A New Approach for Estimating Organic Carbon Oxidation State (C_{ox}) and Oxidative Ratio (OR) in soils and sediments

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Abstract

We present a new approach in the measurement of two interconnected variables useful in the study of organic carbon (OC) storage and decomposition: OC oxidation state (C_{ox}) and oxidative ratio (OR). OR is a measure of mols CO_2 released/mols O_2 consumed when a pool of OC decomposes. Although C_{ox} and OR are proportional, we work with both terms because each is useful in different contexts: C_{ox} can be related directly to the chemical composition of OC, while OR is critical in C cycle studies that partition land and ocean C sinks (Keeling et al, 1996).

Equations

C_{ox} is a function of molar concentrations. For $C_xH_yO_zN_w$:

$$(1)\quad C_{ox} = \frac{2z - y + 3w}{x}$$

$C_xH_yO_zN_w$ oxidation to CO_2, H_2O, and NH_3, gives:

$$C_xH_yO_zN_w + \left(x + \frac{1}{4}(y - 3w) - \frac{z}{2}\right) O_2 \longrightarrow$$

$$xCO_2 + \frac{1}{2}(y - 3w)\, H_2O + wNH_3$$

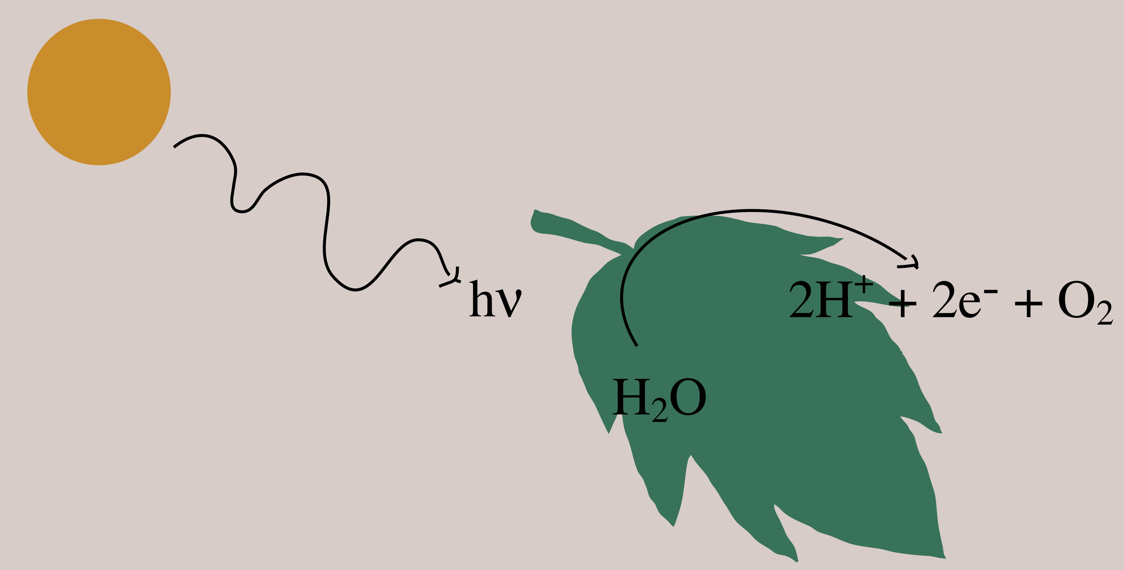
giving the definition of OR as:

$$(2)\quad OR = \frac{O_2}{CO_2} = \frac{x + \frac{1}{4}(y - 3w) - \frac{z}{2}}{x}$$

