



RELATIONSHIP BETWEEN THE CHEMICAL STRUCTURE OF HUMIC SUBSTANCES AND THEIR HYGROSCOPIC PROPERTIES

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ABSTRACT

We investigated the relationship between the hygroscopic properties and chemical structures of humic and fulvic acids. Humic and fulvic acids were extracted from andosol, Canadian peat and Chinese weathered coal using the IHSS method. Fulvic-like organics produced by the ozone oxidation of humic acid were also prepared by a method reported previously. Their main chemical properties related to hygroscopicity were also studied by elemental analysis and the measurement of functional group contents. Humic and fulvic acids were allowed to stand under various relative humidity (RH) conditions and the amounts of water vapor adsorbed were measured by gravimetry. Water adsorption isotherms were similar for both humic and fulvic acids below RH 80%. Above 80%, water vapor adsorption of fulvic acids and fulvic-like organics increased considerably as compared with humic acids. Deliquescence was observed for all fulvic acids and fulvic-like organics at higher RH. The amount of water vapor adsorbed at 97% RH by humic substances from different sources was highly correlated with the ratio of oxygen to carbon contents.

Keywords: Humic structure, hygroscopic properties, humidity, water retention

1. INTRODUCTION

Natural humic materials have been used recently to

ameliorate degraded soils. Under low-moisture conditions, the hygroscopic properties of soil organic materials are important for soil wettability, microbial activity, and the dynamics of soil carbon [1-3]. Humic and fulvic acids are able to adsorb large amounts of water [4]. The hygroscopic properties of humic materials have been well studied; in particular, there have been comparisons between humic acid (HA) and fulvic acid (FA) and the effects of their functional groups and monovalent metal cations [4,5]. Recent studies of the hygroscopic properties of humic materials have been conducted in the field of atmospheric aerosols [6-8]. However, these aerosol studies were mainly based on the interaction of humic substances (and/or humic-like substances) and inorganic salts with respect to the types of inorganic salts.

Clarification of the relation between the chemical structure of humic materials and their hygroscopic properties is important because it attempts to further address the influence of soil organic matter structure on water sorption, and thus its potential influence on soil wettability and other important aspects. The purpose of this paper is to present an evaluation and discussion of water vapor adsorption by HAs and FAs in order to clarify the relationship between their chemical characteristics and their capacity for water vapor adsorption.

2. MATERIALS AND METHODS

2.1. Humic Materials

The humic and fulvic acids used in this study were obtained from Japanese andosol (AS), Canadian peat (CP), and Chinese weathered coal from Xinjiang, (XWC). Humic acid (HA) and fulvic acid (FA) were extracted with the International Humic Substances Society (IHSS) method [9]. AG[®] MP-50 resin (Bio-Rad Laboratories, Inc) was used for cation exchange, and Amberlite[®] XAD7HP resin (Rohm & Haas Co.) was used for the isolation of fulvic acid instead of Amberlite[®] XAD-8 resin, because the production of XAD-8 resin ceased some years ago and XAD7HP resin has the same chemical structure as XAD-8 resin (polymethylmethacrylate). Fulvic-like organics produced by the ozone oxidation of HAs were also prepared as follows [10]. XWC-HA 1.0 g was dissolved in 250 mL of 0.1 N NaOH solution, and this solution was placed in a 500 mL gas-washing bottle as an oxidation reactor. Ozone gas (0.45 mmol/L) was fed into the gas-washing bottle by bubbling at a flow rate of 50 L/h for 0.5, 1.0, 2.0 and 4.0 h, respectively. CP-HA was also used for fulvic-like organics

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production. 0.5 g CP-HA was dissolved in 250 mL of 0.1 N NaOH solution and oxidized for 0.25, 0.5, 0.75 and 1.0 h using the same method as that used for XWC-HA oxidation. All oxidized samples were treated and isolated using the simplified IHSS method (Figure 1). Fulvic-like organic acids produced by XWC-HA oxidation were named XWCS-0.5, XWCS-1.0, XWCS-2.0, XWCS-4.0, and XWCS-0.5+ (Ozone gas, 1.15 mmol/L, 50 L/h; Reaction time, 0.5 h), and those produced by CP-HA were named CPS-0.25, CPS-0.5, CPS-0.75, and CPS-1.0, respectively.

