



Both the **concentrations** and the **stocks** of soil organic carbon vary across the landscape.

Do the amounts of **recalcitrant components** of SOM also vary with landscape position?

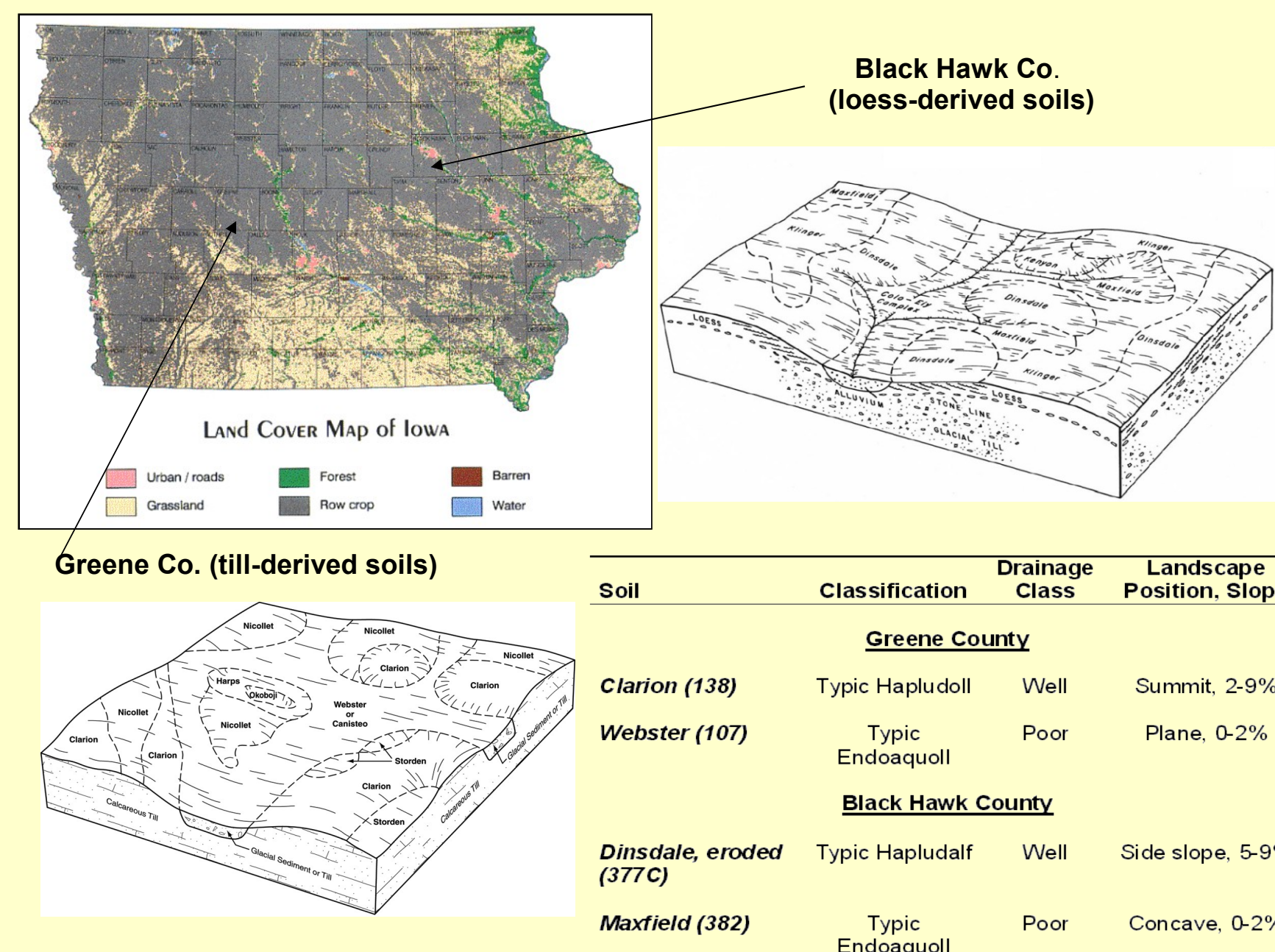
Why they might vary

- Biomass production varies with landscape position
- Intensity of microbial activity varies with water regime
- Type of microbial activity (esp. species of fungi) varies with water regime
- Redistribution of residues by overland flow of water (erosion)
- Preferential association of aliphatics with clay fraction

