

A. FRONT COVER/TITLE PAGE

TITLE OF RESEARCH PROJECT:

EFFECTS OF QUALITY COMPOSTS AND OTHER ORGANIC AMENDMENTS
AND THEIR HUMIC AND FULVIC ACID FRACTIONS ON THE
GERMINATION AND EARLY GROWTH OF
SLICKSPOT PEPPERGRASS (*LEPIDIUM PAPILLIFERUM*) AND SWITCHGRASS
IN VARIOUS EXPERIMENTAL CONDITIONS

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B. BODY OF THE REPORT

(1) SCIENTIFIC WORK DONE DURING THE REPORTING PERIOD

1. Origin and Chemical Characterization of the three Composts used

1.1. Experimental

Three representative and different composts were selected and used in this work: a green compost (GC), a mixed compost (MC) and a green coffee compost (GCC). The GC was obtained by composting for about 120 days in aerated (air-insufflated) piles a mixture of lignocellulose materials consisting mainly of tree and grass cuttings of urban public and private green. The MC was obtained by composting for 80 days in aerated piles a mixture of 60% lignocellulose material and 40% of food industry wastes and the organic fraction of municipal solid wastes. The GCC was obtained by composting for 120-days in aerated turned piles a mixture of 50% coffee husks and 50% tree cuttings. The three composts were characterized by means of conventional methods for several chemical and physical properties, including pH, electrical conductivity (EC), moisture and ash contents, total organic carbon (TOC) content, total N content, C/N ratio and humic acid-like (HAL) content.

1.2. Results and Discussion

The physical and chemical properties of the three compost samples examined are shown in Table 1. No relevant differences appear to exist among the three composts for pH, EC and moisture. The GCC sample shows lower ash content and HAL yield, and higher TOC, total N content and C/N ratio with respect to the other two composts that appear very similar in their properties.

2. Isolation and Chemical and Spectroscopic Characterization of Compost Humic Acid-like (HAL) fraction

2.1. Experimental

The HALs were isolated from the three composts according to the following conventional procedure. Each compost sample was air-dried and then extracted with a 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ + 0.5 M NaOH solution using a sample:extractant ratio=1:20. Suspensions were shaken mechanically in capped plastic bottles for 12 h at room

temperature (RT), and supernatants were separated by centrifugation at $6,000\times g$ for 15 min followed by filtration under vacuum through GF/C filters (particle size retention $1.2\ \mu\text{m}$). The extraction procedure was repeated five times. The combined alkaline supernatants were acidified with HCl to $\text{pH} \sim 1$, and then left standing overnight at RT to allow the complete precipitation of HAL fractions. Precipitated HALs were separated by centrifugation at $6,000\times g$ for 15 min, and subsequently purified by dissolution in 100 ml of 0.2 M KOH + 0.3 M KCl and stirring for 5 h, centrifugation at $6,000\times g$ for 15 min to remove the residues, and acidification of supernatants with HCl to $\text{pH} \sim 1$. The suspensions obtained were left standing overnight at RT, and subsequently centrifuged at $6,000\times g$ for 15 min. The purification steps were repeated twice. The purified HALs obtained were finally resuspended in 100 ml of distilled water, dialyzed through a Spectrapore membrane (6-8,000 Da membrane cut-off), freeze-dried, and stored in plastic vials at RT until analysis.

Each HAL was characterized for moisture and ash contents, acidic functional groups composition, and by Visible spectroscopy to obtain the E_4/E_6 value (see below), Fourier transform infrared (FT IR) spectroscopy, fluorescence spectroscopy in the emission, excitation and synchronous scan modes, and total luminescence (TL) spectroscopy. Moisture and ash contents were measured by heating HALs overnight at 105°C or for 5 h at 550°C , respectively. Total acidity was determined by the $\text{Ba}(\text{OH})_2$ method, the carboxylic group content by the $\text{Ca}(\text{CH}_3\text{COO})_2$ method, and the phenolic hydroxyl group content was calculated by difference. The E_4/E_6 ratio was calculated as the ratio of the absorbances at 465 and 665 nm measured with a Perkin Elmer model Lambda 15 UV-VIS spectrophotometer on solutions of 3.0 mg of each HA in 10 mL of 0.05 M NaHCO_3 . The FT IR spectra were recorded in the range $4000\text{-}400\ \text{cm}^{-1}$ on pellets obtained by pressing a mixture of 1 mg of each HA and 400 mg of dried KBr, spectrometry grade, under reduced pressure. A Thermo Nicolet Nexus FT IR Spectrophotometer equipped with a Nicolet Omnic 6.0 software was used, with $2\ \text{cm}^{-1}$ resolution and $64\ \text{scans min}^{-1}$ for each acquisition. Conventional monodimensional fluorescence spectra in emission, excitation and synchronous-scan modes and TL spectra in the form of excitation/emission matrix (EEM) spectra were obtained on aqueous solution of $100\ \text{mg L}^{-1}$ HA after overnight equilibration at RT, and adjustment to $\text{pH} 8$ with 0.05 M NaOH. All spectra were recorded using a Perkin Elmer model LS 55 luminescence spectrophotometer. Emission and excitation slits were set at 5-nm band width, and a scan speed of $240\ \text{nm min}^{-1}$ was selected for both monochromators. Emission spectra were recorded over the range 380–600 nm at a constant excitation

wavelength of 360 nm. Excitation spectra were recorded over the range 300–500 nm at a fixed emission wavelength of 520 nm. Synchronous-scan excitation spectra were measured by scanning simultaneously both the excitation and the emission wavelengths (from 300 to 550 nm), while maintaining a constant, optimised wavelength difference $\Delta\lambda$ ($\lambda_{em} - \lambda_{exc}$) = 18 nm. The TL spectra were obtained by scanning the wavelength emission over the range 300 to 600 nm, while the excitation wavelength was increased sequentially by 5-nm steps from 250 to 500 nm. The EEM contour spectra were generated from TL spectral data by using the Surfer 8.0 software. The fluorescence intensity (FI) values (in arbitrary unit) were normalized to the TOC content.

2.2. Results and Discussion

The main chemical properties of HAL samples examined are shown in Table 2. Although not relevant some differences appear to exist for HAL properties as a function of their origin. The E_4/E_6 ratio decreases in the order: GCC-HAL > GC-HAL > MC-HAL, whereas an opposite trend is observed for the carboxylic groups content. The phenolic and total acidity contents decrease in the order: MC-HAL > GCC-HAL > GC-HAL. Since the E_4/E_6 ratio is known to be inversely related to aromaticity, polycondensation degree and molecular weight of humic macromolecules, these results suggest a more aliphatic character, a lower polycondensation degree and a smaller molecular weight of GCC-HA with respect to the other HALs.

