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Impact study of the wastewater treatment plant effluents on fluorescence of coastal zone water using fluorescence EEM-PARAFAC

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Stéphane Mounier

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10 **Impact study of the wastewater treatment plant effluents on fluorescence of coastal zone**
11 **water using fluorescence EEM-PARAFAC.**
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65 ABSTRACT : Human activity puts pressures on coastal zone altering dissolved organic matter
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67 quality. No specific self-differentiating fluorescence signal of the anthropogenic DOM in the
68
69 coastal zone is found in the literature. Solar irradiation were conducted on mixed samples of
70
71 River water, sea water, wastewater treatment plant effluent. Excitation Emission Matrices of
72
73 Fluorescence were used to monitor the fate of wastewater treatment plant effluent. Multilinear
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75 regression of CP/PARAFAC components contribution depending on mixing composition were
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77 done and was excellent. Kinetics of decreasing contribution versus irradiation time were
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79 investigated. Second order Kinetics were found for C1 and C2. Distinction between fluorescence
80
81 signal of endmembers was undoable. Wastewater treatment plant endmember after
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83 photodegradation was highly predominant.
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90 Keywords : Fluorescent Organic Matter, EEM-PARAFAC , multilinear regression,
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92 photodegradation, Coastal zone
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96 **1. Introduction**

97
98 Coastal zone is a transitional zone between the terrestrial and oceanic zones (Huguet et al.
99
100 2009) and mixing zone between marine/oceanic waters inputs and the freshwater riverine inputs
101
102 (Parlanti et al. 2000a). Dissolved organic matter (DOM) play an important role in physical,
103
104 chemical functioning of aquatic ecosystems (Hansell 2009) and biogeochemical processes
105
106 (Hansell & Carlson 2014a) and is a heterogenous mixture of organic compounds of both aromatic
107
108 and aliphatic nature (Hansell & Carlson 2014b). Chromophoric Dissolved Organic Matter
109
110 (CDOM) is a fraction of DOM which can interact with light (Coble 1996a; Coble 2007; Lei et al.
111
112 2018) and is ubiquitous in aquatic environmental media (Nelson & Siegel 2013) with a subgroup
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122
123 fluorescing FDOM (Coble 1996b; Mostofa et al. 2012). DOM plays a key role in global carbon
124
125 cycle (Hansell 2001) and is highly influenced by continental inputs (Fichot & Benner 2012;
126
127 Yamashita et al. 2013) and by autochthonous sources (Romera-Castillo et al. 2011). Most of
128
129 organic matter in the coastal zone is of terrestrial origin (Hedges et al. 1997; Parlanti et al.
130
131 2000b).
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135
136 Human activity has contributed to increased inputs of terrestrial CDOM in aquatic ecosystems
137
138 (Massicotte et al. 2017). Urbanization is increasing and expected to triple between 2000 and 2030
139
140 (Seto et al. 2012) with higher population density and migration to the coastal zone (Hugo 2011a;
141
142 Hugo 2011b). In turn, it changes land cover, hence quality and quantity of DOM in rivers (Seto et
143
144 al. 2012). Anthropogenic sources of organic matter vary from industrial (Carvalho et al. 2008),
145
146 agricultural (Manninen et al. 2018), wastewater treatment plants effluents (Maizel & Remucal
147
148 2017) , landfill leachates (Oloibiri et al. 2017). Moreover, it has been found (Williams et al.
149
150 2016) that anthropogenic influence on urban watersheds caused distinct DOM composition.
151
152 However, contribution of anthropogenic signal of FDOM in coastal zone is not yet well defined
153
154 and evaluated in the literature. Biogeochemistry of natural waters is impacted significantly by
155
156 photo-reactivity of CDOM (Andrew et al. 2013; Lønborg et al. 2016) since photochemistry
157
158 affects bioavailability of DOM (Moran & Zepp 1997; Oleinikova et al. 2017), microbial activity
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160 (Piccini et al. 2009) and production of DOM of different character (Zhu, Yang, et al. 2017).
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167 Partial information can be extracted from global analytical techniques (DOC, TOC, BOD,
168
169 etc...) due to complex composition of DOM. And these techniques are time consuming and
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171 require elaborated sample preparation. Optical properties of CDOM and FDOM provides a
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173 valuable tool in delineating DOM sources (Osburn et al. 2016a) and tracking DOM fluxes of
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183 terrigenous origin into ocean (Osburn et al. 2016b) enables online or real-time monitoring in
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185 various media (Helms et al. 2013; Cohen et al. 2014). There are so many advantages of
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187 fluorescence spectroscopy which is useful, less time-consuming, inexpensive, precise qualitative
188
189 and quantitative technique (Fellman et al. 2010; Zhu et al. 2014) used among varying scientific
190
191 fields (Gao et al. 2017b). Excitation Emission Matrix fluorescence spectroscopy (EEM) has
192
193 furthered scientific research in aquatic systems (Kim & Kim 2015; Dainard et al. 2015; Sgroi et
194
195 al. 2017; Cheng et al. 2018). It enables characterization of optical properties of FDOM due to its
196
197 high sensitivity, good selectivity and non-destruction of samples (Coble 1996c). Coupled with
198
199 Canonical Polyadic / Parallel Factor Analysis (CP/PARAFAC) enables deconvolution of
200
201 overlapping independent EEM spectra into distinct components (Stedmon & Bro 2008a). In
202
203 addition, the use of this technique EEM/PARAFAC in tracing the DOM fractions which is
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205 cost-effective and rapid in chemistry and aquatic ecology fields is in fact a significant advance in
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207 those fields (Stedmon et al. 2003a).
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214 To the best of our knowledge, there is no previously found pattern or specific
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216 self-distinguishing fluorescence signal of anthropogenic organic matter in the coastal zone. The
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218 present study is focussing on wastewater treatment plants effluent discharge in urban river
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220 systems. Laboratory endmember mixing experiments was conducted of river water , sea water
221
222 and wastewater treatment plant, to define contributions after mixing and solar irradiation
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224 experiment. The present study is the first of its kind to develop and propose a multivariate linear
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226 regression for the prediction of FDOM signal and its photodegradation kinetic as a function of
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228 the mixing composition and solar exposure.
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245 **2. Material and methods**
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250 **2.1 Sampling Sites**
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252 Gapeau river originates at Signes city (43° 17' 24" N, 5° 52' 59" E) and run till the sea at city
253 of Hyères (43°06'42" N, 6°11'33" E) in southeastern part of France (figure 1) with a length of
254 34.4 km (Ollier 1972) and watershed of 544 km² (Ducros et al. 2018) with a pluvial regime.
255 River water (RW) was sampled roughly 500 m before wastewater treatment plant which is
256 located at (43°08'38.6"N 6°05'36.1"E) whereas wastewater treatment plant effluent (WW) was
257 sampled at its output directly. Wastewater treatment plant of La Crau city has a daily volume of
258 0.17 m³/s. Sea water (SW) was sampled at the coastal area of Hyères city at roughly seven meters
259 far from beach (43°06'10.4"N 6°10'38.3"E). Plastic bottle of one liter (cleaned with ethanol
260 100% and three times rinsed with 18.2 MΩ at 25 °C MilliQ water) was used in sampling.
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Fig. 1. Locations of sampling sites in Southeastern France. RW , WW , SW are the points from left to right colored in red.

