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Combination of 3D Fluorescence/PARAFAC and UV-Vis Absorption for the characterization of agricultural soils from Morocco

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Abstract

The present study, combining UV-Visible absorption and 3D fluorescence supported by PARAFAC chemometric analysis, focused on the characterization of soil water extractable organic matter (WEOM) in the zone of Doukkala located near the Atlantic coast of Morocco. The extracts, in water, of a set of 30 samples covering the four main types of agricultural soils in the region (commonly labeled Tirs, Faid, Hamri and R'mel) were investigated. E_2/E_3 and E_4/E_6 absorbance ratios, $S_{275-295}$ and $S_{350-400}$ spectral slopes, along with their ratios S_R, as well as the fluorescence FI and humification HIX indices were calculated and interpreted. In the four soil types these parameters revealed, on the one hand, organic materials of terrigenous origin with a certain biological component, and showed on the other hand that these materials are in similar stages of humification with an important humic character. The 3D fluorescence crossed with PARAFAC chemometrics highlighted the absence of any protein component and revealed the prevalence of the FAs fraction in the OM humic material in all the soils investigated.

Keywords Morocco . Agricultural Soils . WEOM . UV-Vis. Absorption . Total fluorescence & PARAFAC.

Introduction

Water extractable organic matter (WEOM), like indigenous dissolved organic matter (DOM) passing a filter pore size of 0.4 – 0.7 µm, is composed of an array of molecules generally reflecting the composition of total soil organic matter [1]. Although it generally comprises < 2% of total soil organic matter, its turnover rate and solubility mean that its role is determinant in many chemical and biological processes in the soil fate [2]. Furthermore, while the frontier between DOM and WEOM is not always obvious [3], it is reported that WEOM may likely to contain further material in comparison with indigenous DOM, being thus of larger magnitude [1]. Therefore, the properties of WEOM are important indicators of soil quality, namely its physical-chemical and microbial community characteristics [4].

Regarding the optical properties, depending on the origin of the OM precursor soil, different fluorescence peaks can be observed on the WEOM fluorescence landscape; they may originate from humic fractions (Humic Acids and Fulvic Acide), protein fractions (mainly tryptophan and tyrosine) or even from persistent contaminants [5, 6]. Therefore, WEOM fluorescence landscape is considered as a reliable indicator of the quality of the whole soil organic matter.

The geographical area of Doukkala, at the Atlantic coast of Morocco, is known for its important agricultural activity and the diversity of its soils. However, an anterior study of these soils, relating to a 10 years follow-up between 1987 and 1997, revealed an OM depletion [7]. This is why physical-chemical investigations focusing on soils of this highly agricultural region are required. Additionally, during a previous study on the fluorescence analysis of pesticide remains in these soils [6, 8], the WEOM fluorescence was submerging fluorescence signals of pesticides emitting in the same spectral range. This interference made it difficult to discriminate fluorescence signals originating from pesticide remains having a low fluorescence yield.

The objective of the present investigation is the analysis of WEOM in the principal soil types in the agricultural zone of Sidi Bennour, in the region of Doukkala. The approach consists in combining UV-Visible absorption and 3D fluorescence supported by PARAFAC chemometrics. The goal is to calculate and take mean of the spectroscopic parameters E_2/E_3 and E_4/E_6 absorbance ratios, $S_{275-295}$ and $S_{350-400}$ spectral slopes and slope ratios S_R, as well as fluorescence FI and humification HIX indices. On another side, exploring 3D fluorescence landscapes by visual peak-picking and trough PARAFAC chemometrics will permit the resolution of the underlying fluorescing components.

Such optical spectrometric characteristics should make it possible the characterization of the WEOM in these soils, and the discrimination of fluorescence signals originating from emitting organic pollutants persisting in the soil.

Soil Sampling and Analysis

Soils classification and samples preparation

The investigated soils are classified into four main types according to two previous studies [9, 10]:

- Vertisol, commonly labeled Tirs, (52%): deep and clayey soil, with a low permeability, characterized by a high water retention and considered of good productivity.

