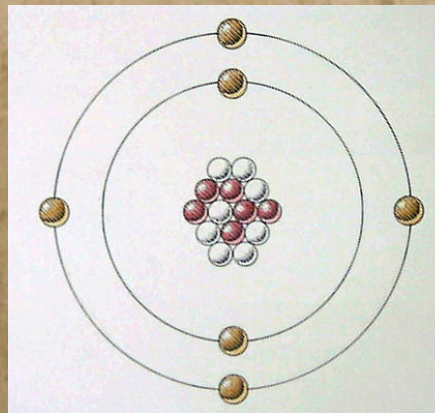


THE DATING GAME: APPLYING ^{14}C AMS IN THE
CHARACTERIZATION OF SOIL CARBON DYNAMICS
WITHIN DOLOMITIC ULTISOL FRACTIONS AT VARYING
DEPTHS



Michael "Mikey" J. Tackett Jr.
University of Arkansas at Little Rock,
Department of Chemistry, Department of Earth Science
Lawrence Livermore National Laboratory

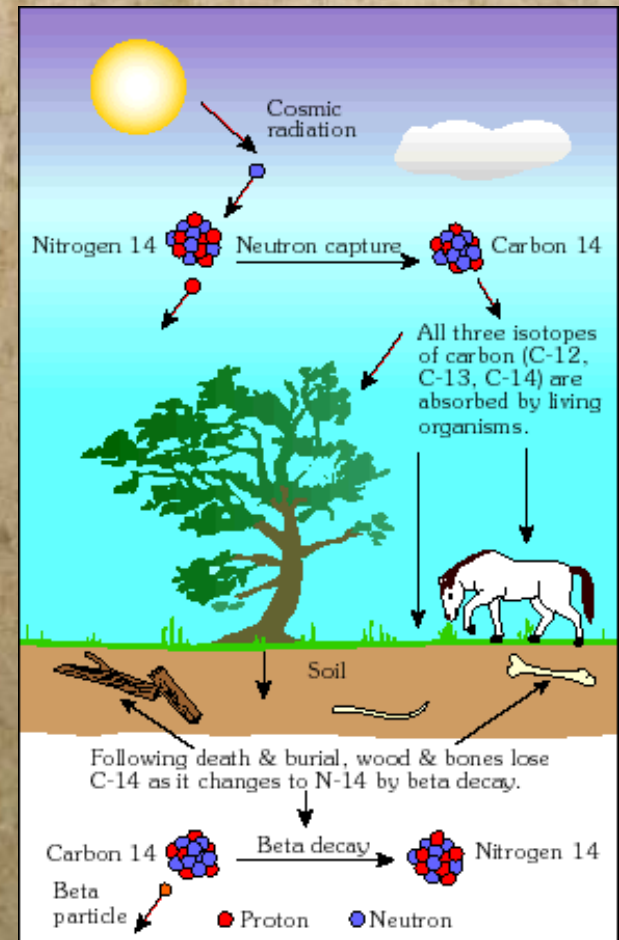
CARBON INPUT AND STABILIZATION

- 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

- $^1_0\text{n} + ^{14}_7\text{N} \rightarrow ^{14}_6\text{C} + ^1_1\text{H}$
- Resulting atoms= 6 protons/8 neutrons
- Half-Life= $\sim 5730 \pm 40$ years

- Decays through Beta Decay
- $^{14}_6\text{C} \rightarrow ^{14}_7\text{N} + e^- + \bar{\nu}_e$
- Emission of electron and antineutrino converts a neutron into proton



WHAT IS ^{14}C AMS?

- AMS=Accelerator Mass Spectrometry



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

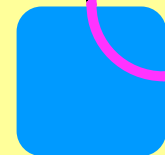
- Sensitive enough to discern between isotopes of similar mass and present in ultra-Low Ratios
- Carbon "Graphite" Targets