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364 2.2. Materials of irradiation experiment
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368 2.2.1. Filtration
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371 RW , SW , WW samples were filtered using MilliPore filters (Type GNWP 0.20 μm , 47 mm
372 diameter) and filtration kit pre-rinsed with acidified water (10% HNO_3). Filterates were put in a
373 new one liter dark glass bottle (pre-rinsed with 10 % HNO_3 and 3 times with 18.2 $\text{M}\Omega\cdot\text{cm}$ at 25
374 $^\circ\text{C}$ MilliQ-water) and transferred to refrigerator at 4 $^\circ\text{C}$ in the dark. Filtrates were used for
375 preparation of 15 mixtures. The measured pH for RW, WW ,SW were 7.4 ± 0.4 .
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383 2.2.2. Preparation of mixtures
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386 Fifteen 50 mL quartz vials were washed with reverse osmosis water then transferred to 10 %
387 HNO_3 bath for 24 hours then rinsed three times with 18.2 $\text{M}\Omega\cdot\text{cm}$ at 25 $^\circ\text{C}$ Milli Q-water. Then
388 burnt in oven at 450 $^\circ\text{C}$ for 24 hours to ensure the elimination of organic/inorganic carbon.
389 Fifteen mixtures were fabricated. The exact mixing percentages for each mixture are summarized
390 in table S1 in supplementary information SI. Percentages were taken by weight, assuming a
391 density of 1.00, 1.00 and 1.025 for WW, RW and SW respectively. A serial number was given to
392 the vial according to its corresponding mixture (table S1). Each vial was shaken gently by hand
393 to insure homogeneity of mixtures.
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410 2.2.3. Irradiation experiments
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423 The mixtures were prepared in quartz vials which then were transferred on August 28th 2015
424
425 in the evening to the roof of laboratory MIO/Toulon University (43° 08' 11.2" N 6° 01' 16.7" E).
426
427 These quartz vials were put at sufficient distances to insure receiving same solar irradiation
428
429 conditions. The irradiation started on August 28th 2015 (Day zero) and finished on September
430
431 11th 2015 for a total of ten days of irradiation.
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438 2.2.4. Solar irradiation/insolation measurement 439 440 441

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443 Daily solar insolation data were measured on place in volts using photovoltaic cell (Solar Cell
444
445 9V/109 mA) for each day of irradiation. A mean irradiance of 2 343 volts per day was detected.
446
447 During this period the irradiation is between 5 to 6 kWh.m⁻² corresponding to 39 mW.cm⁻²
448
449 (www.meteofrance.com).
450
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452