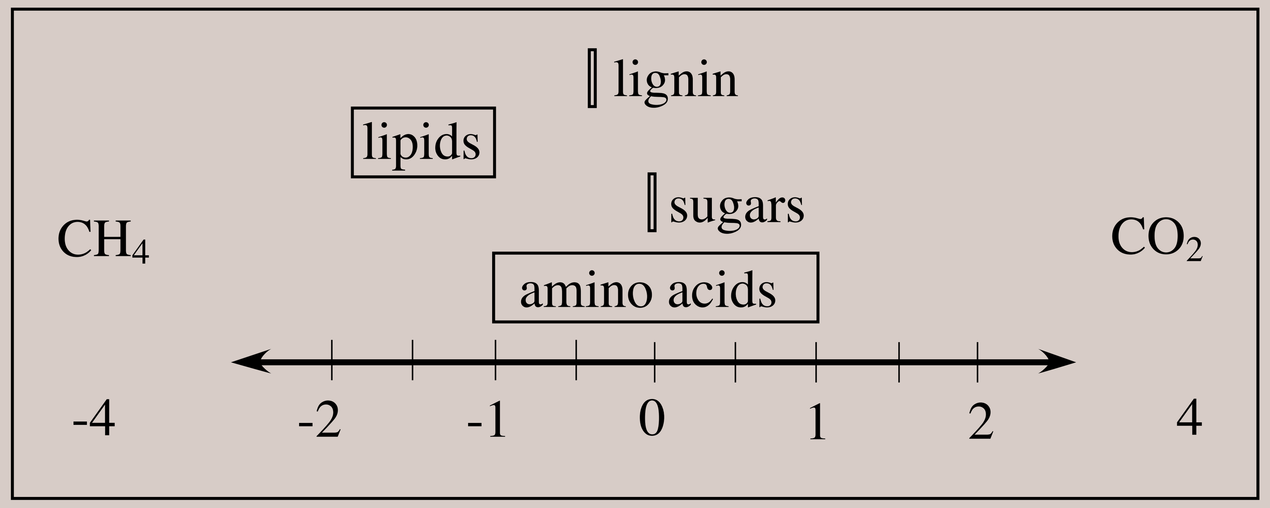
C_{ox} is also a function of the energy stored in the ecosystem.

$$C_{ox} = 4 - \frac{1.6}{[C]_{massfrac}}(0.06968 \bullet \Delta H - 0.065)$$

This can be derived from eqn (1) and Williams et al., 1987.



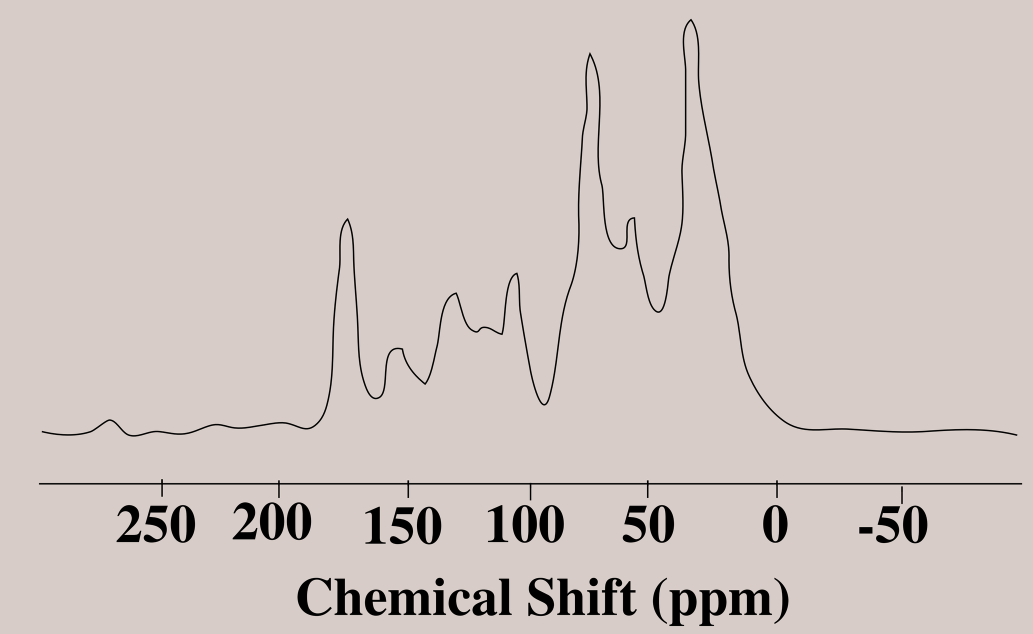
Photosynthesis uses light to split water, generating electrons. These electrons are used to reduce CO_2 to compounds like glucose, lignin, lipids, and amino acids.



C_{ox} values of many natural compounds stay close to zero

Organic matter cannot be nondestructively separated from the host soils, due to the complexity of organo-mineral bonds. This is a particularly serious roadblock in the estimation of the O content of embedded organic matter because O is a major component in virtually all soil minerals. We circumvent this problem using [13]C CP/MAS NMR coupled to a simple mixing model.

