Određivanje udjela biokomponente u tekućim gorivima metodom ^{14}C

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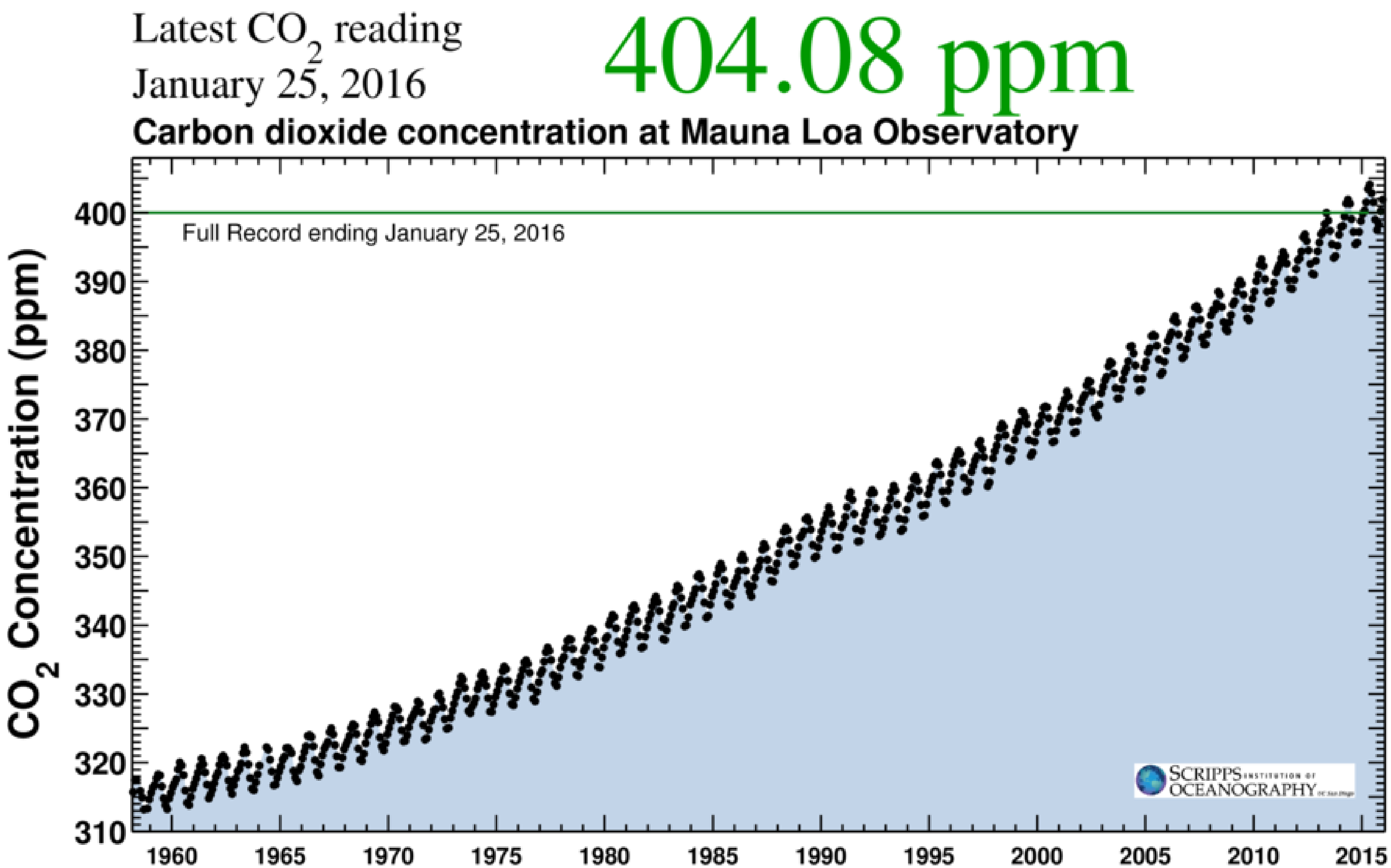
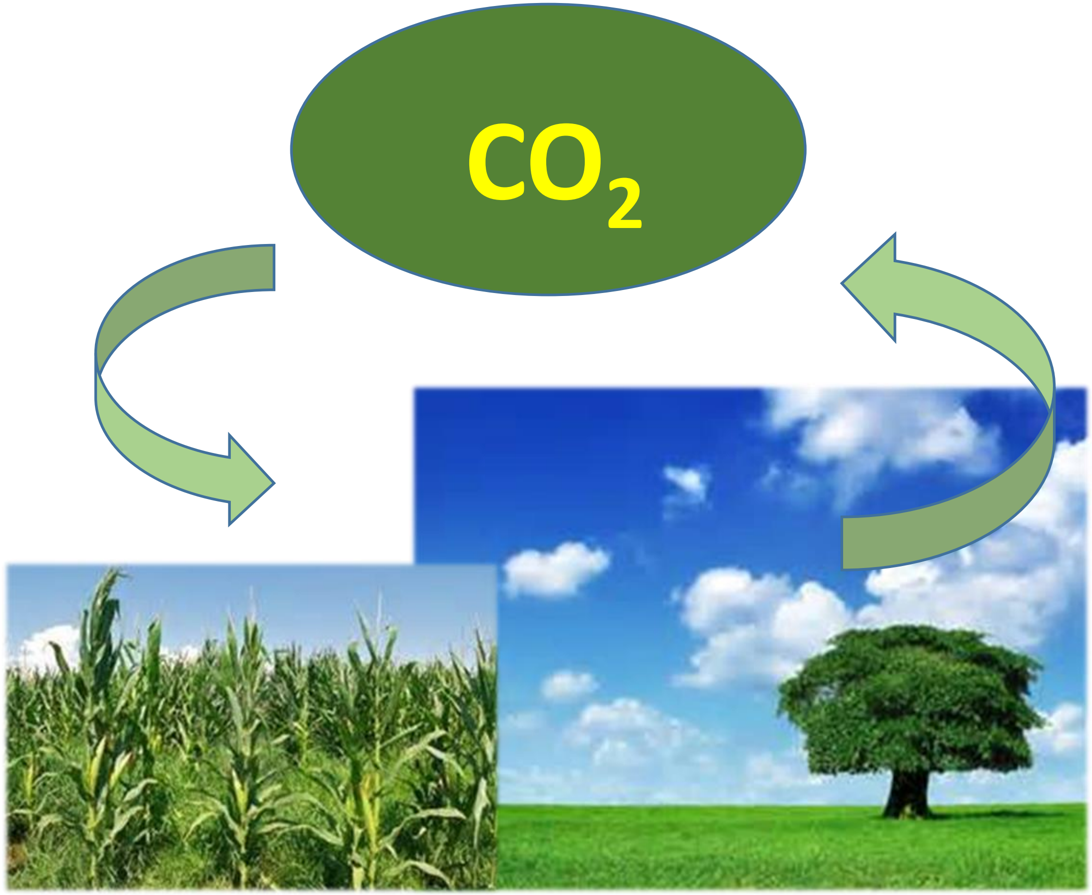


https://scripps.ucsd.edu/programs/keelingcurve/wp-content/plugins/sio-bluemoon/graphs/mlo_full_record.png

