Supporting Material for

Natural organic matter composition determines the molecular nature of silver nanomaterial NOM-corona

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FT-ICR-MS spectra and data analysis

Table S1. Descriptive compound classes in NOM and AgNM NOM-corona. Experiments were performed at 4 mg L^{-1} cit-AgNP and 5 mg L^{-1} NOM concentrations

Class	Criterion
Condensed polycyclic aromatics	AI > 0.66
Phenolic	0.66 ≥ AI ≥ 0.5
Highly unsaturated and phenolic	AI ≤0.5 and H/C <1.5
Aliphatic	2.0 ≥ H/C ≥ 1.5

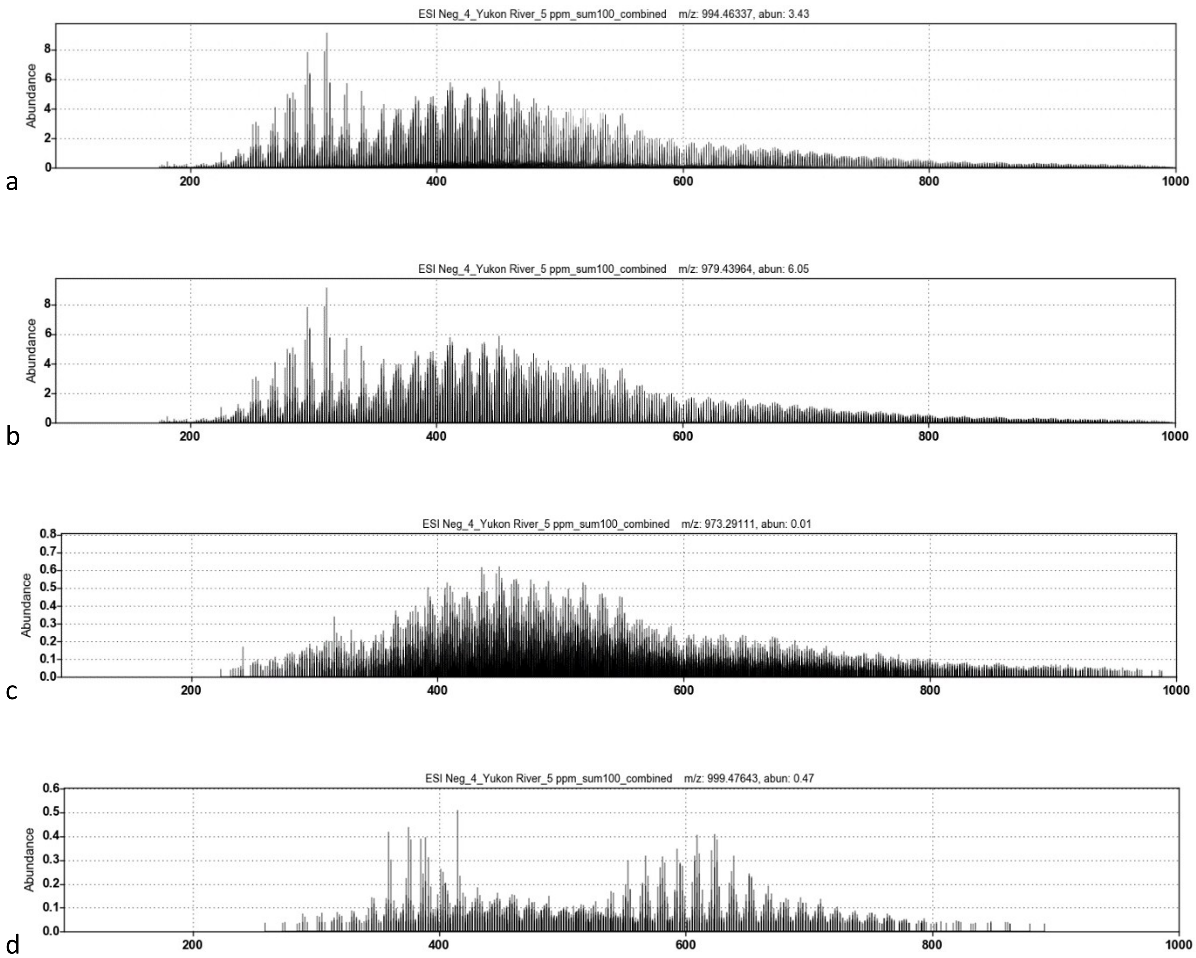


Figure S1. ESI-FT-ICR-MS spectra of the Yukon River NOM: (a) all formulas, (b) CHO, (c) CHOS, and (d) CHON

