soil systems

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Supplementary Materials

Composition-Dependent Sorptive Fractionation of Anthropogenic Dissolved Organic Matter by Fe(III)-Montmorillonite

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Table S1. Summary statistics for the absolute errors (ppm) of the Common Formula assignments.

Sample	Type	n	Median	Mean	Std. Dev.
Anthrop. DOM	Initial	7641	0.02	0.06	0.14
	Sorbed		0.03	0.05	0.06
HiN Fraction	Initial	4392	0.02	0.03	0.04
	Sorbed		0.03	0.07	0.09
HoA Fraction	Initial	2258	0.02	0.02	0.02
	Sorbed		0.02	0.05	0.09
HoN Fraction	Initial	6438	0.02	0.07	0.16
	Sorbed		0.01	0.03	0.04

Table S2. Number of formulas that were present both in the original DOM solution and the corresponding sorbed organic matter extract (Common Formulas), and the percent relative abundance of the Common Formulas in each van Krevelen plot region defined in Figure S3.

Sample	Quartile	Formulas	% Abund.	Sample	Formulas	% Abund.
Anthropogenic DOM	ALIPH-LO	157	1.1	HiN Fraction	151	1.6
	ALIPH-MO	783	9.3		1180	35.0
	ALIPH-HO	402	5.4		662	15.9
	MS-LO	645	4.5		298	2.4
	MS-MO	2785	37.8		1375	34.2
	MS-HO	1228	22.8		444	9.0
	AROM-LO	381	2.3		60	0.3
	AROM-MO	1003	13.0		201	1.3
	AROM-HO	257	3.9		21	0.1
Sample	**Quartile**	**Formulas**	**% Abund.**	**Sample**	**Formulas**	**% Abund.**
HoA Fraction	ALIPH-LO	9	0.3	HoN Fraction	694	13.1
	ALIPH-MO	207	8.6		1121	23.0
	ALIPH-HO	68	3.1		183	2.2
	MS-LO	56	1.5		996	14.5
	MS-MO	940	39.9		2003	29.5
	MS-HO	486	26.1		515	7.5
	AROM-LO	18	0.4		236	1.8
	AROM-MO	355	14.4		564	6.2
	AROM-HO	119	5.7		126	2.2

"ALIPH" = aliphatic (H/C ≥ 1.5); "AROM" = aromatic (ModAI > 0.5); "MS" = mid-saturation (H/C < 1.5 and ModAI ≤ 0.5); "LO" = low oxygen content (O/C ≤ 0.3); "MO" = mid-oxygen content (0.3 < O/C ≤ 0.6); "HO" = high oxygen content (O/C > 0.6); "ModAI" = modified aromaticity index.

Table S3. Number of formulas that were present both in the original DOM solution and the corresponding sorbed organic matter extract (Common Formulas), and the percent relative abundance of the Common Formulas in each elemental class.

Sample	Elements	Formulas	% Abund.	Sample	Formulas	% Abund.
Anthropogenic DOM	CHO	1414	27.7	HiN Fraction	919	17.8
	CHNO	3479	45.6		2859	75.8
	CHOS	827	10.6		136	1.4
	CHNOS	1921	16.1		478	5.0
Sample	**Elements**	**Formulas**	**% Abund.**	**Sample**	**Formulas**	**% Abund.**
HoA Fraction	CHO	620	35.2	HoN Fraction	1974	48.7
	CHNO	990	40.9		2514	24.6
	CHOS	297	13.1		998	19.8
	CHNOS	351	10.8		952	7.0