The FT IR spectra of HALs are shown in Fig. 1. In general, they are similar to FT IR spectra typical of compost HALs and also similar to each other, featuring a number of common absorption bands with small differences in their relative intensity: (a) 3394 cm^{-1} (O-H stretching of inter- and intra-molecular hydrogen bonds); (b) 2923 and 2853 cm^{-1} (asymmetric and symmetric C-H stretching of CH_2 groups, respectively); (c) 1707 cm^{-1} (C=O stretching of various carbonyl groups including COOH); (d) 1633 cm^{-1} (aromatic C=C skeletal vibrations, asymmetric stretching of C=O of quinones and ketones, symmetric stretching of COO^-); (e) 1545 cm^{-1} (N-H bending of amide II band); (f) 1381 cm^{-1} (asymmetric stretching of COO^- , C-H bending of aliphatic groups); (g) 1350 cm^{-1} (C-O asymmetric stretching of COOH groups); (h) 1260 cm^{-1} (C-O stretching of aryl ethers); (i) 1226 cm^{-1} (C-O asymmetric stretching and OH bending of COOH groups and phenols); (l) 1080 cm^{-1} (C-O stretching of primary alcohols and on-plane bending of aromatic C-H); and (m) 1028 cm^{-1} (OH stretching of polysaccharides).

The fluorescence emission, excitation and synchronous scan spectra of the three HAs are shown in Figs. 2, 3, and 4, respectively, and fluorescence parameters are reported in Table 3. The HAL fluorescence spectra and parameters show a maximum fluorescence intensity in the regions of medium wavelengths, which suggests the presence of low substituted aromatic nuclei and/or conjugated systems. The EEMs spectra of HALs (Fig. 5) are characterized by a common peak at 435-440_{ex}/514-520_{em}, which may be associated to the occurrence of aromatic units with a medium polycondensation degree. Further, the GCC-HA sample shows an additional peak at lower wavelengths that would confirm the simpler structural nature of GCC-HA.

3. Isolation and Chemical and Spectroscopic Characterization of Compost Dissolved Organic Matter (fulvic acid-like fraction)

3.1. *Experimental*

The dissolved organic matter (DOM) was extracted from each compost according to the following procedure. An aliquot of 100 g of each air-dried compost was suspended in 1000 ml of distilled water, and mechanically shaken for 15 min. The suspension was then centrifuged at 6000 rpm for 15 min, and finally filtered sequentially through Whatman filters with decreasing particle size retention in the order: 11µm, 2.5µm, 1.2µm and 0.45 µm. The DOM samples were then stored at 4 °C in the dark until analyses.

The electrical conductivity and the pH have been measured by conventional methods. The TOC content was determined by an autoanalyser (Thermo Electron Corporation HiPer TOC) using the difference method (total organic carbon = total carbon – inorganic carbon). Spectrophotometric analysis was conducted on a Perkin Elmer model Lambda 15 UV-VIS spectrophotometer by recording molar absorptivities at 280 nm (the region where the $\pi \rightarrow \pi^*$ electron transitions occur for a number of aromatic substances) and absorbances at 465 and 665 nm to determine the E₄/E₆ ratio.

The FT IR spectra were recorded in the range 4000-400 cm⁻¹ on pellets obtained by pressing a mixture of 3-4 drops of DOM and 400 mg of dried KBr, spectrometry grade, under reduced pressure, after heating overnight the mixture at 30 °C. A Thermo Nicolet Nexus FT IR spectrophotometer equipped with a Nicolet Omnic 6.0 software was used, with 2 cm⁻¹ resolution and 64 scans min⁻¹ for each acquisition. Fluorescence spectra were recorded using a Perkin Elmer model LS 55 luminescence spectrophotometer, in the same conditions described for HALs. Fluorescence intensity (FI) values (in arbitrary

unit) were normalized to the TOC content. The humification index (HI) was calculated as the ratio between the area in the upper quarter (435-480 nm) and the area in the lower quarter (300-345 nm) of the emission spectra. High performance liquid chromatographic (HPLC) analysis of each DOM sample was carried out with a Spectra System pump (Thermo Separation Products) equipped with a Rheodyne 7125 injection valve fitted with a 20 μ l loop and connected to a SupelcosilTM LC-18 chromatographic column (250 mm x 4.5 mm x 5 μ m). The mobile phase used was acetonitrile:H₂O:acetic acid at a ratio of 30:69.8:0.2 (v/v), and a diode array detector (DAD) was used at wavelengths of 230, 280 and 320 nm.

3.2. Results and Discussion

The main chemical and spectroscopic properties of DOM samples are shown in Table 4. The three DOM samples appear quite different one from another (Table 4). The pH value is similar and close to neutrality for MC-DOM and GC-DOM, whereas it is slightly alkaline for GCC-DOM. The EC values are similar for MC-DOM and GC-DOM and higher than that of GCC-DOM. The TOC content, the E₄/E₆ ratio, the ϵ_{280} value and the HI decrease in the order: GCC-DOM>MC-DOM>GC-DOM. It is known that high values of ϵ_{280} and E₄/E₆ ratio suggest the occurrence of low molecular weight aromatic molecules, such as phenolic-like units, aniline-derived compounds, benzoic acid derivatives, polyenes, etc., which are usually present in DOM samples of various origin.

The FT IR spectra of DOM samples are shown in Fig. 6. In general, they are similar one to another, featuring a number of common absorption bands with small differences in their relative intensity: (a) 3450 cm⁻¹ (O-H stretching of inter- and intra-molecular hydrogen bonds and N-H stretching); (b) 2930 and 2853 cm⁻¹ (asymmetric and symmetric C-H stretching of CH₂ groups, respectively); (c) 1636 cm⁻¹ (aromatic C=C skeletal vibrations, asymmetric stretching of C=O of quinones and ketones, symmetric stretching of COO⁻, C=O stretching of amide I band); (d) 1386 cm⁻¹ (asymmetric stretching of COO⁻, C-H bending of aliphatic groups); (e) 1200 cm⁻¹ (C-O asymmetric stretching and OH bending of COOH groups and phenols, C-O stretching of ethers and phenols); (f) 1135 cm⁻¹ (C-O stretching of secondary alcohol, aromatic C-H bending); (g) 1087 cm⁻¹ (C-O stretching of primary alcohols and on-plane bending of aromatic C-H).

