Larger contribution of non-protonated aromatics for organic matter in subsoil than topsoil horizons in Brazilian Ferralsols

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Introduction

- In this study we investigated whether recurring fire events across the Brazilian Cerrado impact soil organic matter (SOM) chemistry in Ferralsols.
- It remains unknown whether inputs of fresh litter-C are constrained by soil depth (topsoil versus subsoil horizons).
- It also remains unclear whether the contribution of pyrogenic materials (e.g. non-protonated aromatics) to SOM depends on soil horizon.

Material and methods

- **Incubation experiment:**
- Complete factorial: 3 Ferralsols, 2 soil horizons (topsoil and subsoil) and 2 litter-C inputs (0 and 40 mg g^{-1} soil). Three blocks were used as replicates.
- Soil samples remained incubated for 12 months.
- Double isotopic labeling (^{13}C and ^{15}N) was used to track down the incorporation of C and N into SOM.
- The amount of litter-C and N remaining in SOM was determined in particle size fractions (PSF) >53 and <53 microns.
- HF was used to treat the PSF <53 microns to remove Fe and concentrate SOM.
- HF-insoluble SOM chemistry was inferred by using Nuclear Magnetic Resonance (NMR) spectroscopy.
- A multi/cross-polarization (multi/CP) pulse sequence was applied to yield a quantitative solid-state magic-angle spinning (MAS) $^{13}C/^{15}N$ NMR.
- Dipolar dephasing was used to determine the contribution of non-protonated aromatics (NPA) to SOM.

Conclusions

A) Despite the fire regime in the Brazilian Cerrado, fresh litter inputs are more important for SOM chemistry in topsoil than in subsoil horizons.

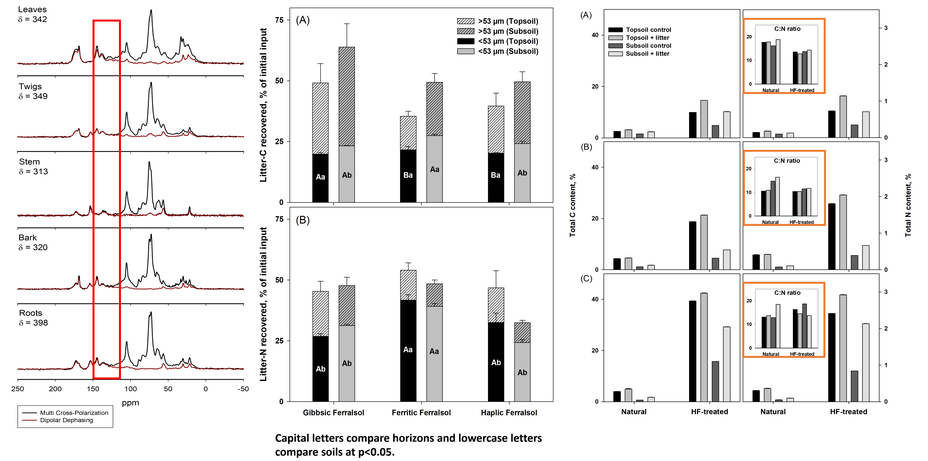
B) NPA appear to be concentrated in subsoil horizons of Ferralsols.

Further research is needed to:

a) determine whether NPA are produced *in loco* or transported from the topsoil;

b) determine whether the accumulation of NPA in the subsoil is absolute or relative, owing to a fast oxidation of NPA in topsoil horizons.

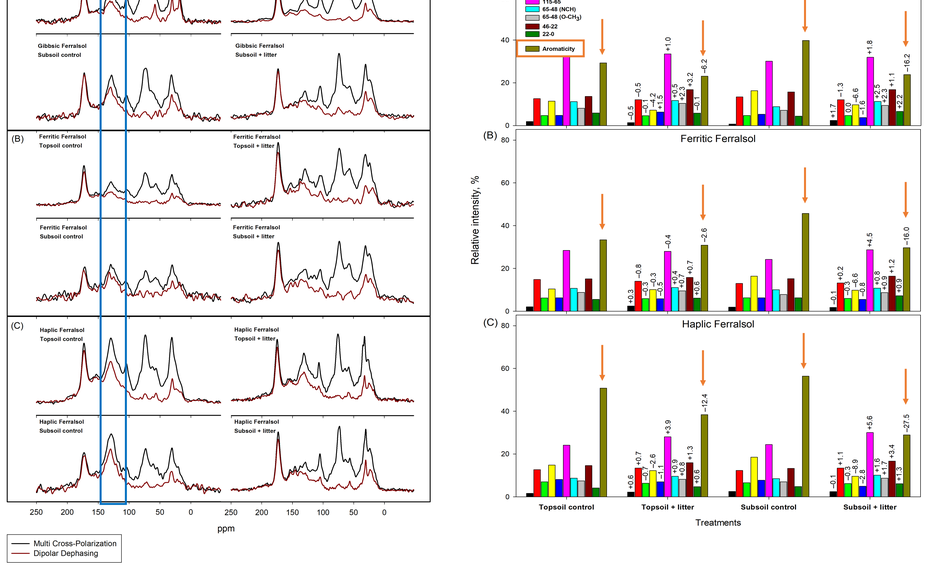
Results and discussion



Capital letters compare horizons and lowercase letters compare soils at p<0.05.

Litter chemistry:
protonated aromatics predominates.

SOM bulk chemistry:
Litter-C retention was higher in subsoil samples; litter-N was retained at similar rates in both horizons.
Litter-C retention was equal within both PSF evaluated.
Litter-N retention was higher within the PSF <53 microns.
HF treatment increased C and N concentration with small changes in C:N ratio.



Molecular chemistry of HF-insoluble SOM:
Plant litter additions had a bigger effect in SOM chemistry in subsoil as compared to topsoil horizons.
NPA contribute proportionally more to SOM chemistry in subsoil than in topsoil horizons.
Upon plant litter addition, the molecular chemistry of SOM in subsoil samples tended to converge towards that observed in topsoil horizons.
Litter addition caused a substantial reduction in SOM aromaticity in both horizons.