Application of ^{14}C method for biogenic component determination in waste and liquid fuels

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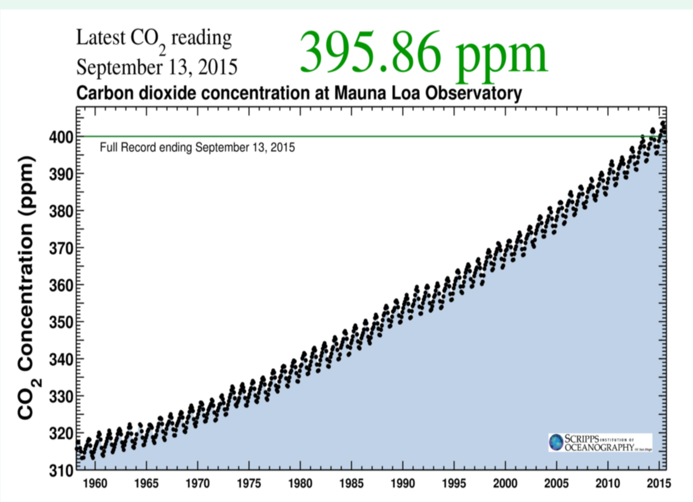
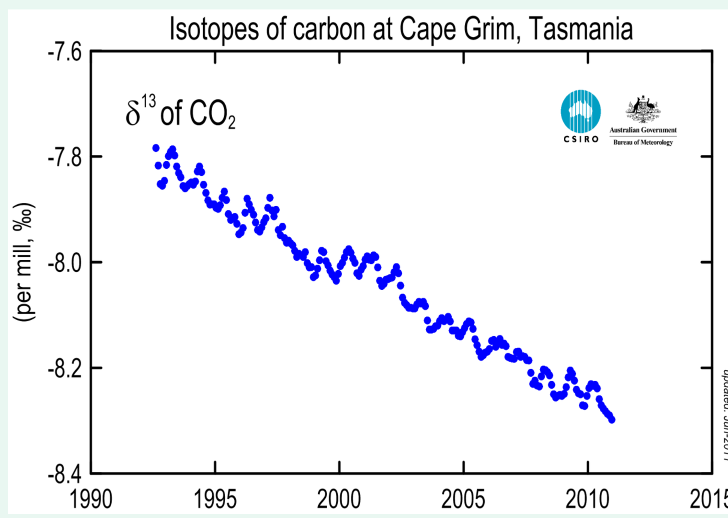
INTRODUCTION

Increase of CO_2 concentration in the atmosphere during 20th century is a consequence of intensive use of fossil fuels. The increase of CO_2 concentration can be slowed down by the use of biogenic materials for energy production and/or transport in addition to the use of renewable energy sources. The "environmentally kind politics" of the European Union stimulates the use of biogenic fuels by lower excise and income tax relief. Thus, there is a need for independent determination of the fraction of the biogenic component in various types of fuels by reliable and accurate methods.

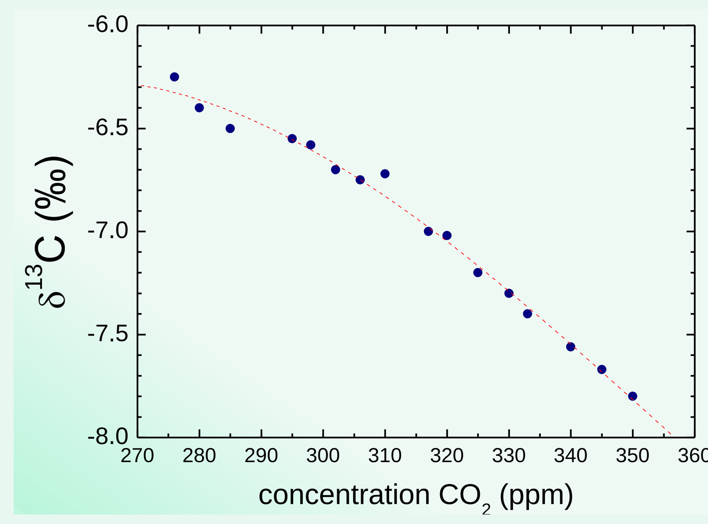
biogenic – produced in natural processes by living organisms but not fossilized or derived from fossil resources



