Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Impact of Bromide Exposure on Natural Organochlorine Loss from Coastal Wetland Soils

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Supplementary Information

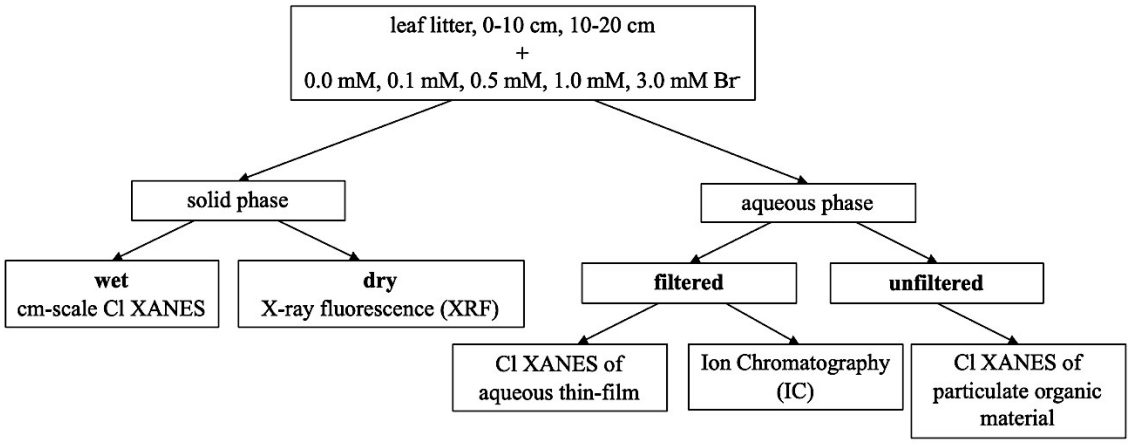

Fig. S1) Methods flow chart indicating solid and aqueous phase extracts and by which method each portion was analyzed.

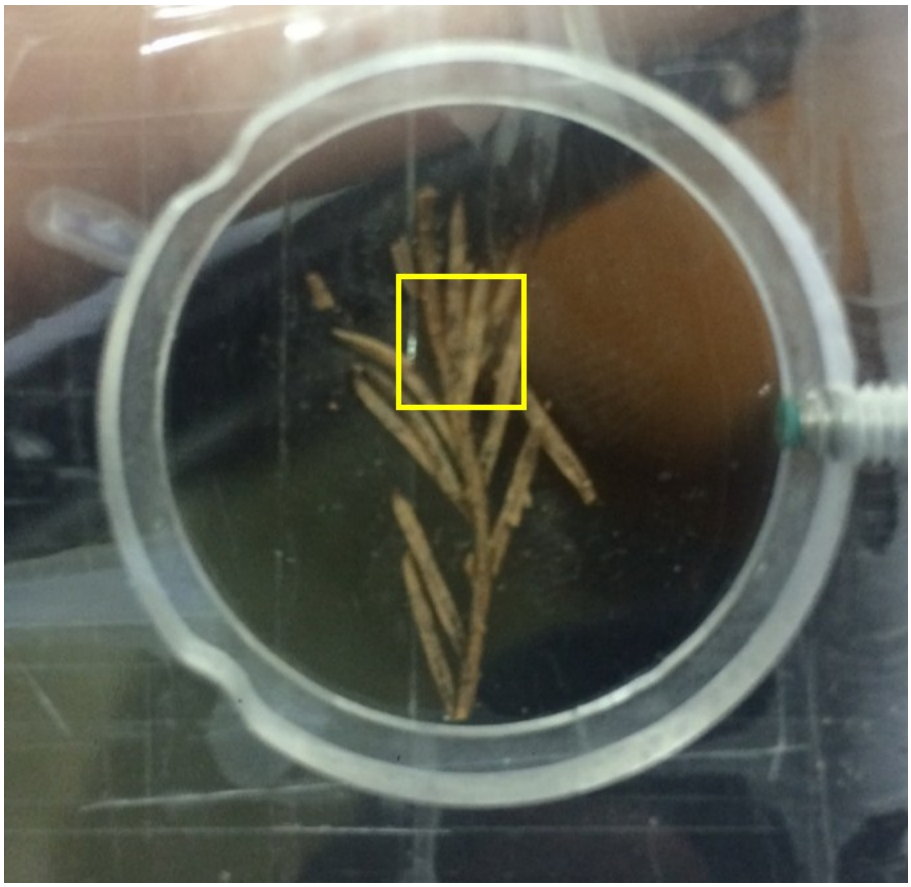

Fig. S2) Example of leaf litter mounted on sample plate for *in-situ* synchrotron XANES spectroscopic analysis. The image shows weathering bald cypress leaf prior to spectromicroscopy mapping at both Cl and Br K-edges, shown in Fig. 3. The yellow box indicates the area of the leaf that was imaged during the X-ray spectromicroscopy.

