Characterization by fluorescence of dissolved organic matter in rural drinking water storage tanks in Morocco

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ABSTRACT

Water storage tanks, fed directly from the river through opened channels, are particular systems used for water supply in rural areas in Morocco. The stored water is used as drinking water by the surrounding population without any treatment. UV-visible spectroscopy and fluorescence spectroscopy (excitation-emission matrices and synchronous fluorescence) have been tested as rapid methods to assess the quality of the water stored in the reservoirs as well as along the river feeding them. Synchronous fluorescence spectra (SFS50), collected with a difference of 50 nm between excitation and emission wavelengths, revealed a high tryptophan-like fluorescence, indicative of a pollution induced by untreated domestic and/or farm wastewater. The best correlations were obtained between the total SFS50 fluorescence and dissolved organic carbon (DOC) and biological oxygen demand, showing that the contribution of humic-like fluorescent substances cannot be neglected to rapidly assess reservoir water quality in terms of DOC by fluorescence spectroscopy.

Key words | dissolved organic matter, drinking water, fluorescence spectroscopy, reservoirs, rural area

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INTRODUCTION

The lack of infrastructure, namely drinking water and sanitation networks, makes the development and sustainable management of water resources difficult in rural areas of countries such as Morocco. When drinking water is not available through a network, rainwater, surface water and groundwater are the only local water supply sources (Skinner 2003). Collecting water in reservoirs is one of the solutions used to meet water needs (Sample *et al.* 2013).

In Morocco, the traditional storage method uses cisterns or 'matfya,' which are buried in the ground to a level of three-quarters of their total height (Aziz *et al.* 2013). These reservoirs are supplied by river and/or rainwater through channels called 'seguia' (Figure 1). The socio-cultural behavior of the population towards water leads them to build more reservoirs than wells, as each family has a hereditary right to its share of surface water whenever it is distributed along the seguias and stored in reservoirs for its own consumption. However, these resources pose drastic problems to human and environmental health because of poor water quality and the lack of water treatment (Taylor *et al.* 2000). In terms of hygiene conditions, the local population does not respect their surroundings, and household rubbish and fecal waste are disposed of anywhere, which explains why runoff water is likely to contaminate the water in reservoirs. If the composition of the water (minerals (including metals), natural and anthropogenic organic matter (dissolved and particulate), and pathogens) guides its uses, the latter also change it considerably.

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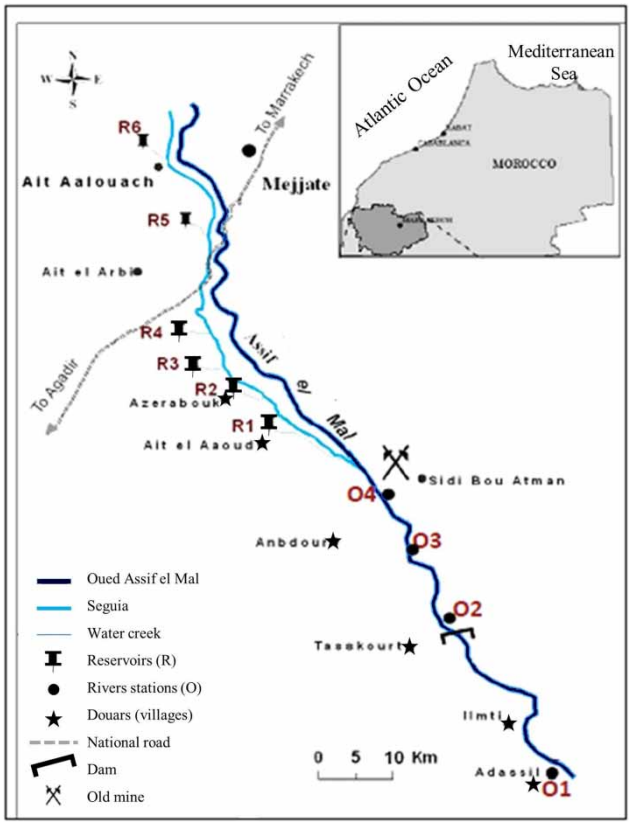

Figure 1 | Map of sampling points along the Assif El Mal valley (R: reservoir, O: river).

