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Characteristics of NOM Released to Water from Different Forest and Agricultural Soils

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Abstract. The characteristics of natural organic matter (NOM) released to water from a soil environment were investigated based on the release potential and the quality indexes of SUVA, fluorescence EEM and molecular weight distribution using eight forest and agricultural soils collected from a representative river catchment (Kani River catchment in Gifu, Japan). The content of organic matter (OM) and its release potential to water differed obviously with type of soil origin, in the following order: vegetable field (VF) < paddy field (PF) < broadleaf forest (BF) < coniferous forest (CF) and VF < PF < CF < BF, respectively. For the released NOM, SUVA under different pH conditions decreased in the following order: neutral condition [3.6-24.0 m^{-1}/(mg/L)] > basic condition [3.5-8.0 m^{-1}/(mg/L)] > acidic condition [2.5-3.0 m^{-1}/(mg/L)]. Humic acids (P1), fulvic acids (P2) and protein-like substances (P3) were the main components of the NOM released under neutral condition. The proportion of P1 and P2 released from the forest soils was lower than that from the agricultural soils. Marked differences in UV-absorbing constituents of NOM between forest and agricultural soils were found in the peak with a molecular weight of about 9800 g/mol identified as PSS (polystyrene sulfonate).

1   Introduction

NOM contained in soils of forest and agricultural fields adjacent to catchments of rivers and lakes, such as broadleaf forests, coniferous forests, paddy fields and vegetable fields, are the main sources of NOM existing in the freshwater environment. Naturally, humic substances (humic and fulvic acids) and protein-like substances are the major components and pH plays a predominant role in determining the final properties of the released NOM in water [1-3]. Guigue, *et al.* [3] have reported that the pH of NOM solution released from different types of soil origin, i.e. forest, grassland and cropland, varied in the range of 5.0-6.4.

Gui, *et al.* [2] found that the molecular weight (MW) of NOM released from the soil of a representative broadleaf forest decreased with conditions that changed from basic to acidic. Moreover, as the major constituting molecules of released NOM, humic substances and protein-like substances in drinking water supplies are causing increasing concern due to their capability to react with chlorine to form hazardous disinfection byproducts and also their capability to adversely affect the removal of synthetic organic compounds (SOCs) by activated carbon through competing for adsorption sites or blocking the access of SOCs to small pores where their adsorption is more effective [2,4,5].

Total organic carbon (TOC) and ultraviolet absorbance at 260 nm (UV260) are normally used to quantify the content of NOM in water. Regarding the composition of NOM, in addition to the index of specific ultraviolet absorbance (SUVA), which reflects the extent of aromaticity of the constituting components [1,2,6,7], fluorescence excitation-emission matrix (EEM) spectroscopy is increasingly used to generate information that cannot be achieved either by TOC, UV260 or SUVA [8-10]. In addition to these, the molecular weight (MW) distribution of NOM can provide valuable information for better understanding the polydisperse nature of NOM and the removal behavior of the constituting components during various physicochemical water treatment processes [2,11,12].

Investigation of the characteristics of NOM released to water from soils of different origin in catchments is important for a comprehensive understanding of the presence and behavior of dissolved organic matter in freshwater environments and for finding optimal operating conditions of drinking water treatment processes for its enhanced removal. The major objective of this study was to evaluate the characteristics of NOM released from different forest and agricultural soils. For this purpose, eight different forest and agricultural soils distributed in a representative river catchment were used. The release potential of NOM in these soils was compared and the characteristics of the released NOM were then evaluated based on the quality indexes of SUVA, fluorescence EEM and MW distribution.

