The Dating Game: Applying $^{14}$C AMS in the Characterization of Soil Carbon Dynamics within Dolomitic Ultisol Fractions at Varying Depths

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Carbon Input and Stabilization

- Degree of contribution to soil carbon from litter vs. root sources still unknown...

- 2 part project:
  - Observing the track of $^{14}$C through soil profile at ORR to gauge input of roots
  - Multi-year reciprocal litter experiment using $^{14}$C-enriched and near background litter to observe input from surface litter

- Whereas, root input was fairly demonstrative, the input from litter over the first year was negligible
The $^{14}$C Cycle

- $^1n + ^{14}N \rightarrow ^{14}C + ^1H$
- Resulting atoms = 6 protons/8 neutrons
- Half-Life = $\sim 5730\pm40$ years

- Decays through Beta Decay
  - $^{14}C \rightarrow ^{14}N + e^- + \bar{\nu}_e$
  - Emission of electron and antineutrino converts a neutron into proton
What is $^{14}$C AMS?

- AMS = Accelerator Mass Spectrometry
- Sensitive enough to discern between isotopes of similar mass and present in ultra-Low Ratios
- Carbon “Graphite” Targets

10MV Tandem Van de Graaff Accelerator & CAMS crew at LLNL
Basic AMS Design

High Energy Mass Spectrometer

13 C4+ Faraday Cup

Rigidity Filter

Tandem Electrostatic Accelerator

C1+...6 +

+7 MV

C−

64 samples

Negative Ion Source

Low Energy Mass Spectrometer

14 C4+

Ion Identification Detector

Velocity (Wien) Filter
EBIS (Enriched Background Isotope Study)

- July/August 1999--large release of radiocarbon near Oak Ridge Reservation (ORR)
- Uptake by vegetation unprecedented in scale
- Ecosystem-scale $^{14}$C tracer used to study outstanding issues in terrestrial carbon cycle
- Reciprocal litter experiment at four sites encompassing two soil types and two levels of $^{14}$C exposure
TVA/WB Site Study Effects of...

WB (A)  
Background Control

TVA (A)  
Roots

WB (E)  
Litter

TVA (E)  
Roots + Litter Enriched Control
Reciprocal Litter Transplant Experiment Design

- Four sites (8 plots each) around ORR

- Two sites $^{14}$C enriched (one Ultisol, one Inceptisol), two sites near background $^{14}$C (one Ultisol, one Inceptisol)

- At each site four of the eight plots were randomly selected, and each year indigenous litter was removed and enriched litter transplanted
Core samples from 3 depths
- 0-15 cm
- 15-30 cm
- 30-60 cm

Samples stored at -20 °C

Thawed, then oven-dried at 105°C

Density fractionation and other sample prep
Study Plot Descriptions

- Ultisols (deep, highly weathered, dolomitic parent material)
- Acidic
- Dominated by kaolinite and interlayered hydroxy-Al vermiculite clays
- Cation exchange capacity = between 4 and 6 cmol/kg
- Clays often coated with 2-4% Fe-oxides, primarily hematite and maghematite
Mean annual precipitation = 1358 mm
Mean annual temperature = 14°C
Upslope, ridgetop positions
Upland oak forest type with scattered pine, mesophytic hardwoods, and some hickory
Soil Fractions

\[ ^{14}\text{CO}_2 \]

Heavy Fraction

Occluded Light Fraction

Free Light Fraction

Scale: 250 μm
Soil Sample Prep for AMS

- Various Pre-Treatments for OC
  - Ex. My soils were ground and density fractionated using liquid sodium polytungstate (LSPT); Other sets may try to chemically distinguish carbon pools (eg. acid hydrolyzable)

- Estimate %C of sample and weigh out for an end product of ~1-2 mg total C

- Addition of enough O$_2$ source (CuO) for complete combustion; Ag powder added to scavenge impurities (ex. sulfur)

- ~900°C/3.5 hours; C now in Form of CO$_2$
Graphitization = Double reduction of CO$_2$ to CO to C in presence of H$_2$ with Fe powder catalyst; if enough CO$_2$ is present, a split can be taken for $\delta^{13}$C analysis at stable isotope mass spectrometer (UC Davis)

