In situ fluorescence measurements of dissolved organic matter: a review

Elfrida M. Carstea[1*], Cristina L. Popa[1], Andy Baker[2], John Bridgeman[3]

[1]National Institute of R&D for Optoelectronics, Atomistilor 409, 077125, Magurele, Romania; elfrida.carstea@inoe.ro, cristina.popa@inoe.ro

[2]Connected Waters Initiative Research Centre, UNSW Sydney, Sydney, NSW 2052, Australia; a.baker@unsw.edu.au

[3]Faculty of Engineering and Informatics, University of Bradford, Richmond Road, Bradford, BD7 1DP, UK; j.bridgeman@bradford.ac.uk

Abstract: There is a need for an inexpensive, reliable and fast monitoring tool to detect contaminants in a short time, for quick mitigation of pollution sources and site remediation, and for characterisation of natural dissolved organic matter (DOM). Fluorescence spectroscopy has proven to be an excellent technique in quantifying aquatic DOM, from autochthonous, allochthonous or anthropogenic sources. This paper reviews the advances in in situ fluorescence measurements of DOM and pollutants in various water environments. Studies have demonstrated, using high temporal-frequency DOM fluorescence data, that marine autochthonous production of DOM is highly complex and that the allochthonous input of DOM from freshwater to marine water can be predicted. Furthermore, river measurement studies found a delayed fluorescence response of DOM following precipitation compared to turbidity and discharge, with various lags, depending on season, site and input of dissolved organic carbon (DOC) concentration. In addition, research has shown that blue light fluorescence ($\lambda_{emission}$ = 430 – 500 nm) can be a good proxy for DOC, in environments with terrestrial inputs, and ultraviolet fluorescence ($\lambda_{emission}$ = UVA – 320 – 400 nm) for biochemical oxygen demand, and also *E. coli* in environments with sanitation issues. The correction of raw fluorescence data improves the relationship between fluorescence intensity and these parameters. This review also presents the specific steps and parameters that must be considered before and

during in situ fluorescence measurement session for a harmonised qualitative and quantitative protocol. Finally, the strengths and weaknesses of the research on in situ fluorescence are identified.

Key words: field fluorimeters, surface water, groundwater, engineered water systems, dissolved organic matter

*** corresponding author: Elfrida M. Carstea, National Institute of R&D for Optoelectronics INOE 2000, Atomistilor 409, 077125, Magurele, Romania; elfrida.carstea@inoe.ro**

1. Introduction

The increase of global economy and population, together with the effects of climate change put a great stress on water resources, increasing the number and quantity of pollutants and threatening to destabilise natural dissolved organic matter (DOM) cycles and composition (Kellerman et al., 2014; Lipczynska-Kochany, 2018; Pagano et al., 2014). Five decades of research have shown that fluorescence spectroscopy has the potential to characterise aquatic DOM, from natural or

anthropogenic sources (Christman and Arnquist, 1969; Hu et al., 2017; Hudson et al., 2007; Jiang et al., 2017; Laane, 1982; Smart et al., 1976). It has been extensively used for cost-effective, reagentless and reliable measurement of water quality from various environments (Bergamaschi et al., 2012; Chen et al., 2015; Chong et al., 2013; Mihalevich et al., 2017; Pesant et al., 2015). Given the above advantages, research has concentrated on optimizing fluorescence spectroscopy for common practice. Thus, the research community and industry developed various portable fluorimeters and fluorescence sensors for water quality monitoring.

Previous reviews have evaluated the potential of fluorescence spectroscopy as an effective monitoring tool in water systems (Carstea et al., 2016; Fellman et al., 2010; Henderson et al., 2009; Hudson et al., 2007; Korshin et al., 2018; Moore et al., 2009; Ruhala and Zarnetske, 2017; Yang et al., 2015; Zielinski et al., 2009). Among these reviews, only Conmy et al. (2014b), Moore et al., (2009), Ruhala and Zarnetske (2017) Zielinski et al. (2009) focused on DOM characterization using field fluorimeters. The reviews of Moore et al. (2009) and Zielinski et al. (2009) were published a decade ago and concentrated on the marine environment. Conmy et al. (2014b) provided an in-depth review of some of the early in situ monitoring studies and the technical details of field fluorimeters, but also with a particular focus on marine and estuarine applications. While Ruhala and Zarnetske (2017) compared optical sensors for the measurement of dissolved organic carbon (DOC) only in freshwater systems. Thus, there are no systematic reviews on in situ fluorescence measurements of different water systems (marine water, freshwater, groundwater and engineered water systems). Moreover, the research in this field has increased, in the past five years, with several in situ measurement studies on the quality of groundwater (for example, Li et al., 2016a; Sorensen et al., 2018a), freshwater (Khamis et al., 2015; Snyder et al., 2018), marine water (Chen et al., 2015; Cyr et al., 2017) and engineered water systems (Carstea et al., 2018; Mladenov et al., 2018; Shutova et al., 2016; Singh et al., 2015). This paper aims to review the advances in water quality measurements using in situ fluorescence devices for detection of fluorescence emitted by DOM in the ultraviolet

(UVA – 320 – 400 nm) and blue light regions (430 – 500 nm), and their characterization, in marine, freshwater, groundwater and engineered water systems. The data correction and calibration strategies for quantitative in situ measurements are described, as multiple factors (such as, suspended particles, dissolved matter or temperature) can affect the fluorescence signal. Based on these strategies, a common protocol for water quality monitoring, using field fluorimeters, is then presented. The protocol will further assist researchers in obtaining the most reliable fluorescence data possible. Finally, the challenges that must be addressed in future studies are identified.

2. Fluorescence in situ measurements

2.1 Fluorescence measurement strategies

Two strategies can be adopted to characterize water, with unknown DOM composition, from different ecosystems using fluorescence spectroscopy. The first one is ex-situ, by collecting samples in order to study them in laboratory. However, this introduces logistical obstacles, which limit the number of samples that can be transported to the laboratory. The samples need to be kept at ~4^{o}C, in order to avoid bacteria overgrowth, in airtight containers to prevent oxidation and in the dark to prevent photodegradation (Spencer et al., 2007a). Also, sampling containers must be thoroughly cleaned to avoid sample contamination with fluorescent and non-fluorescent material. In addition, the samples must be measured as soon as possible from collection, within 24 to 72 h depending on sample source (wastewater and treated drinking water, respectively), to prevent sample degradation. The advantage of laboratory measurements is the access to bench-top spectrofluorimeters, equipped with software able to record different types of spectra, such as excitation-emission matrix or total synchronous fluorescence scans. Excitation-emission matrices can be processed later with sophisticated applications, such as parallel factor analysis or self-organizing maps, for thorough separation of components and correction of data (Bieroza et al., 2009; Bro and Vidal, 2011; Carstea et al., 2010; Murphy et al., 2013; Stedmon and Markager, 2005). Moreover, samples can be easily analysed for additional chemical characteristics.

The second strategy is to test the water in situ with field fluorimeters. The main advantage of this type of measurement is that the water is sampled immediately and without perturbation, thus enabling a more accurate representation of actual environmental conditions. Moreover, the devices can be left unattended at the site for extended periods of time, permitting the generation of time series data and the investigation of changes in fluorescence over time (Carstea et al., 2018; Khamis et al., 2015; Shutova et al., 2016; Singh et al., 2015). In this context, the market offer for equipment able to perform online fluorescence measurements is diverse, regarding price and performance.

When deciding on the type of sensor to use, several optical characteristics and configurations must be considered. The most important characteristics to consider are the excitation and emission wavelengths, and their respective bandwidths, which determine the ratio between the sensitivity and selectivity of the instrument and, consequently, define the targeted fluorophores. Secondly, device configuration is another criterium, depending on the type of application: open-path (right angle detection or intersecting cones – optical window exposed to the environment) or closed-path (flow-through) (Conmy et al., 2014b). In addition, submersible and cuvette-based devices can be adapted for flow-through configuration. Thirdly, the type of light source and detector must be taken into account. The excitation in field fluorimeters is provided by light sources such as Xenon flash lamps, light emitting diodes (LEDs) or lasers (for example, nitrogen, HeCd, Nd-YAG). Devices that use lasers are also known as laser induced fluorescence (LIF) systems. Photomultipliers, photodiodes or charge coupled devices (CCDs) are common detectors for in situ fluorimeters. The excitation and detection units also contain mirrors and lenses for directing and collecting the light. In addition, optical filters are used to select the desired excitation and emission wavelength or to reduce the intensity of light without spectral discrimination (Conmy et al., 2014b). Another important aspect is energy consumption, as it varies between light sources. Finally, the presence of a reference detector should be considered, because it corrects the sensor drift in light source intensity variation. Technical details of instruments are given by Coble et al. (2014), while a detailed analysis of the advantages

and disadvantages of submersible versus cuvette-based fluorimeters is provided by Sorensen et al. (2018a).

Common peaks targeted by most devices, commercial or non-commercial, are: peak T (in the UVA fluorescence region, $\lambda_{excitation}/\lambda_{emission}$ = ~230 & ~275/~340 nm), peak C and peak C^+ (in the blue and green fluorescence region, $\lambda_{excitation}/\lambda_{emission}$ = 300-350/400-500 nm and $\lambda_{excitation}/\lambda_{emission}$ = 250 & 385-420/470-504 nm), as named by Coble et al. (2014) (Fig. 1). Other fluorophores, such as chlorophyll-a, phycocyanin, phycobilin, refined hydrocarbons, dyes, optical brighteners (or fluorescent whitening agents - FWA) may be measured with field fluorimeters, if present at sufficient concentration above the background signal. Additional fluorescence peaks commonly detected with laboratory instruments, which are less frequent at in situ measurements, include peak B ($\lambda_{excitation}/\lambda_{emission}$ = 230 & 275/305 nm, generally referred to as tyrosine-like) (Coble et al 2014), which computational chemistry investigations suggest corresponds to compounds with at least one aromatic ring, and peak A ($\lambda_{excitation}/\lambda_{emission}$ = 260/400-500 nm), usually associated with substances with two aromatic rings (Barsotti et al., 2016; Coble et al., 2014).

In the literature, peak T is also referred to as tryptophan-like and peak C as humic-like or chromophoric DOM. Generally, peak T indicates possible microbial contamination in the water sample (Baker et al., 2015; Fox et al., 2017) and has been associated with an autochthonous source (Coble et al., 2014). Computational chemistry analysis has designated the peak T fluorescence region to compounds with at least one aromatic ring (Barsotti et al., 2016), which may include: indoles, amino acids, polycyclic aromatic hydrocarbons (PAHs), DNA, lignins, etc. (Carstea et al., 2016; Coble et al., 2014). Peaks C and C^+, have been demonstrated using computational chemistry to show the presence of compounds with two or more aromatic rings (Barsotti et al., 2016), and have an allochthonous source (Coble et al., 2014). However, Fox et al. (2017) found that microbially produced (autochthonous) substances can also contribute to peak C^+ fluorescence. The peaks can include several compounds: humic substances, lignins, PAHs, pharmaceutically active compounds,

aromatic ketones, quinones, flavonoids, and FWA (Carstea et al., 2016; Coble et al., 2014). For a simple approach, the nomenclature provided by Coble et al. (2014), namely peaks T, C and C^+, will be used in this review, or the generic name of fluorescent dissolved organic matter (fDOM), irrespective of the naming used in described papers or the name given by the manufacturers.

