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Characterization of organic matter in natural waters by EEM fluorescence properties

Sibel Sen-Kavurmaci*, Nazmiye Cemre Birben, Ayşe Tomruk, Miray Bekbolet

Institute of Environmental Sciences, Bogazici University, 34342 Bebek, Istanbul, Turkey, Tel. +90 212 359 7145; Fax: +90 212 257 5033; emails: sibel.sen@boun.edu.tr (S. Sen-Kavurmaci), cemrebirben@gmail.com (N.C. Birben), atomruk@boun.edu.tr (A. Tomruk), bekbolet@boun.edu.tr (M. Bekbolet)

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ABSTRACT

Natural organic matter (NOM) as the main component of natural colloidal matter is a major concern in drinking water treatment due to well-documented disadvantages. The understanding of NOM properties is a crucial factor to determine the dissolved organic matter treatability. The main purpose of this study is to provide information for realization of physicochemical and compositional properties of NOM in relation to the impact factors related to the surface water quality. To achieve this goal, water samples were collected from major watersources of Istanbul as well as from lakes located in various parts of Turkey. A consistent data-set of basic parameters specifically related to the quantification of organic matter contents, namely dissolved organic carbon and spectroscopic parameters (UV–vis and fluorescence) of selected surface waters were evaluated. Besides UV–vis spectral parameters, fluorescence intensity as represented by the ratio of the emission intensity at λ_{emis}450 nm to that at λ_{emis}500 nm, following excitation at λ_{exc}370 nm was also successfully employed. Moreover, fluorescence fingerprinting of surface waters by using emission excitation matrix (EEM) features as a tool was explored. These analytical techniques could contribute to the knowledge and understanding of the characterization and composition of NOM in surface waters. Based on the attained results, it could be indicated that EEM contour plots could be successfully utilized as a tool in understanding of the organic matter present in natural waters.

Keywords: Natural waters; Organic matter characterization; UV–vis spectral parameters; EEM fluorescence properties

1. Introduction

Natural organic matter (NOM) as the main carbon-based component of natural colloidal matter can range in molecular weight from a few hundred to 100,000 daltons (Da) [1]. NOM is derived from both allochthonous (watershed or terrestrial) and autochthonous (algal or *in situ*) sources. Allochthonous NOM generally exhibits more of a humic signature while autochthonous NOM largely consists of algal organic

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*Corresponding author.

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matter. Polydispersity of molar masses and complex chemical structures give NOM a multifunctional role in natural environment and in water treatment processes [2]. Removal of NOM displays prime importance in water treatment primarily due the formation of possibly carcinogenic disinfection by-products (DBPs) [3–5]. Although the model humic compounds have been used widely, *in situ* investigation of NOM components of which the chemical structure and properties are dependent on environmental conditions and time requires special importance.

Understanding the structural chemistry of NOM components can be useful in designing new water treatment processes to remove these components from drinking water. Fractionation techniques in conjunction with sensitive spectroscopic techniques (e.g. UV–vis absorbance and fluorescence) could be essential for effectively evaluating NOM quality and quantity in source waters and optimizing water treatment processes. Therefore, the additional data available from fluorescence spectroscopy is potentially of great process and commercial value to the water industry. Besides, understanding the quantitative/qualitative chemical nature and reactivity of NOM would bring valuable information to the control of DBPs and their relevance to the respective standards in drinking water treatment operations [6].

Several non-destructive spectroscopic analytical techniques could also be employed for the physicochemical characterization of the organic matrix present in natural waters. Non-destructive spectrophotometric analyses, such as UV–vis absorbance and fluorescence measurements can complement dissolved organic carbon measurement (DOC) in NOM profiling studies [7–9]. Specific UV absorbance (SUVA or $SUVA_{254}$) is defined as the sample's UV absorbance at wavelength $\lambda = 254$ nm divided by the DOC concentration of the solution [10]. High SUVA waters are generally enriched in hydrophobic NOM, such as humic substances. Therefore, SUVA indicates aromatic compounds in the DOC and can be used to estimate the chemical nature of the DOC at a given location. The water industry also uses SUVA as a surrogate parameter to monitor sites for DBPs precursors [11]. Besides chromophores, fluorophores are also associated with the humic portion of NOM. Fluorescence spectroscopy can provide a rapid, real-time method for distinguishing between various pools of DOC [12]. Although less than a 1% of the aromatic moieties in NOM actually emit light as fluorophores, fluorescence spectroscopy has provided new insight into the chemical composition of DOC in natural waters because it is at least an order of magnitude more sensitive to NOM than UV absorbance [13]. In addition to two-dimensional techniques acquired in emission, excitation, and synchronous scan modes, three-dimensional fluorescence spectroscopy and the evaluation of emission excitation matrix (EEM) would be beneficial analytical tools for this goal [14]. EEM produces fluorescence spectra at many different excitation wavelengths providing an overall view of all features existing within a selected spectral range. This technique has been widely used to differentiate the origin of the organic matter in natural environments [15–20]. Recently, this technique found an application area in describing the behavior of organic fluorophores during various water treatment schemes [21–24]. It should also be indicated that EEM fluorescence features cannot be used for estimation of DOC content since not all of the organic compounds (e.g. sugars and lipids) contribute to the overall fluorescence [25].