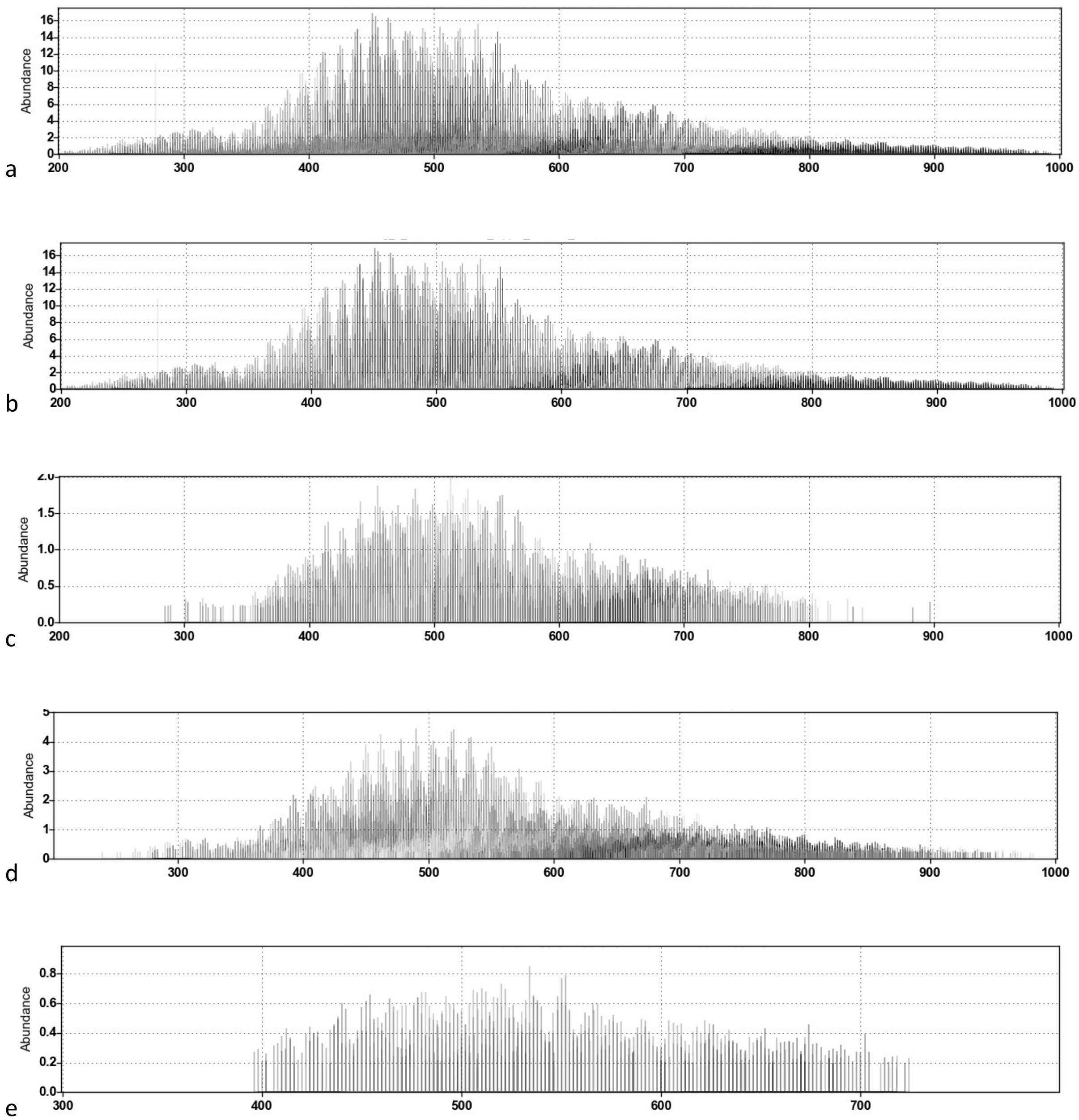


Figure S2. ESI-FT-ICR-MS spectra of the Milwaukee River NOM: (a) all formulas, (b) CHO, (c) CHOS, (d) CHON, and (e) CHONS

