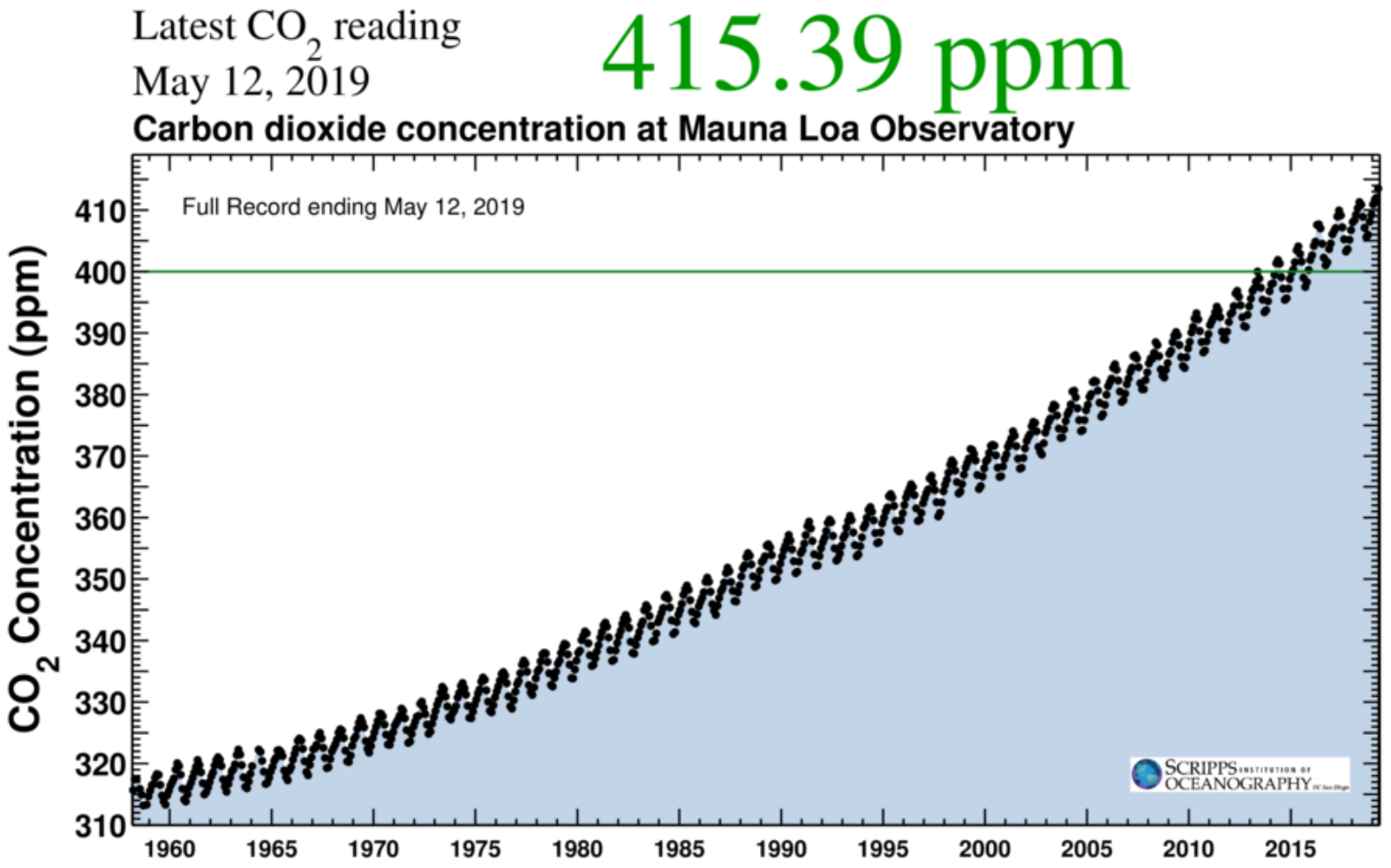
Determination of biogenic component in solids and liquids by the radiocarbon (^{14}C) method