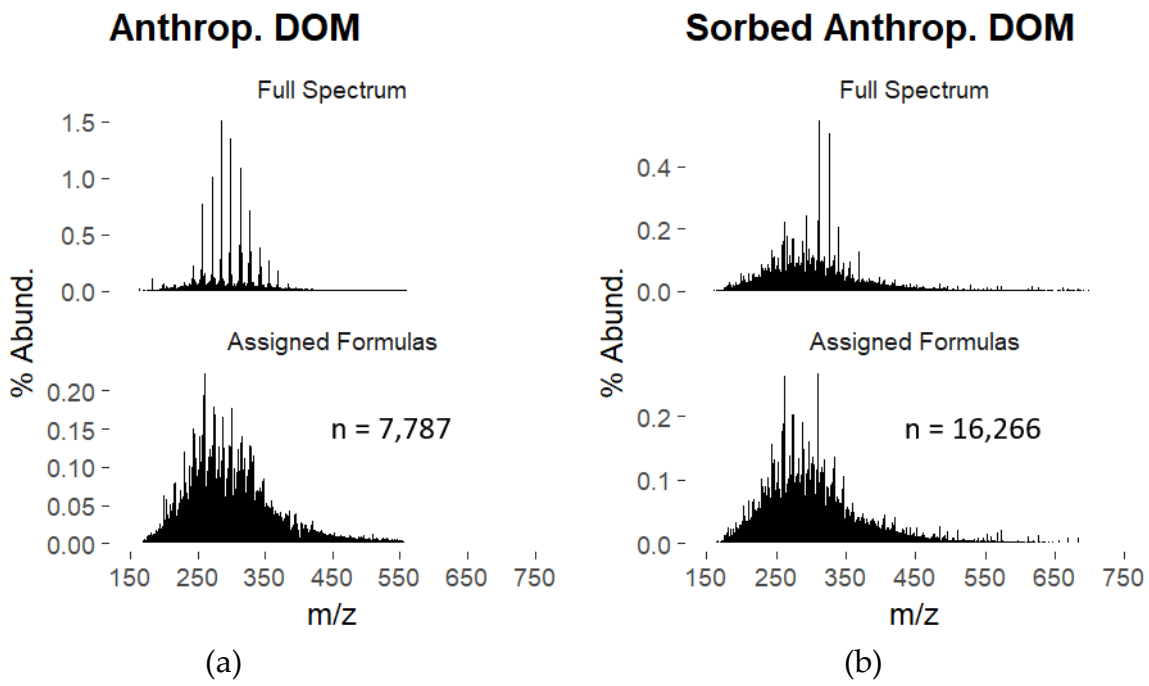

Figure S1. For the (a) anthropogenic DOM solution, and (b) sorbed anthropogenic DOM extract, the top panel contains the full mass spectrum for all peaks with S/N ≥ 6, and the bottom panel contains an extracted mass spectrum containing all of the assigned formulas (n) after excluding the surfactant-like series.

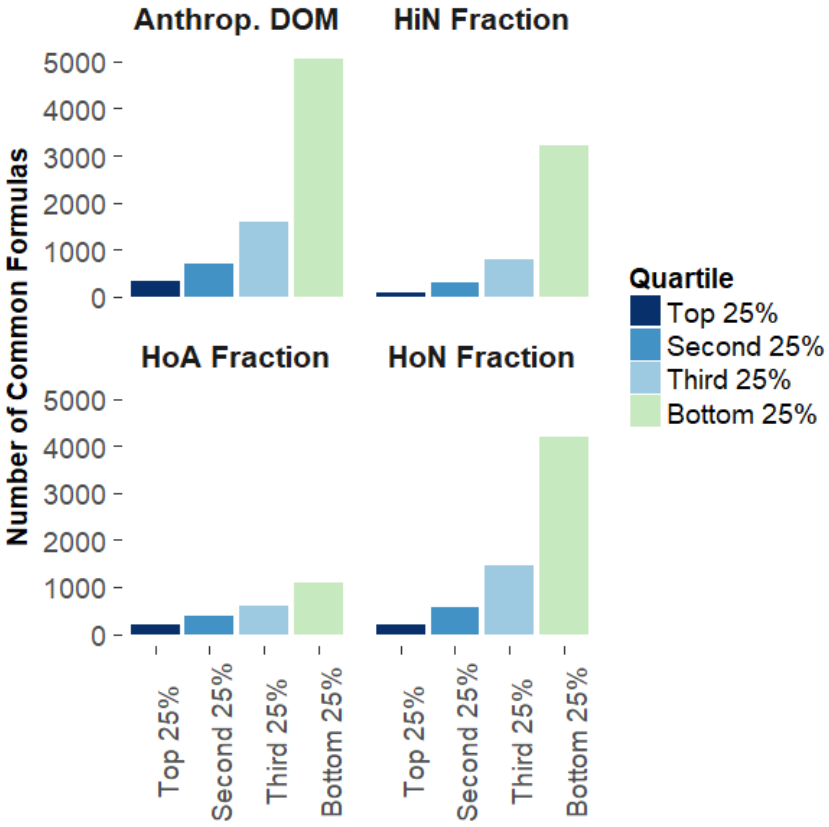

Figure S2. Number of formulas that were present both in the original DOM solution and the corresponding sorbed organic matter extract (Common Formulas), distributed among the quartiles illustrated in Figure 1. The "Top 25%" (dark blue in Figure 1 and above), totaling ~25% of the sample's cumulative abundance, comprised the most abundant Common Formulas. The "Bottom 25%" (light green in Figure 1 and above), also totaling ~25% of the sample's cumulative abundance, comprised the least abundant Common Formulas.