2   Materials and Methods

2.1   Release of NOM from Soils to Water

Eight soil samples from different forest and agricultural origins, including two broadleaf forest soils (BF-1 and BF-2), two coniferous forest soils (CF-1 and CF-2), two paddy field soils (PF-1 and PF-2) and two vegetable field soils (VF-1 and VF-2) were collected from the Kani River catchment (Kani-city, Gifu Prefecture, Japan). Kani River is a major tributary of the Kiso River that has

forest coverage of about 80% and is the largest river system in the central Japan area. It is used as a water supply for drinking, industrial and agricultural purposes. The release of NOM from each soil was made under three different pH conditions (2, 7 and 11) in a temperature controlled room (at 20°C) by mixing 1 kg of soil in 6 L of organic carbon-free tap water at 500 rpm for 7 days, followed by settling for 1 day, centrifuging at 12,000 rpm for 5 min, filtering through a 0.2 μm membrane filter (Toyo Roshi, Japan), and finally storing the filtered solution in a refrigerator at 4 °C prior to analysis. The reason to use organic carbon-free tap water as the solution was for the purpose of eliminating the influence on the concentration and composition of the released NOM. The use of 1 kg of soil in 6 L of water was done for obtaining the total volume of solution needed for the purposes of this study and the purposes of an adsorption experiment conducted for investigation of the adsorbability of the released NOM by activated carbon by referencing previous studies on the release of organic matter from soil [13-15].

2.2   Overall concentration of the Released NOM

The overall concentration of the released NOM was quantified using dissolved organic carbon (DOC) with a total organic carbon analyzer (TOC 5000, Shimadzu Co.) and ultraviolet absorbance at a wavelength of 260 nm (UV260) with a UV-visible spectrophotometer (Model UV-1600, Shimadzu Co.), respectively. The specific ultraviolet absorbance (SUVA), which is defined as the ratio of UV260 to DOC, was calculated in order to investigate the differences in aromaticity of the organic species.

2.3   Fluorescence EEM of the Released NOM

The fluorescence EEM was analyzed using a fluorescence spectrophotometer (RF-5300, Shimadzu Co.). The excitation scan was performed in the range of 220-480 nm with 5 nm increments and the emission spectral ranging from 280-550 nm with 1 nm intervals. The obtained EEM was normalized to the quinine sulfate unit (QSU) by dividing the fluorescence intensity (FI) of all samples with that of 10 ppb quinine sulfate (in 0.05 M H_2SO_4) at the designated wavelengths of Ex/Em = 350/450 nm [2]. To minimize the inner filter effect, all samples subjected to EEM measurement were diluted by Milli-Q to DOC below 2 mg/L.

2.4   MW distribution of the Released NOM

The MW distribution of the NOM released from each soil was analyzed using a high-performance size exclusion chromatography system (HPSEC) that consisted of a silica chromatographic column (GL-W520-X 10.7 × 450 mm, Hitachi Co.) and a UV260 detector (Model LC-10AV, Shimadzu Co.). The

mobile phase containing 0.02 M Na_2HPO_4 and 0.02 M KH_2PO_4 was used as the eluent and was supplied to the column at a constant flow rate of 0.5 mL/min. Based on the obtained MW chromatograms, the weight-averaged (*Mw*) and number-averaged (*Mn*) molecular weight, and the polydispersity of the released NOM were calculated according to the method described in Refs. [2] and [5].

3   Results and Discussion

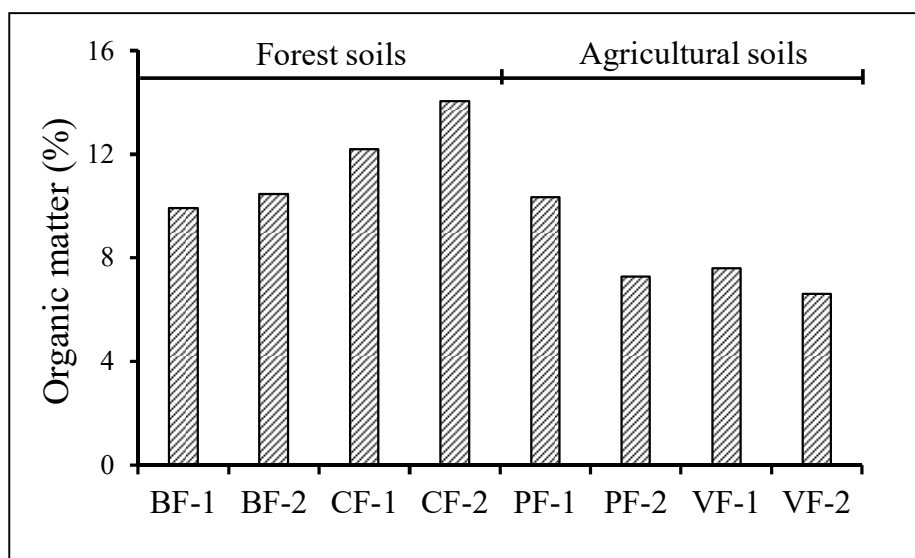### 3.1   NOM Content of Soils and Its Release Potential to Water

Figure 1   The OM content of investigated forest and agricultural soils.

