Characteristics of NOM released from soil under different pH conditions: physicochemical properties and activated carbon adsorbability

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The characteristics of natural organic matter (NOM) released from a representative forest soil under acidic, neutral and basic conditions were investigated based on their physicochemical properties and activated carbon adsorbability. For physicochemical properties, it was found that as the releasing condition changed from acidic to basic, NOM components possessing larger UV absorbing capability and larger molecular weight were released into water. The DOC concentration of NOM released under basic condition was tens of times larger than that under either acidic or neutral condition. On the other hand, based on the batch adsorption experiments and isotherm data analysis with a modified Freundlich isotherm model, the differences in the adsorbability of the released NOM were also demonstrated. Compared to the NOM released under either neutral or basic condition, the NOM released under acidic condition was less adsorbable, and NOM components with larger molecular weight seemed to be more preferentially adsorbed.

Key Words: *natural organic matter, excitation emission matrix, molecular weight distribution, normalized isotherm*

1. INTRODUCTION

Natural organic matter (NOM) is a complicated mixture of organic components with different physicochemical features (including molecular size, functional groups, charge density and hydrophilicity). Consisted mainly of humic and fulvic acids, NOM can react with heavy metals to form complexes, thus altering the fate and behavior of the metal elements in water environment¹⁻³). Moreover, for water treatment, in addition to the well-known fact that NOM is capable of reacting with chlorine to form carcinogenic disinfection byproducts (DBPs)³),

NOM is also reported to be able to compete with synthetic organic compounds (SOCs) for adsorption sites, thus adversely affecting the removal efficiency for SOCs during activated carbon adsorption^{3,4}).

NOM in rivers is mainly released from soils of the adjacent catchments^{2,3,5}). In addition to the physicochemical properties of soils (including soil size, pH, ionic strength, organic matter content and metal element content, etc.), which differ greatly with the land usages (such as lands for forest and farming), the pH levels of water to contact with soils (rain-water, pore water in soils and river water) may significantly affect the extent and composition of or-

ganic matter released to rivers since the solubility of most soil organic species changes with pH ^{1,2,6}. Investigation of the characteristics of NOM released from soils under different pH is important for better understanding the occurrence of NOM in river water sources and for optimizing the treatment conditions for enhanced removal of NOM and hazardous SOC.

For quantification of NOM in water environment and during water treatment, the lumped water quality indices, such as dissolved organic carbon (DOC) and ultraviolet absorbance at the wavelength of 260 nm (UV260), are well used ^{1,4,5}. For evaluation of the composition of NOM, analysis based on the apparent molecular weight (or size) of the constituting components is adopted in many cases ³. In recent years, however, fluorescence spectroscopy is drawing researchers' attention due to its advantages of being simple and cheap for application, and particularly the advantage for being able to provide more information than the well-used UV spectroscopy. The application of this method for investigating the composition of dissolved organic matter in water and wastewater sources is increasing ^{2,7-9}.

Activated carbon (AC) adsorption is considered as one of the best available techniques for removing organic substances in water treatment ^{3,4,10}. When adsorption is applied to water containing NOM, the adsorption capacity may change in accordance with the composition of the constituting components. Therefore, investigation of the characteristics of NOM based on its adsorbability is also important.

The major objective of this study was to evaluate the characteristics of NOM released from soil under different pH conditions. For this, NOM released separately from a representative forest soil under acidic, neutral and basic conditions was targeted. The characteristics of the released NOM were evaluated in terms of the physicochemical properties and activated carbon adsorbability. The physicochemical properties were focused on the specific ultraviolet absorbance, the fluorescence excitation emission matrix (EEM) and molecular weight (MW) distribution. The activated carbon adsorbability was studied based on a series of carefully controlled batch adsorption experiments and data analysis of the observed isotherms with a modified Freundlich isotherm model proposed for normalizing isotherms of heterogeneous organic mixtures.