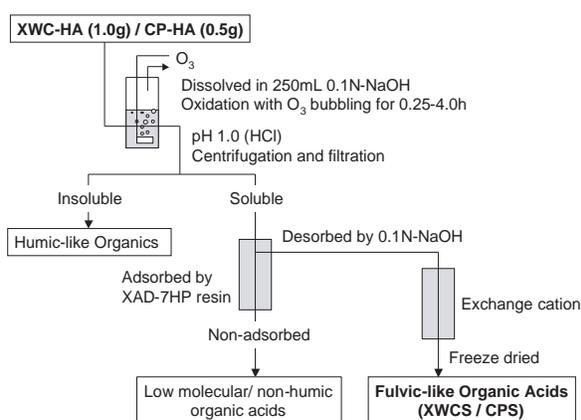


Figure 1 Fulvic-like organics production from humic acids by ozone oxidation.

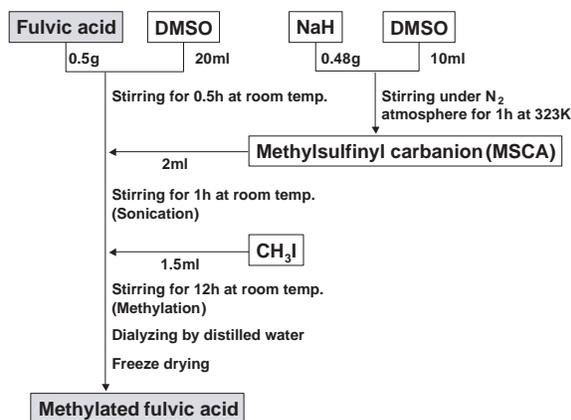


Figure 2 Permethylation of fulvic acid by the Hakomori method.

All samples were freeze-dried and finely ground, and were maintained in glass vessels in desiccators over saturated LiCl solution at room temperature for water adsorption measurements. The amounts of water

vapor adsorbed were determined gravimetrically using an electronic balance (Mettler-Toledo, Inc., AB204-S, Precision: 0.1 mg). Permethylated XWCS-0.5+ (XWCS-0.5+methyl) was also prepared to examine the effect of oxygen functional groups on the capacity for water vapor adsorption of humic substances.

Permethylation was conducted with the Hakomori method [11, 12] shown in Figure 2. The Hakomori method is a rapid permethylation method catalyzed by methylsulfinyl carbanion in dimethyl sulfoxide. This method can be applied to methylate carboxyl and hydroxyl groups. Abbreviations of humic substances are listed in Table 1.

Table 1 Abbreviation, Source, and Character of Humic Substances

Source (Country)	Oxidation, h	Character
Peat (Canada)		
CP-HA	-	HA
CP-FA	-	FA
Weathered coal (China, Xinjiang)		
XWC-HA	-	HA
XWC-FA	-	FA
Andosol (Japan)		
AS-HA	-	HA
AS-FA	-	FA
Peat HA (Canada)		
CPS-0.25	0.25	FA
CPS-0.50	0.5	FA
CPS-0.75	0.75	FA
CPS-1.00	1	FA
Coal HA (China, Xinjiang)		
XWCS-0.5	0.5	FA
XWCS-1.0	1	FA
XWCS-2.0	2	FA
XWCS-4.0	4	FA
XWCS-0.5+	0.5 ^a	FA
XWCS-0.5+ (China, Xinjiang)		
XWCS-0.5+methyl	-	Permethylated

^a Ozone, 1.15mmol/L.

2.2. Analysis of Fundamental Properties

Elemental analysis was performed with a Yanaco CHN Corder type MT-5 (Yanaco Analytical Instruments Corp., Japan). Carboxyl group content was measured with the calcium acetate method [11, 13] and phenolic hydroxyl group content was measured with the Folin-Ciocalteu method [11, 14]. The E_4/E_6 ratio was calculated by measuring absorbance of the humic substances dissolved in 0.1 N NaOH at 400 and 600 nm using a spectrometer (Shimadzu, Model UV-1700).

