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RECEIVED 01 February 2024 ACCEPTED 04 April 2024 PUBLISHED 22 April 2024

CITATION

Kumar M, Khamis K, Stevens R, Hannah DM and Bradley C (2024) *In-situ* optical water quality monitoring sensors applications, challenges, and future opportunities. *Front. Water* 6:1380133. doi: 10.3389/frwa.2024.1380133

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In-situ optical water quality monitoring sensors—applications, challenges, and future opportunities

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Water quality issues remain a major cause of global water insecurity, and real-time low-cost monitoring solutions are central to the remediation and management of water pollution. Optical sensors, based on fluorescence, absorbance, scattering and reflectance-based principles, provide effective water quality monitoring (WQM) solutions. However, substantial challenges remain to their wider adoption across scales and environments amid cost and calibration-related concerns. This review discusses the current and future challenges in optical water quality monitoring based on multi-peak fluorescence, full-spectrum absorbance, light-scattering and remotely sensed surface reflectance. We highlight that fluorescence-based sensors can detect relatively low concentrations of aromatic compounds (e.g., proteins and humic acids) and quantify and trace organic pollution (e.g., sewage or industrial effluents). Conversely, absorbance-based sensors (Ultraviolet-Visible-Infra-red, UV-VIS-IR) are suitable for monitoring a wider range of physiochemical variables (e.g., nitrate, dissolved organic carbon and turbidity). Despite being accurate under optimal conditions, measuring fluorescence and absorbance can be demanding in dynamic environments due to ambient temperature and turbidity effects. Scattering-based turbidity sensors provide a detailed understanding of sediment transport and, in conjunction, improve the accuracy of fluorescence and absorbance measurements. Recent advances in micro-sensing components such as mini-spectrometers and light emitting diodes (LEDs), and deep computing provide exciting prospects of insitu full-spectrum analysis of fluorescence (excitation-emission matrices) and absorbance for improved understanding of interferants to reduce the signalto-noise ratio, improve detection accuracies of existing pollutants, and enable detection of newer contaminants. We examine the applications combining insitu spectroscopy and remotely sensed reflectance for scaling Optical WQM in large rivers, lakes and marine bodies to scale from point observations to large water bodies and monitor algal blooms, sediment load, water temperature and oil spills. Lastly, we provide an overview of future applications of optical techniques in detecting emerging contaminants in treated and natural waters. We advocate for greater synergy between industry, academia and public policy for effective pollution control and water management.

KEYWORDS

optical spectroscopy, fluorescence, absorbance, water quality monitoring, sensors, *in-situ*

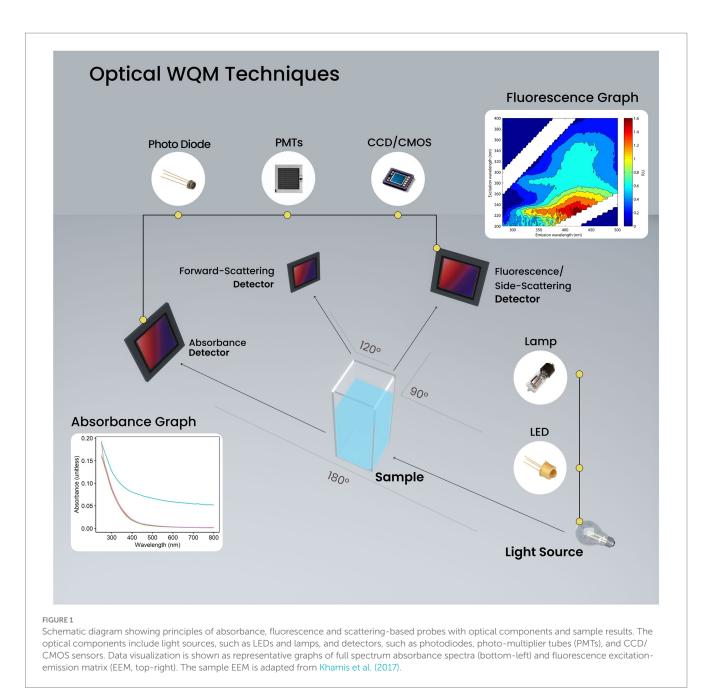
1 Introduction

Water pollution is a major challenge to global water security, with >25% of the world's population unable to access safe drinking water in 2022 (WHO and UNICEF, 2023). After accounting for water quality issues, the fraction increases to 40%, with key hotspots in India, China, the Middle East, the Mediterranean and Mexico (van Vliet et al., 2021; Caretta et al., 2022). Real-time and accurate monitoring of critical water pollution variables, including heavy metals, agricultural nutrients [e.g., nitrate and phosphorus, disease-causing bacteria, viruses and emerging contaminants such as microplastics and pesticides, remains a global challenge (Hannah et al., 2022)]. The lack of infrastructure, financial and technical resources and regulatory oversight significantly hamper water quality monitoring (WQM) efforts in developing countries. Similarly, despite having financial resources, developed countries are constrained by aging infrastructure, lack of investment, and low compliance and accountability (Kirschke et al., 2020; Hannah et al., 2022). Technological improvements can lower some of the financial and infrastructure-related issues and facilitate decision-making by enabling in-situ monitoring of key water quality variables identified under global conventions such as the United Nations's Sustainable Development Goals (SDGs) 6.3.2, European Union (EU) Water Framework Directive (WFD) and World Health Organization's (WHO) water quality guidelines (Warner, 2020; European Union, 2021; WHO, 2022). For example, SDG 6.3.2 details a list of water quality variables, including oxygen, salinity, macronutrients (Nitrogen, Phosphorus) and pH and defines a range of target values that reflect human and ecosystem health perspectives (Warner, 2020). Similarly, in Europe, the WFD focuses on improving the chemical and ecological conditions of both surface and groundwater through monitoring and holistic river basin management (European Union, 2021). However, this monitoring occurs at coarse intervals and often misses critical periods of pollutant transport and transformation (e.g., hot moments; McClain et al., 2003). Recent WHO guidelines advocate developing early-warning systems for predicting harmful algal blooms using in-situ monitoring approaches (WHO, 2022).