Molecular methods have been proposed to identify human and animal sources of pollution (Griffith *et al.* 2009; Cao *et al.* 2013; Ervin *et al.* 2013). However, these methods require highly trained staff and are expensive. The development of appropriate monitoring systems with a rapid assessment of water quality and the performance of treatment processes is a key issue to prevent health problems (Foley *et al.* 2007). Optical methods are particularly attractive for that purpose because they are fast and do not involve reagents that can be harmful to the environment if not disposed of properly. Therefore, UV-visible spectroscopy and fluorescence spectroscopy have received special attention for several years (Hautala *et al.* 2000; Ahmad *et al.* 2002). Fluorescence spectroscopy has been proposed as a monitoring tool for a wide range of applications related to water quality and pollution monitoring in rivers (Hudson *et al.* 2007): the characterization of dissolved natural organic matter in drinking water, wastewater effluent, storm water, and seawater (Baghoth *et al.* 2008); the control of wastewater treatment processes (Hudson *et al.* 2007); and the detection of contaminants during drinking water treatment (Peiris *et al.* 2008). Cumberland *et al.* (2012) have successfully tested a portable LED fluorometer to monitor tryptophan-like fluorescence, one of the components of dissolved organic matter (DOM), which was found to correlate well with bacteria numbers in wastewater treatment plant final effluent and receiving water bodies. DOM has different sources, either natural (runoff from soil, microbial activity in the aquatic systems) or anthropogenic, through the release of ill-treated domestic or farm wastewater (Hudson *et al.* 2007, 2008; Old *et al.* 2012), i.e. exhibiting large intensities of tryptophan-like fluorescence.

For many years fluorescence spectroscopy has been used to characterize aquatic DOM. The conventional fluorescence emission spectra (McKnight *et al.* 2001) provide limited information due to the spectrum shape and the position of the slightly marked maximum. More comprehensive information can be obtained by building excitation-emission matrices, using emission spectra obtained from a series of excitation wavelengths. Specific areas of these matrices have been associated with groups of substances (Coble 1996; Coble *et al.* 1998) related to humic, fulvic or tryptophan-type substances, the last being more particularly bound to proteins. The spectral resolution can also be improved by the use of synchronous fluorescence spectra: they are obtained by keeping the gap constant between the excitation and the emission wavelengths (Patra & Mishra 2002).

Our objective has been to demonstrate the interest of optical methods such as fluorescence spectrometry and absorbance spectroscopy for making rapid diagnosis of the water quality in rural environments, where potable water scarcity is an everyday issue.

MATERIALS AND METHODS

Sampling

A single sampling campaign was performed on April 3, 2012 according to the French standard methods (AFNOR 1997; Rodier *et al.* 2009). At that time of the year the water is plentiful in the river. Water samples (one sample per site) were

collected by directly filling clean polyethylene sampling bottles in the Assif El Mal valley in Morocco from six traditional reservoirs (R1–R6) intended for human use and from four stations (O1–O4) along the river upstream of the diversion point towards the reservoirs (Figure 1 and Table S1 in the Supplementary material, available with the online version of this paper). The sampling depth was 10 cm. The river samples were collected from downstream to upstream, at equal distance between the banks. The reservoirs and river stations were chosen according to four main characteristics: urbanization, intensity of usage, accessibility, and spatial distribution along the valley. The samples were transported to the laboratory in cold boxes on the same day and kept at 4 °C in the dark until analysis began (12 h after sampling).

Analytical methods

Temperature, pH, conductivity, and dissolved oxygen were measured *in situ* using a WTW LF 92 Multiparameter probe. Except for BOD_5 (biological oxygen demand after 5 days) (AFNOR T90-103 in AFNOR (1997)), all analyses were conducted on filtrated samples (cellulose nitrate filters, porosity of 0.45 μm). Nitrates, ammonia, and BOD_5 were measured in the laboratory using French standard methods (AFNOR 1997; Rodier *et al.* 2009). Dissolved organic carbon (DOC) was measured on a VCHS system (Shimadzu, Noisiel, France) by catalytic oxidation at 680 °C and infrared detection of the produced carbon dioxide. Dissolved metals (copper, zinc, and lead) were measured by inductively-coupled plasma atomic emission spectroscopy (ICP-AES with an argon plasma) (Thermo Instruments, Courtaboeuf, France) after digestion. For the digestion (40 min at 180 °C under nine bars in a microwave system), 5 mL of ultra-pure nitric acid is added to the sample (20 mL).

UV-visible spectroscopy

The UV-visible absorbance spectrum of each filtrated sample was recorded using an Anthélie Light UV-visible spectrophotometer (Secomam, Domont, France) in a quartz cuvette (volume = 3.5 mL, optical path length = 1 cm) between 200 and 700 nm. The blank was performed with ultra-pure water for solvent correction.

