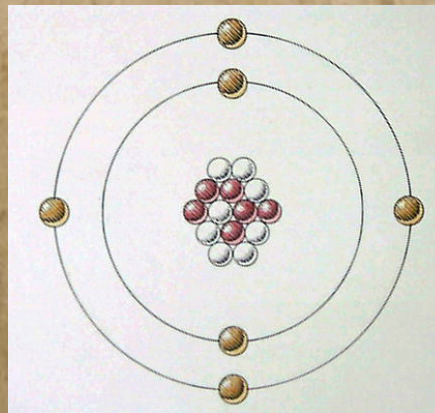


THE DATING GAME: APPLYING ^{14}C AMS IN THE
CHARACTERIZATION OF SOIL CARBON DYNAMICS
WITHIN DOLOMITIC ULTISOL FRACTIONS AT VARYING
DEPTHS



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Department of Chemistry, Department of Earth Science
Lawrence Livermore National Laboratory

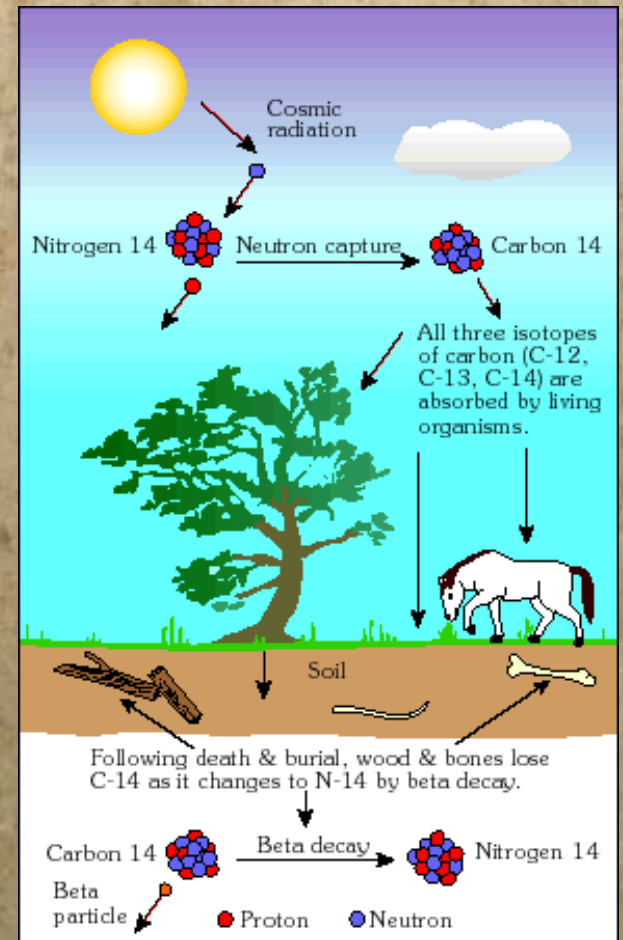
CARBON INPUT AND STABILIZATION

- 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

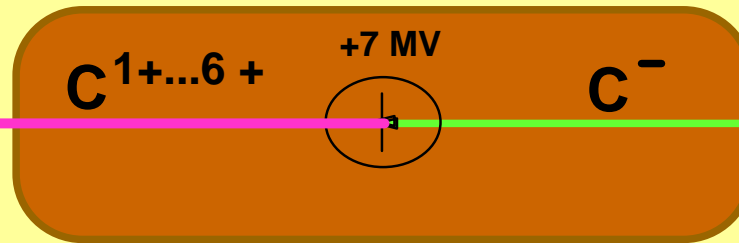
High Energy Mass Spectrometer



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

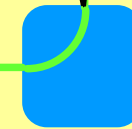


Rigidity Filter



Tandem Electrostatic Accelerator

64 samples
Negative Ion Source

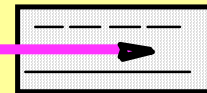


Low Energy Mass Spectrometer

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



Velocity (Wien) Filter



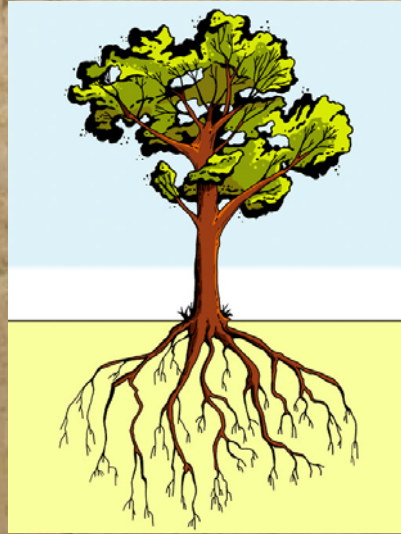
Ion Identification Detector

EBIS (ENRICHED BACKGROUND ISOTOPE STUDY)