Ines Krajcar Bronić
Ruđer Bošković Institute, Zagreb, Croatia

krajcar@irb.hr

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

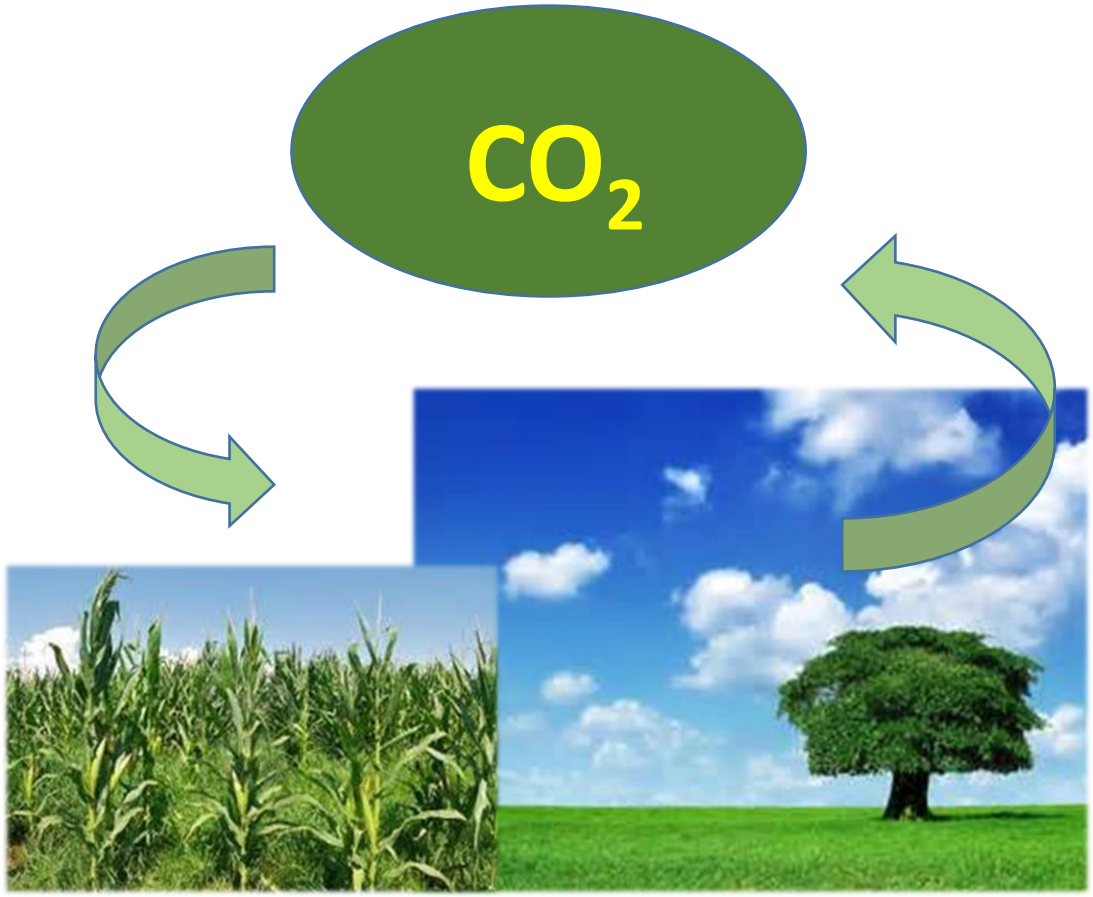


How do we know that excess-CO_2 comes from fossil fuels?

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

Carbon cycle

How do we know that excess-CO_2 comes from fossil fuels?



Biogenic carbon

All carbon isotopes take part

^{12}C: 98.89 %

^{13}C: 1.1 %

^{14}C: 1.18×10^{-10} %

Carbon on Earth

^{12}C: 98.89 %

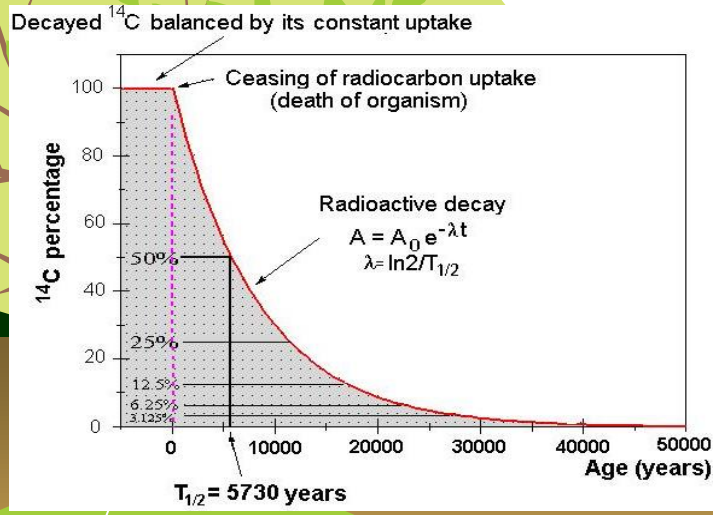
^{13}C: 1.1 %

^{14}C: 1.18×10^{-10} %

$$^{14}N + n \rightarrow {}^{14}C + p$$

O_2

$^{14}CO_2$



$$^{14}C \rightarrow {}^{14}N + e + \bar{\nu}$$

Carbon isotope fingerprint

Atmosphere
$a^{14}C$ = 100 pMC
$\delta^{13}C$ = -8 ‰

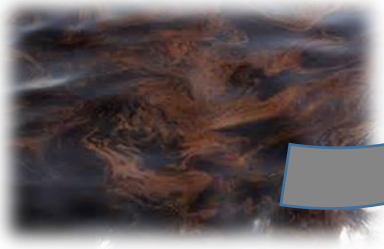
CO_2

CO_2

Biogenic carbon

Plants (biosphere)
$a^{14}C$ = 100 pMC
$\delta^{13}C$ = -25 ‰ (-12 ‰)