The technology for in-situ monitoring of physiochemical variables, such as temperature, electrical conductivity, pH, and dissolved oxygen (DO), is well-established (Banna et al., 2014; Silva et al., 2022). Recent developments have expanded the potential variables that can be monitored in-situ to include total and dissolved organic carbon (TOC and DOC, respectively), biological and chemical oxygen demand (BOD and COD, respectively), dissolved organic matter (DOM), fecal coliforms, agricultural pollutants (e.g., ammonium, nitrate, and phosphorus), ions (chloride, fluoride) and heavy metals (e.g., iron, arsenic) (Raich, 2013; Banna et al., 2014). However, given that human-health-related thresholds are more stringent than those for ecosystem that production and environmental occurrence of emerging contaminants (ECs) continues to increase, there is an urgent requirement for monitoring technology that can detect a wide range of variables accurately and across a broad spectrum of environmental conditions. Alongside sensor technology advances, data transfer (telemetry) and data visualizations support quick and effective stakeholder decision-making (Gholizadeh et al., 2016; Zaidi Farouk et al., 2023). Technological advances are also increasingly informing policy-making and riverine ecosystem restoration efforts toward improving the drinking and bathing qualities of rivers, lakes and marine waters (Johnson et al., 2008; Mouchel et al., 2021; Tiwari et al., 2021).

Recent advances in optical water quality monitoring (OWQM) techniques have improved the understanding of eutrophication and organic pollution in aquatic ecosystems (Baker, 2002; Hudson et al., 2007; Thakur and Devi, 2022). In-situ optical sensors measuring fluorescence, absorbance, and scattering have become particularly important for aquatic monitoring. Advancements in optical components, i.e., light emitting diode (LED) technology, and miniaturization of sensing elements such as photodiodes, photomultiplier tubes, charge-coupled device (CCD), and complementary metal-oxide-semiconductor (CMOS) sensors, etc., have made the optical sensors, such as fluorimeter, absorbance and turbidity sensors, smaller in form-factor, lowered their power requirements and improved their field usability (Mukunda et al., 2022; Zainurin et al., 2022; Goblirsch et al., 2023). Fluorescence spectroscopy relies on the principle of Stokes shift, which is the spectral shift between incident (excitation, ex) light and emitted (em) light (detected orthogonally to incident light) from shorter to longer wavelengths (Figure 1). Fullspectrum applications enable measurement of the fluorescence signature in a three-dimensional excitation-emission matrix (EEM) and use parallel factor analysis (PARAFAC) tools to characterize specific fluorescence peaks associated with specific dissolved organic compounds (Murphy et al., 2013). The key fluorescence peaks include Peak A (ex/em: 260/380-460 nm) and Peak C (ex/em: 350/420-480 nm), both of which have been associated with humic-like material derived from terrestrial environments, Peak B (ex/em: 275/310 nm) and Peak T (ex/em: 275/340 nm), associated with Tyrosine and Tryptophan-like fluorescence (TLF), respectively, and Peak M (ex/em: 310/370-420 nm) associated with humic-like material derived from marine environment. However, EEM applications are still limited primarily to the laboratory, with most in-situ applications focusing on single or dual peak fluorescence to detect dissolved organic compounds (Peak T and Peak C; Khamis et al., 2017; Li et al., 2020).

Absorbance spectroscopy is based on the absorption of incident light at specific wavelengths by the variable of interest, resulting in the loss of transmitted light measured at 180° angle. Fluorescence can provide high specificity and sensitivity for a set of organic compounds but can saturate at high concentrations (i.e., the inner-filtering effect) and is prone to interferences due to the sample temperature and turbidity (Fellman et al., 2010; Carstea et al., 2020; Kimball et al., 2020). Conversely, absorbance can detect a larger pool of organic and inorganic compounds across a wider range of concentrations, albeit with limited specificity (Dai et al., 2022; Carter et al., 2023). Nephelometric sensors detect undissolved/suspended solid/sediment particles in water by measuring scattering at different angles to the incident light (0°), including back-scattering ($30^{\circ} \pm 15^{\circ}$ angle), sidescattering (90° angle) and forward-scattering ($120^{\circ} \pm 15^{\circ}$ angle) (Kitchener et al., 2017; Droujko et al., 2023). These are based on inverse attenuation, i.e., a higher concentration of total suspended solids (TSS) will cause higher scattering and vary considerably with particle size, shape, and wavelength of incident light. The sidescattering-based sensors measure turbidity as a proxy of TSS with good accuracy at low concentrations. In contrast, backward-scattering sensors are accurate at high TSS concentrations, and forwardscattering sensors cover a wider range of concentrations. Together, they provide a detailed understanding of sediment transport in water bodies and are used to improve the accuracy of fluorescence and



absorbance measurements (Khamis et al., 2015; Lee et al., 2015). However, substantial challenges remain to the large-scale deployment of these technologies, given costs, power requirements and calibrationrelated concerns. Increasingly, remotely sensed reflectance-based platforms are being used to monitor water quality events, such as algal blooms, in freshwater lakes and marine habitats, but require validation against *in-situ* ground observations (Shi et al., 2019; Sagan et al., 2020; Windle and Silsbe, 2021).