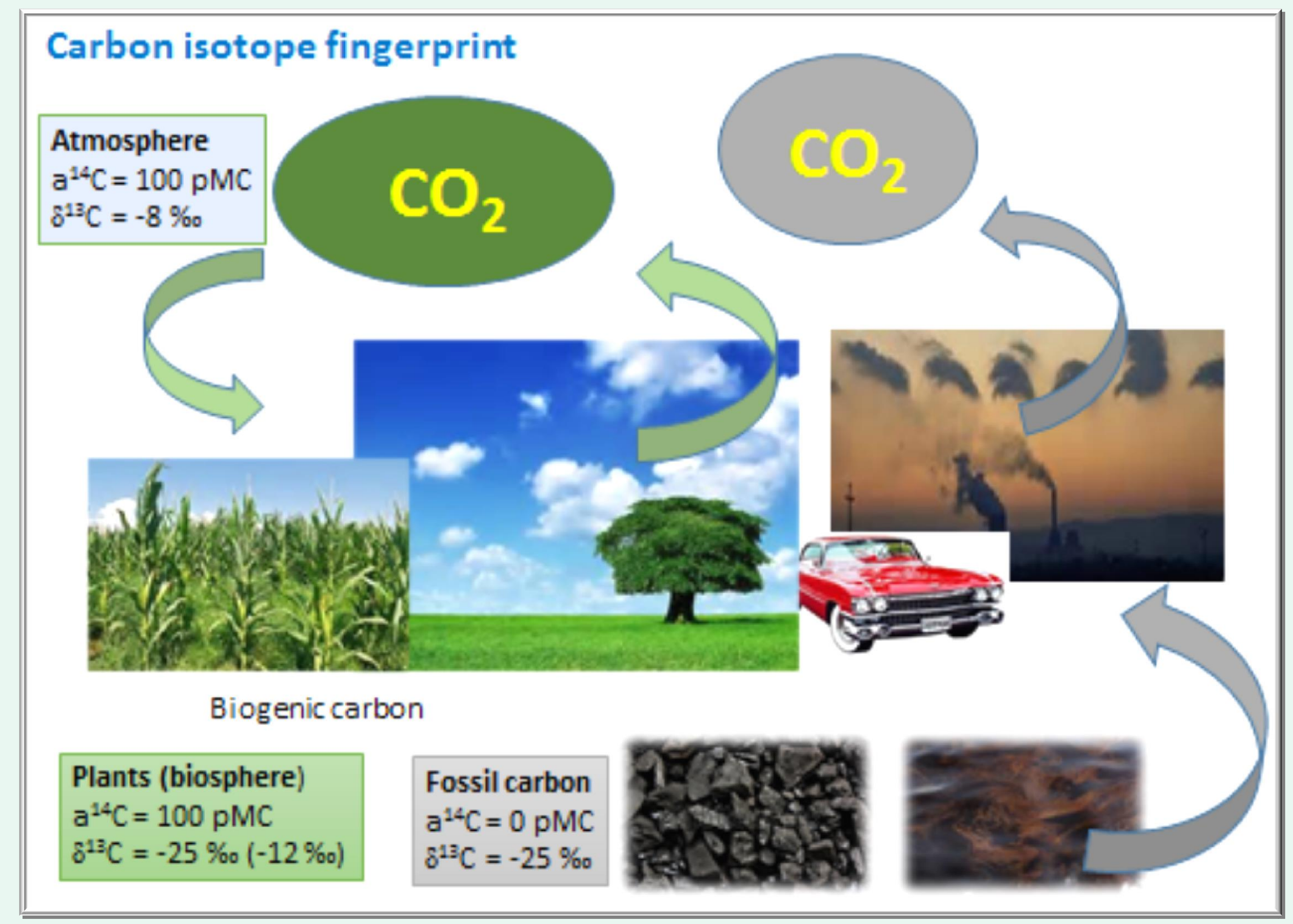
Increase of atmospheric concentration of CO_2



Decrease of $\delta^{13}C$ of atmospheric CO_2



Relation between $\delta^{13}C$ and concentration of atmospheric CO_2 – excess CO_2 has lower $\delta^{13}C$ than the undisturbed atmospheric CO_2



Carbon isotope characteristics ($\delta^{13}C$ and $a^{14}C$) of biogenic carbon, atmospheric CO_2 and fossil carbon. The use of fossil fuels causes introduction of excess CO_2 to the atmosphere.

How can we determine the biogenic fraction in any type of fuel by the ^{14}C method?

^{14}C method is based on different content of ^{14}C in biogenic (reflects the modern atmospheric ^{14}C activity) and in fossil component (no ^{14}C present). The ^{14}C method can be applied to various types of materials, such as solid communal waste, used car tyres, liquid fuels, consumable products, or CO_2 produced by combustion of various fuels.

