The Characteristics of Soil Organic Matter

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The purpose of this study is to illustrate the characteristics of soil organic matter (SOM) and partition coefficient (K_{DOC}). Humic substances (HS) from eight soils of varying properties were extracted by two different methods. The dissolved organic carbon (DOC) concentration was stabilized in 22hrs. The ratio of UV absorbance at 465nm and 665nm (E4/E6 ratio) for HS were similar pattern for 8 soils. The extraction with increasing pH increased dissolution of SOM. The ratio of organic carbon (OC) associated with HA and FA (the HA:FA ratio) was varied widely in accordance with the soils and was highly correlated to OC content(%) of the soils. In modeling metal speciation in soils and soil solutions, assumptions that all DOC in soil solution is associated with FA and that HA:FA ratio in SOM is constant have been made. The results of this study indicate that the validity of these assumptions is questionable. By sequential pH extraction, the K_{DOC} showed in a linear correlation with pH.

Key Words : SOM, Sequential pH extraction, HA:FA ratio, Partiton coefficient

1. Introduction

Windermere Humic Aqueous Model (WHAM) is an equilibrium model for metal speciation which takes into consideration the specific and nonspecific ion binding by humic substance (HS)[1]. It hypothesizes that DOC concentrations depend on the hydrophobicity of HS[2]. Furthermore, Tipping and colleagues have observed that only a fraction of dissolved HS is active. The models have been optimized with respect to this active fraction. In the applications of WHAM for aqueous speciation in surface waters and soil pore waters, only 65-69% of DOC is assumed to be active and all of it is Fulvic Acid (FA). The remaining 35-31% is assumed to be inert with respect to metal binding. In whole soil speciation applications of WHAM, it is assumed that the soil organic matter (SOM) constitutes HA and FA in the ratio 84:16[3]. In this case, the active fraction of SOM is calculated by minimizing the difference between the observed soil pH and the calculated pH. The active fraction of SOM thus determined has an apparent negative correlation with the SOM content of the soils. However, there has been no explanation on why only a fraction of SOM and DOM appears to be active. Therefore, there is a need to better understand the characteristics of DOM and SOM and their partitioning behavior in the soil matrix.

Therefore, the extraction of SOM from soils involves base solubilization at pH >12. The subsequent separation of HA from FA then involves acid precipitation at pH <2. In this study, we extracted SOM from different soils sequentially at incremental pH values (2 to10). Based on this study we illustrate whether HA:FA ration of 84:16 is reasonable for general use or not. The extracted SOM were then acidified to different pH and centrifuged. The supernatants were analyzed for DOC and E4/E6 ratio.

Futhermore, we also investigated dissolved metals (Cu and Zn) associated with the SOM extract[4]. And, we propose a correlation to predict organic matter(OM) partitioning based on pH.

2. Materials and Methods

Eight soils (Matawon, Keyport, Codorus, Matapeake, Boonton Union County, Butte, Illinois and Treaty) were used for this study. The properties and characteristics of these soils have been reported else-

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where[4,5]. Particle size distribution was determined using a hydrometer method[6]. Loss on Ignition (LOI) of the soils were determined by ashing at 550°C. The released metals were determined using ICP-MS (Agilent, 7500 CS). Dissolved organic carbon (DOC) was determined using TOC analyzer (Tekmar Dohrmann, Apollo 9000). The UV-VIS spectra of the final supernatants were carried out using a 1.0cm cell and a scan range of 200~700nm. E4/E6 ratios were calculated from absorbance measurements at 465 and 665nm (Diode Array Spectrophotometer, Hewlett Packard 8452A).

2.1. Characteristics of SOM

The soils (8 g each) were mixed with 40 ml of 0.1 M NaOH and shaken for 24 hr at room temperature. The supernatant was removed by centrifuging for 20 minutes at 4000 rpm. This extraction was repeated three more times to give four supernatants, which were pooled. The pooled supernatants were centrifuged again for 30 minutes at 4000 rpm to ensure complete removal of fine colloidal clay[7]. The supernatants were divided into 11 aliquots, and their pHs were adjusted to 1 to 10 by adding HCl. Then, these samples were centrifuged for 20 minutes at 4000 rpm to remove the precipitates and the supernatants were analyzed for TOC using TOC analyzer (Tekmar Dohrmann, Apollo 9000). The UV-VIS spectra of the adjustable final supernatants were also obtained.