Several review papers have summarized recent advances in water quality monitoring (Raich, 2013; Banna et al., 2014; Gholizadeh et al., 2016; Thakur and Devi, 2022; Zainurin et al., 2022; Zaidi Farouk et al., 2023), and while some have focused explicitly on *in-situ* optical sensors (Hudson et al., 2007; Carstea et al., 2016, 2020; Gunter et al., 2023), there is still a need for deeper understanding of this rapidly evolving technology and its potential for water quality monitoring at different scales. In this review, we provide a concise overview of the current and future challenges in *in-situ* optical monitoring of freshwater and marine bodies, focusing on fluorescence, full-spectrum absorbance, scattering and reflectance-based techniques. Further, we discuss the available market solutions and data sources using fielddeployable optical sensors and their strengths and limitations. Lastly, we provide an overview of future applications of optical techniques in detecting novel/emerging contaminants in water.

2 Status of fluorescence and absorbance spectroscopy for WQM

Early research on the use of fluorescence spectroscopy for WQM used fiber optic sensors for a wide range of applications, including the detection of organic matter (TOC, DOC), oxygen (BOD, DO), biological agents (e.g., bacteria, viruses, algal blooms, etc.) and hydrocarbons (Scully, 1998; Ahmad and Reynolds, 1999). The commercial applications of these techniques were either

limited to benchtop instruments (Phillips et al., 1974) or in the form of optical fiber-based sensors in the 1980s, which, along with electrochemical techniques such as ion selective electrodes (ISEs), have been widely used for a range of aquatic and industrial monitoring activities for more than half a century (Frant, 1997; Scully, 1998; Ahmad and Reynolds, 1999). Similarly, *in-situ* optical turbidity sensors have long been used to measure scattering at different angles to understand the composition of suspended solids in water bodies (Kitchener et al., 2017). In comparison, the application of fluorescence and absorbance spectroscopy for *in-situ* WQM is a recent trend. The emergence of commercial fluorometers and absorbance probes over the last ~20 years is primarily linked to the development of UV LEDs (<400 nm) and photodetectors (Johnson and Coletti, 2002; Rode et al., 2016; Mukunda et al., 2022).

Currently, optical water quality monitoring represents a multibillion US dollar market comprising probes based on various measurement principles, e.g., nephelometry (scattering of light), absorbance and fluorescence. The availability of cost-effective and low-powered LEDs and detectors has driven the expansion of the in-situ OWQM market. Mukunda et al. (2022) provided a comprehensive review of conventional light sources (Arc lamps, Quartz halogen lamps, mercury lamps, etc.) and highlighted cost, bulkiness, short lifespan, drift in output with prolonged flashing and UV phototoxicity as major issues. Conversely, LEDs provide high power, longer lifespan, high signal-to-noise ratio, stable outputs, compact size and low costs, making them ideal for field-deployable OWQM sensors (Hart and JiJi, 2002; Mukunda et al., 2022). The early applications of Ultraviolet-Visible-Near Infra-Red (UV-VIS-NIR) LEDs were for biomedical analytical devices and ecophysiological sensing (i.e., plant chlorophyll), which were later adopted for water quality sensors (Mukunda et al., 2022). Early sensors used single or dual-beam LEDs to focus on fluorescence or absorbance measurements for a single variable of interest, e.g., nitrate and TOC, with a second beam often used for turbidity correction. The two major gaps in the wider adoption of LEDs for OWQM are the low efficiency of deep UV (<280 nm) and scattering-induced noise in the signal. Multi-chip LEDs, which position multiple LEDs on a single chip, along with deep learning techniques, provide a better opportunity to understand the sediment composition and develop robust correction factors (Hart and JiJi, 2002; Ighalo et al., 2021). However, the cost-effectiveness and power requirements of deep UV LEDs remain a significant bottleneck in developing low-cost OWQM probes.

Similar to LEDs, the use of photodetector technology, such as photodiodes, CCDs, PMTs, and, recently, linear CMOS arrays, for WQM has also evolved significantly (Spring, 2001; Mukunda et al., 2022). Photodiodes have a number of desirable properties, namely, low-cost, high specificity, narrow or broad range of wavelengths, low power requirements, and low data processing time. Thus, paired with monochromatic or band-pass filters (which allow transmission of specific wavelengths), low-light photodiodes and PMTs contribute to the affordability and compactness of OQWM probes. Optical detectors can also improve the signal-to-noise ratio by optimizing signal gain and modulating the sensor integration time. However, PMTs and photodiodes have no spatial discrimination, i.e., they convert the intensity of light into an electrical signal and cannot differentiate them according to wavelengths, which limits their applicability to broad spectrum (UV–VIS) sensing (Spring, 2001; Yokota et al., 2021). Miniaturizing traditional benchtop spectrometers into mini and microspectrometers provides new opportunities for developing fielddeployable UV–VIS OWQM probes (Bouyé et al., 2016; Shi et al., 2022; Goblirsch et al., 2023). The mini/micro-spectrometers use a linear CCD or CMOS imaging sensor in a Czerny-Turner design or micrograting to achieve smaller form factors (Bouyé et al., 2016; Chen et al., 2022). However, the significant challenges to adopting mini/micro-spectrometers lie in cost-effectiveness, data analytics and power management.

3 Current *in-situ* applications of optical WQM

The use of fluorescence and absorbance spectroscopy for in-situ WQM, while relatively new in comparison to electrochemical techniques (ion-selective electrodes have been used for half a century), has become well-established over the past 20 years (Johnson and Coletti, 2002; Rode et al., 2016). Fluorescence for monitoring Chlorophyll a and UV absorbance for nitrate measurements are among the most widely cited environmental monitoring applications (Arndt et al., 2022). In this case, the sensors are used to directly measure the variables of interest (Chlorophyll a and nitrate have specific absorbance and fluorescence spectra). Concurrently, there has been increasing interest in the use of absorbance as a surrogate (or proxy) for other difficult-to-measure variables, including the development of multivariate regression models to quantify DOC/TOC (Peacock et al., 2014; Gaviria Salazar et al., 2023), fecal coliforms (Nowicki et al., 2019; Sorensen et al., 2020; Dapkus et al., 2023), and phosphorus fractions (Vaughan et al., 2018). These approaches have recently utilized emerging data science and machine learning tools to develop more robust proxy models (see Carter et al., 2023).