Table 2 Elemental and functional characteristics of humic substances

Abbreviation	Elemental analysis ^a , wt%–d.a.f. ^d				Ash, wt%	Elemental ratio		Functional groups, mmol/g	
	C	H	N	O, diff.		H/C	O/C	COOH ^b	Phe-OH ^c
CP-HA	57.3	5.4	2.0	35.3	3.5	1.13	0.46	3.01	n.d.
CP-FA	52.4	4.7	0.7	42.2	0.2	1.08	0.60	6.31	n.d.
XWC-HA	64.1	3.6	1.5	30.8	3.6	0.67	0.36	4.53	1.41
XWC-FA	43.0	3.5	1.2	52.4	0.0	0.96	0.91	4.28	0.14
AS-HA	59.2	3.5	2.8	34.5	0.7	0.70	0.44	5.50	0.17
AS-FA	48.7	4.3	3.0	44.0	0.2	1.04	0.68	9.12	0.56
CPS-0.25	49.1	3.4	1.3	45.9	0.3	0.82	0.70	7.36	n.d.
CPS-0.50	45.5	3.5	1.3	46.7	3.0	0.91	0.77	7.82	n.d.
CPS-0.75	47.9	3.5	1.5	45.4	1.7	0.86	0.71	8.14	n.d.
CPS-1.0	46.0	3.6	1.6	46.9	1.8	0.94	0.77	8.69	n.d.
XWCS-0.5	38.1	2.7	1.6	57.6	2.2	0.85	1.14	7.81	0.82
XWCS-1.0	36.8	2.7	1.3	59.2	2.0	0.87	1.21	8.31	0.81
XWCS-2.0	43.0	3.2	1.7	52.1	1.1	0.89	0.91	6.52	n.d.
XWCS-4.0	46.0	3.5	1.8	48.6	1.1	0.91	0.79	8.99	1.09
XWCS-0.5+	50.1	3.7	1.4	50.1	2.7	0.87	0.67	9.10	0.93
XWCS-0.5+methyl	54.1	4.2	1.6	40.1	2.9	0.56	0.93	3.11	1.00

^a Yanaco CHN Corder; ^b Calcium acetate method; ^c Folin-Chiocalteu method; ^d d.a.f. Dry ash free basis; n.d.: Not detected.

Table 3 ¹³C NMR estimates of carbon distribution, molecular weight, E₄/E₆ ratio and BET surface area in humic substances

Abbreviation	Carbon distribution, %						M _n ^a	E ₄ /E ₆ ratio	S _a ^b , m ² /g
	Carbonyl	Carboxyl	Phenolic	Aromatic	Substituted	Aliphatic			
CP-HA	7.5	14.0	5.2	14.3	22.2	36.8	17,300	5.2	0.64
CP-FA	n.d.	15.4	3.2	19.0	36.1	26.3	2,600	15.1	n.a.
XWC-HA	10.7	9.6	5.9	39.1	13.0	21.6	8,800	3.3	0.93
XWC-FA	12.3	20.9	14.7	7.6	20.4	24.1	n.a.	n.a.	n.a.
AS-HA	12.0	18.0	15.0	27.0	16.0	12.0	14,000	6.8	n.d.
AS-FA	n.d.	31.4	0.0	30.6	6.1	31.9	1,200	17.3	n.a.
CPS-0.25	7.9	19.6	4.0	21.3	22.3	24.8	8,800	12.4	1.11
CPS-0.50	n.a.						5,000	13.3	n.a.
CPS-0.75	n.a.						3,200	14.8	n.a.
CPS-1.0	n.a.						900	15.3	n.d.
XWCS-0.5	8.7	20.9	4.2	26.9	20.5	18.9	n.a.	8.9	n.a.
XWCS-1.0	n.a.						n.a.	7.6	n.a.
XWCS-2.0	n.a.						n.a.	6.6	n.a.
XWCS-4.0	6.6	20.7	3.4	20.9	25.9	22.5	1,800	6.7	n.a.
XWCS-0.5+	10.3	23.6	2.4	20.6	15.1	28.0	500	7.2	0.95
XWCS-0.5+methyl	n.a.						n.a.	n.a.	n.a.

^a M_n: Number-averaged molecular weight; ^b S_a: Surface area by BET method with nitrogen; n.a.: Not analyzed; n.d.: Not detected.

Carbon distributions were determined by CP/MAS ¹³C-NMR spectrometry (Bruker, AVANCE 300; MAS frequency 6 kHz; contact time 2 ms; repetition time 3 s; number of scans 2000–10000). Molecular masses were investigated by gel permeation chromatography (GPC) using pullulan as the calibrant.

GPC was carried out at 70°C on a Shimadzu LC-10A series apparatus equipped with two Plgel 5 μm Mixed-D GPC columns (Polymer Laboratories Ltd.; linear range of molecular weight, 200–400,000) and a refractive index detector. The mobile phase consisted of DMSO at a flow rate of 0.5 mL/min. The surface

areas were measured by the BET method with nitrogen using a surface area analyzer (Micromeritics ASAP 2020). The analytical characteristics of HAs, FAs and fulvic-like organics are shown in Tables 2 and 3.