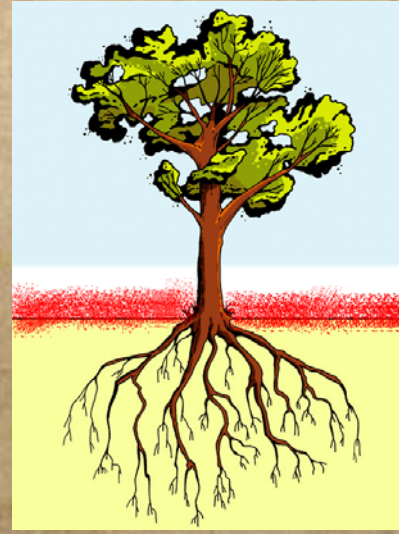
- July/August 1999--large release of radiocarbon near Oak Ridge Reservation (ORR)
- Uptake by vegetation unprecedented in scale
- Ecosystem-scale ^{14}C tracer used to study outstanding issues in terrestrial carbon cycle
- Reciprocal litter experiment at four sites encompassing two soil types and two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

TVA/WB SITE STUDY EFFECTS OF...

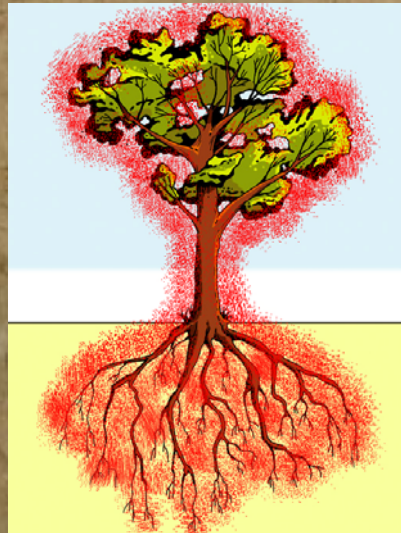
WB (A)
Background
Control



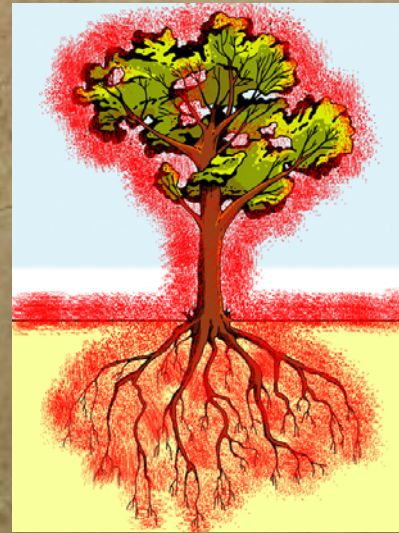
WB (E)
Litter



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 °C
- Thawed, then oven-dried at 105°C
- Density fractionation and other sample prep