In-situ fluorescence monitoring has been used for both quantitative and qualitative WQM. For example, pollution sources are tracked using fluorescence peaks associated with proteinaceous compounds (e.g., TLF; Baker et al., 2004; Lenaker et al., 2023) and optical brightening agents (Finegan and Hasenmueller, 2023) as (non-conservative) tracers of wastewater. Fluorescence has also been used to quantify DOC and BOD (Khamis et al., 2017, 2021) by measuring dual fluorescence peaks (tryptophan and humic-like fluorescence) and turbidity, which is vital for developing reliable proxy models. There has also been growing interest in using fluorescence to quantify microbial contamination in rivers (Baker et al., 2015; Bridgeman et al., 2015), groundwater (Nowicki et al., 2019; Sorensen et al., 2020; Dapkus et al., 2023), and potable water (Sorensen et al., 2018; Gunter et al., 2023). However, it is important to note that most studies to date focus on single or dual fluorescence peaks; hence, the associated models tend to be relatively simple compared to those developed for absorbance sensors.

Optical indices (rather than proxy models) have recently emerged as a viable approach for monitoring water quality. There are a large number of fluorescence indices associated with Excitation Emission Matrix spectroscopy (Fellman et al., 2010; Begum et al., 2023), which have not yet been implemented for field deployable sensors, although the use of the ratio of peak T:peak C fluorescence has been used as an indicator of wastewater/anthropogenic DOM in an urban river (Croghan et al., 2021). For absorbance, it is possible to calculate a broader range of optical indices using full-spectrum measurements *in-situ*. For example, the spectral slope, linked to the molecular weight of DOM, has been used to assess carbon quality dynamics across a land cover gradient (Vaughan et al., 2019).

4 Market solutions using fluorescence and absorbance spectroscopy for WQM

In an exhaustive market survey for current probes based on absorbance and fluorescence spectroscopy, we found more than 32 products catering to various environmental, academic, and industrial applications. The survey results are summarized in Supplementary Table S1. We relied on the datasheets and specifications provided by the retailers to glean the relevant information or lack thereof. The product marketing material (e.g., brochures, webpages, datasheets and manuals) often lacked technological specifications and was thus ignored. However, they provide helpful information on the applications, technology-based demands, supply-side constraints, and insights into their future directions. The surveyed probes were segregated based on the measurement principles: absorbance and luminescence including fluorescence; the light source: LEDs and lamps; the detector: single or arrayed photodiodes; and variables of interest: single or multivariable, design and data postprocessing methods.

4.1 Measurement principles

Absorbance-based sensors dominate the market space (72%, N=31). The single-variable probes (38%) focused on nitrate (NO₃-N), nitrite (NO₂-N), DO and DOM. The multivariable probes use specific wavelength LEDs ranging from 200 to 720 nm to observe absorbance, which is converted to equivalent COD, BOD, DOC, TOC, and Total Suspended Solid (TSS) values using calibration algorithms. The absorbance measurements are taken at 180° angle from the incident light and are particularly susceptible to changes in turbidity. Thus, most surveyed probes had a turbidity compensation component based on nephelometry principles and temperature compensation. Most probes also offer single or dual-beam (more common) corrections for absorbance using reference blanks.

Luminescence probes (28%) form a smaller proportion of the market and use fluorescence-based sensing for organic matter detection, including TLF, Chromophoric Dissolved Organic Matter (CDOM), Chlorophyll a, etc. and derive other variables such as BOD and even fecal coliforms through statistical extrapolation. Fluorescence measurements are prone to matrix-specific interference, such as inner-filtering effects (IFE) and thermal quenching, creating a non-linear relationship between intensity response and concentrations, especially at high fluorophore concentrations. In ex-situ (laboratory-based) experimental studies, absorbance measurements are used to correct the inner-filtering effects and improve the accuracy of the fluorescence measurements (Kimball et al., 2020). The technique is now widely used in benchtop spectrometers with dual-mode features for absorbance and fluorescence (e.g., Duetta, Horiba Pvt. Ltd.). However, combining absorbance and fluorescence measurements to reduce noise, increase the linear range and measurement repeatability and achieve higher detection accuracies remains challenging for *in-situ* water quality monitoring probes.

4.2 Light sources and detectors

More than half of the surveyed sensors used LEDs of specific wavelengths, while less than a third preferred lamps, and some provided no information. The availability of affordable deep-UV LEDs (<280 nm, 41%) has led to the development of multiple commercial probes for nitrate, DO and DOM detection. UV-VIS LEDs (315-550nm, 16%) are frequently used for absorbance and fluorescence measurement of dissolved organic matter (DOM) and algal activities in large water bodies, including marine environments. VIS (~550 nm) and NIR (~850 nm) LEDs are standard for turbidity sensors nowadays. Lamps provide an alternative to multiple LEDs as a single broadband (~190 to ~750 nm) light source, including Xenon flash lamps, Deuterium and Tungsten. In comparison, mercury lamps are used for narrow-band (~254 nm) applications measuring nitrate. They benefit from simpler components and designs and allow simultaneous measurements of multiple variables. However, the tradeoffs with LEDs are in terms of power requirements and component costs, both being considerably higher for lamps. Furthermore, some sensors (24%) use more than one LED in a singlevariable probe, in which case the second LED is used for turbidity or absorbance-based corrections.

