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Adsorption and desorption of agricultural waste-derived DOMs in soil

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Abstract. The sorption and desorption of two forms of dissolved organic matter (DOM) extracted from agricultural wastes were studied by batch experiments. The adsorption of the two DOMs on the soil were well fitted to the Linear and Freundlich isotherms. DOM extracted from cow manure (MDOM) shows higher affinity to the soil than that extracted from wheat straw (SDOM). Significant desorption hysteresis was observed for both DOMs. Due to the desorption of some aromatic substances with larger molecular weight from the soil, the average molecular weight and aromaticity of the DOMs increased at sorption equilibrium compared with those before sorption.

1. Introduction
The incorporation of organic amendments such as straw and animal manure are common farming management practices in China and many other countries around the world [1], thus DOMs originated from these amendments will be released into soil environments. DOM can be bound to the soil via electrostatic adsorption, ligand exchange, complexation, hydrophobic interaction, hydrogen bonding and cation bridging mechanisms [2]. Since DOMs play an important role in the transport of pollutants in soils, their fate has been a subject of considerable interest in recent years.

There are several studies on the sorption of DOMs in soils. For example, Kaiser et al. [3] investigated the sorption of total, hydrophilic, and hydrophobic DOM on 125 forest soil samples and found that the majority of the soils preferentially sorbed hydrophobic dissolved organic carbon. Shen [4] evaluated some important physical-chemical factors determining the sorption of DOM onto natural soil and demonstrated that DOM sorption on soil is largely due to ligand exchange between DOM and hydroxyl groups on the soil mineral surface. He also found that soil sorption capacity of DOM is positively correlated to the soil clay content as well as the soil water solution ionic strength and pH. The sorption of DOMs on soils can decrease the mobility of the associated pollutants. Furthermore, the adsorbed DOMs can change the physicochemical properties of the soil surface, which will have an effect on the fate of some other contaminants. Thus, it is essential to better understand the processes that alter the concentration and properties of DOMs in soils.

The aims of this study was to explore the sorption and desorption behaviors of two DOMs derived from agricultural wastes and the changes in their physiochemical characteristics before and after sorption.

2. Materials and methods

2.1. Materials
$CaCl_2$ and NaN_3 were analytical grade purchased from Sinopharm Chemical Reagent Co. ltd and Sigma-Aldrich, respectively.

An uncontaminated soil was collected from the suburb of Jinan city, China. The soil was air dried and sieved through a 2 mm mesh. The $K_2Cr_2O_7$ titration method was used to determine the soil total organic carbon (TOC). The soil pH was determined in 1:5 soil‒water slurries using a glass electrode. The cation-exchange capacity (CEC) of the soil was determined by the NH_4^+–acetate method. Selected soil properties are shown in Table 1.

Table 1. Selected soil properties

pH	Grain size distribution (%)			CEC (cmol/kg)	TOC (g/kg)
	<0.002 mm	0.002-0.02 mm	0.02-2 mm		
6.8	53.2	24.4	22.4	6.84	7.19

2.2. Dissolved organic matter extraction and characterization

Two forms of dissolved organic matter were used. One form of DOM was extracted from wheat straw (SDOM) and the other from cow manure (MDOM). The DOMs were extracted as described in our previous study [1]. Briefly, wheat straw and cow manure were extracted with deionized water using a solid/water ratio of 1:10 and 1:5 (w/v, dry weight basis), respectively, in a reciprocal shaker at 200 rpm and 25 ˚C for 24 h. The suspensions were centrifuged at 5000 rpm for 30 min, then, vacuum filtered through a filter paper (Whatman 20-25 μm pore size), and a 0.45 μm cellulous acetate filter (Whatman, Maidstone, UK) successively. The filtrates were freeze dried as powders and stored in a desiccator for later use. The concentrations of DOMs were measured at mg L^{-1} dissolved organic carbon (DOC) using a total organic carbon (TOC) analyzer (Shimadzu TOC-L CPH/CPN, Japan). The electrical conductivity (EC) of the DOM solution was measured at 25 °C by a YSI 3100 conductivity instrument (YSI, US). The salt ions in the DOM solution were determined using an inductive coupled plasma atomic emission spectroscopy (ICP-AES) (PerkinElmer, Optima 7000 DV). The molecular weights were measured using the high-pressure size exclusion chromatography method as described by Yue et al. [5]. Specific UV absorbance at 254 nm was used to evaluate the aromaticity of DOM samples [6]. Absorbance of DOM solution at 465 and 665 nm was also measured to calculate the E4/E6 ratio, which is negatively correlated with molecular size [7]. The ^{13}C CP/MAS NMR spectra were obtained using a Varian Infinity Plus-300 spectrometer equipped with a 4 mm double-resonance magic angle spinning probe head, operating at ^{13}C frequency of 75.4 MHz. The aliphatic carbon and aromatic carbon were determined by quantifying the peak area in the 0-109 ppm [8] and 110-160 ppm [9] chemical shift bands, respectively. The polar carbon of the DOMs was determined by quantifying the peak area in the 50-109 ppm and 145-220 ppm chemical shift band [8].

