Understanding "Biobased" and ASTM Standard D6866-16 for measuring biobased content

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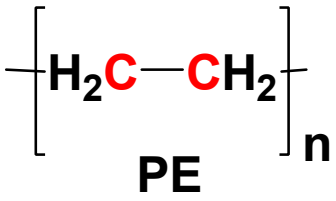
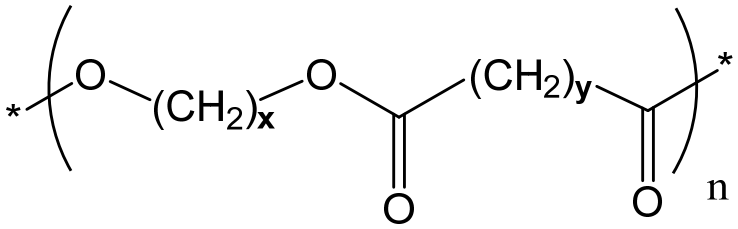
BASICS -- TERMINOLOGY

Biobased plastics and products refers to:

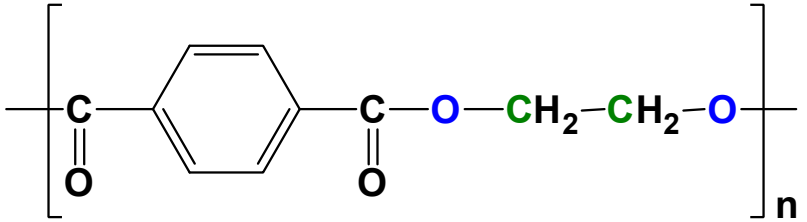
- **Origins of the carbon in the polymer**
- **Plant-biomass feedstock (biobased) vs petro-fossil feedstock**
- **The "beginning of life" and does not address end-of-life**
- **Biobased products are not necessarily and automatically biodegradable-compostable**