453 2.3. Excitation Emission Matrix EEM fluorescence spectroscopy 454 455 456

457 2.3.1. Irradiated water Sampling 458 459 460 461

462 Three mL aliquots from each 50 mL exposed quartz vial were sampled and transferred into
463
464 10x10 mm quartz cell at different irradiation times. EEMs of solar irradiation experiment sample
465
466 were performed using fluorescence spectrophotometer (F4500, Hitachi). Ultrapure Perkin Elmer
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468 deionized water was measured to check spectrofluorimeter stability and measure daily the Raman
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470 peak intensity. Scan speed was set at 2,400 nm.min⁻¹. Emission spectra were collected at 5 nm
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483 intervals between 220 and 420 nm, while excitation spectra were measured between 200 and 400
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485 nm at 5 nm intervals. Slit widths for both excitation and emission wavelengths were set at 5 nm.
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489 2.3.2. EEM Data processing

494 2.3.2.1. Raman measurement

496 Water Raman scans of Perkin Elmer blanks were measured for each irradiation day (from Aug.
497
498 28th to Sept. 11th 2015) using the same fluorescence spectrophotometer (F4500, Hitachi). Scans
499 used an excitation wavelength of 350 nm whereas the emission intensities were measured from
500
501 350 nm to 650 nm with a step of 1 nm. Scan speed was 240 nm.mn⁻¹ with the same slit width of
502
503 5 nm on excitation and emission monochromators.
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509 2.3.2.2. Raman Normalization

512 Each excitation emission matrix values corresponding to each mixture were normalized to the
513
514 integrated Raman signal measured at the corresponding irradiation date. The integrated Raman
515
516 signal was calculated by integration the area under the curve from 370 nm to 420 nm (Lawaetz &
517
518 Stedmon 2009) and used for EEMs normalisation.
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523 Spectral contribution of each CP/PARAFAC components to total EEM fluorescence was
524
525 determined using CP/PARAFAC algorithm (Bro 1997; Stedmon & Markager 2005a). Finally, the
526
527 150 Raman-corrected EEMs were modelled using a MATLAB software (MathWorks R2015b)
528
529 based on Nway toolbox and DOMFluor toolbox (Stedmon & Bro 2008b). Raman and Rayleigh
530
531 scattering were removed according to Zepp method (Zepp et al. 2004). No inner filter correction
532
533 was done as samples were in linearity domain. Nonnegativity constraints were applied for
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541 CP/PARAFAC components for excitation and emission loadings. Accepted correct number of
 542 CP/PARAFAC components and model validation was taken according to evaluation of
 543 CONCORDIA score and split-half analysis. No outliers were found in the dataset and a three
 544 components model was validated. Once decomposition is done, for each mixture, contributions of
 545 each components were normalised to the maximum value in the whole EEM dataset, which is, in
 546 that work, the initial one before the start of solar irradiation for all experiments, according to the
 547 following equation :

$$548 \quad C_i^{T_n} = \frac{c_i^{T_n}}{\max(c_i^{T_n})^{\forall n}} \quad (eq.1)$$

549 Where :

550 T_n is the n^{th} day of irradiation. $c_i^{T_n}$ is value of contribution of CP/PARAFAC component i and
 551 $C_i^{T_n}$ the normalised to the maximum contribution of CP/PARAFAC component i from 1 to 3
 552 components.

553 2.4. Multi-linear regression

554 Considering f_{RW} , f_{SW} which are the percentage (w/w) of RW and SW in the quartz vial
 555 mixture respectively, a multi-linear regression was conducted for all f_{RW} , f_{SW} of a fixed
 556 CP/PARAFAC component i for each irradiation day T_n , considering the following general
 557 multilinear regression formula :

$$Y = a_0 + a_1 \cdot X_1 + a_2 \cdot X_2 + \dots + a_n \cdot X_n \quad (\text{eq. 2})$$

2.4.1. Multilinear regression of three endmember

RW, SW and WW mixture is constrained by mass total sum of three content fraction that should be equal to 100 according to the following equation :

$$f_{SW} + f_{RW} + f_{WW} = 100 \quad (0 < f_i < 100) \quad (\text{eq.3})$$

Where f_{SW} , f_{RW} , f_{WW} are content fraction of SW, RW and WW in mass respectively. All percent fractions obviously positive and less than or equal to 100.

Then

$$f_{WW} = 100 - f_{SW} - f_{RW} \quad (\text{eq. 4})$$

By substituting in eq. 2 for f_{WW} where $n=3$, the different terms, the following equation can be obtained :

$$C_i^{Tn} = a_{i,0} + a_{i,1} \cdot f_{SW} + a_{i,2} \cdot f_{RW} + a_{i,3} \cdot f_{WW} \quad (\text{eq.5})$$

Where C_i^{Tn} is normalised contribution of CP/PARAFAC component number i , and $a_{i,1}$, $a_{i,2}$, $a_{i,3}$ the respective partial contribution to this contribution by the three endmember SW, RW and WW. To simplify, C_i^{Tn} is replaced by C_i^* in the next equations

By substituting for f_{WW} by its expression in (eq.4) the following equations can be obtained :

$$C_i^* = a_{i,0} + a_{i,1}f_{SW} + a_{i,2}f_{RW} + a_{i,3} \cdot (100 - f_{SW} - f_{RW}) \quad (\text{eq.6})$$

$$C_i^* = a_{i,0} + a_{i,1}f_{SW} + a_{i,2}f_{RW} + a_{i,3} \cdot 100 - a_{i,3}f_{SW} - a_{i,3}f_{RW} \quad (\text{eq.7})$$

