Optical Sensors for Water Quality

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Shifts in land use, population, and climate have altered hydrologic systems in the United States in ways that affect water quality and ecosystem function. Water diversions, detention in reservoirs, increased channelization, and changes in rainfall and snowmelt are major causes, but there are also more subtle causes such as changes in soil temperature, atmospheric deposition, and shifting vegetation patterns. The effects on water quality are complex and interconnected, and occur at timeframes of minutes (e.g., flash floods) to decades (e.g., evolving management practices).

However, water-quality monitoring has historically focused on discrete samples collected weekly or monthly, and laboratory analyses that can take days or weeks to complete. Low-frequency data and delayed access hampers a timely response during events, limits the ability to identify specific causes or actions, and may result in poorly quantified effects on ecosystems and human health at local to regional scales.

Recent advancements in commercially available in situ sensors, data platforms, and new techniques for data analysis provide an opportunity to monitor water quality in rivers, lakes, and estuaries on the time scales in which changes occur. For example, measurements that capture the variability in freshwater systems over time help to assess how shifts in seasonal runoff, changes in precipitation intensity, and increased frequencies of disturbances (such as fire and insect outbreaks) affect the storage, production, and transport of carbon and nitrogen in watersheds. Transmitting these data in real-time also provides information that can be used for early trend detection, help identify monitoring gaps, and provide science-based decision support across a range of issues related to water quality, freshwater ecosystems, and human health.

State of the Technology

One of the most promising advances in recent years is the increasing use of optical sensors for water quality studies. Optical sensors rely on the absorbance, fluorescence, or scattering properties of materials that are dissolved or suspended in water (Figure 1). Recent interest has focused on the ability to measure the concentration or type of some dissolved constituents through absorbance and fluorescence. Certain types of dissolved constituents such as nitrate and organic matter (DOM) convert absorbed light into other forms of energy, and include the re-release of energy at longer wavelengths (e.g., fluorescence) by humic substances.

The wavelength and amount of light absorbed and emitted provides important information on the type, size, and concentration of constituents in water. Field optical measurements related to the concentration and types of suspended particles in water have been around for more than 40 years, with turbidity – a measure of the relative clarity of water – perhaps the most common example. While the ability to make relatively simple and inexpensive optical measurements of DOM and nitrate in the laboratory has been known for even longer, advances in