Humic substances as a model compound of NOM typically express fluorescence in the excitation wavelength range of λ_{exc}~300–400 nm and the emission wavelength range of λ_{emis}~400–500 nm. Coble ascribed these fluorophoric centers as humic-like fluorescence (fluorescence excited between λ_{exc}220 and 250 nm, and emitted between λ_{emis}400 and 460 nm), fulvic-like fluorescence (fluorescence excited between λ_{exc}300 and 340 nm, and emitted between λ_{emis}400 and 460 nm), and protein-like (tryptophan and tyrosine) fluorescence (fluorescence excited between λ_{exc}270 and 280 nm and emitted between λ_{emis}330 and 370 nm) [14]. Fluorescence features could also be correlated with UV–vis spectroscopic parameters as well as DOC; with this respect, fluorescence-derived index is defined as fluorescence intensity (FI) represented by the ratio of the emission intensity at λ_{emis}450 nm to that at λ_{emis}500 nm, following excitation at λ_{exc}370 nm [26]. An inverse relationship was elucidated between FI and aromaticity of humic matter. Moreover, $FI \leq 1.4$ represented humic fluorophores of organic matter originating from terrestrial sources whereas $FI \geq 1.9$ mainly attributed to microbially derived organic material.

Water samples collected from the major water sources of Istanbul (Buyukcekmece, Sazlidere, Alibeykoy, Darlik, Omerli and Elmali) and four different lakes in Turkey (Durusu, Abant, Mogan and Eymir) were analyzed in terms of their chemical and spectroscopic properties and their comparisons were presented displaying a general profile. This study presents a data-set of basic physicochemical parameters (specifically DOC) and spectroscopic properties (UV–vis and fluorescence) of surface waters by focusing on NOM characterization. Moreover, it aims to explore fluorescence fingerprinting of natural waters by using EEM contour plots as a tool.

2. Experimental

2.1. Materials

Natural water samples were taken from major drinking water sources of Istanbul-Turkey as Buyukcekmece, Sazlidere, Alibeykoy, Darlik, Omerli, and Elmali. Water samples were also collected from four different lakes as Durusu, Abant, Mogan, and Eymir. All of the water samples were collected during winter season of the year.

2.2. Physicochemical characterization

Natural water samples were filtered primarily through a coarse filter followed by 0.45 µm cellulose acetate membrane filters prior to analysis. Characterization of the water samples were carried out according to the methods outlined in Standard Methods of Analysis. Common anions (Cl^-, Br^-, F^-, NO_2^-, NO_3^-, SO_4^{2-}, and PO_4^{3-}) were analyzed by Ion chromatography (Dionex ICS-3000). Common cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) were analyzed by atomic absorption spectroscopy (Perkin-Elmer AAnalyst 300).Trace metals (Cr, Mn, Fe, Ni, Cu, Zn, Al, Cd, Pb, and Co) were measured by inductively coupled plasma optical emission spectrometer (ICP-OES), Perkin-Elmer Optima 2100DV. DOC (mg OrgC L^{-1}) was measured by using total organic carbon analyzer (Shimadzu TOC-VWP) and reported as a mean value of three valid measurements with an error of ≤5%.