By arranging similar terms together and taking the common factor, the following equation can be obtained :

$$C_i^* = (a_{i,0} + a_{i,3} \cdot 100) + (a_{i,1} - a_{i,3})f_{SW} + (a_{i,2} - a_{i,3})f_{RW} \quad (\text{eq.8})$$

By giving a proper term for the constant and newly modified coefficients to account for f_{WW} term as shown :

$$A_{i,0}^{WW} = (a_{i,0} + a_{i,3} \cdot 100) \quad A_{i,1}^{WW} = (a_{i,1} - a_{i,3}) \quad A_{i,2}^{WW} = (a_{i,2} - a_{i,3})$$

The final multilinear regression equation is obtained as a function of two content fractions of two endmembers :

$$C_i^* = A_{i,0}^{WW} + A_{i,1}^{WW}f_{SW} + A_{i,2}^{WW}f_{RW} \quad (\text{eq.9})$$

721
 722
 723 Where $A^{WW}_{i,0}$, $A^{WW}_{i,1}$ and $A^{WW}_{i,2}$ represent multilinear regression coefficients related to mixing
 724
 725 equation when f_{WW} is expressed in terms of content fraction of the other two endmembers (f_{RW} and
 726
 727 f_{SW}). Any circular permutation can not yield the $a_{i,*}$ coefficients independently.
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732 $A^{WW}_{i,0}$ is the constant in the multilinear regression equation which contains information about
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 734 WW effect in the multilinear regression, $A^{WW}_{i,1}$ is the coefficient of of content fraction of SW
 735
 736 endmember which not only represent its effect but also the effect of the wastewater treatment
 737
 738 plant effluent WW, $A^{WW}_{i,2}$ is the coefficient of of content fraction of RW endmember which not
 739
 740 only represent its effect but also the effect of WW. Determination of $A^{WW}_{i,0}$, $A^{WW}_{i,1}$ and $A^{WW}_{i,2}$ was
 741
 742 done for each exposition day.
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749 2.5. Kinetics

751 The measured irradiation in volts was used as a proxy for photodegradation reaction time . The
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 753 determination of the kinetic order of the multilinear regression parameters/coefficients for all T_n
 754
 755 was conducted. These multilinear regression are expressed mathematically as a function of volts :
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 759

$$\begin{aligned}
 &A^{WW}_{i,0}(V) \\
 &A^{WW}_{i,1}(V) \\
 &A^{WW}_{i,2}(V)
 \end{aligned}
 \tag{eq.10}$$

769
 770 Where V is received solar irradiation in Volts (V) at each day T_n . CP/PARAFAC contribution
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 772 during irradiation experiment can be expressed as a function of content fraction of two
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 774 endmember depending on V, which enable kinetic study:
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$$C^*_i(V) = A^{WW}_{i,0}(V) + A^{WW}_{i,1}(V) \cdot f_{SW} + A^{WW}_{i,2}(V) \cdot f_{RW} \quad (\text{ep.11})$$

The zeroth, 1st, 2nd and 3rd order kinetics were calculated and compared to find out the most linear model which fits the data (Wright 2004).