The organic matter (OM) content of all eight forest and agricultural soils was analyzed according to the method of weight loss on ignition. As plotted in Figure 1, the OM content in the soils varied greatly in the range of 6.6-14.0%. By grouping based on type of soil origin, the average OM content increased in the following order: VF (7.1%) < PF (8.8%) < BF (10.2%) < CF (13.1%). Similar results were found in previous studies [3,4,16]. Celik [16] have reported an increasing order in OM content as follows: farmland < grassland < scrubland < forestland.

Guigue *et al.* [3] concluded that the contents of soil organic carbon (SOC), total nitrogen (TN) as well as the ratio of carbon to nitrogen (C/N) in cropland soil were lower than those in grassland soil, followed by those in forest soil. Liu, *et al.* [4] summarized that the OM content decreased during the conversion process of forest and pasture soils into agricultural soil. All these findings

demonstrate that the OM content of forest soils is higher than that of agricultural soils. The reason for this difference is probably because of the loss of organic matter in agricultural soils due to agricultural activities, such as the application of lime, manure, fertilizer, pesticide and herbicide as well as irrigation and harvesting of crops [17]. As a result of cultivation, the composition of OM in agricultural soils is also found to be more uniform than that in forest soils [18].
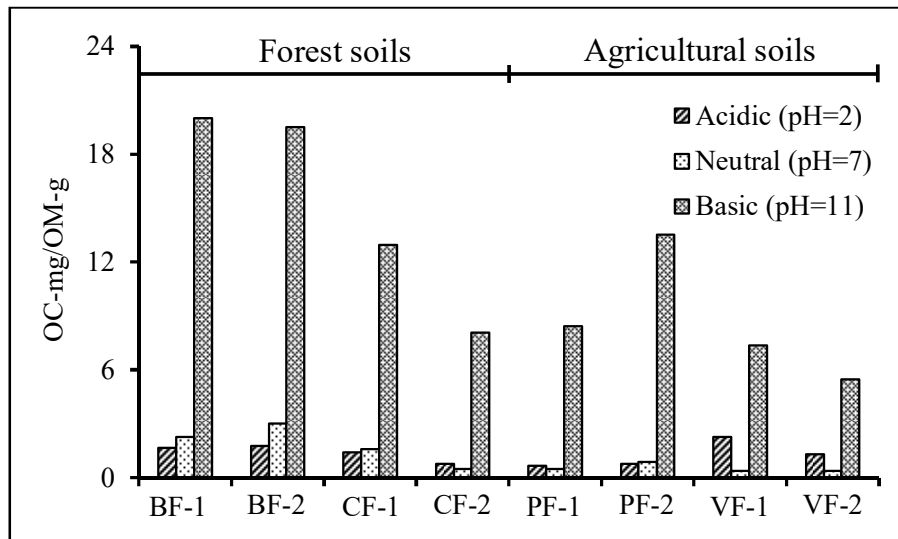

Figure 2 The release potential of NOM from investigated forest and agricultural soils under different pH conditions.

The release potential of NOM from soils under the experimental conditions of this study was defined as the amount of organic matter content released to water (measured as organic carbon, OC) divided by the total content of OM in each soil. The values of the release potential determined for all soils under all three investigated pH conditions are plotted in Figure 2. It is interesting to see that the release potentials of NOM under basic condition (5.5-20.0 mg-DOC/g-OM) were several to tens of times larger than those under neutral (0.4-3.0 mg-DOC/g-OM) and acidic (0.6-2.3 mg-DOC/g-OM) conditions, which reflects significantly enhanced release of OM to water by increasing pH.