2.3. Adsorption and desorption experiments

Batch adsorption experiments were conducted in 30-mL glass vials with teflon-lined caps. Soil sample (3.00 g) was mixed with 30 mL of DOM solution in 0.01 M $CaCl_2$ as the background electrolyte and 0.2 g L^{-1} NaN_3 as a biocide. The initial concentrations of DOMs were in the range of 0–150 mg L^{-1}. The mixtures were shaken for 48 h at 25 ˚C on a rotary shaker (200 rpm) and afterwards centrifuged for 30 min at 5000 rpm. After the sorption period, desorption was conducted by withdrawing 28 mL supernatant and replenishing the samples with the same volume of background electrolyte solution. The vials were sealed, shaken and centrifuged as described in the sorption experiments. The supernatant of sorption and desorption experiments was filtered through a 0.45 μm cellulous acetate filter (Whatman, Maidstone, UK). A portion of the filtrate was used for the determination of TOC and the remaining was used for UV detection at 254 nm, 465 nm and 665 nm.

Sorbed DOM concentration in the sorption experiments was calculated by the following mass balance equation

$$Q_e = \frac{(C_0 - C_e + C_{ck})V}{W} \qquad (1)$$

where C_e is the liquid phase equilibrium concentration in mg L^{-1} and Q_e is the concentration on the solid phase in mg kg^{-1}, C_{ck} is the DOM concentration that released from the soil to the solution when no SDOM and MDOM was added, V (mL) is the volume of solution and W (g) is the mass of soil used.

For the desorption experiments, the desorption amount of DOM can be calculated with the following equation

$$Q_d = \frac{(C'_e - C'_{ck})V - C_e V_1}{W} \qquad (2)$$

where Q_d (mg kg^{-1}) is the desorption amount of DOM at equilibrium, C'_e (mg L^{-1}) is the equilibrium concentration in the liquid phase, C'_{ck} is the DOM concentration that released from the soil to the solution in the desorption treatment with no SDOM and MDOM was added initially, V_1 is the residual solution volume before the desorption experiments.

2.4. Adsorption isotherm models
Linear, Langmiur, Freundlich and Temkin isotherm which have the following forms were used to fit the adsorption data

Linear isotherm: $Q_e = aC_e + b$ $\qquad (3)$

Langmiur isotherm: $\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{kQ_m}$ $\qquad (4)$

Freundlich isotherm: $\ln Q_e = lnK_f + nlnC_e$ $\qquad (5)$

Temkin isotherm: $Q_e = A + BlnC_e$ $\qquad (6)$

where Q_m is the Langmuir parameter related to maximum adsorption capacity (mg kg^{-1}), k is the Langmuir parameter related to energy of adsorption, K_f is the Freundlich affinity coefficient [(mg kg^{-1})/(mg L^{-1})^n], n is the Freundlich nonlinearity factor, A and B are constants.

3. Results and discussion

3.1. Characterization of DOMs
The major properties of the two DOM samples were reported previously [1] and are shown in Table 2. Higher A$_{254}$/DOC values for MDOM indicate that MDOM has relatively higher aromaticity than SDOM. The E4/E6 ratios of SDOM and MDOM were 8.83 and 7.66, respectively, indicating that MDOM had a relatively higher molecular weight. The differences between SDOM and MDOM might affect their adsorption on the soil, thus their interaction with other pollutants. Table 3 presents the molecular weights and structural composition of the two DOMs. It can be seen that MDOM has a higher molecular weight than SDOM. The contents of aliphatic and polar carbon for SDOM are higher than those for MDOM, while the content of aromatic carbon for SDOM are lower than that for MDOM.