3. Results and Discussion

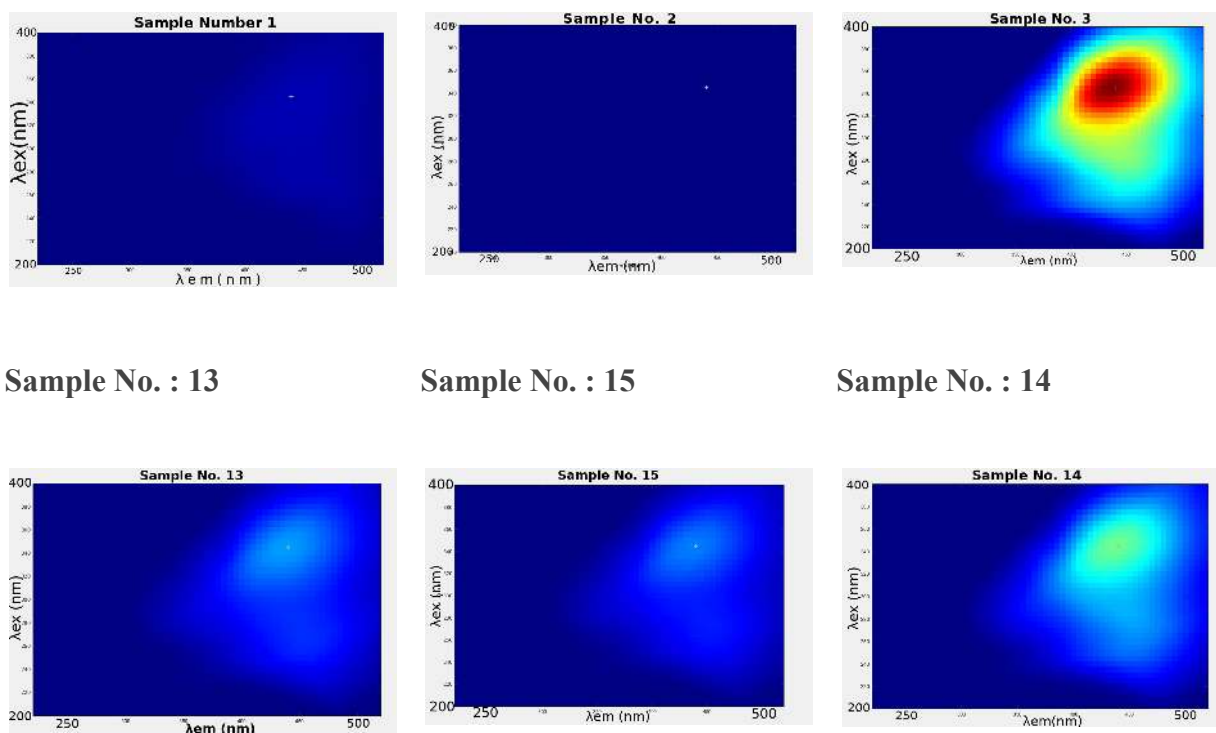
3.1. EEMs Results

Figure 2. shows the excitation emission matrices EEM of fluorescence for the samples numbers 1, 2, 3, 13, 14, 15 which are described in table 2. These EEMs are shown after the removal of Rayleigh and Raman scattering and Raman normalization.

Sample No. :1

Sample No. : 2

Sample No. : 3



Sample No. : 13

Sample No. : 15

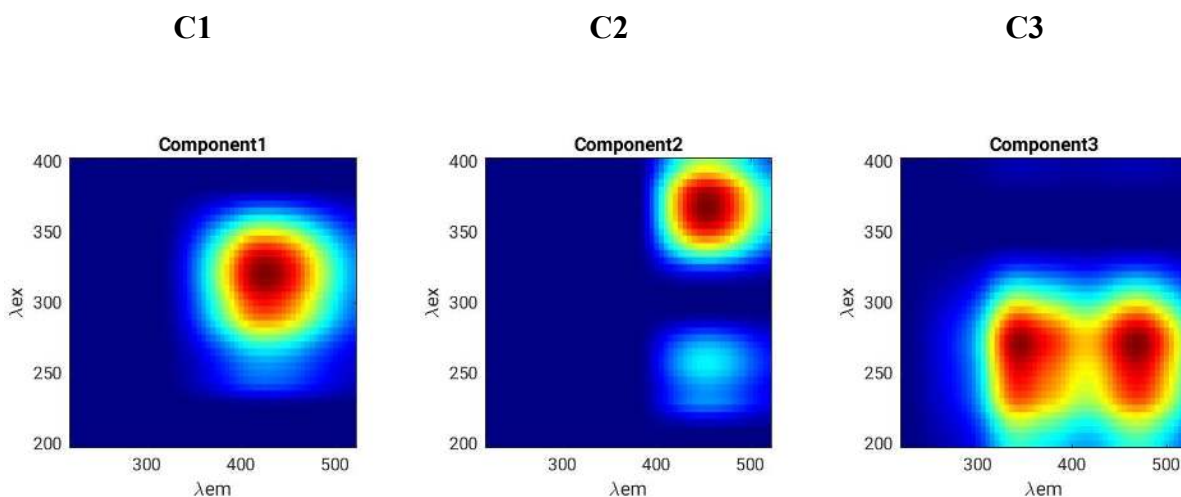
Sample No. : 14

Fig. 2. The excitation emission matrices of Samples number 1 , 2 ,3, 13 , 14 and 15 whose composition is (100,0,0), (0,100,0) ,(0,0,100), (50,0,0), (0,50,0) and (0,0,50) respectively (table S1)

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902
903 Split-half analysis was conducted for three subsets of the EEM-dataset which asserted the
904 non-existence "finding" of any protein-like fluorescent signal. That's because the CP/PARAFAC
905 algorithm doesn't capture what's already not there.
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915 3.2. CP/PARAFAC decomposition results

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918 CORCONDIA analysis showed drop down between four components and five, from near 70 %
919 to less than or around 30 % which surpasses acceptable threshold of 60% where as it showed a
920 value of 80.75 % for three components, indicating that a three-factor model was appropriate. The
921 split-half analysis confirm this three components model. Spectral contour plots of components
922 and their corresponding loadings for both the excitation and the emission wavelengths are shown
923 in figure 3.
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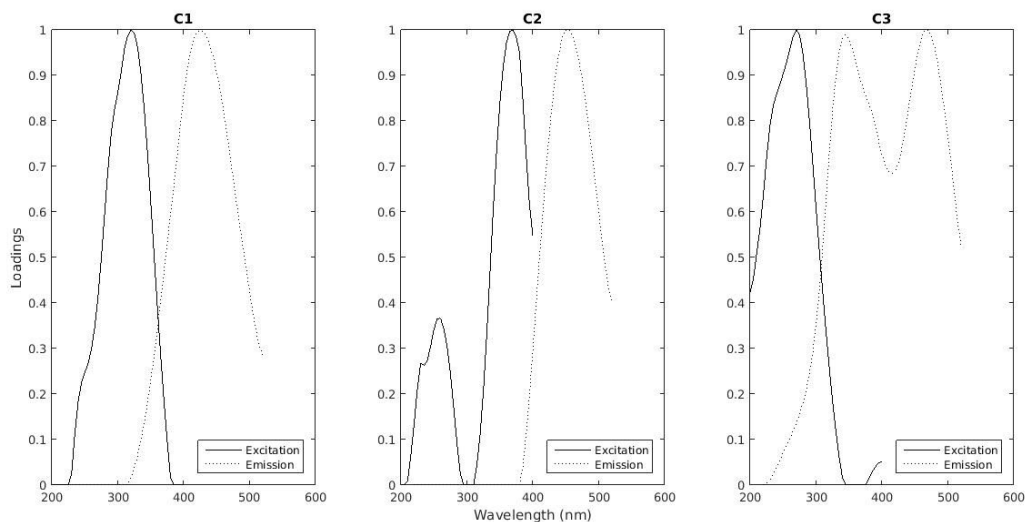