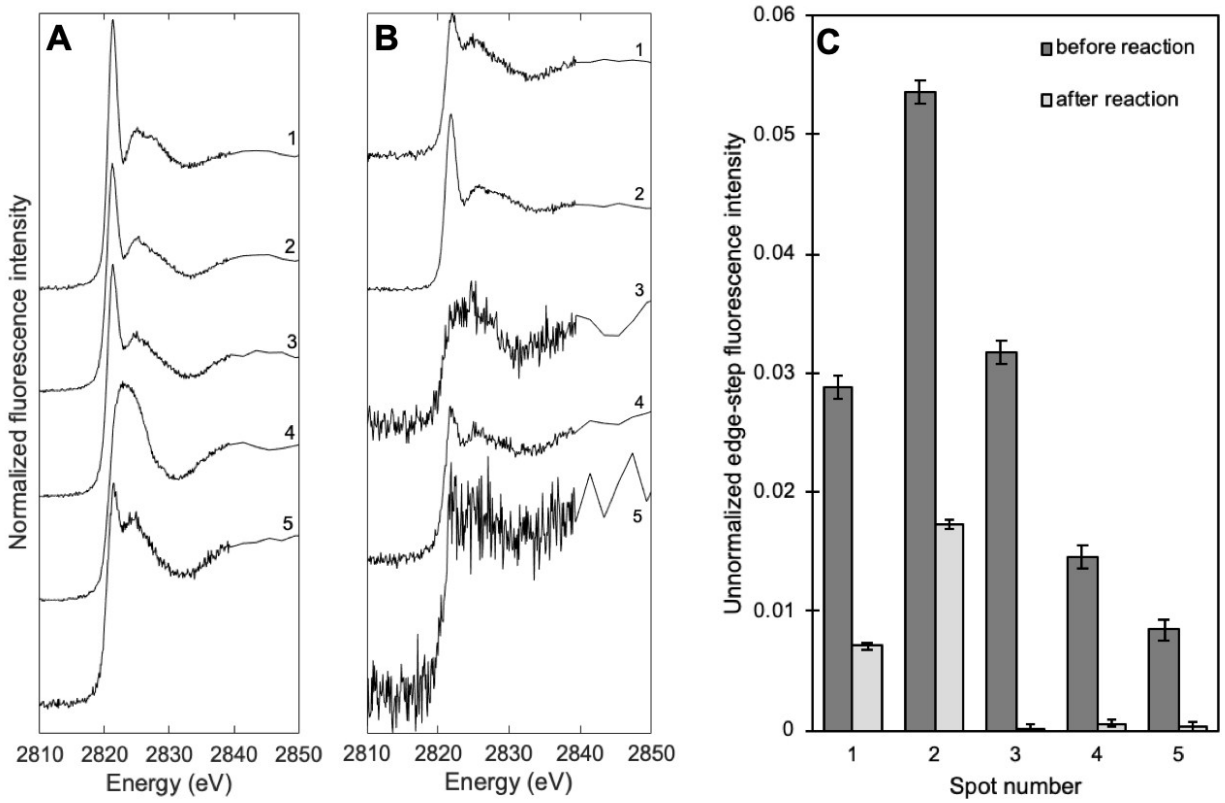

Fig. S3) μ-XANES spectroscopic analysis of Cl hotspots from leaf maps shown in Fig. 3. Spot numbers correspond to spots shown on map **A** in Fig. 3. **A**: Cl μ-XANES spectra of Cl-hotspots before reaction with Br^-; **B**: Cl μ-XANES spectra of same hotspots after reaction with 0.1 mM Br^-; LCF analysis of both spectra before and after reaction is shown in Table S2. **C**: Estimated Cl abundances in hotspots using unnormalized Cl μ-XANES spectra. The same spots were analyzed before and after reaction.