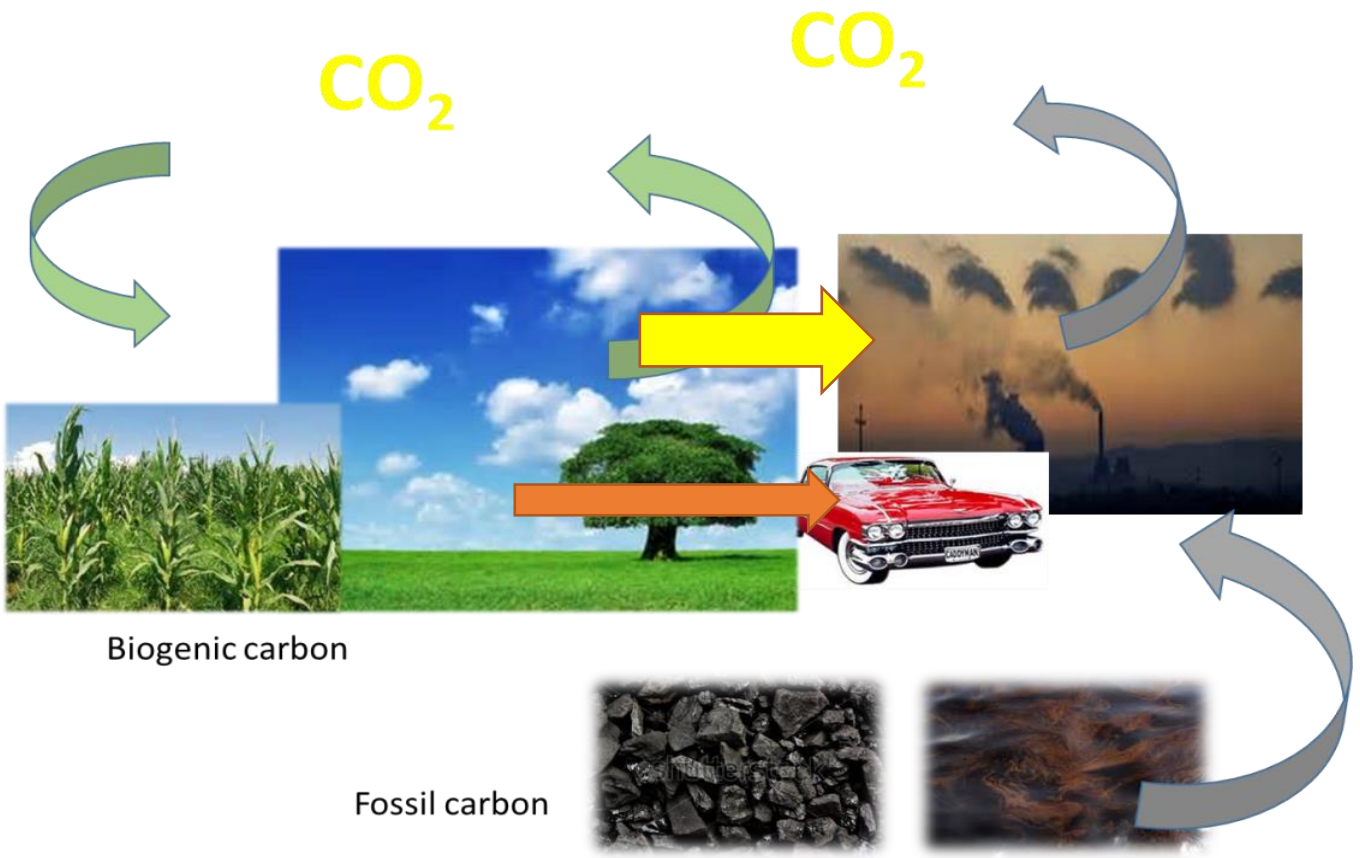
Fossil carbon
$a^{14}C$ = 0 pMC
$\delta^{13}C$ = -25 ‰



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.

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



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.**

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

- Fast, accurate and reliable method of biogenic component determination in various materials (including liquid fuels) is the method based on radiocarbon, ^{14}C,
- Various measurement techniques can be used
- The method principle – different ^{14}C activities in two components – biogenic and fossil
- biogenic component reflects atmospheric ^{14}C activity, there is no ^{14}C in fossil component

Fossil matrix of the fuels is either gasoline (benzine, petrol) or diesel (gas oil) **biogenic components/blends - biofuels** are usually bioethanol, biodiesel, biogas, biomethanol, biodimethylether, bio-ETBE (ethyl-tertio-butyl-ether), bio-MTBE (methyl-tertio-butyl-ether), fatty acid methyl esters (FAMEs), hydrogenated vegetable oil (HVO), synthetic biofuels, biohydrogen and pure vegetable oil.

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

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

^{14}C method can be applied to various materials (mixed communal waste, used car tyres, wooden material, liquid fuels, various consumables, CO_2 obtained by waste combustion).

Depending on the type of the maetrial (and required uncertainties, and costs) various measurement techniques can be applied

- AMS
- LSC-B
- LSC-A
- Direct LSC method

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Comparison of different measurement techniques

Techniques	Sample type	mass	Complexity *	precision *	Cost *	Main defficiency
AMS	all	~2 mg	3	4	4	Sample representativity ##
LSC-benzene#	all	~4 g	4	3	3	long
LSC-CO_2 #	all	~0.6 g	2	2	2	High uncertainty, low precision
LSC-direct	liquid	10 ml	1	1	1	quenching

* Higher number for more complex, more precise, higher costs

\# Oxidation/combustion is a critical step – possible explosion

\## samples should be homogenized before preparation

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

Advantage:

Fast sample preparation

Low cost

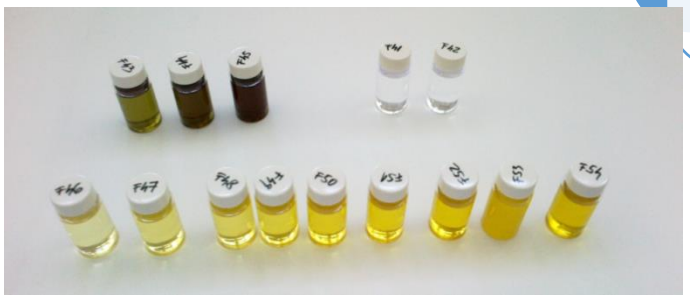
Problems:

Not standardized yet

Higher uncertainty

Color quenching

A large variety of mixtures
fossil matrix + biogenic blend



- Direct LSC method for biogenic component determination has been widely used
- Radiocarbon Laboratory of the Ruđer Bošković Institute (RBI), Zagreb, has developed its own method of evaluation of the measured spectra
- LSC brojač Quantulus 1220

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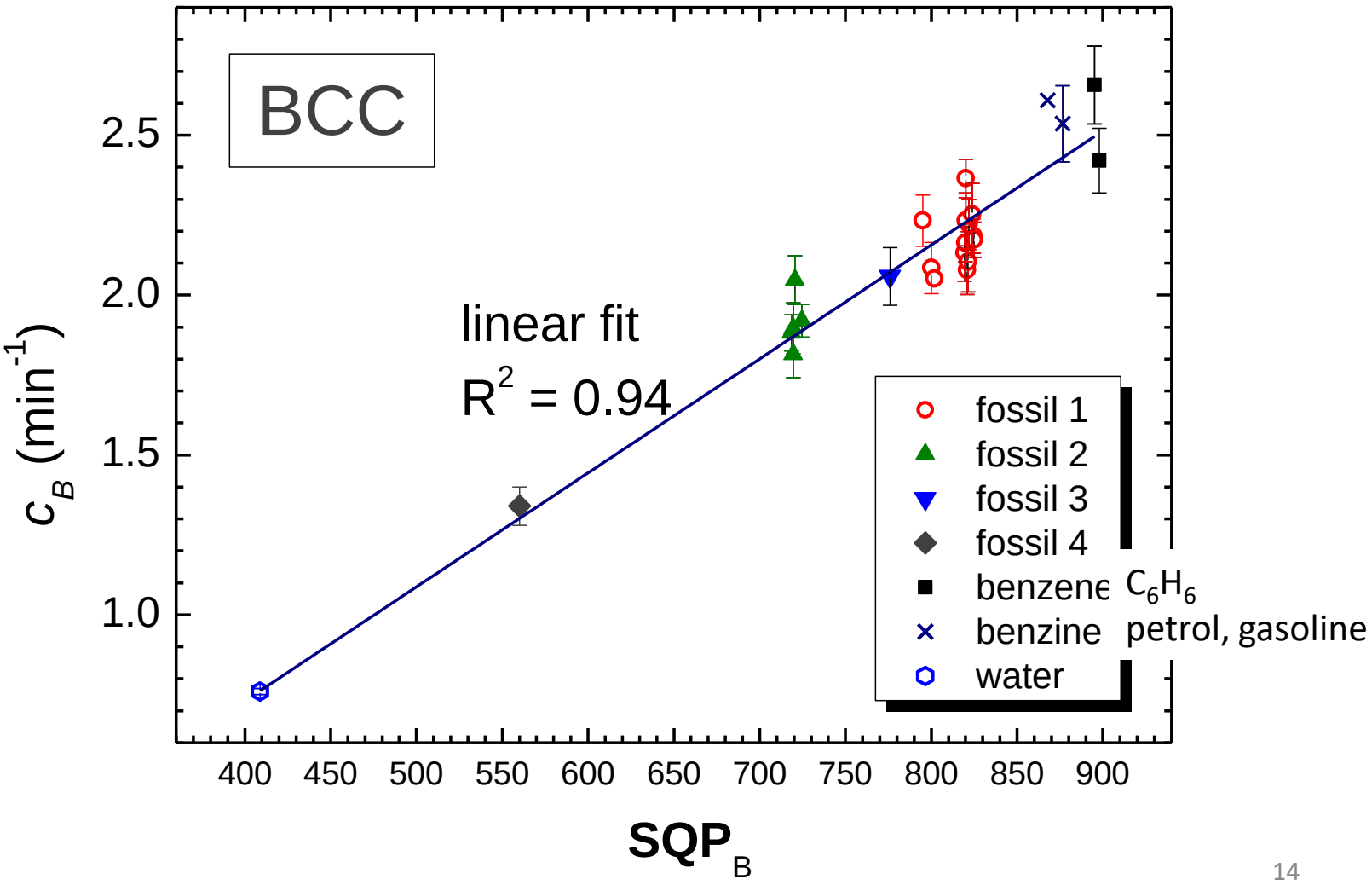
Determination of biogenic component in liquid fuels by the ^{14}C direct LSC method by using quenching properties of modern liquids for calibration ☆