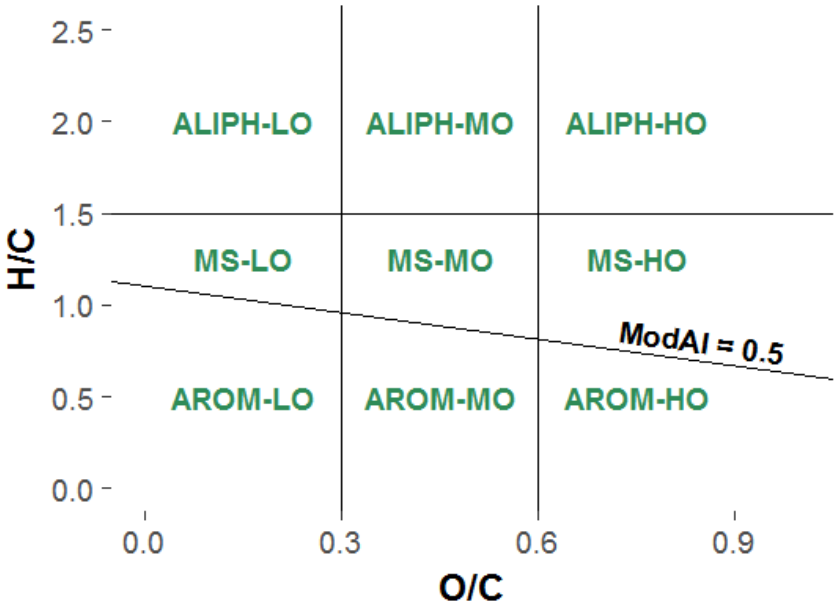

Figure S3. Scheme for determining plot regions in the van Krevelen diagram: "ModAI" = modified aromaticity index; "ALIPH" = aliphatic (H/C ≥ 1.5); "AROM" = aromatic (ModAI > 0.5); "MS" = mid-saturation (H/C < 1.5 and ModAI ≤ 0.5); "LO" = low oxygen content (O/C ≤ 0.3); "MO" = mid-oxygen content (0.3 < O/C ≤ 0.6); "HO" = high oxygen content (O/C > 0.6).

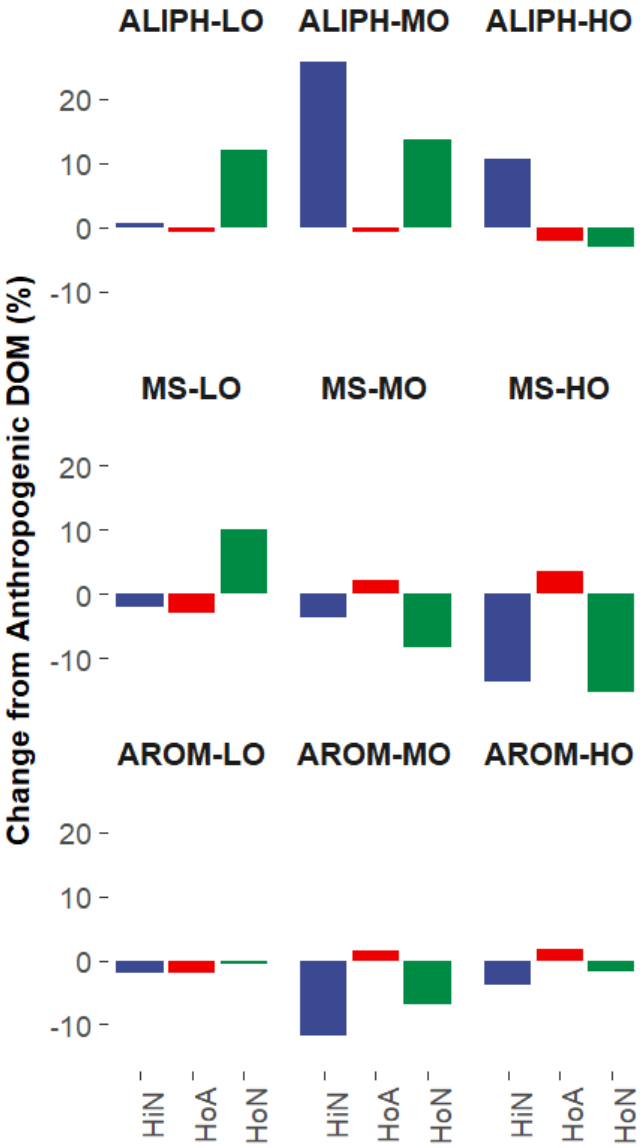

Figure S4. Cumulative percent abundances of the structural fractions in each van Krevelen plot region, relative to the anthropogenic DOM. Each value was computed by subtracting the cumulative percent abundance of the anthropogenic DOM from the cumulative percent abundance of the structural fraction in the same van Krevelen plot region. "ALIPH" = aliphatic (H/C ≥ 1.5); "AROM" = aromatic (ModAI > 0.5); "MS" = mid-saturation (H/C < 1.5 and ModAI ≤ 0.5); "LO" = low oxygen content (O/C ≤ 0.3); "MO" = mid-oxygen content (0.3 < O/C ≤ 0.6); "HO" = high oxygen content (O/C > 0.6); "ModAI" = modified aromaticity index.