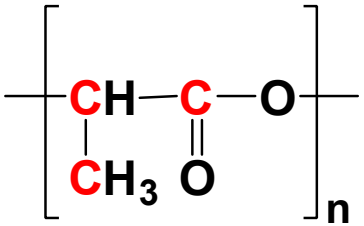
PE



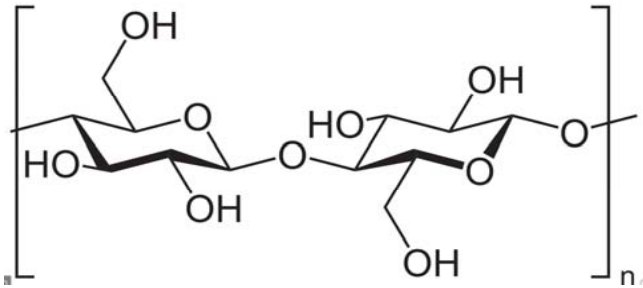
Biobased polyester



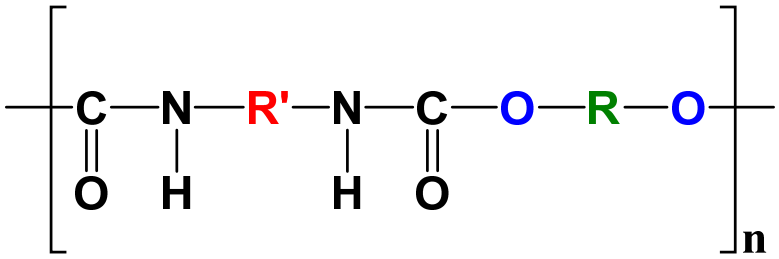
PET



PLA



Cellulose



Biobased polyurethane

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BASICS -- TERMINOLOGY

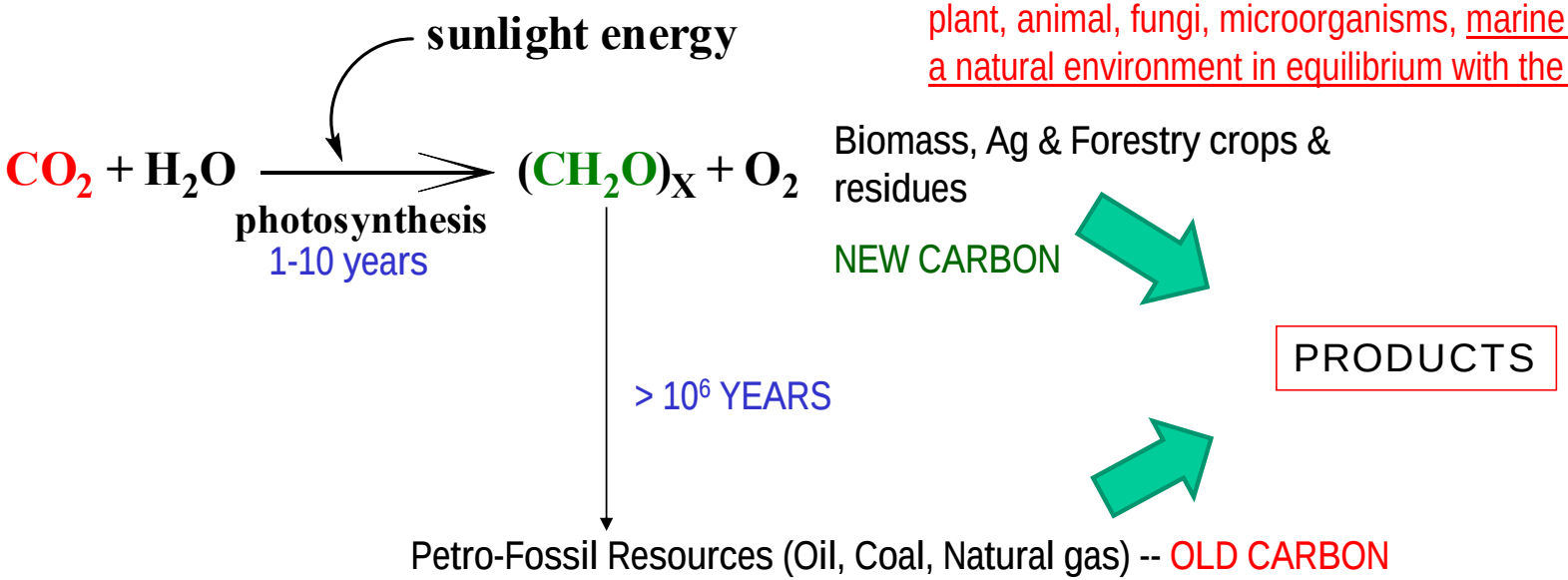
Biodegradable-compostable plastic refers to "end-of-life" in managed, closed loop disposal systems like composting or anaerobic digestion coupled to composting

- **Viable and responsible "end-of-life" solution in harmony with the "circular economy" concepts of closed loop systems**