Ines Krajcar Bronić *, Jadranka Barešić, Nada Horvatinčić, Andreja Sironić

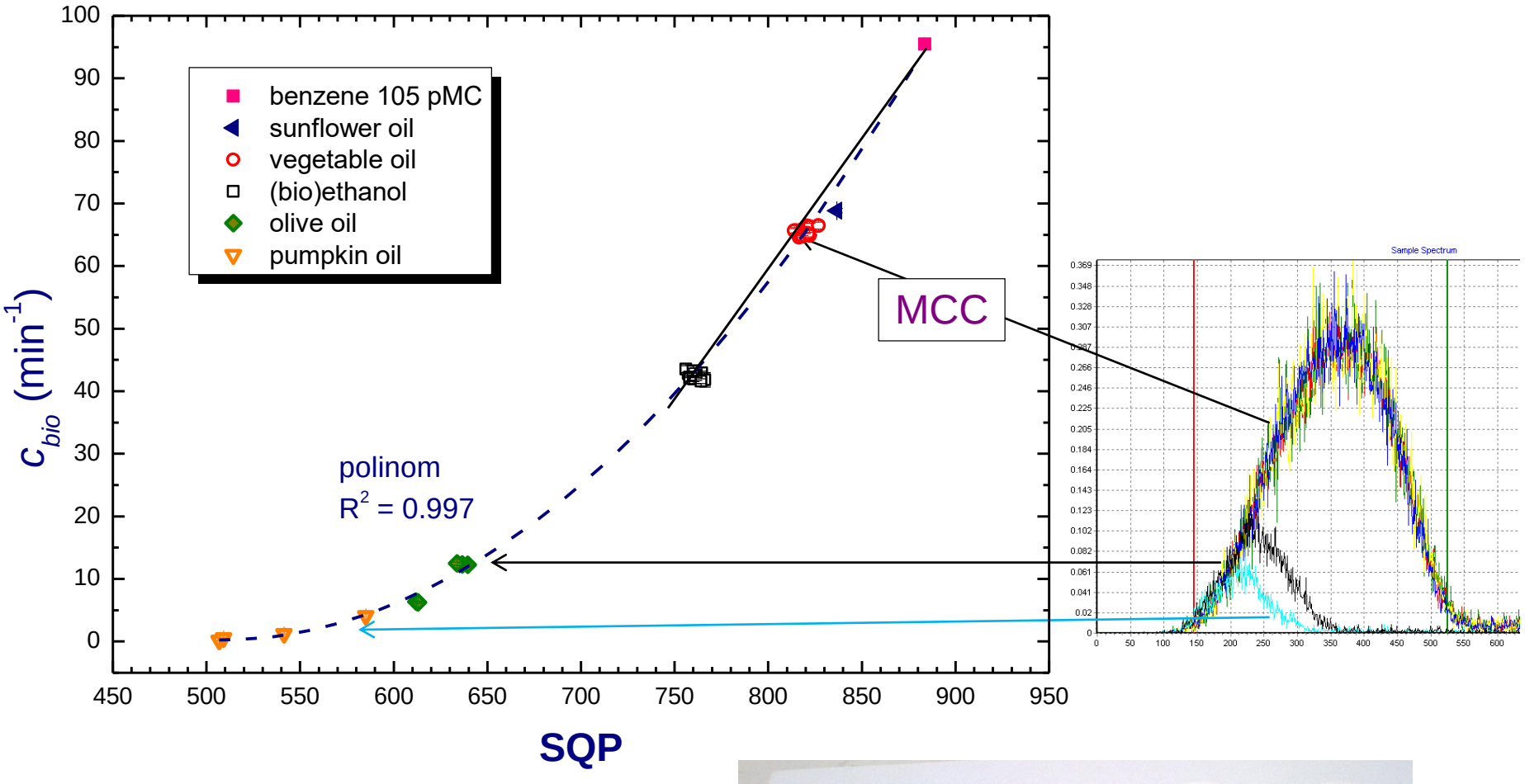
Ruđer Bošković Institute, Zagreb, Croatia

Background calibration curve (BCC)