BASIC AMS DESIGN

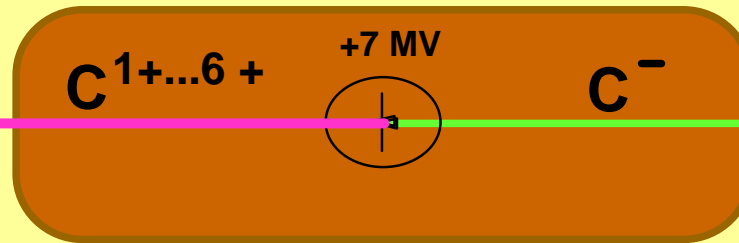
High Energy Mass Spectrometer



$^{13}\text{C}^{4+}$
Faraday Cup



Rigidity Filter

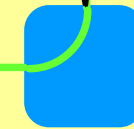


Tandem Electrostatic Accelerator

64 samples



Negative Ion Source

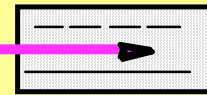


Low Energy Mass Spectrometer



Velocity (Wien) Filter

$^{14}\text{C}^{4+}$



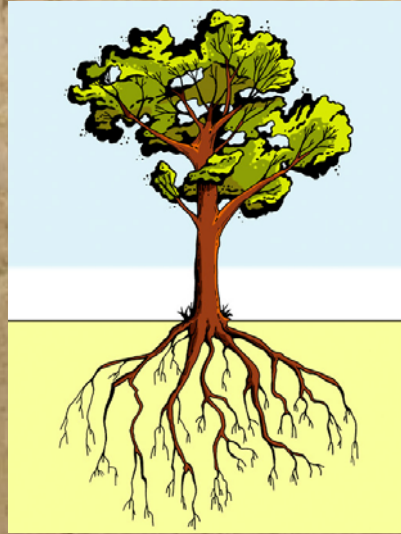
Ion Identification Detector

EBIS (ENRICHED BACKGROUND ISOTOPE STUDY)

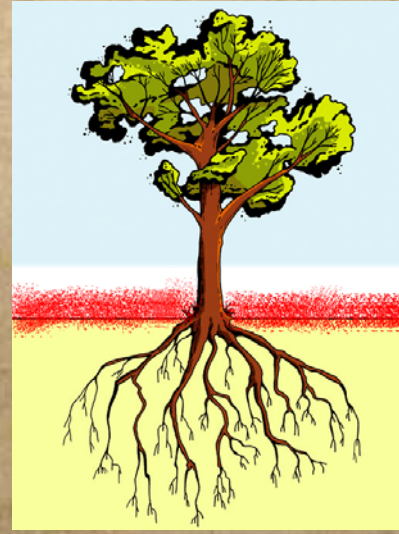
- July/August 1999--large release of radiocarbon near Oak Ridge Reservation (ORR)
- Uptake by vegetation unprecedented in scale
- Ecosystem-scale ^{14}C tracer used to study outstanding issues in terrestrial carbon cycle
- Reciprocal litter experiment at four sites encompassing two soil types and two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

TVA/WB SITE STUDY EFFECTS OF...

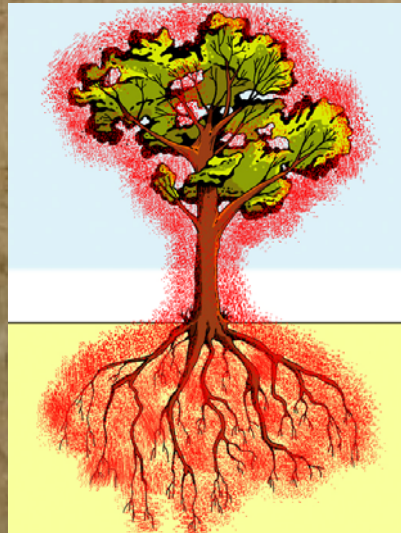
WB (A)
Background
Control



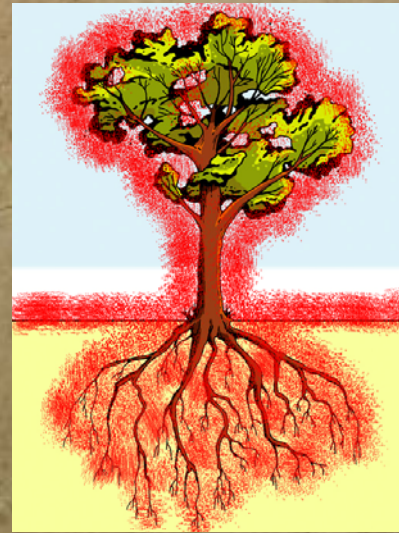
WB (E)
Litter



TVA (A)
Roots



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

CONT'D

- Core samples from 3 depths
 - 0-15 cm
 - 15-30 cm
 - 30-60 cm
- Samples stored at $-20\text{ }^{\circ}\text{C}$
- Thawed, then oven-dried at 105°C
- Density fractionation and other sample prep