Fig. 3. Contour plots of CP/PARAFAC components found in EEM dataset. Spectral loadings of excitation and emission wavelengths of the three identified CP/PARAFAC in the present study.

Description of excitation and emission pairs of main peak positions for CP/PARAFAC components are summarized in Table 1 and compared to previously identified components and peaks in the literature.

Table 1

Descriptions of CP/PARAFAC components and comparison with literature

Component	$\lambda_{EX}/\lambda_{EM}$ (nm)	Description and references in literature
Component C1	320/425	Component 4 (Stedmon et al. 2003b) : terrestrially derived organic matter
		Peak C (Coble 1996d; Coble et al. 1998) : visible humic-like
		Component 2 (Yamashita et al. 2008a) : terrestrial humic-like
		Component 4 (Yamashita et al. 2008b)
Component C2	370/455	Component 3 (Stedmon et al. 2003c)
		Component G3 (Murphy et al. 2011a)
		Component 3 (Li et al. 2014a)
		Component 7 (Osburn et al. 2016a)
		Component 5 (Baghoth et al. 2011)
		Component 1 (Zhu et al. 2017a) Humic-Like
Component C3	270/(340) 470	Component 3 (Yamashita et al. 2008c) : Humic-like component
		Peak T : Tryptophan like fluorescence (Coble 1996d)
		Q2 (Cory & McKnight 2005) Small resemblance to C6 (Zhou et al. 2013) which was Oil-related, degradation product

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1087 Based on maximum peak position, these three components have been previously identified
1088 (Table 1). C1, showed an excitation maximum at 320 nm and an emission maximum at 425 nm
1089 and a range of excitation emission wavelengths ($E_x=300-350$ nm, $E_m=400-450$ nm). Previous
1090 studies have associated this component to UVA humic-like fluorescent CP/PARAFAC
1091 component and Peak C (Coble 2007) and peak “ ∞ ” (Parlanti et al. 2000c; Sierra et al. 2005). It
1092 was previously found from terrestrial, anthropogenic, agricultural sources (Stedmon et al. 2003d;
1093 Stedmon & Markager 2005b). C2 component showed an excitation maximum at 370 nm and an
1094 emission maximum at 455 nm and a range of excitation emission wavelengths ($E_x=340-400$ nm,
1095 $E_m= 400-500$ nm). In addition, spectra of C2 resembles spectra of component “G3” which has
1096 $E_{x_{max}}=350$ nm, $E_{m_{max}}=428$ nm in (Murphy et al. 2011b) who have attributed it to wastewater or
1097 nutrient enrichment tracer. This component has also been identified as humic-like component,
1098 similar to “C3” (Li et al. 2014b) which had two excitation maxima (at 250, 350 nm)
1099 corresponding to the same emission maxima (at 440 nm). Furthermore, C2 has very similar
1100 spectra to “C7” from recycled water studies, which included samples of wastewater, treated
1101 water, gray water (Osburn et al. 2016b). C3, showed an excitation maximum at 270 nm and an
1102 emission maximum at 340 nm and 470 nm which is bimodal in emission. It’s range of excitation
1103 emission wavelengths is $E_x=200-300$ nm, $E_m=300-500$ nm. The 1st peak (270/340 nm) is near
1104 the tryptophan-like peak (Coble 1996e). This component could be protein-like component but it
1105 resembles noise.
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3.3. Multivariate Linear Regression Parameters

Numerical values of multilinear regression coefficients (eq. 9) for each CP/PARAFAC component C1, C2 and C3 are the following for time zero, i.e. Aug. 28th 2015.

For

$$C1 = 100.45 - 0.99 * f_{SW} - 0.93 * f_{RW} \text{ with coefficient of determination } r^2 \text{ value of } 0.99$$

$$C2 = 98.67 - 0.97 * f_{SW} - 0.92 * f_{RW} \text{ with } r^2 \text{ value of } 0.99$$

$$C3 = 72.84 - 0.66 * f_{SW} - 0.64 * f_{RW} \text{ with } r^2 \text{ value of } 0.84$$

From the above substituted equations, it can be seen that the correlation coefficient is greater than 0.95 for C1 and C2 indicating multilinear regression is excellent. Values of the intercept are always greater than values of coefficients of f_{SW} and f_{RW} by two orders of magnitude. These values of the parameters/coefficients of the multilinear regression are calculated after the Raman unit corrections of the EEM-dataset. Knowing that values of the intercept account for effect of f_{WW} on contribution of CP/PARAFAC component, these results show that contribution of CP/PARAFAC component decreases with increasing f_{SW} or f_{RW} . Indeed, all of coefficients f_{SW} , f_{RW} have negative sign. As a consequence, it can be observed that for $f_{SW}=100$ or $f_{RW}=100$, contributions are weak compared to the $f_{WW}=100$, i.e. $f_{SW}=f_{RW}=0$. These indicated that most of fluorescence contributions are due to WW endmember considering the blank fluorescence $a_{i,0}$ as negligible. Considering that WW is the principal contributor to the all components contribution, there is no specific end member response for SW and RW in these mixtures.