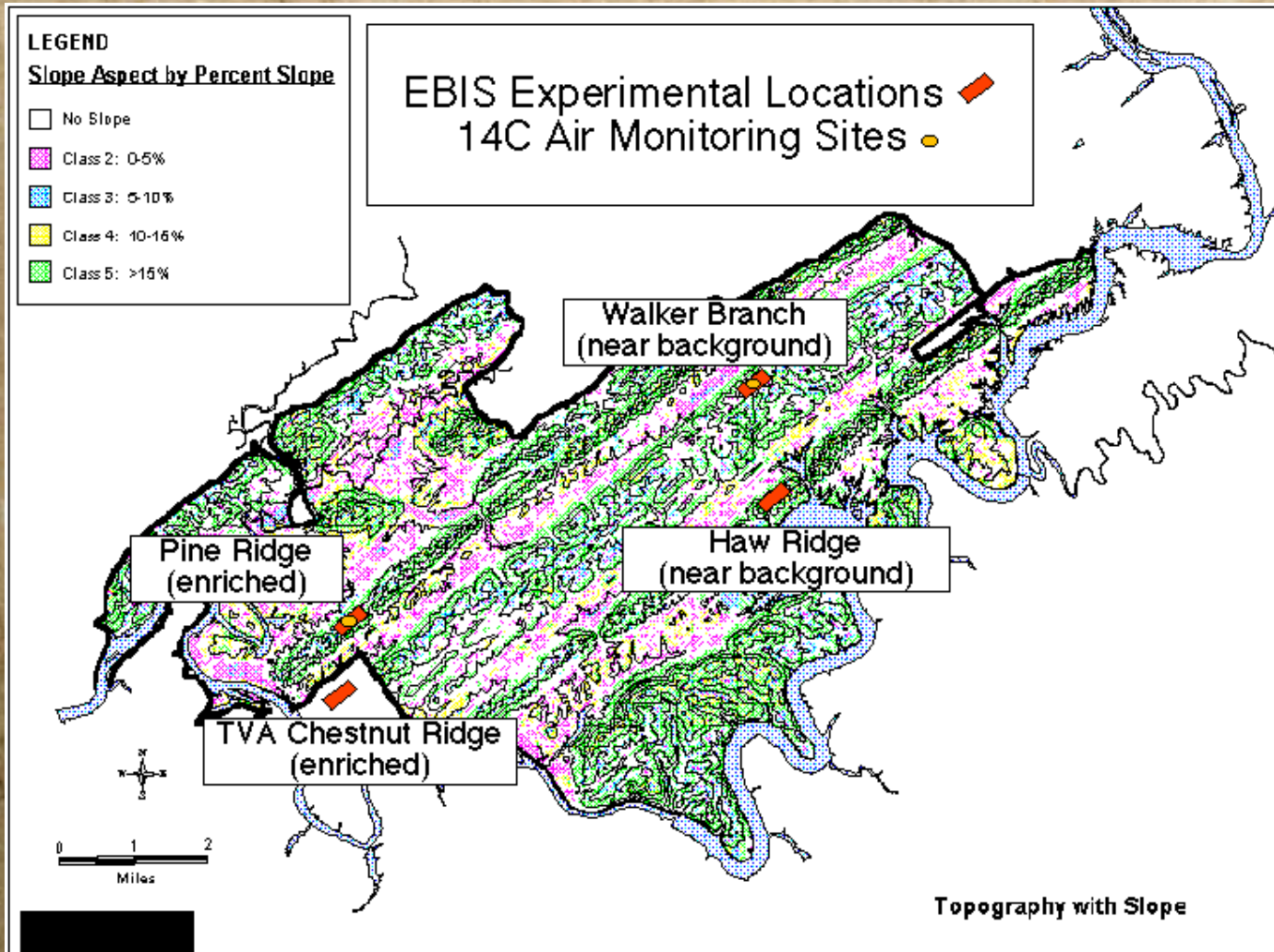
STUDY PLOT DESCRIPTIONS

- 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

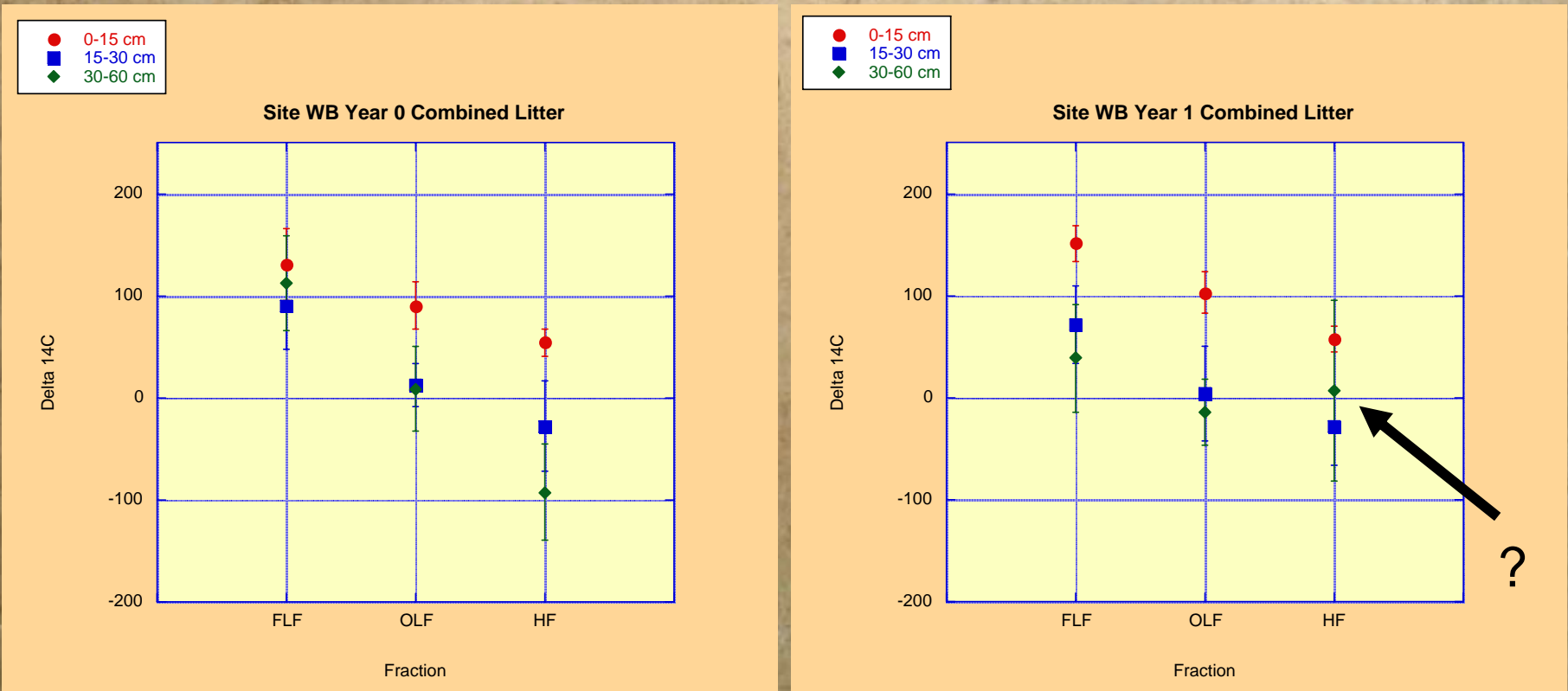
CONT'D

