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In situ fluorescence measurements of dissolved organic matter: a review

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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

27 during in situ fluorescence measurement session for a harmonised qualitative and quantitative
28 protocol. Finally, the strengths and weaknesses of the research on in situ fluorescence are identified.
29
30 **Key words:** field fluorimeters, surface water, groundwater, engineered water systems, dissolved
31 organic matter
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56 1. Introduction

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

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

69 Previous reviews have evaluated the potential of fluorescence spectroscopy as an effective
70 monitoring tool in water systems (Carstea et al., 2016; Fellman et al., 2010; Henderson et al., 2009;
71 Hudson et al., 2007; Korshin et al., 2018; Moore et al., 2009; Ruhala and Zarnetske, 2017; Yang et
72 al., 2015; Zielinski et al., 2009). Among these reviews, only Conmy et al. (2014b), Moore et al.,
73 (2009), Ruhala and Zarnetske (2017) Zielinski et al. (2009) focused on DOM characterization using
74 field fluorimeters. The reviews of Moore et al. (2009) and Zielinski et al. (2009) were published a
75 decade ago and concentrated on the marine environment. Conmy et al. (2014b) provided an in-depth
76 review of some of the early in situ monitoring studies and the technical details of field fluorimeters,
77 but also with a particular focus on marine and estuarine applications. While Ruhala and Zarnetske
78 (2017) compared optical sensors for the measurement of dissolved organic carbon (DOC) only in
79 freshwater systems. Thus, there are no systematic reviews on in situ fluorescence measurements of
80 different water systems (marine water, freshwater, groundwater and engineered water systems).
81 Moreover, the research in this field has increased, in the past five years, with several in situ
82 measurement studies on the quality of groundwater (for example, Li et al., 2016a; Sorensen et al.,
83 2018a), freshwater (Khamis et al., 2015; Snyder et al., 2018), marine water (Chen et al., 2015; Cyr et
84 al., 2017) and engineered water systems (Carstea et al., 2018; Mladenov et al., 2018; Shutova et al.,
85 2016; Singh et al., 2015). This paper aims to review the advances in water quality measurements
86 using in situ fluorescence devices for detection of fluorescence emitted by DOM in the ultraviolet

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

94 ## 2. Fluorescence in situ measurements

95 ### 2.1 Fluorescence measurement strategies

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

112 The second strategy is to test the water in situ with field fluorimeters. The main advantage of
113 this type of measurement is that the water is sampled immediately and without perturbation, thus
114 enabling a more accurate representation of actual environmental conditions. Moreover, the devices
115 can be left unattended at the site for extended periods of time, permitting the generation of time
116 series data and the investigation of changes in fluorescence over time (Carstea et al., 2018; Khamis et
117 al., 2015; Shutova et al., 2016; Singh et al., 2015). In this context, the market offer for equipment
118 able to perform online fluorescence measurements is diverse, regarding price and performance.
119 When deciding on the type of sensor to use, several optical characteristics and configurations
120 must be considered. The most important characteristics to consider are the excitation and emission
121 wavelengths, and their respective bandwidths, which determine the ratio between the sensitivity and
122 selectivity of the instrument and, consequently, define the targeted fluorophores. Secondly, device
123 configuration is another criterium, depending on the type of application: open-path (right angle
124 detection or intersecting cones – optical window exposed to the environment) or closed-path (flow-
125 through) (Conmy et al., 2014b). In addition, submersible and cuvette-based devices can be adapted
126 for flow-through configuration. Thirdly, the type of light source and detector must be taken into
127 account. The excitation in field fluorimeters is provided by light sources such as Xenon flash lamps,
128 light emitting diodes (LEDs) or lasers (for example, nitrogen, HeCd, Nd-YAG). Devices that use
129 lasers are also known as laser induced fluorescence (LIF) systems. Photomultipliers, photodiodes or
130 charge coupled devices (CCDs) are common detectors for in situ fluorimeters. The excitation and
131 detection units also contain mirrors and lenses for directing and collecting the light. In addition,
132 optical filters are used to select the desired excitation and emission wavelength or to reduce the
133 intensity of light without spectral discrimination (Conmy et al., 2014b). Another important aspect is
134 energy consumption, as it varies between light sources. Finally, the presence of a reference detector
135 should be considered, because it corrects the sensor drift in light source intensity variation. Technical
136 details of instruments are given by Coble et al. (2014), while a detailed analysis of the advantages

137 and disadvantages of submersible versus cuvette-based fluorimeters is provided by Sorensen et al.
138 (2018a).