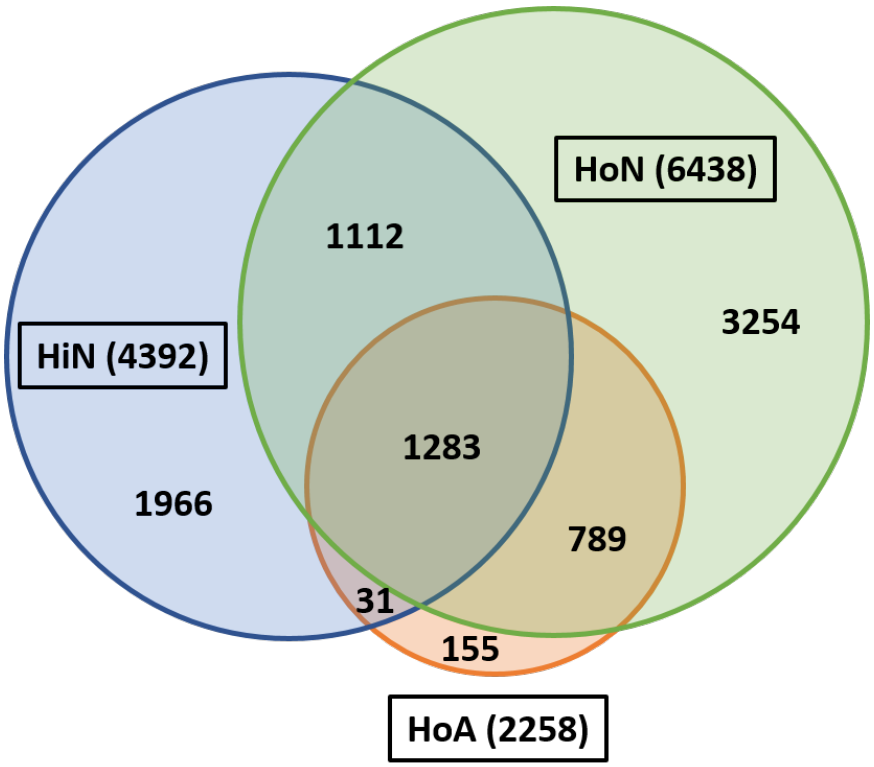

Figure S5. Venn diagram illustrating the number of formulas in each structural fraction (black boxes) that were present both in the original DOM solution and the corresponding sorbed organic matter extract (Common Formulas), and the number of Common Formulas that were unique or shared with other structural fractions (circles).