2.2 Advances in sensor development

In the 1990s CE, field fluorimeters developed from single wavelength fluorimeters to multispectral and hyperspectral devices (Coble et al., 2014). In the past decade, with the advancement of technology in optical and electronical components, fluorimeters became more power-efficient, miniaturized and cheaper than ever before, while providing effective information. One direction of sensor development was oriented towards maximizing the information extracted from the device. For example, Zielinski et al. (2018) have developed a submersible sensor system that is able to record full EEMs, within a high spectral range (($\lambda_{excitation}/\lambda_{emission}$ = 220-750 nm / 200-950 nm). Another example of novel devices is the "one LED & three signals" system developed by Li et al. (2016a) for in situ measurements. The device uses a light source at 280 nm, one photodiode to measure UV 280 absorbance and two photodiodes with bandpass filters to detect peaks T and C fluorescence. Another example is the system developed by Bridgeman et al. (2015), that displays the fluorescence intensity for peaks T and C, the Raman value and the ratio T/C. The intensity of the Raman emission of water is used for normalization and fluorimeter stability check. However, only a limited number of in situ devices, mostly custom, measure this peak. Continuous measurement of the Raman emission of water would be an excellent addition to field fluorimeters to enhance comparison between instruments and sites. Other commercial devices convert fluorescence values to BOD and TOC using a proprietary algorithm and do so in real-time (for example, "The LiquID Station – ZAPS Technologies, LLC," 2018 and "UviLux Fluorometer," 2018), which may be used in wastewater treatment and drinking water plants and distribution systems. Another area of development was directed towards increasing field fluorescence versatility. One example is the next generation

devices, which are sufficiently stable to be installed on gliders, buoys and surface platforms (Cyr et al., 2019; Ferdinand et al., 2017). Also, the novel device constructed by Zielinski et al. (2018) can be installed in a moonpool in a vessel or integrated into an underwater platform.

Field devices, based on LIF, have also been slowly advancing in the past years. Before the 1990s, LIF systems were not as common as standard devices in water quality measurements, despite their elevated sensitivity and selectivity (Chen et al., 2015), due to their relatively high cost and size. LIF instruments were developed in probes with fiber cables (Rudnick and Chen, 1998), flow-through systems (Chen et al., 2015) or in LiDAR (Light Detection And Ranging) systems for remote sensing (Babichenko et al., 2016). The history of LIF and remote sensing is largely discussed by Coble et al. (2014) and since then some further studies have been undertaken with this type of system (Babichenko et al., 2016; Chen et al., 2015). Rudnick and Chen (1998) constructed a LIF system with time-resolved capabilities, which can be mounted on submersible platforms for continuous transects. Chen et al. (2015) developed a compact, low-cost and low-power system that measured Raman scattering value, peak C and Chl-a fluorescence. It used a high pulse repetition frequency laser to increase signal to noise ratio and a broadband spectrometer for effective spectral information. Babichenko et al. (2016) developed a relatively compact hyperspectral LiDAR, in terms of size and weight, increasing the systems practicality on site. The advantage of a LiDAR is that, by measuring the pulsed emitted laser through the water column and by time-gating a secondary laser echo signal, it can measure in real time both surface and subsurface DOM concentration and oil pollution. In addition, LiDARs can be installed on infrastructure (e.g. bridges) and aircraft.

Despite recent developments in field fluorimeters, there are still some limitations in terms of sensitivity, compared with benchtop spectrofluorimeters. For example, the Kallemeter sensor, developed by Zielinski et al. (2018), has a sensitivity of 34 signal-to-noise ratio (SNR) measured for the water Raman peak, while a typical benchtop spectrofluorimeter (Aqualog, Horiba, Japan) has a Water-Raman SNR of > 20,000. It is not known, though, if the water Raman peak was measured at

similar wavelengths and integration times. However, most of the fluorescence sensors do not measure the water Raman peak and instead report the limit of detection (LOD), which is not provided in the technical specifications of benchtop spectrofluorimeters. Research studies on field fluorimeters usually compare the instruments by correlating fluorescence values within a range of concentrations of standards, above the LOD, or with discrete water samples, which are used for device calibration (section 3.1). Research showing the LODs of field and laboratory instruments is scarce. Tedetti et al. (2013) determined substantially better LODs for a benchtop spectrofluorimeter (Hitachi F7000) compared to a field fluorimeter (MiniFluo-UV) with standards of phenanthrene (0.21 µg/L and 0.39 µg/L) and tryptophan (1.43 µg/L and 0.72 µg/L). Wasswa et al. (2019) also found that the benchtop fluorimeter displayed better LODs (0.003-0.677 RU) compared to field fluorimeters (127.35-218.43 RU for peak T and 8.23-3,527.99 RU for peak C) on tertiary effluents and recycled water samples spiked with pharmaceutical and oil pollutants. In addition, Cumberland et al. (2012) showed that both portable fluorimeter and benchtop spectrofluorimeter were able to detect the presence of a few bacteria per 100 mL. They highlighted, however, that instruments LODs could not be determined with accuracy, due to false negative and false positive results, at low concentrations. Also, Wasswa et al. (2019) mentioned that in complex environments, the instruments may not measure towards the minimum LOD due to background fluorescence. Although field fluorimeters have lower sensitivity and LOD ranges compared to benchtop spectrofluorimeters, they are still able to detect the same patterns and trends as laboratory instruments (Mladenov et al., 2018).

3. Steps in fluorescence in situ measurements

Several parameters and steps must be considered before and during in situ fluorescence measurements. Figure 2 presents a summary of the parameters, which have been used in field studies, for fluorimeter calibration, measurement frequency, maintenance and data correction.

3.1 Calibrations

Several steps must be undertaken for sensor calibration, as recommended by D'Ortenzio et al. (2010): a) a pre-calibration to test the precision, pressure and mechanical and electrical stability of the device; b) calibration of signal output by measuring dark and saturation counts (Zielinski et al., 2018); c) calibration of internal temperature to test its impact on sensor optical components (Cyr et al., 2017; Yamashita et al., 2015); d) calibration with distilled water at a certain temperature; e) absolute calibration with known substances.

The first step should determine the instrument drift due to environmental factors, such as pressure and aging. For the second step, D'Ortenzio et al. (2010) recommended to insert the sensor in distilled water and cover the detector with black tape for dark counts measurements. Saturation counts can be measured by placing a fluorescent object (glow stick) in front of the sensor. For the third step, Cyr et al. (2017) developed an internal temperature correction; however, it may depend on instrument, as Yamashita et al. (2015) found that temperature had no impact on optical components during in situ measurements. Two common methods have been proposed for absolute calibration of field fluorimeters: using standard substances (L-tryptophan, quinine sulfate or humic substances) and water collected from the field location (Conmy et al., 2014a; Gutierrez et al., 2014; Khamis et al., 2015). Khamis et al. (2017), (2015) used a tryptophan standard (synthetic, ≥ 98%) in dilutions ranging from 0 to 1,000 ppb on five fluorescence sensors to calibrate peak T, out of which four fluorescence sensors displayed a linear relationship ($r^2 > 0.95$) across the tested range of 0-1,000 ppb. Lee et al. (2015) used quinine sulfate standards from 0 to 100 ppb to calibrate peak C, by diluting a 1,000 ppm of quinine sulfate stock solution. Specific applications, such as measuring PAHs in water, require other standards. Cyr et al. (2019), (2017) used two calibrations for PAHs. The first calibration, included PAH standards and the second, water accommodated fraction of crude oil, which contained methylated and non-methylated hydrocarbons. In some cases, calibrating with the water under assessment (seawater, river water) was considered the best option, since calibrating large

sensors or those attached to CTD platforms with standards is operationally difficult (Baker et al., 2015; Conmy et al., 2014a, 2004; Yamashita et al., 2015). However, validation of field fluorimeters with steady state spectrofluorimeters is needed. Excellent linear relationship (r^2 = 0.70-0.98) between fluorescence measured with a benchtop spectrofluorimeter and with a field device was observed in samples from various locations (Bridgeman et al., 2015; Chen et al., 2015; Graham et al., 2015; Yamashita et al., 2015). Tedetti et al. (2010), obtained a poor correlation (r^2 = 0.55) with seawater samples, compared to correlation with standards (r^2 = 0.96). However, the measurement parameters (such as excitation wavelength or bandwidth) were not perfectly matched between the two instruments (Table S1) and Tedetti et al. (2010) compared 0.20 µm filtered samples, measured with a benchtop spectrofluorimeter, with unfiltered samples measured with the in situ fluorimeter.

3.2 Frequency of in situ measurements

The field measurement frequency should be given careful consideration, as a low measurement frequency may not provide the resolution needed to determine characteristics (Fig. 2). However, high frequency measurements may not be needed in particular environments, with reduced fDOM variation. Downing et al. (2009) found that for flux estimation, sampling intervals of 90 mins or less were sufficient. Carstea et al. (2018) showed that a 15 minutes measurement frequency was needed to determine the daily variation of fDOM concentration and to evaluate treatment process efficiency in a wastewater treatment plant. A 30 minute frequency was tested, but the data points were insufficient to assess adequately the water quality fluctuations (Carstea et al., 2018). Higher measurement frequency, below 5 minutes, was chosen for drinking water sources, rivers or recycled water assessment (Bieroza and Heathwaite, 2016; Khamis et al., 2017; Ryder et al., 2012; Saraceno et al., 2017; Singh et al., 2015), where DOM characteristics and concentration can vary at short time scales (< 2 h) (Fox et al., 2017). In addition, for sensors integrated on mobile platforms the measurement interval may decrease to one recording per second, in order to match the platform speed (Mihalevich et al., 2017).

3.3 Sensor installation and maintenance

Studies showed that field fluorimeters could be installed even in places with hostile conditions, such as a wastewater treatment plant (Carstea et al., 2018), with high humidity, relatively high organic matter in water, high flow, presence of industrial contaminants or in freshwater during winter when ice cover, limited solar power and high flow conditions were recorded (Pellerin et al., 2012). Carstea et al. (2018) found that submersible devices are more practical in wastewater treatment plants, since these were battery operated, which allowed it to work for a longer period of time during a power failure, and required less frequent cleaning (once per month) compared to cuvette-based fluorimeters.

Shutova et al. (2016) found that the choice of probe for installation was important, as one peak C probe (Cyclops C®, Turner Designs, excitation wavelength 368±17 nm, emission wavelength 470±30 nm) was more sensitive to DOM changes in fresh water, in particular at low DOM, than another peak C probe (EXO C®, Xylem YSI, excitation wavelength 365±5 nm, emission wavelength 480±40 nm). However, the latter was more effective in detecting minor changes in wastewater effluent DOM compared to other fluorimeters (Carstea et al., 2018), due to the position of the emission wavelength, close to the FWA peak, which is likely to be detected in wastewater. On the contrary, Snyder et al. (2018) found no bias in the data provided by individual sensors in a year-round monitoring across several streams. Snyder et al. (2018) also showed that no individual site drove the overall trend in the relationship between fDOM and DOC. From a total of 1.18 M data records, Snyder et al. (2018) flagged only 4.6 % of fDOM measurements by automated or manual QC procedures. Flagged data resulted from general sensor malfunctions, such as lamp failures, and localized instream events such as heavy debris deposition Snyder et al. (2018). Performing remote monitoring and knowing the instrument well before deployment, such as potential sensor error messages and erroneous values, can help solve issues immediately after they occur.

309 Routine maintenance of in situ fluorimeters depends on the device, the accessories used and the
310 monitored site, and includes device cleaning, inspection and recalibration. Sorensen et al. (2018b)
311 observed a decrease of over 40 % in fluorescence intensity after two weeks of online operation
312 caused by build-up of ferric deposits on sensor (flow-through configuration, no wipers used). Others
313 (Carstea et al., 2018; Xing et al., 2012) have not observed any reduction of the fluorescence signal
314 after extended periods of time without maintenance of the submersible fluorimeters (no wipers used).
315 For on-line measurements, device cleaning and inspection periods varied from 5 days to 6 weeks,
316 while recalibration was undertaken every week to 3 months (Fig.2). After sensor cleaning, Khamis et
317 al. (2017) detected step changes for peaks T and C, which were corrected with a linear regression
318 model. Minimal maintenance was needed for a LiDAR system for remote sensing monitoring
319 (Babichenko et al., 2016). The embedded software controlled the operation and inspection of the
320 system and provided remote access to the onshore control centre via internet access on the vessel.
321 The LiDAR optical window required cleaning after strong storms and long operation periods, but
322 this process was undertaken by the ship crew when the software prompted the alert (Babichenko et
323 al., 2016).