2.2. The release of DOC by sequential extraction

A batch technique was used to perform all studies. 1.8 ± 0.01g of each soil was mixed with 45 ml of 0.01M $NaNO_3$ in a 50-mL polyethylene centrifuge tube. The pHs were adjusted to approximately 2 using 0.1 M HCl. The samples were then shaken (Orbit, no 3590, Lab-Line Instruments, Melrose Par,

IL) at 100 strokes/min for 22 hr at room temperature (20 ± 2 °C). After 22 hr of equilibration, the samples were centrifuged at 4000 rpm for 20 min and then filtered using 0.45 μm membrane filters. The remaining residues were centrifuged again at 4000 rpm for 5 min and the supernatants (<0.2 ml in volume) were discarded.

To the residues a fresh 45ml portion of 0.01 M $NaNO_3$ was added and the pH adjusted to approximately 3. The above procedure was repeated for each soil sample at incremental pH up to the final extraction pH of approximately 10.5. The pH adjustments for higher pH were made using 0.1 M NaOH.

The resulting filtrate at each pH was divided into three portions. The first portion was used for TOC analyses. This TOC is associated with humic substance (HS). The second portion was acidified to pH 1 and centrifuged to remove HA from the solution. The supernatant was analyzed for TOC. This TOC is associated with to FA. The final portion was used for analyses of pH (Thermo Orion) and dissolved metals (ICP-MS, Agilent 7500 CS). The OC concentration associated with HA was then calculated as the difference between the TOCs before and after the acidification to pH 1 and centrifugation, i.e., HS-FA.

3. Results and Discussion

The soil pHs were recorded below 7 for all the soils (Table 1). The clay contents ranged from 8% to 28%. The LOI ranged from 2.26% to12.49 %. There was, however, no apparent relationship between clay contents and LOIs. The concentrations of total metal (Cu, Zn) were measured by Impellitteri[8].

3.1. Characteristics of SOM

Generally, SOM is extracted and FA and HA are

Table 1. Soil properties

Soil	pH (1:25)	Sand (%)	Cilt (%)	Clay (%)	LOI	Cu (%)	Zn	Fe	Mn	Ca
								mg/kg		
Matawon	6.42	66	22	12	3.36	8.06	39.5	-	-	
Keyport	6.07	27	45	28	5	14.21	58.5	-	-	
Codorus	6.27	36	40	24	4.49	11.25	47.2	-	-	
Metapeak	6.07	13	63	24	4.74	21.4	73.5	-		
Boonton	5.32	49	35	16	11.54	53.2	126.7	17873	2499	1010
Butte	4.64	65	24	11	22.6	585	726	27353	289	1208
Illinois	6.35	19	58	23	10.54	332.9	1089.7	21733	499	13566
Treaty	5.36	61	31	8	124.9	74.3	74.3	10653	1603	841

separated by using some sort of resin. In this study, however, the SOM extracted by 0.1 M NaOH was controlled at different pH. The measured OC and its relation to the pH at which it was controlled are shown in Figure 1. The concentration of OC in the supernatant was significantly affected by pH control. Decrease in pH resulted in decreasing concentration of OC. In general, there was a dramatic decrease in OC concentration as the pH at which the extracted SOM was controlled changed from~7 to ~ 4. At lower pH values, the concentration of OC was small and it increased slightly at pH < 4 for all soils except for Boonton and Treaty soils. This sharp decrease in solubility is due to the precipitation of HA. Also apparent in Figure 1 is the relationship between the OC extracted and the %LOI of the soils. More OC is extracted from the soils with high %LOI (Boonton, Treaty and Illinois).