Ciklus ugljika



Biogeni ugljik

Sudjeluju svi izotopi ugljika

^{12}C

^{13}C

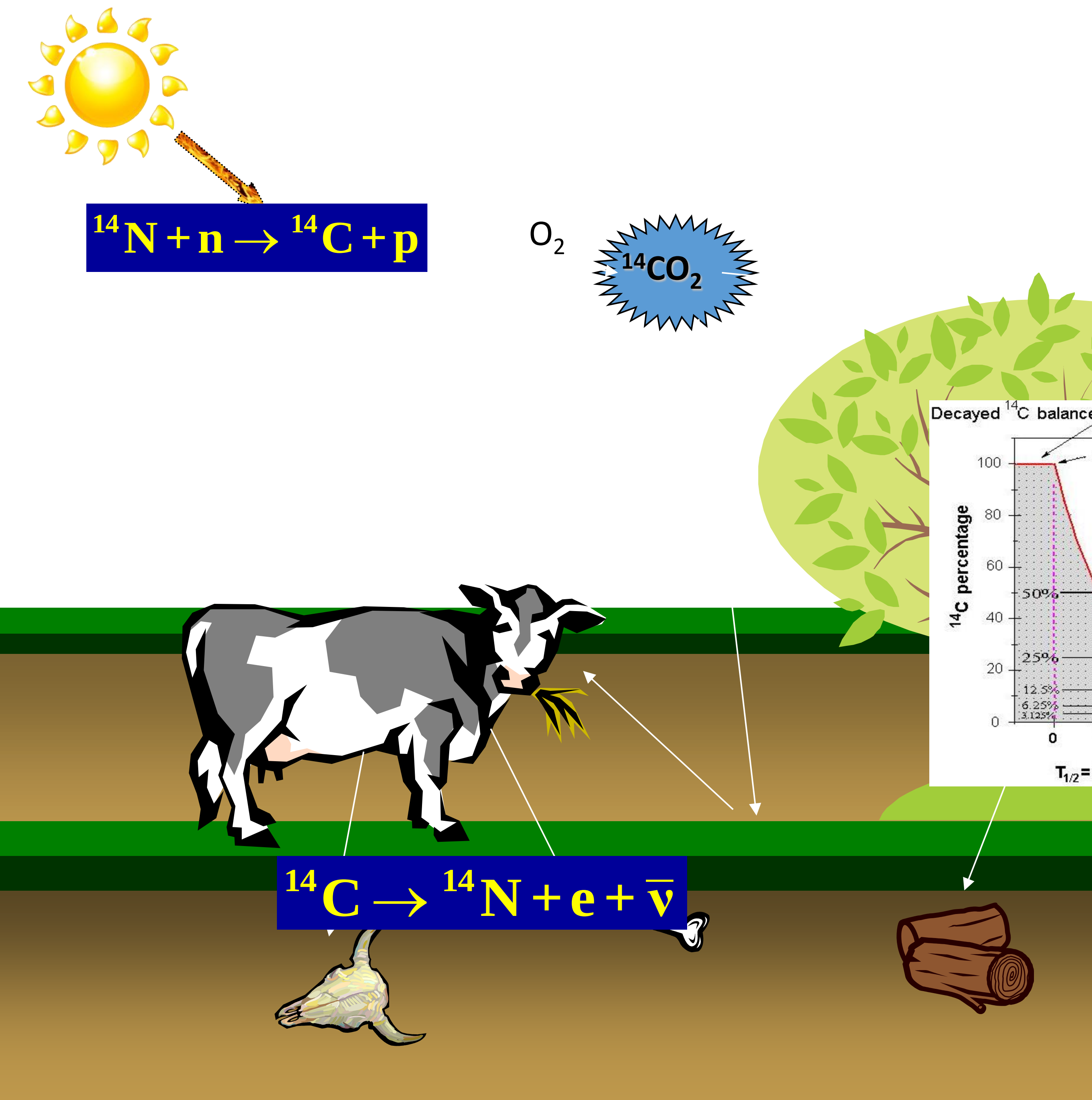
^{14}C

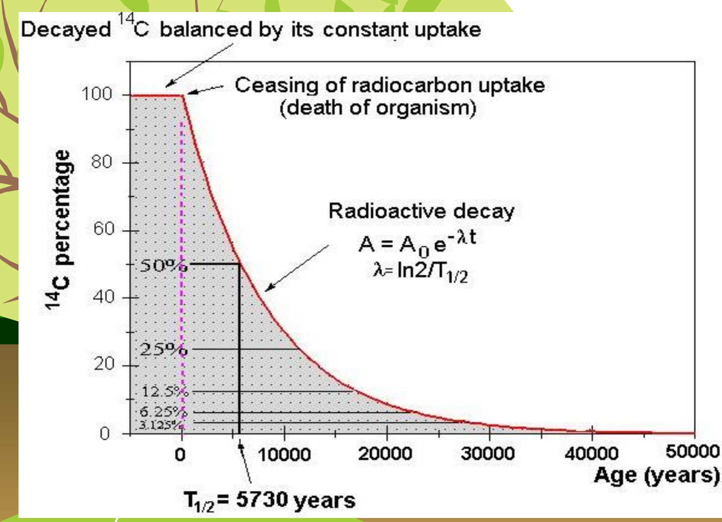
Carbon on Earth

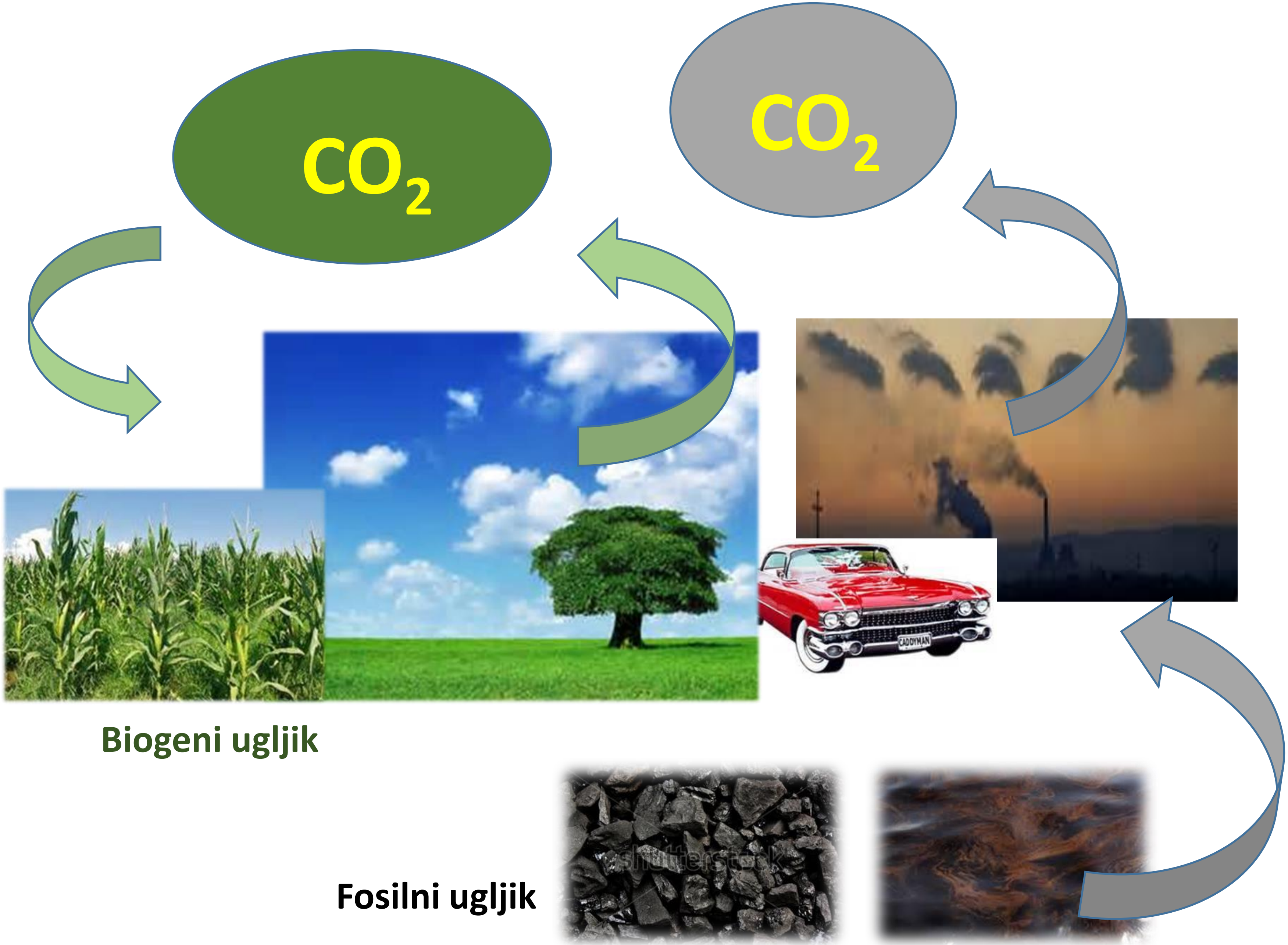
^{12}C: 98.89 %

^{13}C: 1.1 %

^{14}C: 1.18 x 10^{-10} %





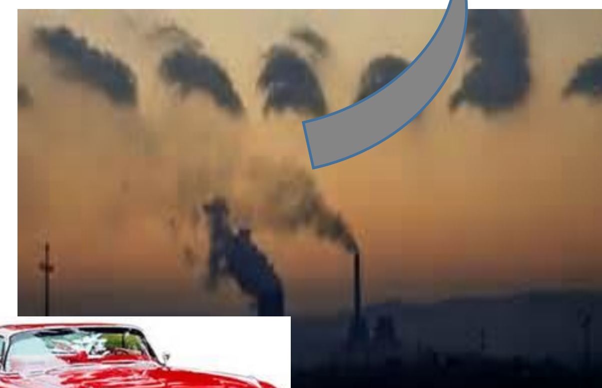

CO_2
CO_2
Biogeni ugljik
Fosilni ugljik

Izotopne karakteristike

Atmosfera
a^{14}C = 100 pMC
δ^{13}C = -8 ‰

CO_2

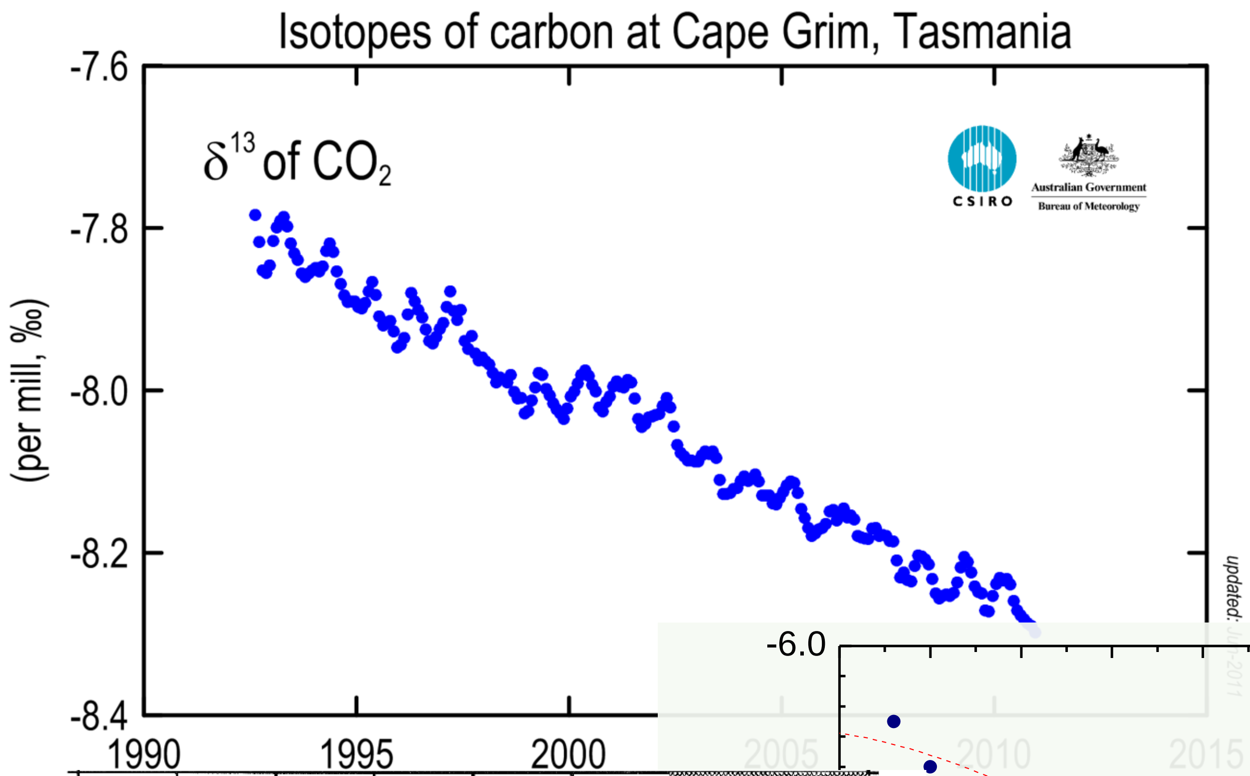
CO_2

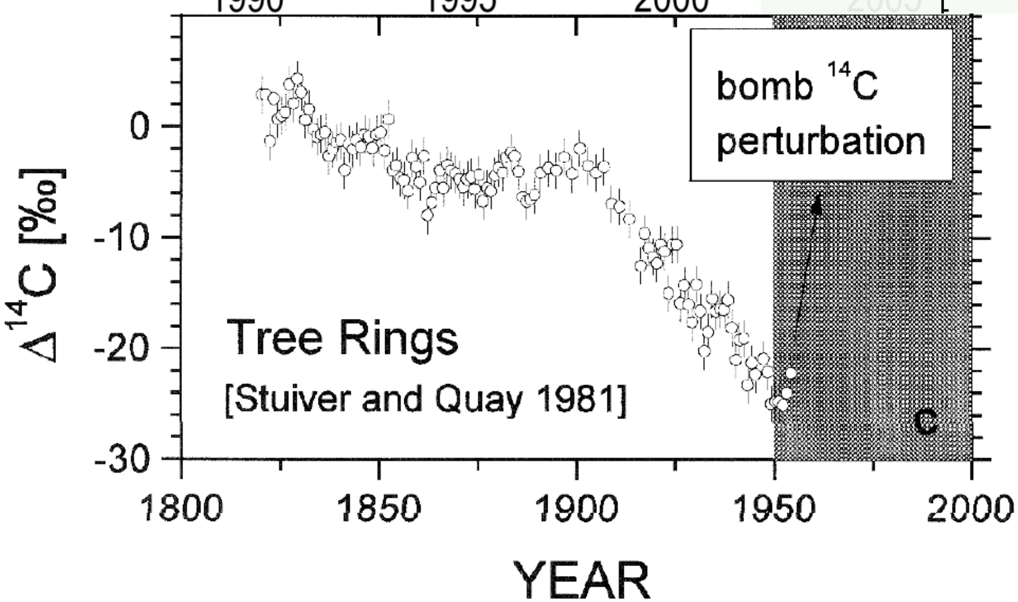


