



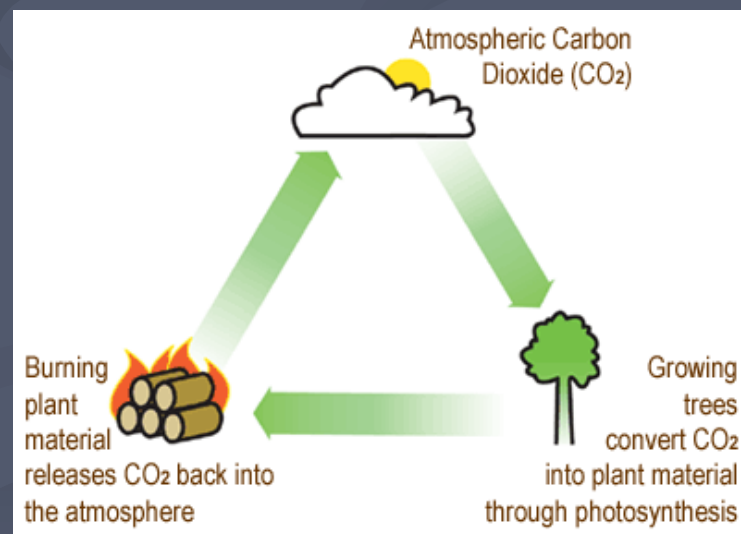
***Quantification of Carbon-Neutral  
Greenhouse Gas Emissions  
Using ASTM D6866***

**Mauricio Larenas**

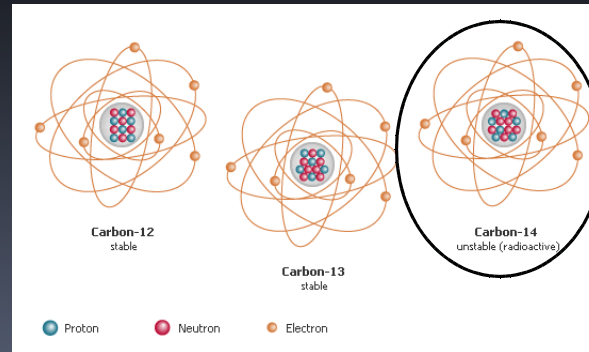
Beta Analytic Inc.

# Carbon Neutral CO<sub>2</sub> (Biogenic CO<sub>2</sub>)

- *Recently respired CO<sub>2</sub>*
- *Plants recently removed it from the air*
- *A by-product of biomass incineration*
- *Can be subtracted from GHG inventories*
- *Has value in the trading markets*



# Carbon-14



*Naturally occurring  
in all biomass,  
absent in fossil fuels*

**ASTM D6866 measures it.**

***Carbon-14 is ubiquitous in all living things.***

***But it doesn't stick around.***

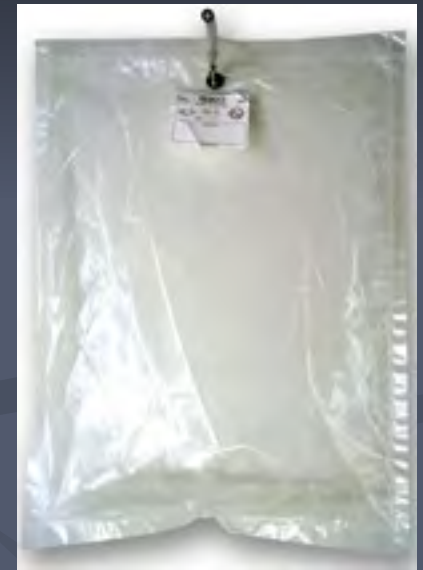
***It slowly and gradually decays away after death, so that by 50,000 years there's none left.***