- Slightly evolved, commonly labeled Faid, (17%): deep soil, little to moderately permeable and characterized by a good permeability.

- Isohumic, commonly labeled Hamri, (16%): deep to moderately deep soil, with a sandy clay texture and characterized by a good permeability.

- Sandy / fersiallitic, commonly labeled R'mel, (13%): sandy in surface and coarse-textured soil, characterized by a high permeability and a low water retention capacity.

These soils are neutral to moderately basic [10].

Thirty representative soil samples were collected in the province of Sidi Bennour in non-cultivated and non-treated areas neither with pesticides nor with fertilizers. The samples were taken at soil depths ranging from 5 to 20 cm, stored in plastic bags and then kept cold.

For each soil type, the samples were mixed and shared into several sub-samples of 20g. Avoiding the use of organic solvents, each sub-sample was mixed with 40 ml of water, as an extractor medium, under 1 hour stirring to improve the dissolution of the organic material. The extraction was made at room temperature (at about 20-24°C), protected from light. The water-soil mixture was then stored in dark bottle in the fridge for 24 to 48 h to decant; the final extracts showed pH values in the range 7.5–8.0. As no significant fluorescence intensity difference has been observed between the spectra of filtered trough 0.45µm size pores and non-filtered supernatants, the measurements were recorded directly on top-supernatants without filtration. These top-supernatants were transferred into a quartz cell of 1 cm optical path for absorption and fluorescence analyses.

UV-Vis. absorption and fluorescence measurements

The absorption spectra were measured on the top-supernatants using a JASCO UV/VIS/ NIR V-570 spectrophotometer; the scans covered the spectral range 200-800 nm.

For each type of soil, the average values of the absorbance ratios $\frac{E_2}{E_3} = \frac{A_{250}}{A_{365}}$ and $\frac{E_4}{E_6} = \frac{A_{465}}{A_{665}}$, the slopes $S_{275-295}$ and $S_{350-400}$ as well as slopes ratio $S_R = \frac{S_{275-295}}{S_{350-400}}$ were calculated. A_{250}, A_{365}, A_{465} and A_{665} denote respectively the measured absorbances at 250, 365, 465 and 665 nm wavelengths. The spectral slopes over the intervals 275-295 nm and 350-400 nm were calculated using a linear regression of $\mathrm{Ln}(a_\lambda)$, where a_λ is the absorption coefficient calculated in m^{-1} according to the equation $a_\lambda = \frac{2.303 \times A(\lambda)}{l}$, with A(λ) and l represent the measured absorbance and the quartz cell thickness (i.e. 0.01 m) [11].

The total fluorescence spectra, or excitation-emission matrices also called TEEMs matrices, were measured using a Shimadzu RF-5301PC spectrofluorimeter controlled by LabSolution software. Continuous fluorescence scans were collected between 250 and 700 nm, varying the excitation wavelength from 220 to 550 nm at a 5 nm step. The excitation and emission slits were set at 3 nm (exc.) / 3 nm (em.) or 5 nm (exc.) / 5 nm (em.) depending on the sample.

The fluorescence matrix representation adopted in this work is the 2D one where the wavelengths $\lambda_{\text{emission}}$ and $\lambda_{\text{excitation}}$ appear explicitly on the X and Y axes, and the fluorescence intensity is coded by colors ranging from blue to red in rising order of values. The fluorescence maxima correspond to peaks, or foci, identified by their wavelengths coordinates λexc./λem. Each TEEM requires the concatenation of an average of 57 conventional fluorescence spectra (excitation from 220 to 500 nm at a 5 nm step). LabSolution package crossed with Origin data analysis and graphing software, allowed the representation and manipulation of the measured TEEMs matrices.