The fluorescence emission, excitation and synchronous scan spectra of the three DOM samples are shown in Figs. 7, 8 and 9, respectively, and related fluorescence parameters

are reported in Table 5. The DOM fluorescence spectra and parameters are characterized by a maximum fluorescence intensity in the regions of short and medium wavelengths, thus suggesting the presence of simple structural components, low degree of aromatic polycondensation, and the possible occurrence on these molecules of electron-donating substituents such as hydroxyl, methoxyl and amino groups. The presence of several peaks and shoulders in the excitation and synchronous scan spectra suggest the presence of various fluorophores. The EEMs spectra of DOM samples are shown in Fig. 10, and are characterized by a common peak at 330-345_{ex}/415-440_{em}, which may be associated to simple aromatic units such as phenolic-like, hydroxy-substituted benzoic and cinnamic acid derivatives. The peak wavelengths observed in all fluorescence spectra of GCC-DOM are generally higher than those of the two other DOM samples, which can be ascribed to a more extended aromatic system and is confirmed by the higher ϵ_{280} value and HI value (inversely related to the H/C ratio).

The HPLC chromatograms obtained for the three DOM samples at 280 nm are shown in Fig. 11. The chromatographic peaks observed indicate a similarity between GC-DOM and MC-DOM, both of which appear slightly different from GCC-DOM, and the possible presence of benzoic acid derivatives such as phthalic and salicylic acids.

4. Germination experiments of slickspot peppergrass (*Lepidium papilliferum*) seeds

4.1. *Experimental*

Twenty (20) seeds of slickspot peppergrass were placed in Petri dishes on filter paper, and different tentative germination experiments were made. Seed treatments were: (a) soaking in distilled water for 12 h at room temperature (SK); (b) soaking in distilled water for 12 h at 35 °C (SK35); (c) SK and scraping (SC) with fine sand paper; (d) SC and then SK; (e) piercing with steel needle (PC); (f) soaking for 12 h in 70% ethylic alcohol and then washing with distilled water (EA); (g-i) soaking for 12 h in 0.2% (P 0.2%) or 2% (P 2%) or 10% (P 10%) pectinase and then washing with distilled water; (l) soaking for 12 h in NaCl 100 ppm and washing with distilled water (NaCl); (m) SK and treatment with 10% GC-DOM (GC-DOM). All experiments were conducted in a Phytotron growth chamber with photoperiod of 12 h and temperature of 23 °C. Germinated seeds were transplanted in glass pots containing fine quartz sand and Nitch nutrient solution.

4.2. *Results and Discussion*

The results of the germination experiments are shown in Table 6. All the germination trials were almost unsuccessful. Germinated seeds obtained in SK and SK + SC treatments presented visible aberrations such as root and shoot alterations and they were viable only for few days and did not grow normally. Further experiments are in course to solve these problems and get the peppergrass seeds germinated appropriately.

(2) RESEARCH PLANS FOR REMAINDER OF THE CONTRACT PERIOD

For the remainder of the contract period of the first financed year (6 months) research plans are the following:

- (a) Further experiments on the pre-treatment of peppergrass seeds in order to obtain a reasonable germination.
- (b) Experiments on germination and early growth of pre-treated peppergrass seeds in the presence of each compost, HAL and DOM sample at various concentrations.
- (c) Correlation of the germination and seedling growth data with chemical and physico-chemical parameters of the composts, HALs and DOMs examined, in order to find out the parameters that influence germination and growth of peppergrass.

(3) SIGNIFICANT ADMINISTRATIVE ACTIONS DURING THE PERIOD REPORTED: NONE.

(4) ANY OTHER INFORMATION : NONE.

(5) ANNEX

- (A) AMOUNT OF UNUSED FUNDS REMAINING ON THE CONTRACT AT THE END OF THE PERIOD COVERED BY THE REPORT: US\$ 25,000.
- (B) IMPORTANT PROPERTIES ACQUIRED WITH CONTRACT DURING THIS PERIOD: NONE.
- (C) METHOD OF REPRODUCTION: E-MAIL ATTACHMENTS, PHOTOCOPYING.

Table 1. Main properties of the three composts.

Sample	pH	EC (dS/m)	Moisture (g kg⁻¹)	Ash (g kg⁻¹)	TOC^a (g kg⁻¹)	Total N (g kg⁻¹)	C/N ratio	HAL Yield (%)
GC	8.4	3.73	163	651	184	15.6	11.7	17.3
MC	8.5	3.64	120	628	196	17.2	11.4	18.1
GCC	9.1	3.30	147	150	424	25.7	16.5	13.9

^aTOC: total organic carbon

Table 2. Moisture, ash and acidic functional group content (on moisture free basis) and E₄/E₆ ratio of HALs examined.

Origin of HAL	Moisture %	Ash %	COOH meq/g	Phenolic OH meq/g	Total acidity meq/g	E₄/E₆ ratio
GC	5.97	3.44	3.34	1.80	5.14	8.24
MC	6.50	3.21	3.38	2.94	6.32	8.08
GCC	4.96	4.96	3.08	2.55	5.63	8.54

Table 3. Wavelengths and fluorescence intensity of peaks and shoulders obtained in the fluorescence spectra of the three HALs examined.

Emission spectrum						
Origin of HALs	E_m	IF				
GC	459	31.7				
MC	462	30.0				
GCC	458	31.1				
Excitation spectrum						
Origin of HALs	E_x	IF	E_x	IF	E_x	IF
GC	307	21.6			443	47.4
MC					444	44.3
GCC			417	32.0	442	34.0
Synchronous scan spectrum						
Origin of HALs	Sy	IF	Sy	IF		
GC			482	22.1		
MC			480	20.2		
GCC	445	13.8	484	13.9		
Excitation/Emission Matrix						
Origin of HALs	E_x/E_m	IF	E_x/E_m	IF		
GC			440/518	50.4		
MC			440/514	46.9		
GCC	400/487	40.0	435/520	36.9		

Table 4. Some chemical and spectroscopic parameters of DOM samples examined.

Sample	pH	EC (dS/m)	TOC (mg L ⁻¹)	$\epsilon_{280\text{nm}}$ (L cm ⁻¹ mol ⁻¹)	E ₄ /E ₆ ratio	Humification index (HI)
GC	7.4	3.14	140	26.8	3.6	124
MC	7.0	3.28	186	32.5	4.3	141
GCC	8.3	1.66	375	38.9	6.9	261

Table 5. Wavelengths and fluorescence intensity of peaks and shoulders obtained in the fluorescence spectra of the three DOM samples.