***Coal and fossil-derived materials do not have any carbon-14 whereas biomass does.***

*Take a good look, Identical?*



Carbon-14  
■ Biomass CO<sub>2</sub>  
Coal CO<sub>2</sub>  
No Carbon-14



***They're NOT the same!***

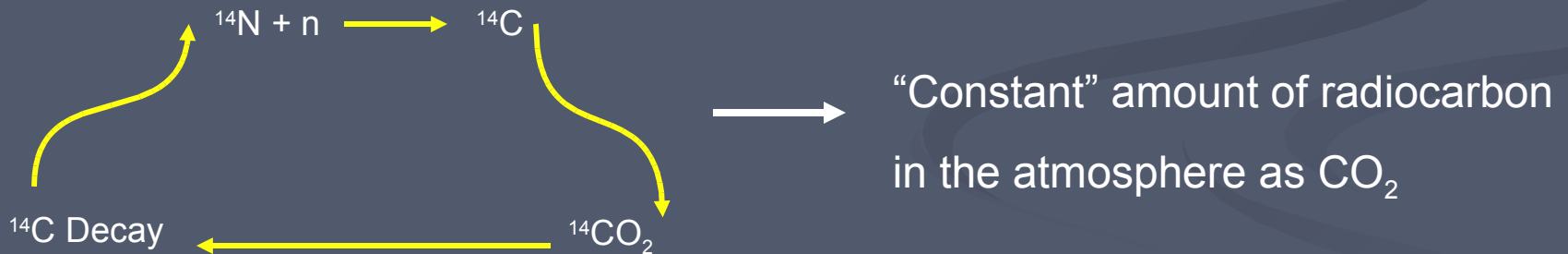
# The Radiocarbon Cycle

## STEP 1: Ongoing formation and decay of radiocarbon within the atmosphere

Nitrogen (  $^{14}\text{N}$  ) + cosmic neutrons  $\longrightarrow$  Radiocarbon ( $^{14}\text{C}$ )

Radiocarbon immediately oxidizes  $\longrightarrow$  Carbon dioxide ( $^{14}\text{CO}_2$ )

The radiocarbon immediately starts to decay ( $T^{1/2} = 5730$  years)

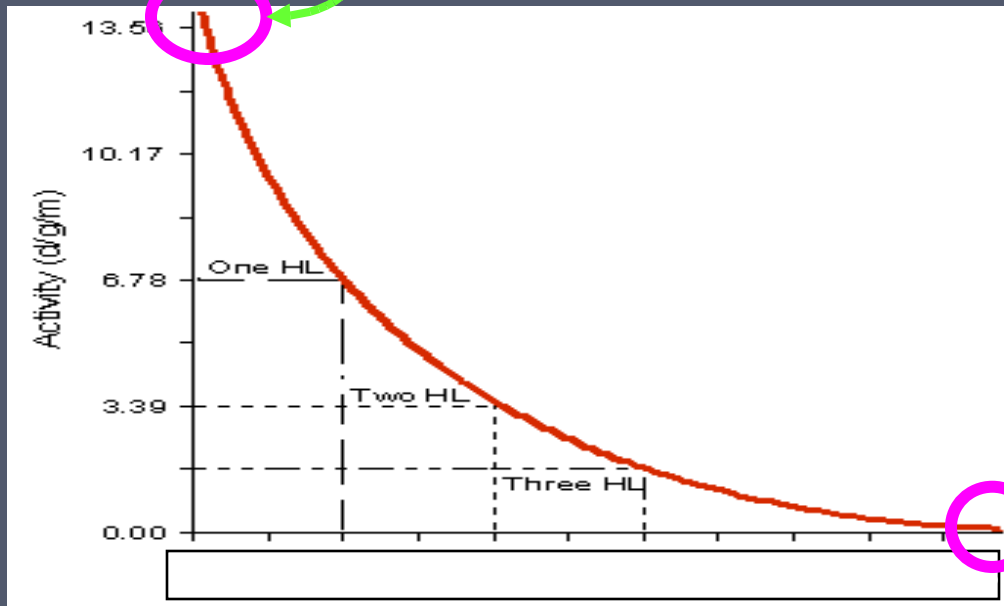


## STEP 2: Radiocarbon is removed from the atmosphere by plants

## STEP 3: Disequilibrium begins upon “death”



100% renewable



The Radiocarbon Decay Curve



0% renewable

# Conventional biomass – CO<sub>2</sub> inventory accounting

(Stationary Combustion Sources – e.g. Cement, Co-firing, Biomass, Waste, etc.)