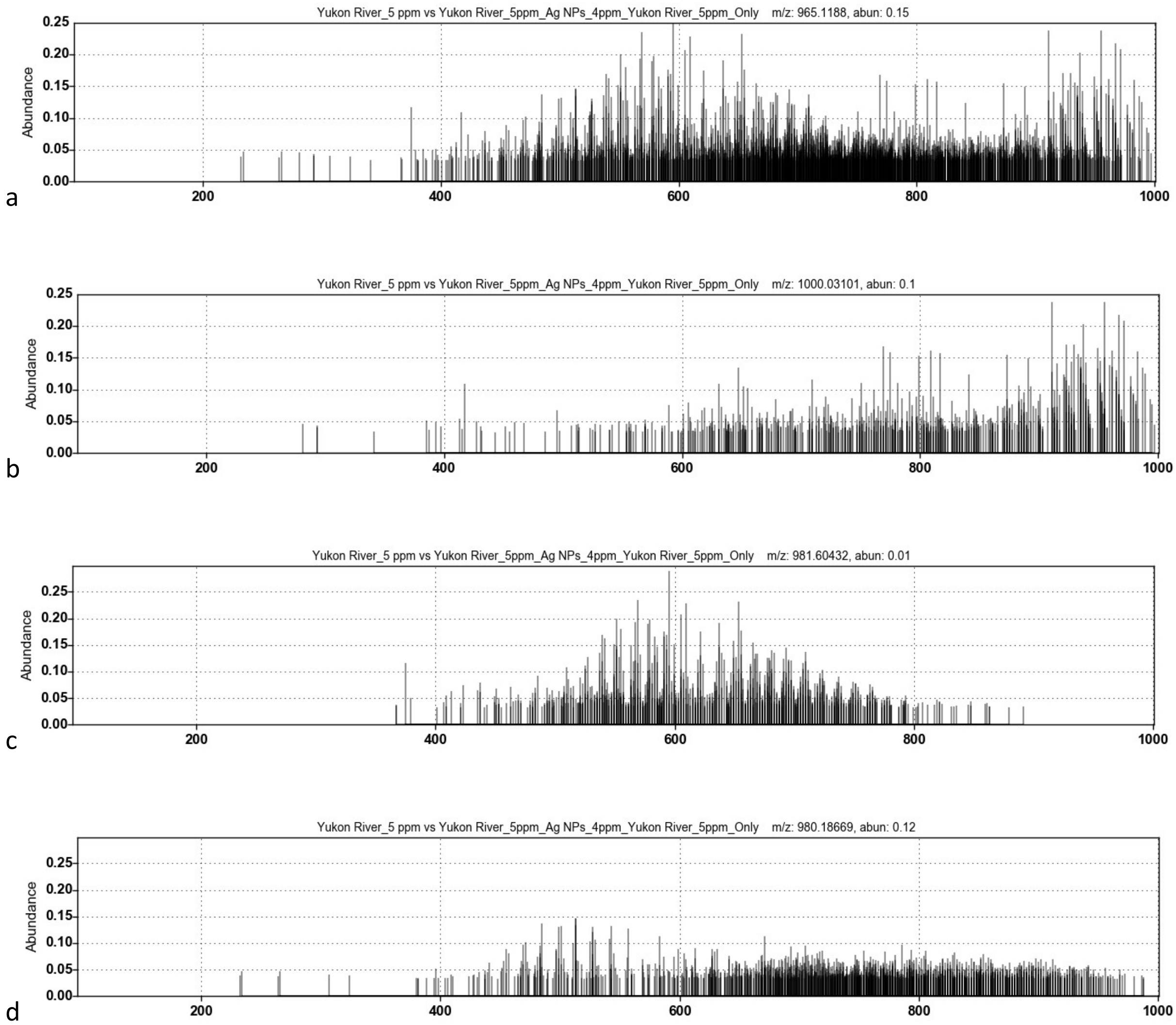


Figure S3. ESI-FT-ICR-MS spectra of the Ag NM NOM-corona formed by interactions with the Yukon River NOM: (a) all formulas, (b) CHO, (c) CHOS, and (d) CHON.