Emission spectrum										
Origin of DOM	E _m	IF								
GC	440	4.7								
MC	440	4.1								
GCC	446	1.1								
Excitation spectrum										
Origin of DOM	E _x	IF	E _x	IF	E _x	IF	E _x	IF	E _x	IF
GC	309	1.3	337	1.4	351	1.4				
MC	313	1.1			351	1.2	373	1.2	385	1.2
GCC									397	0.5
Synchronous scan spectrum										
Origin of DOM	Sy	IF	Sy	IF	Sy	IF				
GC	353	9.7	385	10.0						
MC	356	7.7	387	8.7	423	7.2				
GCC			395	0.2	432	0.3				
Excitation/Emission Matrix										
Origin of DOM	E _x /E _m	IF								
GC	330/415	6.5								
MC	330/418	5.3								
GCC	345/440	1.2								

Table 6. Number of germinated seeds (20 seeds per Petri dish) after different treatments and time periods.

Treatment		Number of germinated seeds				
		7 days	15 days	30 days	60 days	Total number
1	SK	4	0	2	2	8
2	SK35	0	0	0	0	0
3	SK + SC	1	1	0	1	3
4	SC + SK	0	0	0	0	0
5	PC	0	0	0	0	0
6	EA	0	0	0	0	0
7	P 0.2%	0	0	0	0	0
8	P 2%	0	0	0	0	0
9	P 10%	0	0	0	0	0
10	NaCl	1	0	0	nd ^a	nd
11	GC-DOM	0	0	nd	nd	nd

nd^a: not yet determined, experiments still in course.

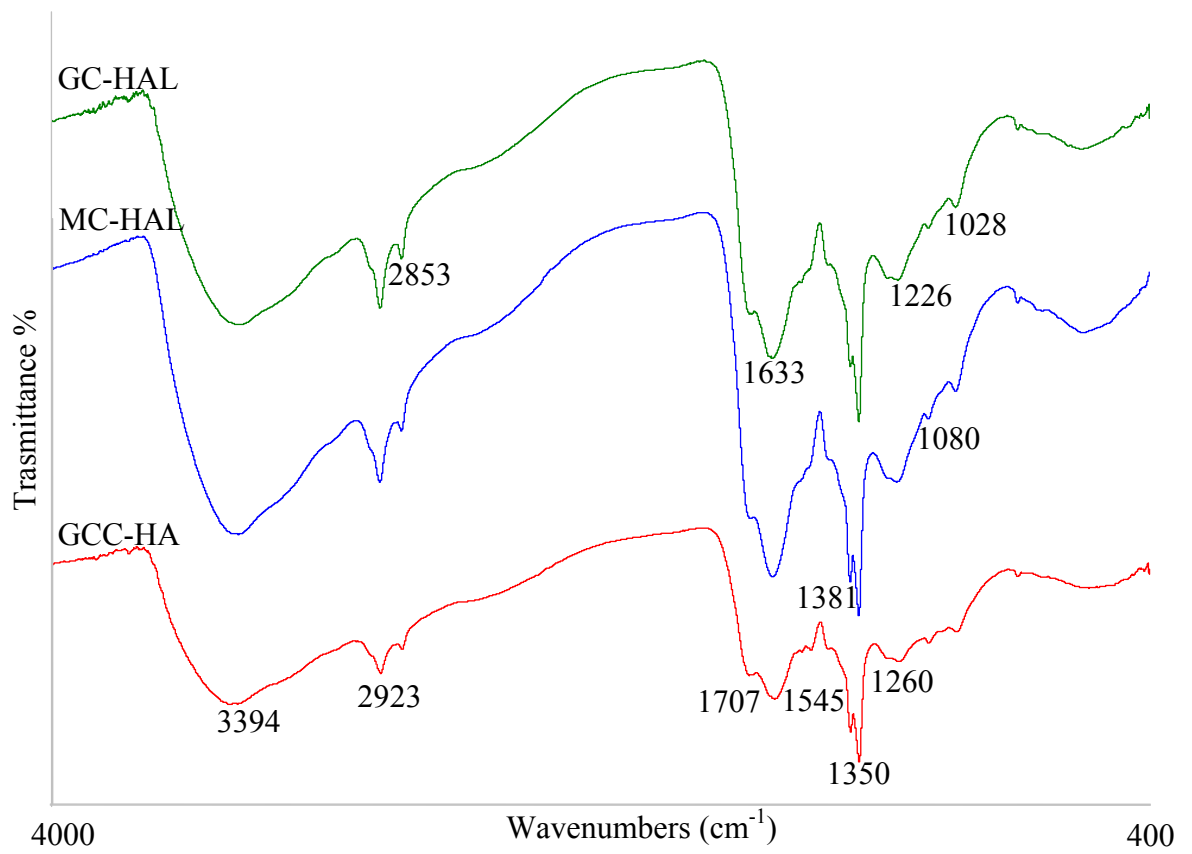


Figure 1. FT IR spectra of HALs examined.

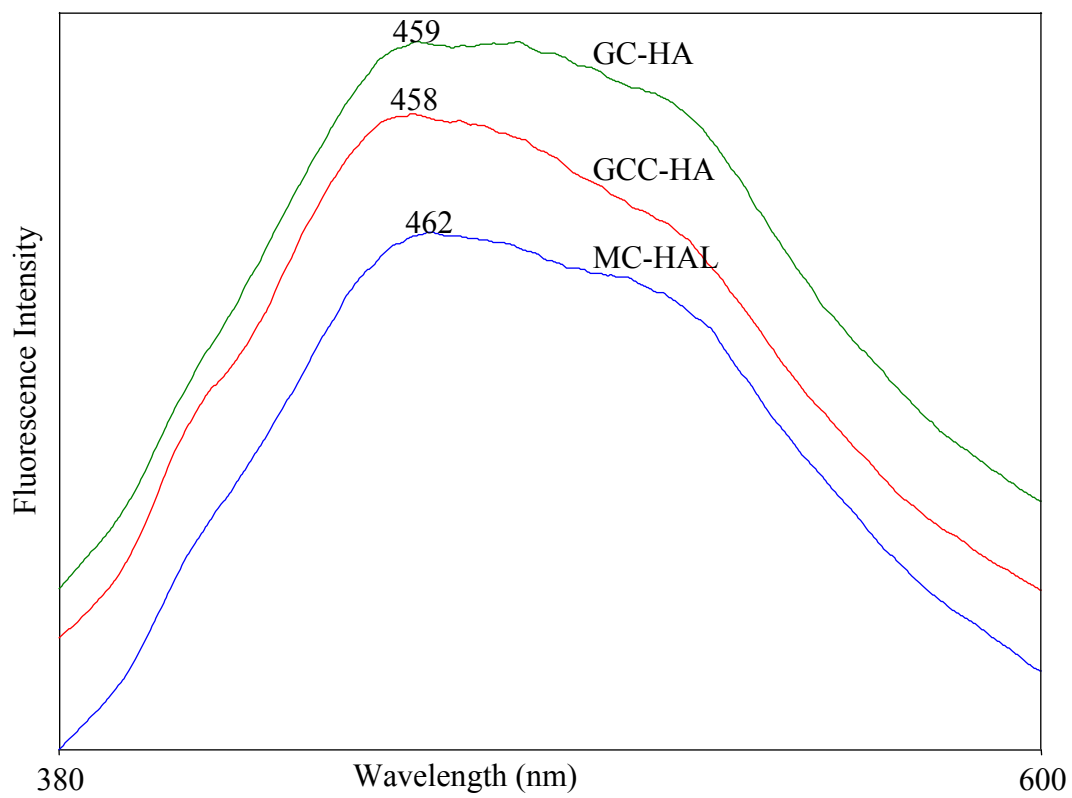


Figure 2. Fluorescence emission spectra of HALs examined.