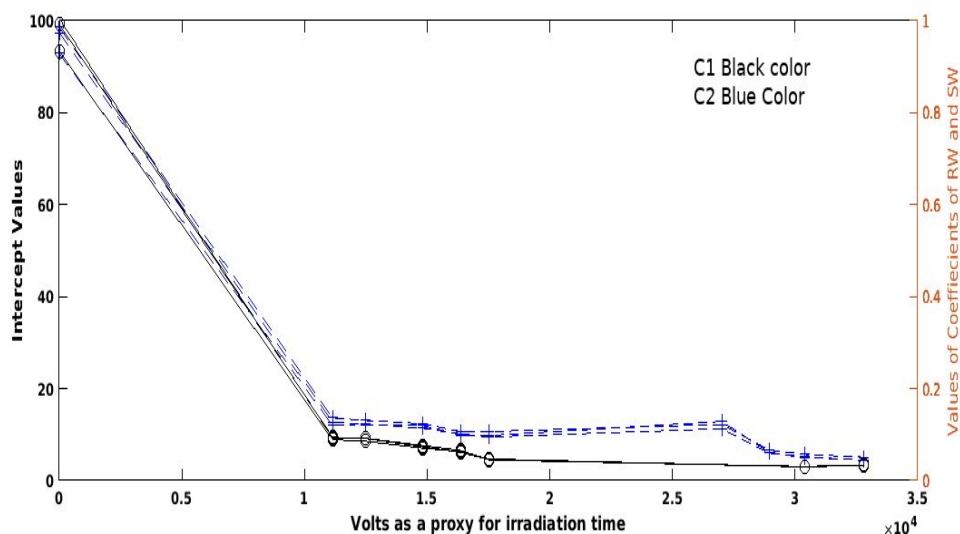


Fig. 4. The variation with irradiation time (volts as proxy for time) of the parameters of multilinear regression (Intercept , absolute values of f_{RW} coefficient, absolute values of f_{SW} coefficient) for C1 and C2 .

The intercept and the coefficients of f_{RW} and f_{SW} of CP/PARAFAC C1 (shown in black) has a faster degradation rate than their counterparts of C2 (shown in blue) as shown in figure 4. which in agreements with the values of the kinetic rate constants as shown in table 6 .

3.4. Determination of kinetic decay coefficient and its kinetic order

The irradiation experiment showed continuous decrease of fluorescence signal with irradiation time. No stable signal or significant fluorescence increase was observed like in other works (; Song et al. 2015; Zhu et al. 2017b). Integrated rate law linear equations of zeroth, 1st, 2nd, and 3rd kinetic order were investigated for each coefficient $A^{WW}_{i,0}$, $A^{WW}_{i,1}$ and $A^{WW}_{i,3}$ to determine kinetics of photodegradation for each multilinear regression parameter. Kinetic order was chosen according to the best coefficient of determination according to kinetic integrated order law,

selecting linear correlation coefficient which must be greater than the threshold 0.75 after eliminating outliers (Wright 2004). Results are presented in table 2 for kinetic order, and kinetic constant are presented in table 3. It was found that all kinetics are 2nd order and are in agreement with a previous work (Yang et al. 2014). Long term photodegradation of fluorescent organic matter is a bimolecular reaction probably involving excited organic matter and organic matter itself. Other work assumed first order kinetic under solar simulated irradiation (Wu et al. 2016) but experiment were done during 12h and under 2.80 mW.cm⁻² (visible) and 70.00 mW.cm⁻², corresponding to the starting point of present irradiation experiment that could be assumed as pseudo-first order kinetic. On the same time, Hee et al 2018 didn't find variation with a 4,2 mW.cm⁻², during 10 hours of exposition.

Table 2

Kinetic order of coefficients of multilinear regression for each CP/PARAFAC with its corresponding r^2 of 2nd order kinetics to the right. "NA" means that correlation coefficient for 2nd order rate was less than 0.75, and was dismissed.

C1						C2						C3		
$A^{ww}_{1,0}$	r^2	$A^{ww}_{1,1}$	r^2	$A^{ww}_{1,2}$	r^2	$A^{ww}_{2,1}$	r^2	$A^{ww}_{2,1}$	r^2	A^{ww}_2	r^2	$A^{ww}_{3,1}$	$A^{ww}_{3,2}$	$A^{ww}_{3,3}$
<i>interpt</i>		(f_{sw})		(f_{rw})		<i>interpt</i>		(f_{sw})		2		<i>interpt</i>	(f_{sw})	(f_{rw})
2	0.94	2	0.95	2	0.96	2	0.83	2	0.78	2	0.82	NA	NA	NA

Table 2 clearly shows that the kinetic order of photodegradation reaction for each parameter of the multi-linear regression for CP/PARAFAC components C1 and C2 are second-order kinetics and the corresponding coefficient of determination r^2 is greater than 0.75 . For the third

CP/PARAFAC component C3 , no order could be found since this component is noise-like component (table 3) and it was neglected from the analysis.