- 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)

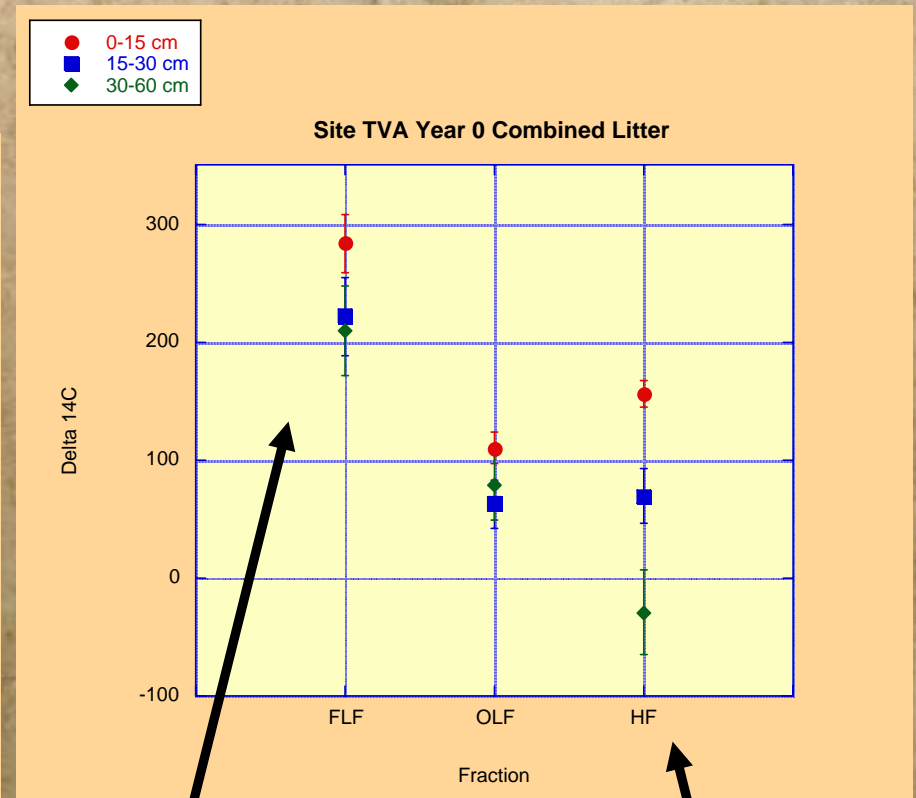
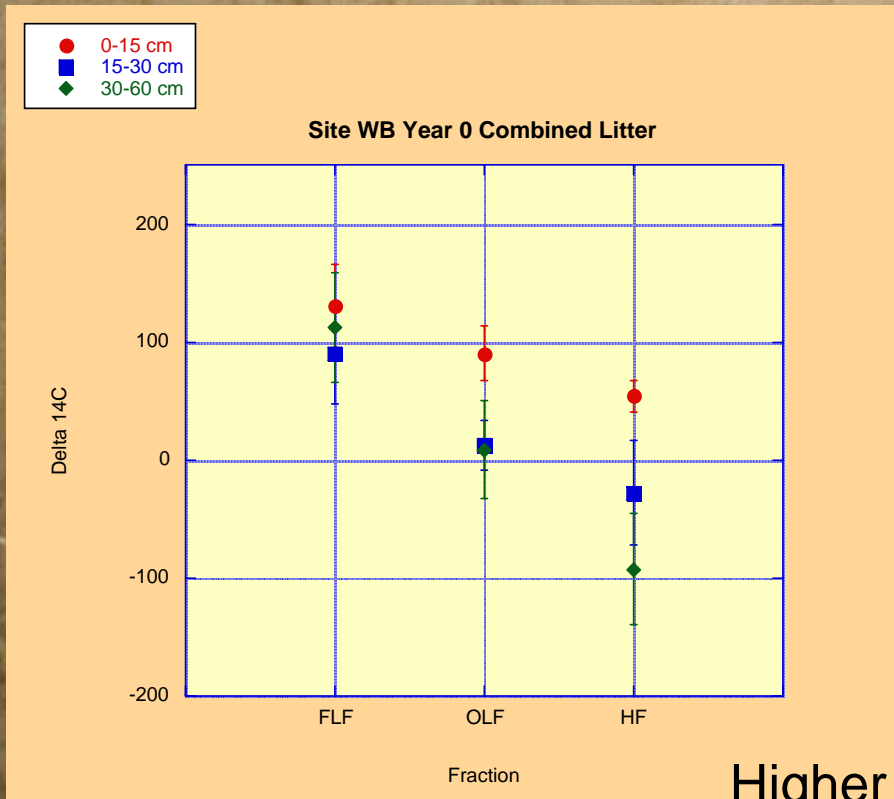
WB YEAR 0 AND YEAR 1 DATA