The enhanced release of NOM to water from soils by increasing pH is a result of enhanced dissociation or desorption of NOM molecules from soils where NOM molecules are fixed on the soil particle surface through sorption onto and/or complexation with minerals of soils [15,19]. As can be seen from Figure 3, by increasing pH, the deprotonation process is promoted, leading to decreases

in the net positive charges at the surface of minerals. For NOM molecules, however, the dissociation of the major functional groups contained in the structure of humic and fulvic acids (COOH groups and phenolic OH groups) is promoted, making the molecules more negatively charged. The changes in charge density of both minerals and NOM molecules weaken the sorption and/or complex formation forces between them, leading to an enhanced release of NOM molecules from soil to water [2,15,19].
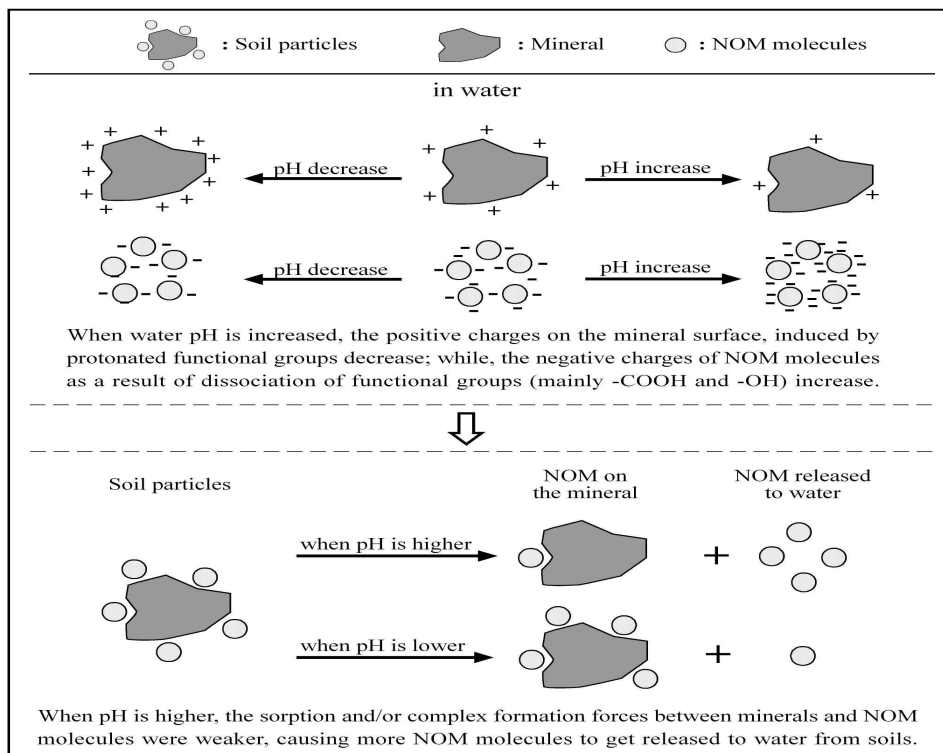

Figure 3 Release mechanism of NOM under different pH conditions.

Under neutral condition, the mean release potential of NOM changed with the investigated type of soil origin in the following order: VF (0.4 mg-DOC/g-OM) < PF (0.7 mg-DOC/g-OM) < CF (1.0 mg-DOC/g-OM) < BF (2.62 mg-DOC/g-OM), an order different from the order of the OM content in the soils discussed earlier: VF (7.1%) < PF (8.8%) < BF (10.2%) < CF (13.1%). This indicates that the release potential of NOM is influenced by the type of soil origin rather than the OM content, and that the release potential of OM from forest soils was generally higher than that from agricultural soils.