PARAFAC chemometric analysis

The PARAFAC "Parallel Factor Analysis" algorithm is a tool which consists in resolving the measured fluorescence matrices into individual sub-matrices corresponding to the fluorophores coexisting in the samples analyzed (supernatants). This chemometric analysis makes it possible to separate the different spectral contributions associated with the different types of fluorophores in these samples. This means that the positions $\lambda_{exc.}/\lambda_{em.}$ of the various underlying signals in a TEEM fluorescence matrix will be determined with a minimal error; the PARAFAC algorithm is considered by several authors to be a mathematical chromatography. Water and soil total fluorescence analysis is the analytical method where PARAFAC is being used the most [12 - 14]. The algorithm has been largely elucidated by various authors [15, 16].

PARAFAC algorithm principle

The algorithm consists in the decomposition of the of the experimental TEEMs data cube, measured on all samples, into a set of trilinear and residual terms as following.

The fluorescence intensity of the sample i for the excitation and emission wavelength pair (k, j) is given by the equation:

$$X_{i,j,k} = \sum_{f=1}^{F} a_{i,.f} b_{j,f} c_{k,f} + \varepsilon_{i,j,k}$$

with $i = 1, 2, \ldots I$; $j = 1, 2, \ldots J$ and $k = 1, 2, \ldots K$. I, J and K designate respectively the numbers of samples, emission wavelengths and excitation wavelengths.

$f = 1, 2, \ldots F$. F is the number of components in the model i.e. the presumed number of the fluorophores coexisting in the samples analyzed.

$X_{i,j,k}$ represents the fluorescence intensity of sample i for the pair of excitation and emission wavelengths (k, j).

$a_{i,f}$ represents the fluorescence factor (the concentration times the fluorescence quantum yield); each PARAFAC component f has I values of a (scores).

$b_{j,f}$ represents the intensity of the emission spectrum of the fluorophore f at the emission wavelength j.

$c_{k,f}$ represents the value of the absorption spectrum of the fluorophore f at the excitation wavelength K (proportional to the specific absorption coefficient).

$\varepsilon_{i,j,k}$ is the residual representing the variability not accounted for by the model, and which the calculation searches to minimize. This term includes instrumental noises and other non-modellable variations.

In this work, the number of components (fluorophores) was varied between 2 and 4. This choice of a reduced number of components is inspired by the measured TEEMs matrices showing a single fluorescence peak, large and extended from 370 to 550 nm. The "split-half analysis" method integrated into the algorithm was chosen during the model validation step. The version of the PARAFAC algorithm used is the online available one [17]; the graphics program used to create the matrices is Matlab.

The successful decomposition of a multi-way data system using the PARAFAC algorithm relies on assumptions about variability, tri-linearity and additivity [15, 16]. In this work, the fluorescence spectra were measured on samples revealing absorbances at 254 nm lower than 0.5 as can be observed on figure 1; no apparent internal filter effect was observed. The experimental matrices were corrected from all of the instrumental response, the internal filter effect and the Raman scattering [16 - 18].

Results and discussion

UV-Visible Absorption: absorbance and slope ratios

In Table 1 are reported, for each type of soil, the average values of the absorbance ratios $\frac{E_2}{E_3} = \frac{A_{250}}{A_{365}}$ and $\frac{E_4}{E_6} = \frac{A_{465}}{A_{665}}$, the slopes $S_{275-295}$ and $S_{350-400}$ as well as the ratios of these slopes $S_R = \frac{S_{275-295}}{S_{350-400}}$.

E_4/E_6 ratio is generally related to the degree of condensation and aromaticity of the organic material in the soil [19, 20]; this ratio varies inversely with respect to the degree of condensation / aromaticity. The values found in the case of the four soil types studied, ranging between 3.26 and 4.82, suggest that these soils contain organic materials in close humification stages. The highest value, 4.82, corresponding to the soil Faid is indicative of an organic material with an aliphatic prevalence of this soil compared to the other ones [20].This result is also confirmed by the values obtained for E_2/E_3 absorbance ratios varying from 3.77 to 4.33, similar to those reported for other soils [21]. E_2/E_3 ratio is associated with the average weight and molecular size of the organic material contained in the soil [22], and reflects the relative contents of humic acids (HAs) and fulvic acids (FAs). In the present case the values found for E_2/E_3 ratios, all greater than 3.5, indicate organic materials with FAs) contents greater than those of HAs [23, 24].