Why they might not vary

- Drainage tile has equalized soil water regimes
- Homogeneous soil management across landscape positions (fertilization and tillage)
- Homogeneous crop cultivars over many years

Study Area



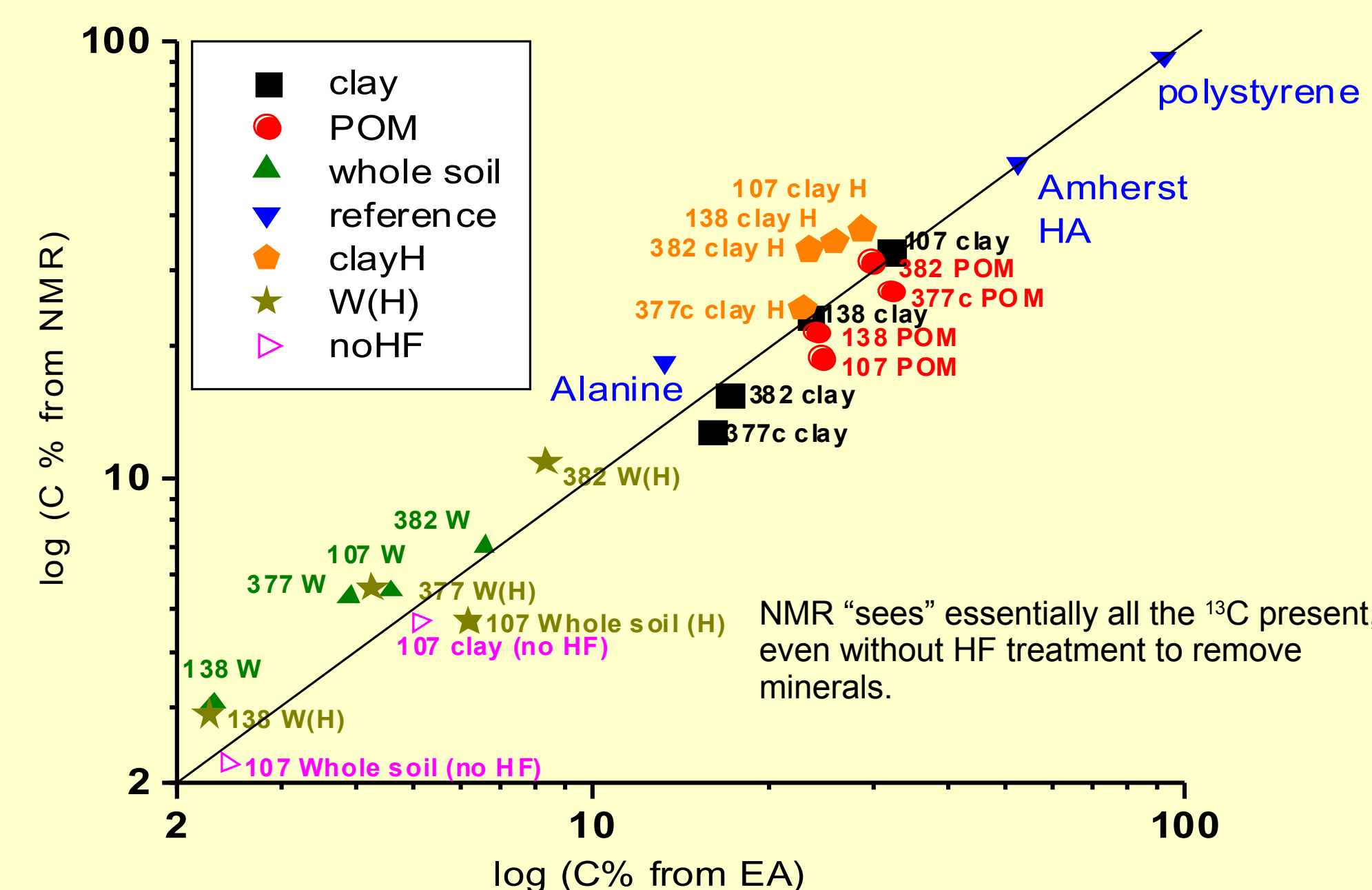
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Soil Characteristics