2.3. Spectroscopic characterization and UV–vis and fluorescence parameters

Fluorescence spectroscopic measurements were conducted using a Perkin-Elmer luminescence spectrometer. Fluorescence EEMs were recorded upon incremental increase of excitation wavelengths (λ_{exc}) from 200 to 500 nm at 10 nm steps and for each excitation wavelength, the emission at longer wavelengths (λ_{emis}) was detected at 0.5 nm steps. Both the excitation and emission slit widths were set to 10 nm and photomultiplier tube voltage was 900 V. Three-dimensional contour plots were generated by plotting fluorescence intensity as a function of emission (x-axis) and excitation (y-axis) wavelength using Matlab R2012a program. The instrument stability was tested by using the Raman peak of water at 348 nm by the supplier. The standard deviation of emission scan fluorescence measurements was <0.5%. UV–vis absorption spectra were recorded in the wavelength range of 200–600 nm by using Perkin-Elmer Lambda 35 UV–vis Spectrophotometer. The standard deviation of UV–vis absorbance in the 200–600 nm wavelength region was <0.4%.

Specified UV–vis parameters were defined as UV–vis absorbance measurements (m^{-1}) recorded at 436 and 254 nm wavelengths and expressed by $Color_{436}$ and UV_{254}, respectively. Fractional UV–vis parameters were also represented by the following ratios; E_{254}/E_{365}; E_{254}/E_{436}; E_{280}/E_{365}; E_{280}/E_{436}, and E_{365}/E_{436}, where for practical reasons, E term designated absorbance measurements at wavelengths 254, 280, 365, and 436 nm. Specific parameters (m^{-1} (mg OrgC $L^{-1})^{-1}$) were defined as SCoA and SUVA that were derived by DOC normalization of the respective specified UV–vis parameters as $Color_{436}$ and UV_{254}.

Fluorescence-derived index defined as FI was described by the ratio of the fluorescence emission intensity recorded at λ_{emis}450 nm to that at λ_{emis}500 nm, following excitation at λ_{exc}370 nm.

3. Results and discussion

Natural water samples that were taken from various sources including drinking water sources as well as lakes located in various parts of Turkey were subjected to physicochemical characterization analysis. Anion contents of the water samples (mg L^{-1}) exhibited variations in the range of 9.4–237.2 mg L^{-1} for chloride, <0.001–0.25 mg L^{-1} for bromide, <0.001–0.20 mg L^{-1} for fluoride, <0.001–0.29 mg L^{-1} for nitrite, 0.89–47.7 mg L^{-1} for nitrate, 9.9–367.0 mg L^{-1} for sulfate, and <0.001–0.8 mg L^{-1} for phosphate. Common cation concentrations were in the range of calcium as 31.4–98.7 mg L^{-1}, magnesium as 3.2–64.0 mg L^{-1}, sodium as 12.5–287 mg L^{-1}, and potassium as 1.3–21.1 mg L^{-1}, respectively.

Since metal ion complexation plays a major role in water quality measurements, a full range of metals including, Cr, Mn, Fe, Ni, Cu, Zn, Al, Cd, Pb, and Co were analyzed as presented in Table 1 [27,28].

Although the water samples were taken from natural drinking water sources and analyzed *as is*, the results displayed quite low concentration levels for all of the physicochemical parameters [29]. Despite the fact that water samples were taken from natural sources without being subjected to any treatment, it could be deduced that the water samples could meet drinking water quality limits. Water samples taken from lakes expressed quite similar common cation contents with the exception of Eymir sample displaying comparatively high contents of Ca^{2+}, Mg^{2+}, and Na^+ ions. Moreover, Mogan Lake water contained quite high Na^+ content.