The composition of the extracted SOM was further characterized by determining the E4/E6 ratio (the ratio of UV absorbance at 465 and 665nm). The UV absorbance is due to smaller molecules at 465nm and large molecules at 665nm. Therefore, the E4/E6 ratio is expected to be smaller for HA and larger FA.

Based on previous studies, the E4/E6 ratio was < 5 for HA[9,10] and 6~18.5 for FA[11,12]. As shown Figure 1, the E4/E6 ratio for solutions (HA+FA) at pH >7 were generally constant within the range 5~7. At low pH (i.e. FA solutions), the E4/E6 ratio were >.8 except for Boonton soil. Additionally, the ratio decreased sharply at the lowest pH (~1).

The relationship between %LOI and %OC for the soils is also shown in Figure 2. In general % LOI is 1.5 times %OC indicating that %LOI could be used to represent the OM content of soils. The regression coefficients (r²) were 0.69 for %LOI and 0.98 for %HA:FA.

Next it was determined the HA:FA ratio in the HS extracted from the soils(Figure 3). Assuming that at low pH (< 2), the solution constituted OC associated only with FA, and at high pH (> 12), the OC represented both FA and HA. The amount of HA (mg/g of soil) was calculated by the difference between the HS-associated OC at high pH (>12) and the FA-associated OC at low pH (<2). The HA:FA ratio ranged from a high of 17.1:1 in Boonton soil to a low of 0.4:1 in Codorus and Butte soils. Tipping et al.[2,3] used a constant ratio of 5.25:1 regardless of the %OC contents of the soils based on model optimization. In
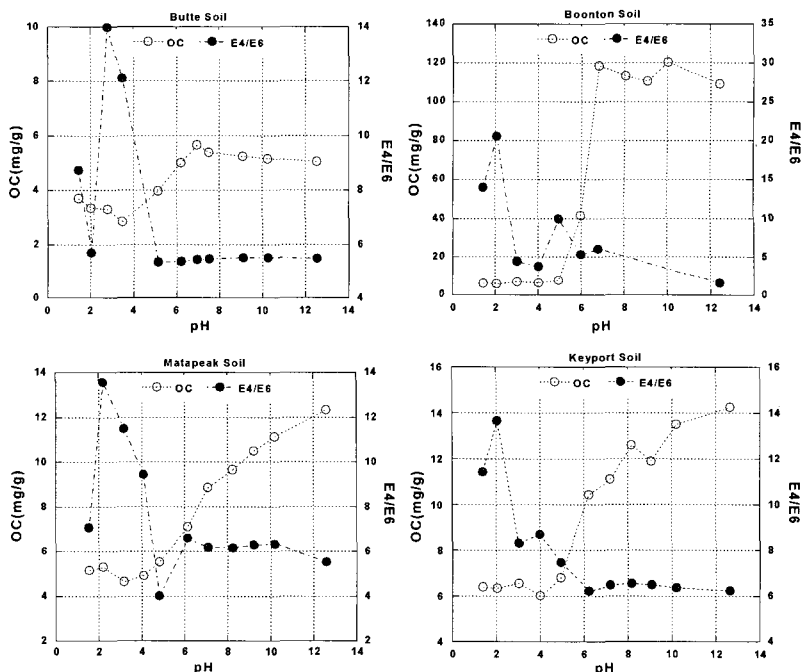