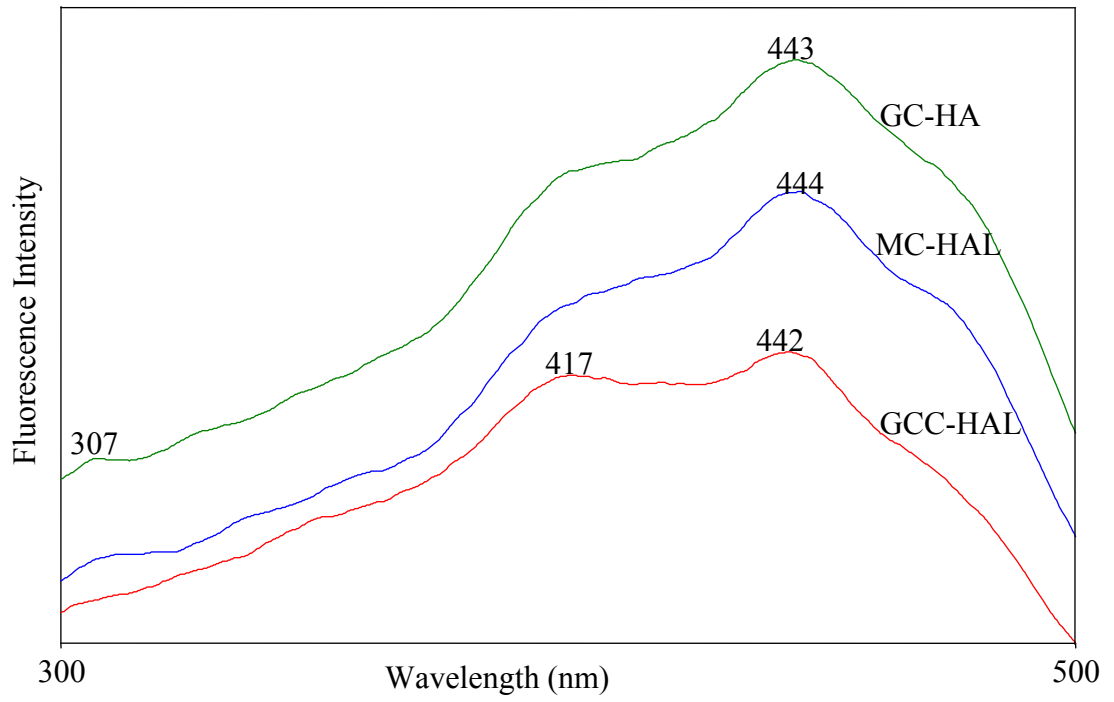


Figure 3. Fluorescence excitation spectra of HALs examined.

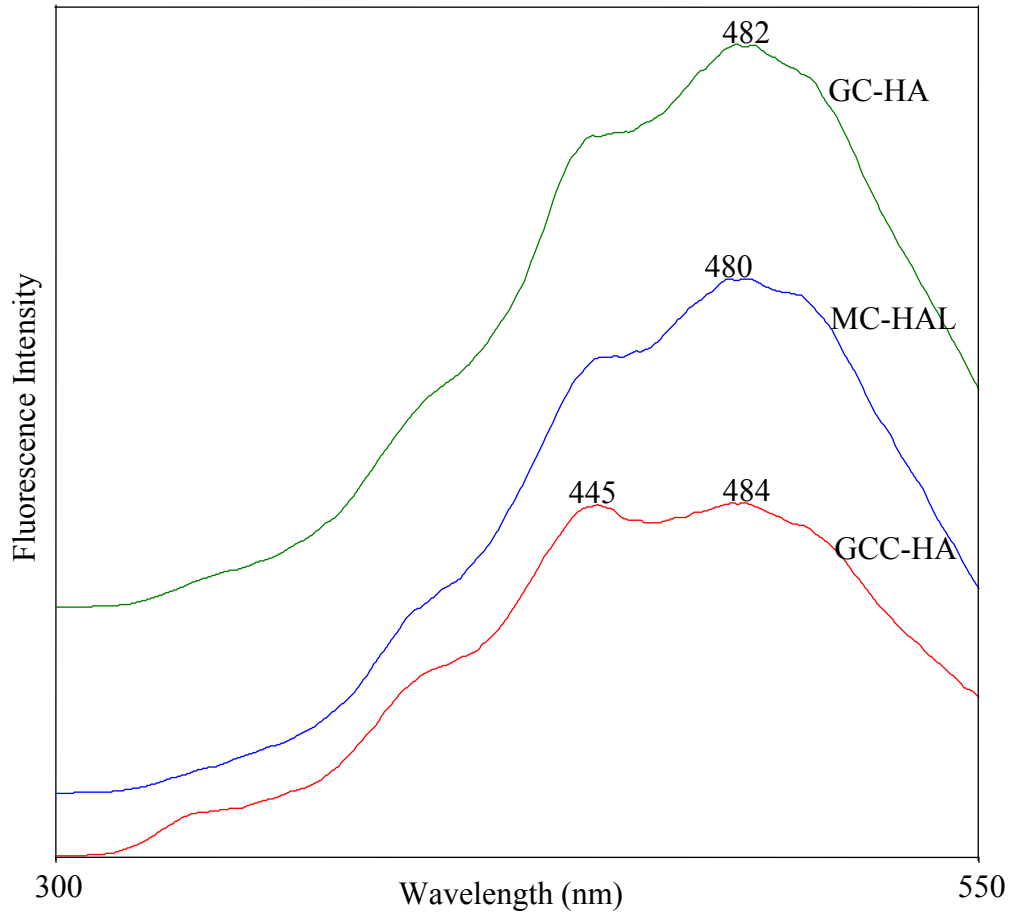


Figure 4. Fluorescence synchronous scan spectra of HALs examined.