- **Unqualified claim of "biodegradable" is misleading, deceptive, wrong and violates CA law and FTC green guides**
- **Not all biobased plastics are biodegradable-compostable; end-of-life is recycling**

Understanding the Value Proposition for biobased vs petro/fossil carbon

Biological Carbon Cycle – the material carbon footprint

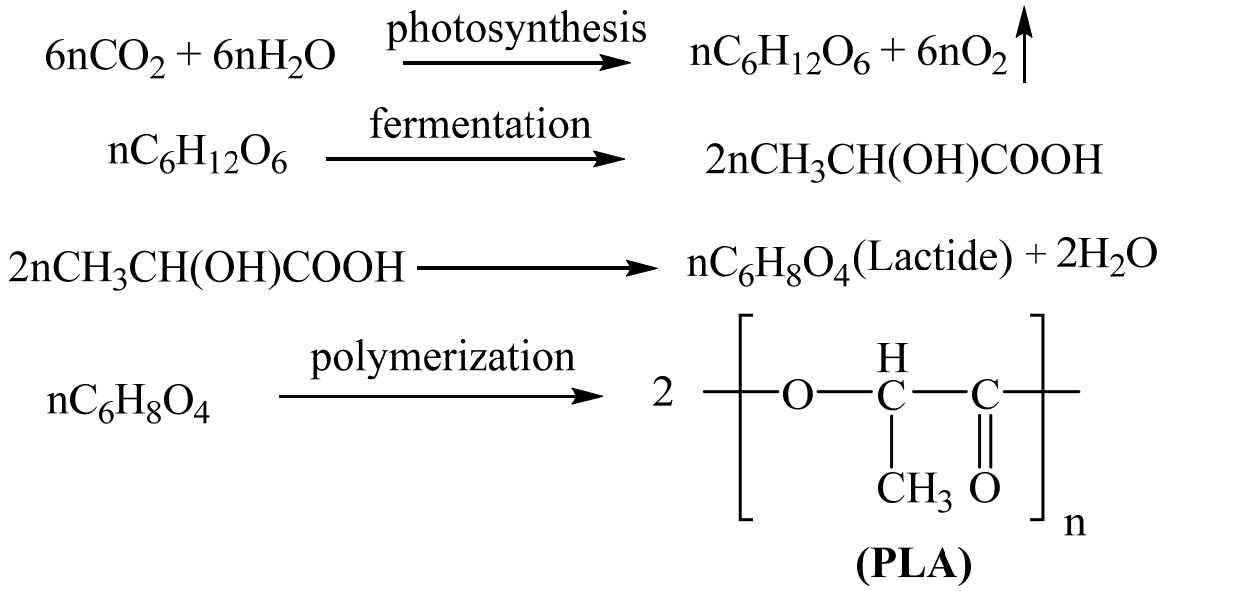
biobased –containing organic carbon of renewable origin like agricultural, plant, animal, fungi, microorganisms, marine or forestry materials living in a natural environment in equilibrium with the atmosphere.



