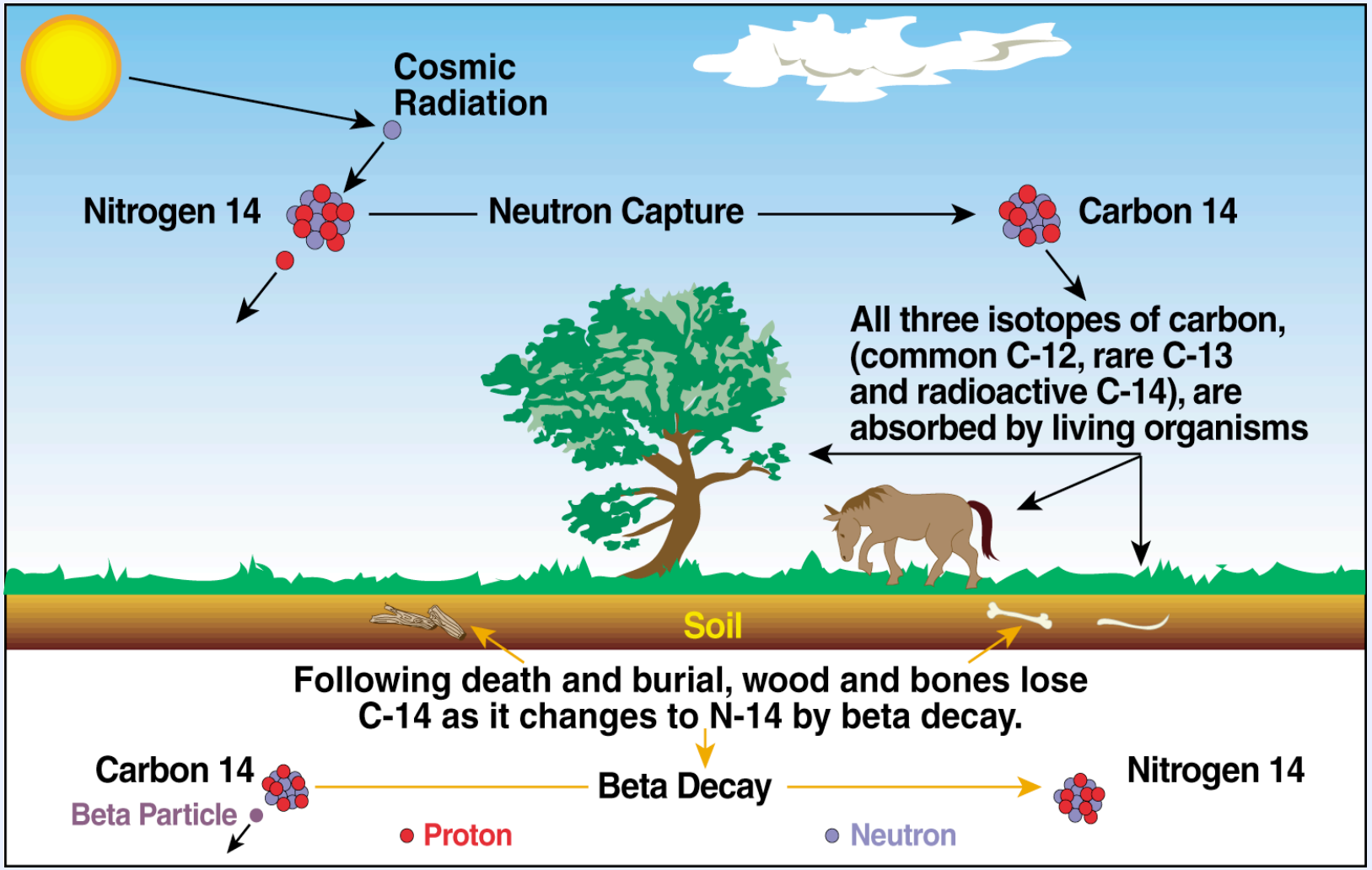
Determination of BioCarbon Content of Transportation Fuels by Carbon-14 Analysis

Bruce Buchholz
Lawrence Livermore National Laboratory
Livermore, CA 94551

LCFS Compliance and Enforcement Working Group Meeting
December 13, 2007

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Cosmic rays naturally produce carbon-14 in the atmosphere that labels every living thing