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

WB YEAR 0 AND TVA YEAR 0

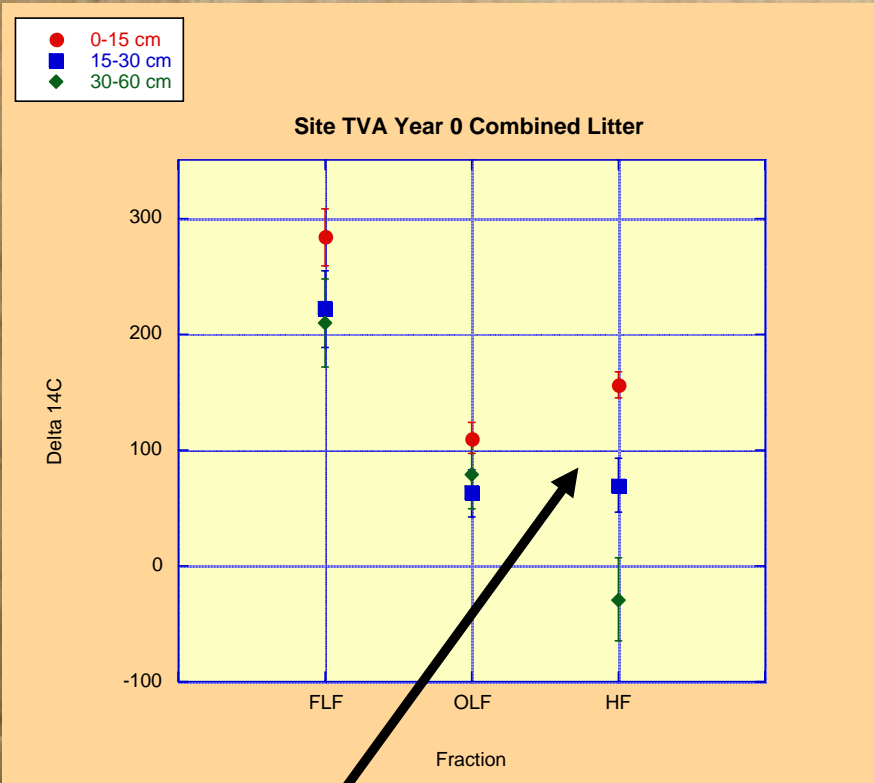
Overall higher 14C
From pulsed site=logical