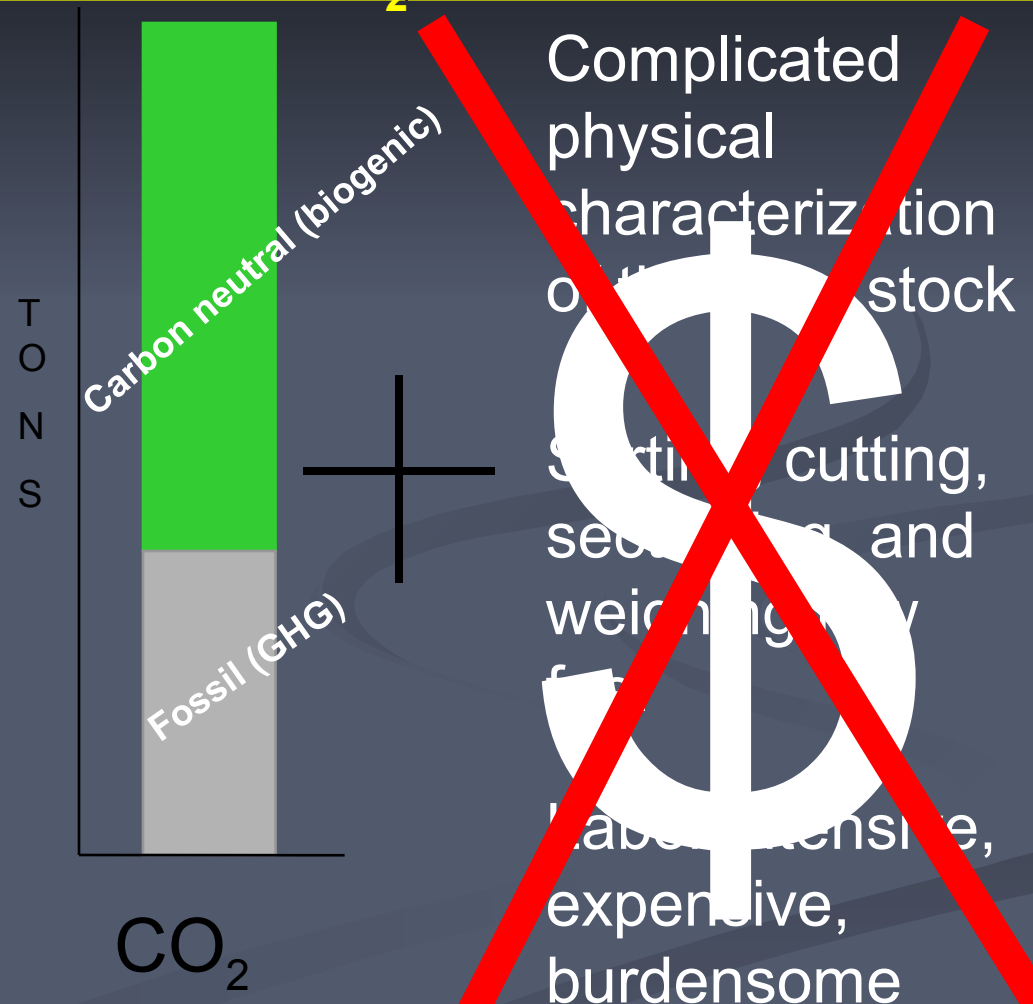
Complicated  
physical  
characterization  
of the feed stock

Sorting, cutting,  
sectioning, and  
weighing raw  
fuel

Labor intensive,  
expensive,  
burdensome

# ASTM D6866 biomass – CO<sub>2</sub> inventory accounting

## Measure CO<sub>2</sub> in the stack effluent



ASTM-D6866 is a standardization of radiocarbon dating methods used by archaeologists to determine the age of fossils.

Methods that have been in use for  
60 years  
(mature technology)

and being a mature industry . . .

- Expertise
- Laboratories
- Well-known sources of error
- Supply Lines
- Venders
- Instrumentation
- Raw materials

Complete pre-existing infrastructure

# **C14 Dating is an internationally recognized method for verification**

**ASTM (American Society for Testing and Materials)**

**CEN (European Committee for Standardization)**

**US EPA (Environmental Protection Agency)**

**ARB (California Air Resources Board)**

**TCR (The Climate Registry)**

**WCI (Western Climate Initiative)**

**Australia (National Greenhouse and Energy Reporting Protocol)**

**EU-ETS (European Union Emission Trading Scheme)**

**ROCs (Renewable Obligation program UK ) \*Currently being Approved**

## Status of ASTM-D6866 in the USA

### California Air Resources Board (CARB) & AB 32

“Fuels like biomass and municipal solid waste (MSW) are so varied that fuel analysis is impractical.”