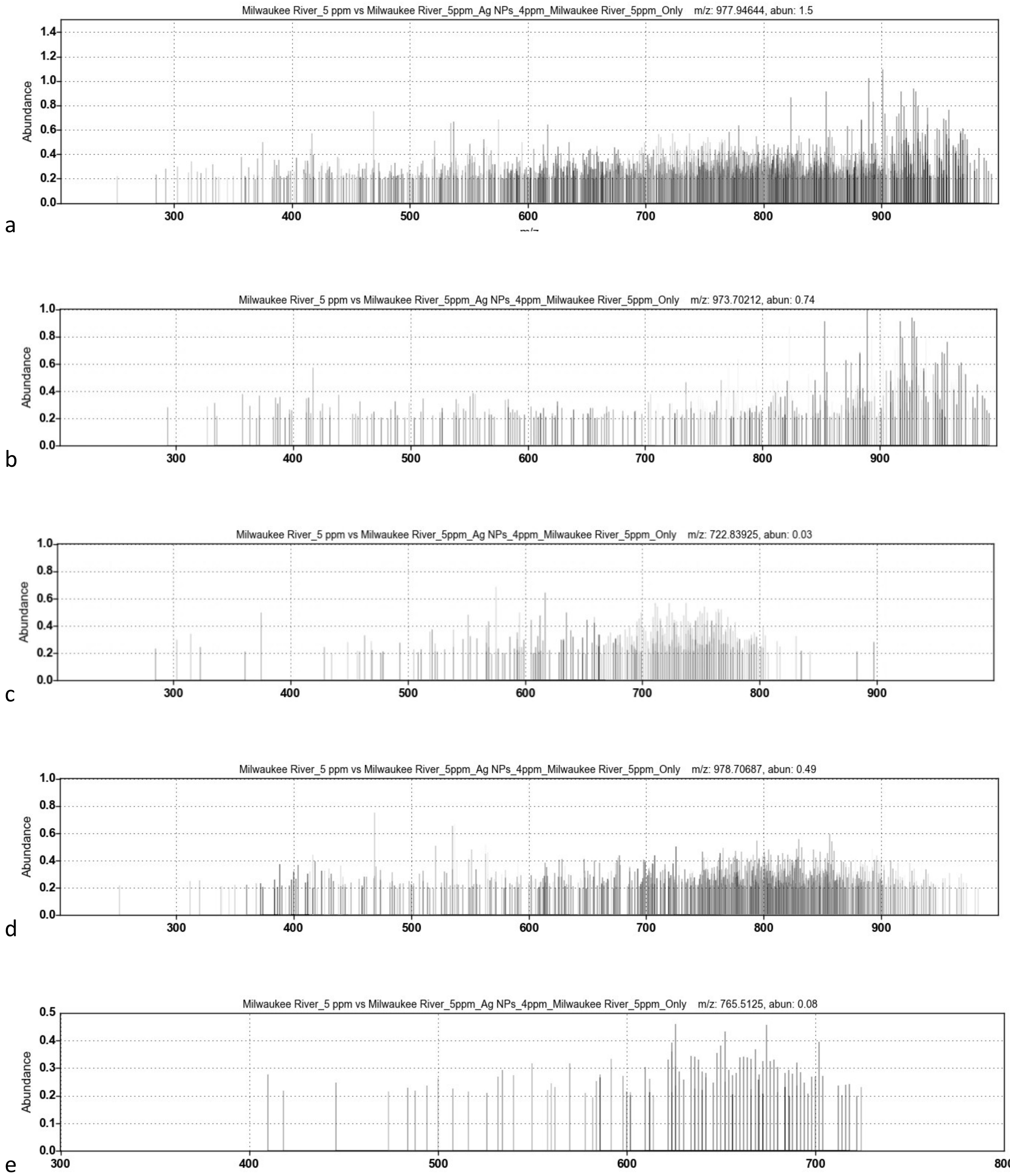


Figure S4. ESI-FT-ICR-MS spectra of the Ag NM NOM-corona formed by interactions with the Milwaukee River NOM: (a) all formulas, (b) CHO, (c) CHOS, (d) CHON, and (e) CHONS.

Fluorescence EEM spectra of NOM

Fluorescence excitation-emission matrices (EEMs) of NOM samples are shown in **Figure S5**. Both samples primarily contain humic-like DOM components. However, the MRNOM sample contains more protein-like fluorescent DOM components compared to the Yukon River NOM.

The humification Index (HIX), the ratio of the integration of fluorescence between 300-345 nm and 435-480 nm / excitation at 254 nm, correlates to the degree of decomposition and humification.[1] Low HIX values (HIX < 5) correlate with biological production and lower degree of decomposition, and high HIX values (HIX >11) indicate mostly highly decomposed and humified humic DOM. The biological index (BIX), the ratio of fluorescence intensity at 380 nm to that at 430 nm at excitation wavelength of 310 nm,[1] could indicate aquagenic DOM [2].