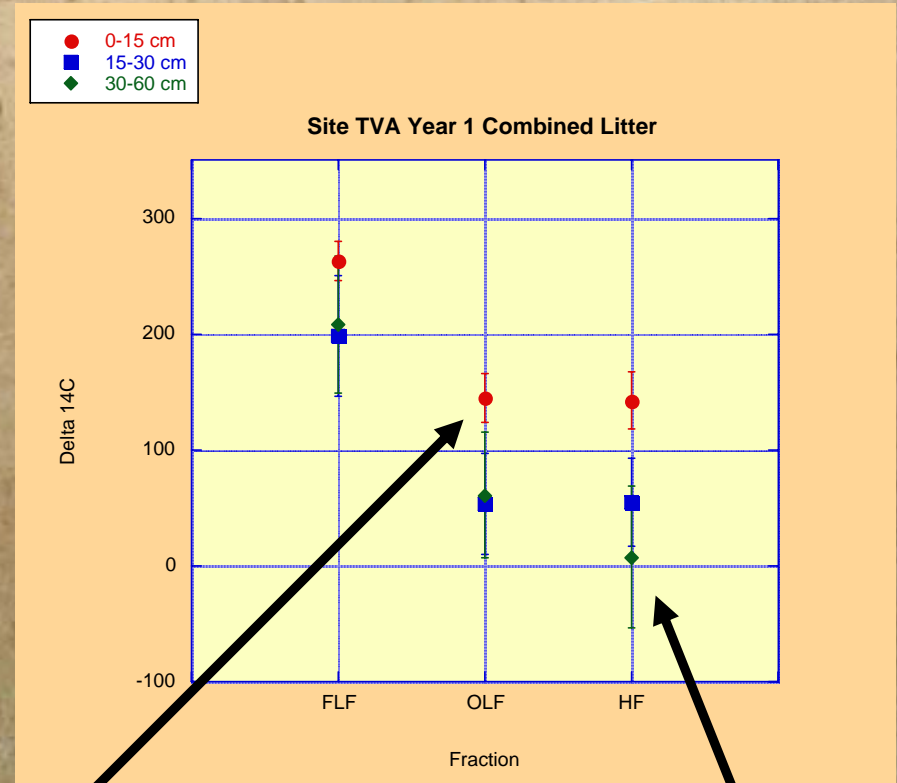
Higher FLF=logical

Higher HF=huh?

TVA YEAR 0 AND YEAR 1 DATA



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



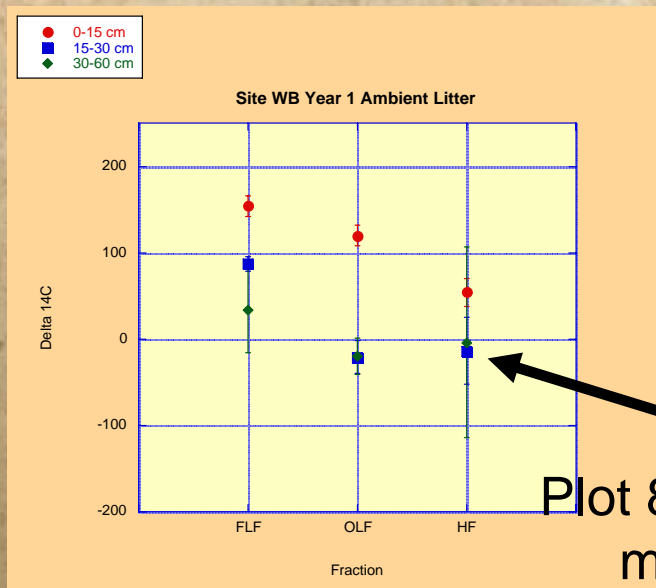
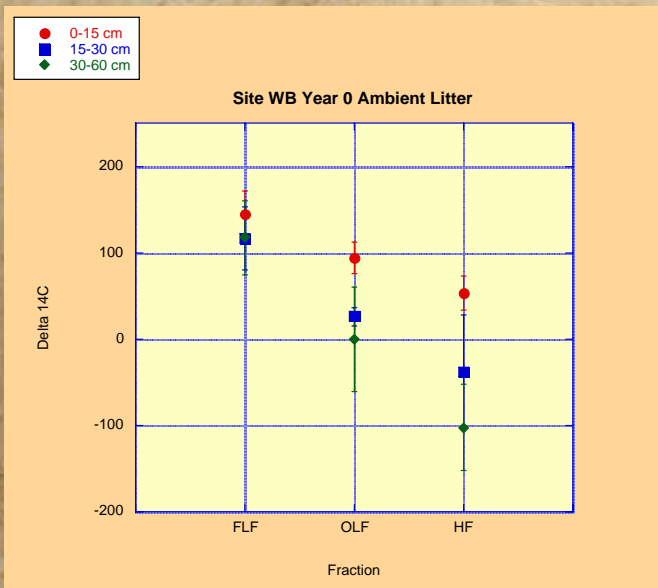
Increase in OLF ^{14}C ?