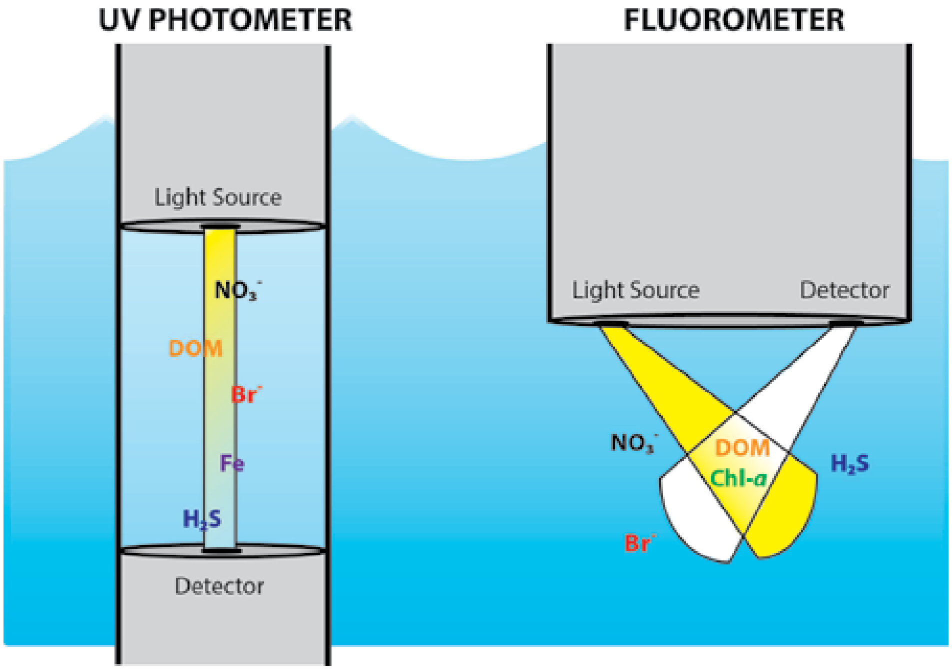

Figure 1. Optical sensors make measurements based on the interactions of light from a sensor with particles or dissolved constituents in water. Certain types of dissolved constituents, such as nitrate and organic matter (DOM), convert absorbed light into other forms of energy, including the re-release of energy at longer wavelengths (e.g., fluorescence) by certain humic substances.

electronics and sensor technology over the past 20 years has led to the development of field-rugged, compact and low power optical sensors for direct measurements of these constituents in water. Nitrate and DOM have been the focus of much recent interest for optical sensor use and development and are further discussed here.

Optical Sensors for Nitrate

On the forefront of new sensor technologies for water-quality monitoring in freshwater systems are ultraviolet (UV) photometers for continuous nitrate measurements (Figure 2). UV nitrate sensors have been used during the past few decades for wastewater monitoring as well as for coastal and oceanographic studies, but have gained broader use in freshwater systems only in the last few years. The current generation of UV nitrate sensors is now being designed specifically for freshwater applications with rugged housings, internal data loggers, built-in wipers, and data processing tools that better account for particles and other interferences common in rivers, streams, and lakes. Optical nitrate sensors operate on the principle that nitrate ions absorb UV light at wavelengths around 220 nanometers. Commercially available sensors utilize this property of nitrate to convert spectral absorption measured by a photometer to a nitrate concentration, using laboratory calibrations and on-board algorithms. This allows for calculating real-time nitrate concentrations without the need for chemical reagents that degrade over time and present a source of waste (Pellerin et al. 2013).

Nitrate is the largest component of total nitrogen in most freshwater systems and, in many locations, represents the most significant concern for algal blooms and human health. One such example is in the Mississippi River Basin, where the addition of optical nitrate sensors at key U.S. Geological Survey (USGS) discharge gaging stations is providing new information about the sources and processes that deliver nitrogen to the coast. For example, USGS discrete and model data on nutrient loads from the Mississippi River basin to the Gulf of Mexico have been critical for understanding the role of nutrients in the formation of a low dissolved oxygen "dead zone" during summer months. The recent deployment of UV nitrate sensors at key locations such as in the lower Mississippi River at Baton Rouge (Figure 3) allows for monthly loading estimates to be refined while reducing the uncertainty in those estimates, leading to a better understanding of the timing and magnitude of nitrate transport within the basin.

Optical Sensors for Organic Matter

Fluorescence-based optical sensors also present an emerging opportunity to better understand organic matter in rivers, streams and lakes. Organic matter includes a broad range of organic molecules of various sizes and composition that are released by all plants and animals (living and dead) and have important implications for drinking water quality, contaminant transport, and ecosystem health. Measuring the fraction of dissolved organic matter (DOM) that absorbs light at specific wavelengths and subsequently releases it at longer wavelengths (e.g., fluorescence) is diagnostic of DOM type and amount. Studies have often used the excitation and emission at 370 and 460 nanometer (nm), respectively, to quantify the fluorescent fraction of colored DOM (referred to as FDOM). Sensors for FDOM have a long history of use in oceanography as an indicator of terrestrial organic matter entering the coastal ocean, but have only recently been adopted for use as water-quality monitors in freshwater systems.

In situ FDOM sensors have been used in many different environments to provide a relatively inexpensive, high-resolution proxy for dissolved organic carbon (DOC) concentrations. This has been useful to understand the transport of DOC from watersheds, but has also been used to better understand the internal sources of DOC in drinking water reservoirs (Downing et al. 2008) and the ability to predict the formation of disinfection by products such as haloacetic acids following drinking water treatment (Carpenter et al. 2013). In some cases, other related biogeochemical variables such as mercury concentrations are also strongly correlated with in situ FDOM measurements. For example, in situ sensors were deployed seasonally on Browns Island, a tidal wetland in the San Francisco Bay-Delta, to measure optical properties related to DOC and dissolved methylmercury (MeHg) across tidal cycles and seasons (Bergamaschi et al., 2011). In situ FDOM measurements explained almost 90% of the variability in dissolved MeHg concentrations across two channels and three seasons, allowing researchers to develop accurate and cost-effective flux estimates of MeHg in a highly dyamic tidal system (Figure 4).