Table 1
Physicochemical characterization of natural water samples

	Water sources						Lakes			
	B.C.*	S.D.*	A.K.*	Darlik	Omerli	Elmali	Durusu	Abant	Mogan	Eymir
Common anions, mg L^{-1}										
Cl^-	41.1	16.2	48.6	15.9	35.3	34.4	22.6	9.4	187.7	237.2
Br^-	0.01	0.17	0.25	0.01	0.16	0.01	0.01	n.d.	n.d.	n.d.
F^-	0.20	0.12	0.10	0.11	0.08	0.14	0.08	n.d.	0.3	0.4
NO_2^-	0.16	0.01	0.01	0.01	0.18	0.29	0.01	n.d.	n.d.	n.d.
NO_3^-	3.15	2.27	2.67	2.07	2.00	2.93	0.89	2.9	2.6	47.7
SO_4^{2-}	56.6	22.4	70.1	20.7	60.2	87.1	15.1	9.9	367.0	238.4
PO_4^{3-}	<0.01	<0.01	<0.01	<0.01	<0.01	0.054	<0.01	0.8	0.8	0.7
Common Cations, mg L^{-1}										
Ca^{2+}	61.7	62.1	58.2	72.2	31.4	50.7	49.1	41.8	40.5	98.7
Mg^{2+}	9.7	4.6	9.7	3.18	4.2	8.1	3.5	6.08	12.8	64.0
Na^+	23.8	14.7	27.7	12.9	14.7	25.1	15.7	12.5	287	183.0
K^+	2.4	4.6	2.6	18.8	3.1	2.9	21.1	1.3	10.9	15.9
Trace metals, mg L^{-1}										
Cr	0.008	0.020	0.011	0.005	0.011	0.005	0.003	0.001	0.000	0.001
Mn	0.007	0.021	0.034	0.017	0.013	0.031	0.016	0.002	0.002	0.002
Fe	0.033	0.028	0.015	0.139	0.055	0.028	0.036	0.000	0.000	0.000
Ni	0.142	0.003	0.005	0.003	0.124	0.032	0.003	0.000	0.000	0.000
Cu	0.015	0.004	0.011	0.001	0.004	0.004	0.005	0.003	0.004	0.004
Zn	0.008	0.006	0.027	0.013	0.017	0.020	0.018	0.001	0.000	0.002
Al	0.021	0.029	0.029	0.101	0.041	0.018	0.021	0.004	0.005	0.011
Cd	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	<0.001	0.002	0.002	0.002	0.002	0.002	0.003	n.d.	n.d.	n.d.
Co	<0.002	0.002	0.004	0.002	0.002	0.005	0.002	0.002	n.d.	n.d.

Note: n.d. below detection limit of 0.001 mg L^{-1}.
*B.C. Buyukcekmece; S.D. Sazlidere; A.K. Alibeykoy.

In aquatic systems, trace metals could be present either solely as hydrated aqua ions or as soluble species formed by complexation with neutral molecules, inorganic anions, and macromolecular humic anions. The presence of trace metals could directly be related to diverse binding capabilities to fulvic and humic fractions of the organic matrix leading to structural and conformational changes [30]. Therefore, all of the water samples were subjected to trace metal analysis the outcome of which was presented in Table 1. From a general perspective, trace metal concentrations were quite low, even lower than the limits set for drinking water standards [29]. A comparison of the results revealed that Alibeykoy water sample contained considerably higher concentrations of Cr, Mn, Zn, and Al.

Organic carbon contents were found to be in the DOC range of 3.18–6.92 mg L^{-1} (Table 2). UV_{254} values were in the range of 0.0436 (Darlik)–0.2902 (Eymir). $Color_{436}$ displayed variations in the range of 0.0027 (Darlik)–0.0136 (Eymir). Contrary to these absorbance values, respective DOC contents were 5.15 mg L^{-1} for Darlik water and 3.44 mg L^{-1} for Eymir Lake water.

Moreover, SCoA and $SUVA_{254}$ values showed slight differences between the samples originating from various sources. The highest $SUVA_{254}$ was calculated for Eymir Lake water followed by Mogan Lake water. The lowest $SUVA_{254}$ was found for Darlik water. $SUVA_{254}$ of water samples taken from water sources could be represented by a decreasing order as Elmali > Alibeykoy > Omerli > Buyukcekmece > Sazlıdere > Darlik. In a similar fashion, $SUVA_{254}$ and SCoA values of lake waters followed a decreasing order as Eymir > Mogan > Durusu > Abant.

In comparison to the UV–vis parameters, fluorescence index (FI) was evaluated displaying FI variations as 1.57–2.01. All water samples except Elmali exhibited FI values greater than 1.4 indicating that NOM might not be originated from terrestrial sources and contain medium aromaticity. Elmali water sample expressed high FI as 2.01 being slightly higher than the reported value of FI = 1.9 stating lower aromatic content and presence of microbially derived organic matter. It was reported that FI could be a useful tool to differentiate fulvic acids of different origins and might not

Table 2
Specified and specific UV–vis and fluorescence spectroscopic parameters of natural water samples

Sources	Color$_{436}$	UV$_{254}$	FI	DOC	SCoA	SUVA$_{254}$
Water sources						
Buyukcekmece	0.0046	0.0980	1.67	6.23	0.074	1.574
Sazlidere	0.0050	0.0910	1.69	6.92	0.073	1.316
Alibeykoy	0.0084	0.1192	1.70	6.47	0.130	1.842
Darlik	0.0027	0.0436	1.72	5.15	0.053	0.847
Omerli	0.0053	0.0749	1.67	4.49	0.118	1.668
Elmali	0.0084	0.1352	2.01	6.07	0.139	2.228
Lakes						
Durusu	0.0072	0.1445	1.57	6.78	0.106	2.130
Abant	0.0034	0.0492	1.71	3.90	0.087	1.262
Mogan	0.0062	0.1747	1.72	3.18	0.195	5.479
Eymir	0.0136	0.2902	1.70	3.44	0.396	8.440

adequately describe humic acids. Moreover, FI would be more suitable for describing aquatic humic substances and fulvic acids rather than humic substances originating from terrestrial sources [17,25,31].