2. MATERIALS AND METHODS

(1) NOM solutions

Three stock solutions of NOM released from the

soil of a representative broad forest in Kani River catchment (Kani-city, Gifu, Japan) by contacting with water adjusted to different pH (2.0, 7.0 and 11.0) were used. The range of pH used was much broader than the differences of pH in real environment. The use of this broader range was intended for achieving obvious changing trend that could reflect the effect of pH on the released extent and composition of NOM from soils by also considering the followings: i) pH of soils and rainwater differs with areas and it may thus bring about changes in the releasing extent of soil organic species; ii) for NOM species released into rivers, precipitation or dissolution may occur as water flows downstream and the occurring extent of these reactions may differ with the changing extent of pH in rivers; iii) the extract of humic acids from water environment is generally conducted at pH around 2.0.

The stock solutions were obtained following the procedures: i) adding 1kg of the soil in 6L of the pretreated tap water of Gifu University by filtration through a fixed bed granular activated carbon (GAC) adsorber for removing dissolved organic matter contained therein, ii) agitating the soil solution with a mixer at 500 rpm for 7 days and then allowing settlement for one day, and iii) centrifuging the supernatant at 12000 rpm for 5 min, then filtering with 0.2 μ m membrane filter (Toyo Roshi, Japan). The use of 7 days for agitating was because intermittent measurement of DOC indicated that the released extent of NOM had reached the maximum level within the time period.

From each stock solution, three working solutions containing different DOC concentrations were prepared by direct dilution with the same pretreated tap water for experiments of this study.

(2) Adsorbent

Pulverized Filtrasorb-400, a coal-based GAC that has been widely used for laboratory research and advanced water applications, was used as the adsorbent for batch adsorption experiments ³. The adsorbent was obtained by pulverizing the market-available GAC and then sieving to particles with sizes below 45 μ m, followed by washing and rinsing with Milli-Q for removal of fines, and drying in an oven (Yamato Co., Japan) at 105 °C overnight. In order to minimize the impacts of ash impurities, prior to pulverizing, the GAC was washed with Milli-Q for several times and subsequently boiled in Milli-Q for about 1 hour before dried at 105 °C.

(3) Batch adsorption experiments

Batch adsorption experiments were carried out

following the bottle-point method of variable AC doses using 500 mL flasks sealed with Teflon-lined rubber septa. To each flask, 100 mL of working solution was added, followed by addition of the adsorbent with a designated dosage within the range of 0-2.0 g/L. All flasks were shaken for 7 days to allow adsorption to reach equilibration. In order to minimize the solution chemistry effect on adsorption caused by dilution³⁾, the ionic strength of all working solutions was adjusted in advance to a same level based on the working solution that had the highest EC value (99.63 mS/m) using 0.5M-NaCl. pH of all working solutions was adjusted to the same value of 7.0 with 0.5 M HCl or NaOH. After reaching equilibration, activated carbon was separated by filtering the solution through 0.2 µm membrane filters and the obtained filtrate was subjected to analysis for DOC, UV260, fluorescence EEM and MW distribution.

(4) Fluorescence EEM

Fluorescence EEM was measured with a spectrofluorometer (RF-5300, Shimadzu Co., Japan). The excitation and emission scans were performed in the range of 220-550 nm with 5 nm increments. The bandwidth for both excitation and emission was 5 nm. The obtained EEM was normalized into the quinine sulfate unit (QSU) by dividing the fluorescence intensity values of all samples with the fluorescence intensity value of 10 ppb quinine sulfate (in 0.05M H₂SO₄ solution) at the designated wavelengths of Ex/Em=350/450 nm^{8,9)}. To minimize the inner filter effect, all samples subjected to EEM measurement were diluted by Milli-Q to DOC below 2 mg/L²⁾.

(5) Molecular weight distribution

The MW distribution of NOM 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) and a UV detector (Model LC-10AV, Shimadzu) with the wavelength of 260 nm^{3,11)}. Pure water containing 0.02 M Na₂HPO₄ and 0.02 M KH₂PO₄ was used as the eluent and was introduced to the column at the constant flow rate of 0.5 mL/min. Since the ionic strength of water samples after adsorption under different doses did not change obviously from that of the samples before adsorption, as judged from the measurement results of EC, for MW analysis, samples after filtration through 0.2 µm membrane filters were directly used without re-adjustment for ionic strength. The calibration of MW was made with three polystyrene sulfonate (PSS) with MW of 1430, 4950 and 6530 g/mol^{3,11)}.