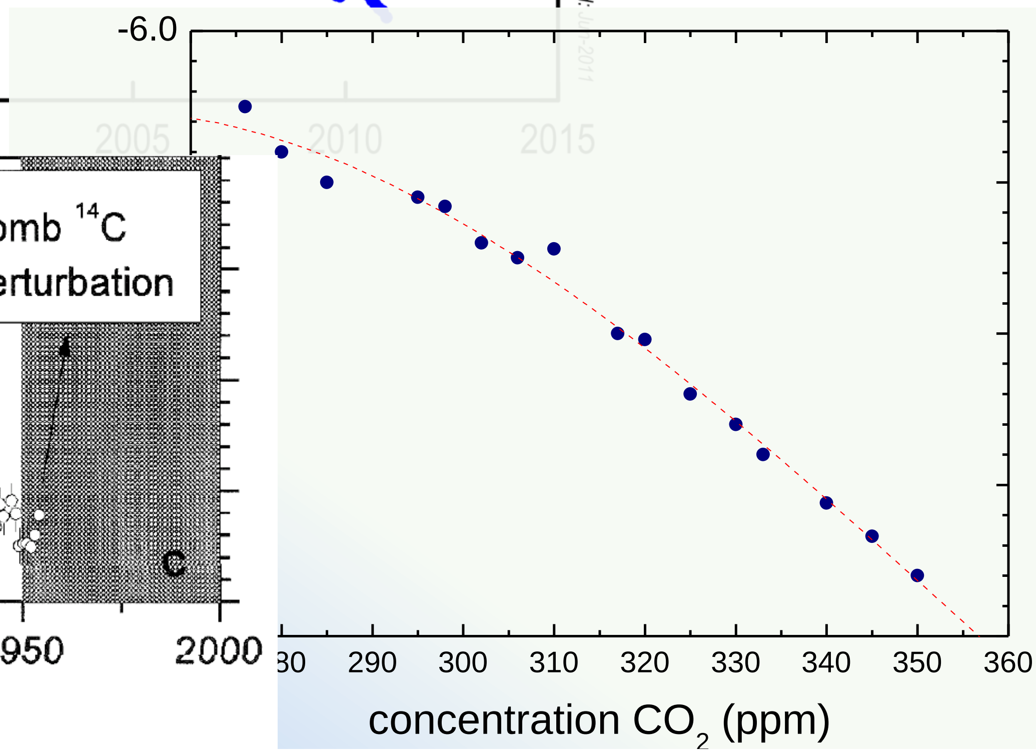
Biogeni ugljik

Biljke (biosfera)
a^{14}C = 100 pMC
δ^{13}C = -25 ‰ (-12 ‰)

Fosilni ugljik
a^{14}C = 0 pMC
δ^{13}C = -25 ‰


Isotopes of carbon at Cape Grim, Tasmania
δ13 of CO2
(per mill, ‰)
-7.6
-7.8
-8.0
-8.2
-8.4
1990
1995
2000
2005
2010
2015
CSIRO
Australian Government
Bureau of Meteorology
updated:

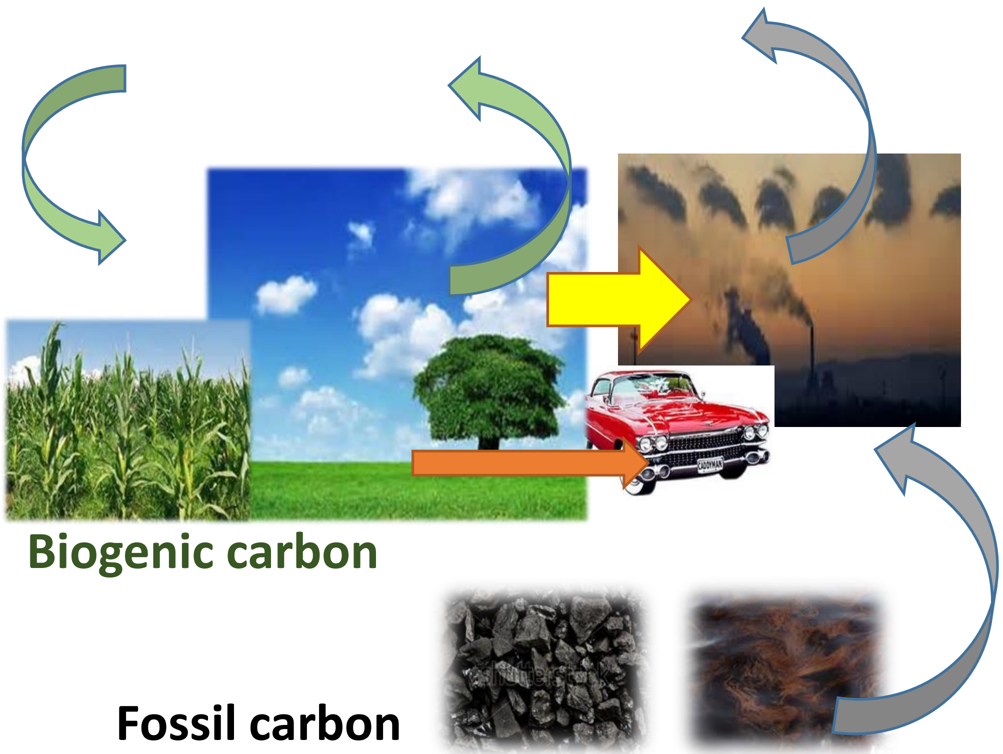

Δ14C [‰]
0
-10
-20
-30
bomb 14C
perturbation
Tree Rings
[Stuiver and Quay 1981]
c
1800
1850
1900
1950
2000
YEAR