Fractional UV–vis parameters could bring about information related to the differences in UV absorbing centers primarily composed of inner core aromatic fractions (E$_{254}$ and E$_{280}$) and absorbances recorded at visible range wavelengths representing color-forming moieties (E$_{365}$ and E$_{436}$) [32]. All of the fractional UV–vis parameters exhibited source-dependent variations. The most significant difference was observed for E$_{254}$/E$_{436}$,especially for water samples taken from lakes. It could be deduced that the use of fractional UV–vis parameters could be effective for the differentiation of the UV–vis spectroscopic character of the water samples provided that a larger data-set of samples would be considered (Fig. 1).

It was reported that specific UV–vis parameters could be correlated to fractional UV–vis parameters under various conditions [33]. Neither SUVA$_{254}$ nor SCoA could be correlated to E$_{254}$/E$_{436}$.

In accordance with the UV–vis parameters, FI of the water samples could not be correlated with the DOC contents. FI values showed an almost constant trend with respect to increasing DOC contents of the water samples irrespective of the source (Table 2). The reason could also be attributed to the non-correlative behavior of the specified UV–vis parameters with respective DOC contents.

To provide a wider perspective, EEM fluorescence matrix contour plots of the water samples taken from water sources and lakes were presented in Figs. 2 and 3, respectively.

From a visual inspection point of view, EEM contour plots were examined in comparison to both UV–vis properties as well as DOC contents. EEM profile of Elmali water sample displayed the presence of fluorophores significantly different than the EEM features of the other samples in relation to the presence

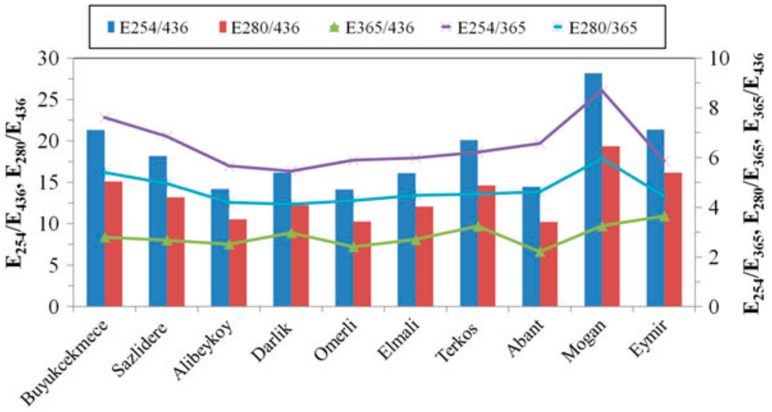

Fig. 1. Fractional UV–vis parameters of natural water samples.