“The proposed regulation requires emissions from biomass-derived fuels to be reported separately from fossil fuels.”

“Municipal solid waste facilities are required to use **ASTM Method D6866 . . .**”

All stationary combustion facilities which co-fire a fossil fuel with a biomass-derived fuel are recommended to use **ASTM Method D6866.**

## Status of ASTM-D6866 in the USA

### California Air Resources Board (CARB) & AB 32

- January 1, 2008 : Establish a statewide GHG emissions cap for 2020 based on 1990 emissions
- January 1, 2009 : Adopt mandatory reporting rules for significant sources of GHG
- January 1, 2010 : Adopt a plan indicating how emission reductions will be achieved
- January 1, 2011 : Adopt regulations to achieve the maximum technologically feasible and cost-effective reductions in GHG

## Status of ASTM-D6866 in the US

### The Western Climate Initiative

Essential Requirements of Mandatory Reporting, Final Draft released May 2009:

“The owner or operator that combusts fuels or fuel mixtures for which the biomass fuel fraction is unknown or cannot be documented (for example, municipal solid waste or tire-derived fuels) shall determine the biomass fuel portion of CO<sub>2</sub> emissions using ASTM D6866....”

An operator who uses CEMS data to report CO<sub>2</sub> emissions from a facility that co-fires fossil fuels with biomass fuels or waste-derived fuels that are partly biomass fuels shall determine the portion of total CO<sub>2</sub> emissions separately assigned to the fossil fuel and the biomass fuels using ASTM D6866.

Operators who combust waste-derived fuels that are not pure biomass fuels shall determine the biomass fuel portion of CO<sub>2</sub> emissions using ASTM D6866.

## *Status of ASTM-D6866 in the US*

### *The Climate Registry – North American GHG Protocol*

Adoption of ASTM D6866 for biomass CO2 emissions monitoring

General Reporting Protocol Version 1.1 May 2008 identified ASTM D6866 as one of the methods to use when quantifying emissions from waste fuels and biomass.

## *Status of ASTM-D6866 in the USA*

### *EPA Proposed Mandatory Greenhouse Gas Reporting Rule*

“Carbon dioxide emissions from the combustion of biogenic fuels shall be excluded from the calculations.”

“For a unit that combusts MSW, the owner or operator shall use, for each quarter, ASTM Methods D6866 and D7459 ... to determine the relative proportions of biogenic and non-biogenic CO<sub>2</sub> emissions when MSW is combusted.”

“The owner or operator shall separate total CO<sub>2</sub> emissions from MSW combustion into biogenic emissions and non-biogenic emissions, using the average proportion of biogenic emissions of all samples analyzed during the reporting year.”

## Status of ASTM D6866 in the UK

**Malcolm Wicks, Minister of Energy, announces in January 2008 a plan for Energy from Waste plants (EfW) to qualify for ROCs**

“Several respondents referred to the [radiocarbon dating](#) approach which has been the subject of a report commissioned by (among others) the Renewable Energy Association.”

“We agree with the principle . . . as long as it produces appropriately accurate and reliable results.”

“We are currently working with Ofgem to consider whether [radiocarbon dating](#) is a valid option and, if it is, to identify any changes to secondary legislation necessary to allow it . . .”

<http://www.betalabservices.com/PDF/ROEfW.pdf>

## *Status of ASTM D6866 in the UK*

### *Howard Leberman - Industry Regulation Policy Advisor UK Environment Agency*

“We accept that the natural rubber content of tyres may be considered as biomass under EU ETS and is in accordance with the definition set out in Section 2(4)(f) of the Commission's monitoring and reporting guidance.”

“We accept your proposed methodology of carbon isotope analysis to determine the non-fossilised carbon content of tyres.”

“This decision has been endorsed by the UK regulators and Defra at the UK regulators telecom on the 17th April 2008 and will apply from the 1<sup>st</sup> January 2008.”