139 Common peaks targeted by most devices, commercial or non-commercial, are: peak T (in the
140 UVA fluorescence region, $\lambda_{excitation}/\lambda_{emission}$ = ~230 & ~275/~340 nm), peak C and peak C^+ (in the
141 blue and green fluorescence region, $\lambda_{excitation}/\lambda_{emission}$ = 300-350/400-500 nm and $\lambda_{excitation}/\lambda_{emission}$ =
142 250 & 385-420/470-504 nm), as named by Coble et al. (2014) (Fig. 1). Other fluorophores, such as
143 chlorophyll-a, phycocyanin, phycobilin, refined hydrocarbons, dyes, optical brighteners (or
144 fluorescent whitening agents - FWA) may be measured with field fluorimeters, if present at
145 sufficient concentration above the background signal. Additional fluorescence peaks commonly
146 detected with laboratory instruments, which are less frequent at in situ measurements, include peak B
147 ($\lambda_{excitation}/\lambda_{emission}$ = 230 & 275/305 nm, generally referred to as tyrosine-like) (Coble et al 2014),
148 which computational chemistry investigations suggest corresponds to compounds with at least one
149 aromatic ring, and peak A ($\lambda_{excitation}/\lambda_{emission}$ = 260/400-500 nm), usually associated with substances
150 with two aromatic rings (Barsotti et al., 2016; Coble et al., 2014).

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

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

166 **2.2 Advances in sensor development**

167 In the 1990s CE, field fluorimeters developed from single wavelength fluorimeters to
168 multispectral and hyperspectral devices (Coble et al., 2014). In the past decade, with the
169 advancement of technology in optical and electronical components, fluorimeters became more
170 power-efficient, miniaturized and cheaper than ever before, while providing effective information.
171 One direction of sensor development was oriented towards maximizing the information extracted
172 from the device. For example, Zielinski et al. (2018) have developed a submersible sensor system
173 that is able to record full EEMs, within a high spectral range (($\lambda_{excitation}/\lambda_{emission}$ = 220-750 nm / 200-
174 950 nm). Another example of novel devices is the “one LED & three signals” system developed by
175 Li et al. (2016a) for in situ measurements. The device uses a light source at 280 nm, one photodiode
176 to measure UV 280 absorbance and two photodiodes with bandpass filters to detect peaks T and C
177 fluorescence. Another example is the system developed by Bridgeman et al. (2015), that displays the
178 fluorescence intensity for peaks T and C, the Raman value and the ratio T/C. The intensity of the
179 Raman emission of water is used for normalization and fluorimeter stability check. However, only a
180 limited number of in situ devices, mostly custom, measure this peak. Continuous measurement of the
181 Raman emission of water would be an excellent addition to field fluorimeters to enhance comparison
182 between instruments and sites. Other commercial devices convert fluorescence values to BOD and
183 TOC using a proprietary algorithm and do so in real-time (for example, “The LiquID Station – ZAPS
184 Technologies, LLC,” 2018 and “UviLux Fluorometer,” 2018), which may be used in wastewater
185 treatment and drinking water plants and distribution systems. Another area of development was
186 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

212 similar wavelengths and integration times. However, most of the fluorescence sensors do not
213 measure the water Raman peak and instead report the limit of detection (LOD), which is not
214 provided in the technical specifications of benchtop spectrofluorimeters. Research studies on field
215 fluorimeters usually compare the instruments by correlating fluorescence values within a range of
216 concentrations of standards, above the LOD, or with discrete water samples, which are used for
217 device calibration (section 3.1). Research showing the LODs of field and laboratory instruments is
218 scarce. Tedetti et al. (2013) determined substantially better LODs for a benchtop spectrofluorimeter
219 (Hitachi F7000) compared to a field fluorimeter (MiniFluo-UV) with standards of phenanthrene
220 (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
221 found that the benchtop fluorimeter displayed better LODs (0.003-0.677 RU) compared to field
222 fluorimeters (127.35-218.43 RU for peak T and 8.23-3,527.99 RU for peak C) on tertiary effluents
223 and recycled water samples spiked with pharmaceutical and oil pollutants. In addition, Cumberland
224 et al. (2012) showed that both portable fluorimeter and benchtop spectrofluorimeter were able to
225 detect the presence of a few bacteria per 100 mL. They highlighted, however, that instruments LODs
226 could not be determined with accuracy, due to false negative and false positive results, at low
227 concentrations. Also, Wasswa et al. (2019) mentioned that in complex environments, the instruments
228 may not measure towards the minimum LOD due to background fluorescence. Although field
229 fluorimeters have lower sensitivity and LOD ranges compared to benchtop spectrofluorimeters, they
230 are still able to detect the same patterns and trends as laboratory instruments (Mladenov et al., 2018).