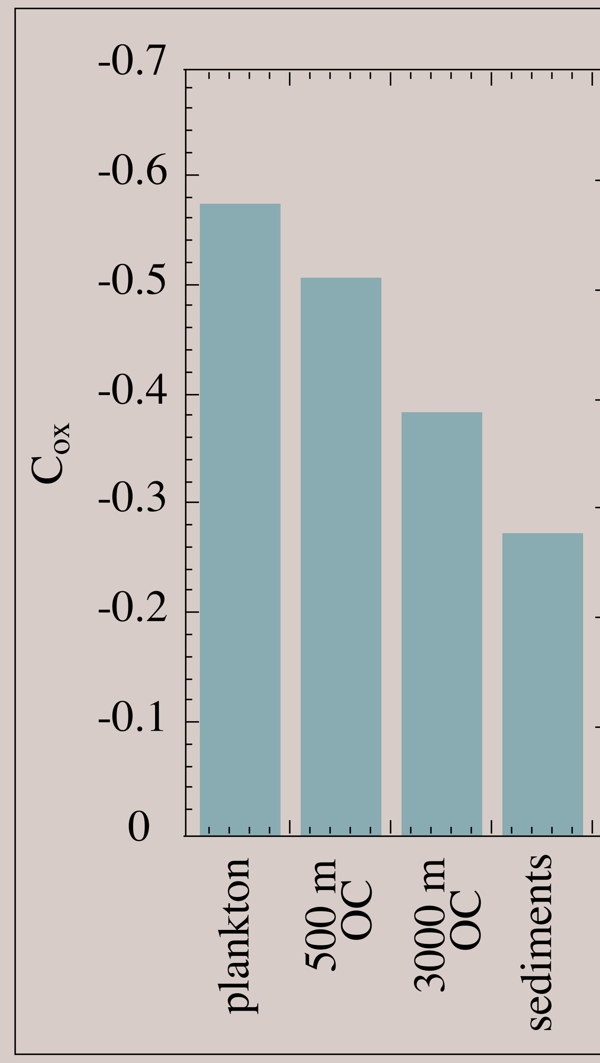
Solid state cross polarization-magic angle spinning (CP/MAS) [13]C NMR does not require separation of organic matter from its mineral matrix and can generally characterize the chemical properties of a sample of whole organic matter embedded in a mineral matrix.



Soil [13]C NMR spectra can be modeled as the sum of 6 biomolecule classes: carbohydrate, protein, lignin, lipid, carbonyl, and char [Nelson and Baldock, 2003]. One output of this model is an estimation of C,H,O, and N content, which allows calculation of C_{ox}.

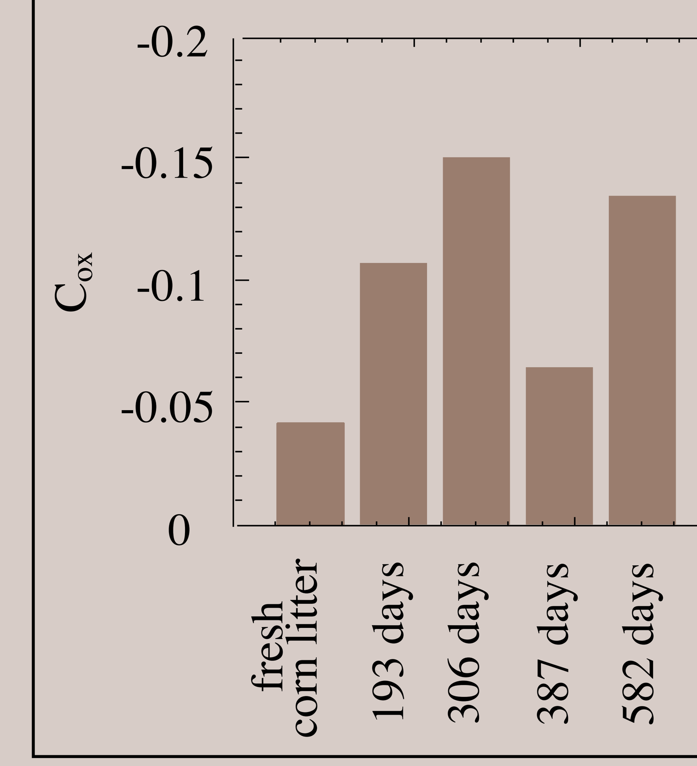
Modeled composition of 0-5 cm (A horizon) Australian Hapludoll