- Removes CO_2 from the environment and incorporates it into a polymer molecule via plant-biomass photosynthesis in a short time scale of one (agricultural crops, algae) to 10 years (short rotation wood and tree plantations) in harmony with Nature's biological carbon cycle
- Petro/fossil resources are formed from plant biomass over millions of years and so cannot be credited with any CO_2 removal from the environment even over a 100 year time scale (the time period used in measuring global warming potential, GWP100)

1. Ramani Narayan, *Carbon footprint of bioplastics using biocarbon content analysis and life cycle assessment,* MRS (Materials Research Society) Bulletin, Vol 36 Issue 09, pg. 716 – 721, 2011
2. Ramani Narayan, *Biobased & Biodegradable Polymer Materials: Rationale, Drivers, and Technology Exemplars;* ACS (an American Chemical Society publication) Symposium Ser. 1114, Chapter 2, pg 13-31, 2012

Exemplar: PLA

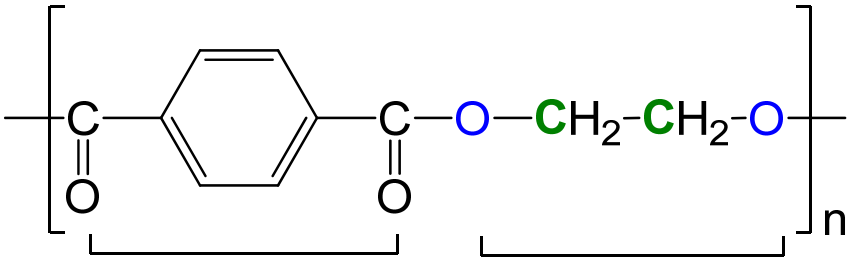


NET $6nCO_2 + 4nH_2O \longrightarrow 2[C_3H_4O_2]_n\ (PLA) + 6nO_2\uparrow$

264 Kg 144 Kg

1.83 Kg of CO_2 removed from the environment to manufacture 1 Kg of PLA

Exemplar -- biobased polyethylene terephthalate -- PET

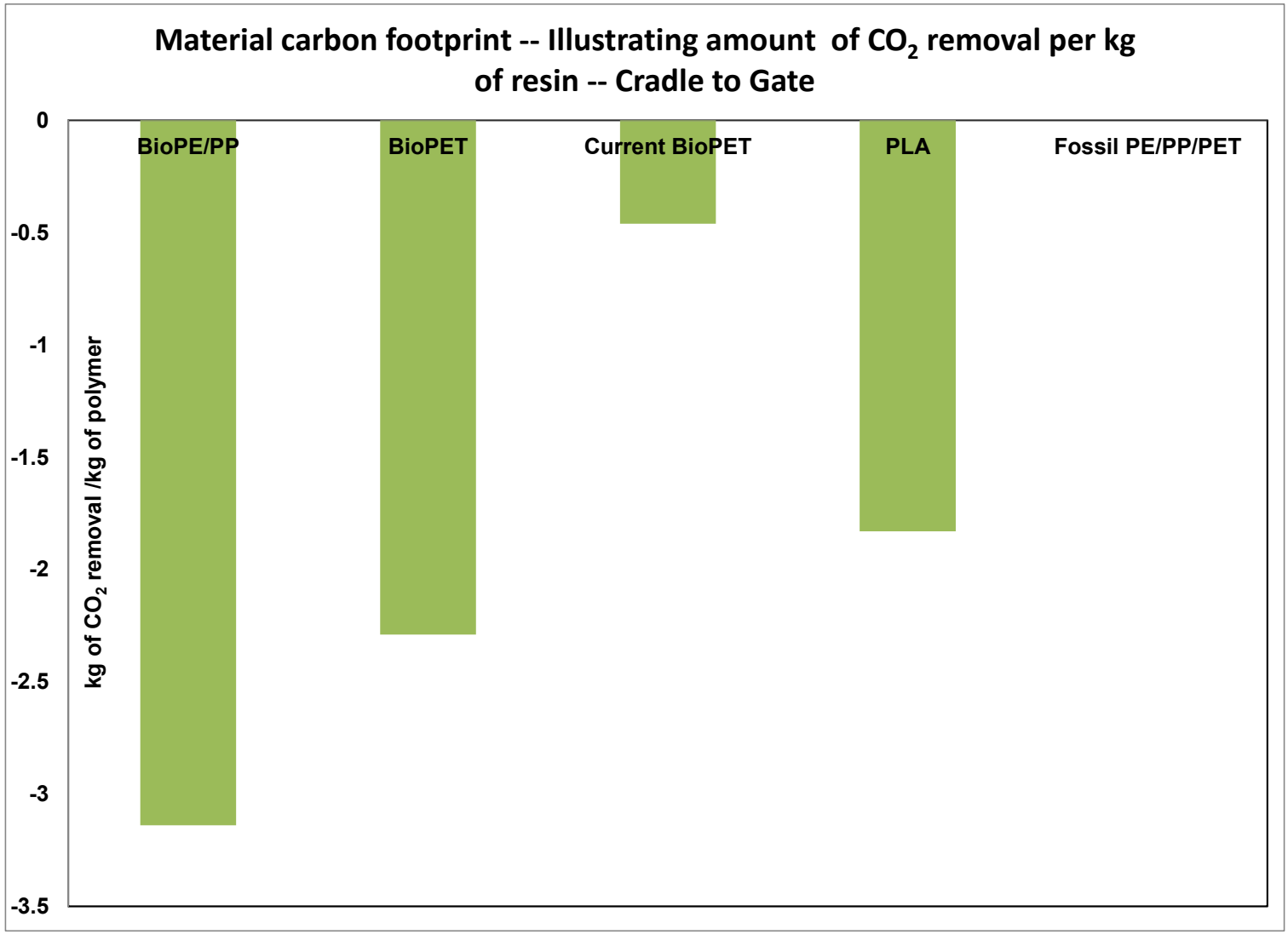


Fossil based acid
8 carbon atoms
68.75% by mass

biobased Glycol
2 carbon atoms
31.25% by mass

20% biobased carbon content [ASTM D6866]
31.25% by weight of plant biomass

For bottles:
37.5 MM tons PET used
17.2 MM tons CO_2 removal from the environment – equivalent to 40 million barrels of oil/yr savings


Material carbon footprint -- Illustrating amount of CO_2 removal per kg of resin -- Cradle to Gate
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
kg of CO_2 removal /kg of polymer
BioPE/PP
BioPET
Current BioPET
PLA
Fossil PE/PP/PET