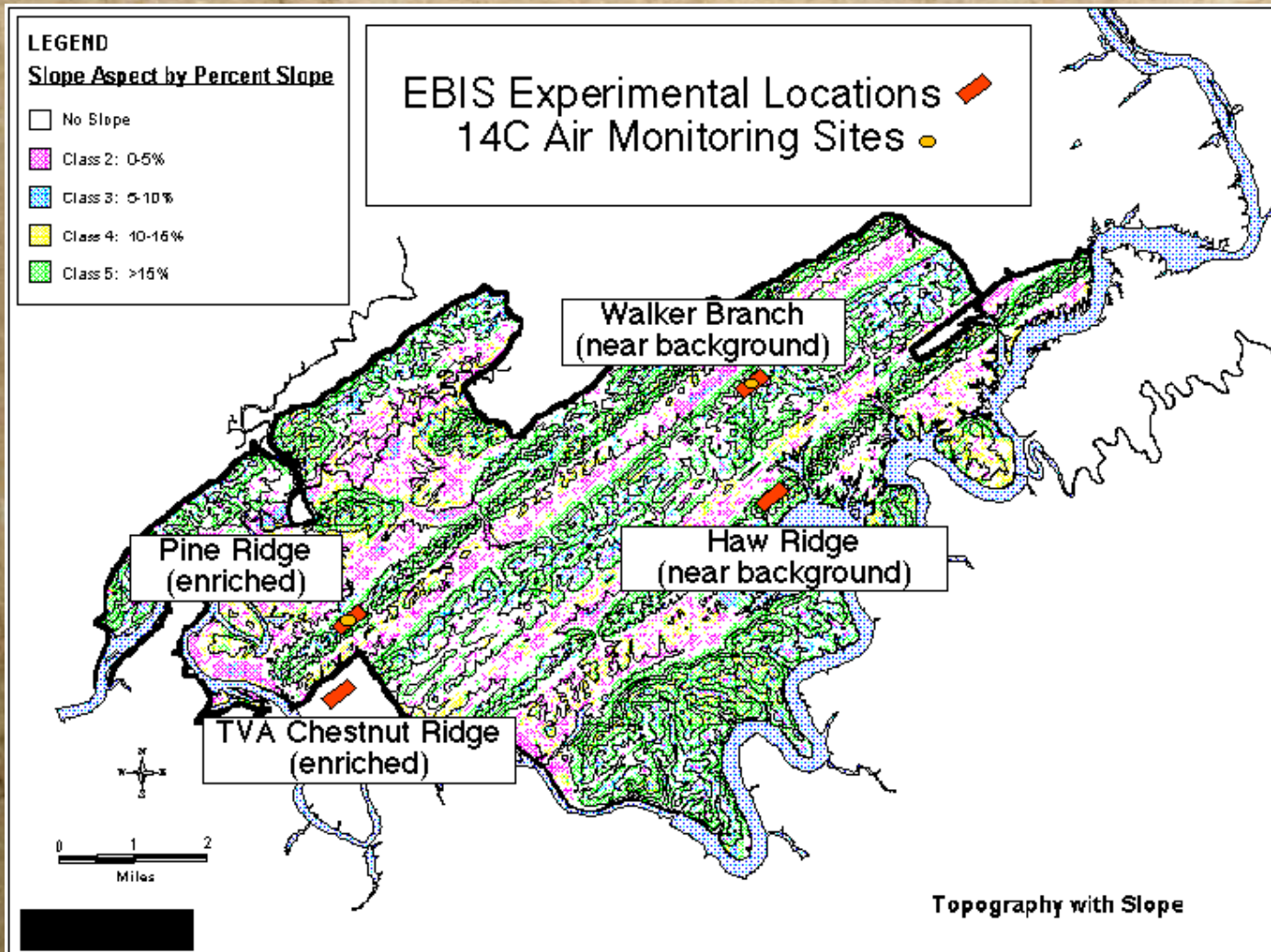
STUDY PLOT DESCRIPTIONS

- Ultisols (deep, highly weathered, dolomitic parent material)
- Acidic
- Dominated by kaolinite and interlayered hydroxy-Al vermiculite clays
- Cation exchange capacity= b/w 4 and 6 cmol/kg
- Clays often coated with 2-4% Fe-oxides, primarily hematite and maghematite

CONT'D

- 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

EBIS SITE MAP



SOIL FRACTIONS

$^{14}\text{CO}_2$



Heavy Fraction

Occluded Light Fraction

Free Light Fraction



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 O₂ source (CuO) for complete combustion; Ag powder added to scavenge impurities (ex. sulfur)
- ~900°C/3.5 hours; C now in Form of CO₂