2.3. Analysis of Amount of Water Vapor Adsorbed

Water vapor adsorption experiments were performed on 200 mg samples maintained in weighting bottles in desiccators at different RH values (33–97%) at 303 K. RH was controlled using selected aqueous saturated salt solutions (MgCl₂, NaHSO₄, NaCl, KCl, KNO₃, and K₂SO₄) [15]. Samples were withdrawn from the desiccators and weighed until constant weights were obtained. At the end of this period, increases in moisture were expressed as grams of H₂O per gram of initial HAs and FAs that were heat-dried at 378K for 24 h. The amount of water vapor adsorbed was calculated as follows:

$$(\text{amount of water vapor adsorbed}) = ([\text{wet sample mass}] - [\text{dry sample mass}]) / (\text{dry sample mass}) \quad (1)$$

3. RESULTS AND DISCUSSION

3.1. Characteristics of Humic Materials

The analytical characteristics of the HAs, FAs and fulvic-like organics are shown in Table 2. The carboxyl and oxygen contents of fulvic-like organics produced by ozone oxidation increased from 4.53 mmol COOH/g (30.8 wt%) for XWC-HA and 3.01 mmol COOH/g (35.3 wt%) for CP-HA to 6.52–9.10 mmol COOH/g (40.1–59.2 wt%) for XWCS and 7.36–8.69 mmol COOH/g (45.4–46.9 wt%) for CPS, depending on the oxidation time. The carboxyl and oxygen contents of permethylated XWCS decreased from 9.10 mmol COOH/g (50.1 wt%) for XWCS-0.5 to 3.11 mmol COOH/g (40.1wt%) for XWCS-0.5+methyl, on permethylation.

3.2. Water Vapor Adsorption

The time courses of weight change on water vapor adsorption by humic substances are shown in Figure 3. Weights of humic substances increased rapidly at an early stage. Reaching a constant weight took about 2 weeks for HAs and 3 weeks for FAs. Deliquescence was observed for all FAs and fulvic-like organics above 80% RH.

Water vapor adsorption isotherms, measured at 303K for HAs, FAs and fulvic-like organics are shown in Figure 4. Isotherms of water vapor

adsorption were similar for humic and fulvic acids below 75% RH. Above 75% RH, water vapor adsorption of FAs and fulvic-like organics increased considerably as compared humic acids. These marked increases in the amount of water vapor adsorbed at high RH are similar to those in previous reports [4, 6–8]. As deliquescence could be observed for all fulvic acids and fulvic-like organics at higher RH values, deliquescent properties may be important in explaining the hygroscopicity of humic substances.

3.3. Relationship between Chemical Characteristics and Amount of Water Vapor Adsorbed by Humic Substances

The relationship between the amount of water vapor adsorbed at 97% RH and the amount of carboxyl carbon (carboxyl C) as a percentage of total carbon (total C) is shown in Figure 5, and that between the water vapor adsorption and the elemental O/C ratio is shown in Figure 6.

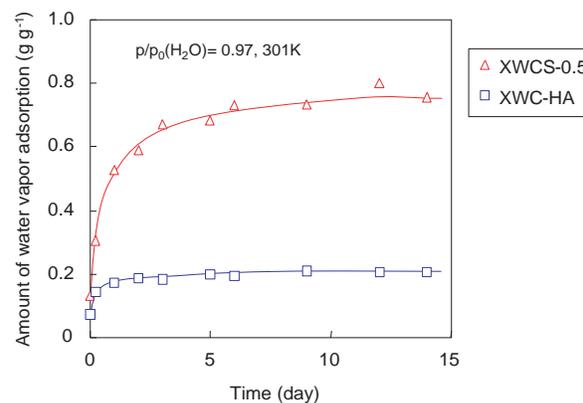


Figure 3 Time courses of the weight changes on water vapor adsorption by humic substances.

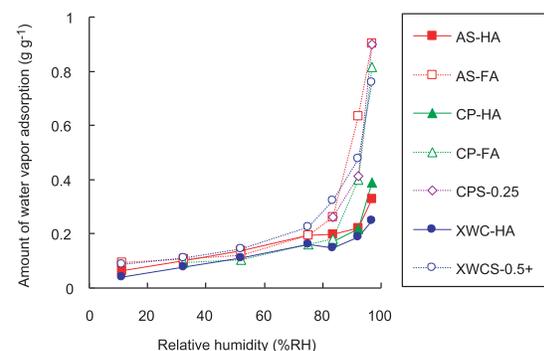


Figure 4 Isotherms for water vapor adsorption by humic substances at 303 K.