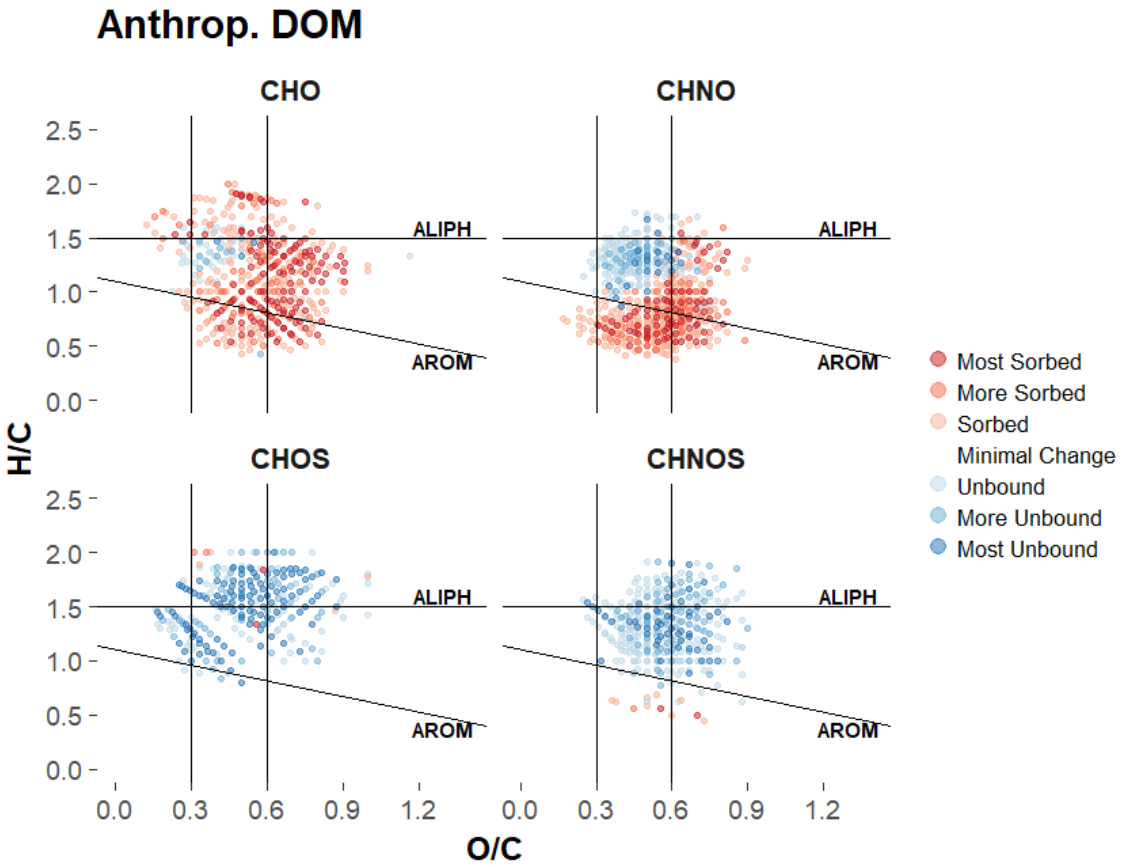

Figure S6. van Krevelen diagrams, separated by elemental composition, illustrating the common formulas that were more abundant in the original anthropogenic DOM (Blue), and more abundant in its sorbed organic matter extract (Red). The vertical lines at O/C = 0.3 and 0.6 correspond to the oxygen content of the van Krevelen plot regions in Figure S3 ("Most Sorbed" = Δ abundance < −0.015%; "More Sorbed" = Δ abundance < −0.010%; "Sorbed" = Δ abundance < −0.005%; "Minimal Change"; "Unbound" = Δ abundance > 0.005%; "More Unbound" = Δ abundance > 0.010%; "Most Unbound" = Δ abundance > 0.015%).