Fluorescence spectroscopy

Two methods of fluorescence measurement were applied with different parameters on filtrated samples with a fluorometer F-2500 (Hitachi, Krefeld, Germany) equipped with a Xenon lamp, using the FL Solution 2.0 software. A quartz cuvette was used (volume = 3.5 mL, optical path length = 1 cm). No correction for inner-filter effect and for the Rayleigh and Raman diffusion was performed, and the spectra were collected at the sample natural pH. The blank was performed with ultra-pure water:

- excitation-emission matrix (EEM): the matrices were obtained by performing a series of emission spectra between 280 and 600 nm (wavelength step = 1 nm) for excitation wavelengths between 250 and 500 nm, with a step of 5 nm.
- synchronous fluorescence: the SFS50 spectra were obtained with a fixed gap (50 nm) between the excitation and emission wavelengths (λ_{ex} and λ_{em}, respectively), with the excitation wavelength varying between 230 and 600 nm (wavelength step = 1 nm). The gap of 50 nm was selected as a compromise to optimize the resolution of both tryptophan-like fluorescence and humic-like fluorescence (Reynolds 2003).

A Raman spectrum and SFS50 spectrum of ultrapure water were collected at the beginning of the measurement series to check the stability of the fluorometer (Spencer *et al.* 2007).

RESULTS AND DISCUSSION

General characteristics

The main water quality parameters are presented in Table 1. Except for copper, all the parameters largely exceed the standards for drinking water production (Moroccan Drinking Water Standards 2006), especially in the reservoirs. The pH is slightly alkaline (average value = 8) and conductivity increases in the river from upstream to downstream. Based on DOC, a spatial variability of the organic pollution is observed. The most polluted reservoirs (R4, R5 and R6) are located in the downstream section of the channel. The dissolved oxygen concentration is lower in the

Table 1 | Characteristics of the collected samples (R: reservoirs, O: river). EC = electrical conductivity; DO = dissolved oxygen; LOQ = limit of quantification

	pH	EC (µS/cm)	DO (mg/L)	NH_4^+ (mg/L)	NO_3^- (mg/L)	BOD_5 (mg/L)	DOC (mg/L)	Cu (mg/L)	Zn (mg/L)	Pb (µg/L)
O1	8.31	260	7.2	0.21	<LOQ	6.3	2.1	<LOQ	1.56	30
O2	8.23	288	7.1	0.23	2.93	5.0	3.3	<LOQ	0.94	41
O3	8.2	320	6.7	0.20	1.2	6.1	3.9	0.56	2.86	52
O4	8.3	403	5.8	0.25	1.7	6.6	4.6	0.94	4.06	55
R1	7.95	757	4.7	0.43	29.4	8.3	4.3	1.04	5.26	51
R2	8.08	1,532	3.8	0.44	33.1	9.1	4.7	0.86	3.04	48
R3	7.86	919	3.1	0.56	54.7	7.4	4.8	0.98	4.16	60
R4	7.79	1,592	2.9	0.52	63.1	12.3	6.4	1.3	5.11	57
R5	7.67	905	3.2	0.45	52.1	13.0	5.8	1.32	3.36	64
R6	7.78	1,809	2.7	0.58	52.8	14.6	8.3	1.14	5.98	61

reservoirs than in the river and is lower than the minimal value set by the drinking water standards (5 mg/L). High ammonia concentrations were measured, especially in the reservoirs, where it varied between 0.43 and 0.58 mg/L. The limit for potable water production is 0.5 mg/L. The nitrate concentrations in the reservoirs located farthest downstream are above the limit of 50 mg/L.

Regarding the metal contamination and with the exception of copper, which is below the limit for drinking water production (3 mg/L), zinc and lead exceed standards (set at 3 and 0.025 mg/L, respectively). Given the presence of dissolved metals (Table 1), it is possible that part of the fluorescence is decreased by the effect of 'quenching' (Frimmel & Hopp 1986; Croué *et al.* 2003; Yamashita & Jaffé 2008; Yang *et al.* 2014).

Information derived from optical methods

No general correlation could be found between the absorbance at 254 nm (A254) and DOC: the coefficient of determination for a linear correlation was less than 0.1. This means that each sample is characterized by a specific ultra-violet absorbance (SUVA, at 254 nm) value (Weishaar *et al.* 2003). The average A254 was 0.04 cm^{-1} (standard deviation = 0.03 cm^{-1}) for the river samples and 0.09 cm^{-1} (standard deviation = 0.03 cm^{-1}) for the reservoir samples.