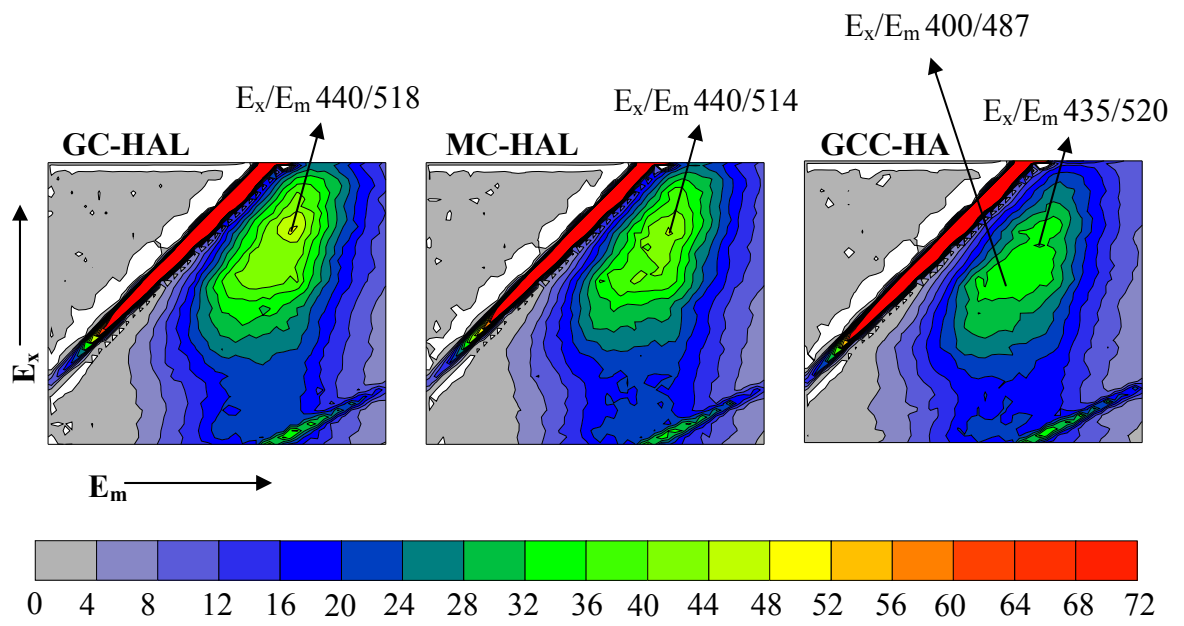


Figure 5. Emission/Excitation Matrices of HALs examined.

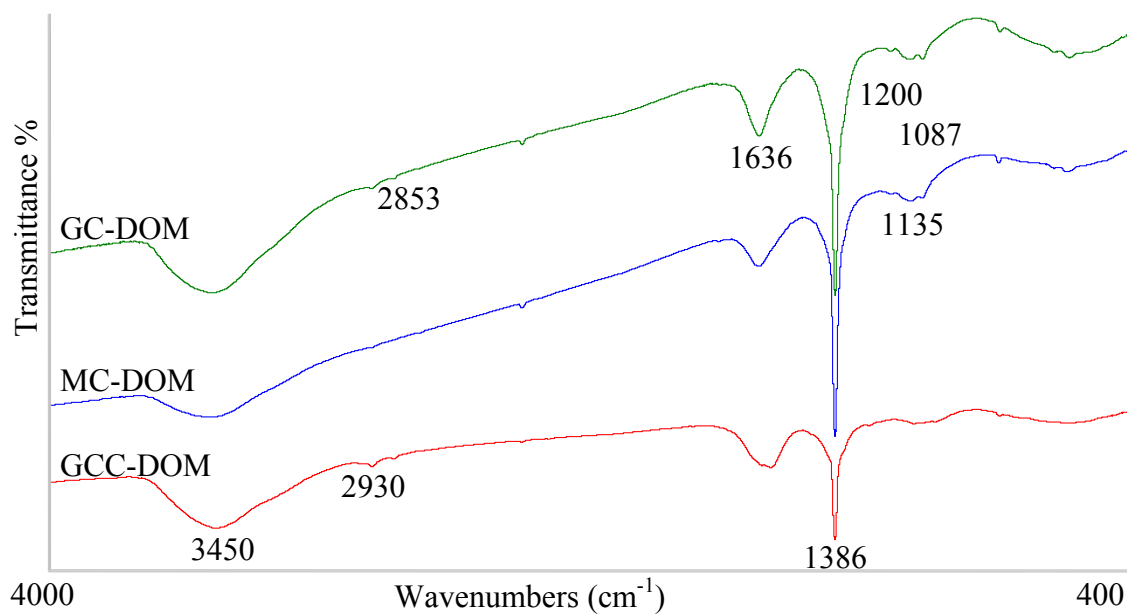


Figure 6. FT IR spectra of DOM samples.