Concerning the slopes $S_{275-295}$ and $S_{350-400}$, the average values found for all soil types range respectively in the intervals 0.0101- 0.0141 nm^{-1} and 0.0122 - 0.0152 nm^{-1}, and are consistent with those reported for other soils [11, 25]. Moreover, the obtained S_R slope ratios, all lower than 1, are reasonably characteristic of terrigenous organic materials generally characterized by $S_{275-295}$ lower than $S_{350-400}$. than $S_{350-400}$. The difference, of about 20%, observed in S_R between Tirs and R'mel may be probably related to a significant difference in chromophoric DOM (CDOM) in these soils which are respectively the darker and the lighter ones. Furthermore, as slopes and slope ratios are commonly related to the average molecular weight of the organic matter, the similarity of these ratios reveals that the four soil kinds contain organic materials with similar molecular weights [11]. Subsequently, these soils are very likely in similar humification levels as indicated before by E_2/E_3 and E_4/E_6 absorbance ratios.

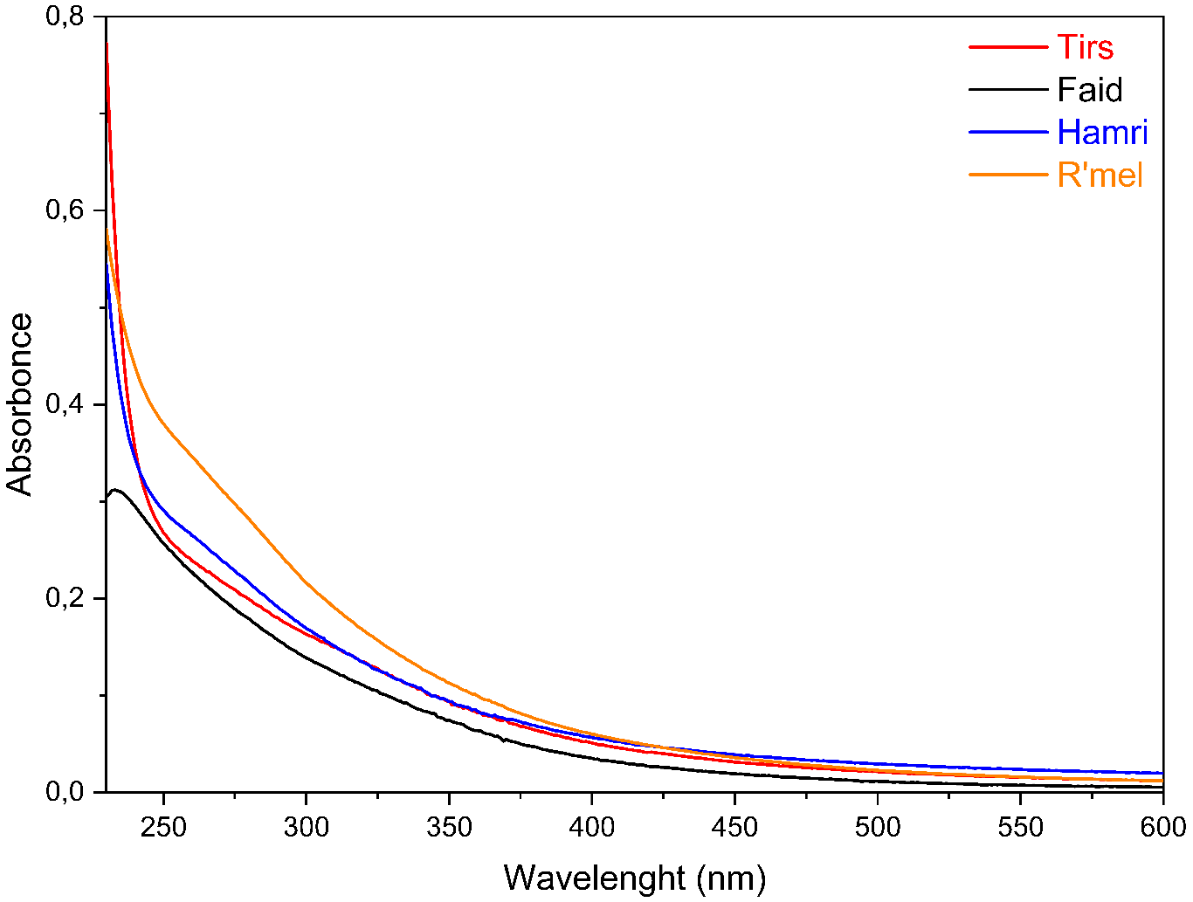

Fig. 1 UV-Vis. Absorption spectra measured on top-supernatants of water-soil mixtures.

Table 1 Averaged spectroscopic parameters calculated from absorption and fluorescence spectra*

Sol	Tirs	Faid	Hamri	R'mel
E_2/E_3	3.85 ± 0.05	4.33 ± 0.18	3.88 ± 0.03	3.77 ± 0.09
E_4/E_6	3.51 ± 0.11	4.82 ± 0.54	3.26 ± 0.24	3.37 ± 0.18
$S_{275-295}(\mathrm{nm}^{-1})$	0.0101 ± 0.0011	0.0141 ± 0.0009	0.0124 ± 0.0001	0.0126 ± 0.0001
$S_{350-400}\ (\mathrm{nm}^{-1})$	0.0122 ± 0.0005	0.0152 ± 0.0009	0.0133 ± 0.0001	0.0128 ± 0.0002
S_R	0.8279 ± 0.0450	0.9276 ± 0.0047	0.9323 ± 0.0007	0.9844 ± 0.0331
FI	1.56 ± 0.01	1.52 ± 0.03	1.61 ± 0.01	1.68 ± 0.04
HIX	9.05 ± 0.77	9.26 ± 0.66	12.25 ± 0.83	11.8 ± 0.60