The fluorescence data were not corrected for absorbance. This choice was made because the ultimate goal is to use the optical methods in the field, where any correction will be difficult to make.

The EEMs of samples taken along the Assif El Mal River and in the reservoirs are presented in Figures S1 (for the river stations) and S2 (for the reservoirs) in the Supplementary material (available with the online version of this paper). The peak ($\lambda_{ex} \approx 285$ nm, λ_{em} centered on 380 nm) for O2, O3 and O4 stations corresponds to the tryptophan-like fluorescence (Baker 2002). The fluorescence intensity at $\lambda_{ex} = 285$ nm/$\lambda_{em} = 380$ nm for O1 is much lower than for the next downstream river station (O2): 300 a.u. for O1 against 3780 for O2. O1 can therefore be considered as a reference with little or no anthropogenic influence. The global intensity of fluorescence increases between R1 and R6, and the wavelength of the maximum of emission for $\lambda_{ex} \approx 280$ nm increases between R1 and R5. This could be explained by an accumulation of various substances, other than tryptophan-like ones. The fluorescence intensity of the region ($\lambda_{ex} \approx 350$ nm/$\lambda_{em} \approx$ 425 nm), which can be associated with humic-like substances (fluorescence C) according to Coble *et al.* (1998), also increases, from 425 a.u. for R1 to 4012 a.u. for R5. The R6 station has an EEM slightly different from the upstream reservoirs along the channel, with a first peak around ($\lambda_{ex} \approx$ 285 nm/$\lambda_{em} \approx 380$ nm) and a second peak at ($\lambda_{ex} = 330$ nm/$\lambda_{em} = 440$ nm). This indicates a different type of organic matter present in this specific sample, which has been reported by Coble (1996) in river waters.

Referring to the works of Westerhoff & Anning (2000) and McKnight *et al.* (2001), two indicators related to the

nature of the DOM were extracted from the emission spectrum obtained for $\lambda_{ex} = 370$ nm (Figure 2): the wavelength of maximum fluorescence or peak wavelength (PW) and the ratio of the fluorescence intensities for the emission wavelengths of 450 and 500 nm (FR). If the PW is lower than 450 nm, the DOM is autochthonous, and if it is larger than 450 nm, the DOC is allochthonous. The fluorescence ratio (FR) is the ratio of the fluorescence intensities for the emission wavelengths of 450 and 500 nm. A value greater than 1.8 indicates an autochthonous source, while a value less than 1.5 indicates an allochthonous source.

The spectra exhibit very similar shapes except at the river station located farthest upstream (O1). This is the only station for which PW is larger than 450 nm, which could indicate an allochthonous origin. However, all the FR values (Table 2) are larger than 1.8, which corresponds to an autochthonous, i.e. bacterial, origin. O1 is the station for which FR is the least (1.83). What cannot be told from the spectra is the origin of the bacterial activity: natural, i.e. related to the decomposition of natural litter (leaves, etc.); or anthropogenic, i.e. related to the presence of domestic or farm ill-treated effluents.

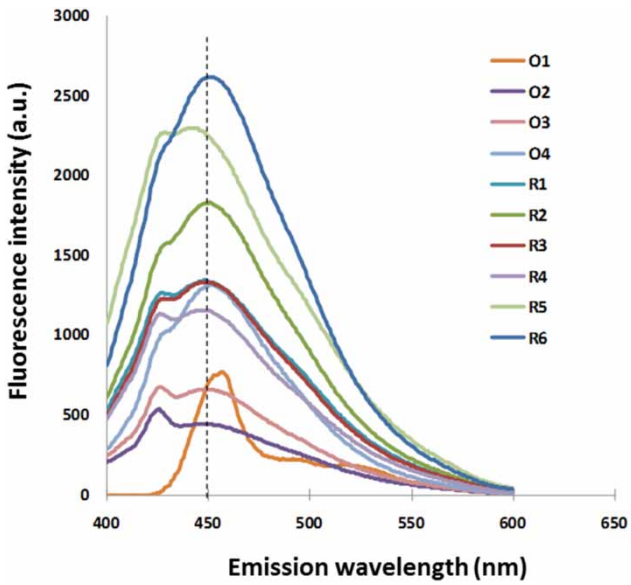

Figure 2 | Fluorescence emission spectra ($\lambda_{ex} = 370$ nm) of the river (O) and reservoirs (R) samples.