Based on the obtained MW chromatograms, the weight-averaged (M_w) and number-averaged (M_n) molecular weights were computed according to the following expressions¹¹⁾:

$$M_w = \frac{\sum_{i=1}^N MW_i(t) h_i(t) \Delta t}{\sum_{i=1}^N h_i(t) \Delta t},$$

$$M_n = \frac{\sum_{i=1}^N h_i(t) \Delta t}{\left(\sum_{i=1}^N h_i(t) \Delta t / MW_i(t) \right)},$$

where, $MW_i(t)$ is the MW as a function of the elution time t , $h_i(t)$ is the detector response and Δt is the time interval. Polydispersity, a parameter calculated by the ratio of computed M_w to M_n (Polydispersity = M_w/M_n) was adopted for evaluating the differences in the heterogeneity of NOM released from soil under different pH conditions and the changes after activated carbon adsorption^{3,11)}.

Like most previous studies^{3,4,11,12)}, in this study, UV detector was used in the HPSEC system. It is thus important to emphasize that the results obtained were not complete and could only reflect the apparent MW characteristics that could be achieved with the detector since, as well-known that, of the total constituting components of NOM, only those possessing UV absorbing features could be detected with the detector and, even for the detected ones, their molar absorbance might be different. Further analysis is expected if easy-approaching new detectors enabling online detection of all constituting components of NOM are developed, for instance, an online DOC detector that could continuously measure trace levels of DOC in eluted solutions.

3. RESULTS AND DISCUSSION

(1) Physicochemical properties of NOM

a) Specific ultraviolet absorbance

The differences in the UV-absorbing capability of NOM released from soil under acidic, neutral and basic conditions were evaluated based on the parameter of specific ultraviolet absorbance (SUVA). As shown in **Table 1**, the values of SUVA increased from about 3.56 to 6.95 [m⁻¹/(mg/L)] as the initial pH used for releasing NOM increased from 2.0-11.0, indicating more species of NOM possessing higher UV-absorbing capability were released from soil. In addition, the values of DOC showed that, compared to neutral (6.81 mg/L), more NOM species were released under acidic (18.53 mg/L) and basic (278.22 mg/L) conditions, with the released content under the basic condition being tens of times larger.

The significant differences in DOC reflected the

Table 1 Physicochemical properties of NOM released from soil under different pH conditions.

Releasing condition	EC	UV260	DOC	SUVA
	(mS/m)	m ⁻¹	mg/L	m ⁻¹ /(mg/L)
Acidic (pH 2.0)	269	66	18.53	3.56
Neutral (pH 7.0)	4.9	27	6.81	3.96
Basic (pH 9.5)	81.3	1934	278.22	6.95

differences in the easiness for soil humic molecules to get released into water under different pH environment and could be interpreted by their solubility differences as reported^{1,2,6)}. In a previous study, Li et al.¹¹⁾ investigated the changes of SUVA for dissolved organic matter brought into Nagara River (Gifu, Japan) during a storm rain. The values of SUVA in the upstream, midstream and downstream of this river varied in the range of 1.3-2.8 [m⁻¹/(mg/L)], showing a trend of increases as the river water level ascended and decreases as de-

scended. Compared to these values, the values of SUVA of this study were comparatively larger, thus indicating the organic matter released from the forest soil was mainly comprised of humic molecules.

Different from DOC and UV260, for the parameter EC that reflects the ionic strength of water, the value under the acidic condition (269 mS/m) was much higher than those under the neutral (4.9 mS/m) and basic (81.3 mS/m) conditions. This is conceivable since under acidic conditions more inorganic ions could release from soil, together with fulvic acids

Fig. 1 Fluorescence EEM of NOM released from soil under different pH conditions (DOC=1.6 mg/L).

Fig. 2 MW distribution of NOM released from soil under different pH conditions.

Table 2 MW characteristics of NOM released from soil under different pH conditions.