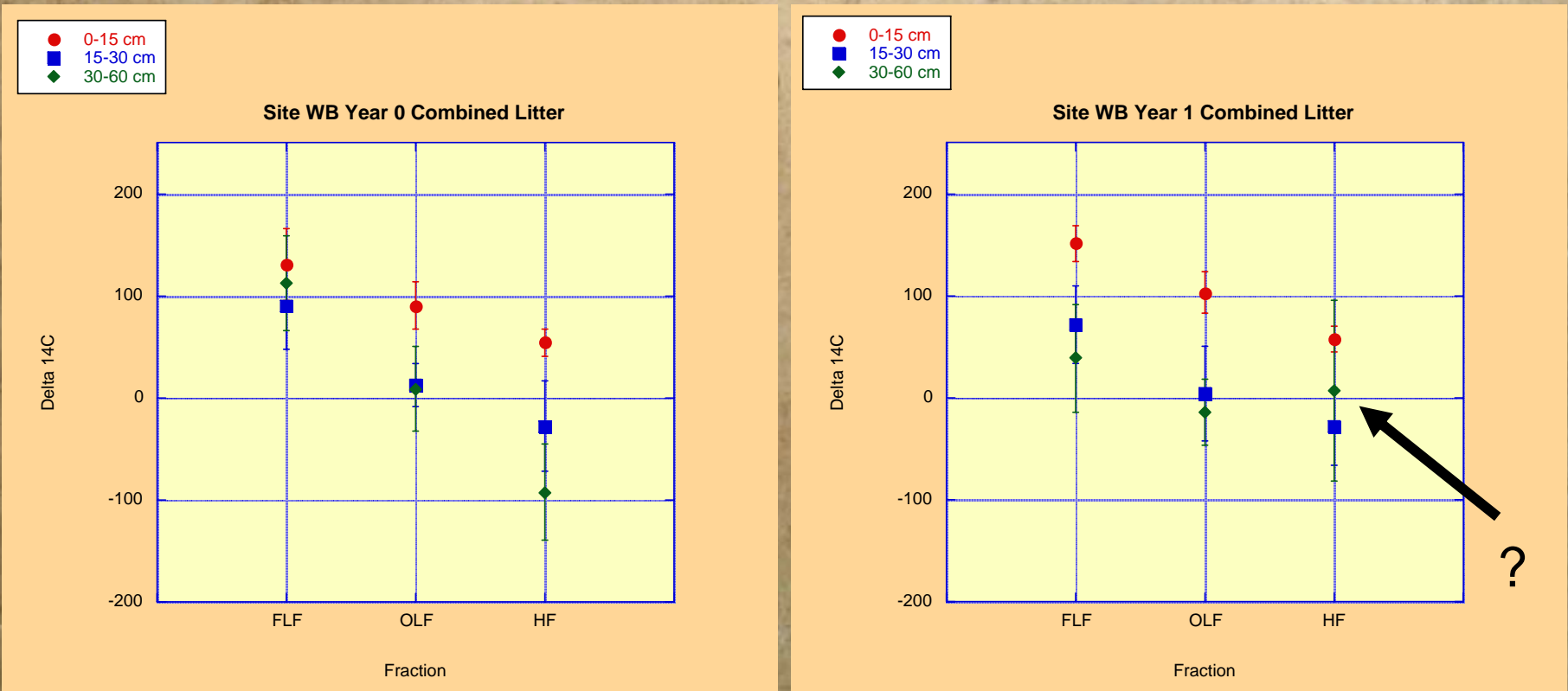
CONT'D

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

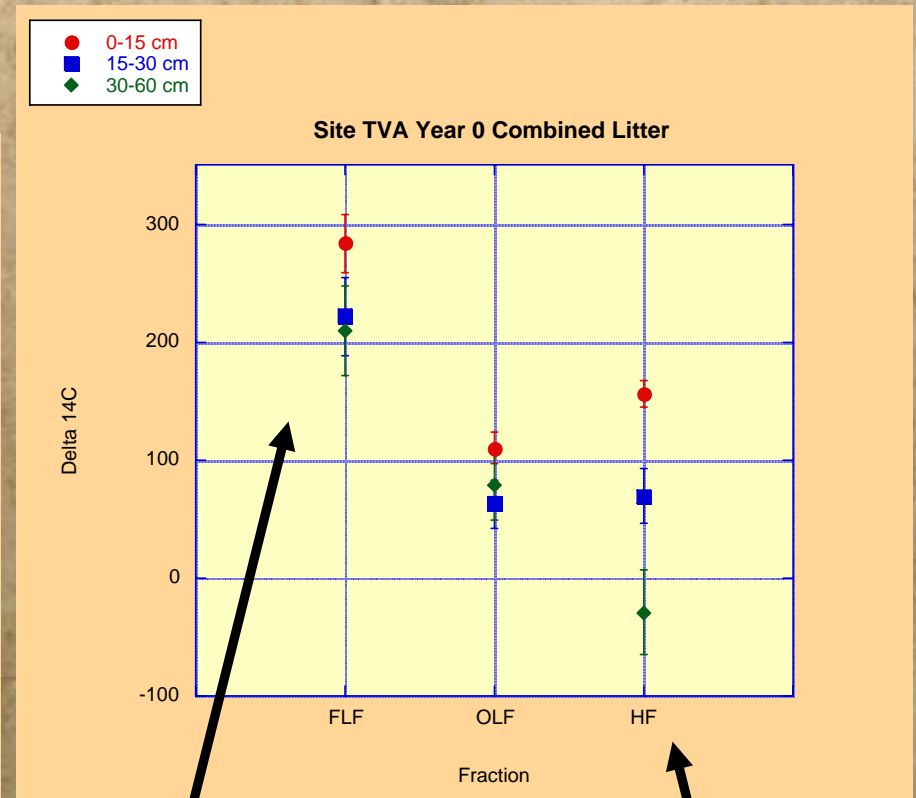
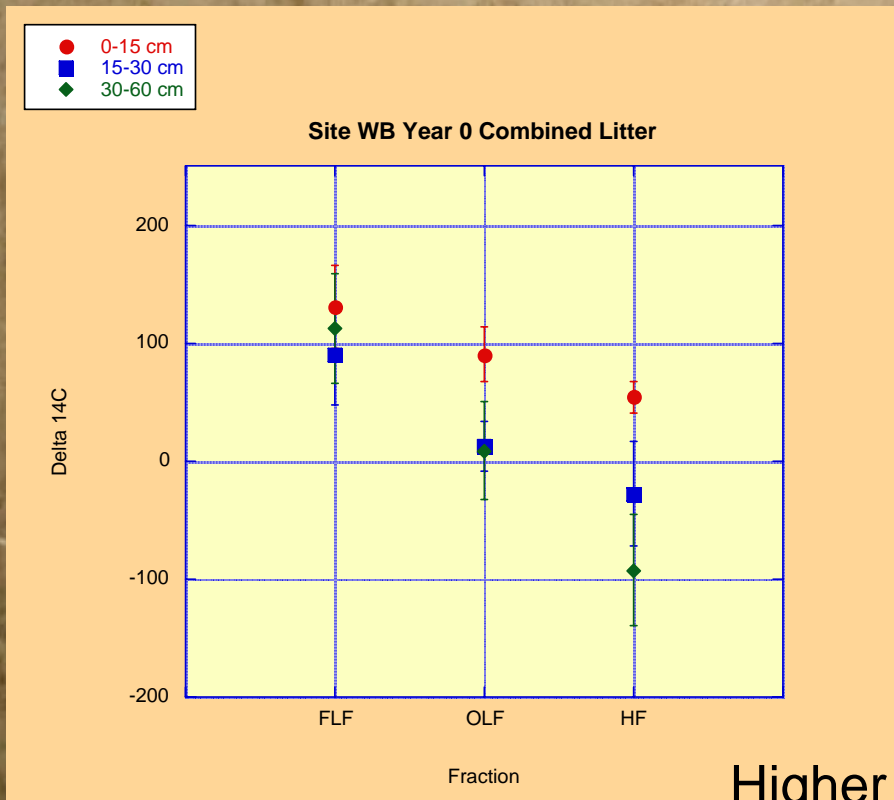
WB YEAR 0 AND YEAR 1 DATA