Approximately two-thirds of the products do not specify the type of detector their probes use. Among the rest, photodiodes are the most common detectors in single or arrayed formations. Like LEDs, advancements in optical technology have made photodiodes affordable and miniaturized them for in-situ deployment. The LED-photodiode specificity allows for precise measurements of specific variables such as nitrate and reduces the scope of interference by other contaminants. However, the specificity limits the potential to account for background interferents, which full spectrum light source and detector combinations can observe and account for in a single measurement (Goblirsch et al., 2023). Current mini-spectrometers in the market are the size of a fingertip (C12880MA and C16767MA, Hamamatsu Pvt. Ltd.) and offer a broad wavelength UV-VIS-NIR range (225-1,000 nm, AFBR-S20M, Broadcom Inc.) in a single body. They use highly-sensitive image sensors such as CCD and CMOS and direct the incident light through optical slits and gratings. Depending on the type of applications, the mini-spectrometers can be tuned to maximum sensitivity at desired blaze angles and are likely to replace the photodiode arrays in future probes aimed at broad-spectrum sensing (Goblirsch et al., 2023). However, only one commercial product (Opus, Trios) is currently mentioned to use a minispectrometer (200-360 nm) as the detector, with most probes relying on an array of photodiodes, sensitive to wavelengths of interest as an alternative way of broad-spectrum sensing.

4.3 Sensor components, design, and interface

The design of the optical window of a probe is largely dependent on measurement principles. As explained earlier, the fluorescence and nephelometry measurements are taken at right angles (15–90°) to the

incident light, and these probes preferred both incident light and detection inlet at the bottom of the sensor, albeit at a slight angle to each other. The design lends itself to better cleaning and antifouling properties. Conversely, the absorbance probes deploy a notched design, allowing the incident light to be 180° to the detector. This design enables path-lengths to be changed as per the application's requirement and varied between 0.3-50 mm in the surveyed probes. Changeable path lengths are a crucial feature of absorbance probes, which allows them to target specific concentration ranges and resolutions based on the type of applications and environments (Jensen and Bak, 2002; Skouteris et al., 2018; Shi et al., 2022). For example, probes appealing to drinking water monitoring require higher sensitivity to low concentrations of pollutants and thus need longer path-lengths (10-50 mm), whereas probes serving effluent treatment plants monitor high concentration loads and require shorter path-lengths (0.3-5 mm). However, the notched design is relatively more susceptible to fouling than downward-facing probes and requires active cleaning mechanisms.

Most probes (85%) deployed one or more automatic cleaning methods such as integrated wipers (47%), compressed air (37%), compressed water (9%) and even the use of ultrasonic waves (NiCaVis, Xylem Analytics). Few probes (22%) were solely based on flowthrough designs, although many offered them as accessories for drinking water and other process applications. Probes with a flowthrough design tend to rely on chemical cleaning or compressed air and have built-in humidity control systems to reduce the noise. Another important approach to minimize the impacts of fouling involves the use of nano-particle coating for optical windows (6%) (Delgado et al., 2021).

The most common method of data interfacing in the probes is via a USB/R232/SI-12 cable, although newer probes come with Bluetooth and WLAN options. Most probes (63%) provided factory calibration of the sensors with optional recommendations of field calibration using standard reagents or comparisons with laboratory-based results. The data analysis and display were primarily server and web-dashboard-based. Despite considerable use in research, fewer probes mention post-processing capabilities or the use of artificial intelligence and machine learning tools, such as Liquid AI (Ighalo et al., 2021; Mustafa et al., 2021, Supplementary Table S1).

5 Challenges and opportunities for WQM using optical spectroscopy

5.1 Scaling from *in-situ* to large water bodies

Ongoing advances in sensor technology and processing algorithms have led to multiple applications of reflectance spectroscopy for real-time monitoring of water bodies at different scales (Huang et al., 2018). Although cloud obscuration may be problematic for some platforms, the absorption and scattering properties of light are now being routinely monitored by various satellite platforms (Tyler et al., 2022), as well as airborne remote sensing and Unmanned Aerial Vehicles (UAVs) (Windle and Silsbe, 2021). In this context, the Inherent Optical Properties (IOPs) and color of water reflect the composition of optically active constituents in the medium, which include living phytoplankton (i.e., Chlorophyll a), dissolved organic matter (DOM) and inorganic matter (i.e., dissolved and particulate matter in water), as well as back-scattering by suspended particles. However, the challenges of using and applying remotely sensed optical data lie in resolving the different components of the reflectance signal, i.e., (a) downwelling irradiance, (b) sky radiance, and (c) water-leaving radiance (Mobley, 2001). While these challenges have somewhat constrained the use of remotely sensed optical data for catchment management, the examples summarized below illustrate their increasing potential to study a variety of applied problems, albeit where the real-time outputs are deemed usable after improved quality control and data processing algorithms (e.g., Matthews and Odermatt, 2015). For example, with respect to CDOM, which is often the main optical component of inland waters, the algorithms target the blue wavelengths of light, where absorption maxima occur. Still, atmospheric correction algorithms are weakest at this part of the spectrum, while studies of algal blooms focus on red wavelengths, where there is less interference from detrital pigments (Wynne et al., 2008).

The utility of satellite data for WQM can be significantly enhanced by integrating the optical output from remote sensing platforms with in-situ hydrological data, yielding increasing quantities of continuous data. Most sensor platforms are positioned in sun-synchronous, low-Earth orbits (Tyler et al., 2016). Inevitably, there is a tradeoff between spatial, spectral and temporal resolution. Their spatial resolution ranges from coarse (>200 m; AVHRR, MODIS, VIIRS), medium resolution (5-100 m; Landsat, SPOT, Sentinel-2) and high resolution (<5 m; IKONOS, RapidEye, CubeSat). The temporal resolution varies from half a day for some coarse platforms (e.g., MODIS) to between 5 and 26 days for medium-resolution sensors and to potentially daily resolution for platforms such as WorldView and RapidEye (Huang et al., 2018). However, there are ongoing challenges with respect to untangling the multiple (dynamic) relationships between reflectance and absorbance for specific locations and conditions (Moshtaghi et al., 2021).