Figure 2. Continuous UV nitrate sensors and other water-quality instruments deployed in the Mississippi River at Baton Rouge (USGS gage 07374000) allows for a better understanding of nitrogen dynamics at the rates in which changes occur.

State of the Art

The advantages offered by in situ optical sensors over discrete sampling or other in situ approaches (ion selective electrodes and wet chemical sensors) are many – rapid sampling rates, low detection limits, low power consumption, no chemicals, easy field

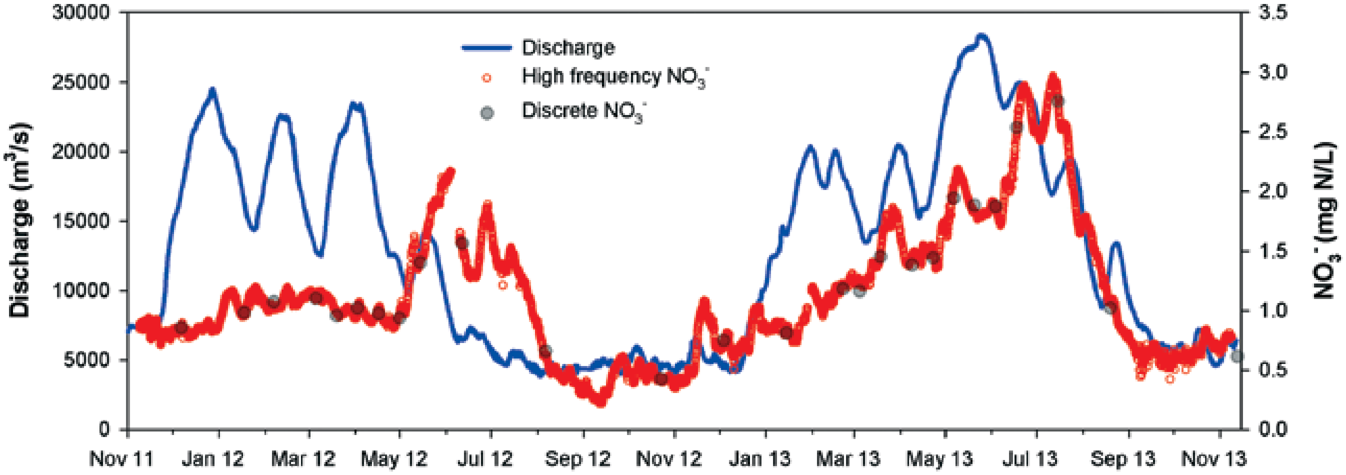

Figure 3. Sensors capture data during all hydrologic events, which results in higher accuracy and lower uncertainty than modeled loads that are based on discrete samples. The data from the USGS site on the Mississippi River at Baton Rouge (USGS gage 07374000) demonstrates the complex relationship between nitrate concentrations and discharge, which reflects both the sources of nitrate within the basin and the accumulation of nitrate in soils prior to flushing.