The HIX values were 16.57 for the YRNOM and 2.66 for the MRDOM, (**Table S1**), which shows a significant humification state where the YRNOM contains organic materials with a higher degree of humification. However, both NOM samples had BIX values <0.6 (**Table S1**), which suggests low abundance of autochthonous or biogenic DOM compounds. The BIX/HIX ratio for the MRNOM sample (0.21) is nearly an order of magnitude higher than the YRNOM sample (0.023) indicating that the MRNOM contains significantly more biogenic DOM compounds, as highlighted in the EEM spectra (**Figure S5**).

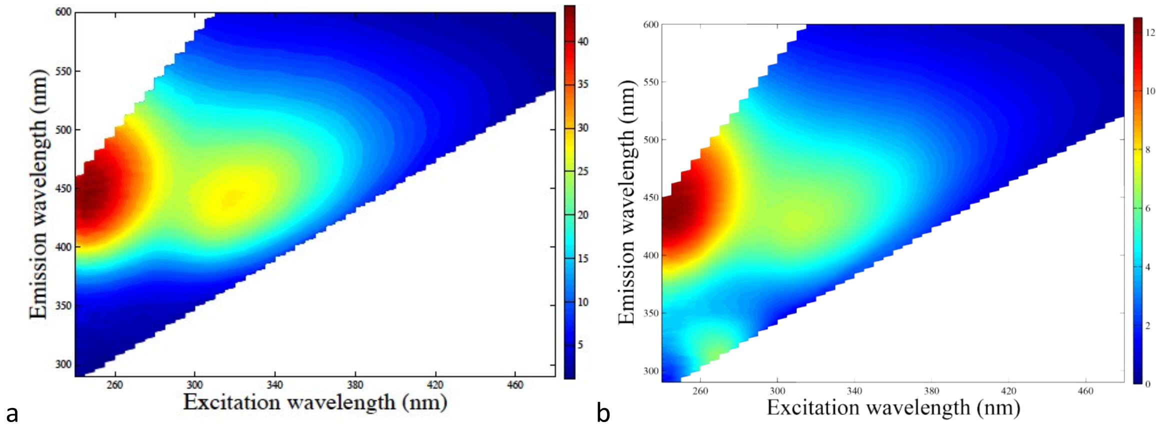


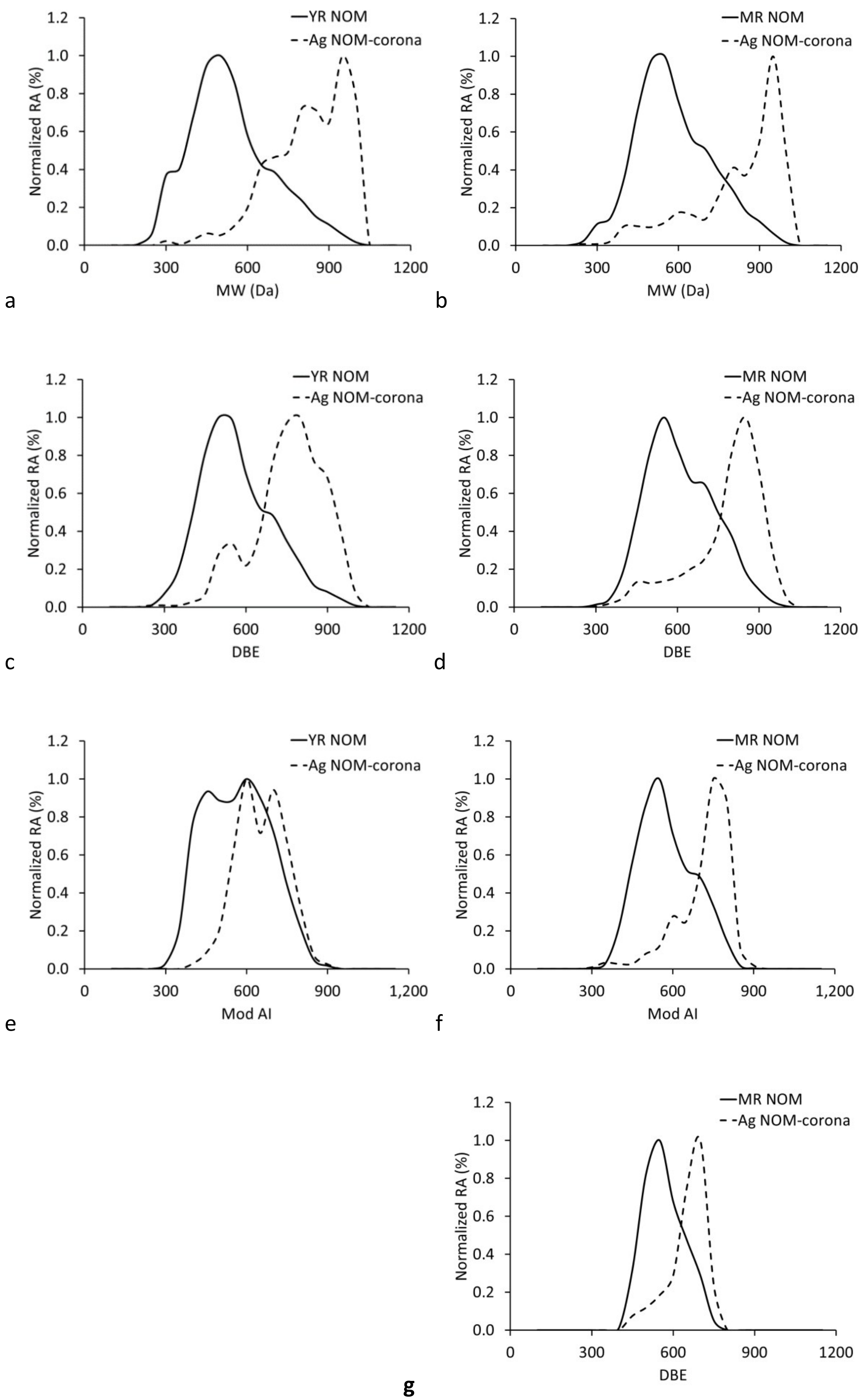
Figure S5. Fluorescence excitation-emission spectra of the two NOM samples from (a) the Yukon River (YRNOM) and (b) Milwaukee River estuary (MRNOM), respectively.

