Supporting Information

Sorption Selectivity in Natural Organic Matter Studied with Nitroxyl Paramagnetic Relaxation Probes

Charisma Lattao[a], Xiaoyan Cao[b], Yuan Li[b], Jingdong Mao[b], Klaus Schmidt-Rohr[c], Mark A. Chappell[d], Lesley F. Miller[d], Albert Leo dela Cruz[e], and Joseph J. Pignatello[a,]*

[a]*Department of Environmental Sciences, The Connecticut Agricultural Experiment Station, P.O. Box 1106, New Haven, Connecticut 06504, USA*

[b]*Department of Chemistry and Biochemistry, Old Dominion University, 4541 Hampton Blvd, Norfolk, Virginia 23529, USA*

[c]*Department of Chemistry,* Iowa State University, Hach Hall, Ames, Iowa 50010, *USA*

[d] *Environmental Laboratory, U.S. Army Corps of Engineers, 3909 Halls Ferry Rd., Vicksburg, Mississippi 39180, USA*

[e]*LSU Superfund Research Center, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70802*

* Corresponding author phone: 203-974-8518; fax: 203-974-8502. Email: Joseph.Pignatello@ct.gov

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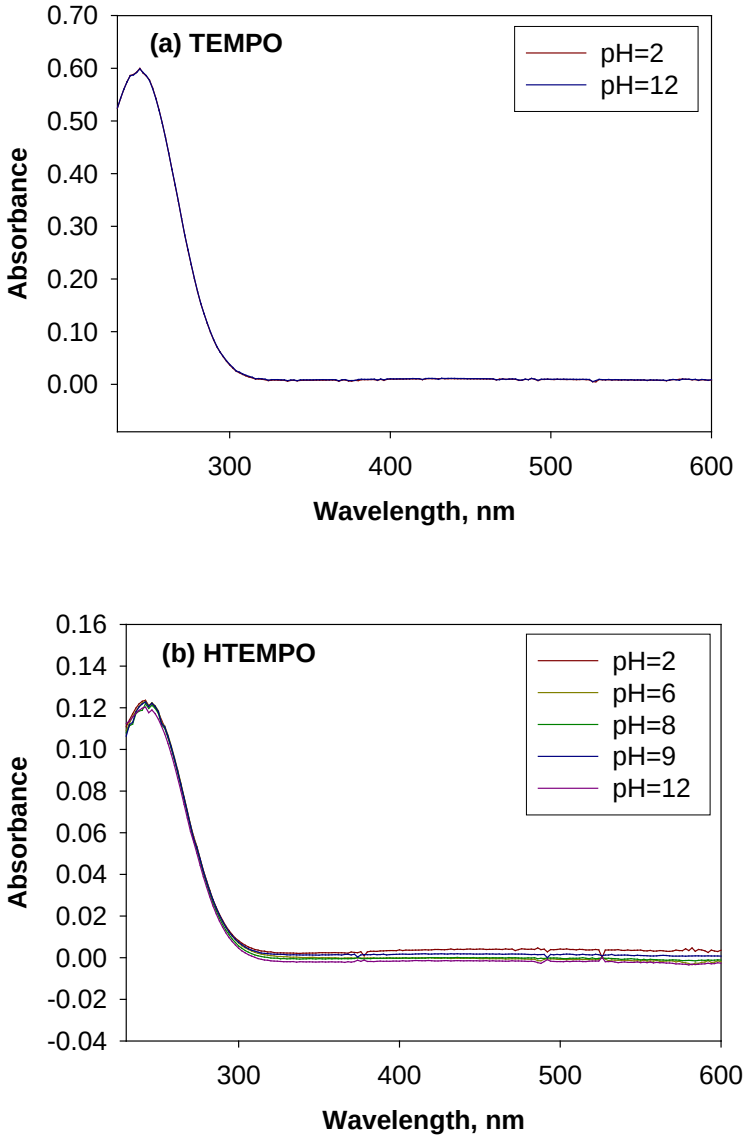


Figure S1. pH dependence of the absorption spectrum of 50 mg/L TEMPO (a) and 10 mg/L HTEMPO (b) in water indicating no acid-base dissociation behavior.

Table S1. Functional group composition (%) of sorbents based on ^{13}C NMR

Sorbent	Ar*, %	Al‡, %	ppm							
			220-192	192-164	164-143	143-110	110-94	94-62	62-46	46-0
			Aldehyde, Ketone	O-C=O, N-C=O	ArC-O, ArC-N	ArC-C, ArC-H	di-O-alkyl	O-alkyl	OCH_3, NCH	C, CH, CH_2, CH_3
Pahokee	23.4	34.2	1.5	9.7	5.7	15.1	4.8	21.5	11.3	30.3
Beulah	54.4	27.4	1.2	5.4	12.0	38.8	5.1	5.1	6.8	25.6

Sorbent	Ar*, %	Al‡, %	ppm				
			159-139	139-119	82-70	63-52	52-31
			Nonpolar ArC_1	Nonpolar ArC_{2-6}	O-alkyl	-CH-Ar, OCH_3	Alkyl
PS-PVME	48.9	37.8	10.9	38.0	5.3	8.1	37.8