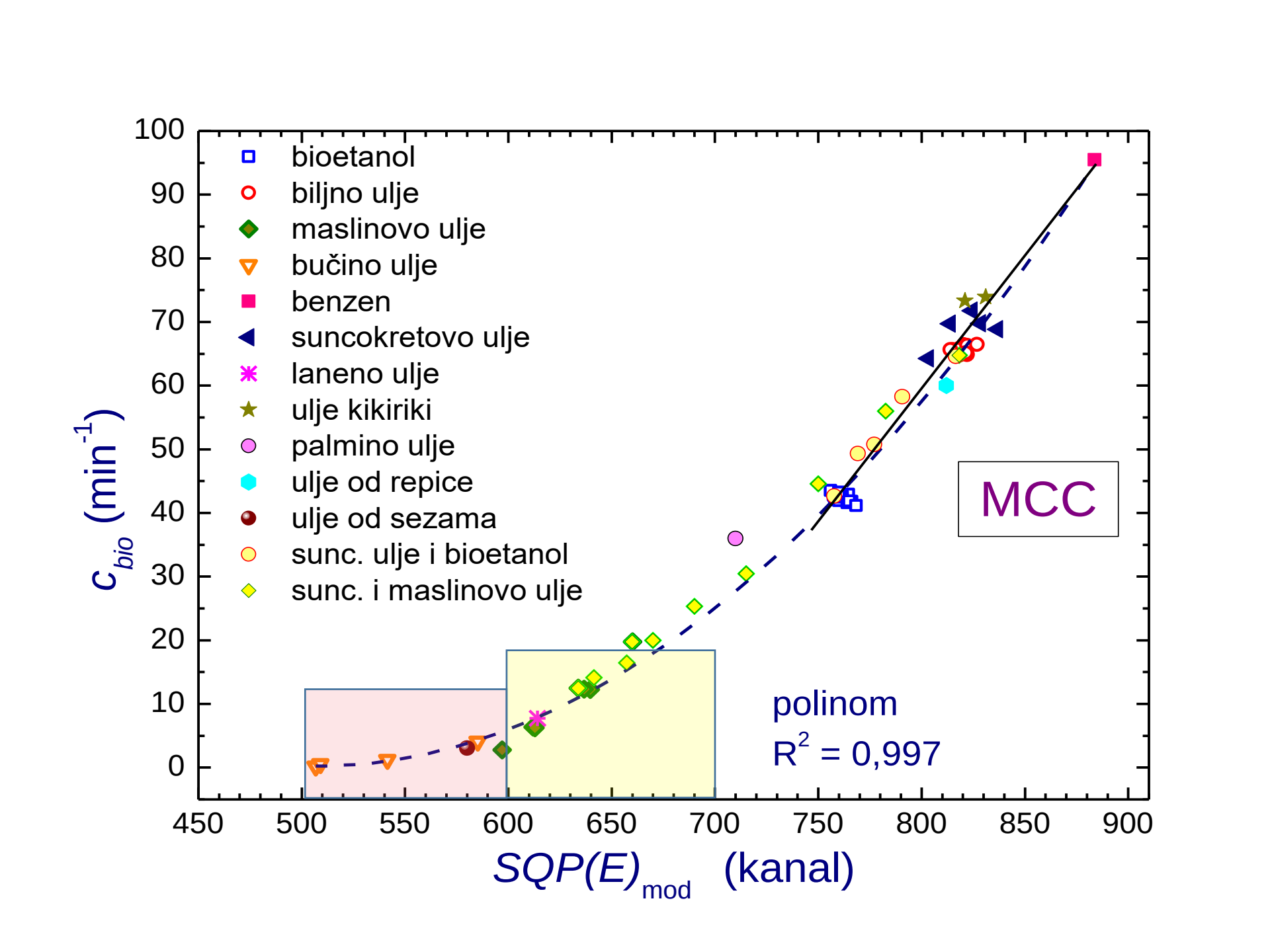
relates the SQP and count rates of various background samples,
i.e. samples that do not contain ^{14}C



Modern calibration curve (MCC)



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


bioetanol
biljno ulje
maslinovo ulje
bučino ulje
benzen
suncokretovo ulje
laneno ulje
ulje kikiriki
palmino ulje
ulje od repice
ulje od sezama
sunc. ulje i bioetanol
sunc. i maslinovo ulje
MCC
polinom
R2 = 0,997
c bio (min-1)
SQP(E)mod (kanal)
0
10
20
30
40
50
60
70
80
90
100
450
500
550
600
650
700
750
800
850
900