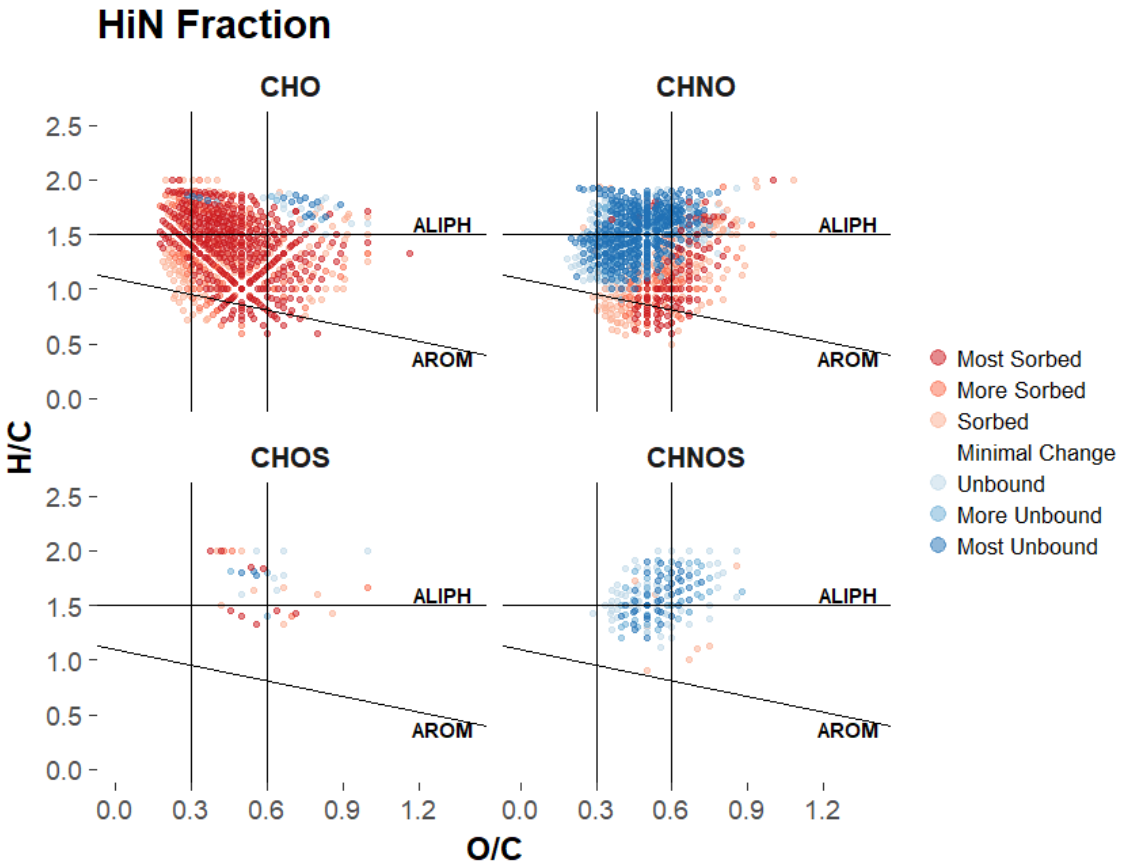

Figure S7. van Krevelen diagrams, separated by elemental composition, illustrating the common formulas that were more abundant in the original HiN fraction (Blue), and more abundant in its sorbed organic matter extract (Red). The vertical lines at O/C = 0.3 and 0.6 correspond to the oxygen content of the van Krevelen plot regions in Figure S3 ("Most Sorbed" = Δ abundance < −0.015%; "More Sorbed" = Δ abundance < −0.010%; "Sorbed" = Δ abundance < −0.005%; "Minimal Change"; "Unbound" = Δ abundance > 0.005%; "More Unbound" = Δ abundance > 0.010%; "Most Unbound" = Δ abundance > 0.015%).