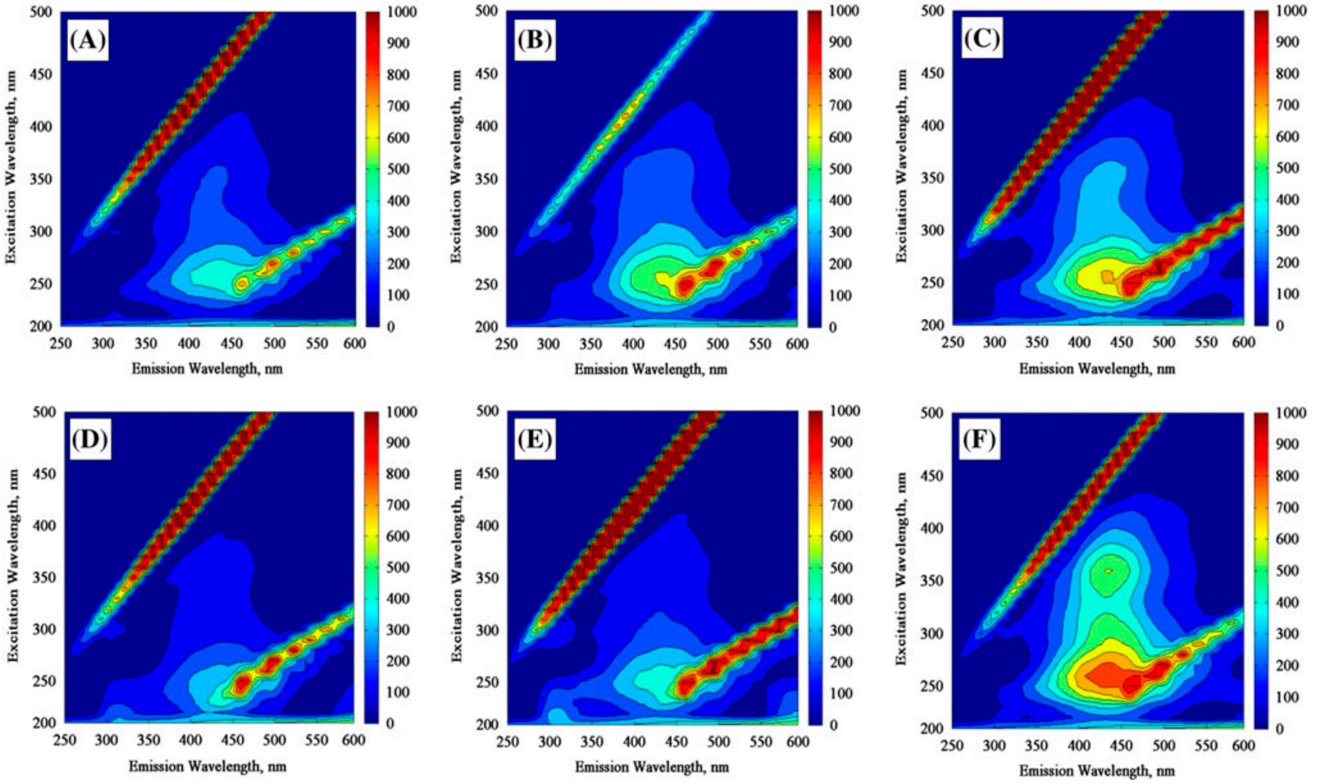

Fig. 2. EEM fluorescence contour plots of natural water samples originating from water reservoirs sources. (A) Buyukcekmece, (B) Sazlidere, (C) Alibeykoy, (D) Darlik, (E) Omerli, (F) Elmali.

of high UV–vis properties (Table 2). Omerli water sample with the lowest DOC content expressed an EEM fluorescence profile with almost non-significant peak formation. Buyukcekmece water sample expressed an EEM fluorescence profile with close similarity to Omerli water sample. It should be indicated that DOC content of Buyukcekmece water sample was 6.23 mg L^{-1} in comparison to the DOC content as 4.49 mg L^{-1} for Omerli water sample. Although Darlik water sample displayed a DOC content of 5.15 mg L^{-1}, the non-appearance of fluorophores could roughly be related to the UV–vis spectroscopic properties of which both UV-absorbing centers and color-forming moieties were considerably lower than the other samples (Table 2). EEM contour plot of Sazlidere water sample could be regarded as similar to the Alibeykoy water sample although all of the UV–vis parameters were significantly different from each other in contrast to the similar DOC contents (Table 2).

EEM fluorescence features of all of the lake waters displayed non-uniform variations with respect to both UV–vis parameters as well as DOC contents. The most significant EEM fluorescence profile was attained for Eymir Lake water followed by Mogan Lake water. These lakes expressed close similarities in DOC contents as 3.18 and 3.44 mg L^{-1}, respectively (Table 2). It should be indicated that Abant Lake water sample showed almost no distinct EEM fluorescence feature in accordance with the lowest UV–vis parameters (Table 2).

Based on the EEM contour plots presented in Figs. 2 and 3, a semi-quantitative approach was directed to the regional speciation of the EEM fluorescence features of the natural water samples (Table 3). Regional speciation of fluorophores was described mainly by five groups [14–20]. Fluorescence intensity strength was indicated by a symbol (+) with reference to the presented color intensity. Besides the aforementioned fulvic-like (Region III) and humic-like fluorophores (Region V), Region I (Aromatic Proteins I, tyrosine-like) and Region II (Aromatic Proteins II, tryptophan-like) signified the fluorophores arising from aromatic proteins either free or as protein constituents. Region IV represented fluorophores attributed to the components of the DOC derived from microbial byproducts [20].