231 **3. Steps in fluorescence in situ measurements**

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

235 **3.1 Calibrations**

236 Several steps must be undertaken for sensor calibration, as recommended by D'Ortenzio et al. 237 (2010): a) a pre-calibration to test the precision, pressure and mechanical and electrical stability of 238 the device; b) calibration of signal output by measuring dark and saturation counts (Zielinski et al., 239 2018); c) calibration of internal temperature to test its impact on sensor optical components (Cyr et 240 al., 2017; Yamashita et al., 2015); d) calibration with distilled water at a certain temperature; e) 241 absolute calibration with known substances.

242 The first step should determine the instrument drift due to environmental factors, such as 243 pressure and aging. For the second step, D'Ortenzio et al. (2010) recommended to insert the sensor 244 in distilled water and cover the detector with black tape for dark counts measurements. Saturation 245 counts can be measured by placing a fluorescent object (glow stick) in front of the sensor. For the 246 third step, Cyr et al. (2017) developed an internal temperature correction; however, it may depend on 247 instrument, as Yamashita et al. (2015) found that temperature had no impact on optical components 248 during in situ measurements. Two common methods have been proposed for absolute calibration of 249 field fluorimeters: using standard substances (L-tryptophan, quinine sulfate or humic substances) and 250 water collected from the field location (Conmy et al., 2014a; Gutierrez et al., 2014; Khamis et al., 251 2015). Khamis et al. (2017), (2015) used a tryptophan standard (synthetic, ≥ 98%) in dilutions 252 ranging from 0 to 1,000 ppb on five fluorescence sensors to calibrate peak T, out of which four 253 fluorescence sensors displayed a linear relationship ($r^2 > 0.95$) across the tested range of 0-1,000 ppb. 254 Lee et al. (2015) used quinine sulfate standards from 0 to 100 ppb to calibrate peak C, by diluting a 255 1,000 ppm of quinine sulfate stock solution. Specific applications, such as measuring PAHs in water, 256 require other standards. Cyr et al. (2019), (2017) used two calibrations for PAHs. The first 257 calibration, included PAH standards and the second, water accommodated fraction of crude oil, 258 which contained methylated and non-methylated hydrocarbons. In some cases, calibrating with the 259 water under assessment (seawater, river water) was considered the best option, since calibrating large

260 sensors or those attached to CTD platforms with standards is operationally difficult (Baker et al., 261 2015; Conmy et al., 2014a, 2004; Yamashita et al., 2015). However, validation of field fluorimeters 262 with steady state spectrofluorimeters is needed. Excellent linear relationship (r^2 = 0.70-0.98) between 263 fluorescence measured with a benchtop spectrofluorimeter and with a field device was observed in 264 samples from various locations (Bridgeman et al., 2015; Chen et al., 2015; Graham et al., 2015; 265 Yamashita et al., 2015). Tedetti et al. (2010), obtained a poor correlation (r^2 = 0.55) with seawater 266 samples, compared to correlation with standards (r^2 = 0.96). However, the measurement parameters 267 (such as excitation wavelength or bandwidth) were not perfectly matched between the two 268 instruments (Table S1) and Tedetti et al. (2010) compared 0.20 μm filtered samples, measured with a 269 benchtop spectrofluorimeter, with unfiltered samples measured with the in situ fluorimeter.

270 **3.2 Frequency of in situ measurements**

271 The field measurement frequency should be given careful consideration, as a low measurement 272 frequency may not provide the resolution needed to determine characteristics (Fig. 2). However, high 273 frequency measurements may not be needed in particular environments, with reduced fDOM 274 variation. Downing et al. (2009) found that for flux estimation, sampling intervals of 90 mins or less 275 were sufficient. Carstea et al. (2018) showed that a 15 minutes measurement frequency was needed 276 to determine the daily variation of fDOM concentration and to evaluate treatment process efficiency 277 in a wastewater treatment plant. A 30 minute frequency was tested, but the data points were 278 insufficient to assess adequately the water quality fluctuations (Carstea et al., 2018). Higher 279 measurement frequency, below 5 minutes, was chosen for drinking water sources, rivers or recycled 280 water assessment (Bieroza and Heathwaite, 2016; Khamis et al., 2017; Ryder et al., 2012; Saraceno 281 et al., 2017; Singh et al., 2015), where DOM characteristics and concentration can vary at short time 282 scales (< 2 h) (Fox et al., 2017). In addition, for sensors integrated on mobile platforms the 283 measurement interval may decrease to one recording per second, in order to match the platform 284 speed (Mihalevich et al., 2017).