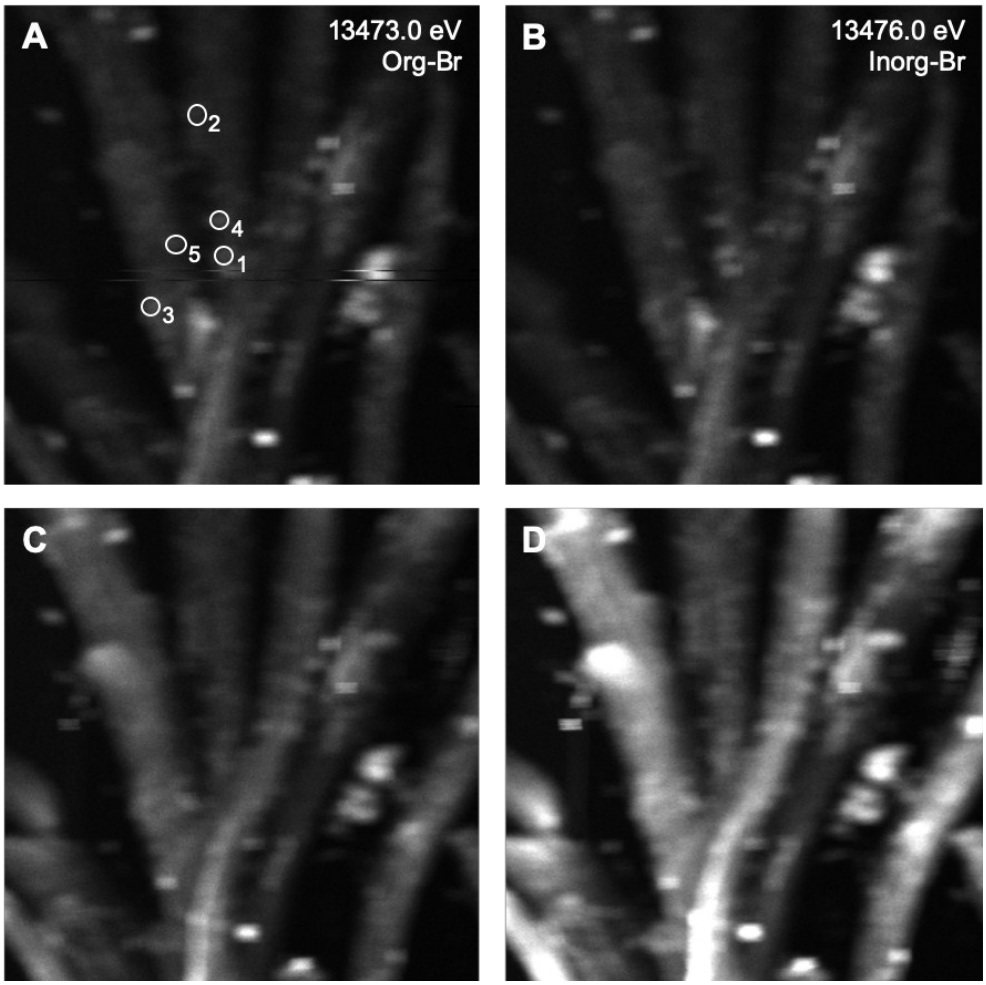

Fig. S4) Br-speciation (spectromicroscopy) maps of leaf litter before and after reaction with 0.1 mM Br^-. Maps **A** and **B** show the leaf samples before reaction with Br^-, and **C** and **D** show the same after reaction with Br^-. Maps **A** and **C** were collected at the org-Br edge (13473.0 eV). Maps **B** and **D** were collected at the inorg-Br edge energy (13476.0 eV). Because the energy difference between org-Br_{ali} and org-Br_{arom} is too small to differentiate for speciation maps, only one map at the org-Br edge energy was collected. Spots 1-5, marked in map **A**, are locations where Br K-edge μ-XANES were collected both before and after reaction with Br^- (Fig. S5).