A material can be composed of a biogenic fraction (f_{bio}) and a fossil fraction (f_f): $f_f + f_{bio} = 1$

The measured ^{14}C activity of such a mixed material, $a^{14}C_{mix}$, is a combination of the biogenic and fossil components:

$$a^{14}C_{mix} = f_f\, a^{14}C_f + f_{bio}\, a^{14}C_{bio}$$

In fossil fuels all ^{14}C had been decayed, $a^{14}C_f = 0$ pMC, → the fraction of the biogenic component can be determined as

$$f_{bio} = a^{14}C_{mix} / a^{14}C_{bio}$$

$a^{14}C$, relative specific ^{14}C activity, expressed in percent of modern carbon (pMC), **100 pMC = 226 Bq/kgC**

Recommendation: ASTM 6866 recommends the use of **$a^{14}C_{bio}$ = 105 pMC** for biogenic material originating from last several years.

ASTM D6866-12 Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis. ASTM International. 2012.

Measurement tehniques

Any measuring technique used in ^{14}C laboratories could be used.

Radiometric measurement techniques are based on counting ^{14}C decay rate by liquid scintillation counters (LSC). A sample can be prepared in form of benzene or as CO_2 absorbed in a cocktail

Accelerator mass spectrometry (AMS) technique counts the number of ^{12}C, ^{13}C and ^{14}C atoms. A sample is usually prepared as graphite target.

Comparison of characteristics (precision, complexity, and price) of various techniques for biogenic fraction determination by the ^{14}C method.

Measurement technique	Sample types	Required mass of carbon	Complexity *	Precision *	Price *	Main drawback
AMS	all	~1 mg	3	4	4	representativeness of the sample ##
LSC-benzene #	all	~4 g	4	3	3	time-consuming
LSC-CO_2 abs#	all	~0.6 g	2	2	2	high uncertainty, low sensitivity
LSC-direct	liquid fuels	10 ml of liquid	1	1	1	quenching

* The higher the number, the more complex the method / the lower the uncertainty / the higher the price

\# Oxidation is critical because samples tend to explode (liquid fuels)

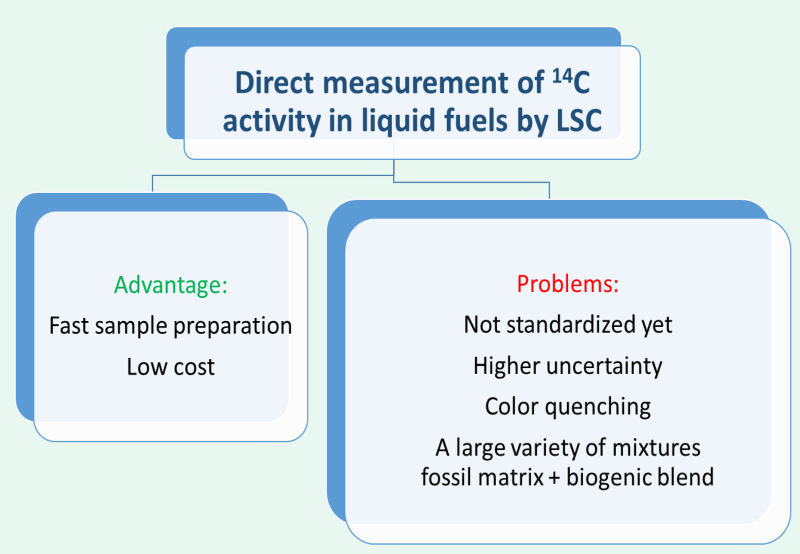
\## Sample heterogeneity: Better to use gram size quantities and LSC

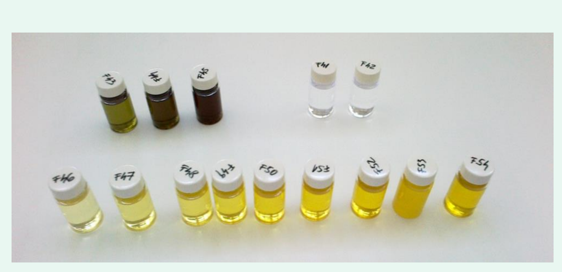
Fossil matrix: either gasoline (benzine) or diesel (gas oil)

Biogenic blends: bioethanol, fatty acid methyl esters (FAMEs), hydrogenated vegetable oil (HVO) and others

Biofuels are liquid or gaseous fuels for transport produced from biomass.