carbohydrate		28.3
protein	28.9	
lignin	19.8	
lipid	19.1	
carbonyl	1.3	
char	2.5	

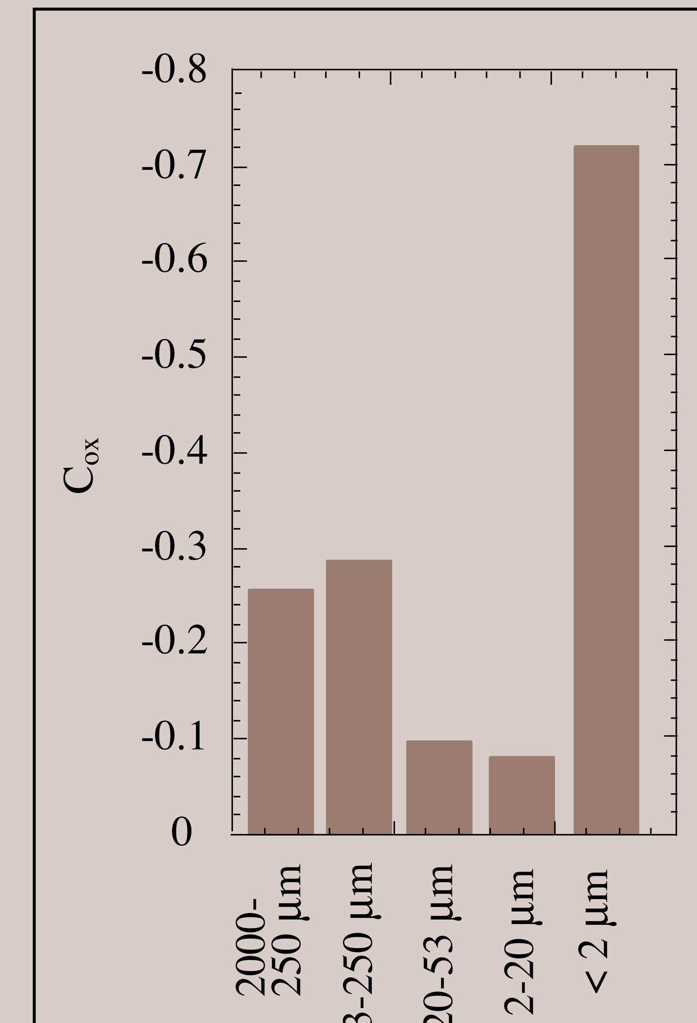


In contrast to terrestrial material, as marine material decomposes, it becomes more oxidized. In these organic matter samples taken from equatorial Pacific sinking particle traps, molecular modeling suggests that as organic matter is processed, the relative proportion of carbohydrate increases, while lipid and protein decreases.

First look at results



Corn litter buried in agricultural soil becomes slightly more reduced as it decomposes, due to initial preferential loss of carbohydrates (stable by 306 d). This is followed by fluctuation in the relative amounts of lipid, lignin, and protein.



Size fractions of an Australian Mollisol become increasingly oxidized down to 20 microns. A large jump in the relative proportion of lipid causes the smallest size fraction to become quite reduced.

Conclusions

C_{ox} and OR are two tracers that can be used to link soil carbon cycling to ecosystem energy storage and trace gas emissions;

soil OC becomes more reduced as it decomposes, possibly due to enrichment in microbial materials;

because soil OC becomes more reduced, there may be an offset between the OR of soil respiration and the OR of carbon accumulated over decades/centuries;

marine organic C_{ox} values suggest different decomposition processes in oceanic samples.

Keeling, R.F., Piper, S.C., Heimann, M. Global and Hemispheric CO_2 Sinks Deduced from Changes in Atmospheric O_2 concentration. Nature, 381, 218-221, 1996.

Williams, K., Percival., F., Merino, J., Mooney, H.A. Estimation of Tissue Construction Cost from Heat of Combustion and Organic Nitrogen Content. *Plant, Cell, and Environment*, v. 10, p. 725-734, 1987.

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