According to the regional speciation profiles, the absence of Region I could be indicated for Buyukcekmece and Eymir water samples. All of the other water samples displayed a very slight presence of fluorophores attributed to the presence of aromatic proteins

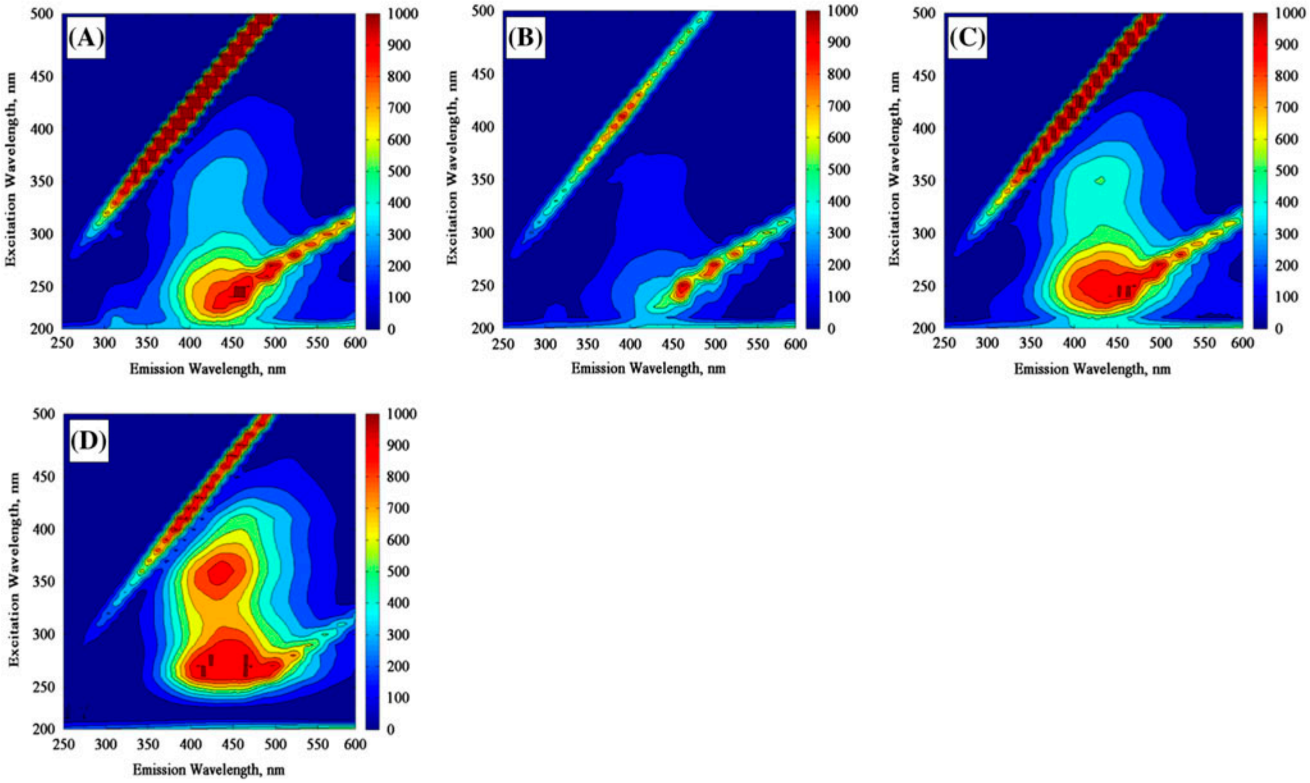

Fig. 3. EEM fluorescence contour plots of lakes, (A) Durusu, (B) Abant, (C) Mogan, (D) Eymir.

giving fluorescence upon excitation at λ_{exc}220–250 nm and emission at λ_{emis}280–332 nm. The presence of Region II was more significant in Mogan Lake water followed by Eymir and Elmali water samples. The least significant presence of Region II could be indicated for Darlik, Omerli, and Abant water samples. The presence of Region IV could be classified as being more intense in Elmali water sample followed by Alibeykoy ~ Mogan ~ Eymir and Buyukcekmece ~ Sazlidere ~ Omerli ~ Durusu. The least significance presence of Region IV was visualized for both Darlik and Abant water samples. The highest FI was calculated for Elmali water sample of which Region IV composed of fluorophores derived from microbial byproducts was more pronounced (Table 3).