Ar*: aromatic; Al‡: aliphatic

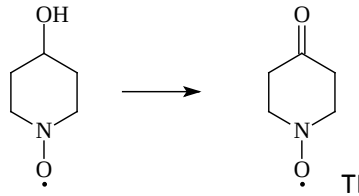
Solvent-Water and Cellulose-Water Partition Coefficients. Solvent-water partition coefficients were determined according to OECD methodology for octanol-water (shake flask method) except for the use of nanopure water rather than distilled water. The organic solvents were 1-octanol (Aldrich, 99+%, anhydrous), n-hexadecane (Acros Organics, 99%), toluene (Sigma-Aldrich, Chromasolv-Plus for HPLC, ≥99.9%) and anisole (Acros Organics, 99%). In triplicate, 2 mL water-saturated solvent, 7 mL solvent-saturated water, and 1 mL of 5000 mg/L aqueous solution of HTEMPO or TEMPO were added to 10 mL vials with PTFE-lined screw caps and the vials shaken vigorously by hand for 5 min. The vials were then centrifuged (Marathon 3000R; Fisher scientific, PA, USA) at 2000 rpm for 15 min and allowed to stand for 24 h to facilitate phase separation. The temperature during water saturation with solvent and

solvent saturation with water, centrifugation and incubation was 20±1 °C. Aliquots of water and organic phase were analyzed using HPLC or UV-Vis spectrophotometry. Calibration curves were constructed in the respective pre-saturated liquids. For the determination of partition coefficients in cellulose (20 μm, Sigma), 7 mL of 5 mg/L TEMPO or HTEMPO was added to 1g of cellulose and incubated for 6 d.

Spin Probe Extraction Recovery. Recovery of TEMPO or HTEMPO from the solid after sorption was quantified by the following procedure. First, about ≥90% of the supernatant was withdrawn, leaving the solid and ~1 mL residual liquid (the exact amount, determined by weight). The solid was then twice-extracted with 4 mL of 3:1 acetonitrile-water (ratio includes the residual water), each time tumbling for 16 h at 20 ^{o}C. The total amount of recovered sorbed probe A_{rec} was the sum of the amounts in the two extracts, after subtracting from each the amount in the supernatant of the previous step. Additional recovery in the second extraction was always less than 6% of total recovery for TEMPO (Figure S2 and S3); for HTEMPO, it was always less than 6% for Pahokee and less than 15% of the total recovery for Beulah, except in rare cases (Figure S4). EPR analysis showed that solvent extraction of the natural solids had completely removed the spins (Figure S5). Therefore, a third extraction was deemed unnecessary. The fractional recovery was calculated as the ratio of A_{rec} to the theoretical amount in the solid phase after sorption equilibrium calculated on the basis of the amount in solution and amount added and assuming no losses. Recovery of HTEMPO from PS-PVME could not be determined due to partial dissolution of polymer, which interfered with HPLC analysis.

Identification of a Spin Probe Degradation Product. The HPLC chromatograms of supernatant solutions (Figure S6a) and solvent extracts (data not shown) after sorption of HTEMPO to Pahokee reveal a peak at longer retention time than HTEMPO identified by GC-MS

per Kroll and Borchert[1] as 4-oxo-2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPONE), (Figure S6b-c):



TEMPONE (1)

TEMPONE was absent in the controls without sorbent. If TEMPONE is assumed to have the same molar absorptivity as HTEMPO, the percent recovery calculated on the basis of both compounds improves by ~3-9% depending on equilibrium concentration. The origin of TEMPONE is unclear at this time. The EPR hyperfine coupling constant is affected by the polarity of the 4-substituent[2] , suggesting the possibility that nitroxyl may facilitate oxidation of the alcoholic group at the 4-position of HTEMPO. Oxidation by iron oxides is unlikely, as addition of 1:1 mole ratio of $FeCl_3$ to HTEMPO solution did not form TEMPONE. No additional peaks in HPLC-UV and GC-MS chromatograms of sorption supernatants (Figure S7a-b) and solvent extracts (data not shown) besides parent compound were observed for TEMPO.

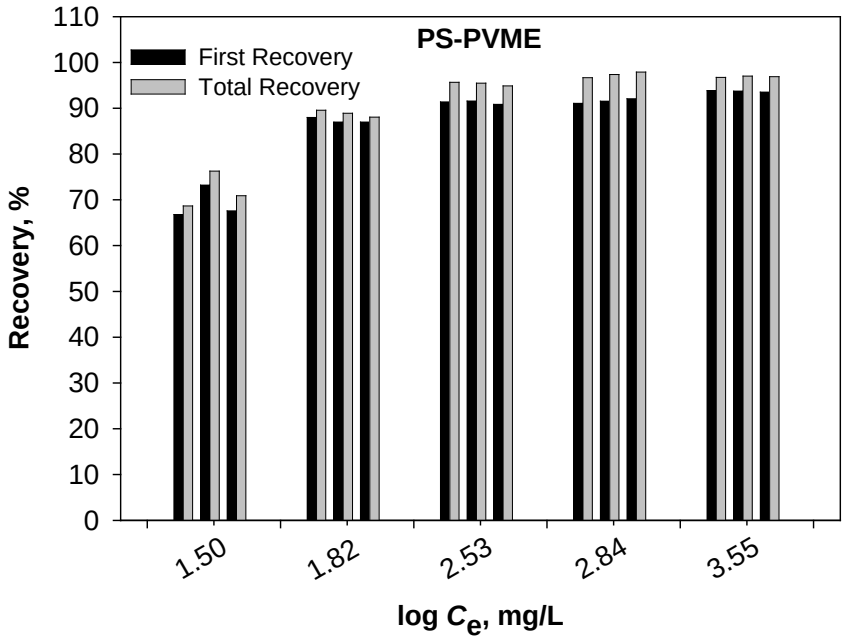


Figure S2. Recovery of TEMPO in PS-PVME in triplicate.