Fig. 1. The measured OC (mg/g of soil) and E4/E6 ratios as a function of pH at which the NaOH extracted SOM was controlled.
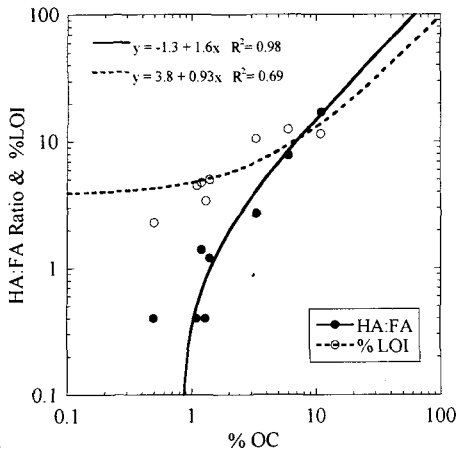
Fig. 2. Relationship between % LOI, HA:FA ratio and the % OC of the soils. The equations represent the linear regression.
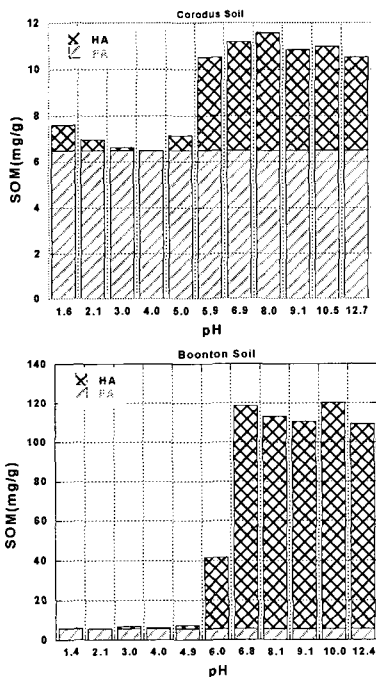

Fig. 3. The HA:FA ratio in the NaOH extracted SOM as a function of pH at which it was controlled.

Fig. 4. Concentration of DOC in the extraction solutions (soil:water = 1:25) due to SOM release.

this study, The HA:FA ratio was highly correlated with the %OC of the soils (Figure 2). This relationship implies that use of a single HA:FA ratio for SOM in different soils may not be reasonable.

3.2. Sequential extraction at incremental pH

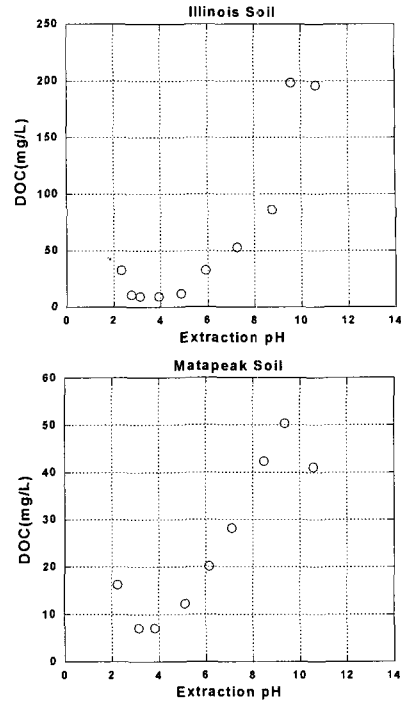In the sequential extraction of SOM, the extraction pH had a significant effect on the release of SOM. As shown in Figure 4, increasing the pH increased the concentration of DOC in the extractants. At the lowest pH (~ 2), with the exception of Matawon soil, the concentration of DOC increased slightly compared to a relatively higher pH of (< 4). Except for Codorus and Butte soils, the lowest concentration of DOC occurred near pH 4.

The reason for the initial decrease in the extraction of OC as depicted in Figure 4 is not clear. De Wit et al.[13] found that adding increasing amounts of Al to batch titration experiments on an Oe horizon soil produced small(<10 mg /L) increases in the concentration of DOC at pH <3.5. It is possible that the higher OC extracted at pH < 4 represent OC associated with Al-OM complexes possessing net positive charge[14,15].