3.2   Aromaticity of the Released NOM

For all four forest soils (BF-1, BF-2, CF-1 and CF-2), the magnitude of SUVA of the released NOM under different pH conditions decreased in the following order: neutral condition [3.6-24.0 m^{-1}/(mg/L)] > basic condition [3.5-8.0 m^{-1}/(mg/L)] > acidic condition [2.5-3.0 m^{-1}/(mg/L)]. Meanwhile, for the four agricultural soils, the changing trends in the magnitude of SUVA with pH were not unique and differed between soils, as can be seen from Figure 4. Under acidic condition, the released NOM from the agricultural soils was found to possess higher aromaticity than that from the forest soils. On the other hand, under neutral condition, the average SUVA from the BF soil [17.3 m^{-1}/(mg/L)] was larger than that of the PF [6.3 m^{-1}/(mg/L)], the CF [4.1 m^{-1}/(mg/L)] and the VF soil [3.7 m^{-1}/(mg/L)]. This is different from the findings of Guigue *et al.* [3], who has reported that the SUVA of NOM extracted from forest soils was lower than that from cropland soils, indicating that the content of aromatic organic molecules contained in and released from soils is affected by the type of soil origin and the pH of water [3].
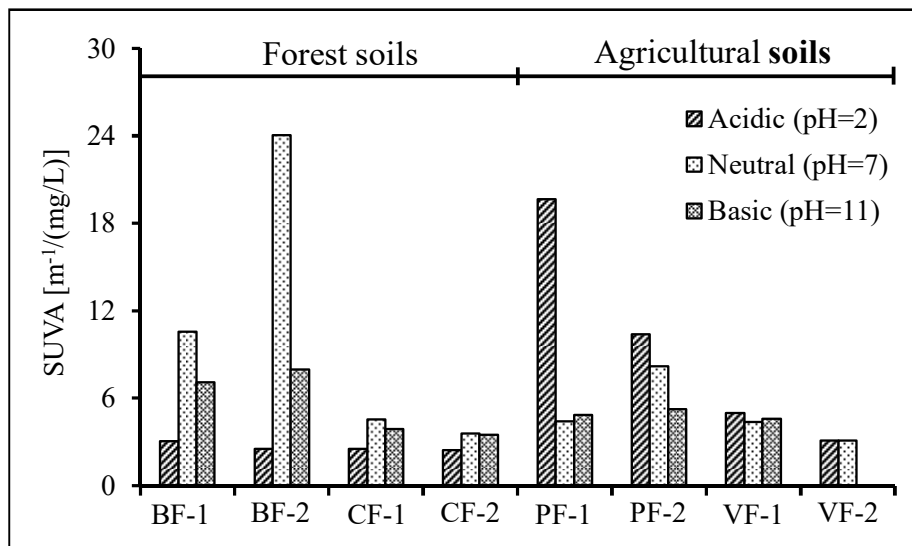

Figure 4 SUVA of released NOM from investigated forest and agricultural soils under different pH conditions.

In addition, compared to the SUVA of dissolved OM in reservoir, lake and river water [1,6,7], the SUVA of the released NOM under neutral condition in this study was larger. For instance, the SUVA of NOM in Maji ya Chai River [1], originated from a tropical swamp, changed in the range of 2.3-5.7 m^{-1}/(mg/L) with the seasons, while the SUVA of a surface area in Masaka [7] showed a value of 4 m^{-1}/(mg/L). This may indicate that the NOM directly released from

soils possess relatively higher aromaticity or a larger content of humic substances [6].