LSC direct measurement of ^{14}C activity in liquid fuels

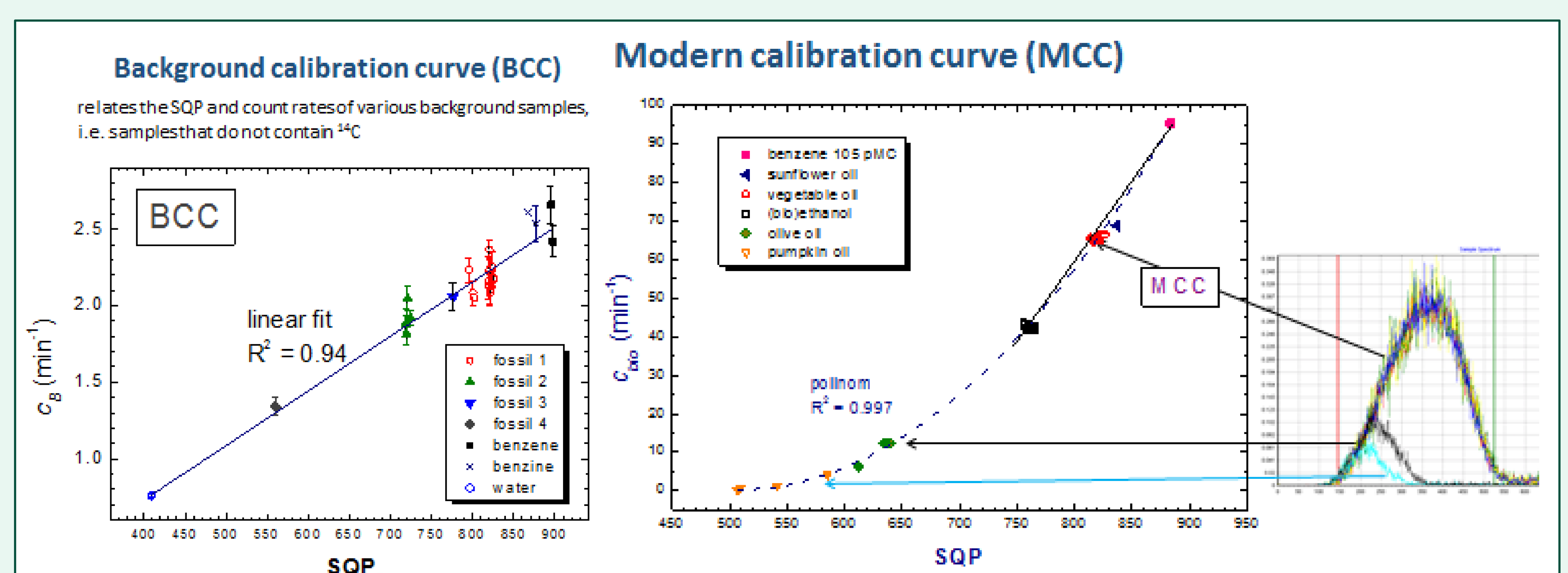




Liquids of different colours have different quenching properties and measurement efficiencies.

New data evaluation technique is proposed!

A new technique uses liquids of different colours and their different quenching properties to construct background and modern calibration curves.



All samples should be measured under the same conditions:

- low-potassium glass vials of 20 ml
- scintillation cocktail UltimaGoldF (UGF)
- Cocktail - sample 10 ml : UGF 10 ml
- spectra recorded by LSC Quantulus evaluated in the window 124 – 570 channels

The lowest detectable biogenic fraction is 0.5 % for measurement duration of 600 minutes

The procedure of data evaluation for the unknown sample:

- measurement of SQP and count rate of the sample (**c**)
- determination of background count rate corresponding to the measured SQP value by using BCC (**b**)
- determination of the count rate of the biogenic sample (**c_{bio}**) corresponding to the measured SQP values by using MCC

The fraction of the biogenic component in the sample is calculated as the ratio of net count rates of the sample to the biogenic material.

$$f_{bio} = (c - b) / (c_{bio} - b)$$

Intercomparison of the new data evaluation techniques with the „standard" evaluation technique:
I. Krajcar Bronić, J. Barešić, N. Horvatinčić, R. Krištof and J. Kožar-Logar: New technique of determination of biogenic fraction in liquid fuels by the ^{14}C method. Proc. 10th Symp. of Croatian Radiation Protection Association, pp. 390-395, Šibenik, Croatia, 15-17 April 2015. HDZZ, Zagreb, 2015.

CONCLUSION

Determination of the biogenic fraction in various materials is an interesting topic for the scientists, for various industries and for the global environment. The ^{14}C method is a very powerful method for determination of the biogenic fraction. The innovative data evaluation technique of the direct measurement of ^{14}C activity of liquid fuels in LSC depends neither on the fossil matrix or the biogenic additive type, it does not require ^{14}C spikes or other expensive standards. One does not need to know the qualitative composition of the fuels, as it is the case for other evaluation techniques. The method still needs some improvements, especially for highly quenched liquids, but it gives comparable results with other data evaluation techniques.

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