285 ### 3.3 Sensor installation and maintenance

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

294 Shutova et al. (2016) found that the choice of probe for installation was important, as one peak
295 C probe (Cyclops C®, Turner Designs, excitation wavelength 368±17 nm, emission wavelength
296 470±30 nm) was more sensitive to DOM changes in fresh water, in particular at low DOM, than
297 another peak C probe (EXO C®, Xylem YSI, excitation wavelength 365±5 nm, emission wavelength
298 480±40 nm). However, the latter was more effective in detecting minor changes in wastewater
299 effluent DOM compared to other fluorimeters (Carstea et al., 2018), due to the position of the
300 emission wavelength, close to the FWA peak, which is likely to be detected in wastewater. On the
301 contrary, Snyder et al. (2018) found no bias in the data provided by individual sensors in a year-
302 round monitoring across several streams. Snyder et al. (2018) also showed that no individual site
303 drove the overall trend in the relationship between fDOM and DOC. From a total of 1.18 M data
304 records, Snyder et al. (2018) flagged only 4.6 % of fDOM measurements by automated or manual
305 QC procedures. Flagged data resulted from general sensor malfunctions, such as lamp failures, and
306 localized instream events such as heavy debris deposition Snyder et al. (2018). Performing remote
307 monitoring and knowing the instrument well before deployment, such as potential sensor error
308 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

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

339 *Suspended and dissolved matter*

340 Suspended and dissolved particles have a combined effect of scattering and absorption leading
341 to source light attenuation, redirection of light from the detector and increase of the photons optical
342 path (Mbaye et al., 2018; Saraceno et al., 2009). Various correction methods have been proposed to
343 reduce the impact of suspended matter (Table 2). For example, Mbaye et al. (2018) developed a
344 scattering correction to estimate the quantity of suspended particles in water. Others proposed
345 correction equations depending on turbidity thresholds (de Oliveira et al., 2018; Downing et al.,
346 2012; Khamis et al., 2017; Lee et al., 2015) (Table 2). However, at groundwater or drinking water
347 treatment plants, (Khamis et al., 2015; Nowicki et al., 2019; Shutova et al., 2016; Sorensen et al.,
348 2018a) reported low turbidity values and negligible impact on in situ fluorescence data, which
349 required no correction. Khamis et al. (2017) stressed the importance of calibrating the sensors using
350 sediment collected from the field location, while Downing et al. (2012) recommended to determine a
351 correction factor for the specific turbidimeter that is paired with the in situ fluorimeter.

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

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

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

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

383 *Temperature*

384 DOM fluorescence intensity is inversely related to temperature (Henderson et al., 2009), due to
385 the impact of temperature on the rate of radiationless decay mechanisms (McKay et al., 2018a). High
386 temperature fluctuations, during in situ studies, significantly impact the measurement session
387 outcome (Table 1). To reduce this impact, Watras et al. (2011) developed a temperature
388 compensation tool for peak C region using a linear regression equation and a reference temperature
389 of 20° C (Table 2). Later, Ryder et al. (2012) proposed a similar temperature correction equation for
390 peak C, which uses the water temperature at the time of measurement. Recently, McKay et al.
391 (2018b) developed a correction method that accounts for apparent quantum yields changes caused by
392 temperature. They showed that the bias in fluorescence intensity due to changes in quantum yield
393 vary from +10% at 10°C to -30% at 55°C.

394 Watras et al. (2011) showed that the temperature coefficient did not depend on DOM
395 concentration and Downing et al. (2012) observed no variation between instruments when applying
396 the temperature correction. Nevertheless, Khamis et al. (2017) recommended calculation of a
397 compensation coefficient specific to each instrument before deployment. In addition, Khamis et al.
398 (2017) found that peak T required a higher compensation coefficient and was more unstable during
399 the experiment compared to peak C. Peak T is more susceptible to thermal quenching compared to
400 peak C, irrespective of the DOM source (Baker, 2005; Carstea et al., 2014; Khamis et al., 2017;
401 Wasswa and Mladenov, 2018).