Pounded into aluminum target for $^{14}$C-AMS analysis
Calculations and Reporting of $^{14}$C Data

- Measurements and calculations reported using Stuiver and Polach (1977) and elaboration by Reimer et al. (2004) as a guide

- $\Delta^{14}$C (‰) = the deviation of the activity, in per mil, of the $\delta^{13}$C corrected sample from that of the $\delta^{13}$C and decay corrected standard (Ox I)
WB Year 0 and Year 1 Data

Not much difference in the data for Site WB except...
WB YEAR 0 AND TVA YEAR 0

Overall higher 14C
From pulsed site=logical

Higher FLF=logical
Higher HF=huh?
TVA Year 0 and Year 1 Data

Site TVA Year 0 Combined Litter

0-15 cm
15-30 cm
30-60 cm

Delta 14C

FLF OLF HF

Increase in OLF 14C?

HF 14C generally higher than OLF; atypical

Heavy Fraction at depth beginning to increase in 14C
What does this Mean?

- Strong pulse signal in the TVA site data
- Unusual results help to further support the idea that the HF is not necessarily as stable as classically thought
WB Ambient vs. Enriched Litter

Plot 8 - southern most plot closest to $^{14}$C exposure; Possible Contamination?

Plot 7 - increase in $^{14}$C at depth first?
What does this mean for litter?

- No significant difference of between years 0 and 1 at site WB or between enriched and ambient plots...at least in a one year time period

- Now in its later years, data beginning to suggest a slight elevation of enriched litter plot $^{14}$C levels

- BUT, out of litter measuring $\sim$1000‰, only about 100‰ increase in $^{14}$C measurements
Further Study

- MORE DATA!

- More intense study of the role of cation exchange within expansive clay mineral soils

- Separation of HF into 2 distinct fractions to further characterize its variations in carbon stabilization (Go Rachel!)
References

“Enriched Background Isotope Study (EBIS)” [http://ebis.ornl.gov](http://ebis.ornl.gov)


Special thanks to:

- GCEP, Jeff Gaffney, Nancy Marley, Milton Constantin
- Lawrence Livermore National Lab, CAMS
- Dr. Tom Guilderson, LLNL
- Dr. Chris Swanston
- Paula Zermeño and Dot Kurdyla, Graphite Lab Staff
Units, Calculations, & Expressions of $^{14}$C Data

- To normalize for isotopic fractionation:
  
  $$A_{SN} = A_s \left(1 - \frac{2(25 + \delta^{13}C)}{1000}\right)$$

  - Sample activity-

  $$A_{ON} = 0.95A_{Ox} \left(1 - \frac{2(19 + \delta^{13}C)}{1000}\right)$$

  - Standard activity-

- To correct for Ox I decay since 1950:

  $$A_{abs} = A_{ON} e^{\lambda(y-1950)}, \quad \text{where } \lambda = \frac{1}{8267} \text{ yr}^{-1}$$
CONT’D

- Using the $\delta^{13}C$ normalized sample activity ($A_{SN}$) along with the $\delta^{13}C$ normalized and age corrected absolute standard ($A_{abs}$)...

\[
F' = \frac{A_{SN}}{A_{abs}} = \frac{\left( \frac{^{14}C}{^{12}C + ^{13}C} \right)_{\text{sample}(-25)}}{\left( \frac{^{14}C}{^{12}C + ^{13}C} \right)_{\text{abs}(-19)}}
\]

$\Delta^{14}C$ (per mil, ‰)- $\Delta^{14}C = (F' - 1) \times 1000$

...can be calculated!
**Density Fractionation**

1. **Soil**
2. Add SPT & gently invert
3. Centrifuge mixture
4. Aspirate free light fraction (FLF)
5. Mix and sonicate sediment
6. Centrifuge mixture
7. Aspirate occluded light fraction (OLF), remaining sediment is DF
8. FLF: rinse and dry
9. OLF: rinse and dry
Litter Pictures