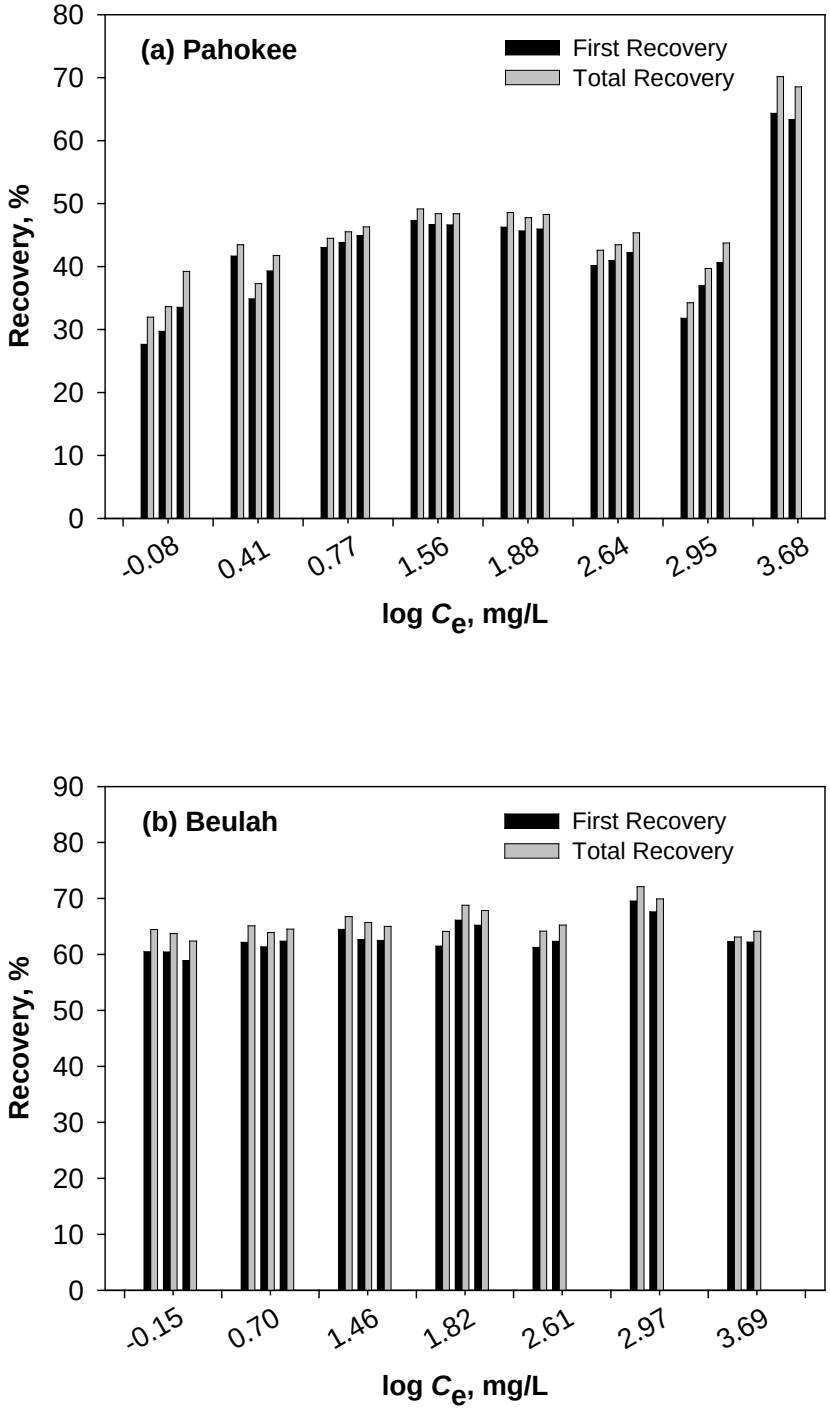
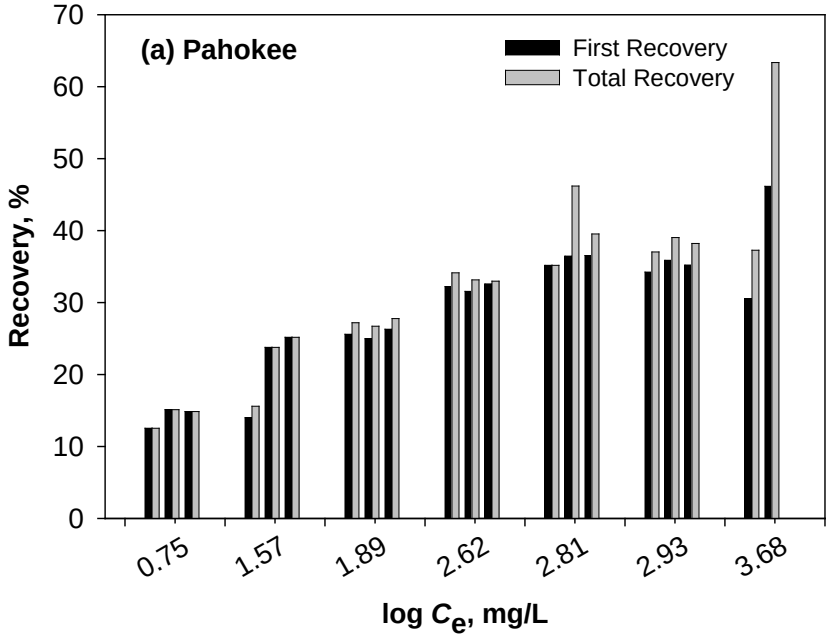


Figure S3. Recovery of TEMPO in Pahokee (a) and Beulah (b) in triplicate or duplicate.