Not much difference in the data for Site WB except...

WB YEAR 0 AND TVA YEAR 0

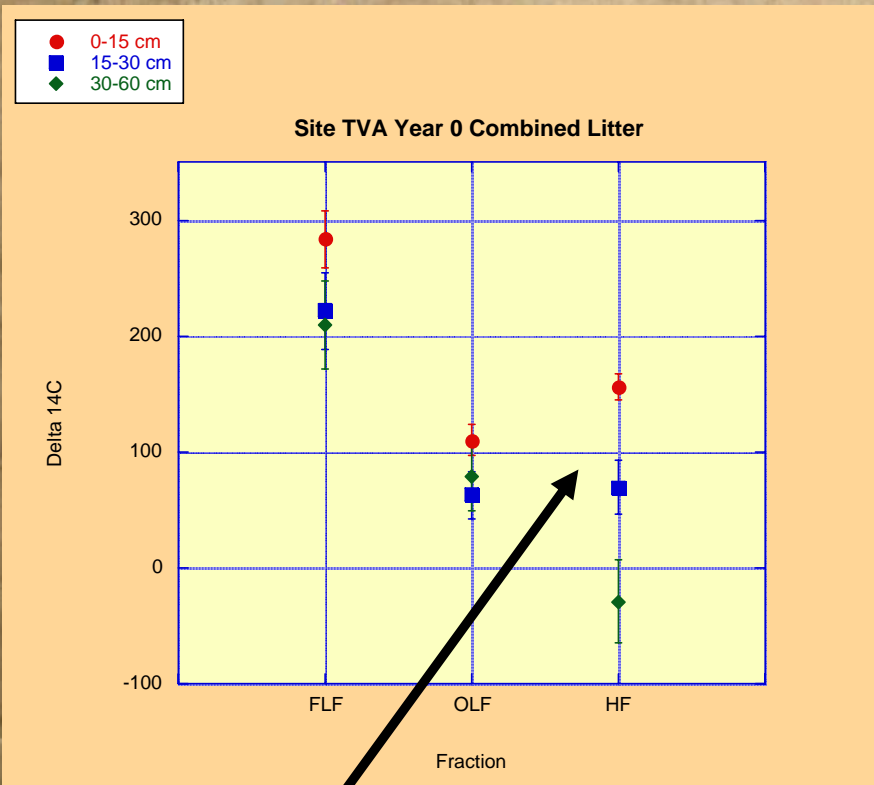
Overall higher 14C
From pulsed site=logical