MW characteristics	Acidic	Neutral	Basic
Mw (g/mol as PSS)	4608	6923	8320
Mn (g/mol as PSS)	3999	6200	7597
Polydispersity	1.15	1.12	1.10

that have higher hydrophilic nature than humic acids.

b) Fluorescence excitation emission matrix

The characteristics of NOM released under different pH conditions based on fluorescence EEM are shown in **Fig. 1** using samples with the same DOC concentration (1.6 mg/L). No matter which pH condition is concerned, the released NOM revealed two apparent peaks. The first and more intense peak appeared in the excitation wavelengths of 220-240 nm, and the second less intense one in the range of 315-335 nm. For both peaks, the emission wavelengths are nearly identical, falling in the range of 420-450 nm, a range well reported as the range for humic-like molecules in rivers and marines ⁷⁾. Besides, although the concentration of DOC was same, the fluorescence intensity was markedly different. As shown in the single-scan excitation spectra drawn at the emission wavelength of 435nm as done by others ^{8,9)}, the fluorescence intensity increased as the releasing pH condition changed from acidic to basic, indicating the differences in the structure of organic molecules that could be released from the soil.

In addition to the above-mentioned two peaks, two less intent peaks with the wavelengths at Ex/Em = 230/335 nm and 225/370 nm were also observed, both representing protein-like substances ^{2,13)}.

c) Molecular weight distribution

The profiles of the MW distribution of NOM are shown in **Fig. 2**. It is clear that, compared to the MW

Fig. 3 Adsorption isotherms of NOM released from soil under neutral pH normalized in terms of AC doses.

Table 3 Estimated parameters of modified Freundlich isotherm model for NOM released from soil under different pH.

	Parameters	Acidic	Neutral	Basic
DOC	$K_F \text{ (mg/g)}^{1-1/n_F}$	5.06	9.55	5.22
	$1/n_F$	0.461	0.257	0.256
	R^2	0.926	0.911	0.938
UV260	$K_F [\text{m}^{1/n_F-1}/(\text{g/L})^{1-1/n_F}]$	6.23	30.69	29.12
	$1/n_F$	0.542	0.228	0.225
	R^2	0.953	0.951	0.820

distribution for NOM released under the neutral pH condition, under the acidic condition more organic components possessing smaller molecular weight were released; while, under the basic condition, more components possessing larger molecular weight were released. The first peak appeared corresponded to the apparent molecular weight of 6500, 7685 and 10122 g/mol as PSS for pH of acidic, neutral and basic, respectively. In addition, comparison of the MW distribution under the neutral pH with reported ones for dissolved organic matter in the less polluted Nagara River water and an underground peaty water

and Tokoro River water in Hokkaido made clear that their patterns were very close, thus indicating NOM released from the forest soil is representative ³⁾.

The computed values for M_w , M_n and polydispersity are shown in **Table 2**. For both M_w and M_n from acidic to basic, the averaged molecular weight for NOM molecules released from the soil increased by about 80% and 90%, respectively, clearly indicating that more fulvic acids were released under the acidic condition and more humic acids were released under the basic condition. In regard of the heterogeneity in molecular weight, with a magnitude similar to Nagara River before and after a storm rain (1.11-1.23) ³⁾, the computed parameter of polydispersity showed slight decreases (from 1.15 to 1.10) as the releasing pH changed from acidic to basic, indicating the released NOM molecules were slightly more heterogeneous under the acidic condition if judging from both their individual molecular weight and concentrations. The values of polydispersity were in close similarity with Nagara River, but were obviously smaller than the market available humic acids or isolated humic substance by following ex-

traction and purification ^{1,14)}.

(2) Activated carbon absorability

a) Adsorption isotherms and parameters

Like adsorption isotherms of previous studies with humic substances or dissolved organic matter in water and wastewater sources ^{10,12,15-16)}, the observed isotherms of NOM released from different pH conditions (data not shown here) exhibited the common features of adsorption for polydisperse organic matrix with unknown compositions: the isotherm is not linear no matter if the adsorption data are analyzed by Freundlich equation or Langmuir equation and it changes with the initial concentrations of either DOC or UV260. To enable comparisons, in this study, the isotherm data obtained with three different initial concentrations for each NOM were analyzed using the following modified Freundlich model ¹⁰⁾, which was proposed for describing the adsorption of multicomponent organic mixtures:

$$q = K_F (C_e / D_{AC})^{1/n_F},$$

Fig. 4 Changes of fluorescence EEM of NOM released from soil under neutral condition with AC doses

Fig. 5 Changes of MW distribution of NOM released from soil under different pH conditions with AC doses.

where, q is adsorption capacity, C_e liquid concentration, D_{AC} activated carbon dose, and K_F and $1/n_F$ are adsorption parameters reflecting the adsorption strength of the adsorbate and its affinity with the adsorbent, respectively.