* More details on the shown parameters are in the text.

Fluorescence: FI and HIX indices

The fluorescence index $\mathrm{FI} = \frac{I_{\mathrm{fl.}(\lambda_{\mathrm{em}}=450\ \mathrm{nm})}}{I_{\mathrm{fl.}(\lambda_{\mathrm{em}}=500\ \mathrm{nm})}}$, calculated as the fluorescence intensities ratio at the excitation wavelength $\lambda_{\mathrm{exc.}} = 370$ nm, provides information on the origin of the soil organic material; it highlights in particular the relative importance of the terrigenous material with respect to the microbial biomass one [26].

An FI index above 1.8 corresponds to a material with a microbial precursor, while an FI index close to 1.2 is indicative of a material with a rather terrigenous precursor [27]. In the case of the investigated soils, the FI indices range in the interval 1.52-1.68. This order of magnitude indicates organic materials from terrigenous sources with a certain microbial biological component. A similar result was observed in soils from China [28]. The humification index HIX calculated as the ratio of fluorescence intensity areas $\mathrm{HIX} = \frac{\sum_{\lambda_{\mathrm{em}}=435}^{\lambda_{\mathrm{em}}=480} I_{\mathrm{fl.}}}{\sum_{\lambda_{\mathrm{em}}=300}^{\lambda_{\mathrm{em}}=345} I_{\mathrm{fl.}}}$, while excitation wavelength is set at 254 nm, is a parameter positively correlated with the humification / maturation degree of the soil organic matter [26]. It is often taken as an indicator of DOM variation in agricultural soils [29]. In the present case, the HIX indices vary from 9 to 12. In comparison with the reference intervals given by various authors [30, 31] the investigated soils can be considered as materials with an important humic character as a consequence of an advanced maturation stage.