324 **3.4 Additional measurements and corrections**

325 After all calibrations are undertaken, careful consideration must be given to factors influencing
326 fluorescence signal as local conditions may impair the quality of the measurements (Table 1). Many
327 factors can influence the fluorescence sensor output: particles, bubbles, DOM concentration range,
328 temperature, pH, metals ions in water and biofouling (Conmy et al., 2014b; Henderson et al., 2009).
329 For example, pH may increase or decrease the fluorescence signal depending on pH range, water
330 sample and measured peak (Henderson et al., 2009). Biofouling of sensor may also significantly
331 interfere with fluorescence measurements, as biofilm can block the optical path, but it may also
332 exhibit fluorescence in the sensor range (Conmy et al., 2014b). Metal ions are also known to quench
333 fluorescence intensity, at various degrees depending on water environment or DOM composition

(Conmy et al., 2014a; Yang et al., 2017). In addition, these factors may interfere with establishing relationships between fluorescence and standard parameters, such as *E.coli* and BOD measurements (Baker et al., 2015; Khamis et al., 2017). Although fluorescence is affected by these factors (Henderson et al., 2009), two main factors are commonly corrected at in situ fluorescence data: particles (suspended and dissolved matter) and temperature.

Suspended and dissolved matter

Suspended and dissolved particles have a combined effect of scattering and absorption leading to source light attenuation, redirection of light from the detector and increase of the photons optical path (Mbaye et al., 2018; Saraceno et al., 2009). Various correction methods have been proposed to reduce the impact of suspended matter (Table 2). For example, Mbaye et al. (2018) developed a scattering correction to estimate the quantity of suspended particles in water. Others proposed correction equations depending on turbidity thresholds (de Oliveira et al., 2018; Downing et al., 2012; Khamis et al., 2017; Lee et al., 2015) (Table 2). However, at groundwater or drinking water treatment plants, (Khamis et al., 2015; Nowicki et al., 2019; Shutova et al., 2016; Sorensen et al., 2018a) reported low turbidity values and negligible impact on in situ fluorescence data, which required no correction. Khamis et al. (2017) stressed the importance of calibrating the sensors using sediment collected from the field location, while Downing et al. (2012) recommended to determine a correction factor for the specific turbidimeter that is paired with the in situ fluorimeter.

Filtration may be used to mechanically remove suspended particles before fluorescence measurements. Kowalczuk et al. (2010) found an absolute difference between filtered and unfiltered samples of -2.05 %, but with high values of RMSE of up to 35 %. They stated that a correction factor based on the correlation between filtered and unfiltered water can be applied to in situ measurements, based on a regression analysis, which must be determined for each water body. Carstea et al. (2010) and Downing et al. (2009) achieved long deployments through the addition of large surface area filters to remove large particles. Saraceno et al. (2009) showed that in situ filtered fDOM

measurements (10 µm and 0.2 µm pore size filters) displayed a stronger correlation with laboratory discrete samples measurements (r^2 = 0.99) compared to unfiltered ones. However, small pore size filtration may also remove particulate and colloidal matter that fluoresces in the peak T region (Baker et al., 2007; Bridgeman et al., 2013). This depends on the site, as Graham et al. (2015) observed no significant differences in fluorescence intensity between filtered and unfiltered groundwater samples at a landfill contaminated site. In addition, Sorensen et al. (2016) found at groundwater samples that peak T fluorescence was mostly given by the size fraction below 0.22 µm, although turbidity decreased after filtration (0.22 µm pore size filters).

Dissolved matter produces an inner filtering effect (IFE) of the fluorescence signal (Downing et al., 2012; Snyder et al., 2018). The IFE is a reduction of the emitted fluorescence intensity and/or a distortion of the band shape due to the sample matrix, which may absorb the excited and emitted radiation (Henderson et al., 2009). The traditional approach is to correct the fluorescence signal with the absorption value at 254 nm (Downing et al., 2012; Henderson et al., 2009; Snyder et al., 2018). The thresholds used for absorption are shown in Table 1. Absorption values may be determined with laboratory spectrophotometers, on discrete samples, or using field spectrophotometers. UV sensors would provide immediate results and if an online algorithm can be developed, the fluorescence data may be corrected in situ. However, UV sensors are more expensive and have relatively limited selectivity of components compared to field fluorimeters. Ruhala and Zarnetske (2017) discuss the application in tandem of UV and fluorescence sensors in freshwater systems, and present the advantages and disadvantages of both types of sensors.

Another approach to reduce the impact of IFE is to use closed-path fluorimeters. According to Downing et al. (2012), closed-path instruments suffered less signal loss from IFE compared to open-path, when water with either dissolved or suspended particulate matter was tested. However, this means that corrections should be not only site specific but also instrument specific.

Temperature

DOM fluorescence intensity is inversely related to temperature (Henderson et al., 2009), due to the impact of temperature on the rate of radiationless decay mechanisms (McKay et al., 2018a). High temperature fluctuations, during in situ studies, significantly impact the measurement session outcome (Table 1). To reduce this impact, Watras et al. (2011) developed a temperature compensation tool for peak C region using a linear regression equation and a reference temperature of 20° C (Table 2). Later, Ryder et al. (2012) proposed a similar temperature correction equation for peak C, which uses the water temperature at the time of measurement. Recently, McKay et al. (2018b) developed a correction method that accounts for apparent quantum yields changes caused by temperature. They showed that the bias in fluorescence intensity due to changes in quantum yield vary from +10% at 10°C to -30% at 55°C.

Watras et al. (2011) showed that the temperature coefficient did not depend on DOM concentration and Downing et al. (2012) observed no variation between instruments when applying the temperature correction. Nevertheless, Khamis et al. (2017) recommended calculation of a compensation coefficient specific to each instrument before deployment. In addition, Khamis et al. (2017) found that peak T required a higher compensation coefficient and was more unstable during the experiment compared to peak C. Peak T is more susceptible to thermal quenching compared to peak C, irrespective of the DOM source (Baker, 2005; Carstea et al., 2014; Khamis et al., 2017; Wasswa and Mladenov, 2018).

To improve correction efficiency, two or more parameters were included in the fluorescence signal correction protocols (Table 2). For example, de Oliveira et al. (2018) developed a sequential compensation procedure to correct temperature, turbidity and IFE on peak C fluorescence. Also, the temperature compensation tool, developed by Watras et al. (2011), was included in a robust equation that also corrected the signal attenuation caused by particles using absorption at 254 nm and turbidity (Downing et al., 2012). Saraceno et al. (2017) later developed a site- specific equation. They found that the Downing et al. (2012) initial equation overcompensated the fluorescence values by a factor

409 of 2.5 at peak turbidity, in comparison to the site-specific correction, potentially caused by different
410 particle size distributions. They recommended the equation of Downing et al. (2012) as a starting
411 point, which may perform well if the particle size is similar to the initial model.

412 In particular studies, no corrections were applied, due to low concentration of dissolved or
413 suspended matter and narrow temperature ranges in the monitored water. For example, Carstea et al.
414 (2018), Mladenov et al. (2018) and Singh et al. (2015) used uncorrected data to monitor fluctuations
415 in the fluorescence intensity of wastewater and recycled water. Since in situ fluorimeters were able to
416 detect minor changes in effluent DOM without any data correction, Carstea et al. (2018)
417 recommended using them without any corrections only for qualitative data, preliminary testing and
418 early warning of underperformance issues. Sorensen et al. (2018a) observed that groundwater sites
419 with high turbidity (>10 NTU) showed low peak T fluorescence (<1 ppb), which suggested low
420 scattering from particles. Temperature was also constant at groundwater sites (Nowicki et al., 2019;
421 Sorensen et al., 2018a). Also, Khamis et al. (2015) found little improvement of errors when the
422 temperature correction was applied to the groundwater fluorescence data. For the only in situ
423 fluorescence measurement study of drinking water treatment, Shutova et al. (2016) applied no
424 turbidity correction as the values were below 5 FNU and were considered insignificant. They found
425 that the slopes and intercepts values of fluorescence intensity curves in response to temperature were
426 different for each water type and device. However, the temperature coefficients were similar between
427 water types and devices and also similar to coefficients determined in freshwater measurements
428 studies.

429 **3.5 Towards a common protocol**

430 The large volume of studies on in situ fluorescence measurements enhances the development
431 of a common protocol, irrespective of the application and field fluorimeter. This represents one step
432 forward from reducing the gap between current experiment level and the level of fluorescence as a

standard practice in water quality monitoring. The protocol, for qualitative and quantitative monitoring, and the thresholds for data correction and calibrations are presented in Figure 3.

Either the qualitative or quantitative protocol may be used for high frequency, long-term measurements of water quality. Qualitative measurements may be achieved without any fluorimeter calibration or data correction. However, turbidity, temperature and absorption should be measured, along with fluorescence, to ensure that dissolved and particulate matter or temperature do not interfere with the fluorescence signal. For precise data, calibration with standard solutions and/or water from the source should be undertaken prior to and after the measurement sessions. Also, data correction should be achieved, either post-measurement or in real-time, to reduce the impact of IFE, scattering and temperature, using water and sediments from the site. At sites with industrial pollution, other parameters, such as metal ions, should also be measured. It was shown, for example that Cu(II) quenches the fluorescence intensity up to 28 % at municipal effluent (Yang et al., 2017) and up to 40 % at sewage (Reynolds and Ahmad, 1995). In addition, quenching varies between metals ions, fluorescence peaks and ecosystem (Coble et al., 2014), which makes their impact difficult to predict. If metal ions are detected, quenching experiments should be undertaken in the laboratory, prior to in situ measurements, with water samples from the measurement site.

The measurement frequency depends on the site. However, a frequency of at least 4 measurements/hour should be used in case of short-term monitoring on fixed platforms. The frequency may be reduced to 2 measurements/hour if long-term sessions are undertaken to prolong battery life. In case of mobile platforms, a high measurement frequency (for example one measurement per 5 seconds) may be used.

4. Fluorescence field measurement applications

4.1 Marine water

Since the early 1970s CE (Karabashev and Solovev, 1973), fluorescence sensors have been used to track pollution, such as sewage and oil spills (Cyr et al., 2019; Petrenko et al., 1997) and to

458 study the characteristics and distribution of fDOM in coastal and open oceans (Chen, 1999; Chen et
459 al., 2002; Conmy et al., 2004; Guay et al., 1999). The studies published in the last 10 years on
460 marine in situ measurements are presented in Table S1. Sewage marine pollution was tracked mostly
461 with peak T sensors. Tedetti et al. (2010) observed a sewage plume in the marine environment up to
462 850 m from the discharge point. However, when peak T was compared to *E. coli* and enterococci,
463 Tedetti et al. (2010) found a moderate to no correlation between them (Table 3), potentially due to
464 the presence, in the coastal waters, of non-microbial fluorophores contributing to peak T region.

465 Peak T fluorescence sensors were also used to track oil pollution after the Deepwater Horizon
466 oil spill in the Gulf of Mexico (Joint Analysis Group for the Deepwater Horizon Oil Spill, 2012).
467 The oil spill was detected 300 km from the source. Nevertheless, no correspondence was found
468 between the concentration of subsurface oil spill, detected with the fluorescence sensors, and
469 chemical analyses. An excellent relationship (r=0.96) between peak T fluorescence and oil
470 compounds were obtained in simulated oil pollution (Conmy et al., 2014a). However, marine water
471 contains a myriad of fluorophores, overlapping in the peak T region, making it difficult to pinpoint a
472 specific compound. Three of the most common PAHs, fluorene ($\lambda_{excitation}/\lambda_{emission}$ – 260/315 nm),
473 naphthalene ($\lambda_{excitation}/\lambda_{emission}$ – 275/340 nm) and phenanthrene ($\lambda_{excitation}/\lambda_{emission}$ – 255/360 nm),
474 which are usually detected during an oil spill, appear close to or in the region of peak T, overlapping
475 other components listed in section 2.1. For example, Tedetti et al. (2013) and Cyr et al. (2017) found
476 phenanthrene-like fluorescence in harbours and coastal areas. Nevertheless, Tedetti et al. (2013)
477 showed that the high fluorescence intensity of the phenanthrene-like peak was actually caused by
478 fluorene, another PAH. Potential solutions to this problem are to use a combination of field
479 fluorimeters, operating at wavelengths specific for each fluorophore, or to use in situ devices that
480 measure at multiple wavelengths, like the ones used by Cyr et al. (2017), Puiu et al. (2015), Tedetti
481 et al. (2010) and Zielinski et al. (2018). In addition, Tedetti et al. (2010) showed that the different
482 quantum yield of fluorophores may help at separating between compounds.