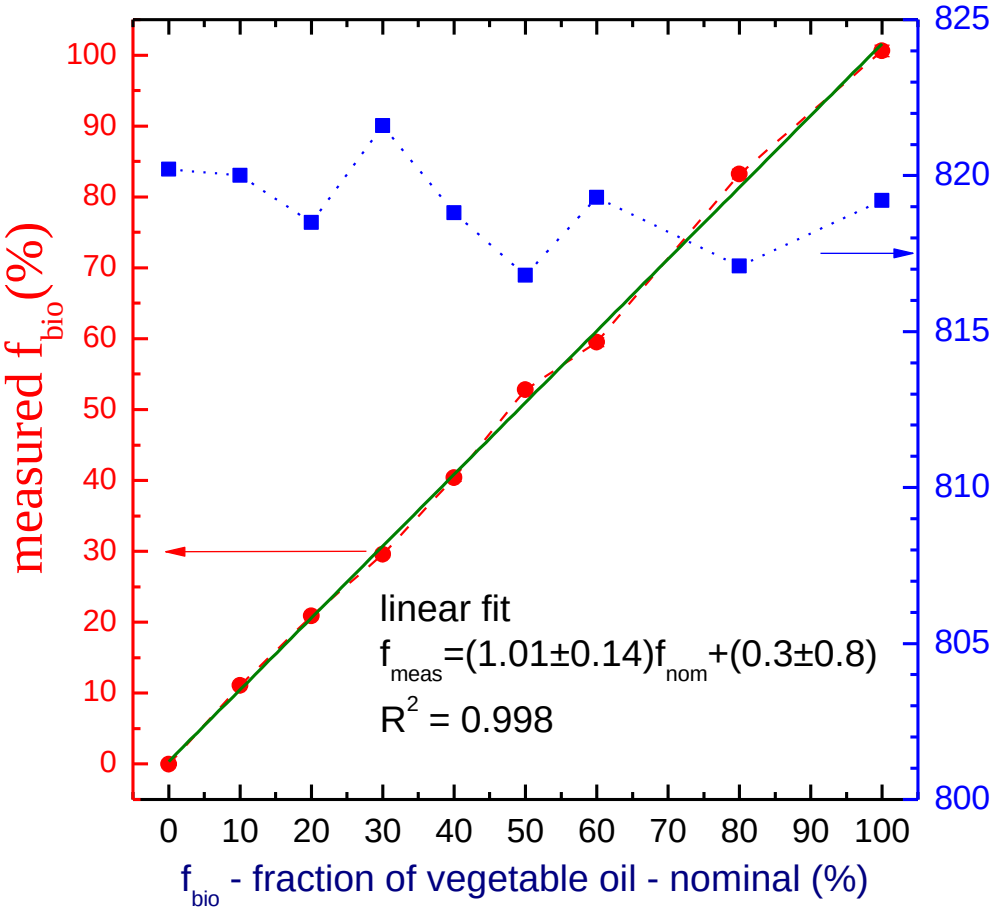
Test and validation

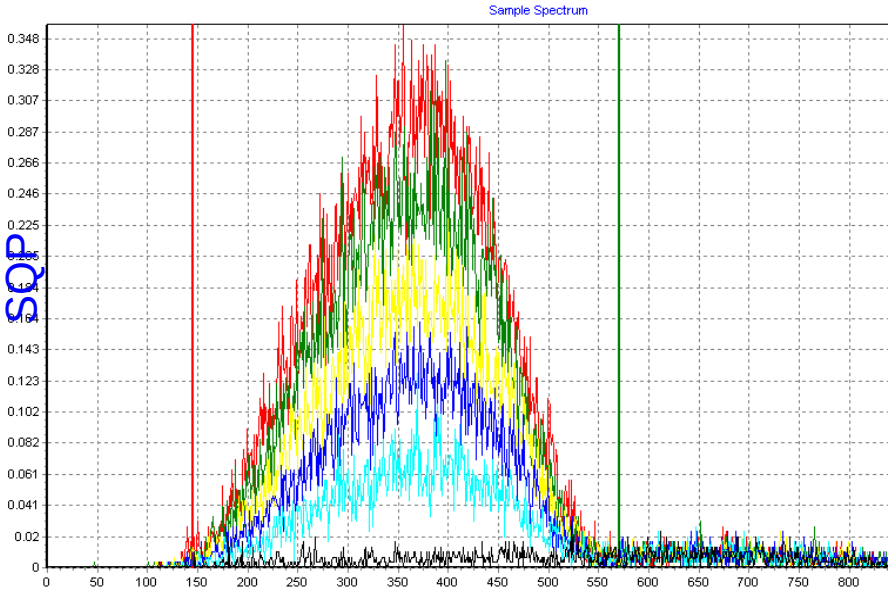
various mixtures of fossil and biogenic liquids in the nominal concentration ranges of the biogenic component from 0 % to 100 %.

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

In all (laboratory) experiments, the calculated biogenic fraction agreed well with the nominal fraction.

Example: vegetable oil (modern sample) and fossil fuel; similar SQP, various concentrations





Intercomparison (4)

- In 2018 international intercomparison study ILC/2018 „Content of biocomponent in liquid fuel samples“ organized by the Institute of Ceramics and Building Materials (Opole, Poland).

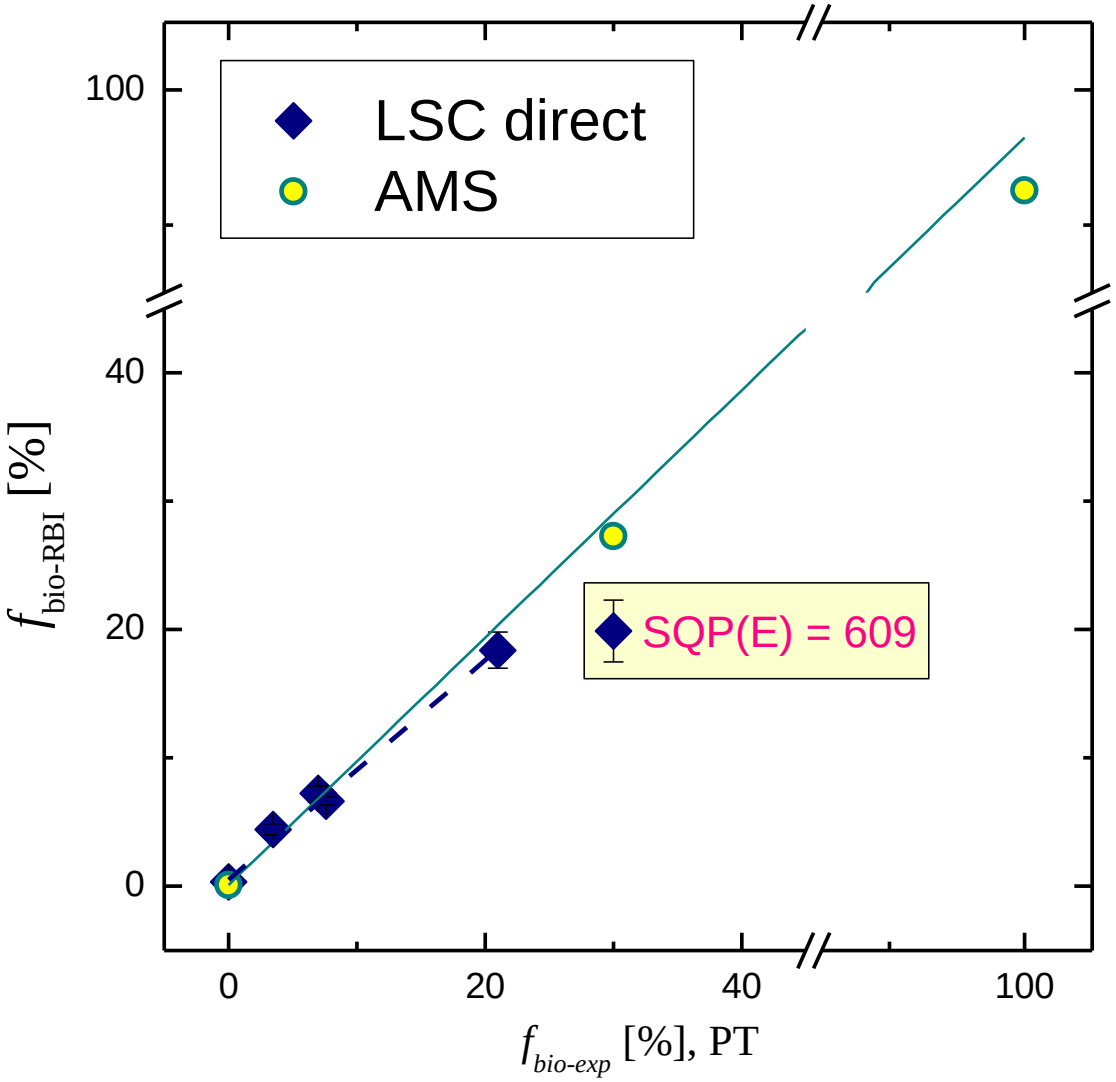
10 mL scintillation cocktail UltimaGold F + 10 mL of sample, glass vials