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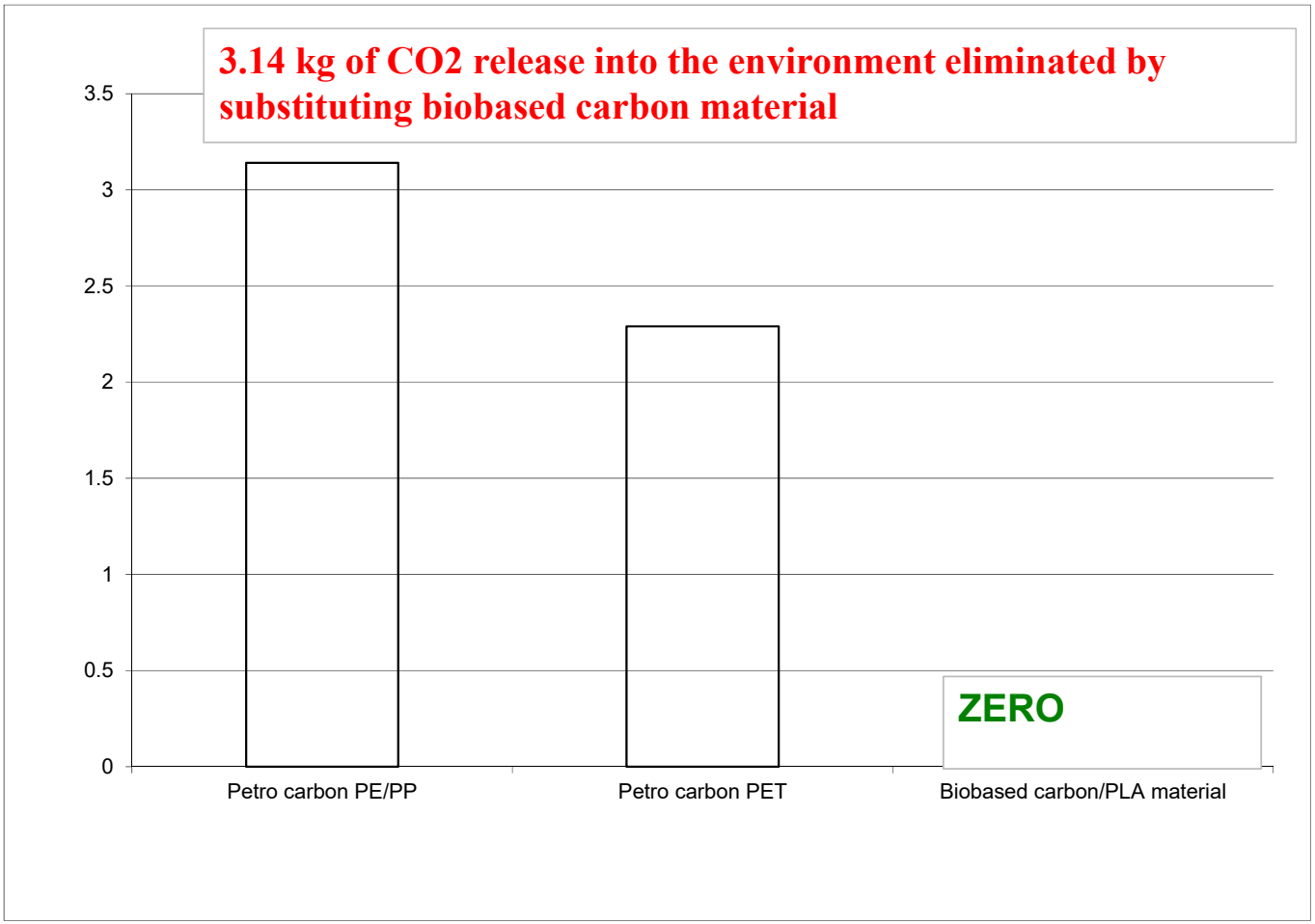
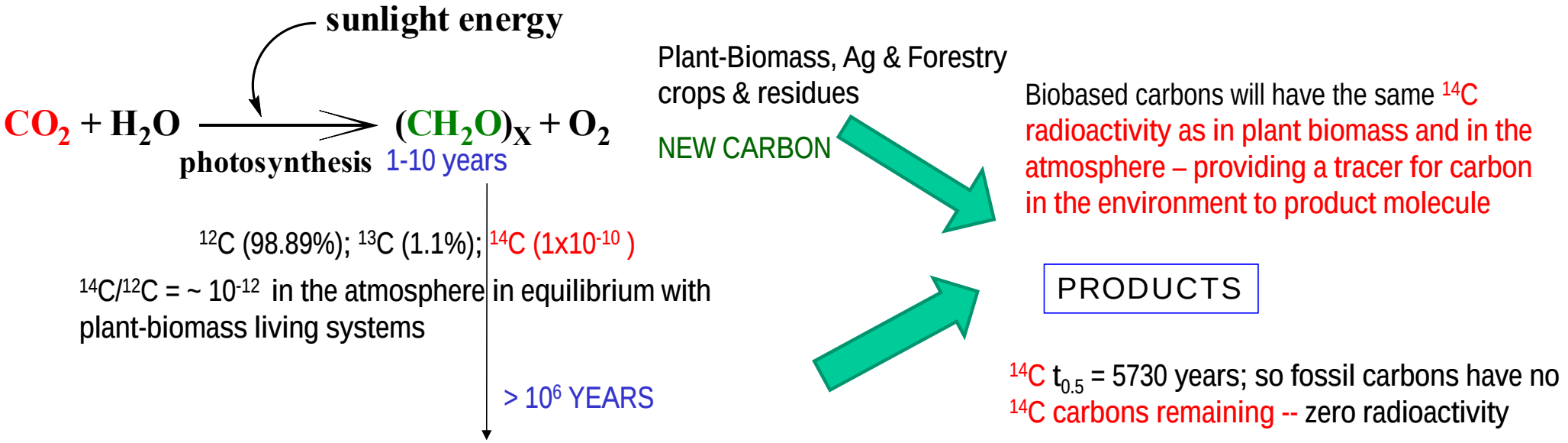