As the spatial and temporal resolution of optical data has improved, reflectance-based technology has been successfully applied for water quality monitoring in more optically complex environments, such as lake-water bodies (Kutser et al., 2005; Andrzej Urbanski et al., 2016; Botha et al., 2020), rivers (e.g., Sultana and Dewan, 2021), and marine pollution (Thorhaug et al., 2007; Lu et al., 2013; Moshtaghi et al., 2021). Further work in this area requires paired optical and biogeochemical sampling, as demonstrated by Castagna et al. (2022) in their dataset from nine coastal and inland water bodies in Belgium, which included IOPs (e.g., absorption, scattering, beam attenuation and turbidity) and biogeochemical (e.g., suspended sediment, mineral fraction, particle size distribution, pigment concentration, etc.) properties. Specifically, within boreal lakes, Erlandsson et al. (2012) investigated the UV-VIS absorbance spectra in 983 water bodies in Sweden to report that alkaline lakes generally had lower absorbance and steeper spectral slopes than acidic lakes with a shorter water retention time while providing a comparable (and cost-effective) measure of the quantity and quality of dissolved organic matter (DOM).

Given public health concerns, many studies have investigated the efficacy of using optical sensors to monitor cyanobacteria (algal blooms) in different water bodies. While cyanotoxins cannot be directly quantified, *Chlorophyll a* can determine algal concentrations (Stumpf et al., 2016), with an absorption peak at 620 nm. Ambrose-Igho et al. (2021) tested algorithms enabling reflectance data from Sentinel-2 for monitoring algal blooms in two reservoirs in Illinois, United States. Coffer et al. (2020) investigated the optical properties of >2,300 lakes of various sizes in the contiguous USA using data from Envisat's Medium Resolution Imaging Spectrophometer and Sentinel 3 to examine the seasonal growth and decay of algal blooms and using a spectral shape algorithm previously described by Wynne et al. (2008). The latter suggests that cyanobacteria are present if absorbance at 681 nm is below a baseline (defined by a line drawn between the 665 nm and 709 nm absorbance bands).

This selection of studies illustrates the increasing possibilities of using and applying optical sensors on various platforms to manage water resources at different scales. While problems with data accessibility and interoperability remain (e.g., Agnoli et al., 2023), some studies have successfully combined data from other satellite platforms (e.g., Zhao et al., 2020), as well as UAVs and *in-situ* sensors. Shi et al. (2019) highlight the need for automated processing algorithms that can be validated at increasing spatial and temporal resolution. However, the utility of these data is likely to be enhanced when combined with information from other sources, including *in-situ* monitoring, laboratory analyses and numerical modeling.

5.2 Low-cost sensors—testing and field validation

The recent emergence of low-cost microcontrollers and other electronic components has led to an increase in the development of "Do It Yourself (DIY)" environmental monitoring solutions for varied applications (Mao et al., 2019). A wide range of sensors and associated data loggers have been proposed for monitoring water quantity and quality (Chan et al., 2021), from non-contact water level sensors using ultrasonic (Pereira et al., 2022) or Light Detection and Ranging (Lidar) technology (Paul et al., 2020) to water quality sondes (Kinar and Brinkmann, 2022). However, most developments have been linked to physical or electrochemical sensors, with optical sensors for monitoring water quality largely neglected, except for turbidity (Kelley et al., 2014; Droujko et al., 2023).

While there have been some examples of field deployable spectroscopy-based sensors, notably low-cost fluorometers for measuring Chlorophyll a (Leeuw et al., 2013) or organic matter (Bridgeman et al., 2015), examples of absorbance (UV-VIS) based sensors are limited, but note a recent study by Goblirsch et al. (2023). The lack of UV-VIS probes has been primarily due to technological limitations, such as the challenges associated with LED costs and stability (Kneissl et al., 2019) at the deeper UV wavelengths required for nutrient or organic matter detection (Etheridge et al., 2014). Furthermore, a lack of suitable off-the-shelf detector solutions has impeded the development of lower-cost full-spectrum absorbance sensors (Ruhala and Zarnetske, 2017). Historically, expensive and bulky monochromators have been required for precise measurements, with the recent emergence of lower-cost solutions often lacking the needed range, resolution or measurement repeatability (e.g., AS7262 Visible Spectral Sensor). The few low-cost spectrophotometers/ fluorometers reported in the literature leave many critical unanswered questions. Most studies report on short-term field deployments (Leeuw et al., 2013) or laboratory testing (Power et al., 2023). Hence, understanding measurement stability (electronic drift) or fouling rates (devices lack an automated cleaning system) remains limited (Delgado et al., 2021). Further, there has been a lack of multiple devices fabricated to enable cross-comparisons between sensors to quantify inter-sensor measurement uncertainty (Deutsch et al., 2018; Fettweis et al., 2019). Also, challenges associated with the calibration of multi-node sensor networks (lower-cost sensors will potentially facilitate more extensive networks of optical sensors) and best practices for using calibration reference standards, mainly when sensors are deployed in remote locations, are poorly defined (Earp et al., 2011).