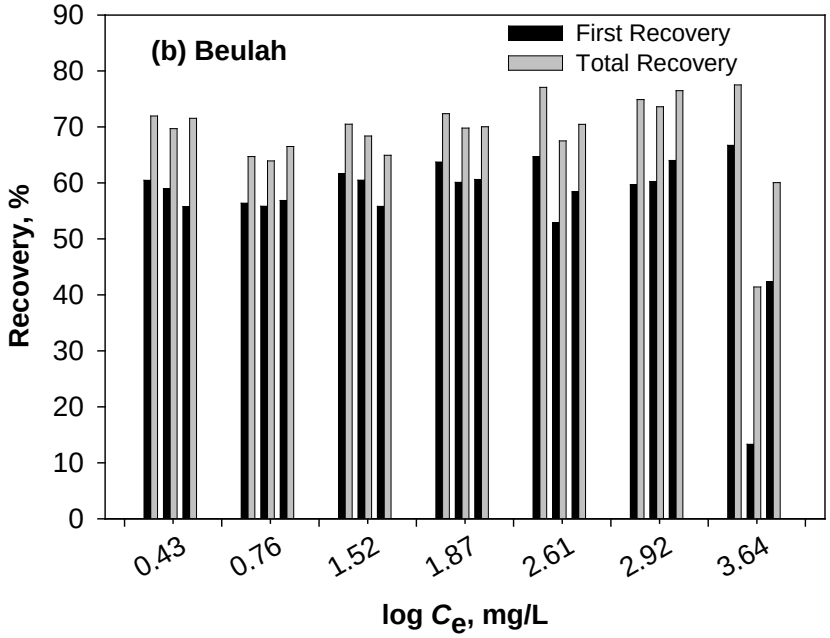


Figure S4. Recovery of HTEMPO in Pahokee (a); and Beulah (b) in triplicate or duplicate.

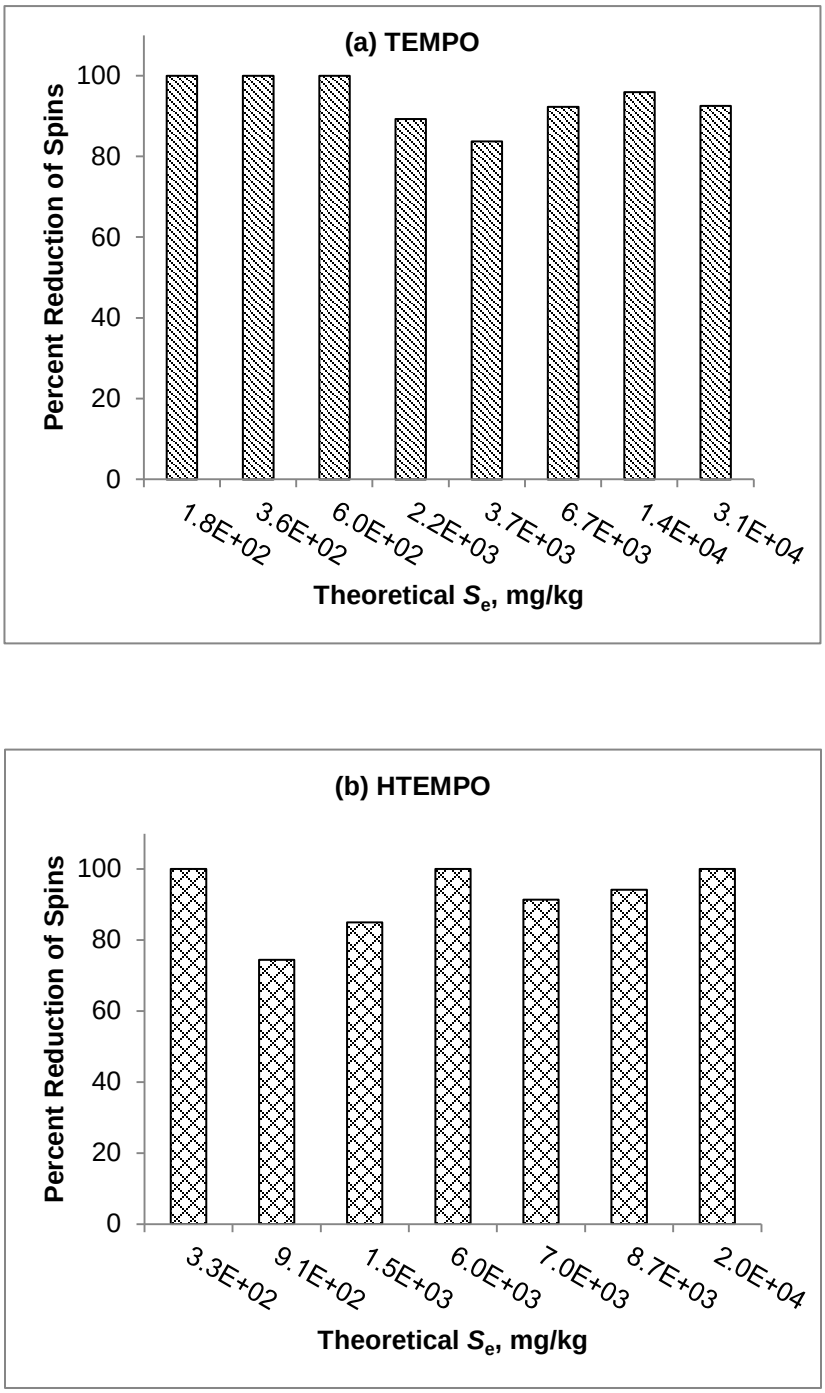


Figure S5. Recovery of spin probe based on EPR analysis of unextracted versus solvent extracted Pahokee sorbed with TEMPO (a) and HTEMPO (b).