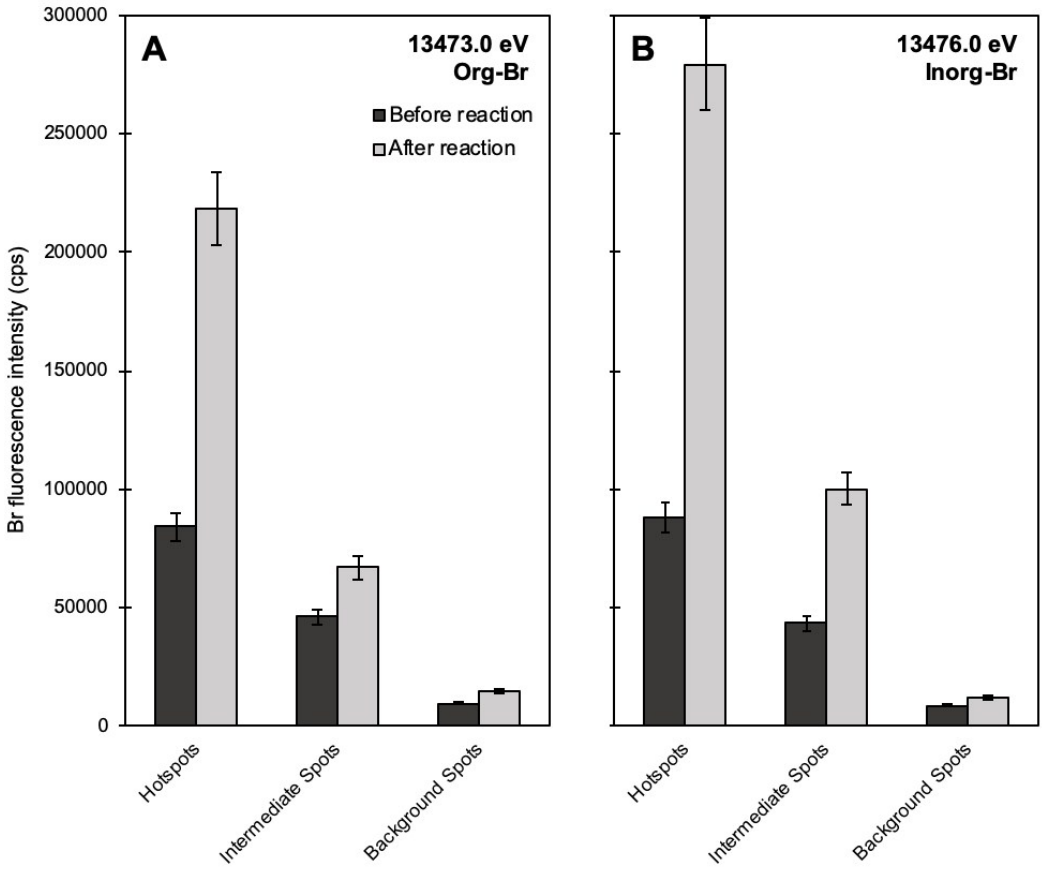

Fig. S5) Changes in Br abundance in hotspots, intermediate spots, and background spot regions in leaf litter before and after reacting with 0.1 mM Br^-. These data are derived from spectromicroscopy studies of leaf litter shown in Fig. S3. **A:** Org-Br (13473.0 eV) and **B:** Inorg-Br (13476.0 eV). The same spots were measured before and after reaction for comparison. Description of CPS used in distinguishing hotspots from others is included in main text.