402 To improve correction efficiency, two or more parameters were included in the fluorescence
403 signal correction protocols (Table 2). For example, de Oliveira et al. (2018) developed a sequential
404 compensation procedure to correct temperature, turbidity and IFE on peak C fluorescence. Also, the
405 temperature compensation tool, developed by Watras et al. (2011), was included in a robust equation
406 that also corrected the signal attenuation caused by particles using absorption at 254 nm and turbidity
407 (Downing et al., 2012). Saraceno et al. (2017) later developed a site- specific equation. They found
408 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

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

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

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

454 4. Fluorescence field measurement applications

455 4.1 Marine water

456 Since the early 1970s CE (Karabashev and Solovev, 1973), fluorescence sensors have been
457 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.

483 The allochthonous and autochthonous input of marine DOM were also studied with in situ
484 fluorimeters (Table S2). The early studies on fDOM allochthonous input revealed that peak C
485 fluorescence intensity had the highest levels in locations close to river mouths (Chen, 1999;
486 Klinkhammer et al., 2000). These findings were confirmed by later studies (Babichenko et al., 2016;
487 Bergamaschi et al., 2012; Chen et al., 2015) who found high fluorescence in estuaries and bays
488 water. For example, in the Norwegian Sea, peak C fluorescence increased 3-4 times in the estuaries
489 (Babichenko et al., 2016). Chen et al. (2002) concluded that only 10 % of the fDOM in the Mid-
490 Atlantic Bight was supplied by rivers, although 50 % of river fDOM reached the Chesapeake Bay.
491 Bergamaschi et al. (2012) also showed that a mangrove system supplied the estuary with an
492 estimated 180 (± 12.6) gC cm^{-1} value, which varied depending on storm, wind or rising global sea
493 level. The rest of fDOM was produced through marine biological activity (Chekalyuk et al., 2014;
494 Chen et al., 2015). Without terrestrial influences, the fluorescence intensity was found as constant
495 (Babichenko et al., 2016; Bergamaschi et al., 2012; Chen et al., 2002).
496 Early studies (Chen, 1999; Chen et al., 2002) showed that net production of marine fDOM
497 occurred in spring, while net degradation occurred in summer, which was later confirmed by
498 Kowalczuk et al. (2010), who found late-summer photodegradation of DOM. Conversely, Cyr et al.
499 (2017) found higher peak T fluorescence intensity during the autumn months, compared to summer
500 and spring. Cyr et al. (2017) suggested that the relationship between FOM and primary marine
501 production may be more complex and proved that fDOM may be a good proxy for processes
502 influencing the DOM pool. The incubation studies undertaken by Jørgensen et al. (2014), revealed
503 highly complex processes of microbial DOM production. They found a link between DOM lability
504 and microbial fDOM production. Jørgensen et al. (2014) suggested that fDOM formation is more
505 pronounced at microbial degradation of semilabile DOM and speculated that this process
506 corresponded to in situ fDOM production.

4.2 Freshwater

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

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

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

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

540 In addition to studying natural organic matter dynamics in freshwater, in situ fluorescence was
541 used to detect anthropogenic DOM. For example, Carstea et al. (2010) detected oil pollution in an
542 urban river, which was reflected in a sudden increase of high peak T fluorescence. They separated
543 the signal of the oil pollution from the regular peak T fluorescence by the ratio between the peak at
544 $\lambda_{excitation}$ = 225 nm and $\lambda_{excitation}$ = 280 nm and by processing the recorded in situ EEMs with self
545 organising maps (SOM), which identified a separate cluster for oil pollution. Another important
546 example is the application of field fluorimeter is to screen freshwater that serve as drinking water
547 sources for the presence of bacteria. Cumberland et al. (2012) showed, in an ex-situ study, that
548 portable devices may be used to detect low levels of total coliforms and *E.coli*. Later, Baker et al.
549 (2015) found that the response of field fluorimeters in the presence of *E.coli* was variable (Table S3).
550 However, they recommended using fluorescence as an initial screening tool in areas with poor
551 sanitation.