Table 2. Properties of dissolved organic matters extracted from wheat straw (SDOM) and cow manure (MDOM) [a]

Sample	pH	EC (μS/cm)	K$^+$ (mg L^{-1})	Na$^+$ (mg L^{-1})	Ca^{2+} (mg L^{-1})	Mg^{2+} (mg L^{-1})	A$_{254}$/DOC (L·mg^{-1}·cm^{-1})	E4/E6
SDOM	8.86	254	12.4	1.68	1.19	0.79	1.6	8.83
MDOM	9.06	192	9.49	2.94	0.36	0.57	1.8	7.66

[a] Data measured at DOM concentration of 50 mg/L DOC.

3.2. Sorption-desorption isotherms of DOMs
The DOM concentration at sorption/desorption equilibrium and the sorption/desorption amounts are shown in table 4. In the sorption experiments, when no SDOM or MDOM was added to the solution, a concentration of 18.4 mg L^{-1} was measured at equilibrium, implying that DOM was released from the soil. The desorption amount is 184 mg kg^{-1}. Significant desorption hysteresis was observed for both

Table 3. Molecular weight, polydispersity, aliphatic carbon, aromatic carbon and polar carbon of DOM samples

Sample	Mw [a]	Mn [b]	Polydispersity (ρ)	Aliphatic C (%)	Aromatic C (%)	Polar C (%)
SDOM	2632	1255	2.1	75.6	3.2	77.0
MDOM	3542	1964	1.8	71.1	3.8	69.1

[a] Weight-averaged molecular weight; [b] Number-averaged molecular weight.

DOMs. For SDOM, the percentage that can be desorbed is 9.86%-50%. While for MDOM, the percentage is only 2.52%-25.2%. This means that MDOM are more difficult to be desorbed than SDOM. As can be seen from table 5, the linear equation and the Freundlich equation can well fit the adsorption of the two DOMs in the soil. The sorption isotherms were also shown in figure 1. In the concentration range studied, the adsorption amount of DOM was linearly correlated with the

Table 4. Sorption/desorption amount of DOMs

Treatment	Initial concentration $(mg \cdot L^{-1})$	Concentration at sorption equilibrium $(mg \cdot L^{-1})$	Sorption amount $(mg \cdot kg^{-1})$	Concentration at desorption equilibrium $(mg \cdot L^{-1})$	Desorption amount $(mg \cdot kg^{-1})$
DOM-0	0	18.4	-184 [a]	2.98	17.5
SDOM-25	25	36.6	72.5	8.01	38.2
SDOM-50	50	55.5	142	8.67	32.2
SDOM-75	75	73.9	216	10.2	34.8
SDOM-100	100	99.1	223	10.6	22.3
SDOM-150	150	127	455	16.6	63.2
MDOM-25	25	34.2	88.5	4.37	3.38
MDOM-50	50	51.8	164	9.45	42.5
MDOM-75	75	66.8	265	6.88	6.77
MDOM-100	100	83.0	354	9.82	25.4
MDOM-150	150	113	554	11.2	19.6

[a] Negative number means the desorption amount from soil.

Table 5. Fitting parameters of adsorption isotherms

	SDOM			MDOM		
Linear isotherm	a	b	R^2	a	b	R^2
	4.25	-8.02	0.998	5.97	-17.8	0.995
Langmiur isotherm	Q_m	k	R^2	Q_m	k	R^2
	1111	0.006	0.862	769	0.006	0.972
Freundlich isotherm	K_f	n	R^2	K_f	n	R^2
	4.06	0.999	0.998	5.34	0.989	0.992
Temkin isotherm	A	B	R^2	A	B	R^2
	-579	211	0.905	-652	250	0.887