Total fluorescence and PARAFAC chemometrics

Experimental TEEMs

All soil extracts in water, prepared as described above, were subjected to total fluorescence measurements. In Figure 2 are presented four examples of the collected raw experimental TEEMs matrices. Likewise, these typical matrices show a single large fluorescence peak extended, in emission, from 370 to 550 nm. This signal is attributable to humic substances in the soil organic matter [32, 33]. However, no signal attributable to any protein fraction has been observed.

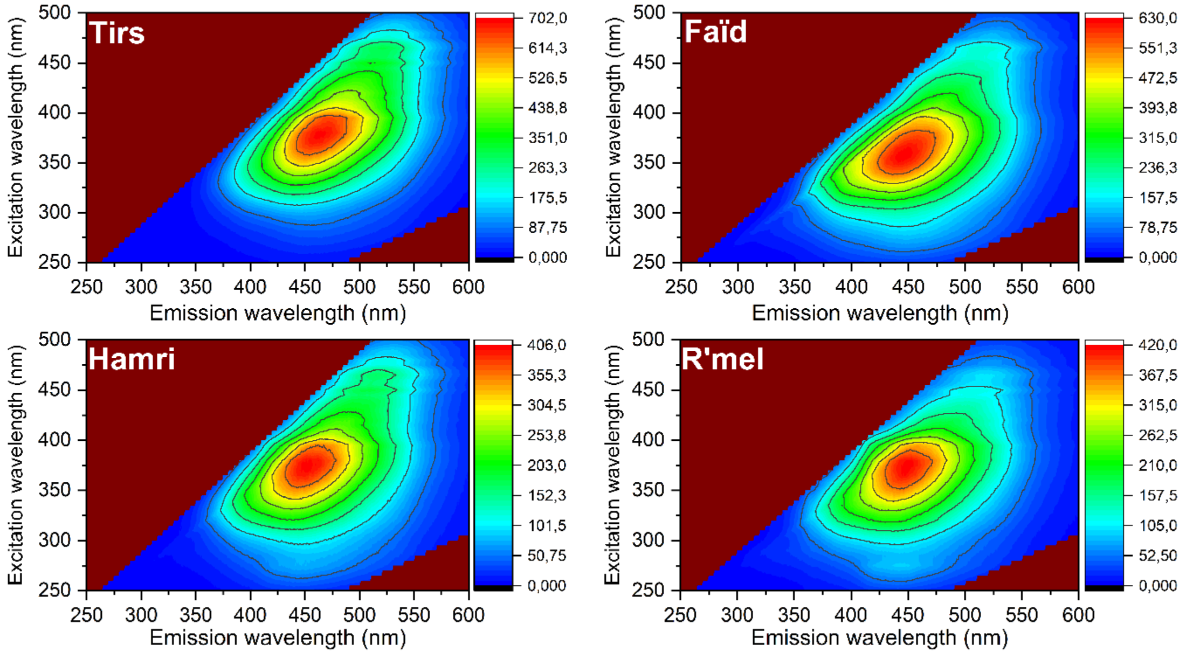

Fig. 2 Examples of experimental total excitation emission matrices (TEEMs).

PARAFAC Analysis

The PARAFAC chemometric analysis has made it possible to discriminate the fluorescent components previously overlapping each other in the experimental TEEMs matrices; the procedure is described above. For all soils, the validated model corresponds to a number of components equal to two, C_1 and C_2. This model is entirely consistent with the experimental TEEMs that did not reveal any fluorescence signal outside the spectral emission range 370-550 nm. Figure 3 shows the individual matrices corresponding to the PARAFAC components obtained for the four soil types. In all cases the component C_1 appearing around 340exc./442em. corresponds to the fulvic acid (FAs) fraction while the component C_2 appearing around 385exc./465em. corresponds to the humic acid (HAs) one of the soils WEOM. Indeed, these fractions are generally observed in the respective intervals (320-350 nm) exc./ (400-450 nm) em. and (370-390 nm) exc./ (460-500 nm) em. [34, 35].