The allochthonous and autochthonous input of marine DOM were also studied with in situ fluorimeters (Table S2). The early studies on fDOM allochthonous input revealed that peak C fluorescence intensity had the highest levels in locations close to river mouths (Chen, 1999; Klinkhammer et al., 2000). These findings were confirmed by later studies (Babichenko et al., 2016; Bergamaschi et al., 2012; Chen et al., 2015) who found high fluorescence in estuaries and bays water. For example, in the Norwegian Sea, peak C fluorescence increased 3-4 times in the estuaries (Babichenko et al., 2016). Chen et al. (2002) concluded that only 10 % of the fDOM in the Mid-Atlantic Bight was supplied by rivers, although 50 % of river fDOM reached the Chesapeake Bay. Bergamaschi et al. (2012) also showed that a mangrove system supplied the estuary with an estimated 180 (± 12.6) gC cm^{-1} value, which varied depending on storm, wind or rising global sea level. The rest of fDOM was produced through marine biological activity (Chekalyuk et al., 2014; Chen et al., 2015). Without terrestrial influences, the fluorescence intensity was found as constant (Babichenko et al., 2016; Bergamaschi et al., 2012; Chen et al., 2002).

Early studies (Chen, 1999; Chen et al., 2002) showed that net production of marine fDOM occurred in spring, while net degradation occurred in summer, which was later confirmed by Kowalczuk et al. (2010), who found late-summer photodegradation of DOM. Conversely, Cyr et al. (2017) found higher peak T fluorescence intensity during the autumn months, compared to summer and spring. Cyr et al. (2017) suggested that the relationship between FOM and primary marine production may be more complex and proved that fDOM may be a good proxy for processes influencing the DOM pool. The incubation studies undertaken by Jørgensen et al. (2014), revealed highly complex processes of microbial DOM production. They found a link between DOM lability and microbial fDOM production. Jørgensen et al. (2014) suggested that fDOM formation is more pronounced at microbial degradation of semilabile DOM and speculated that this process corresponded to in situ fDOM production.

507 **4.2 Freshwater**

508 River assessment with field fluorescence aimed mainly to understand DOM concentration and
509 dynamics, in relation to autochthonous production and allochthonous input (Table S3). Several
510 studies (Carstea et al., 2010; Downing et al., 2009; Khamis et al., 2017; Saraceno et al., 2009;
511 Spencer et al., 2007b) found diurnal and semi-diurnal variation of fDOM under steady river flow
512 conditions, which indicated a variation in source and processing of DOM. For example, Spencer et
513 al. (2007b) measured high peak C values after dawn and low values in the evening. A secondary
514 peak imposed on the daily cycle was observed and was associated with zooplankton grazing
515 (Spencer et al., 2007b) or with river cross-connections with sewer systems (Carstea et al., 2010).
516 Contradicting results were found for peak T. Bieroza and Heathwaite (2016) and Carstea et al.
517 (2010) observed a daily trend for online peak T measurements, but Khamis et al. (2017) found no
518 diurnal pattern; however, variations between studies were probably caused by subtle changes in the
519 water, local fDOM characteristics or sensor sensitivity (details regarding sensors in Table S3). .

520 Fluorescence sensors allowed high resolution measurements of DOM dynamics in streams and
521 rivers over several precipitation events of various intensity and frequency. Rainfall increased the
522 river flow and terrestrial DOM input, leading to high fluorescence intensity. The degree of increase
523 varied depending on the frequency and quantity of precipitation (Bergamaschi et al., 2012; Carstea et
524 al., 2010; Mihalevich et al., 2017; Tunaley et al., 2016). In storm conditions, the first flush generated
525 the highest concentrations of fDOM, with a strong allochthonous and terrestrially derived character
526 (Mihalevich et al., 2017).

527 Several studies have shown that, after rainfall, DOM fluorescence intensity lagged behind
528 turbidity and discharge. However, reports varied from site to site, starting with < 1 h lag behind peak
529 streamflow (Pellerin et al., 2012), to 11 h behind discharge and 15 h behind turbidity (Saraceno et al.,
530 2009) and to a full day after discharge (Bergamaschi et al., 2012). It was hypothesized that this
531 relationship indicated a delayed input of high DOC concentrations from surface and shallow flow

paths on the hillslope or from a riparian source (Pellerin et al., 2012; Tunaley et al., 2016). In addition, Tunaley et al. (2016) found that warm seasons generated higher DOC concentrations compared to cold seasons, at peak discharges, with 123 % and 10 % increase respectively. Therefore, high frequency data from the fluorescence sensors enabled the study of the impact of temperature, discharge, antecedent conditions, flow paths, connectivity and the age of water sources on the temporal dynamics of DOC (Tunaley et al., 2016), helping to detect even subtle shifts in biogeochemical cycles over time scales that are difficult to measure with discrete sampling (Pellerin et al., 2012).

In addition to studying natural organic matter dynamics in freshwater, in situ fluorescence was used to detect anthropogenic DOM. For example, Carstea et al. (2010) detected oil pollution in an urban river, which was reflected in a sudden increase of high peak T fluorescence. They separated the signal of the oil pollution from the regular peak T fluorescence by the ratio between the peak at $\lambda_{excitation}$ = 225 nm and $\lambda_{excitation}$ = 280 nm and by processing the recorded in situ EEMs with self organising maps (SOM), which identified a separate cluster for oil pollution. Another important example is the application of field fluorimeter is to screen freshwater that serve as drinking water sources for the presence of bacteria. Cumberland et al. (2012) showed, in an ex-situ study, that portable devices may be used to detect low levels of total coliforms and *E.coli*. Later, Baker et al. (2015) found that the response of field fluorimeters in the presence of *E.coli* was variable (Table S3). However, they recommended using fluorescence as an initial screening tool in areas with poor sanitation.

4.3 Groundwater

Studies of groundwater contamination field measurements focused on landfill leachate (Graham et al., 2015) and microbial pollutants (Nowicki et al., 2019; Sorensen et al., 2015a, 2016, 2018b, 2018a) (Table S4). Graham et al. (2015) identified variations in fluorescence intensity in an aquifer affected by landfill leachate. The results implied that the in situ fluorimeter most probably

557 detected a combination of reprocessed, allochthonous humic material and FWAs (Graham et al.,
558 2015). fDOM decreased with an order of magnitude from the landfill site to the edge of the plume,
559 ~650 m away. Despite the positive results, Graham et al. (2015) recommended the addition of
560 electrical conductivity or other methods in the monitoring scheme for higher precision in delineating
561 the leachate plume.

562 A series of studies (Baker et al., 2015; Nowicki et al., 2019; Sorensen et al., 2018b, 2018a,
563 2016, 2015a, 2015b) was undertaken to determine if peak T fluorescence can be used as a real-time
564 indicator of fecal contamination. Peak T fluorescence was found to be the best predictor of
565 presence/absence and number of thermotolerant coliforms (Sorensen et al., 2015a). Peak T
566 fluorescence is more mobile and resilient in groundwater compared to thermotolerant coliform
567 (Sorensen et al., 2015b), as fluorescence can also measure the degradation by-products of bacteria.
568 Peak T fluorescence was also elevated at water supplies polluted with bacterial DNA markers. Baker
569 et al. (2015) showed that the relationship between peak T fluorescence and *E. coli* weakened in
570 complex environments, with multiple pollution sources and a large array of fluorophores unrelated to
571 microbial contamination.

572 Later, Sorensen et al. (2016) were able to determine a sanitary risk score of drinking water
573 sources depending on the distance from a toilet. They found that 91 % of the water supplies that
574 presented thermotolerant coliforms were located within 10 m of a toilet, presenting high sanitary risk
575 scores. Based on these initial studies on peak T fluorescence measurements, Sorensen et al. (2018a)
576 set up threshold values to classify contamination with thermotolerant coliforms. They suggested a
577 peak T threshold of >1.3 ppb for low risk, >2.4 ppb for medium, > 6.9 ppb for high and > 27.1 ppb
578 for very high.

579 Similarly, Nowicki et al. (2019) developed risk classes based on *E. coli* and peak T measured,
580 in real-time, in groundwater. Using three World Health Organization defined classes (very high,
581 high, and low/intermediate), they demonstrated that the risk indicated by peak T fluorescence was

not significantly different from that indicated by *E. coli* (p=0.85). Nowicki et al. (2019) recommended not to use peak T fluorescence as a proxy for *E. coli* on an individual sample basis, but for groundwater risk assessments, by identifying priority sample sites, and to understand spatiotemporal variability. In addition, peak T fluorescence may be used for high frequency measurements and communication of risk, followed by thorough laboratory investigation.

4.4 Engineered water systems

The development of new and powerful in situ fluorimeters, in the past five years, encouraged researchers to test the performance and robustness of the devices in engineered water systems. Although few studies were conducted, the results were promising in determining the effectiveness of treatment processes. Studies on field fluorescence assessment of engineered water systems included drinking water treatment plants (Shutova et al., 2016), wastewater treatment plants (Carstea et al., 2018; Mladenov et al., 2018) and recycled water plants (Singh et al., 2015) (Table S5). Shutova et al. (2016) identified daily changes in DOM at the untreated water and a stable DOM at the treated water. In addition, Shutova et al. (2016) observed that the character of DOM changed after each treatment process, by analyzing the ratio between peaks C and T. They concluded that this parameter may be used to determine DOM removal in drinking water treatment plants.

Despite multiple indications in the literature that fluorescence sensors can be used for in situ measurements of wastewater treatment processes (Carstea et al., 2016; Chong et al., 2013; Mesquita et al., 2017), only two studies have been published so far (Carstea et al., 2018; Mladenov et al., 2018). The main reason for the slow advancement is the difficulty of using this technique in the hostile environment of a wastewater treatment plant (i.e. high humidity, high quantity of particulate and DOM even in treated wastewater, high susceptibility to biofilm formation on optical surfaces etc.). Moreover, Wasswa et al. (2019) found that the LOD of fluorescence sensors increases due to the high background DOM fluorescence in effluents. They showed, in an ex-situ experiment, that pharmaceutical, personal care products and oil contaminants were more difficult to discern in tertiary

effluents than in final treated water. Despite these issues, Carstea et al. (2018) reported minor changes in fluorescence caused by underperformance issues, following power failures at the treatment plant. In addition, they detected changes in DOM concentration due to the addition of activated sludge mixed liquor, dilution by precipitation and increased flowrate due to peak household water usage. Mladenov et al. (2018) also found that fDOM varied depending on the patterns of household wastewater generation. Mladenov et al. (2018) showed that peak T fluorescence was preferentially removed by the anaerobic baffled reactor, while peak C was effectively removed by wetland cells.