Cradle to Grave Scenario

ASTM D6868 -16 -- Fundamentals

biobased –containing organic carbon of renewable origin from agricultural, plant, animal, fungi, microorganisms, marine or forestry materials living in a natural environment in equilibrium with the atmosphere.



Petro-Fossil Resources (Oil, Coal, Natural gas) -- OLD CARBON

The amount of 14C is measured relative to a more abundant isotope (i.e., 13C or 12C) in the ion beam of an AMS (accelerator mass spectrometry) or by decay counting. **Absolute quantification** comes from comparing the sample's measured isotope ratio to that of pre 1950 biobased oxalic acid radiocarbon Standard Reference Material (NIST SRM) 4990c, (referred to as HOxII) after correcting for isotopic fractionation. Values must also be corrected for the C-14 pulse injected into the atmosphere (1950-63) from atmospheric testing of nuclear weapons

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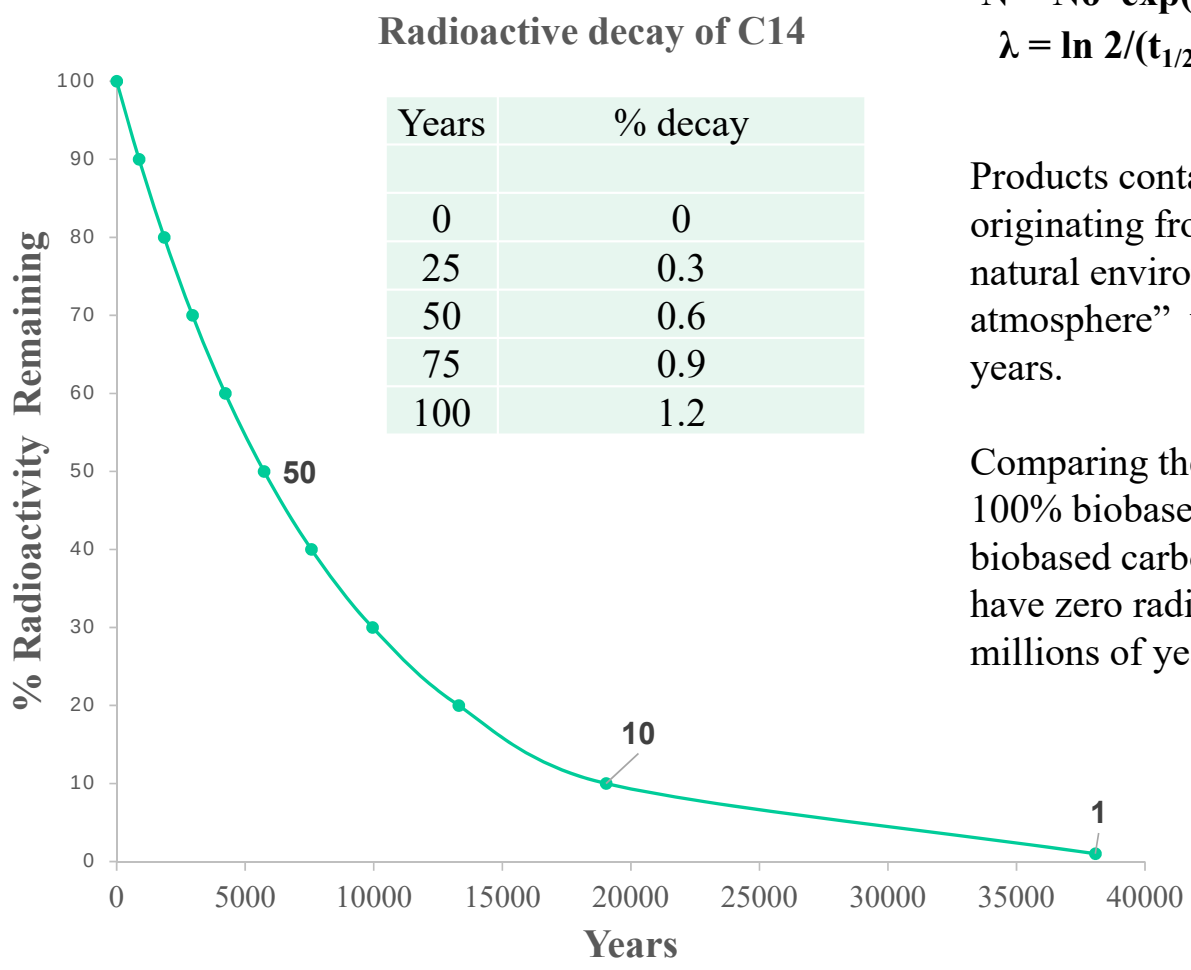
(-dN/dt=λ*N)