In all soils, the ordering of FAs fraction as component C_1 and HAs fraction as component C_2 is entirely consistent with the obtained values of E2/E3 absorbance ratios which are greater than 3.5 indicating an organic material with FAs prevalence. Hence, in the whole of the investigated soils, these findings reflect a dominance of the FAs fraction with respect to the HAs one [36]. Furthermore, the absence of any PARAFAC component compatible with a protein fraction, such as tyrosine or tryptophan, reveals highly humified organic materials as previously highlighted by the HIX humification indices ranging between 9 and 12. The absence of any protein-type fluorescence signal indicates the absence or, at least, the weakness of proteins microbiological activity in the soil lands investigated; this is a consequence of the revealed advanced stage of humification. Probably, in the present soils, the formation of humic subtances may be governed by the lignin mechanism putting forward the hypothesis of the transformation of HAs into FAs [37]. Soil humification means the process leading to the increasing of the humic material content (namely FAs and HAs); an advanced humification stage may be associated with an increase in FAs concentration with a decrease in HAs concentration [38]. The formation of humic substances (HAs, FAs and Humins) is one of the least understood aspects of humus chemistry and one of the most intriguing.

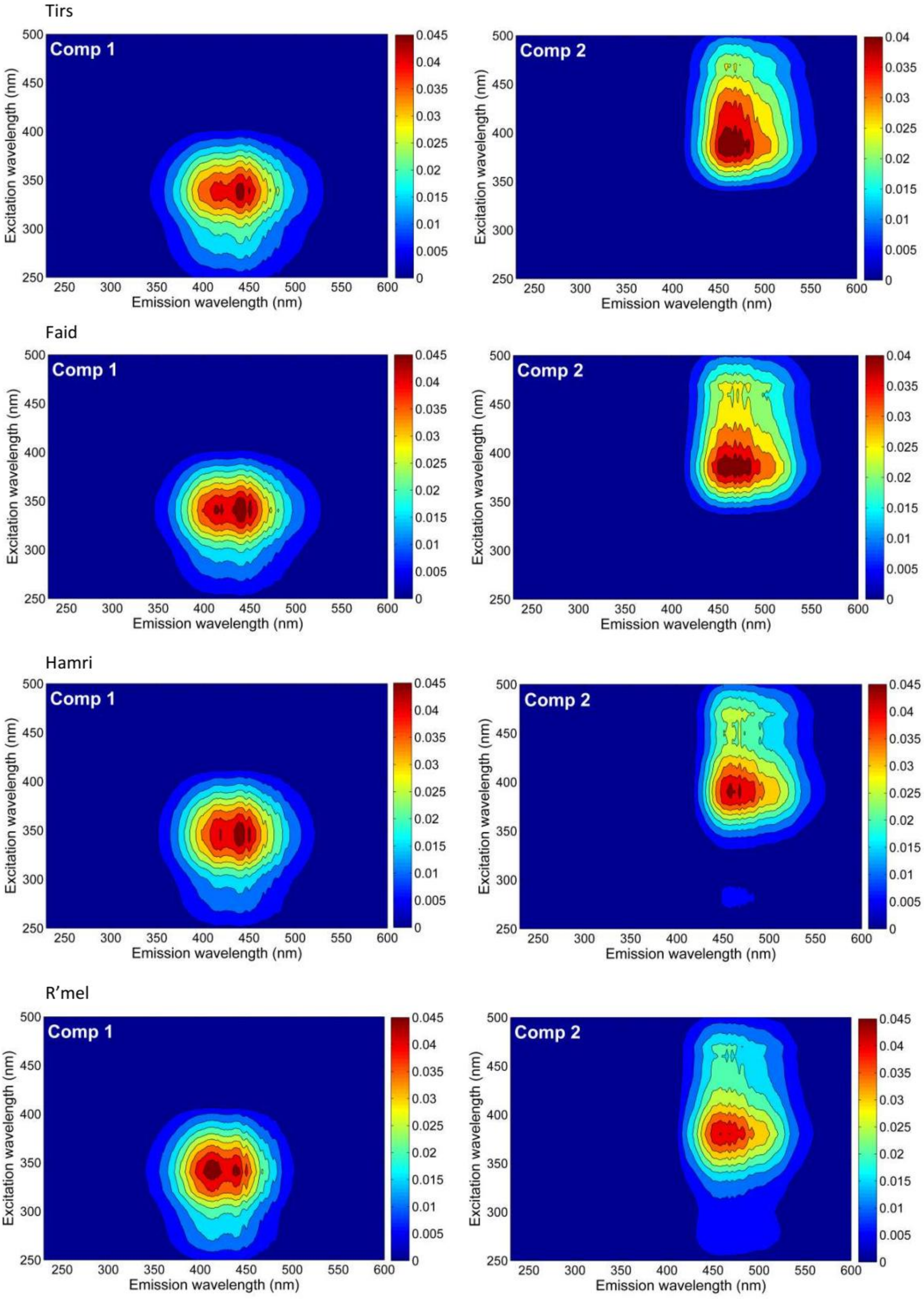

Fig. 3 Individual total excitation emission matrices of PARAFAC components.
Comp1 and Comp2 designate respectively C1 and C2 components.

Conclusion

The present study focused on the WEOM in a set of thirty agricultural soil samples collected from the zone of Doukkala in Morocco. The set has covered the four types of agricultural soil (Tirs, Faid, Hamri and R'mel), while the analysis was performed on the soils extracts in water by means of UV-visible absorption and total fluorescence combined to PARAFAC chemometrics.

E_4/E_6 and E_2/E_3 absorbance ratios, ranging respectively in the intervals 3.26 - 4.82 and 3.77- 4.33, revealed that all soils contain organic materials in similar humification stages, with a predominance of FAs fractions with respect to HAs ones. The average spectral slopes $S_{275-295}$ and $S_{350-400}$ varying respectively in the intervals 0.0101-0.0141 nm^{-1} and 0.0122 - 0.0152 nm^{-1}, with