Some attention was also given to fluorescence online measurements of recycled water systems. Hambly et al. (2015) showed that field fluorimeters may be used to detect cross-connections between recycled water supply and the potable water supply. Also, Singh et al. (2015) monitored fluorescence at reverse osmosis feed and permeate stages within two recycled water treatment plants. They observed that the relationship between peak C fluorescence and transmembrane pressure increased as flow decreased due to biofouling on membrane. These results may help to identify fouled membranes or membranes suspected of integrity breaches. Recently, Aftab et al. (2019) found that peak T fraction was the main foulant component in membranes and showed this peak may also be used to monitor membrane permeability and flux recovery. Singh et al. (2015) suggested placing multiple sensors at strategic locations to obtain the best compromise between costs involved in installing a sensor network in large reverse osmosis systems and the information needed to detect underperformance issues. They also suggested interfacing fluorescence devices to supervisory control and data acquisitions (SCADA) systems of water treatment plants.

5 Future perspectives

Fluorescence devices represent excellent tools in long-term, high frequency, in situ measurements of aquatic environments. Most of the in situ fluorescence studies, between 2009-2018, were undertaken of freshwater and the least on engineered water systems (Fig. 4). However, there are

still some challenges to be addressed in future studies (Table 3). One challenge is to separate between compounds whose fluorescence emission overlaps. Since in situ fluorimeters can be left unattended for weeks or even months, this can only be achieved by measuring at multiple fluorescence emission wavelengths, more specific fluorescence emission regions, or multiple water quality parameters. Separation of components may be undertaken post-measurement using complex data processing algorithms. Parallel Factor Analysis (PARAFAC), SOM or Constraint Randomised Non-negative Factor Analysis (CRNFA) have been proposed and used separate or combined mainly to correct data, remove scattering and decompose peaks (Carstea et al., 2010; Cuss et al., 2019; Kumar, 2018; Murphy et al., 2013). The main disadvantages in using complex processing techniques, are that they require training, some basic knowledge in data modeling and a database of fluorescence spectra as input data. Steps have been taken to simplify PARAFAC processing, which is the most common method, with the EEMizer (Bro and Vidal, 2011), while an on-line database was created to enhance comparison and data interpretation (Murphy et al., 2014). These tools are freely available, ensuring that a growing number of researchers can apply and improve them for in situ measurements. Until then, however, observing relative changes in the fluorescence signal, with single or two wavelengths devices, may be useful in most water quality monitoring applications, such as assessing daily fDOM variation, water treatment process control or pollution early warning.

Another challenge is to predict online the disinfection by-products formation potential, in drinking water treatment plants, using field fluorimeters. Disinfection by-products are formed mainly by the reaction between disinfectants and natural OM (Mian et al., 2018). Past studies have proven the link between disinfection by-products precursors and fluorescence (Bridgeman et al., 2011; Watson et al., 2018; Williams et al., 2019), and developed predictive models based on this relationship (Peleato et al., 2018). Li et al. (2016a) used a portable device to evaluate ex-situ the potential to predict disinfection by-products and found a good relationship with peak C (r^2 = 0.71-0.73). There are no truly predictive models for disinfection by-products (Brown et al., 2011), but

fluorescence may help improve their predictive power and may further facilitate the control of drinking water treatment processes.

Another research gap is to establish relationships between water quality parameters and fluorescence peaks across environments. The obstacles arise from the complex nature of fDOM, varied fDOM behaviour in the environment and the lack of standards to quantify main fluorescence peaks. As shown in section 3.1, a partial quantification of field fluorimeters may be achieved with standards, such as tryptophan, humic substances or PAHs. However, the actual composition of fDOM in water is relatively unknown, with potential several other fluorophores contributing to peaks T and C fluorescence, at the same degree or higher compared to the used standards. Consequently, in situ fluorescence measurements may only proxies for chemical and biological properties, which are of fundamental interest to water managers and scientists. Also, the fluorescence sensors effectiveness as proxies must be continuously evaluated. So far, in situ fluorescence studies showed that the relationship between DOC and peak C is strong in most environments: r^2 = 0.49-0.99 at coastal sites, r^2 = 0.74-0.99 at freshwater sites and r^2 = 0.85-0.93 at engineered water systems (Tables 3 and S2-S5). Thus, peak C can be an excellent, direct proxy for DOC concentration, in environments where the influence of terrestrial input is high. However, the relationship between fluorescence and DOC improves when corrections (for turbidity in particular) are applied or when samples are filtered (Downing et al., 2012; Khamis et al., 2017; Kowalczuk et al., 2010). Correction of data or removal of particles would improve prediction of DOC, especially during storms when high quantities of particles may underestimate DOM fluxes (Downing et al., 2012). In addition, peak C can be an indirect proxy of salinity, in particular cases (Kowalczuk et al., 2010) (Table S2). In situ fluorescence studies also showed that peak T correlated with *E. coli* (r^2 = 0.71-0.95 at freshwater, r^2 = 0.59-0.77 at groundwater and r^2 = 0.66 at marine water), but only at sites with sanitation problems (Tables S2-S4). Peak T also correlated with COD (r^2 = 0.75) at engineered water systems (Table S5). Nevertheless, the relationship between peak T and BOD is valid at most sites (Baker et al., 2014;

682 Coble et al., 2014; Hudson et al., 2008). However, at in situ measurements, the relationship was
683 strong only at turbidity corrected peak T data (Khamis et al., 2017) (Table S3). A common protocol
684 may help at improving some of the correlation coefficients and at harmonizing the output of various
685 studies. Once harmonized, fluorescence data may be included in predictive models for improved
686 environmental scenarious and for understanding the combined effect and transport of pollutants.
687 Furthermore, field fluorimeters may be part of Wi-Fi based wireless sensor networks for water
688 quality monitoring in smart cities concept, using various communication protocols under the idea of
689 the Internet of Things (Chen and Han, 2018; Dong et al., 2015; Pule et al., 2017). Finally, by
690 increased promotion of the technique to the water utilities, a platform of long-term, high-frequency
691 data would be developed, useful for early warning, immediate response from the practitioners and for
692 research on fDOM dynamics, provided that access to data is allowed.

693 **6 Conclusions**

694 High frequency UVA and blue light fluorescence data helped to model DOC flux, to evaluate
695 temporal dynamics of DOC production and to determine subtle changes in biogeochemical cycles, in
696 streams and rivers. Additionally, fluorescence sensors helped to understand the processes responsible
697 of DOM production in marine environments. In engineered water systems, fluorescence devices were
698 effective in detecting DOM removal and treatment process failure. Moreover, fluorescence served as
699 a tool for prescreening and for establishing sanitary risk scores in rivers and groundwaters, including
700 potable water sources in regions of poor sanitation. All this information is difficult to obtain with
701 current methods or with discrete sampling.

702 Across the world, the water quality is deteriorating at a pace never before encountered.
703 Although successful in monitoring and detecting pollution in serious cases throughout the USA,
704 water authorities face budget cuts coupled with a continuous reduction in water quality (van Beynen,
705 2018), threatening to overwhelm the capacity to take immediate actions for the environment and
706 public health protection. In Europe, only developed industrialized countries managed to reduce the

environmental impact of pollutants after the first cycle of the Water Framework Directive implementation, in 2015 (Müller-Grabherr et al., 2014). Overall, the number of European surface water bodies in "good ecological status" increased with only 10 % (van Rijswick and Backes, 2015). These issues call for the use of an effective monitoring tool that includes cheap, reliable and fast methods, such as fluorescence spectroscopy, which has demonstrated use as a proxy for DOC, BOD and in regions of poor sanitation, *E. coli*. Field fluorimeters are a key component in powerful monitoring tools, leading to better decisions in water management and environmental policy.

Acknowledgements

Authors, E.M. Carstea and C.L. Popa, acknowledge the support of the Ministry of Research and Innovation, CNCS-UEFISCDI, project number PN-III-P1-1.1-TE-2016-0646, within PNCDI III, project number 18N/2019, under the Core Program OPTRONICA VI, project number 19PFE/17.10.2018 and project number 152/2016, SMIS 108109. The graphical abstract was prepared using Mind the Graph.

References

Aftab, B., Ok, Y.S., Cho, J., Hur, J., 2019. Targeted removal of organic foulants in landfill leachate in forward osmosis system integrated with biochar/activated carbon treatment. Water Res. 160, 217–227. https://doi.org/10.1016/J.WATRES.2019.05.076

Babichenko, S., Poryvkina, L., Rebane, O., Sobolev, I., 2016. Compact HLIF LiDAR for marine applications. Int. J. Remote Sens. 37, 3924–3937. https://doi.org/10.1080/01431161.2016.1204479

Baker, A., 2005. Thermal fluorescence quenching properties of dissolved organic matter. Water Res. 39, 4405–4412. https://doi.org/10.1016/j.watres.2005.08.023

Baker, A., Andersen, M.S., Marjo, C.E., Zainuddin, N.S., Rutlidge, H., Graham, P.W., Henderson,

732 R.K., 2014. Investigation of Pollution in Rivers and Groundwater by Fluorescence. Encycl.
733 Anal. Chem. https://doi.org/10.1002/9780470027318.a9412
734 Baker, A., Cumberland, S.A., Bradley, C., Buckley, C., Bridgeman, J., 2015. To what extent can
735 portable fluorescence spectroscopy be used in the real-time assessment of microbial water
736 quality? Sci. Total Environ. 532, 14–19. https://doi.org/10.1016/j.scitotenv.2015.05.114
737 Baker, A., Elliott, S., Lead, J.R., 2007. Effects of filtration and pH perturbation on freshwater
738 organic matter fluorescence. Chemosphere 67, 2035–2043.
739 https://doi.org/10.1016/j.chemosphere.2006.11.024
740 Barsotti, F., Ghigo, G., Vione, D., 2016. Computational assessment of the fluorescence emission of
741 phenol oligomers: A possible insight into the fluorescence properties of humic-like substances
742 (HULIS). J. Photochem. Photobiol. A Chem. 315, 87–93.
743 https://doi.org/10.1016/j.jphotochem.2015.09.012
744 Belzile, C., Roesler, C.S., Christensen, J.P., Shakhova, N., Semiletov, I., 2006. Fluorescence
745 measured using the WETStar DOM fluorometer as a proxy for dissolved matter absorption.
746 Estuar. Coast. Shelf Sci. 67, 441–449. https://doi.org/10.1016/j.ecss.2005.11.032
747 Bergamaschi, B.A., Krabbenhoft, D.P., Aiken, G.R., Patino, E., Rumbold, D.G., Orem, W.H., 2012.
748 Tidally driven export of dissolved organic carbon, total mercury, and methylmercury from a
749 mangrove-dominated estuary. Environ. Sci. Technol. 46, 1371–1378.
750 https://doi.org/10.1021/es2029137
751 Bieroza, M., Baker, A., Bridgeman, J., 2009. Exploratory analysis of excitation-emission matrix
752 fluorescence spectra with self-organizing maps as a basis for determination of organic matter
753 removal efficiency at water treatment works. J. Geophys. Res. Biogeosciences 114, 1–8.
754 https://doi.org/10.1029/2009JG000940
755 Bieroza, M.Z., Heathwaite, A.L., 2016. Unravelling organic matter and nutrient biogeochemistry in
756 groundwater-fed rivers under baseflow conditions: Uncertainty in in situ high-frequency