All of the water samples presented fulvic-like fluorophores (Region III) being more significant in lake samples except Abant Lake water. Region III displayed a decreasing order of lake water samples as Eymir ~ Mogan ~ Durusu > Abant. Moreover, water samples taken from water sources expressed a decreasing order of Elmali being significantly higher than the other source waters as Alibeykoy > Buyukcekmece ~ Sazlidere > Omerli ~ Darlık. The presence of humic-like fluorophores recorded at λ_{emis}380–580 nm upon excitation at λ_{exc}250–470 nm (Region V) was evident in all water samples. Darlik and Abant water samples displayed considerably lower humic-like fluorophores. The highest Ca content of Darlik water sample could be related to the lower humic and fulvic like fluorophores in comparison to the DOC content (5.15 mg L^{-1}) [34]. However, EEM fluorescence profile of Eymir water sample containing higher amount of Ca ions (98.7 mg L^{-1}) displayed the presence of Regions III and V in spite of low DOC content (3.44 mg L^{-1}). It should be indicated that the presence of divalent cations could not be directly related to the appearance or disappearance of fulvic/humic like fluorophores due to fluorescence quenching via complexation. Since high $SUVA_{254}$ values indicated the presence of high humic-like fractions mostly composed of aromatic moieties, the presence of Region V could be verified by the decreasing order of $SUVA_{254}$. Region V displayed a decreasing order of lake water samples as Eymir ~ Mogan ~ Durusu >> Abant (Table 2). The presence of both fulvic-like (Region III) and humic-like (Region V) fluorophores expressed source dependent close similarities expressing that DOC matrix of all of the water samples were mainly composed of humic substances. Lowest DOC content, considerably lower UV–vis parameters as well as fractional UV–vis parameters, lowest Ca content,

Table 3
Regional speciation of the EEM fluorescence spectral features of natural water samples

Sources	Region I aromatic proteins I λ_{exc}220–250 λ_{emis}280–332	Region II aromatic proteins II λ_{exc}220–250 λ_{emis}332–380	Region III fulvic-like λ_{exc}220–250 λ_{emis}380–580	Region IV microbial byproducts λ_{exc} 250–470 λ_{emis}280–380	Region V, humic-like λ_{exc}250–470 λ_{emis}380–580
Water sources					
Buyukcekmece	n.o.	++	++++	++	+++
Sazlidere	+	++	++++	++	++++
Alibeykoy	+	+++	+++++	+++	+++++
Darlik	+	+	+++	+	++
Omerli	+	+	+++	++	+++
Elmalı	+	++++	++++++	++++	++++++
Lakes					
Durusu	+	+++	++++++	++	++++++
Abant	+	+	+++	+	++
Mogan	+	+++++	+++++++	+++	+++++++
Eymir	n.o.	++++	+++++++	+++	+++++++

Note: n.o.: not observed.

and insignificant degree of fulvic-like and humic-like fluorophores indicated that Omerli water source could serve as a good drinking water source for the metropolitan city of Istanbul. The presence of various trace metals and metal-binding capabilities of humic fractions leading to diminished fluorescence intensities could not be visualized by EEM fluorescence features possibly due to the low metal concentrations (Table 1).

Referring to the above given characterization features of the natural water samples, EEM plots distinctly expressed the structural and compositional variations of the organic matter in relation to the water matrix components. Therefore, EEM contour plots could be successfully utilized as a tool in understanding of the organic matter present in natural waters.

4. Conclusion

Water samples were taken from major drinking water sources of Istanbul and four lakes from various locations in Turkey. Water samples were subjected to UV–vis and fluorescence spectroscopic characterization. Physicochemical characterization was also carried out for the elucidation of the possible effects on the spectroscopic properties. Specific and specified UV–vis and UV–vis fractional parameters were discussed in relation to DOC contents. Moreover, fluorescence spectroscopic properties were elucidated by using fluorescence index values. From a broader perspective, EEM fluorescence contour plots were also presented and discussed.

All of the water samples expressed diverse properties that could not be explained solely by their respective DOC contents. The results indicated that DOC determination by itself could not be accepted as sufficient for the understanding of organic matrix components that determines the different reactivities of NOM.

It should also be taken into account that, this study was comprised of very limited number of samples without considering any regional, seasonal, and/or real-time dependent variations. Despite this fact, the attained results indicated that elucidation of the EEM fluorescence contour plots would be a versatile tool for understanding of NOM properties. Therefore, a further study focusing on sampling principles is highly recommended.

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