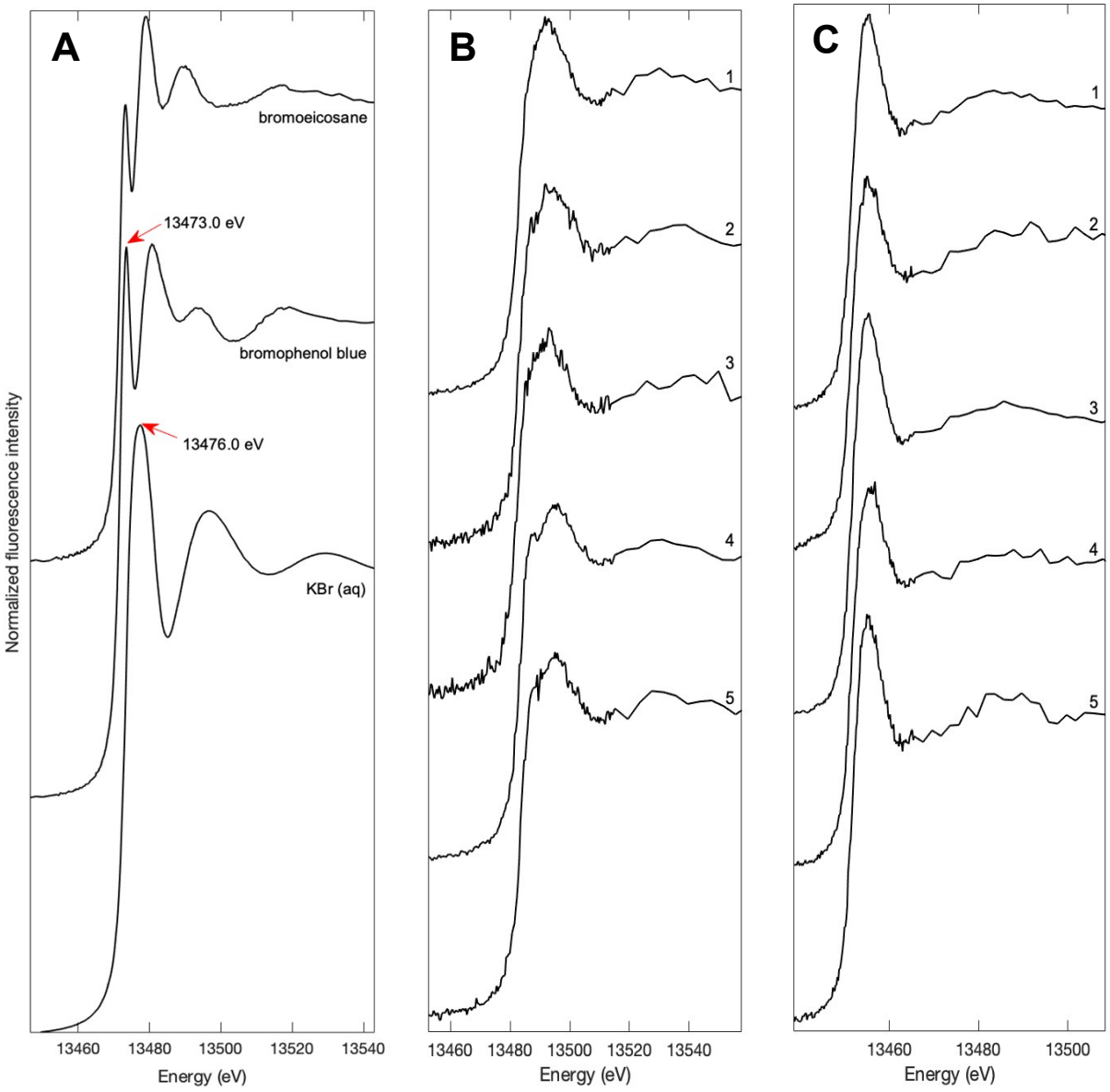

Fig. S6) Br XANES standards (A) and μ-XANES analysis of Br spots from leaf maps shown in Fig. S3. Spot numbers correspond to spots shown on map A in Fig. S3. **B:** μ-XANES of Br spots before reaction with 0.1 mM Br^-, **C**: μ-XANES of Br spots after reaction with 0.1 mM Br^-. The same spots were analyzed before and after reaction. Arrows in panel **A** indicate edge energies for Br in different bonding environments, and these energies are used in Br-speciation maps presented in Fig. S3. LCF analysis of these spectra is shown in Table S3.