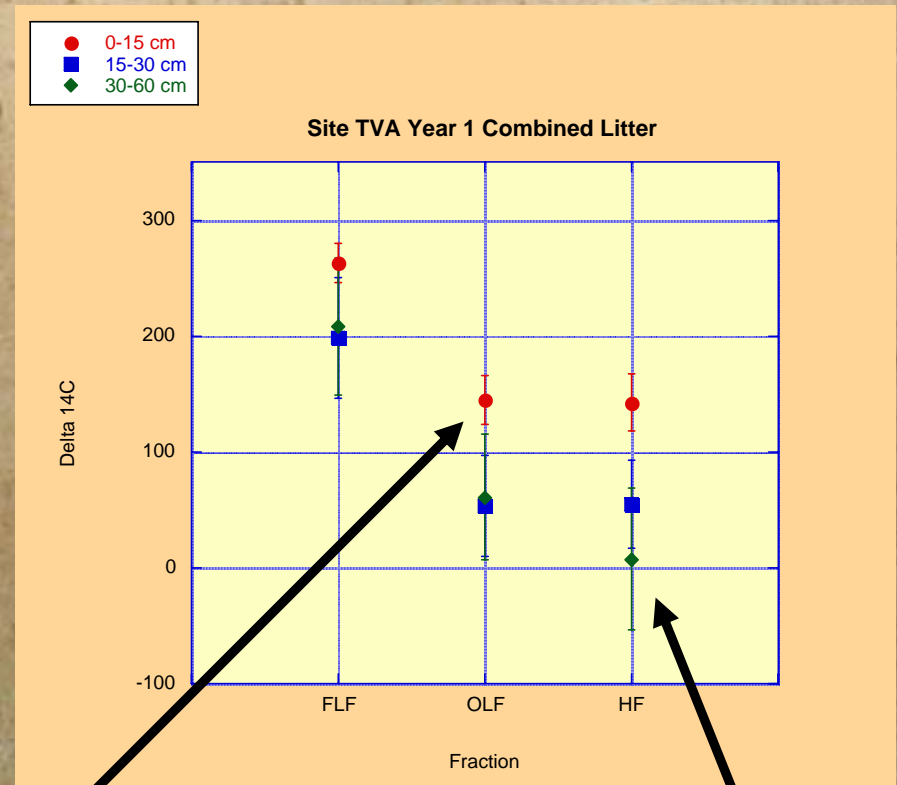
Higher FLF=logical

Higher HF=huh?

TVA YEAR 0 AND YEAR 1 DATA



HF ^{14}C generally higher than OLF; atypical



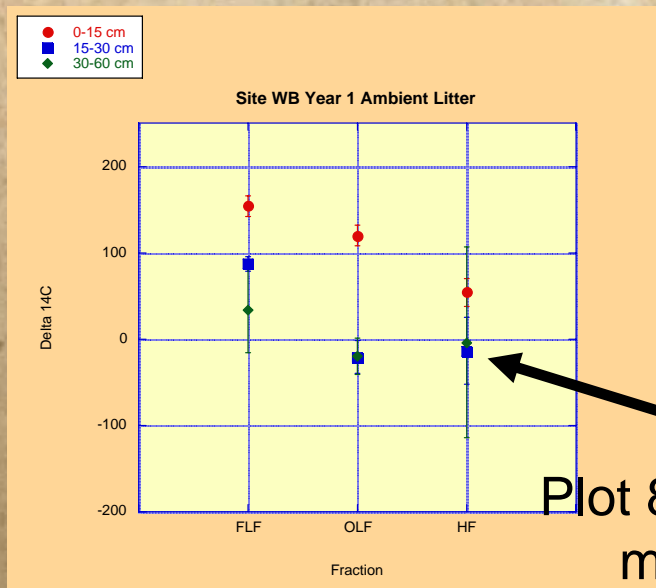
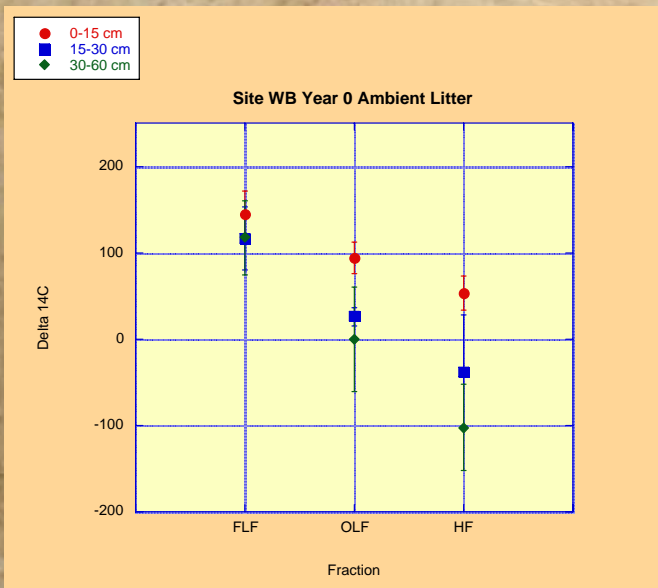
Increase in OLF ^{14}C ?