Table S2. Comparisons in optical properties between the two DOM samples used for the experiments

Sample ID	Description	FIX	HIX	BIX	BIX/HIX
YRNOM	From the Yukon River, > 1 kDa HMW-DOM	1.03	16.57	0.39	0.023
MRNOM	From the Milwaukee River, > 1 kDa HMW-DOM	1.14	2.66	0.56	0.210

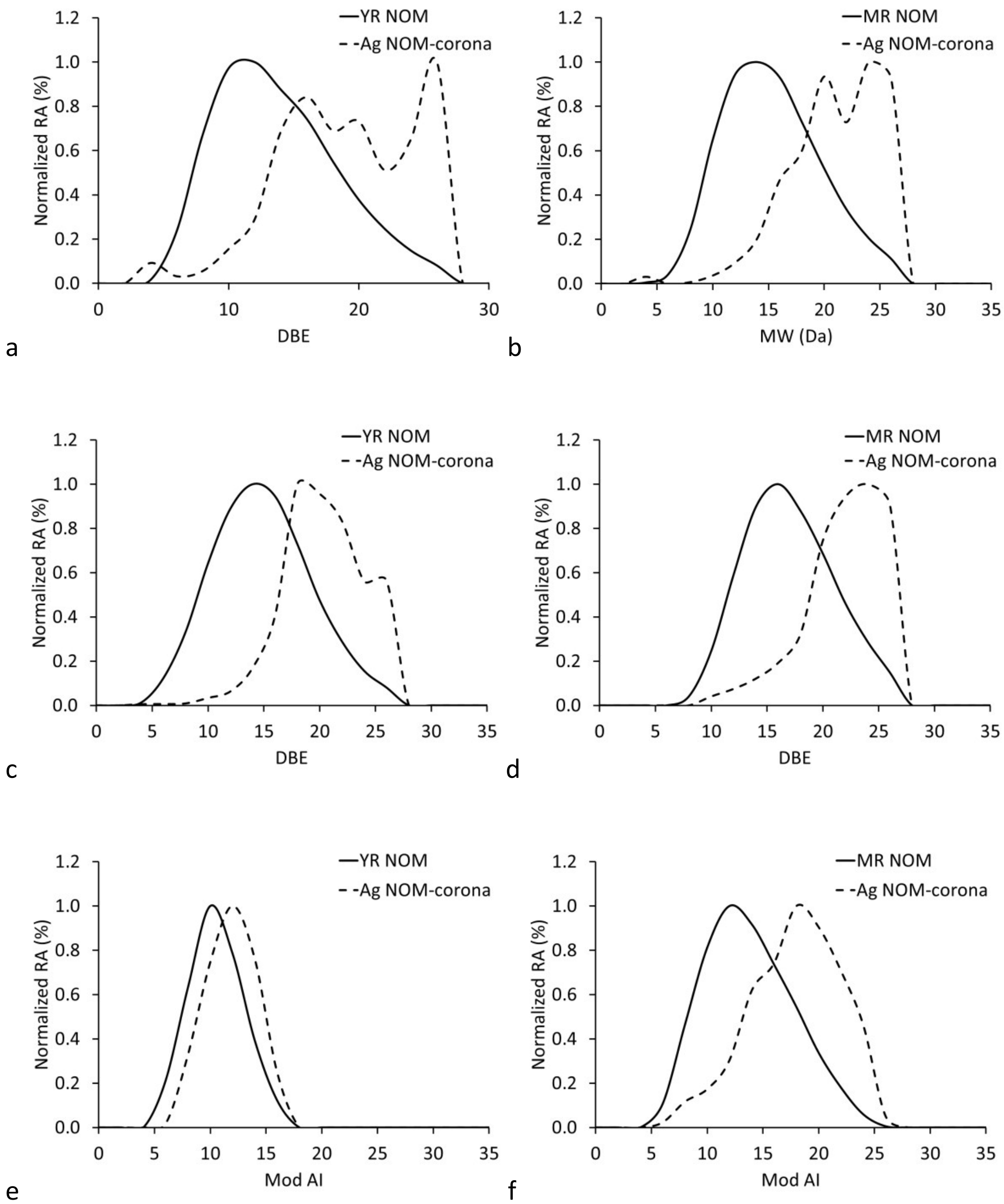
Table S3. Biogeochemical classes of NOM and Ag NOM-corona and their relative abundance in each class of heteroatom class of compounds