Soil	5 – 15 cm depth				POM (0 – 5 cm)		
	Clay	Sand	Silt	pH	TC	TN	C/N
-----g kg ⁻¹ -----							
Black Hawk County							
Dinsdale 377 (W)	330	100	570	5.4	320	15	21
Maxfield 382 (P)	360	90	550	6.2	296	17	17
Greene County							
Clarion 138 (W)	250	400	350	4.8	241	14	17
Webster 107 (P)	280	340	380	4.9	244	13	19

Fractionation of Soil Organic Matter Samples

- Surface horizon samples
- 50 g ≤2-mm soil dispersed in 250 mL H₂O using 22 J mL⁻¹ sonification
- Suspension passed through a 53-μm sieve
- Sieved residue treated with Na polytungstate (density = 1.8 g cm⁻³) to collect **POM**
- Clay + silt dispersed at 450 J mL⁻¹ and < 2 μm material separated by sedimentation of the silt
- Clay coagulated with MgCl₂, then dialyzed, freeze-dried
- Whole soil and clay fraction treated with HCl followed by four 10% HF treatments to dissolve minerals
- The washed residue was freeze-dried and ground



Nuclear Magnetic Resonance Spectroscopy

Bruker DSX400 spectrometer at 400 MHz for ¹H and 100 MHz for ¹³C.

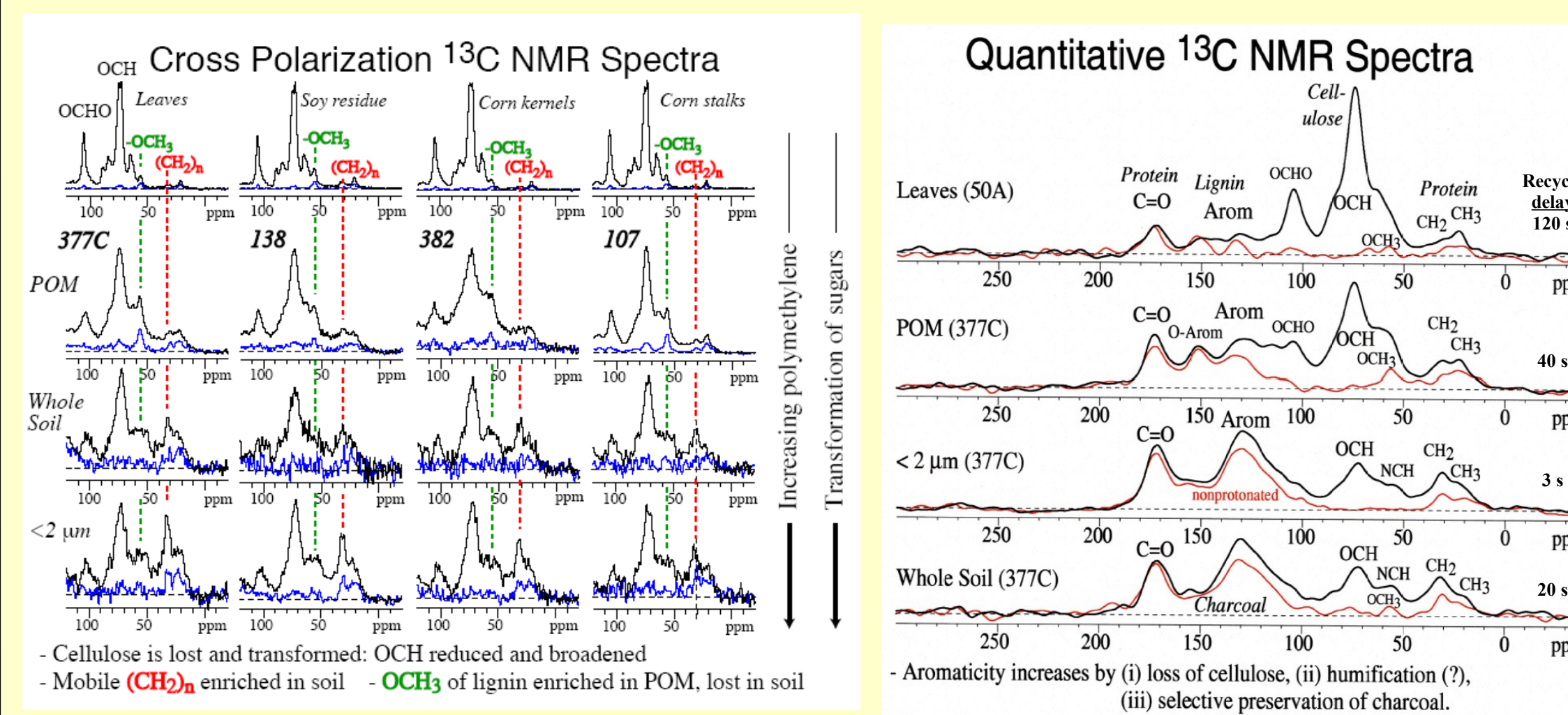
- 4-mm double-resonance magic-angle spinning (MAS) probe head
- ¹³C and ¹H chemical shifts referenced to tetramethylsilane, using glycine as a secondary reference for ¹³C and hydroxyapatite as a secondary reference for ¹H.
- Two-pulse phase modulation decoupling on the ¹H channel.