Figure 5 shows that at low pH values (typically < 4), the extracted OC is predominantly FA as determined by the precipitation method described previously. At higher pH, although the increase in OC was primarily due to increasing release of HA, significant contribution by FA release at each incremental pH is also evident. The fraction of FA extracted at pH 2.27 with respect to the total cumulative FA extracted is only ~15% and ~22% for Metapeak and Boonton soils, respectively.
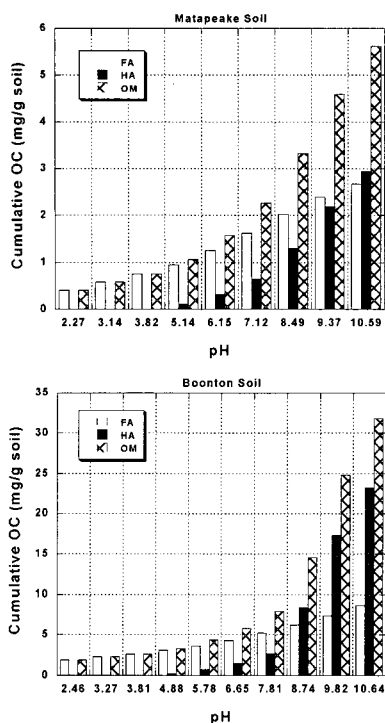
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Fig. 5. Cumulative OC (mg/g soil) associated with FA and HA (and the total OM) extracted from the soils at incremental pH. (soil:water = 1:25, pH from ~2 to ~10)

That not all of FA is extracted at acidic pHs and that a significant amount of FA is extracted in each sequence are at odds with the determination of FA by base extraction followed by acid precipitation.

In the extracted SOM, the HA:FA calculated for pH >8 was on average 83:17 and 68:32 for Boonton and Matapeake soils, respectively. These values are not consistent with the SOM results. This discordance is probably caused by the difference in water contents.

The trend shown in Figure 5 is consistent with Figure 1. In the precipitation of the base extracted HS represented in Figure 1, HA becomes increasingly more soluble with increasing pH. In the sequential extraction represented in Figure 5, incremental amounts of HA are being released in the solution as the extraction pH increases.

Between the pH of 5-7, where in lies most of soils, significant amount of HA is still soluble. This *is more so for soils with higher %LOI.* These observations imply that the assumption[3,16,17] that all of the soil solution DOC is associated with FA may not

be reasonable.

3.3. The partition coefficients

It was assumed that the SOM content of the soils represents the amount of OM that can be extracted by 0.1 M NaOH (Based on % LOI) and the DOC in the extraction solution is due to the extracted SOM. The results are expressed in terms of a partition coefficient (KDOC), according to the following equation:

$$K_{DOC} = \frac{C_{SOM} - V_{EX} \times C_{DOC}}{C_{DOC}}$$

where,

K_{DOC} = Partition coefficient (L/kg)

C_{SOM} = Total soil organic matter based on % LOI (mg/kg)

C_{DOC} = Concentration of organic carbon released in sequential extraction (mg/L)

V_{EX} = The extraction volume (L)

Figure 6 shows the relationship between the partition coefficient (log K_{DOC}) and the pH for the 8 soils. The coefficient of variation is 0.81. But, at low pH values (< 4), the log K_{DOC} values increased with increasing pH. This result probably eschewed the regression coefficient towards a lower value than it would otherwise have been.

Based on the concentration of metals in the extracted solutions and the total metals in the soils as shown in Table 1, the partition coefficients for Copper and Zinc were calculated (log K_{Cu} and log K_{Zn}, respectively). There was no apparent relationship between these values and the extraction pH. Next, the
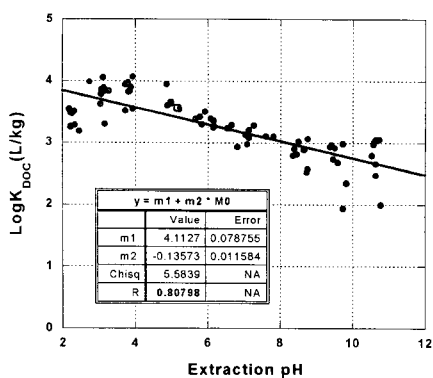