Heavy Fraction at depth beginning to increase in ^{14}C

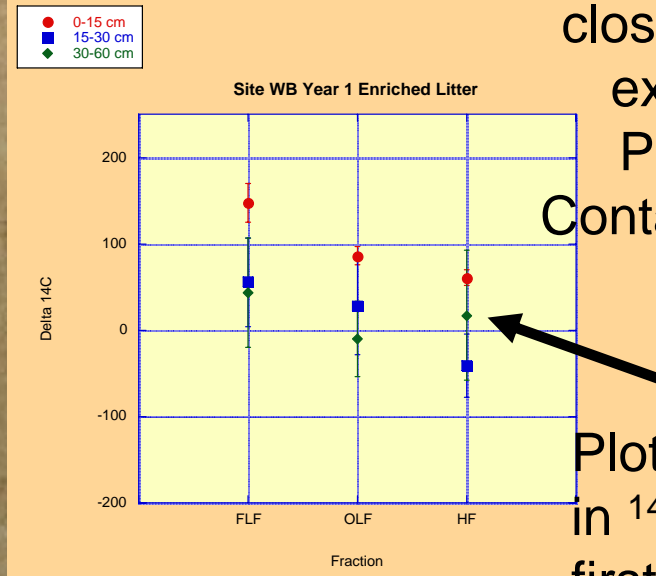
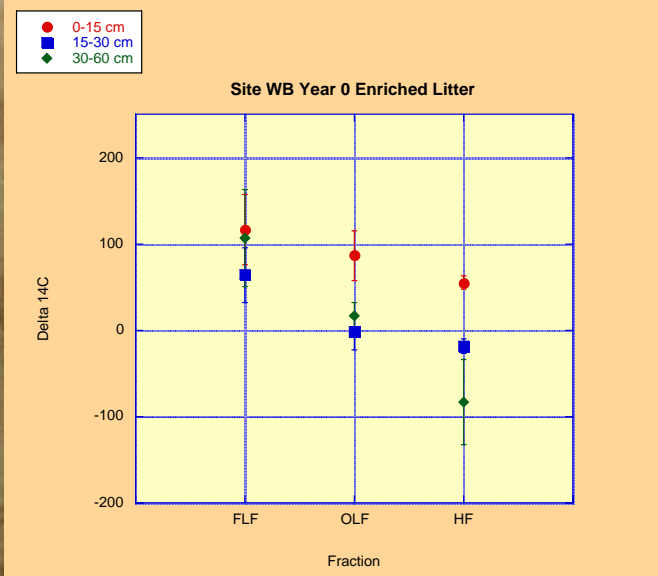
WHAT DOES THIS MEAN?

- 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 $\sim 1000\text{‰}$, 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>

Fröberg, M, et al. 2007. Low dissolved organic carbon input from fresh litter to deep mineral soils. *SSSAJ* **71**, no. 2, 347-54.

Reimer, PJ, et al. 2004. Discussion: reporting and calibration of post-bomb ^{14}C data. *Radiocarbon* **46**, 1299-1304.

Stuiver, M, and Polach, HA. 1977. Discussion: reporting of ^{14}C data. *Radiocarbon* **19**, 355-63.

Swanston, CW, et al. 2005. Initial characterization of processes of soil carbon stabilization using forest stand-level radiocarbon enrichment. *Geoderma* **128**, 52-62.

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

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

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TIFF (Uncompressed) decompressor
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UNITS, CALCULATIONS, & EXPRESSIONS OF ^{14}C DATA

- To normalize for isotopic fractionation:

- Sample activity-
$$A_{SN} = A_S \left(1 - \frac{2(25 + \delta^{13}\text{C})}{1000} \right)$$

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

- 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

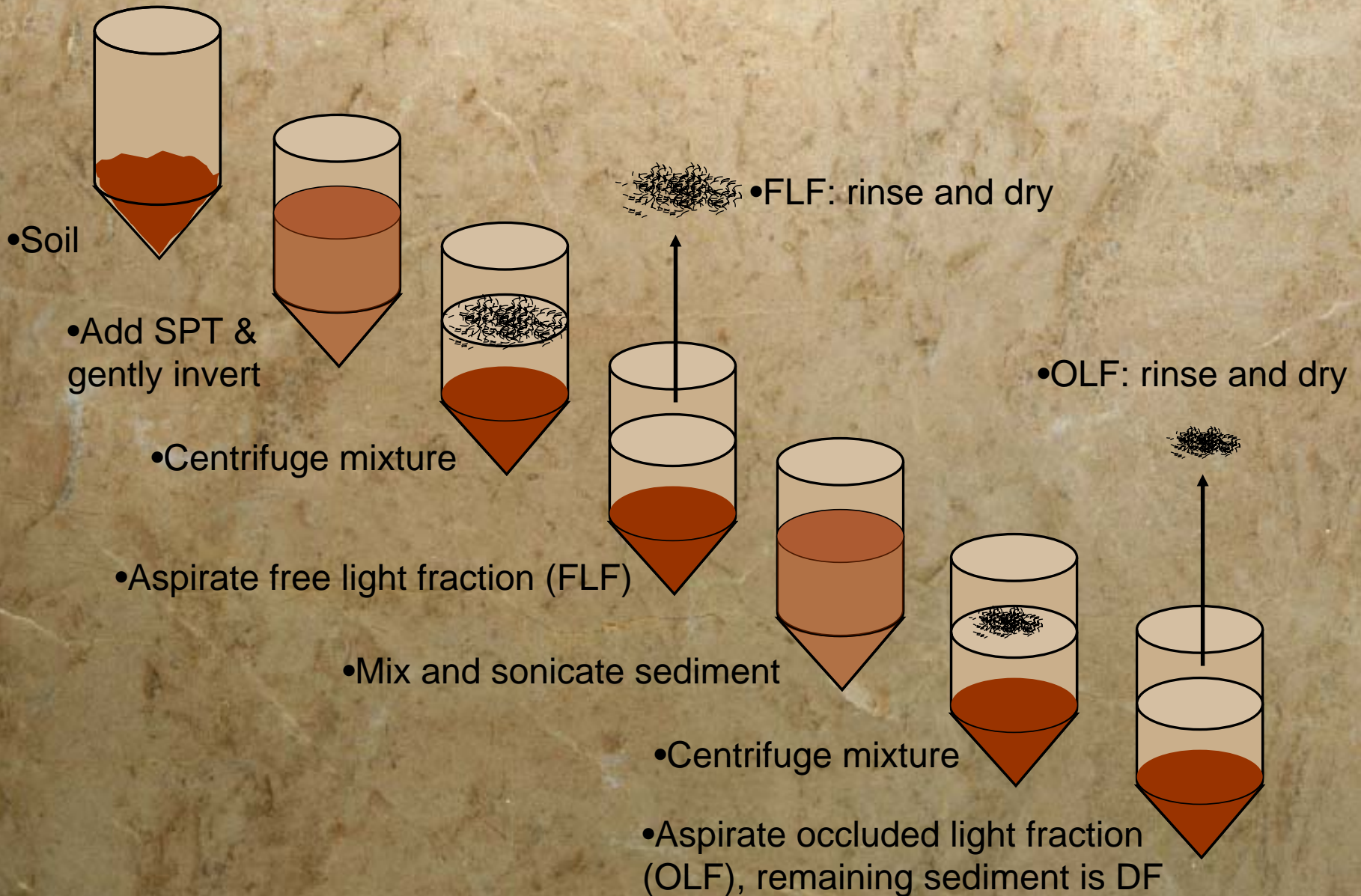
- Using the $\delta^{13}\text{C}$ normalized sample activity (A_{SN}) along with the $\delta^{13}\text{C}$ normalized and age corrected absolute standard (A_{abs})...