High-speed quantitative ¹³C DP/Echo/MAS NMR.

- Direct polarization (DP)/Hahn echo/MAS NMR spectra were acquired at 14 kHz MAS.
- Measuring times: 5.5 - 14.5 h per spectrum, except for the untreated samples, which were measured for about 38 hours each.

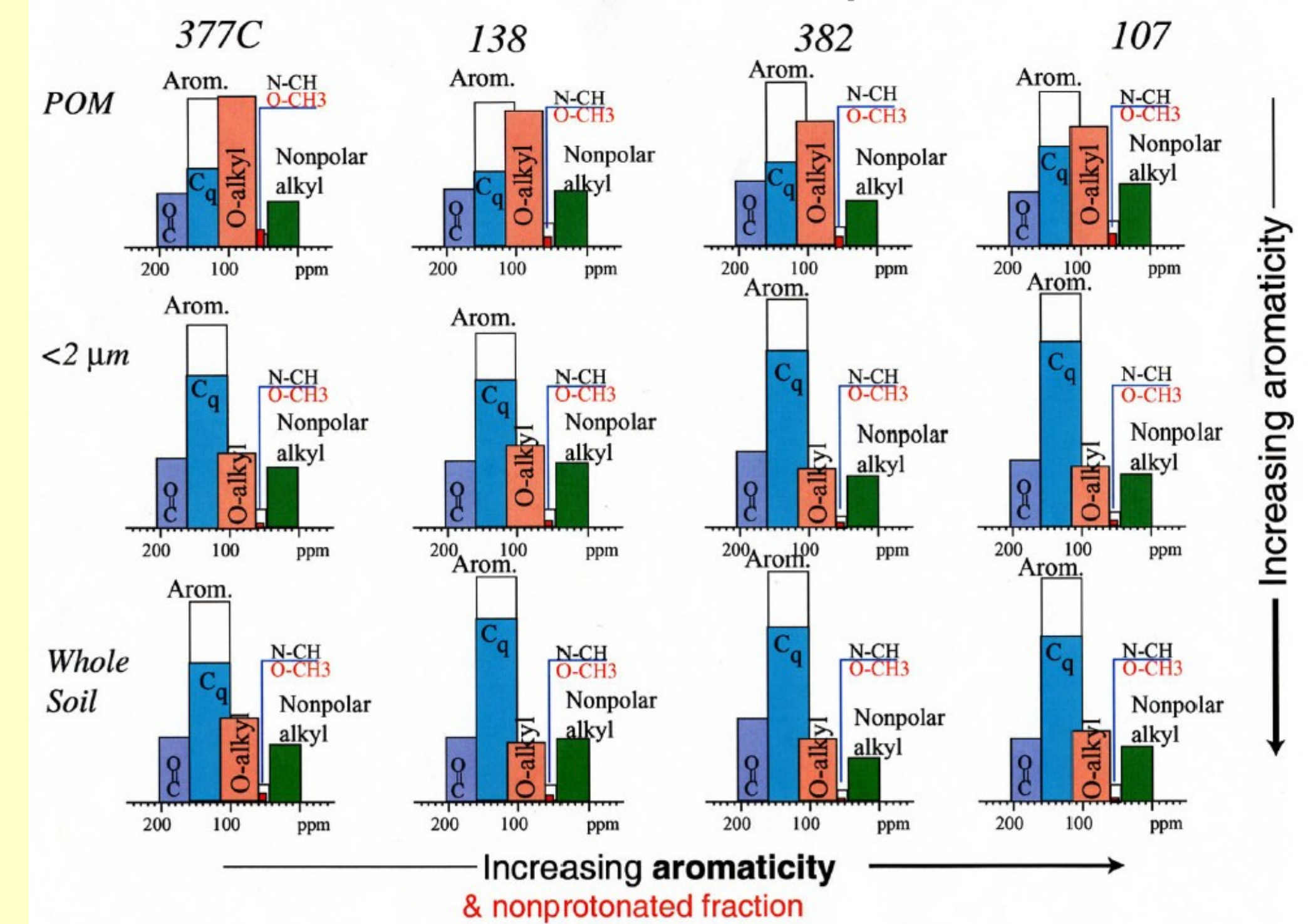
CP/TOSS experiment

- ¹H-¹³C cross polarization (CP) combined with four-pulse total suppression of sidebands (TOSS) spectra were recorded at 6.5 kHz MAS.
- The CP contact time was 1 ms, with a 0.5-s recycle delay.
- The T_{1,C} filtering time, where the remaining signal is less than 5% of the full intensity, was set as the recycle delay of the quantitative DP/MAS experiments.



Soil	Ketone	COO	Polar aromatic C		Total nonpolar aromatic C		Nonpolar aromatic Cq		O-alkyl	NCH	O-CH ₃	Non-polar alkyl
			ppm	% of total C	ppm	% of total C	ppm	% of total C				
	205-185	185-160	160-145	160-145	145-100	145-100	115-60	60-49	60-50	49-0		
Plant tissue												
Corn leaves	0	7	3	3	21	4	53	5	2	9		
Corn stalks	0	5	5	5	22	5	54	4	3	8		
Particulate organic matter												
Dinsdale (W)	2	11	8	7	23	12	38	3	4	12		
Clarion (W)	2	12	8	7	22	11	34	4	2	15		