-6.0
290
300
310
320
330
340
350
360
concentration CO2 (ppm)

From the presented data we can conclude

- Intensive use of fossil fuels for energy production and transport during 20th century caused an increase of CO_2 concentration in the atmosphere

What to do to stop or at least slow-down the increase of atmospheric CO_2 concentration?



The increase of CO_2 concentration can be slowed down **by the use of biogenic materials for energy production and/or transport.**

Production of biofuel is more expensive than the use of fossil fuel

The "environmentally kind politics" of the European Union stimulates the use of biogenic fuels by lower excise and income tax relief.

Countries throughout the world have set new targets for the minimum content of biogenic materials in fuel (5.75% until 2010 in Europe, 2003/30/EC; EU Directive 2009/28/EC at least 10 % of bio-fuel in all (liquid) fuels by 2020).

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.**

Methods for determination of fraction of biogenic component in any type of fuel or waste used in waste-to-energy plants

1 - manual sorting

2 - chemical dissolution

3 - ^{14}C method

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

^{14}C method is based on different content of ^{14}C in biogenic and in fossil component: while the biogenic component reflects the modern atmospheric ^{14}C activity, no ^{14}C is present in fossil fuels.
The ^{14}C method is the most reliable method of determination of the biogenic fraction in fuels. It can be applied to various types of fuels used, such as solid communal waste, used car tyres, liquid fuels.
It can be used also to determine the biobased content of **various manufactured products** (e.g., solvents and cleaners, lubricants, construction material, carpets…)

Alternatively, the ^{14}C method can be applied to determine **^{14}C content of the CO_2** produced by combustion of various fuels in waste-to-energy plants

How to determine biogenic fraction by the ^{14}C method

Results of measurement are presented as relative specific ^{14}C activity, a^{14}C, expressed in percent of modern carbon (pMC)
100 pMC = 226 Bq/kgC

A material can be composed of a biogenic component (of fraction f_{bio}) and a fossil component (f_f)

$$f_f + f_{bio} = 1$$

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

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

Since in fossil fuels all ^{14}C had been decayed, and $a^{14}C_f = 0$ pMC, it follows that the fraction of the biogenic component can be determined as

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

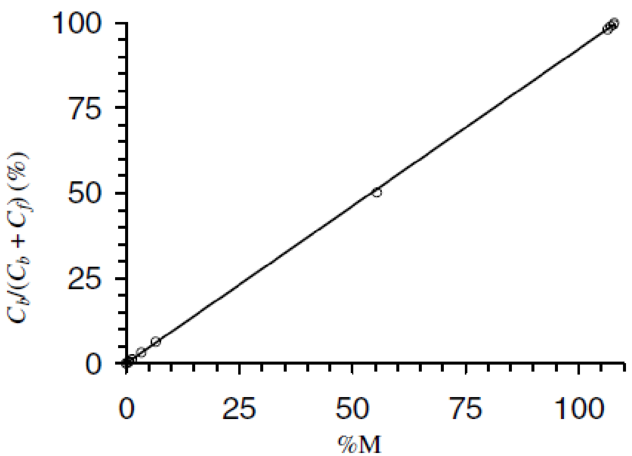
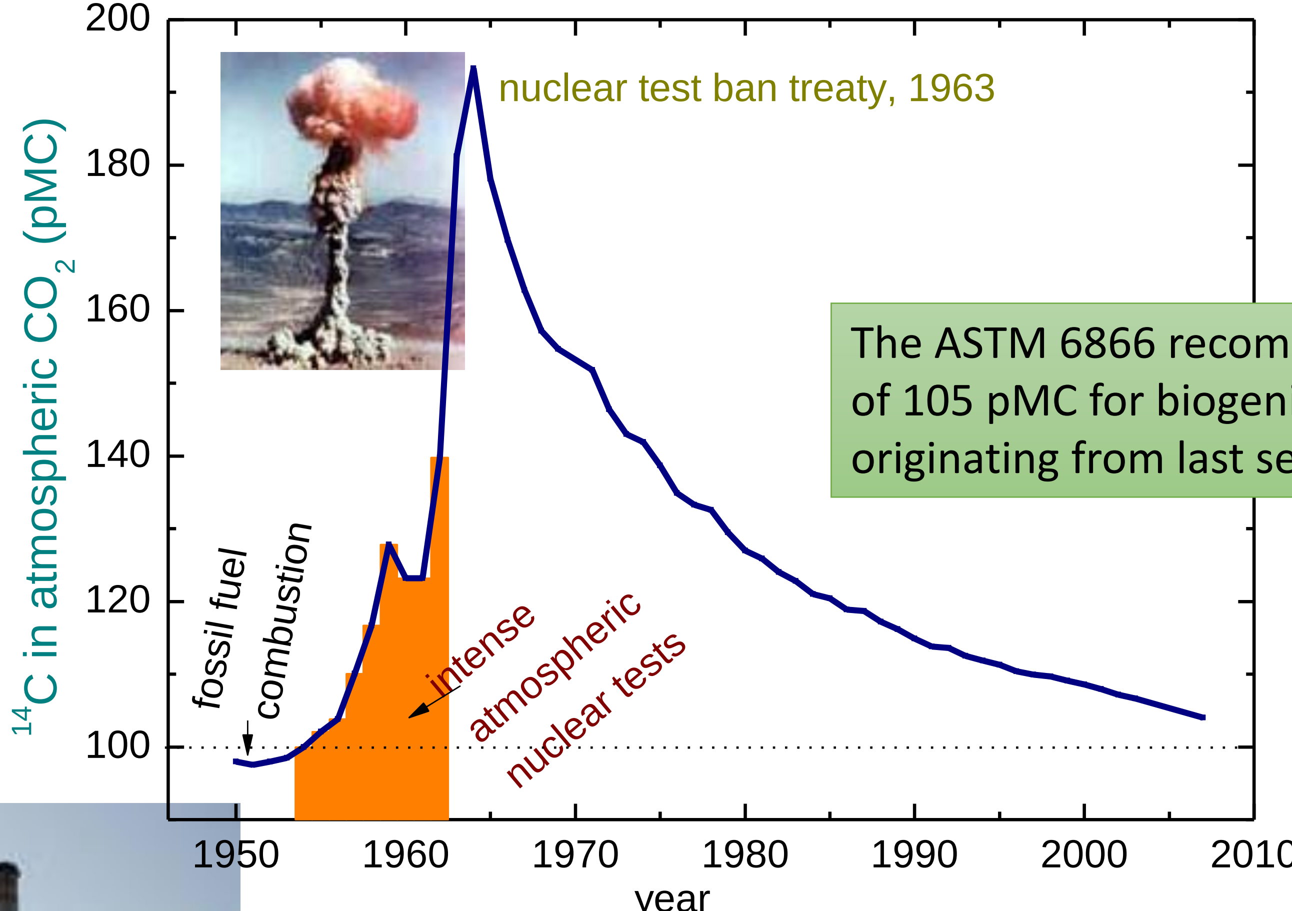


Figure 2 Biofuel carbon : total carbon ratio in the fuel sample ($C_b/(C_b + C_f)$) versus percent Modern (%M) by ^{14}C LSC, 5.5 hr counting; linear fit: $C_b/(C_b + C_f) = 0.9231 \times$ %M, $R^2 = 0.9999$.