As displayed in **Fig. 3** with the data of NOM released under the neutral condition as examples, both the DOC-based and UV260-based isotherms were well converged to a line that could be described by the modified Freundlich model. The estimated parameters for NOM released under different pH conditions are summarized in **Table 3**. For DOC, K_F for NOM released under the neutral condition [$9.55 \text{ (mg/g)}^{1-1/n_F}$] was higher than that for NOM released under either the acidic [$5.06 \text{ (mg/g)}^{1-1/n_F}$] or the basic condition [$5.22 \text{ (mg/g)}^{1-1/n_F}$], indicating NOM released under the neutral condition possessed higher adsorbability. Similarly, for UV260, K_F for NOM

Fig. 6 Effect of AC dosage on mean molecular weight and polydispersity of NOM released under different pH.

released under the neutral condition [$30.69 \text{ m}^{1/n_F-1}/(\text{g/L})^{1-1/n_F}$] was much higher than that for NOM released under the acidic [$6.23 \text{ m}^{1/n_F-1}/(\text{g/L})^{1-1/n_F}$] condition and was almost the same as that for NOM released under the basic condition [$29.12 \text{ m}^{1/n_F-1}/(\text{g/L})^{1-1/n_F}$].

For both DOC and UV260, it was common that the K_F value for NOM released under the acidic condition was the smallest, suggesting fulvic acids were less adsorbable than humic acids that released more under basic conditions. In addition to their differences in molecular weight, their differences in the hydrophobic or hydrophilic feature were probably the reason behind the differences in adsorption. The higher values of $1/n_F$, a parameter considered reflecting the affinity between the adsorbate and the adsorbent, for the NOM released under the acidic condition (0.461 for DOC, 0.542 for UV260) may

serve as the evidence supporting this assumption.

b) Fluorescence EEM changes with adsorption

The changes of EEM with increases of the activated carbon (AC) dosage are displayed in **Fig. 4**. It could be clearly seen that the fluorescence intensity of NOM gradually decreased as the AC dosage increased from 0 to 1.0 g/L. Simultaneously, the two corresponding apparent peaks of humic molecules ⁷⁾ gradually disappeared. Under the dosage of 1.0 g/L, the DOC and UV removals reached 99.1% and 99.7% respectively. It was thus reasonable to conclude that almost all humic molecules released from the forest soil chosen for use in this study could be removed. Similar results were also obtained for NOM released under both acidic and basic conditions (data not shown). For the less intense peak representing protein-like substances, even at the AC dosage of 1.0 g/L, it could still be seen, thus suggesting protein-like substances from the soil were less adsorbable than humic ones.

c) MW distribution changes with adsorption

The changes of molecular weight distribution with increases of the AC dosage are displayed in **Fig. 5**. It was clear that by increasing the AC dosage, NOM components over broader molecular weight ranges were removed. The chromatograms shifted downwards over the whole ranges for NOM released under all three pH conditions.

The changes in *M_w*, *M_n* and polydispersity with adsorption were computed. As could be seen in **Fig. 6**, in reflective of the preferential adsorption for larger NOM molecules, *M_w* and *M_n* displayed a decreasing trend with increases of the AC dosage. For polydispersity, a trend of slight increases was noticed as the AC dosage increased; indicating that, although *M_w* and *M_n* decreased with adsorption, the decrease for the former was slower than the latter.

4. CONCLUSIONS

The characteristics of NOM released from a representative forest soil under different pH conditions were investigated based on their physicochemical properties and activated carbon adsorbability. Compared to NOM released from basic condition, NOM released from acidic condition contained molecules with smaller molecular weight, smaller UV absorbing capability and relatively weaker adsorbability by activated carbon. It was also found that large NOM molecules were preferably adsorbed than smaller ones.

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(Received May 22, 2015)