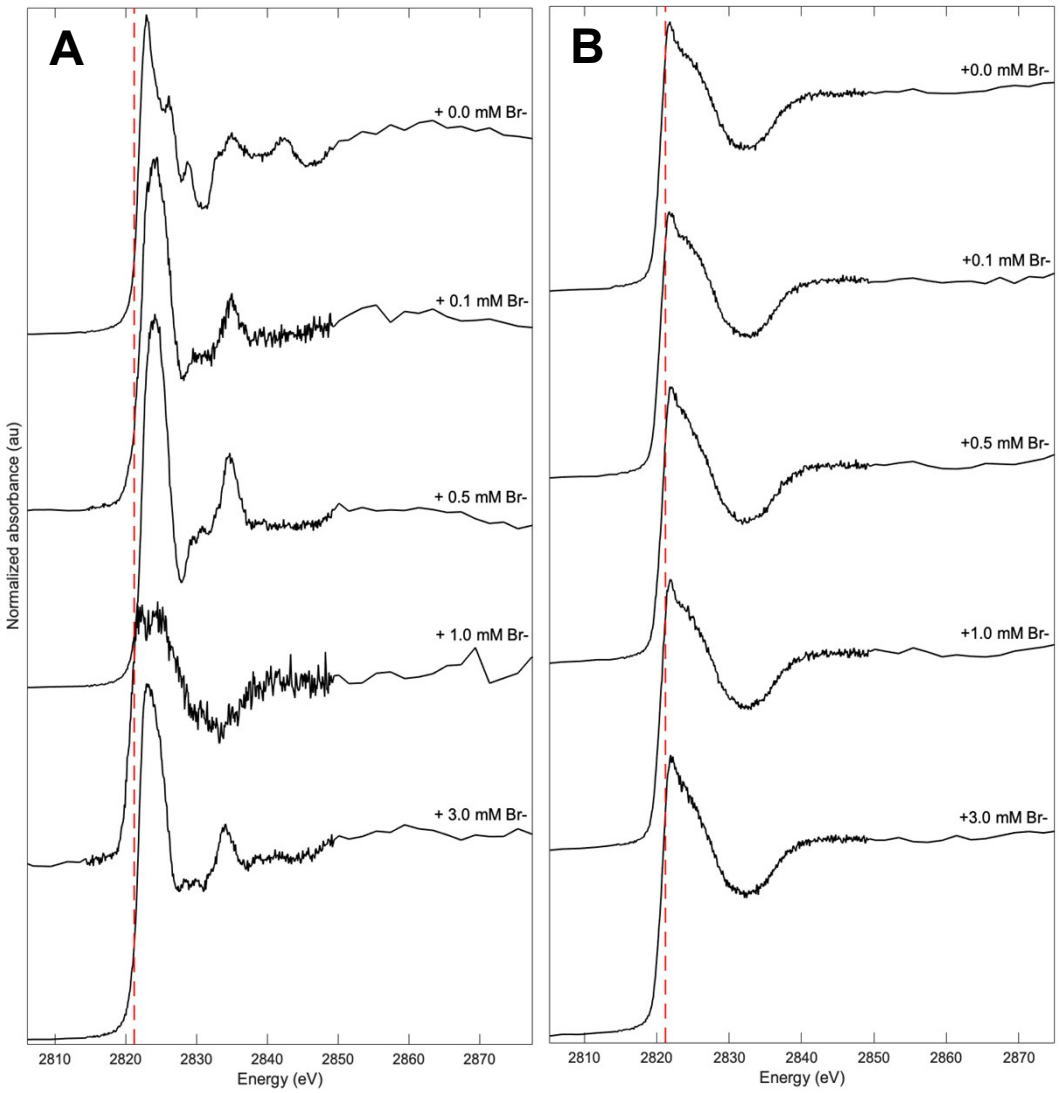

Fig. S7) Cl speciation analyzed using XANES spectroscopy. **A:** aqueous filtrates collected from leaf litter samples reacted with Br^- and analyzed with IC, **B**: particulate organic matter filtered from leaf litter samples reacted with Br^-. The red dashed line indicates the org-Cl_{arom} edge energy at 2821.1 eV (the org-Cl_{ali} edge energy falls below this at 2820.5 eV), showing that particulate organic matter contains a higher percentage of org-Cl character, whereas the aqueous phase contains majority inorg-Cl species (Table S4).

Table S1: Cl speciation variations in leaf litter and soil samples exposed to Br^-. Weighted speciation is from LCF analysis of bulk XANES spectra of samples with Cl standards (Fig. 1). R-factor indicates precision of fit. Estimated fit error is ±3%.

Depth	Br^- added (mM)	Inorganic Cl^-	Inorganic H-Cl	Org-Cl_{ali}	Org-Cl_{arom}	R-factor
Leaf Litter	**0**	0.00	0.50	0.11	0.39	0.0027
	0.1	0.00	0.40	0.29	0.31	0.0025
	1.0	0.00	0.60	0.11	0.33	0.0080
	3.0	0.07	0.61	0.09	0.23	0.0745
0-10 cm	**0**	0.45	0.00	0.30	0.31	0.0138
	0.1	0.00	0.41	0.21	0.35	0.0041
	1.0	0.00	0.44	0.11	0.50	0.0076
	3.0	0.24	0.54	0.05	0.13	0.0233
10-20 cm	**0**	0.11	0.50	0.13	0.21	0.0099
	0.1	0.00	0.52	0.22	0.31	0.0063
	1.0	0.00	0.50	0.13	0.38	0.0040
	3.0	0.48	0.30	0.08	0.13	0.0356

Table S2. Cl hotspot speciation variations in leaf litter surface exposed to Br^-. Weighted speciation is from LCF analysis of μ-XANES spectra of samples with Cl standards (Fig. S2). R-factor indicates precision of fit. Estimated fit error is ±3%.