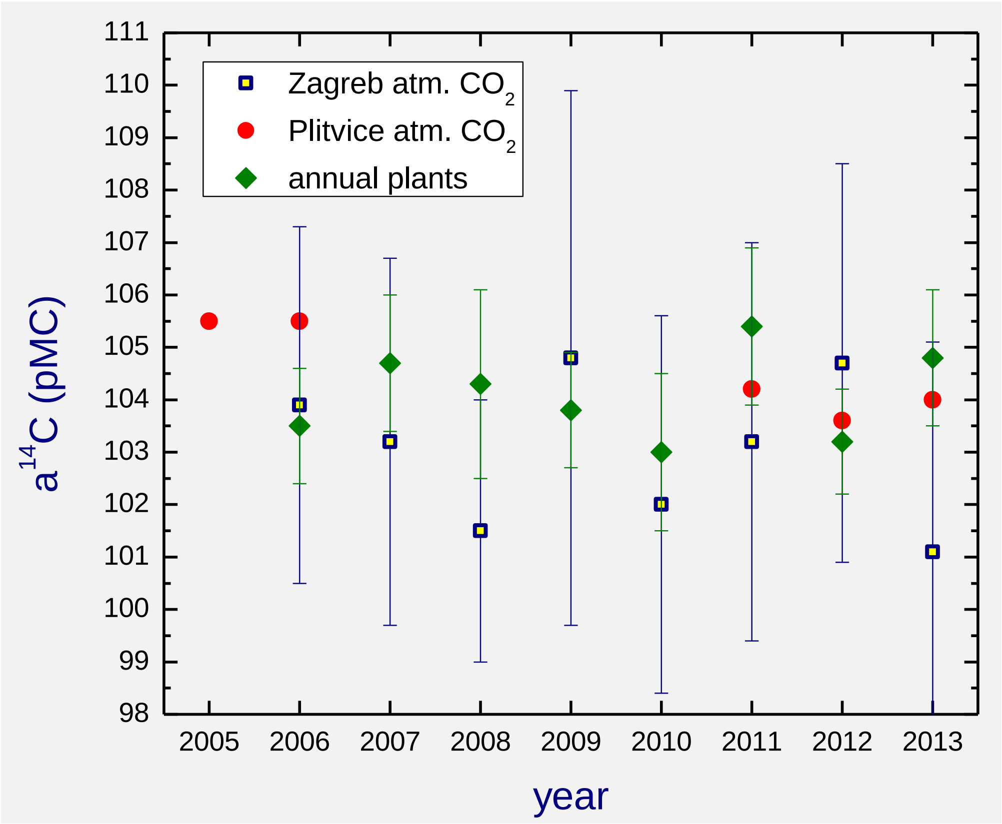
Anthropogenic activities

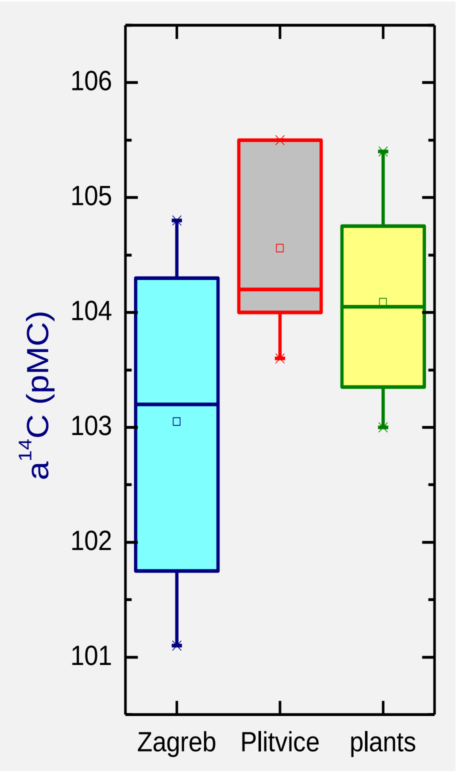
^{14}C in atmospheric CO_2 on the Northern Hemisphere



The ASTM 6866 recommends the use of 105 pMC for biogenic material originating from last several years.

- any derivative of short rotation crops can be used (harvesting year should be known) as modern standard
- mean ^{14}C activity of the atmosphere has not significantly changed over last 10 years → biogenic material produced in this period has also constant ^{14}C activity → no need to know the exact ^{14}C activity of modern biogenic material
- ISO 13833/ASTM D6866: ^{14}C activity of modern biogenic fuels is taken/defined as 105 pMC, or 1.05*226 Bq/kgC





Note: that the value of 105 pMC can be safely used for short-lived biomass that grew during last ~10 years.

When the wood, wooden products or wooden pellets produced from a wood grown in the second half of the 20th century are used as fuels, ^{14}C activities may lie in the range between 105 pMC and even ~190 pMC, depending of the year of growth. Such values would yield unrealistic f_{bio} values of >100%, if the correct $a^{14}C_{bio}$ values were not used.

Z-	Code	Sample type	LSC-B $a^{14}C$ (pMC)	σ
3871	X	Mixture of plants and plastics, #1	58.48	0.31
3872	D	Wood, sawdust, #2	140.25	0.59
3873	D	Paper, #3	109.82	0.64
3874	X	Plastics, #4	7.61	0.19
3875	X	Plastics, various colours, #5	1.45	0.08
3876	X	Mixed communal waste, #6	57.31	0.31

Measuring techniques for ^{14}C

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

- graphite targets are prepared (or CO_2)

Comparison of some characteristics (mass C, precision, complexity, 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 #	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: Advantageous to use gram size quantities and LSC

Liquid fuels

According to the EU Directive 2009/28/EC [14] all (liquid) fuels have to contain at least 10 % of bio-fuel, i.e., blend of biogenic origin, by 2020.

Fossil matrix of the fuels is either gasoline (benzine, petrol) or diesel (gas oil), while **biogenic blends** are usually bioethanol, fatty acid methyl esters (FAMEs), hydrogenated vegetable oil (HVO) and others.

Biofuels - definition

are liquid or gaseous fuels for transport produced from biomass.

Directive 2003/30/EC on the promotion of the use of biofuels or other renewable fuels for transport - at least the following products shall be considered as biofuels:
bioethanol, biodiesel, biogas, biomethanol, biodimethylether,
bio-ETBE (ethyl-tertio-butyl-ether), bio-MTBE (methyl-tertio-butyl-ether),
synthetic biofuels, biohydrogen and pure vegetable oil.

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

Advantage:

Fast sample preparation

Low cost

Problems:

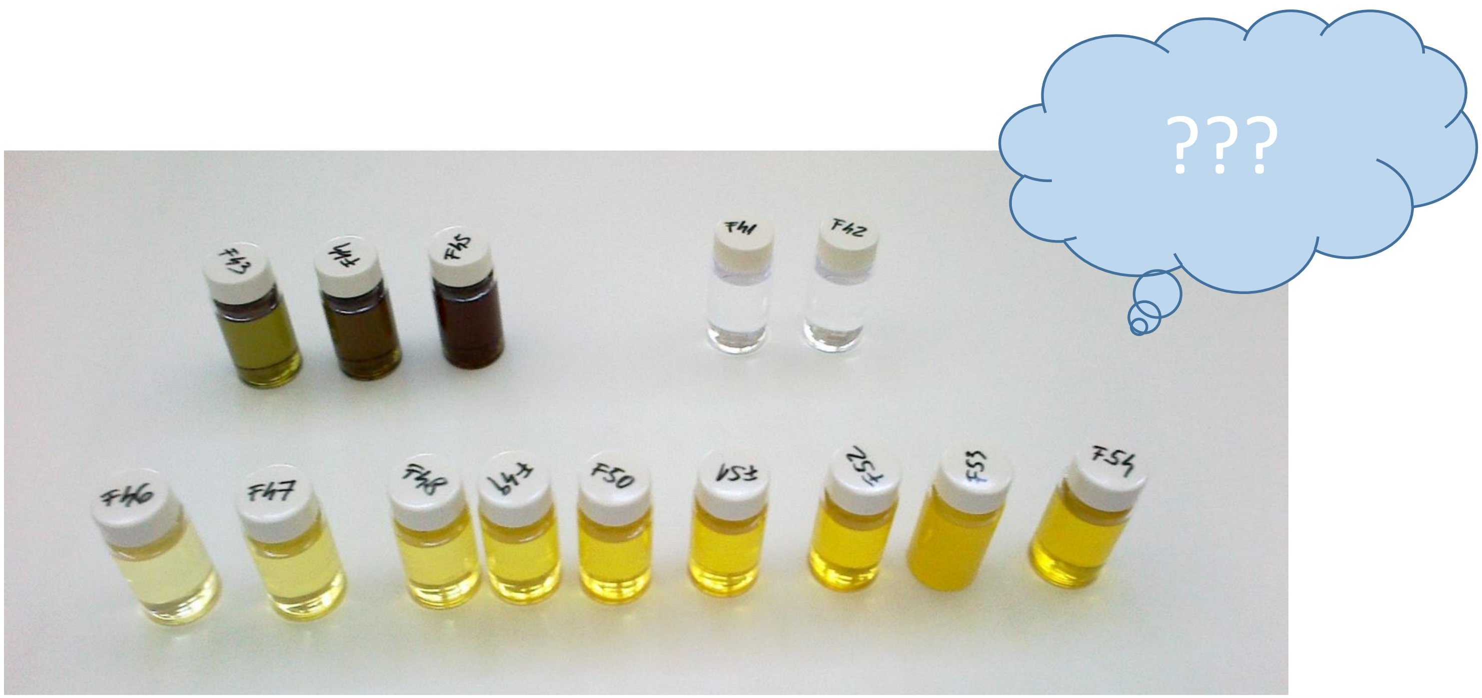
Not standardized yet

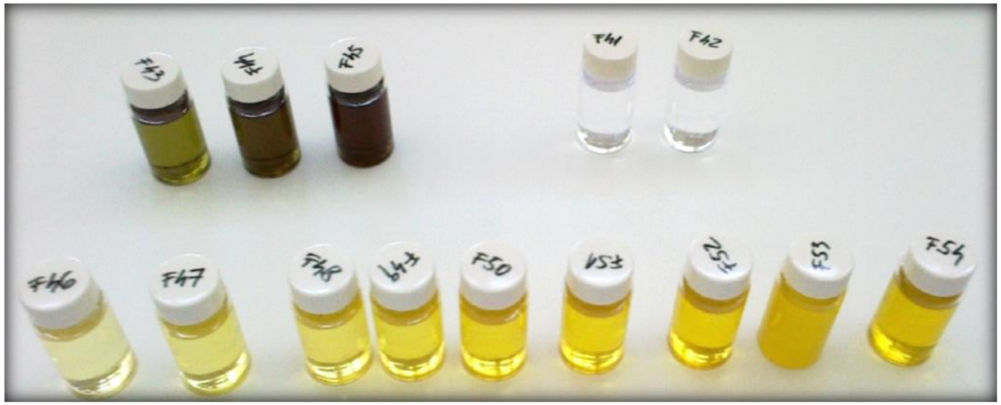
Higher uncertainty

Color quenching

A large variety of mixtures
fossil matrix + biogenic blend

We were looking for a simple, fast, robust technique, though reliable and accurate, that would depend neither on the type of the fossil matrix nor on the type of the biogenic blend





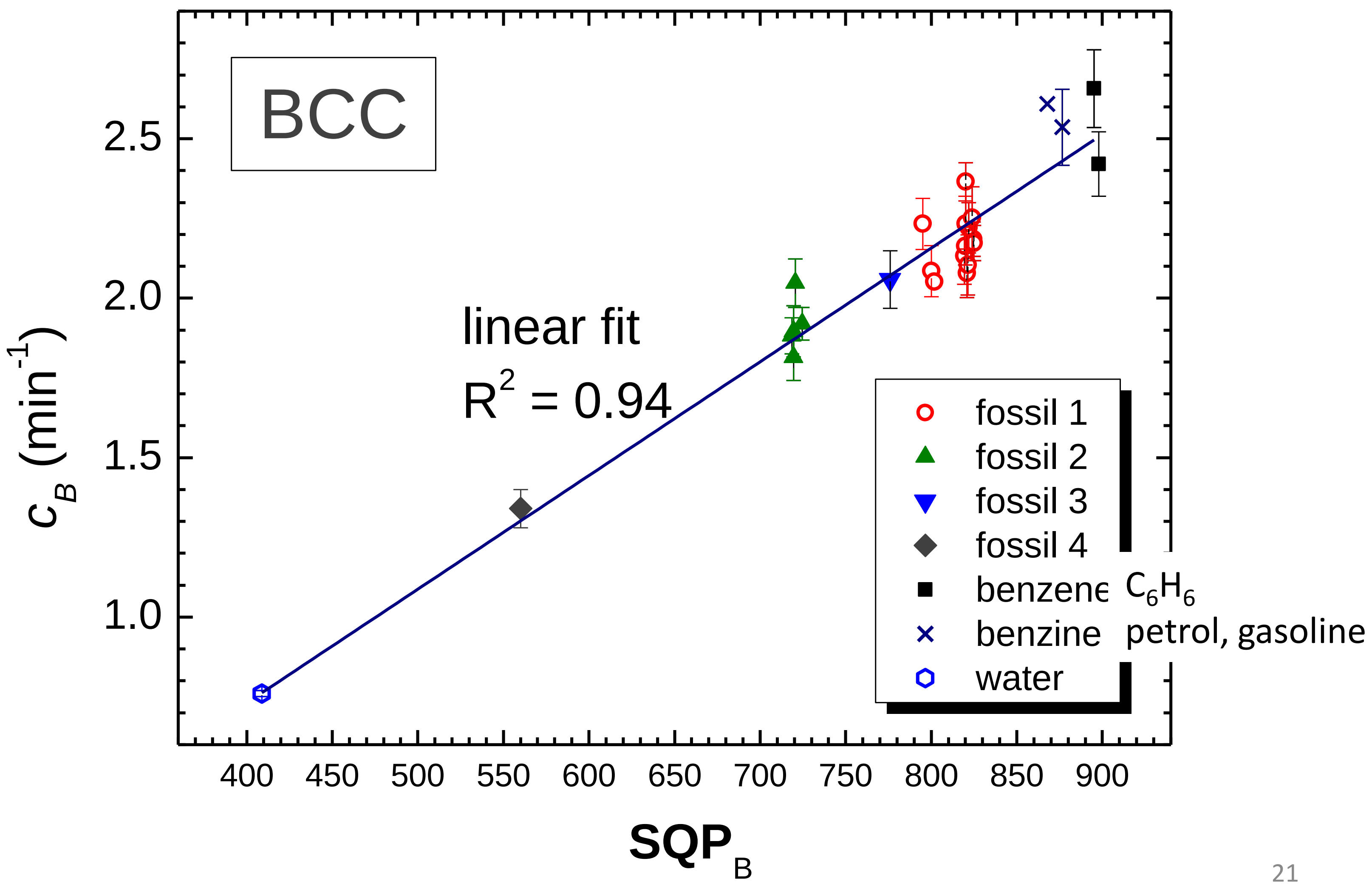
Idea!

Convert the problem/main drawback to the advantage - **quenching parameter of various samples use as the calibration parameter**!

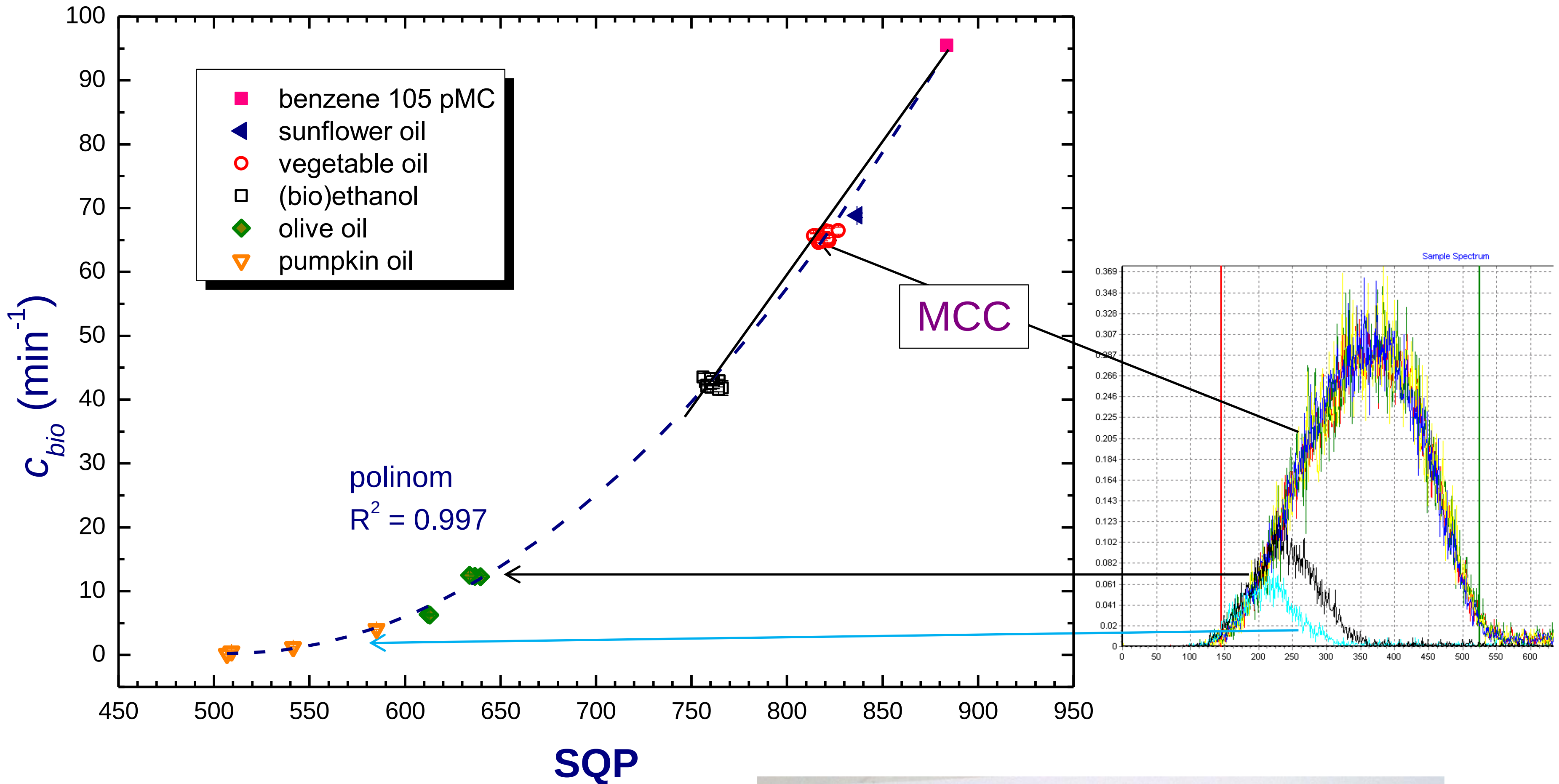
By using different 100% biogenic and 100% fossil liquids of different colors we determined a relation between the two quantities measured by LSC Quantulus: SQP parameter and count rate