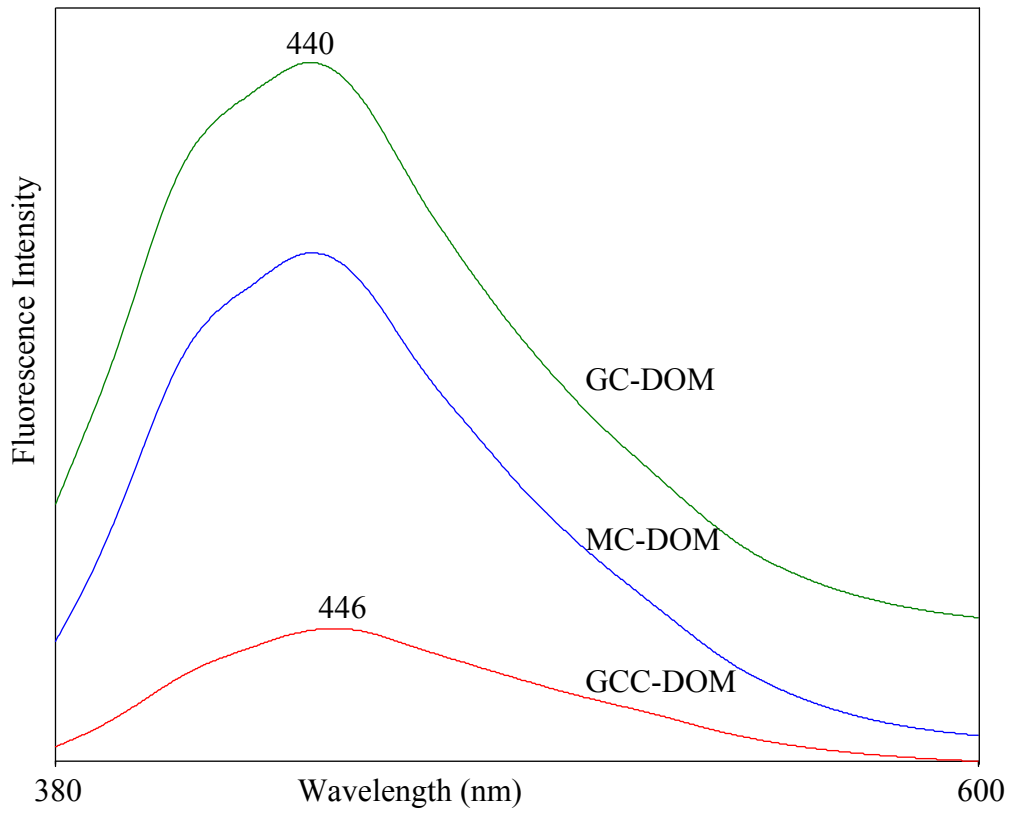


Figure 7. Fluorescence emission spectra of DOM samples.

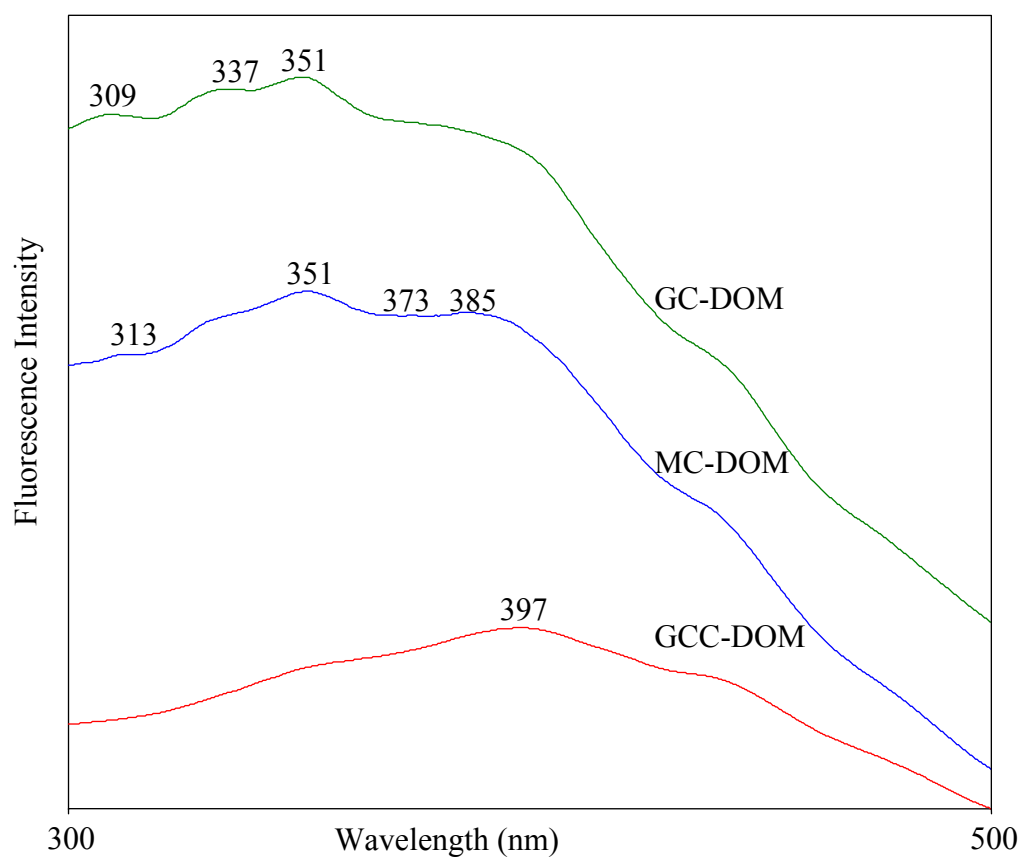


Figure 8. Fluorescence excitation spectra of DOM samples.

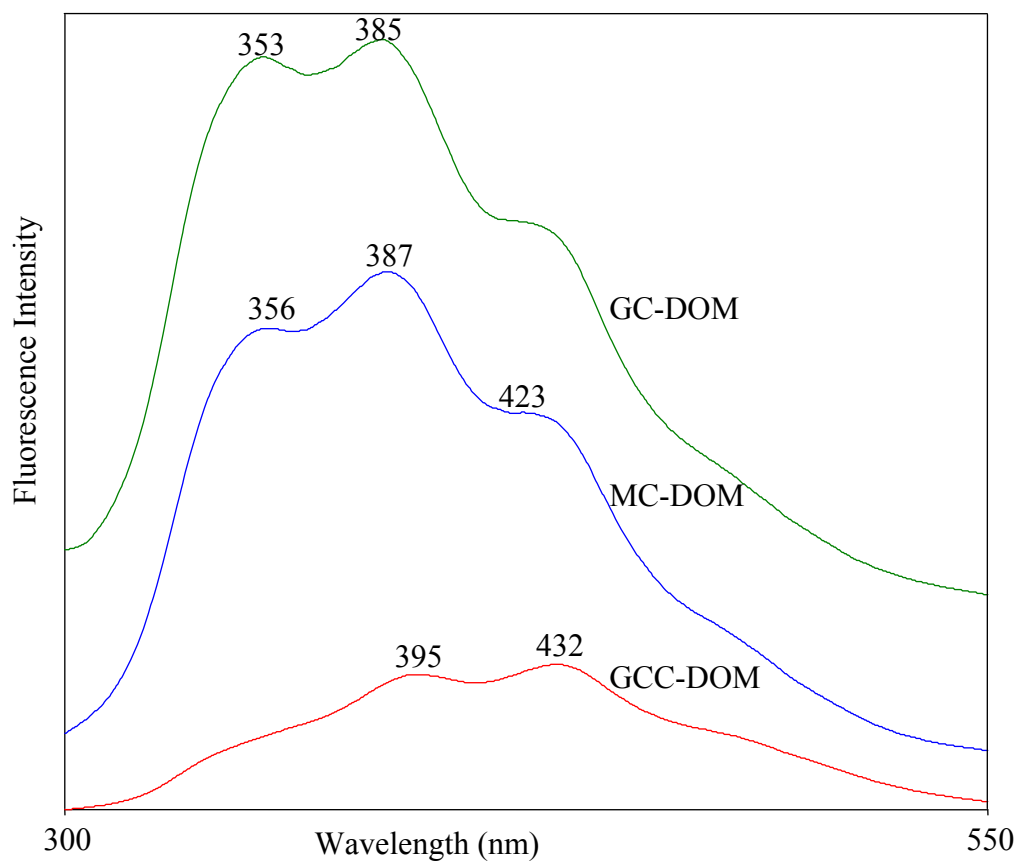


Figure 9. Fluorescence synchronous scan spectra of DOM samples.