Maxfield (P)	3	13	9	8	25	14	32	3	2	12		
Webster (P)	1	12	9	8	25	13	30	4	3	16		
Unfractionated sample												
Dinsdale (W)	2	15	7	5	37	27	22	3	1	14		
Clarion (W)	2	16	7	7	41	32	16	3	1	16		
Maxfield (P)	3	17	7	7	44	34	16	3	1	11		
Webster (P)	1	16	7	6	45	36	16	3	1	12		
Clay (< 2 μm)												
Dinsdale (W)	1	17	7	6	39	32	19	4	0	13		
Clarion (W)	1	16	7	5	38	29	19	4	0	14		
Maxfield (P)	2	17	7	5	45	34	16	3	1	12		
Webster (P)	3	16	7	6	44	33	15	2	1	11		

Quantitative ¹³C NMR Spectra



Conclusions

The quantitative NMR analyses allowed us to conclude:

- that HF treatment (with or without heat) had little impact on the organic C functional groups in the samples,
- that organic C was detectable even in untreated soil materials,
- that the aromatic components of SOM were enriched to ~52% in the poorly drained soils, compared with ~46% in the well-drained soils, and
- that nonpolar, non-protonated aromatic C, interpreted as a proxy for charcoal C, dominated the aromatic C in all soil samples. It composed 71 – 82% of aromatic C and 27 – 36 % of total organic C in the unfractionated soil and clay-fraction samples.

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