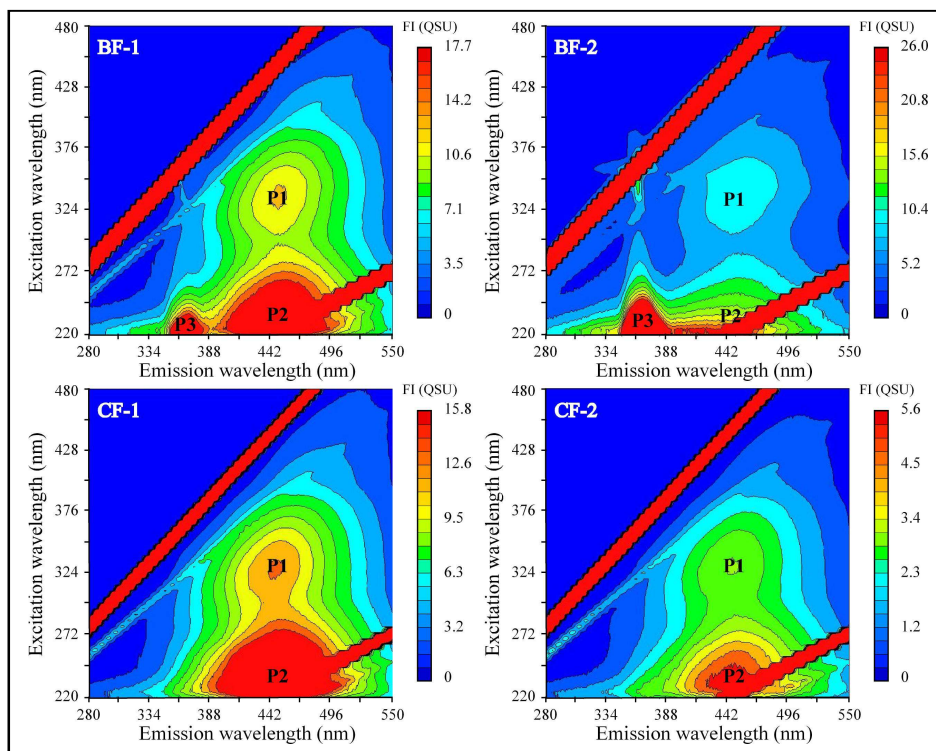## 3.3   Fluorescence Characteristics of Released NOM

Figure 5 Fluorescent components of released NOM from investigated forest soils under neutral condition.

The characteristics of NOM released under neutral condition from soils of forest and agricultural origin based on fluorescence EEM are displayed in Figures 5 and 6. In coincidence with previous studies [8-10,20], two apparent peaks, reported to reflect humic acids (P1) and fulvic acids (P2) with Ex/Em at 325/445 nm and 230/445 nm, were found in all of the soils, while the obvious peak (P3) that represents the protein-like substances with Ex/Em at 230/370 nm appeared only in soils BF-1 and BF-2 (broadleaf forest) and PF-2 (paddy field). As for the three peaks, they have been widely detected in river, marine, domestic wastewater and the drinking water system [8-10]. Baker [8] has reported that humic acids, fulvic acids and tryptophan were the main components of the River Tyne, and that fluorescence EEM spectrophotometry has the potential to be used for pollution detection and monitoring of river systems. Through investigation of the fluorescence components in dissolved

organic matter from Ise Bay, Yamashita [9] identified humic acids, fulvic acids and two protein-like components and then exemplified the potential applicability of fluorescence EEM in studies for evaluating the dynamics of NOM in estuaries. By evaluating the fluorescence components in drinking water and wastewater treatment systems, Yang, *et al.* [10] classified humic acids, fulvic acids and protein-like substances, and analyzed the corresponding composition of dissolved OM.
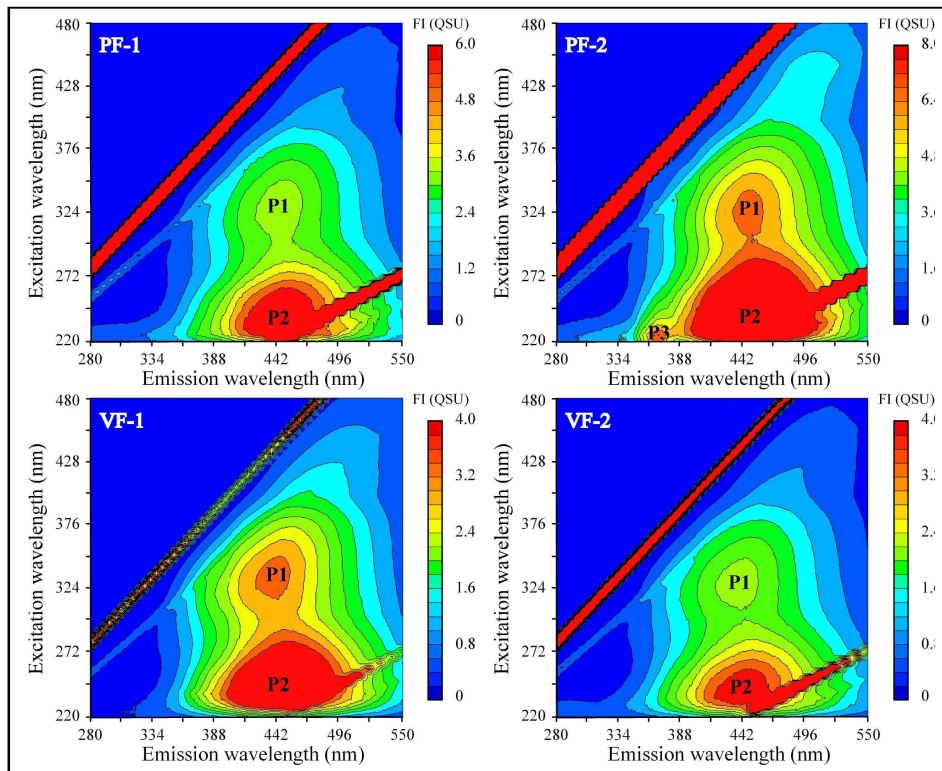