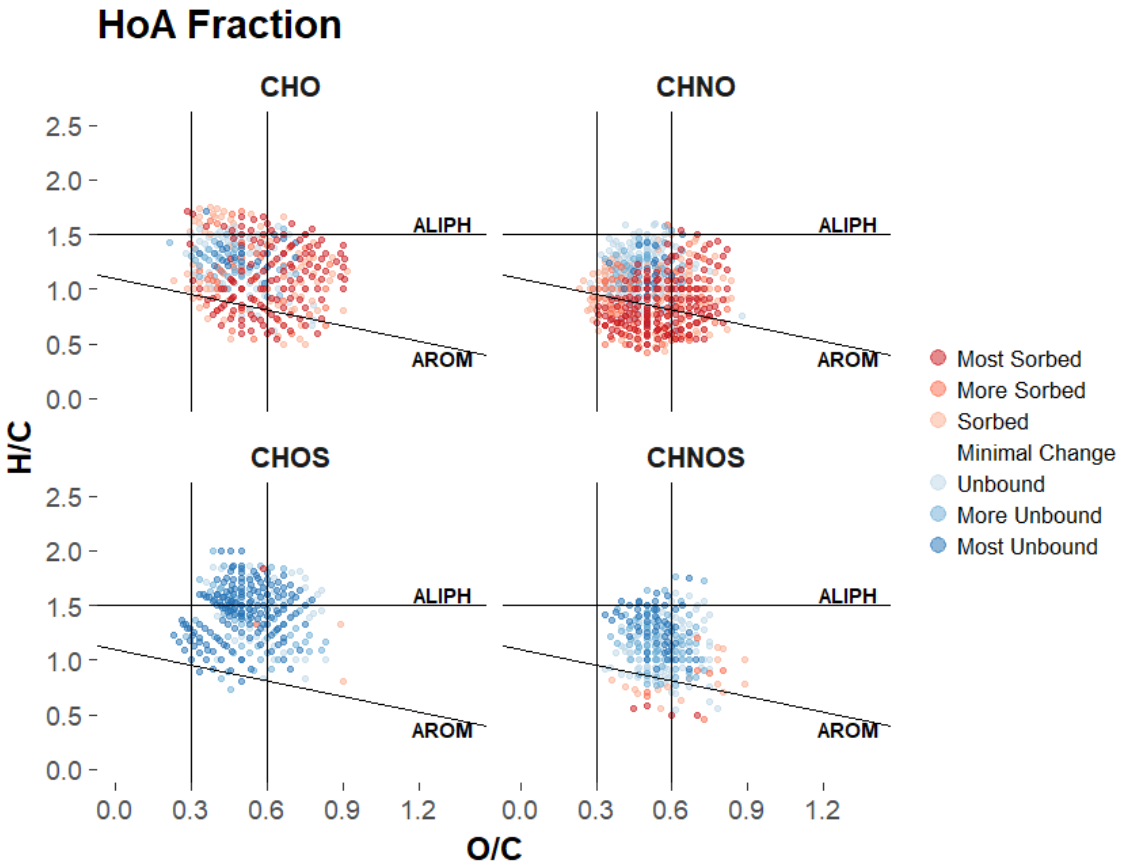

Figure S8. van Krevelen diagrams, separated by elemental composition, illustrating the common formulas that were more abundant in the original HoA fraction (Blue), and more abundant in its sorbed organic matter extract (Red). The vertical lines at O/C = 0.3 and 0.6 correspond to the oxygen content of the van Krevelen plot regions in Figure S3 ("Most Sorbed" = Δ abundance < −0.015%; "More Sorbed" = Δ abundance < −0.010%; "Sorbed" = Δ abundance < −0.005%; "Minimal Change"; "Unbound" = Δ abundance > 0.005%; "More Unbound" = Δ abundance > 0.010%; "Most Unbound" = Δ abundance > 0.015%).

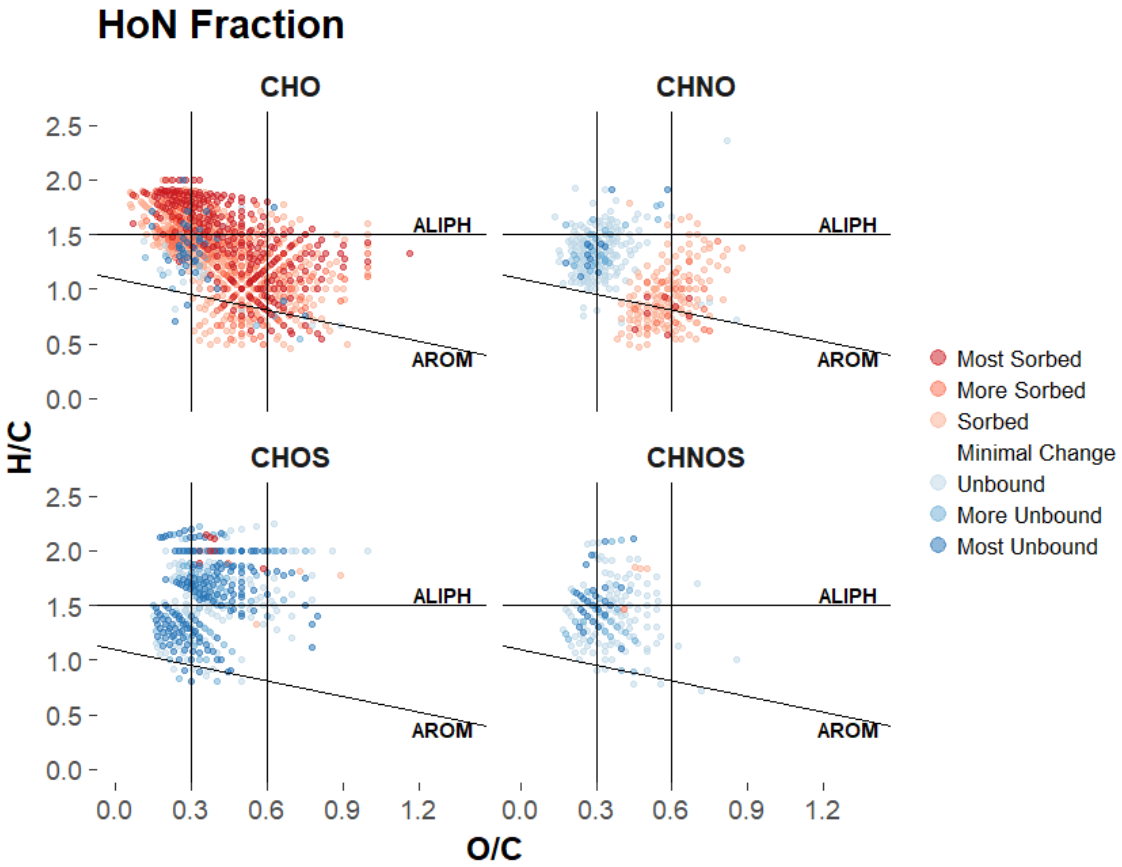

Figure S9. van Krevelen diagrams, separated by elemental composition, illustrating the common formulas that were more abundant in the original HoN fraction (Blue), and more abundant in its sorbed organic matter extract (Red). The vertical lines at O/C = 0.3 and 0.6 correspond to the oxygen content of the van Krevelen plot regions in Figure S3 ("Most Sorbed" = Δ abundance < −0.015%; "More Sorbed" = Δ abundance < −0.010%; "Sorbed" = Δ abundance < −0.005%; "Minimal Change"; "Unbound" = Δ abundance > 0.005%; "More Unbound" = Δ abundance > 0.010%; "Most Unbound" = Δ abundance > 0.015%).