slope ratios S_R lower than 1, are characteristic of terrigenous organic materials. In addition, the FI fluorescence indices found between 1.52 and 1.68 revealed organic materials from terrigenous sources, having some microbial biological component. In parallel, HIX humification indices ranging from 9 to 12 indicated that the soils are in advanced humification stages.

3D fluorescence did not detect any protein fraction in the soils WEOM studied, highlighting thus poor fresh organic matter soils. The PARAFAC chemometric analysis, in full agreement with experiments, revealed only two fluorescent components in the humic material with FAs fraction classified as component 1 while HAs one classified as component 2.

Consequently, the four types of agricultural soils are compartments in similar humification stages, containing organic materials dominated by FAs fractions and very poorly provided in fresh organic matter.

Considering the issue of pesticide remains, the accomplished 3D fluorescence/PARAFAC characterization of the WEOM in the investigated soils will make it possible to discriminate additional fluorescence signals originating from any fluorescent contaminants persisting in the soil.

Authors' contributions. Hassan Ba-Haddaou: (Experimental investigations, first draft preparation and submission). Hicham Hassoun: (Sampling, material preparation and experimental investigations). Salim Foudeil: (Data collection, first draft preparation and submission). Saadia Ait Lyazidi: (Supervision, methodology, final draft reviewing and project administration). Mustapha Haddad: (Discussion, validation and funding acquisition). Matthieu Masson: (Discussion and validation). Marina Coquery: (Discussion and validation). Christelle Margoum: (Experimental logistics, discussion and validation).

All authors read and approved the final manuscript.

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Data Availability Not applicable.

Declarations

Conflicts of interest/Competing interests The authors declare they have no conflicts of interest and no competing interests.

Ethics Approval Not applicable as the study does not include any use of animals and humans.

Consent to Participate All authors consent to participate in the research.

Consent for Publication All authors consent to participate in the publication of the research.

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