Patterns of Change in Permanganate Oxidizable Soil Organic Matter from Semiarid Drylands Reflected by Absorbance Spectroscopy and Fourier Transform Ion Cyclotron

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Labile-C pools of soil organic matter (OM) can be quantified or indexed by chemical or physical procedures. Recently, permanganate oxidizable carbon (POXC) has emerged as a promising and affordable labile-C test for soil health frameworks. POXC measurements are based on the oxidation of OM by 0.2 M $KMnO_4$. Yet, qualitative information on POXC is very scarce. Since the actual POXC fraction is released as CO_2 during the extraction procedure, conclusions regarding the composition of POXC are generally drawn by relating POXC bulk concentrations with other C fractions. Advanced molecular analytical techniques, such as Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), may unravel the water extractable OM molecular composition contributing to the turnover of POXC.

Soil samples were collected from three long-term studies conducted in Montana. The samples encompassed a wide range of textural properties, soil depths, land uses, and cropping systems. The molecular composition of the POXC fraction was determined indirectly following the equation:

$$POXC = DOC_T - POXC_{NL} \qquad [1]$$

where DOC_T represents the total pool of dissolved OM composition present in soil before the $KMnO_4$ reaction; $POXC_{NL}$ represents the non-oxidizable C, or the pool of DOC_T that was not released as CO_2 during $KMnO_4$ oxidation reaction. Molecular formulae of each fraction were determined by 9.4 T FT-ICR MS at the NHMFL, Tallahassee, Florida. The POXC molecular constituents were then inferred from the difference between the two measurable fractions.

Examples of OM molecular markers before (DOC_T) and after ($POXC_{NL}$) $KMnO_4$ treatment are represented in **Fig. 1**. The chemical character of OM obtained from $POXC_{NL}$ was very different from that of DOC_T, with no formula matches between them. The $POXC_{NL}$ samples were strongly depleted in unbound Mn-OM constituents relative to DOC_T, indicating that all DOC_T compositions participated in some part of the $KMnO_4$ reaction. The concentration of POXC increased as a function of labile DOC_T constituents (**Fig. 2**); implying $KMnO_4$-reactive OM was favored by the increasing proportion of aliphatic chemical species. The $KMnO_4$ reaction, however, also removed molecules typically regarded as aromatic-C. Our ESI FT-ICR MS results implied the aqueous POXC fraction represents a mixture of OM chemical species at varying levels of aromaticity and lability. The view of POXC as a merely labile, simple biodegradable OM fraction needs to be reconsidered.

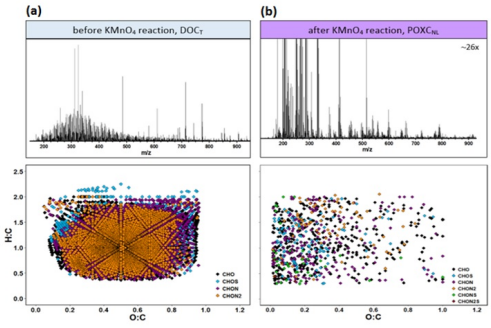

Fig. 1 Negative ESI FT-ICR mass spectra and van Krevelen diagrams of representative (a) dissolved OM (DOC_T) and (b) $KMnO_4$ non-oxidizable OM ($POXC_{NL}$) pools.

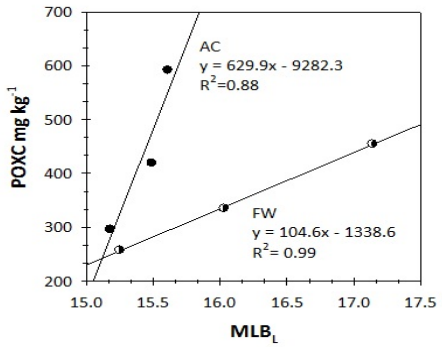

Fig. 2 Relationship between POXC concentration and OM labile molecular composition percentages (MLB_L).

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References

[1] Romero, C.M., *et al.*, Organic Geochemistry, **120**, 19-30 (2018).