		Condensed polycyclic aromatics	Phenolics	Highly unsaturated and phenolics	aliphatic
NOM					
YR NOM	All	4.1	16.1	75.6	4.2
	CHO	4.2	16.3	75.8	3.7
	CHOS	0.0	2.3	75.3	22.4
	CHON	4.3	17.2	74.1	4.4
	CHONS	-	-	-	-
MR NOM	All	3.8	19.9	75.3	1.0
	CHO	4.0	19.2	75.6	1.2
	CHOS	1.3	14.9	80.5	3.3
	CHON	3.9	22.3	73.7	0.1
	CHONS	3.1	28.4	68.5	0.0
Ag NOM-corona					
YR NOM-corona	All	5.8	12.1	70.7	11.4
	CHO	11.2	15.2	65.6	8.0
	CHOS	0.1	2.6	68.5	28.8
	CHON	6.9	17.2	75.2	0.8
	CHONS	-	-	-	-
MR NOM-corona	All	9.3	18.2	71.8	0.7
	CHO	14.0	15.7	69.0	1.3
	CHOS	2.1	16.1	79.7	2.0
	CHON	9.3	19.3	71.5	0.0
	CHONS	8.6	27.9	63.5	0.0



YR NOM
Ag NOM-corona
Normalized RA (%)
MW (Da)
a
MR NOM
Ag NOM-corona
Normalized RA (%)
MW (Da)
b
YR NOM
Ag NOM-corona
Normalized RA (%)
DBE
c
MR NOM
Ag NOM-corona
Normalized RA (%)
DBE
d
YR NOM
Ag NOM-corona
Normalized RA (%)
Mod AI
e
MR NOM
Ag NOM-corona
Normalized RA (%)
Mod AI
f
MR NOM
Ag NOM-corona
Normalized RA (%)
DBE
g

Figure S6. Molecular weight distributions of different classes of compounds in original YRNOM and MRNOM and the corresponding AgNM-NOM-corona (a, b) CHO, (c, d) CHON, (e, f) CHOS, and (g) CHONS



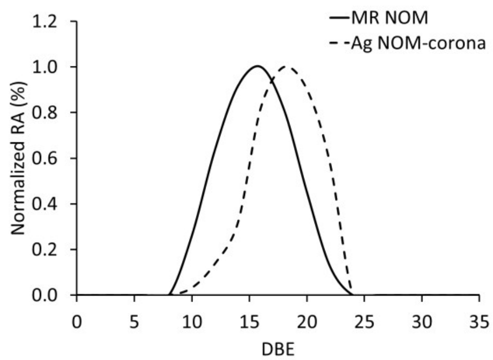


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Figure S7. DBE distribution of different classes of compounds in original YRNOM and MRNOM and the corresponding Ag NOM-corona (a, b) CHO, (c, d) CHON, (e, f) CHOS, and (g) CHONS