The synchronous fluorescence spectra (Figure 3) enable us to better appreciate the changes of the tryptophan-like fluorescence ($\lambda_{ex} \approx 285$ nm, $\lambda_{ex} \approx 335$ nm) for river stations and reservoirs (Reynolds 2003). As identified on the EEMs, the R4 and R6 reservoirs are particularly polluted with very high tryptophan-like fluorescence intensities (2640 a.u. for R4 and 3090 a.u. for R5), whereas the most polluted river samples exhibit tryptophan-like intensities of approximately 900 a.u. This fluorescence is mainly due to substances similar to tryptophan, including structures containing an indole group. There is still debate over its origin (Hudson *et al.* 2007): a natural origin due to bacterial transformations in the aquatic environment and/or discharges of untreated domestic (Baker *et al.* 2003) and/or farm effluents (Baker 2002). However, with the very large intensities of tryptophan-like fluorescence observed here and compared to the O1 station, it is likely that untreated sewage is polluting the reservoirs. If some quenching of the tryptophan-like fluorescence occurs due to humic-like components, the situation concerning tryptophan-like substances discharge will worsen (Wang *et al.* 2015).

Correlations between fluorescence and pollution indicators

Linear correlations with high coefficients of determination were obtained between the total synchronous fluorescence $TF = \int_{250}^{500} SFS50(\lambda)d\lambda$ on one hand and BOD_5 ($R^2 = 0.91$) and DOC ($R^2 = 0.95$) on the other (Figure 4). Both correlations were meaningful and could allow estimation quickly and without a sophisticated instrument BOD_5 and DOC: the calculated value of the Fisher–Snedecor test statistic F was equal to 88.3 and 155 respectively, whereas the tabulated value of F for a significance level $\alpha = 0.05$ is 2.02. No general correlation could be obtained between ammonia and the tryptophan-like fluorescence intensity (F285 measured at $\lambda_{ex} = 285$ nm/$\lambda_{em} = 335$ nm). Such a

Table 2 | Fluorescence ratio (ratio of the fluorescence intensities for the $\lambda_{em} = 450$ and $\lambda_{em} = 500$ nm) (O: river; R: reservoir)

Station	O1	O2	O3	O4	R1	R2	R3	R4	R5	R6
Fluorescence ratio	1.83	1.88	2.10	2.31	1.88	2.02	1.95	2.03	1.92	1.95

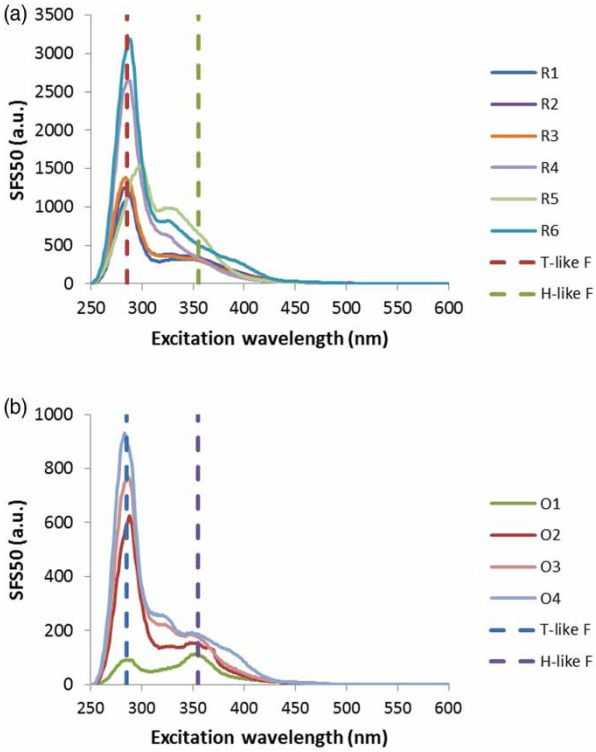

Figure 3 | Synchronous fluorescence spectra for $\lambda_{em} - \lambda_{ex} = 50$ nm (SFS50): (a) reservoirs, (b) river stations.