	Before reaction with 0.1 mM Br^-				
Spot Number	**Inorganic Cl^-**	**Inorganic H-Cl**	**Org-Cl_{ali}**	**Org-Cl_{arom}**	**R-factor**
1	0.00	0.27	0.02	0.68	0.0049
2	0.00	0.298	0.164	0.48	0.0029
3	0.00	0.38	0.12	0.48	0.0035
4	0.00	0.85	0.15	0.09	0.0051
5	0.00	0.55	0.18	0.33	0.0046
	After reaction with 0.1 mM Br^-				
Spot Number	**Inorganic Cl^-**	**Inorganic H-Cl**	**Org-Cl_{ali}**	**Org-Cl_{arom}**	**R-factor**
1	0.04	0.65	0.00	0.26	0.0271
2	0.27	0.317	0.00	0.37	0.0572
3	0.46	0.31	0.12	0.002	0.0746
4	0.00	0.68	0.02	0.35	0.0337
5	0.00	1.00	0.12	0.36	0.1242

Table S3. Br hotspot speciation variations in leaf litter surface exposed to Br^-. Weighted speciation is from LCF analysis of μ-XANES spectra of samples with Br standards: 1-bromoeicosane (aliphatic C-Br), bromophenol blue (aromatic C-Br), and KBr (aq) and ethidium bromide (inorganic Br^-) (Fig. S5). Estimated fit error is ±3%.

Before reaction with 0.1 mM Br^-				
Spot Number	**Inorganic Br^-**	**Org-Br_{ali}**	**Org-Br_{arom}**	**R-factor**
1	0.60	0.11	0.39	0.0094
2	0.57	0.13	0.41	0.0076
3	0.47	0.26	0.40	0.0275
4	0.45	0.22	0.39	0.0034
5	0.55	0.11	0.41	0.0025
	After reaction with 0.1 mM Br^-			
Spot Number	**Inorganic Br^-**	**Org-Br_{ali}**	**Org-Br_{arom}**	**R-factor**
1	0.64	0.09	0.35	0.0271
2	0.63	0.10	0.35	0.0293
3	0.75	0.02	0.34	0.0241
4	0.64	0.12	0.34	0.0158
5	0.76	0.01	0.34	0.0224

Table S4: Cl speciation variations in filtrates and particulate organic matter from bulk leaf litter and 0-10 cm samples exposed to Br^-. Weighted speciation is from LCF analysis of bulk XANES spectra of samples with Cl standards (Fig. S6). R-factor indicates precision of fit. Estimated fit error is ±3%.

Aqueous Filtrates:						
Depth	**Br^- added (mM)**	**Inorganic Cl^-**	**Inorganic H-Cl**	**Org-Cl_{ali}**	**Org-Cl_{arom}**	**R-factor**
Leaf Litter	**0**	0.51	0.49	0.00	0.00	0.0354
	0.1	0.80	0.26	0.00	0.00	0.0242
	0.5	1.00	0.06	0.00	0.00	0.0323
	1.0	0.21	0.52	0.11	0.12	0.0157
	3.0	0.59	0.47	0.00	0.00	0.0359
0-10 cm	**0**	0.99	0.07	0.00	0.00	0.0254
	0.1	1.00	0.07	0.00	0.00	0.0344
	0.5	1.00	0.10	0.00	0.00	0.0498
	1.0	0.14	0.95	0.00	0.00	0.0559
	3.0	0.32	0.76	0.00	0.00	0.0779
Particulate Organic Matter:						
Depth	**Br^- added (mM)**	**Inorganic Cl^-**	**Inorganic H-Cl**	**Org-Cl_{ali}**	**Org-Cl_{arom}**	**R-factor**
Leaf Litter	**0**	0.32	0.37	0.09	0.17	0.0059
	0.1	0.35	0.35	0.11	0.15	0.0057
	0.5	0.22	0.52	0.07	0.16	0.0056
	1.0	0.29	0.40	0.10	0.16	0.0063
	3.0	0.20	0.54	0.06	0.17	0.0058
0-10 cm	**0**	0.06	0.59	0.25	0.08	0.0011
	0.1	0.37	0.13	0.37	0.07	0.0597
	0.5	0.29	0.43	0.18	0.07	0.0048
	1.0	0.36	0.40	0.15	0.04	0.0042
	3.0	0.46	0.00	0.38	0.09	0.1003