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

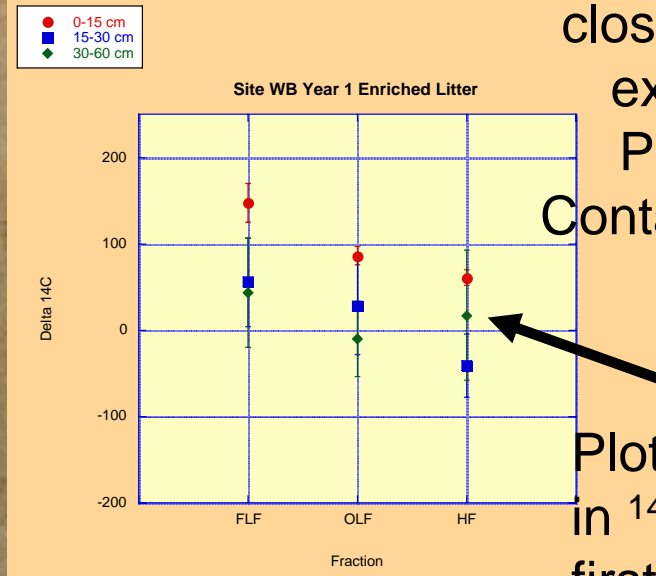
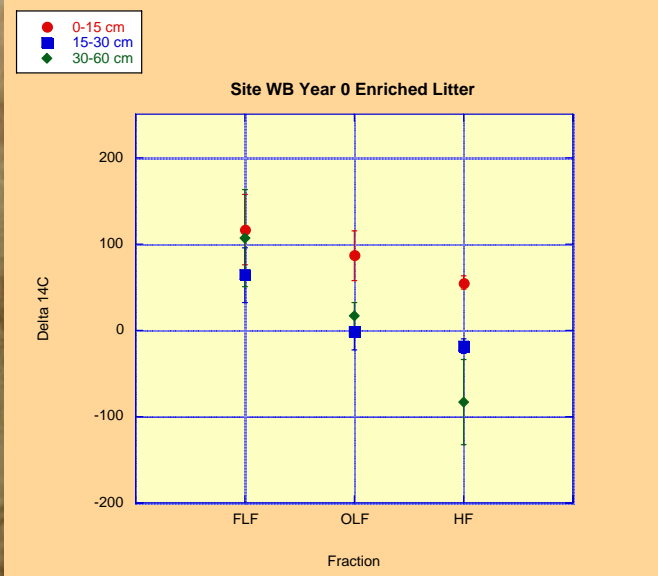
WHAT DOES THIS MEAN?

- 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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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

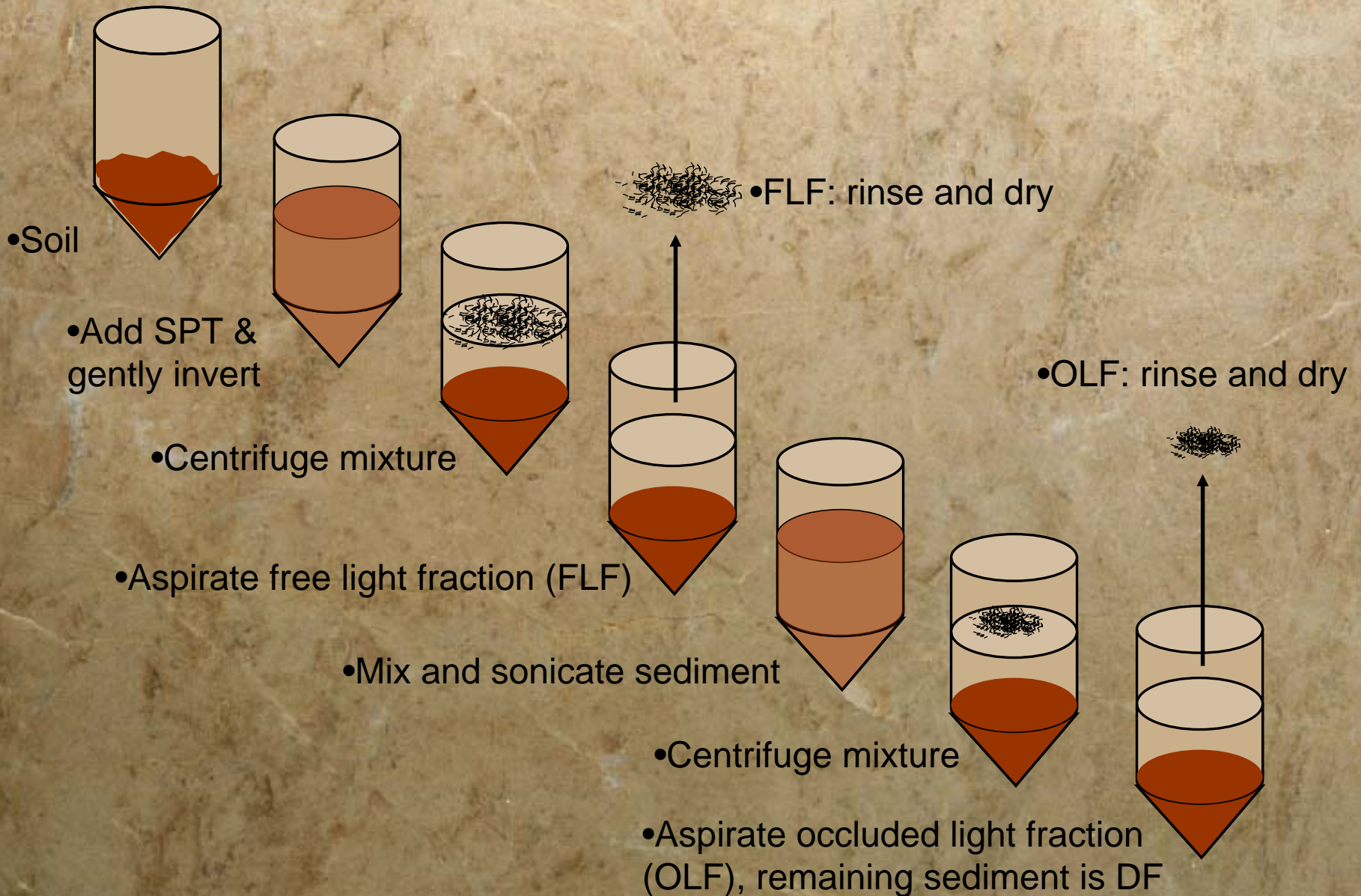
- Using the $\delta^{13}\text{C}$ normalized sample activity (A_{SN}) along with the $\delta^{13}\text{C}$ normalized and age corrected absolute standard (A_{abs})...