N = No*exp(-λ*t)

$\lambda = \ln 2/(t_{1/2})$; $t_{1/2}$ = 5730 years

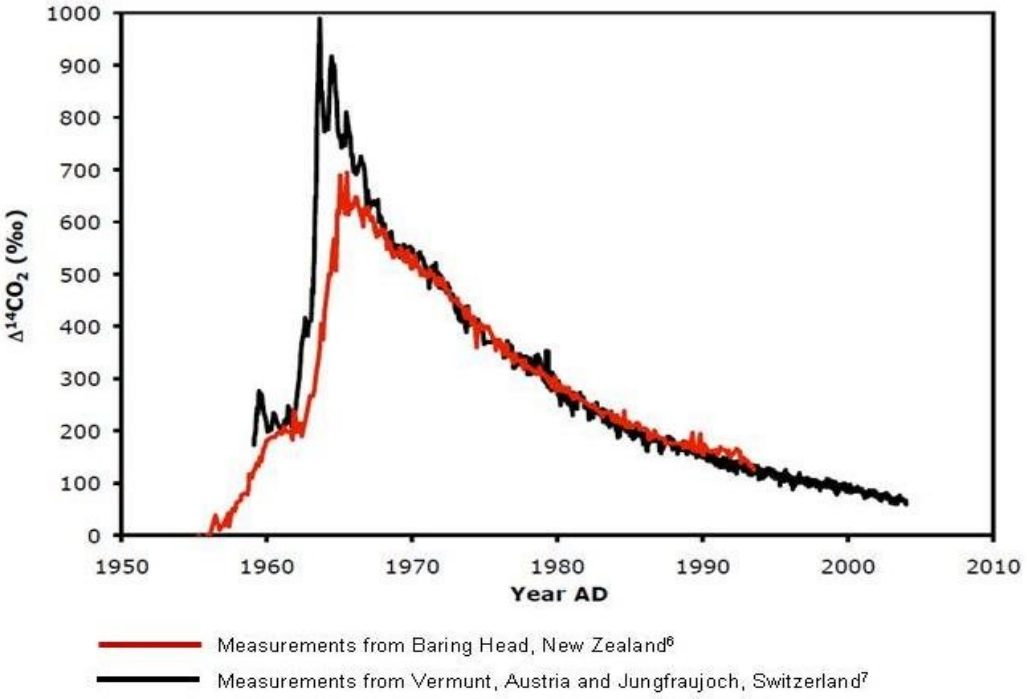


Years	% decay
0	0
25	0.3
50	0.6
75	0.9
100	1.2

Products containing biobased carbons -- carbon originating from " living systems (plant biomass) in a natural environment in equilibrium with the atmosphere" will retain the same isotopic ratio for 100 years.

Comparing the isotopic ratio of the test product with a 100% biobased standard product provides the amount of biobased carbons in the test product. Fossil carbons will have zero radioactivity left as they are formed over millions of years.