757 analysis. Sci. Total Environ. 572, 1520–1533.
758 https://doi.org/10.1016/J.SCITOTENV.2016.02.046
759 Bridgeman, J., Baker, A., Brown, D., Boxall, J.B., 2015. Portable LED fluorescence instrumentation
760 for the rapid assessment of potable water quality. Sci. Total Environ. 524–525, 338–346.
761 https://doi.org/10.1016/j.scitotenv.2015.04.050
762 Bridgeman, J., Baker, A., Carliell-Marquet, C., Carstea, E.M., 2013. Determination of changes in
763 wastewater quality through a treatment works using fluorescence spectroscopy. Environ.
764 Technol. 34, 3069–3077. https://doi.org/10.1080/09593330.2013.803131
765 Bridgeman, J., Bieroza, M., Baker, A., 2011. The application of fluorescence spectroscopy to organic
766 matter characterisation in drinking water treatment. Rev. Environ. Sci. Biotechnol. 10, 277–290.
767 https://doi.org/10.1007/s11157-011-9243-x
768 Bro, R., Vidal, M., 2011. EEMizer: Automated modeling of fluorescence EEM data. Chemom. Intell.
769 Lab. Syst. 106, 86–92. https://doi.org/10.1016/j.chemolab.2010.06.005
770 Brown, D., Bridgeman, J., West, J.R., 2011. Predicting chlorine decay and THM formation in water
771 supply systems. Rev. Environ. Sci. Biotechnol. 10, 79–99. https://doi.org/10.1007/s11157-011-
772 9229-8
773 Carstea, E.M., Baker, A., Bieroza, M., Reynolds, D., 2010. Continuous fluorescence excitation-
774 emission matrix monitoring of river organic matter. Water Res. 44, 5356–5366.
775 https://doi.org/10.1016/j.watres.2010.06.036
776 Carstea, E.M., Baker, A., Bieroza, M., Reynolds, D.M., Bridgeman, J., 2014. Characterisation of
777 dissolved organic matter fluorescence properties by PARAFAC analysis and thermal
778 quenching. Water Res. 61, 152–161. https://doi.org/10.1016/j.watres.2014.05.013
779 Carstea, E.M., Bridgeman, J., Baker, A., Reynolds, D.M., 2016. Fluorescence spectroscopy for
780 wastewater monitoring: A review. Water Res. 95, 206–219.
781 https://doi.org/10.1016/j.watres.2016.03.021

782 Carstea, E.M., Zakharova, Y.S., Bridgeman, J., 2018. Online fluorescence monitoring of effluent
783 organic matter in wastewater treatment plants. J. Environ. Eng. 144, 1–9.
784 https://doi.org/10.1061/(ASCE)EE.1943-7870.0001360.
785 Chekalyuk, A., Barnard, A., Quigg, A., Hafez, M., Zhao, Y., 2014. Aquatic laser fluorescence
786 analyzer: field evaluation in the northern Gulf of Mexico. Opt. Express 22, 21641–21656.
787 https://doi.org/10.1364/OE.22.021641
788 Chen, P., Pan, D., Mao, Z., Tao, B., 2015. Detection of water quality parameters in Hangzhou Bay
789 using a portable laser fluorometer. Mar. Pollut. Bull. 93, 163–171.
790 https://doi.org/10.1016/j.marpolbul.2015.01.023
791 Chen, R.F., 1999. In situ fluorescence measurements in coastal waters. Org. Geochem. 30, 397–409.
792 https://doi.org/10.1016/S0146-6380(99)00025-X
793 Chen, R.F., Zhang, Y., Vlahos, P., Rudnick, S.M., 2002. The fluorescence of dissolved organic
794 matter in the Mid-Atlantic Bight. Deep. Res. Part II Top. Stud. Oceanogr. 49, 4439–4459.
795 https://doi.org/10.1016/S0967-0645(02)00165-0
796 Chen, Y., Han, D., 2018. Water quality monitoring in smart city: A pilot project. Autom. Constr. 89,
797 307–316. https://doi.org/10.1016/J.AUTCON.2018.02.008
798 Chong, S.S., Aziz, A.R.A., Harun, S.W., 2013. Fibre optic sensors for selected wastewater
799 characteristics. Sensors 13, 8640–8668. https://doi.org/10.3390/s130708640
800 Christman, R., Arnquist, J., 1969. Fluorescence techniques in detection of organics in water.
801 A.S.T.M. Spec. Tech. Publ. 448, 96–115.
802 Cisek, M., Colao, F., Demetrio, E., Di Cicco, A., Drozdowska, V., Fiorani, L., Goszczko, I., Lazic,
803 V., Okladnikov, I.G., Palucci, A., Piechura, J., Poggi, C., Sighicelli, M., Walczowski, W.,
804 Wieczorek, P., 2010. Remote and local monitoring of dissolved and suspended fluorescent
805 organic matter off the svalbard. J. Optoelectron. Adv. Mater. 12, 1604–1618.
806 Coble, P.G., Spencer, R.G.M., Baker, A., Reynolds, D.M., 2014. Aquatic Organic Matter

807 Fluorescence, in: Coble, P.G., Lead, J., Baker, A., Reynolds, D.M., Spencer, R.G.M. (Eds.),
808 Aquatic Organic Matter Fluorescence. Cambridge University Press, New York, pp. 75–122.
809 Conmy, R.N., Coble, P.G., Del Castillo, C.E., 2004. Calibration and performance of a new in situ
810 multi-channel fluorometer for measurement of colored dissolved organic matter in the ocean.
811 Cont. Shelf Res. 24, 431–442. https://doi.org/10.1016/j.csr.2003.10.010
812 Conmy, R.N., Coble, P.G., Farr, J., Wood, M., Lee, K., Pegau, W.S., Walsh, I., Koch, C.,
813 Abercrombie, M., Miles, S., Lewis, M., Ryan, S., Robinson, B., King, T. a, Kelble, C.R.,
814 Lacoste, J., 2014a. Submersible optical sensors exposed to chemically-dispersed crude oil: wave
815 tank simulations for improved oil spill monitoring. Environ. Sci. Technol. 48, 1803–1810.
816 https://doi.org/10.1021/es404206y
817 Conmy, R.N., Del Castillo, C.E., Downing, B.D., Chen, R.F., 2014b. Experimental design and
818 quality assurance: in situ fluorescence instrumentation, in: Coble, P.G., Lead, J.R., Baker, A.,
819 Reynolds, D.M., Spencer, R.G.M. (Eds.), Aquatic Organic Matter Fluorescence. Cambridge
820 University Press, New York, pp. 190–230.
821 Cumberland, S., Bridgeman, J., Baker, A., Sterling, M., Ward, D., 2012. Fluorescence spectroscopy
822 as a tool for determining microbial quality in potable water applications. Environ. Technol. 33,
823 687–693. https://doi.org/10.1080/09593330.2011.588401
824 Cuss, C.W., Donner, M.W., Noernberg, T., Pelletier, R., Shotyk, W., 2019. EEM-PARAFAC-SOM
825 for assessing variation in the quality of dissolved organic matter: simultaneous detection of
826 differences by source and season. Environ. Chem. 16, 360-374.
827 https://doi.org/10.1071/EN19016
828 Cyr, F., Tedetti, M., Besson, F., Beguery, L., Doglioli, A.M., Petrenko, A.A., Goutx, M., 2017. A
829 new glider-compatible optical sensor for dissolved organic matter measurements: test case from
830 the NW Mediterranean Sea. Front. Mar. Sci. 4, 1–19. https://doi.org/10.3389/fmars.2017.00089
831 Cyr, F., Tedetti, M., Besson, F., Bhairy, N., Goutx, M., 2019. A glider-compatible optical sensor for

the detection of polycyclic aromatic hydrocarbons in the marine environment. Front. Mar. Sci. 6, 110. https://doi.org/10.3389/fmars.2019.00110

D'Ortenzio, F., Thierry, V., Eldin, G., Claustre, H., Testor, P., Coatanoan, C., Guinet, C., Poteau, A., Prieur, L., Lefevre, D., Bourrin, F., Carval, T., Goutx, M., Garçon, V., Thouron, D., Lacombe, M., Lherminier, P., Loisiel, H., Mortier, L., Antoine, D., 2010. White book on oceanic autonomous platforms for biogeochemical studies : instrumentation and measure. PABIM Wihte B. https://doi.org/10.13140/RG.2.1.3706.5763

de Oliveira, G., Bertone, E., Stewart, R., Awad, J., Holland, A., O'Halloran, K., Bird, S., 2018. Multi-parameter compensation method for accurate in situ fluorescent dissolved organic matter monitoring and properties characterization. Water 10, 1146,1–20. https://doi.org/10.3390/w10091146

Dong, J., Wang, G., Yan, H., Xu, J., Zhang, X., 2015. A survey of smart water quality monitoring system. Environ. Sci. Pollut. Res. 22, 4893–4906. https://doi.org/10.1007/s11356-014-4026-x

Downing, B.D., Boss, E., Bergamaschi, B. a., Fleck, J. a., Lionberger, M. a., Ganju, N.K., Schoellhamer, D.H., Fujii, R., 2009. Quantifying fluxes and characterizing compositional changes of dissolved organic matter in aquatic systems in situ using combined acoustic and optical measurements. Limnol. Oceanogr. Methods 7, 119–131. https://doi.org/10.4319/lom.2009.7.119

Downing, B.D., Pellerin, B.A., Bergamaschi, B.A., Saraceno, J.F., Kraus, T.E.C., 2012. Seeing the light: The effects of particles, dissolved materials, and temperature on in situ measurements of DOM fluorescence in rivers and streams. Limnol. Oceanogr. Methods 10, 767–775. https://doi.org/10.4319/lom.2012.10.767

Fellman, J.B., Hood, E., Spencer, R.G.M., 2010. Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review. Limnol. Oceanogr. 55, 2452–2462. https://doi.org/10.4319/lo.2010.55.6.2452

857 Ferdinand, O.D., Friedrichs, A., Miranda, M.L., Vos, D., Zielinski, O., 2017. Next generation
858 fluorescence sensor with multiple excitation and emission wavelengths - NeXOS MatrixFlu-
859 UV. Ocean. 2017 - Aberdeen 2017-Octob, 1–6.
860 https://doi.org/10.1109/OCEANSE.2017.8084809
861 Fox, B.G., Thorn, R.M.S., Anesio, A.M., Reynolds, D.M., 2017. The in situ bacterial production of
862 fluorescent organic matter; an investigation at a species level. Water Res. 125, 350–359.
863 https://doi.org/10.1016/j.watres.2017.08.040
864 Graham, P.W., Baker, A., Andersen, M.S., Acworth, I., 2015. Field measurement of fluorescent
865 dissolved organic material as a means of early detection of leachate plumes. Water. Air. Soil
866 Pollut. 226, 1–18. https://doi.org/10.1007/s11270-015-2475-6
867 Guay, C.K., Klinkhammer, G.P., Kenison Falkner, K., Benner, R., Coble, P.G., Whitledge, T.E.,
868 Black, B., Bussell, F.J., Wagner, T.A., 1999. High-resolution measurements of dissolved
869 organic carbon in the Arctic Ocean by in situ fiber-optic spectrometry. Geophys. Res. Lett. 26,
870 1007–1010. https://doi.org/10.1097/HMR.0000000000000021
871 Gutierrez, A., Zhang, Y., Assaad, A., France, X., Adouani, N., Pons, M.N., 2014. Assessment of
872 field fluorometers. Water Sci. Technol. 70, 1335–1340. https://doi.org/10.2166/wst.2014.381
873 Hambly, A.C., Henderson, R.K., Baker, A., Stuetz, R.M., Khan, S.J., 2015. Application of portable
874 fluorescence spectrophotometry for integrity testing of recycled water dual distribution systems.
875 Appl. Spectrosc. 69, 124–129. https://doi.org/10.1366/14-07513
876 Henderson, R.K., Baker, A., Murphy, K.R., Hambly, A., Stuetz, R.M., Khan, S.J., 2009.
877 Fluorescence as a potential monitoring tool for recycled water systems: A review. Water Res.
878 43, 863–881. https://doi.org/10.1016/j.watres.2008.11.027
879 Hu, B., Wang, P., Wang, C., Qian, J., Hou, J., Cui, X., Zhang, N., 2017. The effect of anthropogenic
880 impoundment on dissolved organic matter characteristics and copper binding affinity: Insights
881 from fluorescence spectroscopy. Chemosphere 188, 424–433.

https://doi.org/10.1016/J.CHEMOSPHERE.2017.09.023

Hudson, N., Baker, A., Reynolds, D., 2007. Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters—a review. River Res. Appl. 23, 631–649. https://doi.org/10.1002/rra.1005

Hudson, N., Baker, A., Ward, D., Reynolds, D.M., Brunsdon, C., Carliell-Marquet, C., Browning, S., 2008. Can fluorescence spectrometry be used as a surrogate for the Biochemical Oxygen Demand (BOD) test in water quality assessment? An example from South West England. Sci. Total Environ. 391, 149–158. https://doi.org/10.1016/j.scitotenv.2007.10.054

Jiang, T., Skyllberg, U., Björn, E., Green, N.W., Tang, J., Wang, D., Gao, J., Li, C., 2017. Characteristics of dissolved organic matter (DOM) and relationship with dissolved mercury in Xiaoqing River-Laizhou Bay estuary, Bohai Sea, China. Environ. Pollut. 223, 19–30. https://doi.org/10.1016/J.ENVPOL.2016.12.006

Joint Analysis Group for the Deepwater Horizon Oil Spill, N., 2012. Review of subsurface dispersed oil and oxygen levels associated with the Deepwater Horizon MC252 spill of national signifi cance, NOAA Technical Report NOS.