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!

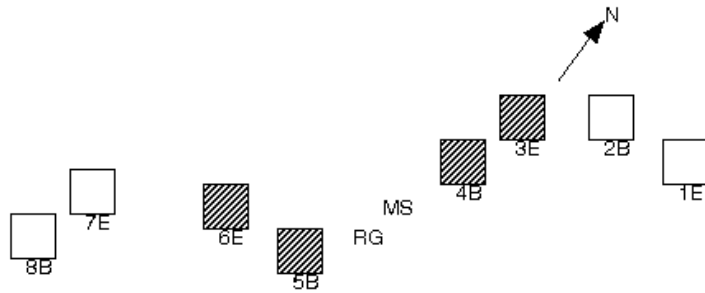
DENSITY FRACTIONATION




PLOT LAYOUTS

Walker Branch Site

Approximate Map of Numbered Plots and Treatments



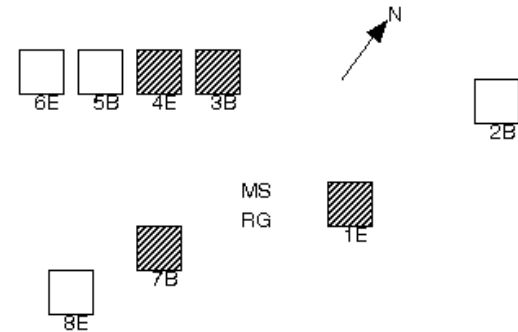
Access from Powerline Right-of-way at Bird Survey Point #3


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

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

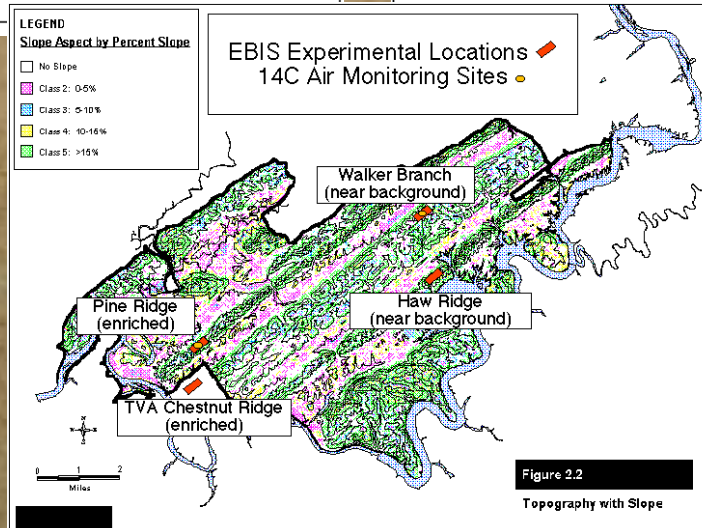
TVA Site

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