Fig. 6. Partition coefficient (log K_{DOC}) as a function of pH for 8 soils. (water:soil = 45ml:1.8g, T=20±2°C)
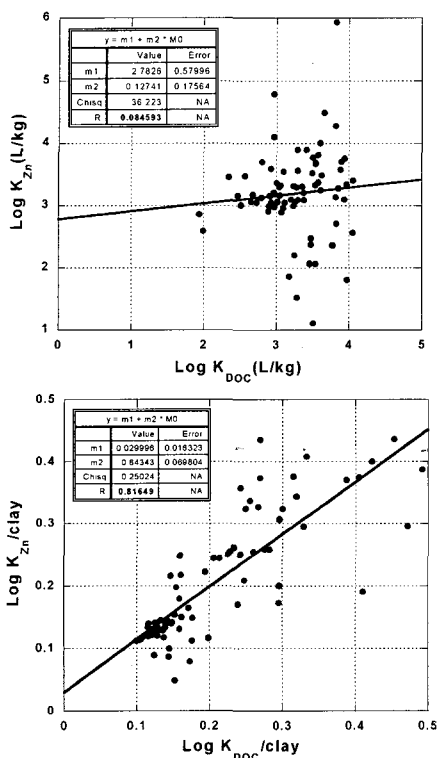
y = m1 + m2 * M0		
	Value	Error
m1	2 7826	0.57996
m2	0 12741	0 17564
Chisq	36 223	NA
R	0.084593	NA

y = m1 + m2 * M0		
	Value	Error
m1	0 029996	0.016323
m2	0 84343	0 069804
Chisq	0 25024	NA
R	0.81649	NA

Fig. 7. The correlation between log K_{Zn} and log K_{DOC}.

y = m1 + m2 * M0		
	Value	Error
m1	0.88443	0 43293
m2	0 56957	0 13149
Chisq	16 687	NA
R	0.47613	NA

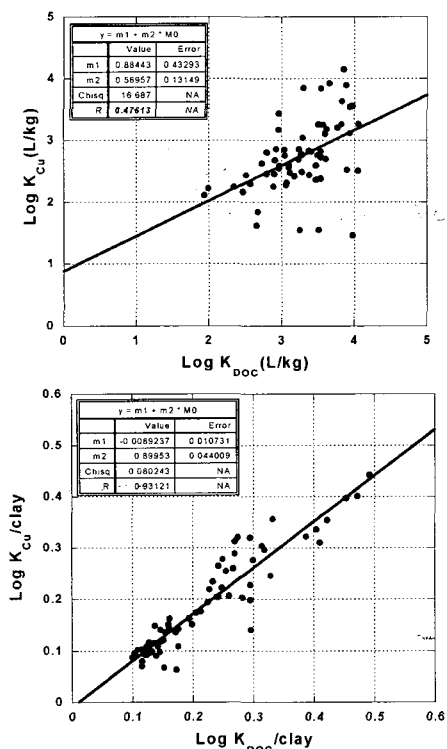| y = m1 + m2 * M0		
	Value	Error
m1	-0 0089237	0 010731
m2	0 89953	0 044009
Chisq	0 080243	NA
R	0 93121	NA

Fig. 8. The correlation between log K_{Cu} and log K_{DOC}.

effects of soil properties on OM, Cu and Zn partitioning were investigated at the experimental pH values.

As shown in Figures 7 and 8, there was no significant correlation between log K_{DOC} and log K_{Cu}, log K_{Zn}. By normalizing the log K with respect to clay content of the soils, better correlations of log K_{Cu} and log K_{Zn} to log K_{DOC} were obtained. The regression coefficient increased from near 0 to 0.8 for Zn and 0.5 to 0.9 for Cu[4]. For the analysis involving Cu, the total extracted Cu was found to be greater than those reported in Table 1 for Matapeake soil. Thus it was excluded in the analysis for Cu.

4. Conclusion

This study demonstrates that HA:FA ratio in SOM varies significantly among different soils and that there is an indication that HA progressively dominates the composition as %LOI of the soil increases. This is of importance in the application of models (such as WHAM, SHM) in which this HA:FA ratio has to be defined. % LOI is 1.5 times %OC indicating that %LOI could be used represent the OM content of soils.

The E4/E6 ratio for solutions at pH >7 were general constant within the range 5~7. At low pH were > 8 except for Boonton soil. But, the ratio decreased sharply at the lowest pH (~1).

The relationship (R) between the partition coefficient (log K_{DOC}) and pH is 0.8. But there was no significant correlation between logK_{DOC} and log K_{Cu}, log K_{Zn}.

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