Table 3

Kinetic constant for coefficients of multilinear regression for each CP/PARAFAC component. Values in parenthesis are standard deviation for kinetic constant. All values should be multiplied by 10^6 . NA : Not Available

	C1	C2	C3
$A^{WW}_{*,0}$	9.68(1.00)	4.85(0.78)	NA
<i>interpt</i>			
$A^{WW}_{*,1}$	-987.35(92.31)	-542.80(101.97)	NA
(f_{SW})			
$A^{WW}_{*,2}$	-977.67(83.84)	-552.56(91.70)	NA
(f_{RW})			

Values of kinetic constant for intercept for both C1 and C2 are smaller than those values of kinetic constant for $A^{WW}_{1,1}$ which is coefficient of f_{SW} and $A^{WW}_{1,2}$ which is coefficient of f_{RW} (table 3). This result could be interpreted as follows: C1 and C2 contributions of RW and SW are more sensitive to photodegradation than WW which in turn decays approximately 100 times slower under irradiation suggesting its dominance in the residual fluorescence of both C1 and C2 after long term irradiation. Hence even if there is no specific endmember CP/PARAFAC

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1383 contribution, it exist a photosensitivity difference between WW and RW or SW. Under long
1384 irradiation, WW contribution is more resilient and refractory to photodegradation. This difference
1385 of behavior depending on endmember mixing was already observed between terrestrial and
1386 autochthonous organic matter (Zhu et al. 2017c). Small differences were also observed on
1387 reclaimed water using fluorescence matrix regional integration between humic-like and
1388 protein-like under high irradiation (Wu et al. 2016). Therefore, it can be said that wastewater
1389 treatment plant fluorophores are somehow similar to natural fluorophores but more refractory to
1390 photodegradation. Anthropogenic dissolved organic matter, in the present study, remains and
1391 constitute the greatest contribution of CP/PARAFAC components along irradiation process.
1392 Fluorescence signal going to the coastal zone should mainly come from WW endmember.
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1408 Comparing C1 versus C2 degradation kinetic, it was observed that humic-like FDOM is more
1409 reactive than protein-like FDOM (Yang et al. 2014). However, results above demonstrated that
1410 it's not so simple. CP/PARAFAC components are constituted by several types of FDOM
1411 fluorophores which behave differently depending on their origin and photosensitivity.
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1419 (Timko et al. 2015) found increasing rates of photochemical fluorescent DOM loss with
1420 increasing pH studied thru measurements on the EEMs not between the parameters of multilinear
1421 regression between CP/PARAFAC components and mixing composition . However, *pH* of RW ,
1422 SW and WW were constant ($pH=7.4 \pm 0.4$) in this study suggesting no effect of *pH* in the results
1423 of the kinetic analysis
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4. Conclusions

In this study, fluorescent conservative behaviour and natural solar changes on three endmember mixing laboratory experiment were investigated leading to the following conclusions

(1) Multilinear regression model for contribution of CP/PARAFAC components is excellent and could be done for the three endmembers in addition to being able to study the kinetic evolution.

(2) Two of the three fluorescence CP/PARAFAC extracted component (C1 “terrestrial humic like” and C2 “humic-like of longer wavelength”) showed a second order photodegradation toward the irradiation process whatever the endmember mixture composition.

(3) Search for specific self-distinguishing fluorescence signal or signature for river water, wastewater treatment plants and sea water couldn’t be done in this work, which could be attributed to the complexity of the anthropogenic and natural dissolved organic matter.

(4) The fluorescence signal of wastewater treatment plant effluent is predominant in the studied coastal zone, according to the results of photodegradation kinetic constant which favour anthropogenically-impacted organic matter contribution (100 times less sensitive to photobleaching). However, its exact contribution couldn’t be found due to inability to calculate or find its coefficient $a_{i,3}$ in the multilinear regression model independently.

(5) In human impacted coastal zone, residual fluorescent organic matter comes from wastewater treatment plant effluent, and no specific fluorescence signal either from sea water or from wastewater treatment plant effluent could be detected near the coast.

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1516 **Declarations of interest** none
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1518 **Appendix A. Supplementary Information (SI)**

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1520 Supplementary Information to this article can be found in the Supplementary Information (SI)
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Table S1

Percentages by weight of RW , SW ,WW used in the preparation of fifteen mixtures in Quartz vials for mixing and solar irradiation experiment

	Sample Serial Number														
Endmember	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
f_{RW}	100	0	0	75	50	25	75	50	25	0	0	0	50	25	25
f_{SW}	0	100	0	25	50	75	0	0	0	25	50	75	25	25	50
f_{WW}	0	0	100	0	0	0	25	50	75	75	50	25	25	50	25