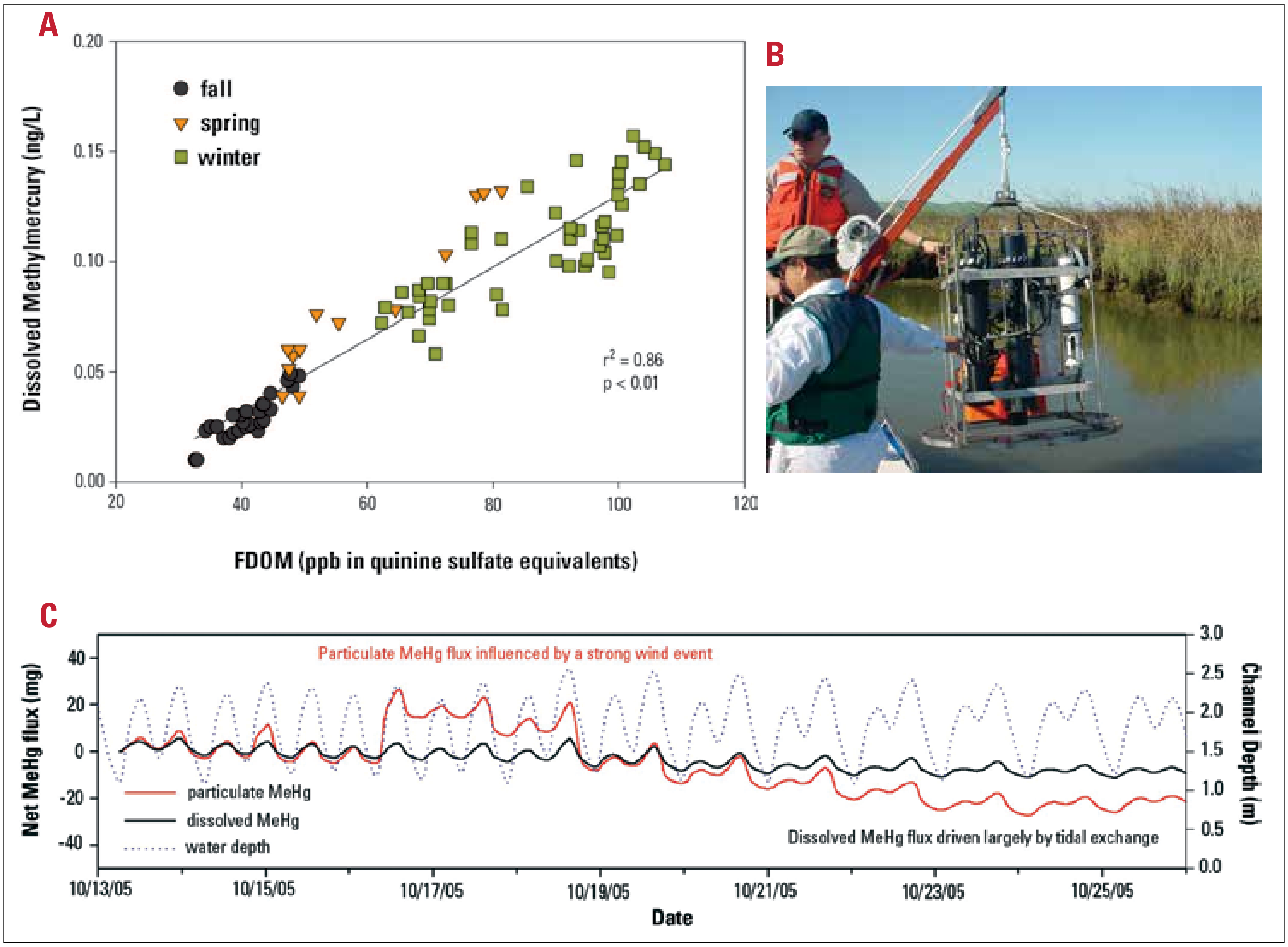

Figure 4. Data from an instrument deploying at a tidal wetland (Browns Island) in the San Francisco-Bay Delta. (A) the correlation between in situ FDOM sensor measurements and dissolved methylmercury concentrations from discrete samples. (B) Picture of the in situ sensor deployment package that includes FDOM and a variety of other optical sensors. (C) Time series data of methylmercury (MeHg) fluxes from Browns Island, indicating a net off-island flux across the spring-neap tide. High-resolution data also illustrate the influence of tidal cycles and wind events on MeHg flux in the San Francisco Bay-Delta system. See Bergamaschi et al. (2011) for more detail.

servicing, and long-term deployment capability. Optical sensor technology is sufficiently developed to warrant their broader application, but generating data that meet high standards requires future investments into common methodologies and protocols for sensor characterization and data management. For example, optical nitrate sensors were originally developed for very different environments – coastal oceans with very low turbidity and color, versus wastewater treatment facilities with very high turbidity and color. Therefore, use in rivers, streams, and lakes requires careful consideration of instrument design, such as the appropriate optical path length and wipers or other anti-fouling techniques.