552 **4.3 Groundwater**

553 Studies of groundwater contamination field measurements focused on landfill leachate
554 (Graham et al., 2015) and microbial pollutants (Nowicki et al., 2019; Sorensen et al., 2015a, 2016,
555 2018b, 2018a) (Table S4). Graham et al. (2015) identified variations in fluorescence intensity in an
556 aquifer affected by landfill leachate. The results implied that the in situ fluorimeter most probably

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

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

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

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

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

587 **4.4 Engineered water systems**

588 The development of new and powerful in situ fluorimeters, in the past five years, encouraged
589 researchers to test the performance and robustness of the devices in engineered water systems.
590 Although few studies were conducted, the results were promising in determining the effectiveness of
591 treatment processes. Studies on field fluorescence assessment of engineered water systems included
592 drinking water treatment plants (Shutova et al., 2016), wastewater treatment plants (Carstea et al.,
593 2018; Mladenov et al., 2018) and recycled water plants (Singh et al., 2015) (Table S5). Shutova et al.
594 (2016) identified daily changes in DOM at the untreated water and a stable DOM at the treated
595 water. In addition, Shutova et al. (2016) observed that the character of DOM changed after each
596 treatment process, by analyzing the ratio between peaks C and T. They concluded that this parameter
597 may be used to determine DOM removal in drinking water treatment plants.

598 Despite multiple indications in the literature that fluorescence sensors can be used for in situ
599 measurements of wastewater treatment processes (Carstea et al., 2016; Chong et al., 2013; Mesquita
600 et al., 2017), only two studies have been published so far (Carstea et al., 2018; Mladenov et al.,
601 2018). The main reason for the slow advancement is the difficulty of using this technique in the
602 hostile environment of a wastewater treatment plant (i.e. high humidity, high quantity of particulate
603 and DOM even in treated wastewater, high susceptibility to biofilm formation on optical surfaces
604 etc.). Moreover, Wasswa et al. (2019) found that the LOD of fluorescence sensors increases due to
605 the high background DOM fluorescence in effluents. They showed, in an ex-situ experiment, that
606 pharmaceutical, personal care products and oil contaminants were more difficult to discern in tertiary

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

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

628 5 Future perspectives

629 Fluorescence devices represent excellent tools in long-term, high frequency, in situ
630 measurements of aquatic environments. Most of the in situ fluorescence studies, between 2009-2018,
631 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

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

659 Another research gap is to establish relationships between water quality parameters and
660 fluorescence peaks across environments. The obstacles arise from the complex nature of fDOM,
661 varied fDOM behaviour in the environment and the lack of standards to quantify main fluorescence
662 peaks. As shown in section 3.1, a partial quantification of field fluorimeters may be achieved with
663 standards, such as tryptophan, humic substances or PAHs. However, the actual composition of
664 fDOM in water is relatively unknown, with potential several other fluorophores contributing to peaks
665 T and C fluorescence, at the same degree or higher compared to the used standards. Consequently, in
666 situ fluorescence measurements may only proxies for chemical and biological properties, which are
667 of fundamental interest to water managers and scientists. Also, the fluorescence sensors effectiveness
668 as proxies must be continuously evaluated. So far, in situ fluorescence studies showed that the
669 relationship between DOC and peak C is strong in most environments: r^2 = 0.49-0.99 at coastal sites,
670 r^2 = 0.74-0.99 at freshwater sites and r^2 = 0.85-0.93 at engineered water systems (Tables 3 and S2-
671 S5). Thus, peak C can be an excellent, direct proxy for DOC concentration, in environments where
672 the influence of terrestrial input is high. However, the relationship between fluorescence and DOC
673 improves when corrections (for turbidity in particular) are applied or when samples are filtered
674 (Downing et al., 2012; Khamis et al., 2017; Kowalczuk et al., 2010). Correction of data or removal
675 of particles would improve prediction of DOC, especially during storms when high quantities of
676 particles may underestimate DOM fluxes (Downing et al., 2012). In addition, peak C can be an
677 indirect proxy of salinity, in particular cases (Kowalczuk et al., 2010) (Table S2). In situ
678 fluorescence studies also showed that peak T correlated with *E. coli* (r^2 = 0.71-0.95 at freshwater, r^2
679 = 0.59-0.77 at groundwater and r^2 = 0.66 at marine water), but only at sites with sanitation problems
680 (Tables S2-S4). Peak T also correlated with COD (r^2 = 0.75) at engineered water systems (Table S5).
681 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

707 environmental impact of pollutants after the first cycle of the Water Framework Directive
708 implementation, in 2015 (Müller-Grabherr et al., 2014). Overall, the number of European surface
709 water bodies in "good ecological status" increased with only 10 % (van Rijswick and Backes, 2015).
710 These issues call for the use of an effective monitoring tool that includes cheap, reliable and fast
711 methods, such as fluorescence spectroscopy, which has demonstrated use as a proxy for DOC, BOD
712 and in regions of poor sanitation, *E. coli*. Field fluorimeters are a key component in powerful
713 monitoring tools, leading to better decisions in water management and environmental policy.
714

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