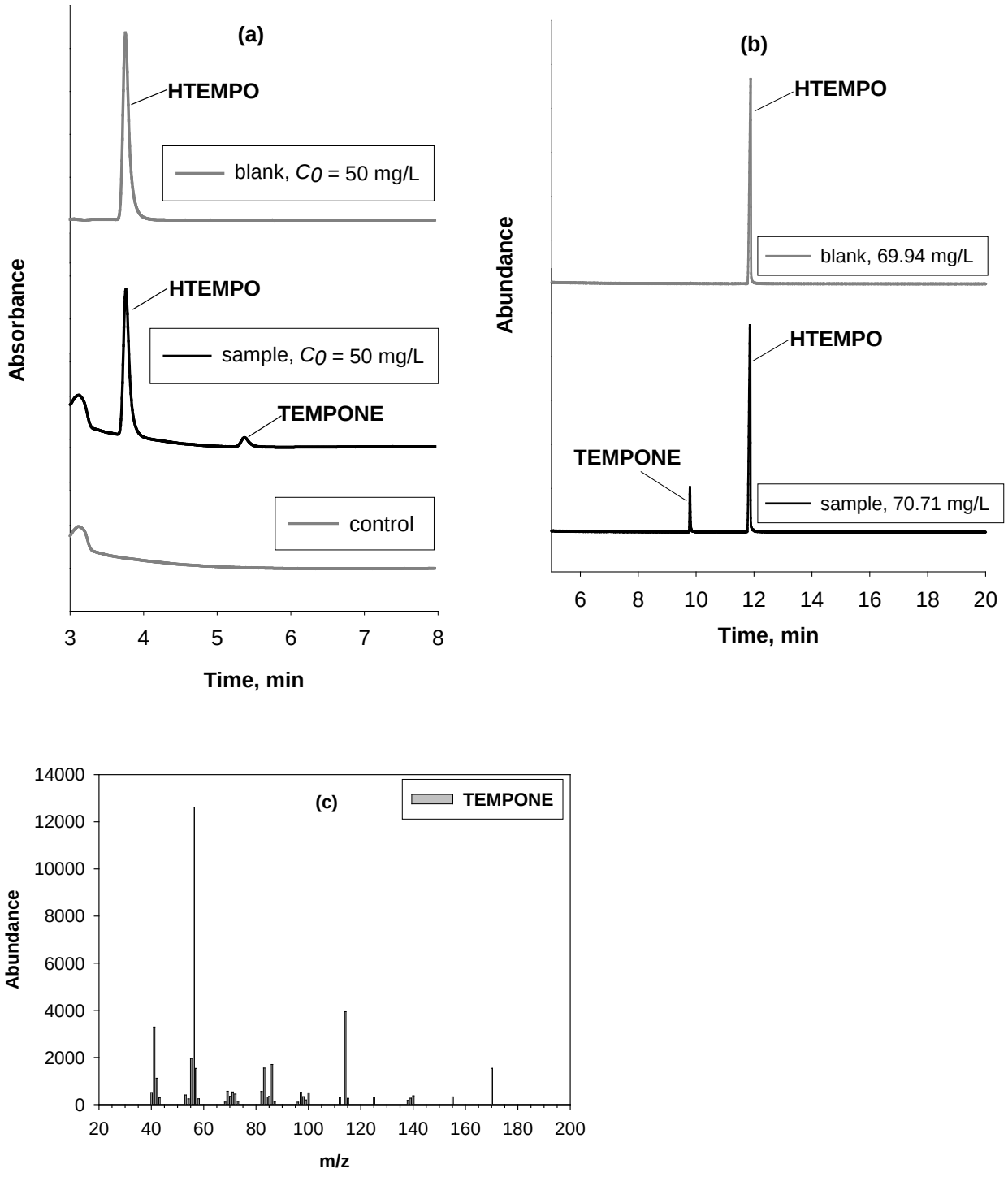


Figure S6. HPLC chromatogram of aqueous supernatant solution from HTEMPO sorption to Pahokee (a); GC-MS ion chromatogram of chloroform-extracted supernatant solution from HTEMPO sorption to Pahokee (b); and m/z ratio of GC-MS peak at retention time 9.96 min, corresponding to TEMPONE (c).