Similarly, optical sensor measurements may be influenced by a variety of matrix effects including water temperature, inner filter effects from highly colored water, turbidity, and the presence of bromide (for UV photometers). Some in situ optical sensors require further characterization for interferences and correction schemes prior to widespread use in river, stream, and lake monitoring. For example, laboratory tests with standard reference materials demonstrated that measured FDOM values were strongly influenced by temperature, turbidity, and DOC concentrations in matrix conditions similar to those observed in many rivers and streams (Downing et al. 2012, Figure 5). However, these interferences appear to be predictable and corrections may be possible across a wide range of turbidities and DOC concentrations.

Interferences, matrix effects, and other challenges for collecting high quality water-quality data in situ will best be solved by continuing to work with manufacturers and the broader user community to fully characterize sensors and develop mechanical solutions and/or correction schemes that will work across the typical range of conditions encountered in rivers, streams and lakes.

Similarly, continued development of common methodologies and protocols are critical to ensuring comparable measurements across sites and over time (Pellerin et al. 2012). Such investments will continue to increase the number of sites at which these technologies are used as well as increase the types of parameters that can be measured by sensors in real-time.

Evaluating the Need for Continuous Data

Given the current costs to purchase optical sensors alone (approximately $2,000-5,000 for FDOM and $15,000-25,000 for UV nitrate) and the ongoing expenses related to instrument service and maintenance, potential users may want to carefully consider whether "continuous" data (for example, multiple samples per hour or day) are really needed. Although explicit guidance is not available, basic time-series analysis requires that the rate of sampling be greater than the rate of change to observe the true time-dependence. Sampling bias can occur when constituent concentrations change significantly between samples, which can lead to overestimates or underestimates of watershed loads, inaccurate pollution assessments, and potentially obscured seasonal or long-term trends. Traditional monthly discrete sampling approaches may be particularly susceptible to bias in more dynamic freshwater systems such as streams and small rivers.

There are many instances where high temporal resolution data are critical for understanding drivers of water quality and effects on human health, ecosystem function, or water management. For example, continuous measurements may improve upon nutrient load estimation techniques if discrete sampling does not fully capture the concentration-discharge range or where the concentration-discharge relationship is poor. However, not all freshwater systems are subject to rapid changes in water quality, and some monitoring or research goals may be sufficiently addressed with less frequent, discrete data collection. Potential users should assess existing discrete water quality data and continuous sensor data for other parameters (such as specific conductance and dissolved oxygen) to determine if a site would benefit from continuous measurements from an optical sensor. Temporary sensor deployments could also provide short-term data on the