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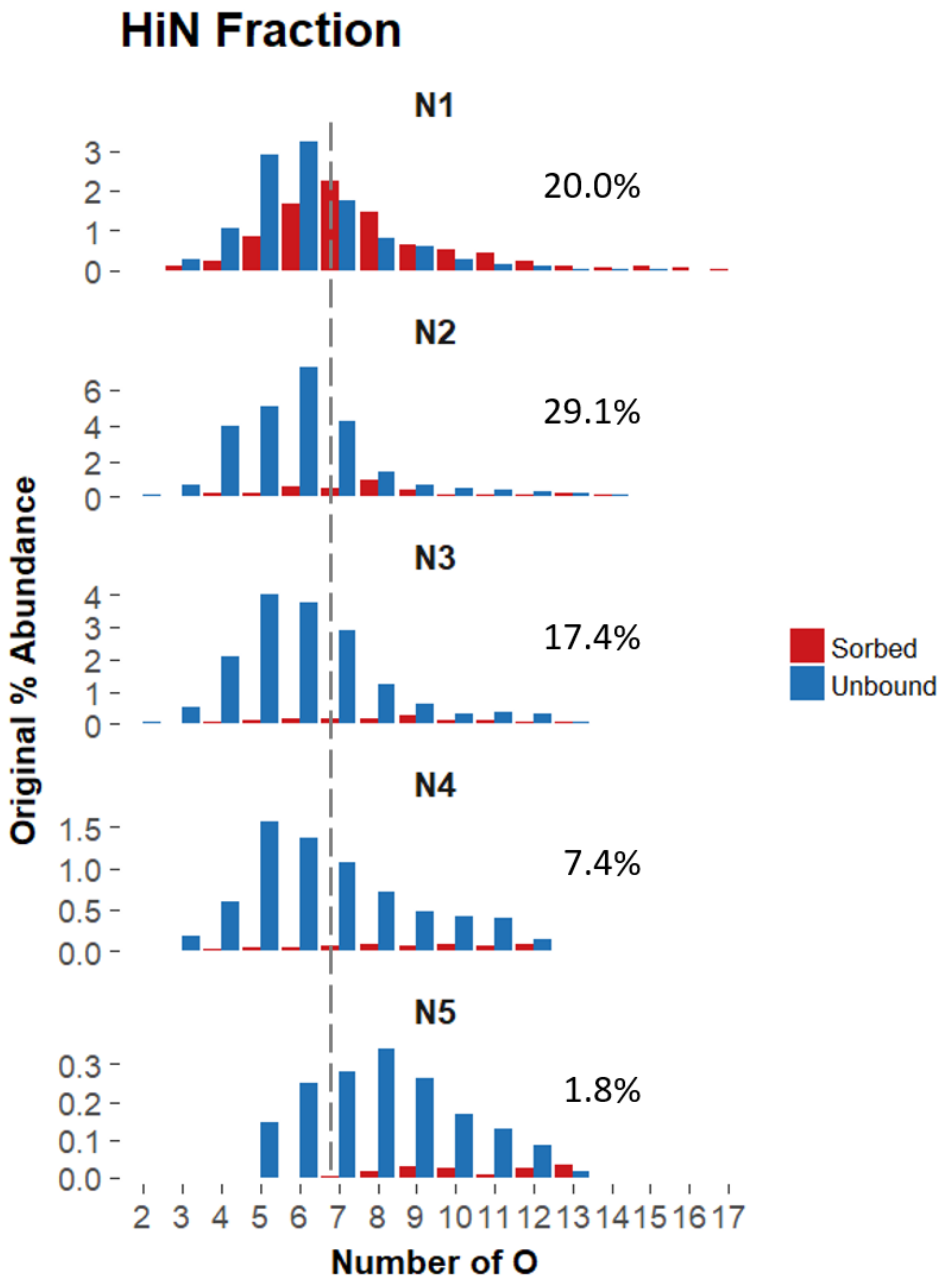

98 **Figure S10.** Distribution of the ionizable CHNO content in the HiN fraction as a function of its original
99 abundance, nitrogen content, oxygen content, and status as Sorbed" or "Unbound". The stated
100 percentage for each $N_{1\text{-}5}$ heteroatom class is its aggregate original percent abundance. The dashed line
101 indicates the number of oxygen atoms at or above which the N_1 heteroatom class favors sorption to
102 the Fe(III)-montmorillonite.