The amounts of water vapor adsorbed at 97% RH by humic substances increased with increasing carboxyl content and O/C ratio, and the O/C ratio showed a stronger correlation ($r^2 = 0.83$) than the carboxyl content ($r^2 = 0.67$) for the different sources. XWCS-0.5+methyl (the permethylated fulvic-like organic sample) adsorbed less water vapor than the other XWCSs, related to the decreased O/C ratio and carboxyl content. This result shows that the O/C ratio and the carboxyl group directly influence the water vapor adsorption capacity of humic substances.

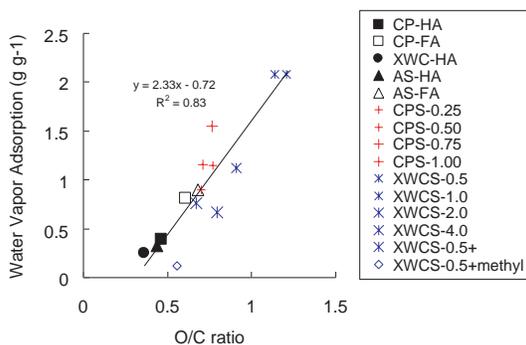


Figure 5 Relationship between the elemental O/C ratio and the amount of water vapor adsorbed by humic substances.

The E_4/E_6 ratio is an index of light absorption in the visible range. A high E_4/E_6 ratio corresponds to a relatively low molecular weight, and a low ratio corresponds to a relatively high molecular weight [16, 17]. Figure 7 shows that, although the E_4/E_6 ratios were correlated with the amount of water adsorbed within the natural humic substances or in XWCSs or in CPSs, the E_4/E_6 ratios varied among the different sources of humic substances. This variation suggests that water vapor adsorption capacity depends on oxygen functional group, and not on the molecular weight.

Schnitzer [4] reported that oxygen functional groups affect water vapor adsorption capacity by HA and FA obtained from Podzol. In our experiment, we confirmed that the O/C ratio is an important factor affecting the water adsorption capacity of several kinds of humic substances extracted with the IHSS method from peat (Canada), weathered coal (China) and Andosol (Japan) at higher humidities, and that the water adsorption capacity of humic substances roughly could be explained only by the O/C ratio.

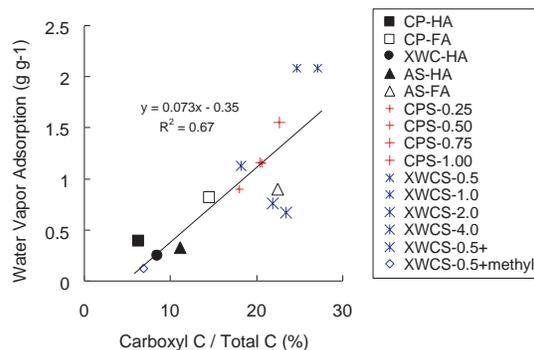


Figure 6 Relationship between the carboxyl content and the amount of water vapor adsorbed by humic substances.

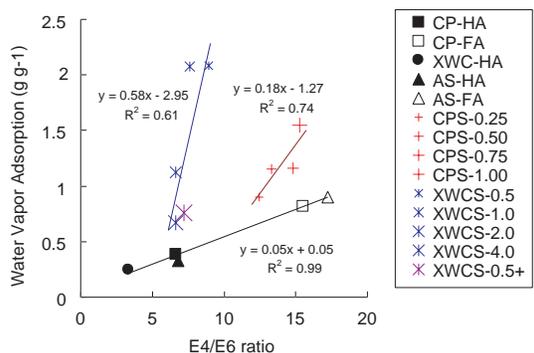


Figure 7 Relationship between the E_4/E_6 ratio and the amount of water vapor adsorbed by humic substances.

4. CONCLUSIONS

We aimed to clarify the relationship between the water vapor adsorption capacities of various humic substances and their chemical characteristics. In our studies, we used humic materials from several sources and their oxidized products, which have fulvic-like characteristics. Although the amount of water vapor adsorbed varied among the various sources of humic substances, the water vapor adsorption of the humic substances was well correlated with their O/C ratio. Humic substances differ in hygroscopicity, and this difference might affect the wettability, the microbial activity and carbon sequestration when degraded soils in arid lands are ameliorated with humic substances from different sources.

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