Jørgensen, L., Stedmon, C.A., Granskog, M.A., Middelboe, M., 2014. Tracing the long-term microbial production of recalcitrant fluorescent dissolved organic matter in seawater. Geophys. Res. Lett. 41, 2481–2488. https://doi.org/10.1002/ 2014GL059428

Karabashev, G.S., Solovev, A.N., 1973. The IPF 70 submersible pulse fluorometer for marine research. Oceanology 13, 361–366.

Kellerman, A.M., Dittmar, T., Kothawala, D.N., Tranvik, L.J., 2014. Chemodiversity of dissolved organic matter in lakes driven by climate and hydrology. Nat. Commun. 5, 1–8. https://doi.org/10.1038/ncomms4804

Khamis, K., Bradley, C., Stevens, R., Hannah, D.M., 2017. Continuous field estimation of dissolved organic carbon concentration and biochemical oxygen demand using dual-wavelength

907 fluorescence, turbidity and temperature. Hydrol. Process. 31, 540–555.
908 https://doi.org/10.1002/hyp.11040
909 Khamis, K., Sorensen, J.P.R., Bradley, C., Hannah, D.M., Lapworth, D.J., Stevens, R., 2015. In situ
910 tryptophan-like fluorometers: assessing turbidity and temperature effects for freshwater
911 applications. Environ. Sci. Process. Impacts 17, 740–752. https://doi.org/10.1039/c5em00030k
912 Klinkhammer, G.P., McManus, J., Colbert, D., Rudnicki, M.D., 2000. Behavior of terrestrial
913 dissolved organic matter at the continent-ocean boundary from high-resolution distributions.
914 Geochim. Cosmochim. Acta 64, 2765–2774. https://doi.org/10.1016/S0016-7037(99)00370-1
915 Korshin, G. V., Sgroi, M., Ratnaweera, H., 2018. Spectroscopic surrogates for real time monitoring
916 of water quality in wastewater treatment and water reuse. Curr. Opin. Environ. Sci. Heal. 2, 12–
917 19. https://doi.org/10.1016/j.coesh.2017.11.003
918 Kowalczuk, P., Zabłocka, M., Sagan, S., Kuliński, K., 2010. Fluorescence measured in situ as a
919 proxy of CDOM absorption and DOC concentration in the Baltic Sea. Oceanologia 52, 431–
920 471. https://doi.org/10.5697/oc.52-3.431
921 Kumar, K., 2018. Processing Excitation-Emission Matrix Fluorescence and Total Synchronous
922 Fluorescence Spectroscopy Data Sets with Constraint Randomised Non-negative Factor
923 Analysis: a Novel Fluorescence Based Analytical Procedure to Analyse the Multifluorophoric
924 Mixtures. J. Fluoresc. 28, 1075–1092. https://doi.org/10.1007/s10895-018-2271-y
925 Laane, R.W.P.M., 1982. Influence of pH on the fluorescence of dissolved organic matter. Mar.
926 Chem. 11, 395–401.
927 Lee, E.J., Yoo, G.Y., Jeong, Y., Kim, K.U., Park, J.H., Oh, N.H., 2015. Comparison of UV-VIS and
928 FDOM sensors for in situ monitoring of stream DOC concentrations. Biogeosciences 12, 3109–
929 3118. https://doi.org/10.5194/bg-12-3109-2015
930 Li, W.T., Jin, J., Li, Q., Wu, C.F., Lu, H., Zhou, Q., Li, A.M., 2016a. Developing LED UV
931 fluorescence sensors for online monitoring DOM and predicting DBPs formation potential

during water treatment. Water Res. 93, 1–9. https://doi.org/10.1016/j.watres.2016.01.005

Li, W.T., Majewsky, M., Abbt-Braun, G., Horn, H., Jin, J., Li, Q., Zhou, Q., Li, A.M., 2016b. Application of portable online LED UV fluorescence sensor to predict the degradation of dissolved organic matter and trace organic contaminants during ozonation. Water Res. 101, 262–271. https://doi.org/10.1016/j.watres.2016.05.090

Lipczynska-Kochany, E., 2018. Effect of climate change on humic substances and associated impacts on the quality of surface water and groundwater: A review. Sci. Total Environ. 640–641, 1548–1565. https://doi.org/10.1016/J.SCITOTENV.2018.05.376

Mast, M.A., Murphy, S.F., Clow, D.W., Penn, C.A., Sexstone, G.A., 2016. Water-quality response to a high-elevation wildfire in the Colorado Front Range. Hydrol. Process. 30, 1811–1823. https://doi.org/10.1002/hyp.10755

Mbaye, M., Diaw, P.A., Gaye-Saye, D., Le Jeune, B., Cavalin, G., Denis, L., Aaron, J.J., Delmas, R., Giamarchi, P., 2018. Development of online automatic detector of hydrocarbons and suspended organic matter by simultaneously acquisition of fluorescence and scattering. Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 192, 117–121. https://doi.org/10.1016/j.saa.2017.11.004

McKay, G., Korak, J.A., Erickson, P.R., Latch, D.E., McNeill, K., Rosario-Ortiz, F.L., 2018a. The Case Against Charge Transfer Interactions in Dissolved Organic Matter Photophysics. Environ. Sci. Technol. 52, 406–414. https://doi.org/10.1021/acs.est.7b03589

McKay, G., Korak, J.A., Rosario-Ortiz, F.L., 2018b. Temperature Dependence of Dissolved Organic Matter Fluorescence. Environ. Sci. Technol. 52, 9022–9032. https://doi.org/10.1021/acs.est.8b00643

Mesquita, D.P., Quintelas, C., Amaral, A.L., Ferreira, E.C., 2017. Monitoring biological wastewater treatment processes: recent advances in spectroscopy applications. Rev. Environ. Sci. Biotechnol. 16, 395–424. https://doi.org/10.1007/s11157-017-9439-9

Mian, H.R., Hu, G., Hewage, K., Rodriguez, M.J., Sadiq, R., 2018. Prioritization of unregulated

957 disinfection by-products in drinking water distribution systems for human health risk
958 mitigation: A critical review. Water Res. 147, 112–131.
959 https://doi.org/10.1016/J.WATRES.2018.09.054
960 Mihalevich, B.A., Horsburgh, J.S., Melcher, A.A., 2017. High-frequency measurements reveal
961 spatial and temporal patterns of dissolved organic matter in an urban water conveyance.
962 Environ. Monit. Assess. 189, 1–19. https://doi.org/10.1007/s10661-017-6310-y
963 Mladenov, N., Bigelow, A., Pietruschka, B., Palomo, M., Buckley, C., 2018. Using submersible
964 fluorescence sensors to track the removal of organic matter in decentralized wastewater
965 treatment systems (DEWATS) in real time. Water Sci. Technol. 77, 819–828.
966 https://doi.org/10.2166/wst.2017.573
967 Moore, C., Barnard, A., Fietzek, P., Lewis, M.R., Sosik, H.M., White, S., Zielinski, O., 2009. Optical
968 tools for ocean monitoring and research. Ocean Sci. 5, 661–684. https://doi.org/10.5194/os-5-
969 661-2009
970 Müller-Grabherr, Dietmar, Florin, M.V., Harris, B., Crilly, D., Gugic, G., Vegter, J., Slob, A.,
971 Borowski, I., Brils, Jos, 2014. Integrated River Basin Management and Risk Governance, in:
972 Brils, J., Brack, W., Müller-Grabherr, D., Négrel, P., Vermaat, J. (Eds.), Risk-Informed
973 Management of European River Basins. The Handbook of Environmental Chemistry. Springer,
974 Berlin, Heidelberg, pp. 241–264. https://doi.org/10.1007/978-3-642-38598-8_9
975 Murphy, K.R., Stedmon, C. a, Wenig, P., Bro, R., 2014. OpenFluor- an online spectral library of
976 auto-fluorescence by organic compounds in the environment. Anal. Methods 6, 658–661.
977 https://doi.org/10.1039/c3ay41935e
978 Murphy, K.R., Stedmon, C.A., Graeber, D., Bro, R., 2013. Fluorescence spectroscopy and multi-way
979 techniques. PARAFAC. Anal. Methods 5, 6557–6566. https://doi.org/10.1039/c3ay41160e
980 Nowicki, S., Lapworth, D.J., Ward, J.S.T., Thomson, P., Charles, K., 2019. Tryptophan-like
981 fluorescence as a measure of microbial contamination risk in groundwater. Sci. Total Environ.

646, 782–791. https://doi.org/10.1016/j.scitotenv.2018.07.274

Pagano, T., Bida, M., Kenny, J., Pagano, T., Bida, M., Kenny, J.E., 2014. Trends in Levels of Allochthonous Dissolved Organic Carbon in Natural Water: A Review of Potential Mechanisms under a Changing Climate. Water 6, 2862–2897. https://doi.org/10.3390/w6102862

Peleato, N.M., Legge, R.L., Andrews, R.C., 2018. Neural networks for dimensionality reduction of fluorescence spectra and prediction of drinking water disinfection by-products. Water Res. 136, 84–94. https://doi.org/10.1016/J.WATRES.2018.02.052

Pellerin, B.A., Saraceno, J.F., Shanley, J.B., Sebestyen, S.D., Aiken, G.R., Wollheim, W.M., Bergamaschi, B.A., 2012. Taking the pulse of snowmelt: In situ sensors reveal seasonal, event and diurnal patterns of nitrate and dissolved organic matter variability in an upland forest stream. Biogeochemistry 108, 183–198. https://doi.org/10.1007/s10533-011-9589-8

Pesant, S., Not, F., Picheral, M., Kandels-Lewis, S., Le Bescot, N., Gorsky, G., Iudicone, D., Karsenti, E., Speich, S., Trouble, R., Dimier, C., Searson, S., 2015. Open science resources for the discovery and analysis of Tara Oceans data. Sci. Data 2, 1–16. https://doi.org/10.1038/sdata.2015.23

Petrenko, A.A., Jones, B.H., Dickey, T.D., LeHaitre, M., Moore, C., 1997. Effects of a sewage on the biology, optical characteristics, and particles size distributions of coastal waters. J. Geophys. Res. 102, 25061–25071.