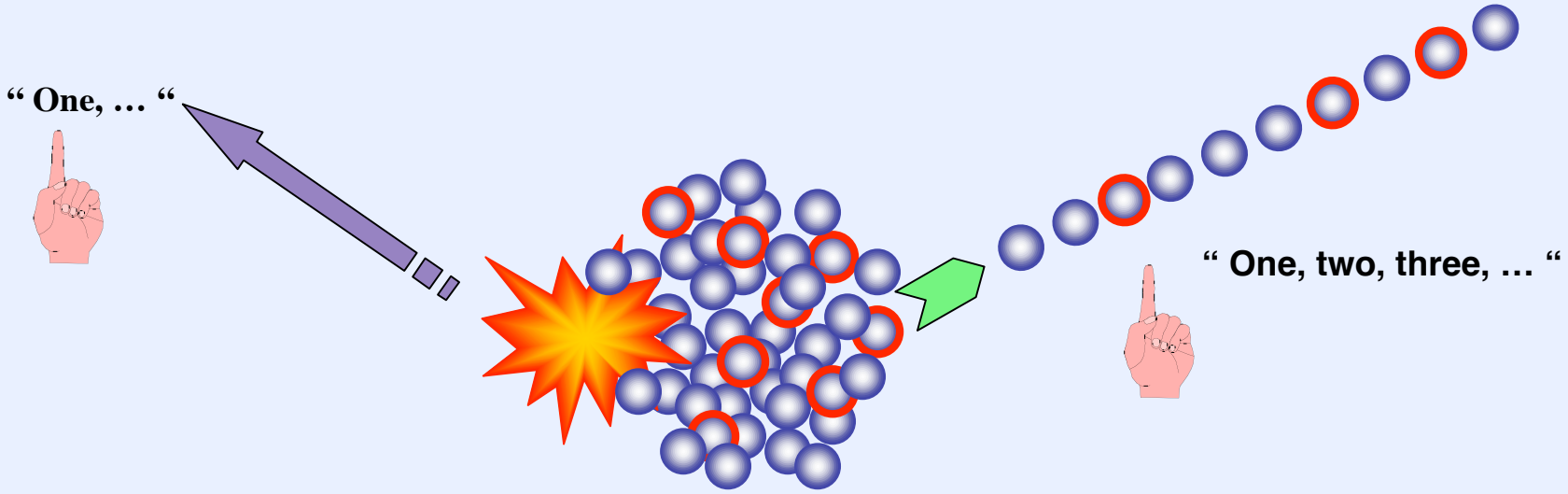


Natural contemporary level of carbon-14 is 1.2 parts per trillion carbon

Carbon-14 can be measured by counting radioactive decays or by counting atoms

Decay Counting

Mass Spectrometry



Decay counting is inefficient when counting long-lived isotopes like carbon-14 (5700 y half-life)

Older technology, lower cost

Retail fuel challenges sensitivity

Count atoms, not decays

10,000 ^{14}C can be counted in <30 sec for contemporary sample

Sensitivity is part per quadrillion

Technical requirements for measurement of carbon-14 in biofuels

- Must be capable of accurately measuring C-14 concentrations similar to radiocarbon dating and distinguish between different petroleum-biofuel blends likely to be encountered (1-2% precision).
- C-14 levels based on same carbon content of petroleum and biofuel components.
  - 100% biofuel: C-14/C = 1.2 parts per trillion
  - 80 % biofuel: C-14/C = 1.0 parts per trillion
  - 10% biofuel: C-14/C = 100 parts per quadrillion
  - 5% biofuel: C-14/C = 50 parts per quadrillion
  - 0% biofuel: C-14/C less than 5 parts per quadrillion
  - E10 (vol%): C-14/C = 60 parts per quadrillion

Instrument and facility requirements for measuring carbon-14 content of biofuels

Must be capable of measuring hundred(s) of samples accurately with reasonable turnaround

Decay Counting

- **Simple sample preparation**
- **Counter occupies 4'x5' space**
- **Measure 1 - 7 samples per day using 10-mL samples**
- **Low level biofuel blends difficult to measure precisely**
- **LSC counters common**
- **Low background counters found at some universities, contract labs, environmental monitoring facilities**

Mass Spectrometry

- **Specialized sample preparation**
- **Spectrometer fills 20'x20' lab**
- **Measure 100 - 250 samples per day**
- **All biofuel blends in standard operating range**
- **9 facilities in U.S., 3 in CA**
- **Sample turnaround depends on facility, existing sample load, and capacity**