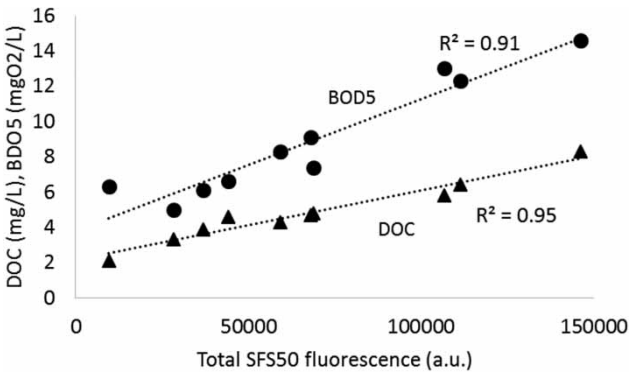

Figure 4 | Correlations between the total synchronous fluorescence, BOD_5 and DOC.

correlation would help in quick estimation of the field ammonia. Partial correlations were obtained for the river samples ($R^2 = 0.23$) and for the reservoir samples ($R^2 = 0.54$) (Figure 5(a)). However, only the linear correlation for the reservoir sample was meaningful: F was equal to 4.75, whereas the tabulated value of F for a significance level $\alpha = 0.05$ is 2.02. It should be noted that the relation between the substances related to tryptophan-like

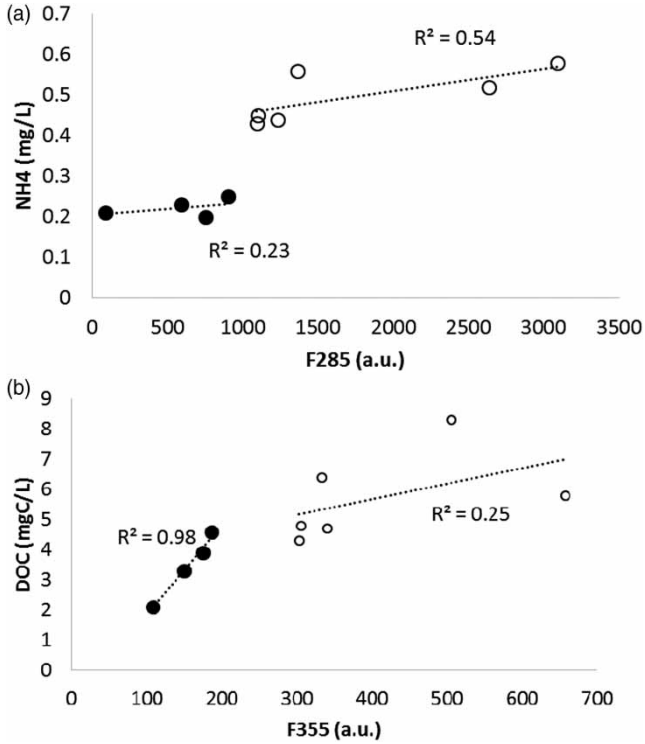

Figure 5 | Correlations (a) between ammonia and the tryptophan-like fluorescence intensity (measured at $\lambda_{ex} = 285$ nm/$\lambda_{em} = 335$ nm), (b) between DOC and the humic-like fluorescence intensity (measured for $\lambda_{ex} = 355$ nm/$\lambda_{em} = 405$ nm). Close symbols = river stations (O1–O4), open symbols = reservoirs (R1–R6).

fluorescence and ammonia is not straightforward, and different trends have been reported in literature (Baker *et al.* 2003; Baker & Inverarity 2004). A meaningful linear correlation with a high coefficient ($R^2 = 0.98$, with $F = 77.7$ against a tabulated value of F for a significance level $\alpha = 0.05$ of 2.13) was found for the river stations between DOC and the humic-like fluorescence (F355, measured at $\lambda_{ex} = 355$ nm/$\lambda_{em} = 405$ nm), but not for the reservoir samples ($R^2 = 0.25$) (Figure 5(b)). Linear correlations between F285 and DOC ($R^2 = 0.88$) and BOD_5 ($R^2 = 0.67$) had lower coefficients of determinations than the correlations with the total synchronous fluorescence.

CONCLUSIONS

The high tryptophan-like fluorescence intensity detected on synchronous fluorescence spectra collected with a gap of 50 nm between excitation and emission did not correlate

well with ammonia, although the intensity is typical of foul waters, polluted by untreated domestic or farm wastewater. The tryptophan-like fluorescence intensity (F285) and humic-like fluorescence intensity (F355) correlated well with ammonia for reservoir samples and DOC for river samples, respectively. These correlations may be sufficient to give a rapid indication of the pollution level. However, a more precise monitoring of the DOC is possible using a full SFS50 spectrum. This finding should prompt the development of portable devices able to provide this type of information, or at least dual-systems for tryptophan-like and humic-like fluorescence.

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