Spatial distribution and fluorescence properties of chromophoric dissolved organic matter in the surface waters of the coastal area of Sfax (Tunisia)

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Abstract

The Sfax coast, located in the south eastern Mediterranean Sea, hosts one of the main harbours in the Gulf of Gabes and is considered as the main fishing zone in Tunisia. However, during the last few decades, a continuous and increasing degradation of the local marine ecosystems has been reported, mainly due to the discharge of many untreated industrial and domestic wastewaters in seawater. Fluorescence excitation–emission matrix (EEM) spectroscopy combined with parallel factor (PARAFAC) analysis can be successfully used to track and fingerprint anthropogenic inputs in estuaries and rivers (Tedetti et al., 2012). Accordingly, hydrochemical parameters (table 1) and fluorescent dissolved organic matter (FDOM) were monitored for samples collected from coastal marine waters highly impacted by industrial and domestic wastewaters discharge (Oued Ezzit, PK4, fishing harbour, Sidi Salem, Oued El Hakmouni, etc).

Table 1. Distribution of hydrochemical parameters from samples collected in Sfax coastal waters

Variable	Min	Max	Mean ± SD
T (°C)	18.5	31.1	26.8 ± 3.8
pH	3.4	8.81	7.85 ± 1.20
Salinity (mg/L)	3.88	43.11	32.02 ± 11.13
Dissolved oxygen (mg/L)	0.04	12.96	6.90 ± 3.81
Turbidity (NTU)	0.01	303.6	39.3 ± 79.6
Suspended matter (mg/L)	4.96	542	76.71 ± 109.46
$[NO_2^-]$ (µM)	0.007	40.84	1.72 ± 7.40
$[NO_3^-]$ (µM)	0.00	104.5	5.2 ± 19.2
$[SiOH_4]$ (µM)	1.35	2480.4	165.7 ± 528.9
$[PO_4^{3-}]$ (µM)	0.16	3467.5	240.7 ± 846.8
DOC (µM C)	81.9	5722	846.1 ± 1501.4
C1 (Tryptophane) (QSU)	0.24	626.6	68.2 ± 138.8
C2 (A+M) (QSU)	1.11	560.8	85.0 ± 142.4
C3 (A+C) (QSU)	0.55	173.6	33.9 ± 51.4

Three components (C1–C3) were identified by the PARAFAC model validated on 77 EEM samples. These components exhibited two Ex maxima and one Em maximum. According to the Coble designation (Coble, 1996), C1 ($\lambda_{Ex}/\lambda_{Em}$ of 235, 275/352 nm) corresponded to a protein-like fluorophore with Ex and Em maxima analogous to those of tryptophan. C2 ($\lambda_{Ex}/\lambda_{Em}$ of 235, 310/420 nm) and C3 ($\lambda_{Ex}/\lambda_{Em}$ of 260, 360/464 nm) corresponded to humic-like fluorophores and their fluorescence peaks are referred to A+M and A+C respectively.

When moving away from the discharge zones, a gradient appeared, with decreasing FDOM intensities, decreasing turbidity values, dissolved organic carbon, suspended matter and nutrients concentrations and increasing pH, salinity values and dissolved oxygen concentration.

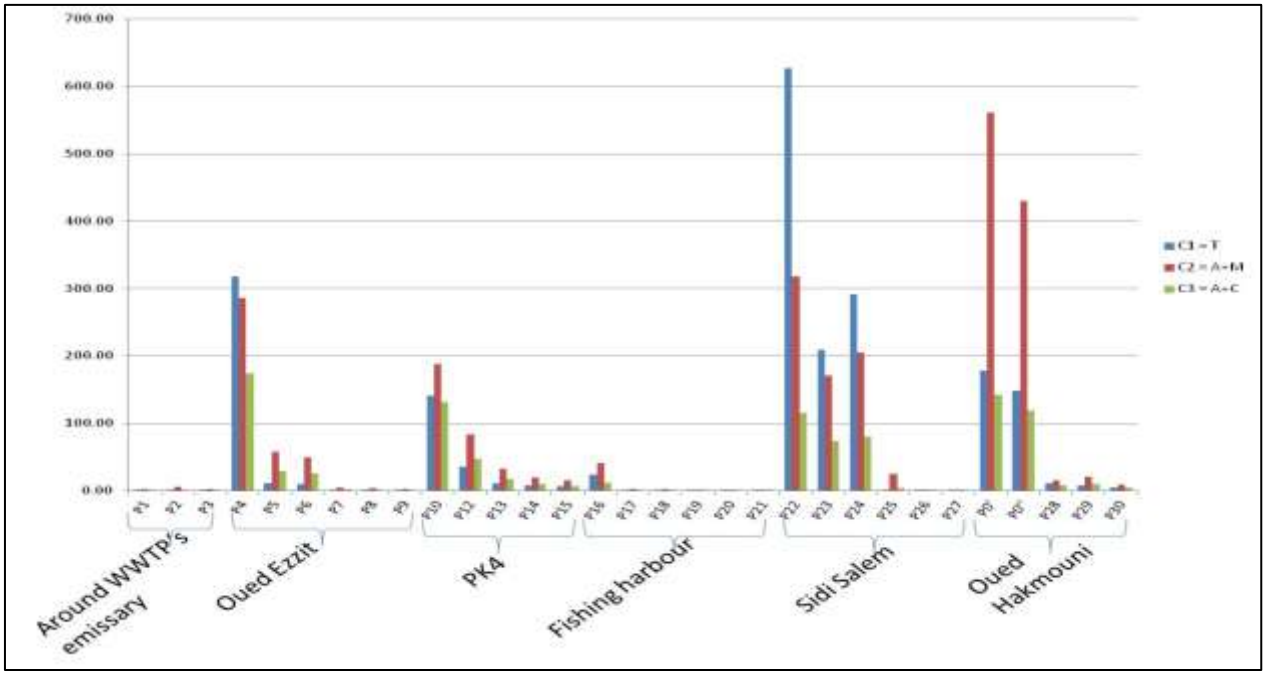

Fig. 1. Spatial variation of F_{max} values (QSU) of Components identified by PARAFAC

Protein- and humic-like materials may have different origins in the aquatic environment: autochthonous, terrestrial or anthropogenic. Identified components (T, A+M and A+C) have been previously reported in many studies conducted on municipal or industrial wastewaters (Carstea et al., 2016). In this study (fig. 1), tryptophan signal was extremely high and dominant for some regions affected by organic wastewaters inputs (626 QSU and 318 QSU for Sidi Salem and Oued Ezzit, respectively). Accordingly, higher correlations with biogeochemical parameters (dissolved oxygen, turbidity, suspended matter, etc) were reported. Also, regions receiving chemical wastewater inputs showed a dominance of A+M fluorophore, i.e., 560 QSU in Oued Hakmouni receiving inputs from the phosphate industry and higher correlations with biogeochemical parameters (pH and $[PO_4^{3-}]$).

References

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