Atmospheric correction factor



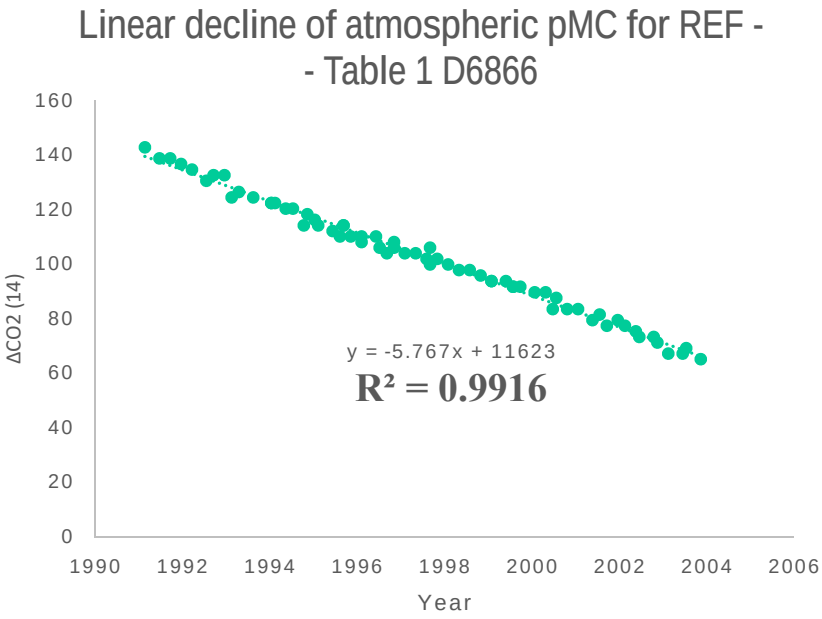


TABLE 1 Percent Modern Carbon (pMC) Reference

Year	REF (pMC)
2015	102.0
2016	101.5
2017	101.0
2018	100.5
2019	100.0
2020	to be determined

% biobased carbon content = pMC (from AMS) x 100
102; REF (2015)

% biobased carbon content = biobased **carbon** content by mass
total organic **carbon** content by mass

Biobased content is on a carbon basis

So what does 50% biobased (carbon) content of your product mean?

- pMC (percent modern carbon) = 50%
- obtained by comparing the isotopic (14C/12C; 4C/13C) ratio of the test sample with the isotopic ratio of a pre-1950 oxalic acid (from wood) standard sample and assigning the oxalic acid standard sample 100 pMC (percent modern carbon) – 100% biobased (carbon) content
- **Zero** pMC represents the entire lack of measurable 14C atoms in a material above background signals thus indicating a fossil carbon source (old carbon). **One hundred** pMC indicates all the carbons originate from biobased (plant-biomass feedstock (new carbon). A pMC value between 0 and 100 indicates a product containing both fossil and biobased carbons.
- There are 50 kg of biobased **carbon** for every 100 kg of organic **carbon** present in the product (can substitute any other mass unit for kg, like g, lbs, ton) ✓
- There are 50 kg of biobased **carbon** for every 100 kg **mass** of product **X**

Derivations from the primary biobased carbon content value

% Biobased Carbon Content (mass basis)
= [% total organic carbon/100
× (% biobased carbon content/100)] × 100

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Exemplar: biobased PET has experimental pMC value = 20%; i.e., 20% biobased (carbon) content) – **carbon basis**
Elemental analysis of PET shows that there is 62.5% carbon in PET, so:

% biobased carbon content on a mass basis = (0.625 x 0.20) x 100 = **12.5 %**

Biobased carbon content of complex assemblies (product) containing "n" organic components

18.9 For an assembly containing "n" organic components, this can be achieved using Eq 1.

% Biobased Carbon Content of Product

$$= \sum_{i=1}^{n} M_i * BCC_i * OCC_i / \sum_{i=1}^{n} M_i * OCC_i \qquad (1)$$

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where:

M_i = mass of the nth component present in the assembly,
BCC_i = % biobased carbon content of the nth component, and
OCC_i = % organic carbon content of the nth component.

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Biobased vs Biogeneic

The difference between “biobased” and “biogeneic” relates to using “organic carbon” vs “total carbon (organic + inorganic)”

$$\%\ \textbf{biobased}\ \text{carbon content} = \frac{\text{biobased } \textbf{carbon} \text{ content by mass}}{\text{total organic } \textbf{carbon} \text{ content by mass}}$$

$$\%\ \textbf{biogeneic}\ \text{carbon content} = \frac{\text{biobased } \textbf{carbon} \text{ content by mass}}{\text{total } \textbf{carbon (organic + inorganic)} \text{ content by mass}}$$

The USDA biopreferred program uses “biobased content” and is synonymous with “biobased carbon content”
EN and ISO is harmonized to the use of this terminology as well.