5.3 Detecting emerging contaminants using spectroscopy

Globally, 27% of the population drinks water contaminated from fecal sources (bio-pollution), of which the majority are in Southeast Asia (34%) and rural areas (41%) (Bain et al., 2014). Changing agricultural practices and urbanization have added or enhanced several emerging contaminants (ECs), such as pesticides, microplastics, pharmaceuticals, etc., creating a cocktail of water pollutants (Rochman, 2018; Sharma et al., 2019). Besides their potentially carcinogenic effects, ECs, like microplastics, are also seen as vectors and substratum for pathogenic bacteria, particularly in low-concentration groundwater environments (Rochman, 2018; Ma et al., 2020). Thus, detecting ECs in effluents and natural waters is a high priority, although limited to traditional "gold standard" laboratory-based methods using benchtop instruments and techniques (Manivannan et al., 2022). Sgroi et al. (2017) analyzed the EEMs of samples from two river systems in Italy to report significant correlations between known fluorescence indexes and EC groups, e.g., humic-like peaks correlating with sucralose, sulfamethoxazole and carbamazepine, and ibuprofen and caffeine correlating with tyrosine-like (Peak B) fluorescent peaks. Similarly, Wasswa et al. (2019) used the PARAFAC method to analyse fluorescent signals from treated wastewater and natural waters in the USA using benchtop and portable fluorometers and reported significant associations between TLF and ibuprofen (a pharmaceutical drug), diesel and gasoline, and tyrosine-peaks with diesel, gasoline, caffeine, isoxathion (a pesticide) and lopinavir (a pharmaceutical drug). They also recommended using portable fluorometers for in-situ tracking of ECs by proxy associations, especially in waters with high background CDOM and TLF concentrations, such as tertiary wastewater, and during events of high EC contamination, such as spills and leakages. Paradina-Fernández et al. (2023) demonstrated the very-low detection limits achieved by a benchtop fluorometer and PARAFAC modeling while quantifying organic micropollutants (e.g., pharmaceuticals) in surface and wastewater in Sweden. Moshtaghi et al. (2021) used experimental VIS-IR reflectance data to validate the algorithms used to remotely detect marine microplastics. The significant challenges to using fluorescence spectroscopy lie in moderating the fluorescent quenching and reducing inner-filtering effects. Similarly, UV-VIS absorbance measurements could provide additional information for screening ECs in natural waters (Romão et al., 2017).

Aspects	Strengths	Challenges	Opportunities	Key references
Technology	Rapid, non-invasive, real-time and <i>in-situ</i> measurements	Relatively higher power requirements and costs compared to established technologies	Technological advances will lower the costs and power requirements of LEDs and detectors	Mukunda et al. (2022), Bouyé et al. (2016)
	Lower maintenance costs than other sensor technology (e.g., membrane-based ISEs)	Prone to biofouling and require automated cleaning systems (e.g., wipers, pressurized air or water)	Combining automated cleaning systems with nano-coated optical windows	Delgado et al. (2021)
	Less prone to sensor drift-related errors	Can require application or site-specific calibrations using laboratory-analyzed samples before/during installation	Open data policy on sensor calibrations and use of AI-ML techniques to develop universal calibration algorithms	Carter et al. (2023), Ighalo et al. (2021)
	High specificity for single variables (nitrate, DOC) while simultaneously scalable to multiple variables (full spectrum absorbance, multi-peak fluorescence and scattering)	Full-spectrum fluorescence (EEMs) measurements are still limited to benchtop instruments	Combining multiple LEDs of overlapping wavelengths with broad-spectrum detectors to measure the full spectrum EEMs <i>in-situ</i>	Goblirsch et al. (2023)
Pollutants	High specificity for organic and inorganic variables	CDOM, TLF and Turbidity are proxies for main variables of interest, i.e., TOC/ DOC, BOD/Bacteria and TSS, respectively, and proxy modeling is constrained by the unavailability of large datasets	Multi-wavelength approach combining absorbance, fluorescence, and turbidity with AI-ML tools can distinguish interferents and improve the accuracy of proxy models	Carter et al. (2023), Ighalo et al. (2021)
		Overlapping signals from other interferents (e.g., hydrocarbons) with TLF/CDOM can lead to false positives		Gunter et al. (2023)
Applications	Can be customized to a specific variable range based on applications by changing optical path-lengths and integration time	Measurement accuracy and minimum detection are significantly affected at high pollutant and TSS concentrations	Multivariable probes combining absorbance, fluorescence and scattering data will significantly improve accuracy for high concentrations and extreme environmental conditions	Shi et al. (2022)
			Multi-angle turbidity measurements for improved sediment characterization	Kitchener et al. (2017)
			Coupling with smart samplers can enable flood event monitoring for improved calibrations in aquatic bodies	Khamis et al. (2023)
			Potential to track emerging contaminants	Wasswa et al. (2019)
Scaling	Point-to-regional scaling is possible by combining <i>in-situ</i> sensor data with aerial and remotely sensed reflectance	Data accessibility and validation challenges hamper interpolation across landscapes and in complex environments	Improved sensor infrastructure, access to remotely sensed data, and use of AI-ML tools for validation and interpolation	Shi et al. (2019)
Regulations	Optical sensors are being incorporated into national and international regulatory frameworks and guidelines	Significant time lag between technology improvements and updating regulatory requirements	Improving the synergy between academia- industry and regulatory bodies through open dialog and combined-action projects	WHO (2022), Hannah et al. (2022)

TABLE 1 A summary table of the strengths, challenges, and opportunities in OWQM.

6 Future of optical WQM sensors

Table 1 summarizes the strengths and challenges of using optical sensors for *in-situ* water quality monitoring and the potential way forward. Currently, there is a wide range of commercially available sensors for *in-situ* monitoring of fluorescence and absorbance at high frequency (seconds to minutes resolution) (Banna et al., 2014; Bouyé et al., 2016; Mukunda et al., 2022). However, these remain expensive and inhibit widespread

statutory or regulatory use (Hannah et al., 2022; Mukunda et al., 2022). Furthermore, high costs have constrained the development of distributed sensor networks in large river catchments, which could have helped identify sources of pollution, assess propagation and persistence and validate scaling up solutions using remotely sensed datasets. We suggest that recent reductions in component costs, both in terms of light sources (e.g., UV LEDs) and detectors (e.g., mini-spectrometers), previously barriers to the development of lower cost and power sensors, are likely to herald a new wave of

affordable optical water quality sensors over the next 5 years (Goblirsch et al., 2023).