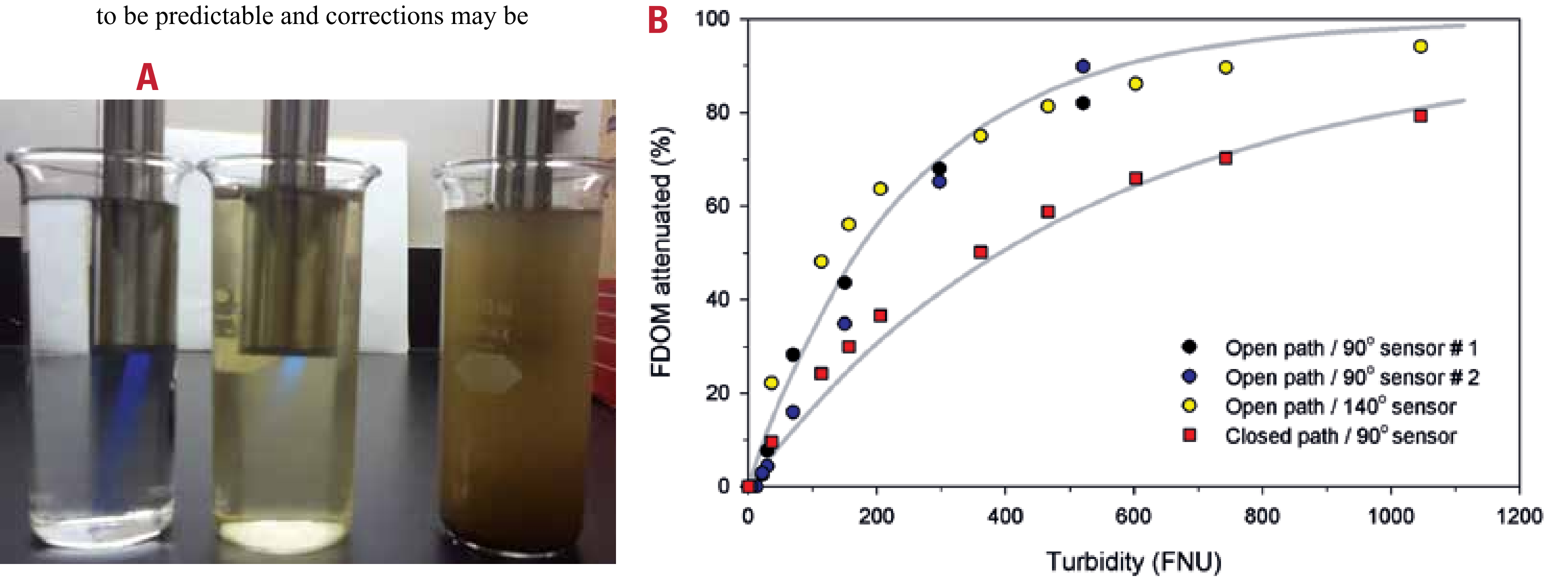

Figure 5. (A) Attenuation of the FDOM signal in an optically clear standard solution (left), as well as a solution with DOM (center) and suspeneded particles (right). (B) The percentage of FDOM attenuated with several types of in situ FDOM sensors as a function of turbidity. See Downing et al. (2012) for more detail.

degree of variability before investing in a longer-term continuous measurement effort.

Looking to the Future

The current generation of commercially available optical sensors will significantly improve the temporal resolution for measurements of nutrients, organic matter, and other parameters. However, a variety of new and improved sensors for applications in rivers, streams, and lakes are on the horizon. For example, recent improvements in LED technology in the lower UV range (e.g., 250-290 nanometers) will open up new avenues for the use of custom fluorometers for the detection of wastewater and other contaminants from urban and agricultural landscapes (Figure 6). Several wet chemical sensors also show significant promise for long-term, in situ monitoring of soluble reactive phosphorus and ammonium in freshwater systems. In addition, advancements in real-time data transmission and communication with sensors will provide numerous benefits including monitoring sensor performance, providing an early warning of water-quality issues, allowing for adaptive sampling, and increasing public awareness. The user community should also continue to work with software developers to continue development of tools for automating quality-assurance and quality-control (QAQC), storage and retrieval, and visualization of real-time in situ optical sensor data and statistics.

Perhaps the greatest scientific "bang for the buck" lies in the development of inter-calibrated networks of water-quality sensors that provide information about water quality across the continuum from headwater streams to lakes, reservoirs, and ultimately coastal rivers and estuaries across the United States. The information provided by such a network would assist environmental and water-quality managers as an early warning of problems, help assess long-term trends, and provide data to evaluate the effects of management and mitigation actions across multiple scales. However, standardized sensor measurement protocols, data-collection strategies, and common QAQC approaches will be necessary to develop an inter-calibrated network of in situ optical sensors with different agencies and users.

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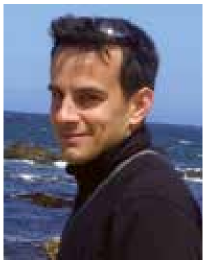
Figure 6. Field testing a custom in situ fluorometer for detecting wastewater effluent near Madison, Wisconsin. Photo: Steve Corsi, USGS.



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