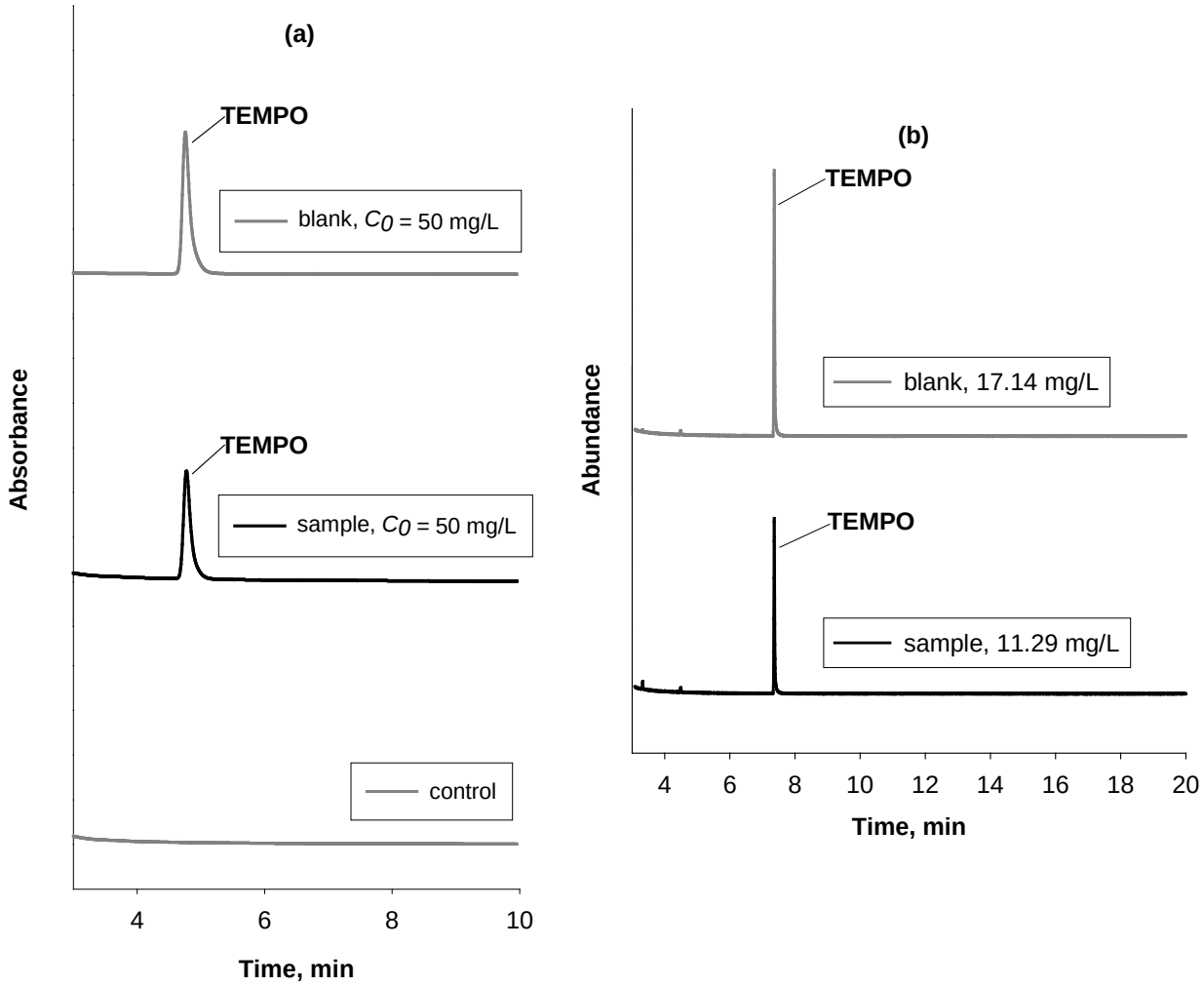


Figure S7. HPLC chromatogram of aqueous supernatant solution from TEMPO sorption to Pahokee (a); and GC-MS ion chromatogram of chloroform-extracted supernatant solution from TEMPO sorption to Pahokee (b).

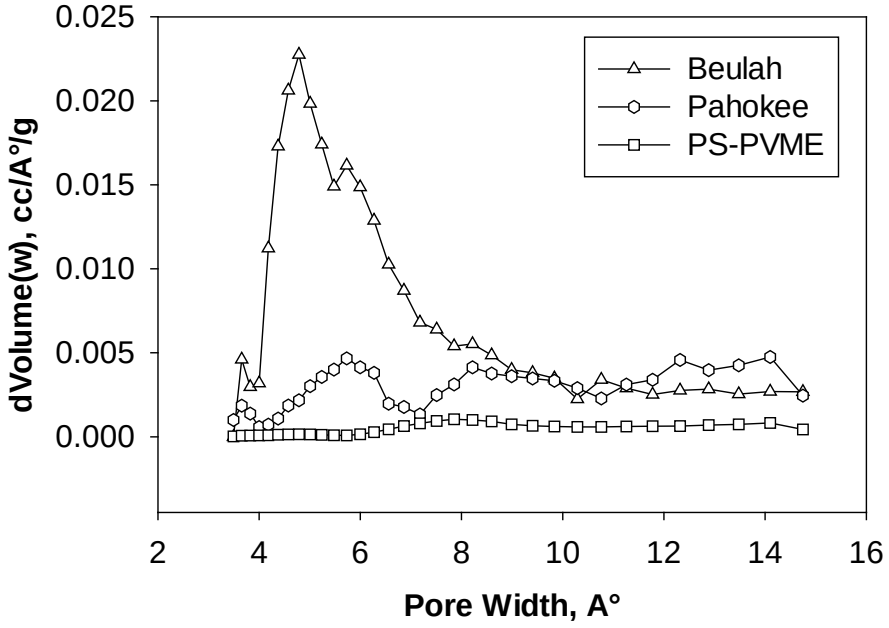


Figure S8. Pore volume histogram of sorbents determined from CO_2 adsorption at 273 K.