Some promising areas for future research involve integrating fluorescence, absorbance, and remote sensing (e.g., reflectance) to increase spatial coverage, particularly in large river networks (Cao et al., 2022; Castagna et al., 2022; Fang et al., 2022). Future sensor networks (i.e., node locations) should, whenever possible, align with statutory monitoring locations where manual sampling occurs routinely (Kinar and Brinkmann, 2022; Gaviria Salazar et al., 2023). This will ensure coupled datasets of laboratory and in-situ measurements, which are of comparable quality and can lead to the development of more rigorous calibration algorithms and proxy models (Ighalo et al., 2021; Paradina-Fernández et al., 2023). With the potential for more measurement data from more locations, there is a clear need for the community to embrace emerging artificial intelligence and machine learning (AI-ML) approaches to aid calibration, reduce the signal-to-noise ratio, and capture and correct drift and outliers. It will also facilitate the development of more robust proxy models for hard-to-measure variables such as phosphorus and critical classes of emerging contaminants such as pharmaceuticals and pesticides (Ighalo et al., 2021; Mustafa et al., 2021; Carter et al., 2023) and microplastics (Moshtaghi et al., 2021). Further, despite remaining unexplored, merging multiple data streams from in-situ WQM, i.e., absorbance, fluorescence, scattering and reflectance, with remotely sensed surface reflectance data can facilitate the development of predictive water quality models and early warning systems for aiding tracking and managing large-scale events, such as, e.g., nutrient enrichment and harmful algal blooms (Briciu-Burghin et al., 2023).

7 Conclusion

In this review, we have highlighted the current state of optical water quality monitoring and identified several challenges and future opportunities. The key concerns are high costs and power requirements, biofouling-induced sensor drift (particularly in dynamic environments with variable turbidity), the need for site-specific calibrations, and the limitation of current commercial WQM probes in performing fullspectrum EEMs in-situ. The rapid growth in UV-LED and fullspectrum detector technologies will likely address these issues. At the same time, the emergence of AI-ML-based data analytics holds the potential to develop universal sensor correction algorithms and proxy models for key variables of interest. Fluorescence spectroscopy may be useful in certain scenarios to detect novel/emerging contaminants in treated and natural waters. We suggest that attention should shift toward multivariable and multi-method (fluorescence, absorbance, scattering and reflectance) optical water quality monitoring, which can enhance existing water management and lead to the development of new applications. Augmenting remotely sensed surface-reflectance datasets with improved on-ground WQM infrastructure would be critical for remote monitoring of large water bodies, including marine and coastal pollution. An emerging application for multimethod monitoring and data fusion is linked to the control and monitoring of stormwater systems and combined sewer overflows. With increasing public awareness and newer environmental laws pushing for stricter monitoring of our water resources, the commercial scope of optical WQM sensors is bound to increase significantly. Thus, we advocate for greater synergy between industry, academia and public policy to ensure technological development supports effective pollution control and water management.

Author contributions

MK: Conceptualization, Formal analysis, Methodology, Visualization, Writing – original draft, Writing – review & editing. KK: Conceptualization, Funding acquisition, Writing – original draft, Writing – review & editing. RS: Funding acquisition, Writing – review & editing. DH: Conceptualization, Funding acquisition, Project administration, Writing – review & editing. CB: Conceptualization, Funding acquisition, Methodology, Writing – original draft, Writing – review & editing.

Funding

The author(s) declare that financial support was received for the research, authorship, and/or publication of this article. This research is supported by Innovate UK and represents outcomes from a Knowledge Transfer Partnership (KTP) between The University of Birmingham and Proteus Instruments Limited (KTP no. 13235). KK and CB are also supported by a Natural Environmental Research Council grant, NE/X011178/1.

Acknowledgments

The authors are thankful to Joshua Walmsley-Scotland, Donald Miller and Pillip Tierney at Proteus Instruments Limited for their knowledge-sharing and input. The authors thank Mayank Singh for graphical design support.

Conflict of interest

RS was employed by Proteus Instruments Ltd.

The authors declare that this study received funding from Innovate UK (KTP Grant no. 13235) in partnership with the University of Birmingham and Proteus Instruments Limited. RS is employed by Proteus Instruments Limited; and he was involved in the writing and editing of this article.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

The author(s) declared that they were an editorial board member of Frontiers, at the time of submission. This had no impact on the peer review process and the final decision.

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Supplementary material

The Supplementary material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/frwa.2024.1380133/ full#supplementary-material

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Glossary

AVHRR	Advanced very high resolution radiometer
AI-ML	Artificial intelligence and machine learning
BOD	Biological oxygen demand
CCD	Charge-coupled device
COD	Chemical oxygen demand
СДОМ	Chromophoric dissolved organic matter
CMOS	Complementary metal-oxide-semiconductor
DOM	Dissolved organic matter
DOC	Dissolved organic carbon
DO	Dissolved oxygen
EC	Emerging contaminants
IOPs	Inherent optical properties
IFE	Inner-filtering effect
em	Emission
EU	European Union
ex	Excitation
EEM	Excitation emission matrix
LEDs	Light emitting diodes
MODIS	Moderate resolution imaging spectroradiometer
OWQM	Optical water quality monitoring
PARAFAC	Parallel factor analysis
PMTs	Photo-multiplier tubes
SDG	Sustainable development goal
TSS	Total suspended solids
TOC	Total organic carbon
TLF	Tryptophan-like fluorescence
UV-VIS-NIR-IR	Ultraviolet-visible-near-infrared-infrared
UAVs	Unmanned aerial vehicles
VIIRS	Visible infrared imaging radiometer suite
WFD	Water framework directive
WQM	Water quality monitoring
WHO	World Health Organization