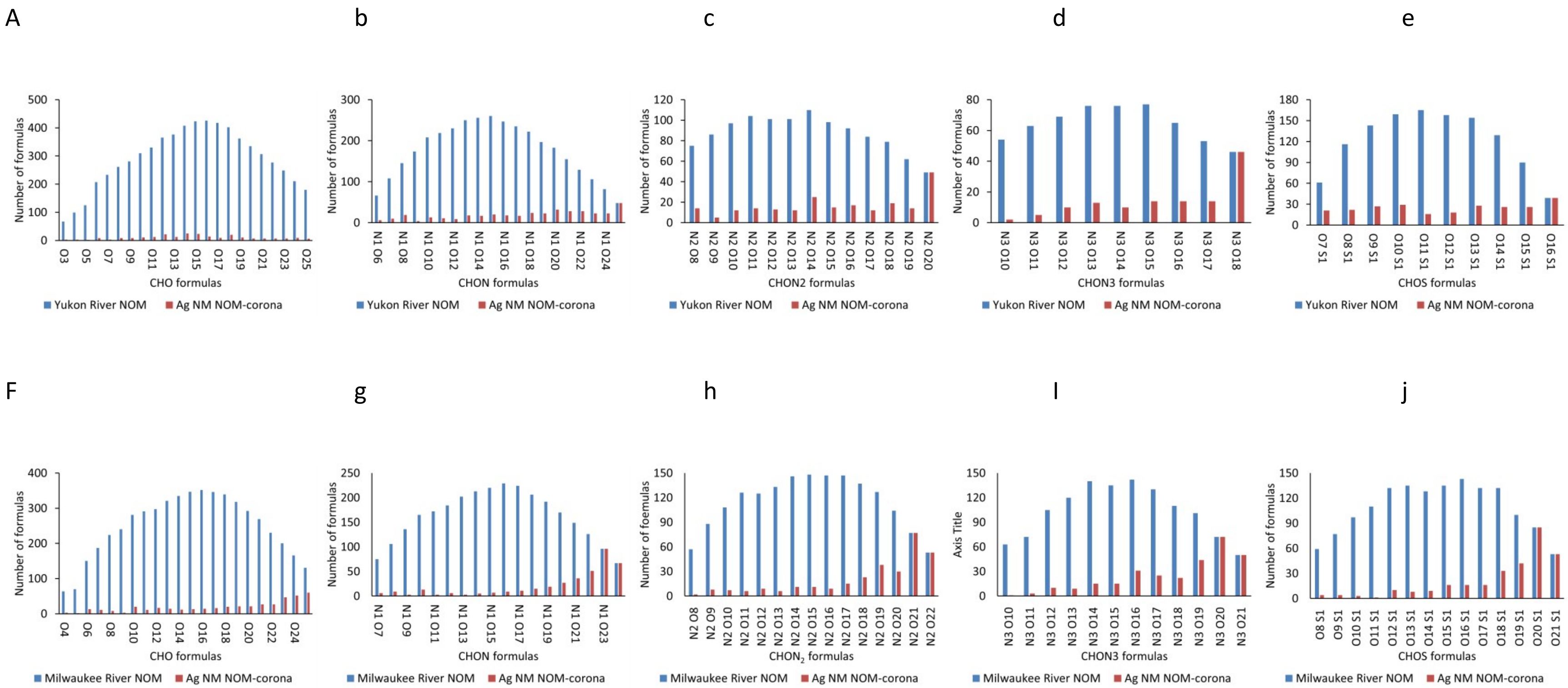

Figure S8. Number of molecules in (first raw) Yukon River NOM and (second raw) Milwaukee River NOM and Ag NM NOM-corona formed from the corresponding NOM as a function of number of oxygen in each formula for each class of formula

References

1. **Huguet, A.; Vacher, L.; Relexans, S. p.; Saubusse, S.; Froidefond, J. M.; Parlanti, E. Properties of fluorescent dissolved organic matter in the Gironde Estuary. *Organic Geochemistry* 2009, *40* (6), 706-719.**

2. **Zhou, Z.; Guo, L.; Minor, E. C. Characterization of bulk and chromophoric dissolved organic matter in the Laurentian Great Lakes during summer 2013. *Journal of Great Lakes Research* 2016, *42* (4), 789-801.**