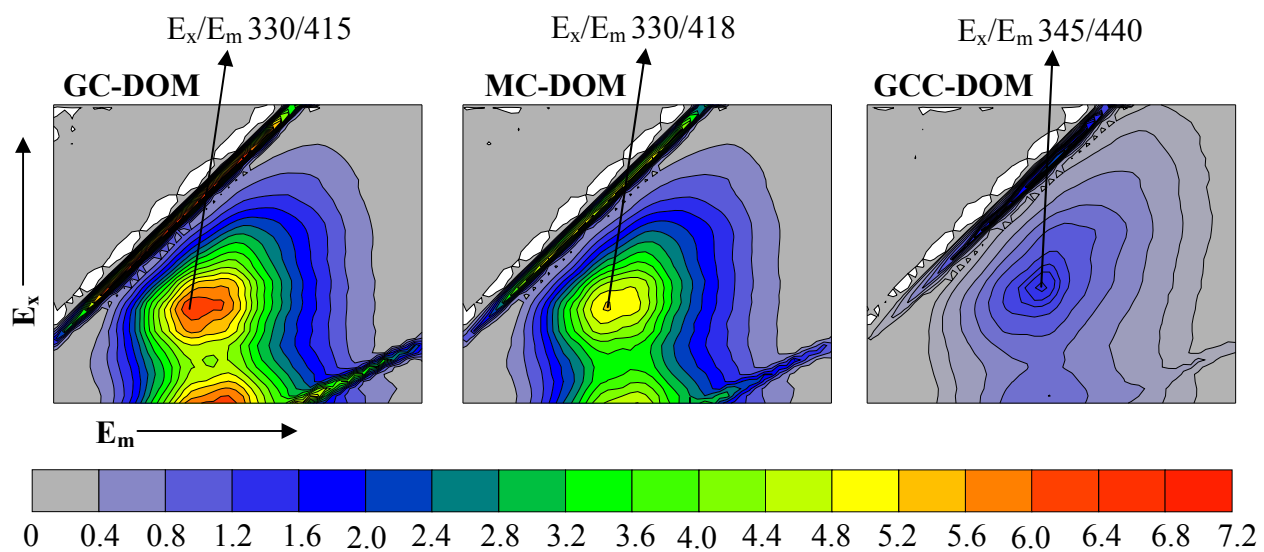


Figure 10. Emission/Excitation Matrices of DOM samples.

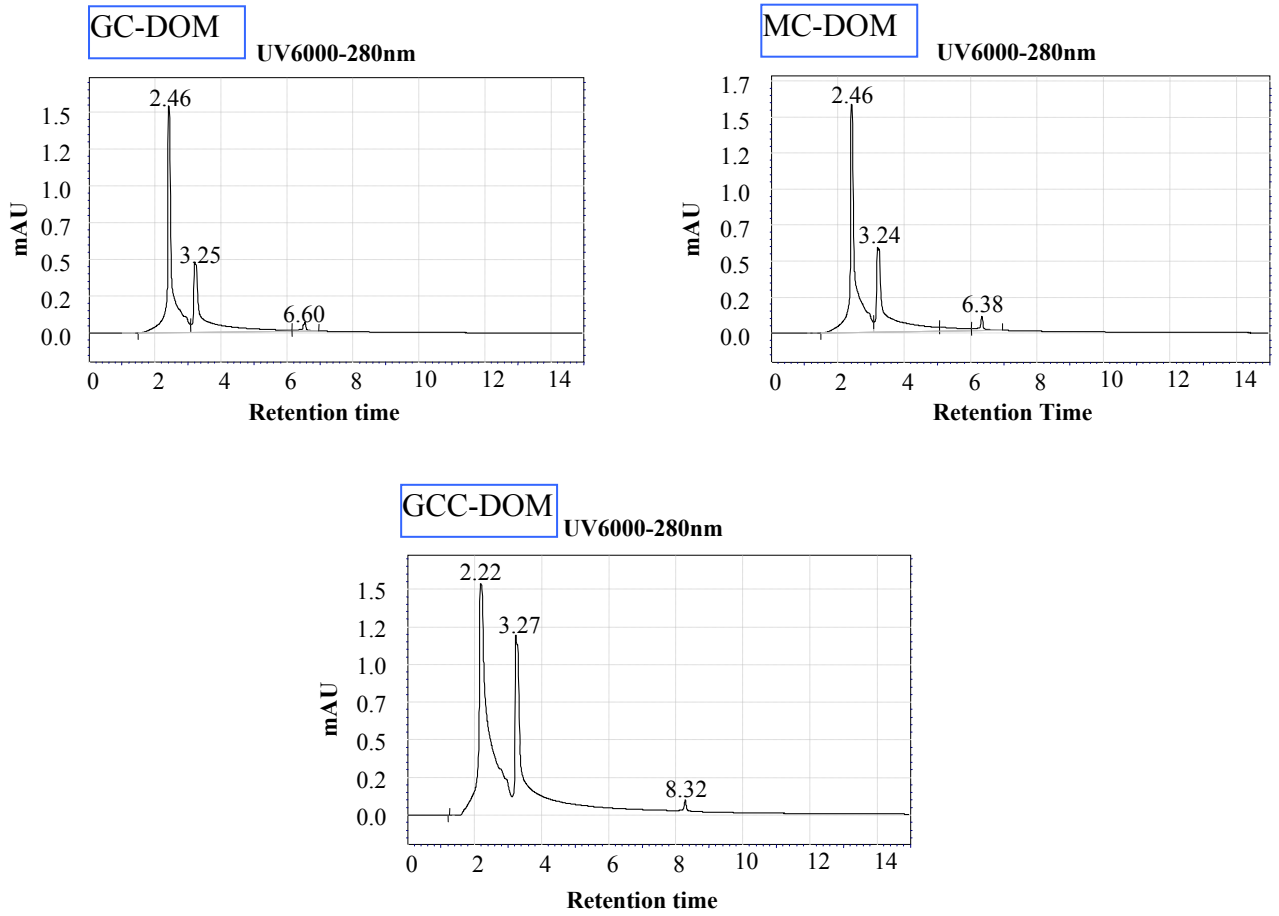


Figure 11. HPLC chromatograms of DOM samples.