Puiu, A., Fiorani, L., Menicucci, I., Pistilli, M., Lai, A., 2015. Submersible spectrofluorometer for real-time sensing of water quality. Sensors 15, 14415–14434. https://doi.org/10.3390/s150614415

Pule, M., Yahya, A., Chuma, J., 2017. Wireless sensor networks: A survey on monitoring water quality. J. Appl. Res. Technol. 15, 562–570. https://doi.org/10.1016/J.JART.2017.07.004

Reynolds, D.M., Ahmad, S.R., 1995. The effect of metal ions on the fluorescence of sewage wastewater. Water Res. 29, 2214–2216. https://doi.org/10.1016/0043-1354(95)00046-N

1007 Rudnick, S.M., Chen, R.F., 1998. Laser-induced fluorescence of pyrene and other polycyclic
1008 aromatic hydrocarbons (PAH) in seawater. Talanta 47, 907–919. https://doi.org/10.1016/S0039-
1009 9140(98)00160-X
1010 Ruhala, S.S., Zarnetske, J.P., 2017. Using in-situ optical sensors to study dissolved organic carbon
1011 dynamics of streams and watersheds: A review. Sci. Total Environ. 575, 713–723.
1012 https://doi.org/10.1016/J.SCITOTENV.2016.09.113
1013 Ryder, E., Jennings, E., De Eyto, E., Dillane, M., NicAonghusa, C., Pierson, D.C., Moore, K.,
1014 Rouen, M., Poole, R., 2012. Temperature quenching of CDOM fluorescence sensors: Temporal
1015 and spatial variability in the temperature response and a recommended temperature correction
1016 equation. Limnol. Oceanogr. Methods 10, 1004–1010.
1017 https://doi.org/10.4319/lom.2012.10.1004
1018 Saraceno, J.F., Pellerin, B.A., Downing, B.D., Boss, E., Bachand, P.A.M., Bergamaschi, B.A., 2009.
1019 High-frequency in situ optical measurements during a storm event: Assessing relationships
1020 between dissolved organic matter, sediment concentrations, and hydrologic processes. J.
1021 Geophys. Res. Biogeosciences 114, 1–11. https://doi.org/10.1029/2009JG000989
1022 Saraceno, J.F., Shanley, J.B., Downing, B.D., Pellerin, B.A., 2017. Clearing the waters: Evaluating
1023 the need for site-specific field fluorescence corrections based on turbidity measurements.
1024 Limnol. Oceanogr. Methods 15, 408–416. https://doi.org/10.1002/lom3.10175
1025 Shutova, Y., Baker, A., Bridgeman, J., Henderson, R.K., 2016. On-line monitoring of organic matter
1026 concentrations and character in drinking water treatment systems using fluorescence
1027 spectroscopy. Environ. Sci. Water Res. Technol. 2, 749–760.
1028 https://doi.org/10.1039/C6EW00048G
1029 Singh, S., Henderson, R.K., Baker, A., Stuetz, R.M., Khan, S.J., 2015. Online fluorescence
1030 monitoring of RO fouling and integrity: analysis of two contrasting recycled water schemes.
1031 Environ. Sci. Water Res. Technol. 1, 689–698. https://doi.org/10.1039/C5EW00090D

1032 Smart, P.L., Finlayson, B.L., Rylands, W.D., Ball, C.M., 1976. The relation of fluorescence to
1033 dissolved organic carbon in surface waters. Water Res. 10, 805–811.
1034 https://doi.org/10.1016/0043-1354(76)90100-7
1035 Snyder, L., Potter, J.D., McDowell, W.H., 2018. An evaluation of nitrate, fDOM, and turbidity
1036 sensors in New Hampshire Streams. Water Resour. Res. 54, 2466–2479.
1037 https://doi.org/10.1002/2017WR020678
1038 Sorensen, J.P.R., Baker, A., Cumberland, S.A., Lapworth, D.J., MacDonald, A.M., Pedley, S.,
1039 Taylor, R.G., Ward, J.S.T., 2018a. Real-time detection of faecally contaminated drinking water
1040 with tryptophan-like fluorescence: defining threshold values. Sci. Total Environ. 622–623,
1041 1250–1257. https://doi.org/10.1016/j.scitotenv.2017.11.162
1042 Sorensen, J.P.R., Lapworth, D.J., Marchant, B.P., Nkhuwa, D.C.W., Pedley, S., Stuart, M.E., Bell,
1043 R.A., Chirwa, M., Kabika, J., Liemisa, M., Chibesa, M., 2015a. In-situ tryptophan-like
1044 fluorescence: A real-time indicator of faecal contamination in drinking water supplies. Water
1045 Res. 81, 38–46. https://doi.org/10.1016/j.watres.2015.05.035
1046 Sorensen, J.P.R., Lapworth, D.J., Read, D.S., Nkhuwa, D.C.W., Bell, R.A., Chibesa, M., Chirwa, M.,
1047 Kabika, J., Liemisa, M., Pedley, S., 2015b. Tracing enteric pathogen contamination in sub-
1048 Saharan African groundwater. Sci. Total Environ. 538, 888–895.
1049 https://doi.org/10.1016/j.scitotenv.2015.08.119
1050 Sorensen, J.P.R., Sadhu, A., Sampath, G., Sugden, S., Dutta Gupta, S., Lapworth, D.J., Marchant,
1051 B.P., Pedley, S., 2016. Are sanitation interventions a threat to drinking water supplies in rural
1052 India? An application of tryptophan-like fluorescence. Water Res. 88, 923–932.
1053 https://doi.org/10.1016/j.watres.2015.11.006
1054 Sorensen, J.P.R., Vivanco, A., Ascott, M.J., Gooddy, D.C., Lapworth, D.J., Read, D.S., Rushworth,
1055 C.M., Bucknall, J., Herbert, K., Karapanos, I., Gumm, L.P., Taylor, R.G., 2018b. Online
1056 fluorescence spectroscopy for the real-time evaluation of the microbial quality of drinking

1057 water. Water Res. 137, 301–309. https://doi.org/10.1016/J.WATRES.2018.03.001
1058 Spencer, R.G.M., Bolton, L., Baker, A., 2007a. Freeze/thaw and pH effects on freshwater dissolved
1059 organic matter fluorescence and absorbance properties from a number of UK locations. Water
1060 Res. 41, 2941–2950. https://doi.org/10.1016/J.WATRES.2007.04.012
1061 Spencer, R.G.M., Pellerin, B.A., Bergamaschi, B.A., Downing, B.D., Kraus, T.E.C., Smart, D.R.,
1062 Dahlgren, R.A., Hernes, P.J., 2007b. Diurnal variability in riverine dissolved organic matter
1063 composition determined by in situ optical measurement in the San Joaquin River (California,
1064 USA). Hydrol. Process. 21, 3181–3189. https://doi.org/10.1002/hyp.6887
1065 Stedmon, C.A., Markager, S., 2005. Resolving the variability in dissolved organic matter
1066 fluorescence in a temperate estuary and its catchment using PARAFAC analysis.
1067 Limnol.Oceanogr. 50, 686–697.
1068 Tedetti, M., Guigue, C., Goutx, M., 2010. Utilization of a submersible UV fluorometer for
1069 monitoring anthropogenic inputs in the Mediterranean coastal waters. Mar. Pollut. Bull. 60,
1070 350–362. https://doi.org/10.1016/j.marpolbul.2009.10.018
1071 Tedetti, M., Joffre, P., Goutx, M., 2013. Development of a field-portable fluorometer based on deep
1072 ultraviolet LEDs for the detection of phenanthrene- and tryptophan-like compounds in natural
1073 waters. Sensors Actuators, B Chem. 182, 416–423. https://doi.org/10.1016/j.snb.2013.03.052
1074 The LiquID Station – ZAPS Technologies, LLC [WWW Document], 2018. URL
1075 http://www.zapstechnologies.com/the-liquid-station/ (accessed 12.20.18).
1076 Tunaley, C., Tetzlaff, D., Lessels, J., Soulsby, C., 2016. Linking high-frequency DOC dynamics to
1077 the age of connected water sources. Water Resour. Res. 52, 5232–5247.
1078 https://doi.org/10.1002/2015WR018419.Received
1079 UviLux Fluorometer [WWW Document], 2018. URL https://www.chelsea.co.uk/products/marine-
1080 science/fluorometers/uvilux-fluorometer (accessed 12.20.18).
1081 van Beynen, P.E., 2018. Editor's Message: Impact of politics on USA water quality monitoring,

protection and management. Hydrogeol. J. 26, 1763–1765. https://doi.org/10.1007/s10040-018-1791-5

van Rijswick, H.F.M.W., Backes, C.W., 2015. Ground Breaking Landmark Case on Environmental Quality Standards? J. Eur. Environ. Plan. Law 12, 363–377. https://doi.org/10.1163/18760104-01204008

Wasswa, J., Mladenov, N., 2018. Improved temperature compensation for in situ humic-like and tryptophan-like fluorescence acquisition in diverse water types. Environ. Eng. Sci. 35, 1–7. https://doi.org/10.1089/ees.2017.0315

Wasswa, J., Mladenov, N., Pearce, W., 2019. Assessing the potential of fluorescence spectroscopy to monitor contaminants in source waters and water reuse systems. Environ. Sci. Water Res. Technol. 5, 370–382. https://doi.org/10.1039/C8EW00472B

Watras, C.J., Hanson, P.C., Stacy, T.L., Morrison, K.M., Mather, J., Hu, Y.H., Milewski, P., 2011. A temperature compensation method for CDOM fluorescence sensors in freshwater. Limnol. Oceanogr. Methods 9, 296–301. https://doi.org/10.4319/lom.2011.9.296

Watson, K., Farré, M.J., Leusch, F.D.L., Knight, N., 2018. Using fluorescence-parallel factor analysis for assessing disinfection by-product formation and natural organic matter removal efficiency in secondary treated synthetic drinking waters. Sci. Total Environ. 640–641, 31–40. https://doi.org/10.1016/J.SCITOTENV.2018.05.280

Williams, C.J., Conrad, D., Kothawala, D.N., Baulch, H.M., 2019. Selective removal of dissolved organic matter affects the production and speciation of disinfection byproducts. Sci. Total Environ. 652, 75–84. https://doi.org/10.1016/J.SCITOTENV.2018.10.184

Wilson, H.F., Saiers, J.E., Raymond, P.A., Sobczak, W. V., 2013. Hydrologic Drivers and Seasonality of Dissolved Organic Carbon Concentration, Nitrogen Content, Bioavailability, and Export in a Forested New England Stream. Ecosystems 16, 604–616. https://doi.org/10.1007/s10021-013-9635-6

Wymore, A.S., Potter, J., Rodríguez-Cardona, B., McDowell, W.H., 2018. Using in-situ optical sensors to understand the biogeochemistry of dissolved organic matter across a stream network. Water Resour. Res. 54, 2949–2958. https://doi.org/10.1002/2017WR022168

Xing, X., Morel, A., Claustre, H., D'Ortenzio, F., Poteau, A., 2012. Combined processing and mutual interpretation of radiometry and fluorometry from autonomous profiling Bio-Argo floats: 2. Colored dissolved organic matter absorption retrieval. J. Geophys. Res. Ocean. 117, 1–16. https://doi.org/10.1029/2011JC007632

Yamashita, Y., Lu, C.-J., Ogawa, H., Nishioka, J., Obata, H., Saito, H., 2015. Application of an in situ fluorometer to determine the distribution of fluorescent organic matter in the open ocean. Mar. Chem. 177, 298–305. https://doi.org/10.1016/j.marchem.2015.06.025

Yang, L., Hur, J., Zhuang, W., 2015. Occurrence and behaviors of fluorescence EEM-PARAFAC components in drinking water and wastewater treatment systems and their applications: A review. Environ. Sci. Pollut. Res. 22, 6500–6510. https://doi.org/10.1007/s11356-015-4214-3

Yang, Y., Ma, X., Yang, X., Xu, H., 2017. Influence of heavy metal ions on the spectra and charge characteristics of DOM of municipal sewage secondary effluent. Water Sci. Technol. 77, 1098–1106. https://doi.org/10.2166/wst.2017.639

Zielinski, O., Busch, J.A., Cembella, A.D., Daly, K.L., Engelbrektsson, J., Hannides, A.K., Schmidt, H., 2009. Detecting marine hazardous substances and organisms: sensors for pollutants, toxins, and pathogens. Ocean Sci 5, 329–349.

Zielinski, O., Rüssmeier, N., Ferdinand, O., Miranda, M., Wollschläger, J., Zielinski, O., Rüssmeier, N., Ferdinand, O.D., Miranda, M.L., Wollschläger, J., 2018. Assessing fluorescent organic matter in natural waters: towards in situ excitation–emission matrix spectroscopy. Appl. Sci. 8, 1–25. https://doi.org/10.3390/app8122685