Figure 6 Fluorescent components of released NOM from investigated agricultural soils under neutral condition.

As displayed in Figures and 6, P1, P2 and P3 were the main fluorescent components of the released NOM from the investigated forest and agricultural soils, though P3 was not obvious in some soils. In order to investigate the differences in proportion of these three components, the relative ratios (P1/P2, P1/P3 and P2/P3) that are usually used for discriminating organic matter sources [21] and that may imply structural differences in the released organic matters [22], were calculated as displayed in Table 1. For all the released NOM, the three average ratios increased in the order BF < CF < PF < VF, indicating

that the fractions of P1 and P2 increased while the fraction of P3 decreased as in the above order, i.e. the proportions of P1 and P2 in the NOM released from forest soils were lower than those from agricultural soils, though the average DOC and UV260 concentrations of released NOM from the former were tens of times larger than those from the latter.

Table 1   Characteristics of NOM released from investigated forest and agricultural soils under neutral condition.

Samples	DOC	UV260	Relative ratios of constituting components			M_w	M_n	Polydispersity
	mg/L	m^{-1}	P1/P2	P1/P3	P2/P3	g/mol as PSS		
BF-1	37.1	391.6	0.56	0.57	1.02	8013	7494	1.07
BF-2	52.3	1257.8	0.43	0.12	0.29	7864	7248	1.09
CF-1	32.0	145.3	0.56	1.34	2.38	7805	7381	1.06
CF-2	11.3	40.7	0.56	1.14	2.04	7704	7239	1.06
PF-1	8.1	35.7	0.53	1.43	2.70	7617	7173	1.06
PF-2	10.8	88.3	0.59	1.07	1.82	7639	7197	1.06
VF-1	4.5	19.5	0.78	2.13	2.74	7407	6831	1.08
VF-2	4.0	12.5	0.63	1.52	2.40	7413	6856	1.08