equilibrium concentration in the solution phase, indicating that the adsorption of DOM onto soil may not reach saturation state, and there are still vacant adsorption sites on the soil surface. The higher the value of parameter a in the linear adsorption equation, the easier the adsorption of DOM by soil. The value of parameter a for MDOM was higher than that for SDOM, indicating that MDOM was more easily adsorbed by soil. This might be originated from the difference in composition and structure of the two DOMs. The aromaticity of MDOM is higher than that of the SDOM, implying it is more hydrophobic and more easily to be adsorbed by soil. This is also verified by the higher K_f value of MDOM.
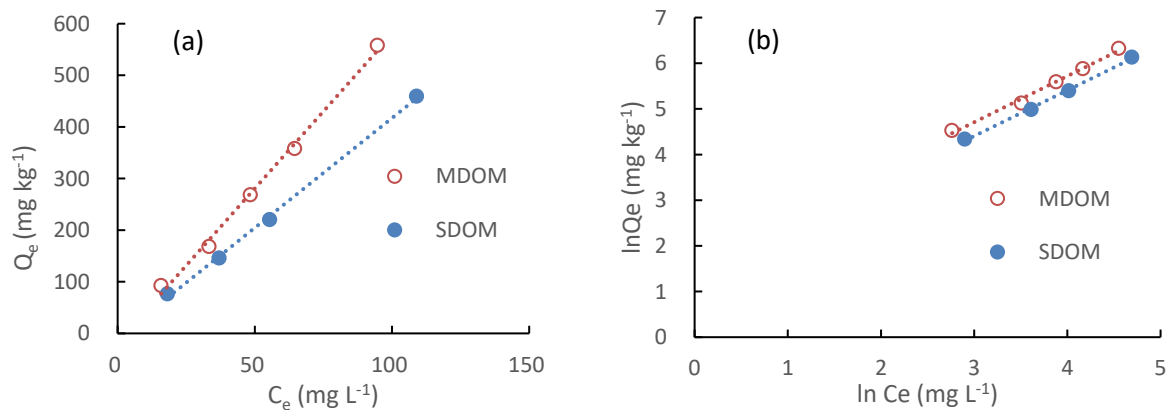
Figure 1. Adsorption isotherms of DOM: (a) Linear isotherm and (b) Freundlich isotherm

3.3. Aromaticity and molecular weight characteristics before and after sorption

Table 6 shows the aromaticity and molecular weight characteristics at sorption equilibrium. The E4/E6 values of SDOM and MDOM before adsorption were 8.83 and 7.66 (Table 2), respectively. At adsorption equilibrium, the E4/E6 values of SDOM and MDOM were 2.29-2.53 and 2.07-3.26, respectively, which both decreased significantly. It is indicated that the average molecular weight of DOMs greatly increased. Some researchers [3] have reported the substance with large molecules in DOMs were preferentially adsorbed on the surface of the soil, thus the molecular weight would decrease if only the sorption process being considered, which contradicted the result of this study. The increase in molecular weight might be attributed to desorption of some substances with large molecules from the soil used in this study, which proved by the lower E4/E6 (1.89) value of DOM-0 treatment (Table 6). Comparing the data in Table 1 and Table 6, it can be found that the A_{254}/DOC values at equilibrium was higher than those before sorption, indicating an increase in aromaticity. This might be explained by desorption of some aromatic substances from the soil, which was proved by the higher A_{254}/DOC value (34.8) of DOM-0 treatment.

Table 6. Aromaticity and molecular weight characteristics at sorption equilibrium

Treatment	A_{254}/DOC ($L·mg^{-1}·cm^{-1}$)	E4/E6
DOM-0	34.8	1.89
SDOM-25	19.9	2.47
SDOM-50	17.3	2.28
SDOM-75	16.7	2.58
SDOM-100	14.4	2.53
SDOM-150	16.0	2.98
MDOM-25	24.7	2.07
MDOM-50	17.3	2.28
MDOM-75	14.7	3.10
MDOM-100	13.5	2.63
MDOM-150	14.0	3.26

4. Conclusions

The adsorption of the two DOMs on the soil were well fitted to the Linear and Freundlich isotherms. Significant desorption hysteresis was observed for both DOMs. Compared with SDOM, MDOM are more easily to be adsorbed by soil and more difficult to be desorbed. Due to the desorption of some

aromatic substances with larger molecular weight from the soil, the average molecular weight and aromaticity of the DOMs increased at sorption equilibrium compared with those before sorption.

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