Background calibration curve (BCC)

relates the SQP and count rates of various background samples, i.e. samples that do not contain ^{14}C



Modern calibration curve (MCC)



Liquid of biogenic origin: various brand of domestic oil, (bio)etanol p.a., benzene (modern samples)

The procedure of data evaluation for the unknown sample:

- measurement of SQP and count rate of the sample (SQP, 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

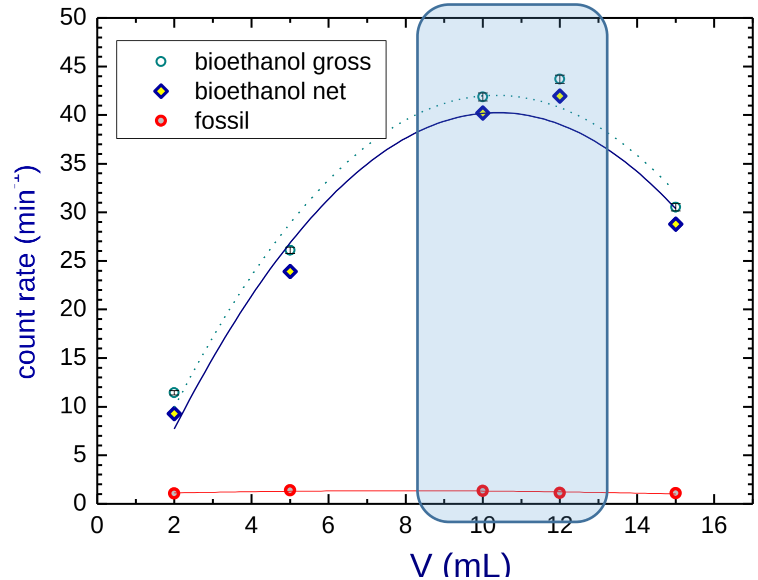
The fraction of the biogenic component in the sample is calculated as the ratio of net count rates of the sample to the biogenic material.

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

All samples should be measured under the same conditions:

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

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



Test and validation

various mixtures of fossil and biogenic liquids in the nominal concentration ranges of the biogenic component from 0 % to 100 %.

- vegetable oil and fossil fuel that both have approximately the same value of the SQP parameter
- bioethanol and fossil fuel with different SQP values
- bioethanol and ^{14}C-free benzine

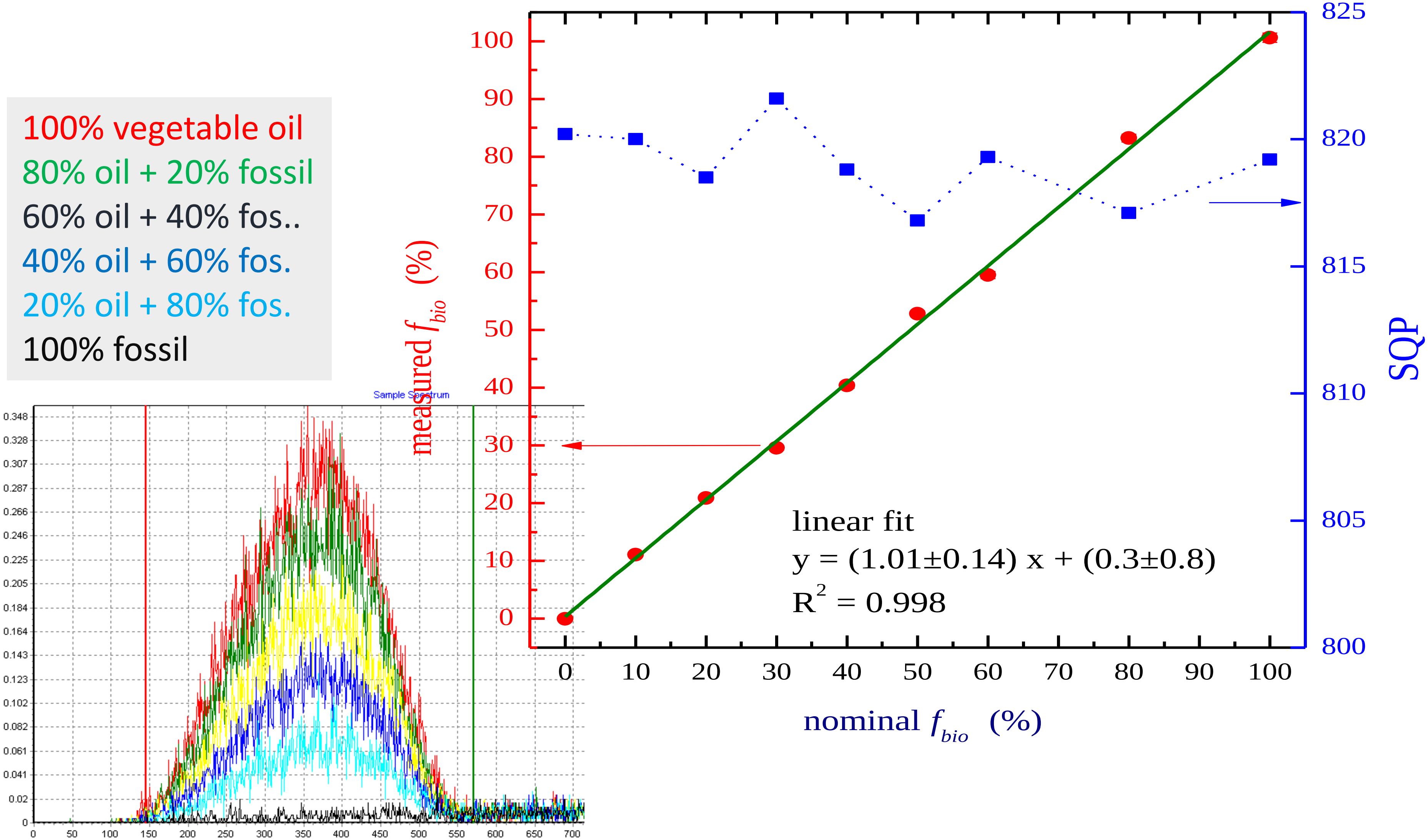
In all cases, the calculated biogenic fraction agreed well with the nominal fraction.

- mixtures of two different biogenic liquids (vegetable oil and bioethanol, vegetable oil and olive oil) having different SQP

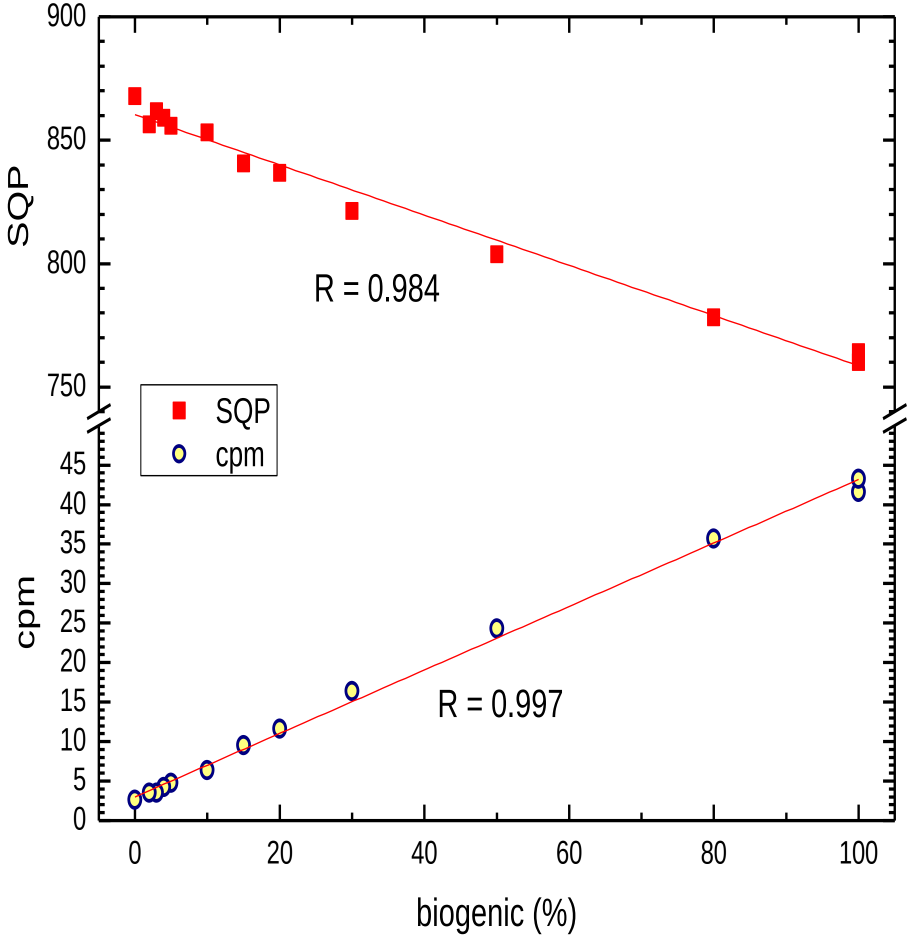
mixtures of vegetable oil and fossil fuel, similar SQP