3.4   Molecular Weight Characteristics of Released NOM

The profiles of MW distribution of the NOM released from eight forest and agricultural soils under neutral condition are shown in the Figure 7. It is clear that the HPSEC profiles of the NOM released from forest soils and agricultural soils are similar, but were obviously different between forest and agricultural soils. For the HPSEC profiles of the forest soils, aside from the differences in UV absorbance intensity, slight changes in the peak pattern were observed. A similar finding was seen for the agricultural soils. It is also worth noting that the levels of detected absorbance intensity could be an indication of NOM enrichment with various aromatic functional groups released from the soils [11]. These observations may be useful for explaining the increased concentration of aromatic carbon compounds in water after a storm [12]. However, the most remarkable differences in the HPSEC profiles between the forest and agricultural soils appeared in the peak with the molecular weight of 9795 g/mol identified as PSS, as it can clearly be seen that the peak only appears in the profiles of the forest soils, indicating that forest soils can provide more compounds with comparatively larger molecular weight than the agricultural soils.
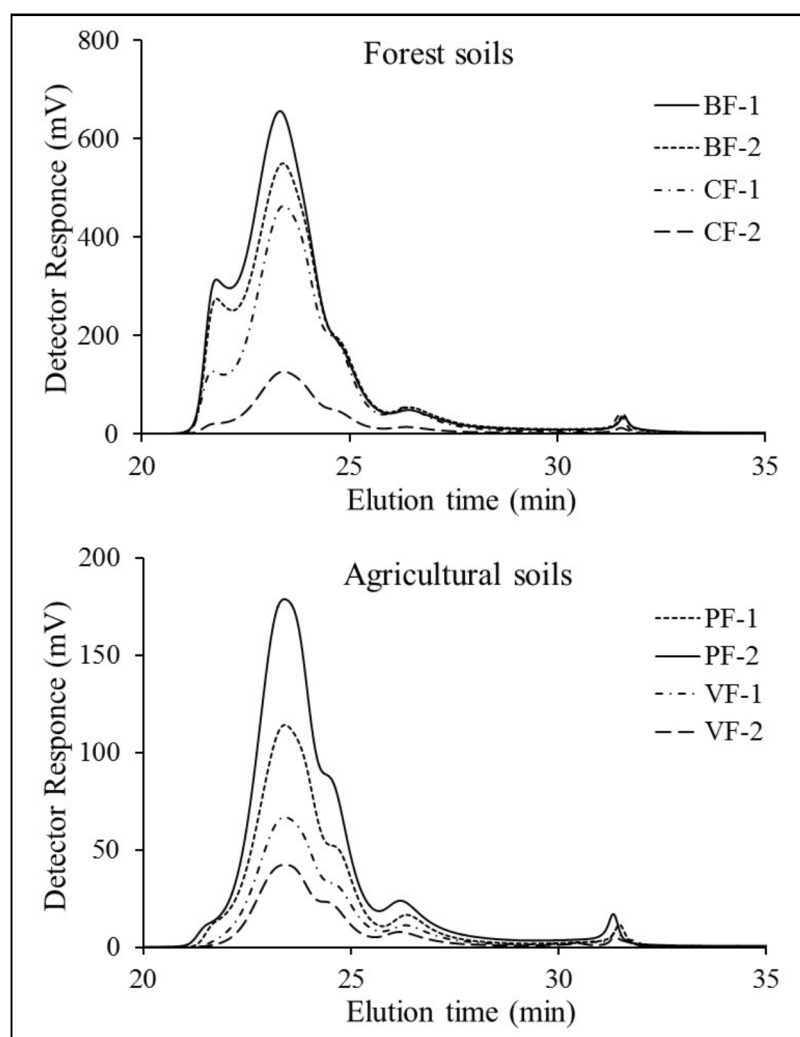
Figure 7 MW distribution of NOM released from investigated forest and agricultural soils under neutral condition.

In order to get more information about the MW characteristics, the *Mw*, *Mn* and polydispersity of the released NOM were computed as displayed in Table 1. For the NOM released from the forest soils, *Mw* and *Mn* changed within the range of 7704-8013 and 7239-7494 g/mol as PSS, while for the NOM released from the agricultural soils, *Mw* and *Mn* changed in the range of 7407-7617 and 6831-7197 g/mol as PSS. This indicates that the constituents of the NOM released from the forest soils possessed comparatively larger molecular weight than those released from the agricultural soils. On the other hand, the slight differences in polydispersity (1.06-1.09) indicate that the differences in the

constituting organic components released from the forest and the agricultural soil were less significant. Compared to NOM in river water [5,11], the released NOM from the soils investigated in this study had a comparatively larger molecular weight but was less heterogeneous.

4   Conclusion

The characteristics of the NOM released to water from forest and agricultural soils were investigated. It was found that the release potential of NOM from soils of different types of origin is significantly influenced by water pH. The aromaticity of NOM released under neutral condition was higher than that under basic or acidic condition. For the released NOM under neural condition, humic acids, fulvic acids and protein-like substances were the predominant components and the proportion of the former two components for forest soils was lower than that for agricultural soils. Additionally, the forest soils released more NOM species with relatively larger molecular weight than the agricultural soils.

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