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

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

...can be calculated!

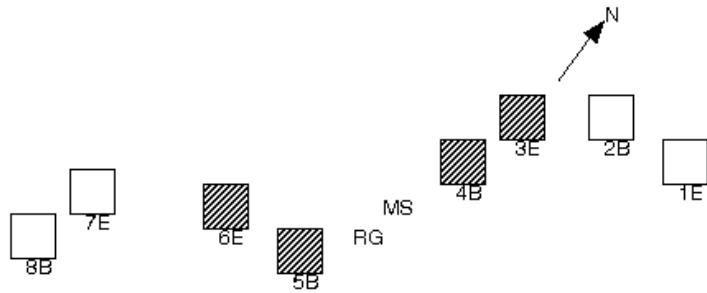
DENSITY FRACTIONATION




PLOT LAYOUTS

Walker Branch Site

Approximate Map of Numbered Plots and Treatments



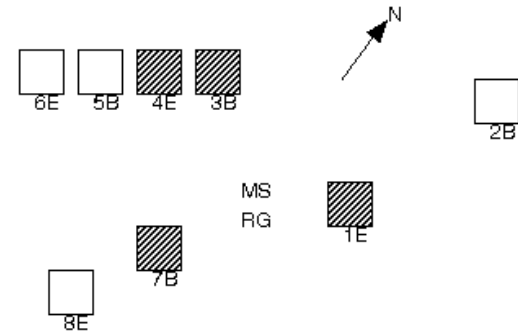
Access from Powerline Right-of-way at Bird Survey Point #3


 = Plots with lysimeters, soil pits, and soil water and temperature sensors.

B = background litter
E = enriched litter
MS = met station
RG = rain gauge

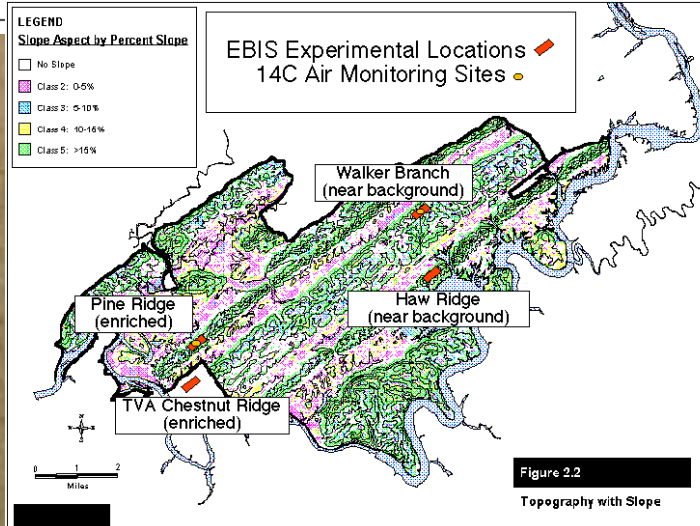
TVA Site

Approximate Map of Numbered Plots and Treatments



 = Plots with lysimeters, soil pits, and soil water and temperature sensors.

B = background litter
E = enriched litter
MS = met station
RG = rain gauge



LITTER PICTURES