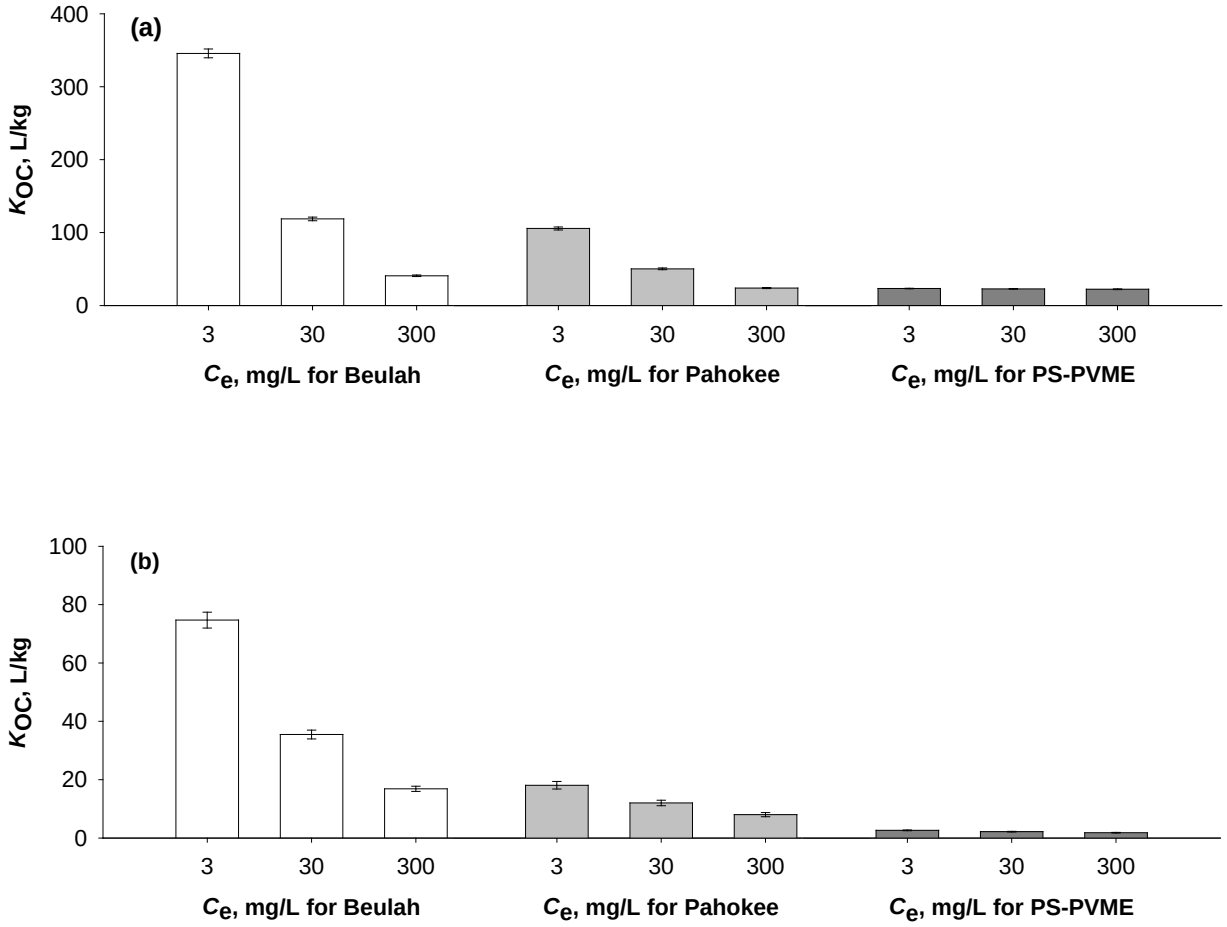


Figure S9. Organic-carbon normalized distribution coefficient at various equilibrium solution concentration for TEMPO (a) and HTEMPO (b).

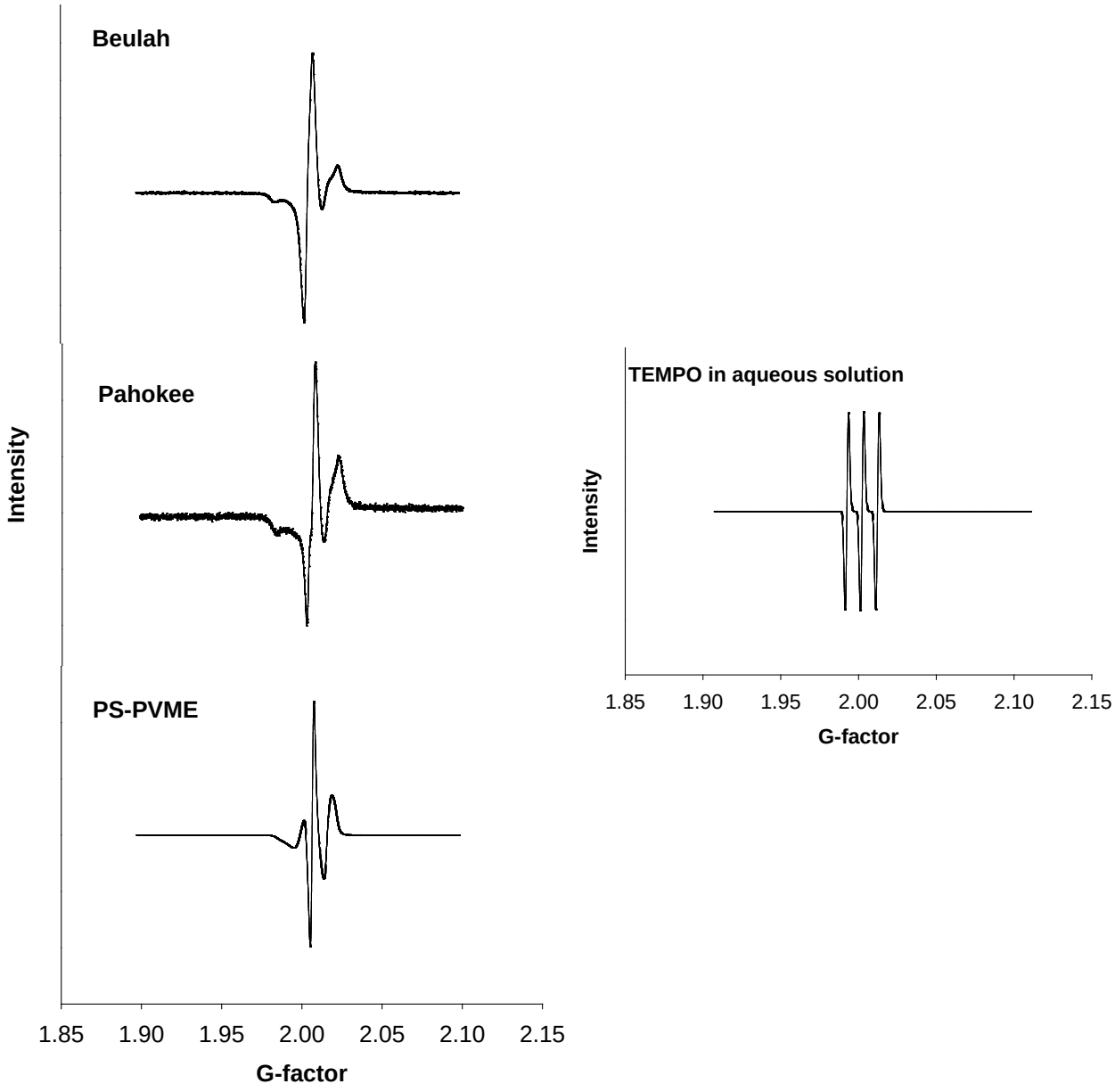


Figure S10. Electron paramagnetic resonance spectra of sorbed TEMPO from an initial solution concentration of 100 mg/L (left) and simulated EPR spectra of TEMPO in aqueous solution using an electron paramagnetic hyperfine splitting constant of 17 G (right). The axis is the g-factor.