The measured f_{bio} values agree very well with the nominal f_{bio} values while the SQP values of all mixtures remained more-or-less constant.

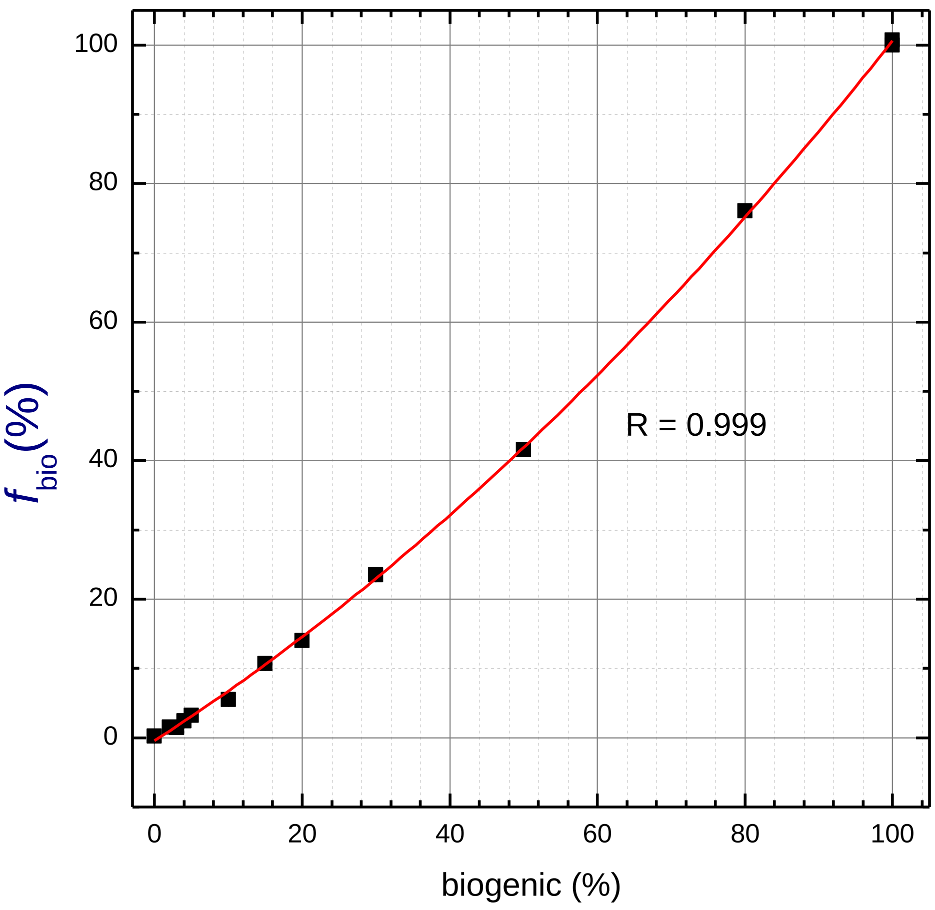
100% vegetable oil
80% oil + 20% fossil
60% oil + 40% fos..
40% oil + 60% fos.
20% oil + 80% fos.
100% fossil



Bioethanol and benzine p.a. mixtures (different SQP)



benzine + bioethanol



Intercomparison

The obtained results were in good agreement with those obtained by different evaluation technique, both for the gasoline and diesel as the fossil matrix and various biogenic blends.

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 14C method. Proc. 10th Symp. of Croatian Radiation Protection Association, pp. 390-395, Šibenik, Croatia, 15-17 April 2015. HDZZ, Zagreb, 2015

no.	Fuel matrix	RBI Zagreb		JSI Ljubljana	
		SQP	f_{bio} (%)	SQP	f_{bio} (%)
1	diesel	636.3	8.2 ± 0.8	657.3	7 (nominal)
2	diesel	716.9	2.2 ± 0.3	742.4	1.73 ± 0.10
3	diesel	758.3	5.8 ± 0.3	771.8	5.17 ± 0.26
4	diesel	885.8	0 (< 0.5)	880.3	0.5 ± 0.3 (< 0.52)
5	diesel	776.8	0.64 ± 0.30	776.2	0.62 ± 0.37
6	gasoline	841.6	0.1 ± 0.1 (< 0.5)	838.9	0.26 ± 0.19 (< 0.57)
7	gasoline	790.7	3.1 ± 0.2	790.6	5.22 ± 0.57
8	gasoline	823.4	3.4 ± 0.2	828.4	4.44 ± 0.43

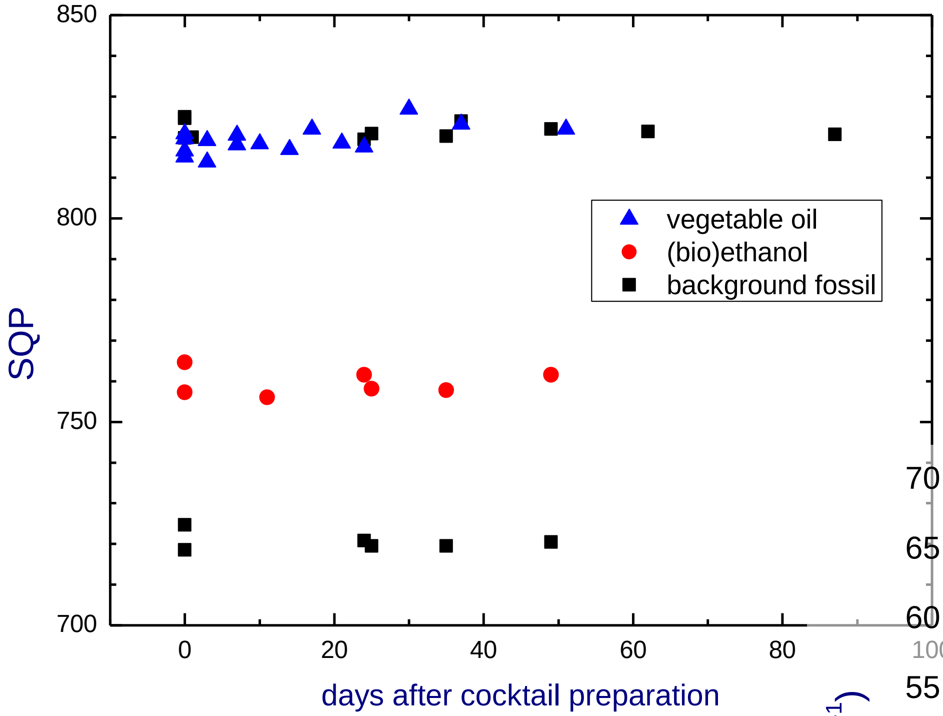
Zaključak (1)

- Određivanje udjela biogene komponente u različitim materijalima je područje istraživanja zanimljivo za znanost, za industriju, ali i za očuvanje okoliša, jer korištenje biogenih materijala za stvaranje energije mmože usporiti porast koncentracije atmosferskog CO_2 (fosilnog podrijetla).
- ^{14}C metoda se uspješno koristi za određivanje biogenog udjela
- Različite mjerne tehnike razvijene za ^{14}C datiranje mogu se uspješno primijeniti.

Zaključak (2)

- Ovdje je prikazana nova tehnika obrade podataka dobivenih direktnom metodom mjerenja aktivnosti ^{14}C u tekućinama u LSCu. Za kalibraciju se koriste uzorci jednake aktivnosti ^{14}C, ali različitih svojstava gašenja zbog različitog obojenja.
- Dobiveni rezultati usporedivi su s onima dobivenima „klasičnom" tehnikom obrade podataka

Long-term stability of SQP and count rate - aging



No change in either SQP or count rate was observed - the prepared cocktails are stable during at least 3 months after preparation.