## ASTM D6866 and CEN 15747

- ~ ASTM D6866 is part of the mandatory reporting requirements of California's AB 32, Western Climate Initiative, The Climate Registry and the EPA's GHG protocol.
- ~ The European Union allows the use of ASTM D6866 for monitoring various types of heterogeneous fuels.
- ~ The Australian government has recommended the use of ASTM D6866 for blended fuels.
- ~ The Renewable Obligation Certificate program in the United Kingdom is also considering this method for monitoring biomass energy production.
- ~ CEN 15747 is used to monitor refuse-derived fuels for the European Union's Emission Trading Scheme.

# ASTM D7459

## Standard Practice for Collection of Integrated Samples for the Speciation of Biomass (Biogenic) and Fossil-Derived Carbon Dioxide Emitted from Stationary Emissions Sources

Established for the EPA Proposed Mandatory Greenhouse Gas Reporting Rule

Written by stack testing community including The Avogadro Group

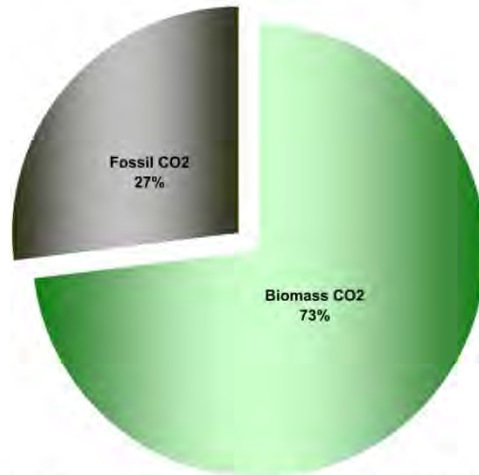
Used as basis for international ISO standard under development

### Report of Biomass CO<sub>2</sub> Content Analysis using ASTM-D6866

Submitter: ABC Company  
Submitter Label: Gas Bag 1  
Laboratory Number: Beta-00001  
Material Analyzed: CARBON DIOXIDE  
Date Received: October 13, 2006  
Date Reported: October 17, 2006

**Biomass CO<sub>2</sub>:** **73% \***  
(carbon-neutral CO<sub>2</sub>) (renewable carbon to total carbon)

Proportions Biomass CO<sub>2</sub> vs. Fossil CO<sub>2</sub>  
indicated by C14 content



\* ASTM-D6866 cites precision on the mean Biomass CO<sub>2</sub> Result as +/- 3% (absolute). This is the most conservative estimate of error in the measurement of complex biomass containing solids and liquids based on empirical results. Real precision for readily combustible and homogenous materials (e.g. gasoline) and especially samples received as CO<sub>2</sub> (e.g. flue gas or CEMS exhaust) can be as low as +/- 0.5-2%. The result only applies to the analyzed material. Fluctuations in carbon content within a batch of product, gasoline or flue gas must be determined separately (e.g. averaged measurements of multiple solids or liquids, and single measurement of the combination of gas aliquots collected over time). The accuracy of the result as it applies to the analyzed product, fuel, or flue gas relies upon all the carbon in the analyzed material originating from either recently respired atmospheric carbon dioxide (within the last few decades) or fossil carbon (more than 50,000 years old). "Percent biomass" specifically relates % renewable (or fossil) carbon to total carbon, not to total mass or molecular weight. Mean Biomass CO<sub>2</sub> estimates greater than 100% are assigned a value of 100% for simplification.

## Reporting

## Simple Visual Report

## Easy Inter-comparison

## Instinctively Obvious

How much does it cost?

**\$595 USD per analysis**

**(Off-setting labor, liabilities and hazards  
associated with feedstock characterization)**

How long does it take to get a result?

**One week, but as little as 2-3 days**

# LSC Counter Room



# One of the Chemistry Line Rooms



# Accelerator Mass Spectrometry Room



## ***Company Background***

- 30 years in business, considered the leader of our field
- Fast turn-around times (as little as 24 hours)
- Confidentiality of all results
- Large throughput operation [52 LSC counters, 2 mass spectrometers, 2 accelerator mass spectrometers (4 ions sources), 16 chemistry lines]
- 18 dedicated full-time professionals, no part-time students learning on your samples
- ISO/IEC 17025:2005 accredited

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