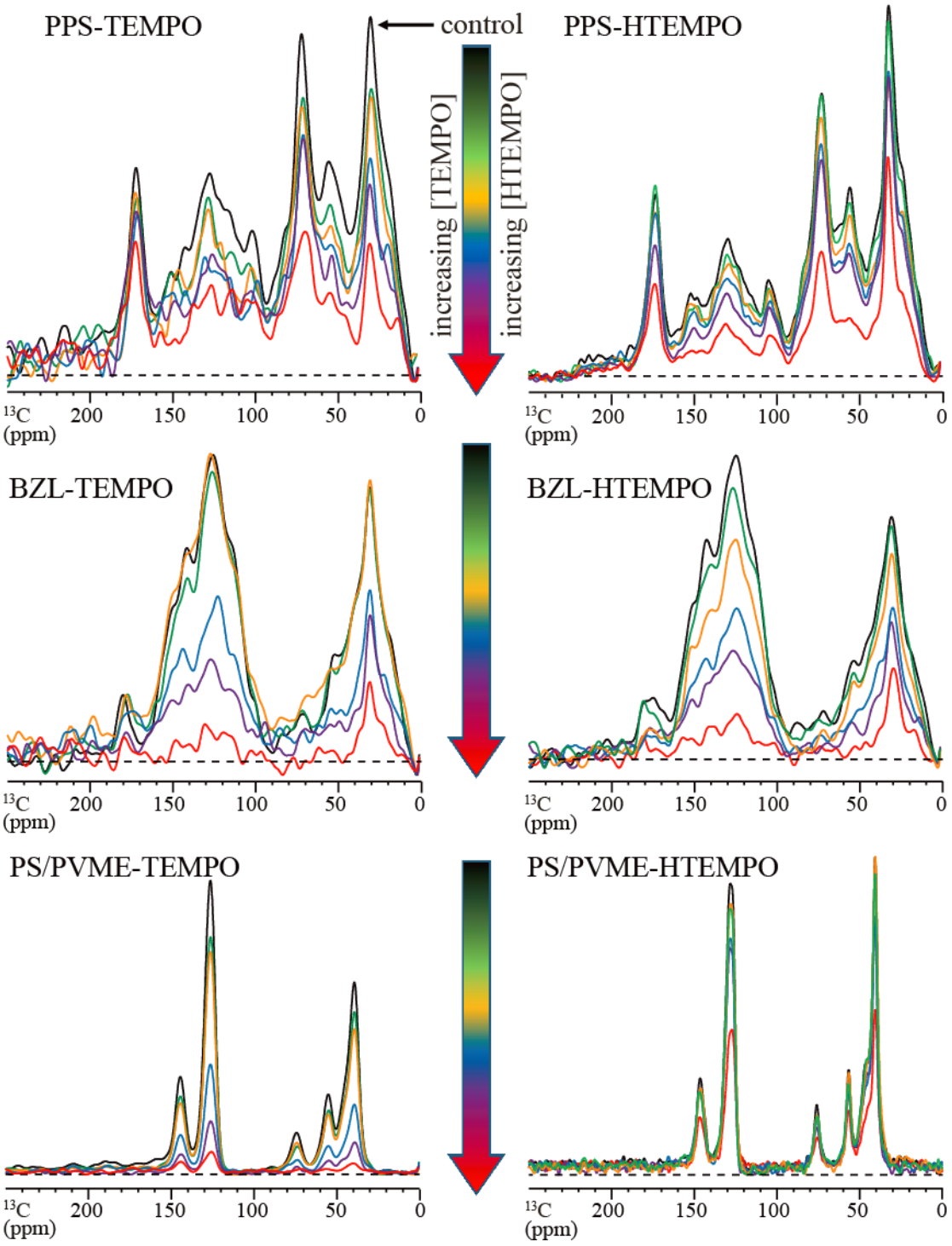


Figure S11. ^{13}C CP/TOSS NMR spectra of control sorbents (zero spin probe—black lines) and sorbents sorbed with increasing amounts of TEMPO or HTEMPO.

Table S2. Mole fraction solvent-water and cellulose-water partition coefficients for TEMPO and HTEMPO

Solvent System	$K'_{org\text{-}w,}$ mole %/mole%	
	TEMPO	HTEMPO
toluene/water	451±16	0.86±0.01
anisole/water	277±22	3±0.1
hexadecane/water	238±6	0.63±0.02
cellulose/water*	21±2	20±4
octanol/water	590±4	23±1

Starting concentration of TEMPO or HTEMPO in the solvent mixture was 500 μg/mL. *****TEMPO or HTEMPO is added at 5 μg/mL, 7 mL to 1g of cellulose. Values after ± are absolute errors at 95% confidence level.

REFERENCES

(1) Kroll, C.; Borchert, C. Metabolism of the stable nitroxyl radical 4-oxo-2,2,6,6,-tetramethylpiperidine-N-oxyl (TEMPONE). *Eur. J. Pharm.Sci.* **1999**, *8*, 5-9.
(2) Lemaire, H.; Rassat, A. Structure hyperfine due a l'azote dans les radicaux nitroxydes. *Journal De Chimie Physique* **1964**, *61*, 1580.