Intercomparison (5)

Sample code	Sample name	$SQP(E)_{IRB}$	Expected $f_{bio\text{-}exp}$ [%]	RBI result $f_{bio\text{-}IRB}$ [%]	JSI results $f_{bio\text{-}IJS}$ [%]
A	LL/18/0805	**804**	**0.0**	**0.34 ± 0,25** 0.09 ± 0.01 [a]	**0.87 ± 0.81**
B	LL/18/0806	**724**	**7.0**	**7.23 + 0.60**	**7.09 ± 1,59**
C	LL/18/0807	**581**	**100.0**	**--** 92.58 ± 0.25 [a]	**--** **92.6 ± 19.5** [b]
D	LL/18/1264	**758**	**3.5**	**4.44 ± 0.43**	**4.69 ± 0.98**
E	LL/18/1265	**609**	**30.0**	**19.9 ± 2.4** 27.3 ± 0.1 [a]	**26.07 ± 3.40**
F	LL/18/1266	**648**	**21.0**	**18.4 ± 1.4**	**19.71 ± 2.63**
G	LL/18/1267	**872**	**7.6**	**6.64 ± 0.30**	**7.79 ± 0.93**

a – AMS
b – LSC - CO_2 absorption

Intercomparison (6)



Conclusion

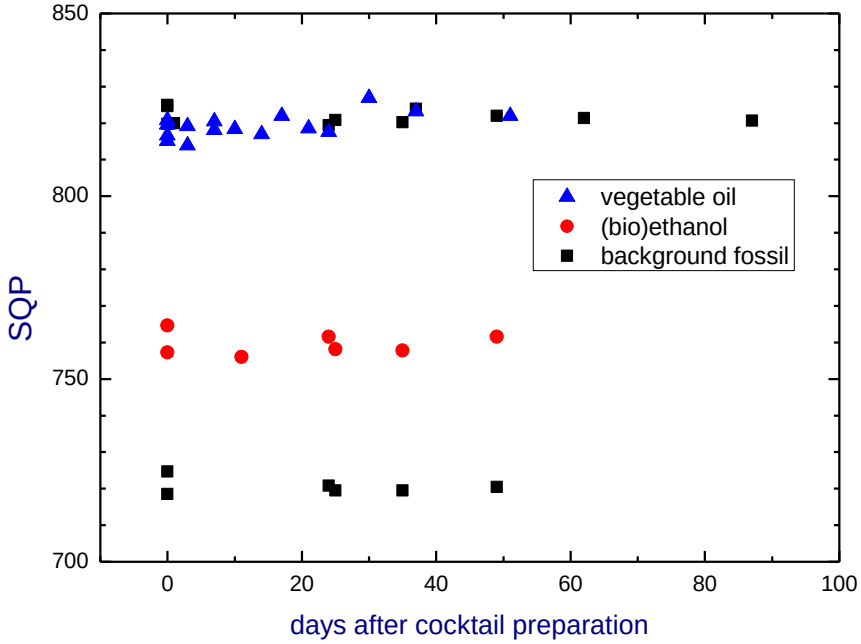
Determination of the biogenic fraction in various materials (liquid fuels especially) is an interesting topic for the scientists, for various industries and for the global environment, because the use of biogenic materials for energy production and transport may slow down the increase of atmospheric CO_2 concentration of fossil origin.

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. Lowest detectable biogenic fraction is 0.5 %.

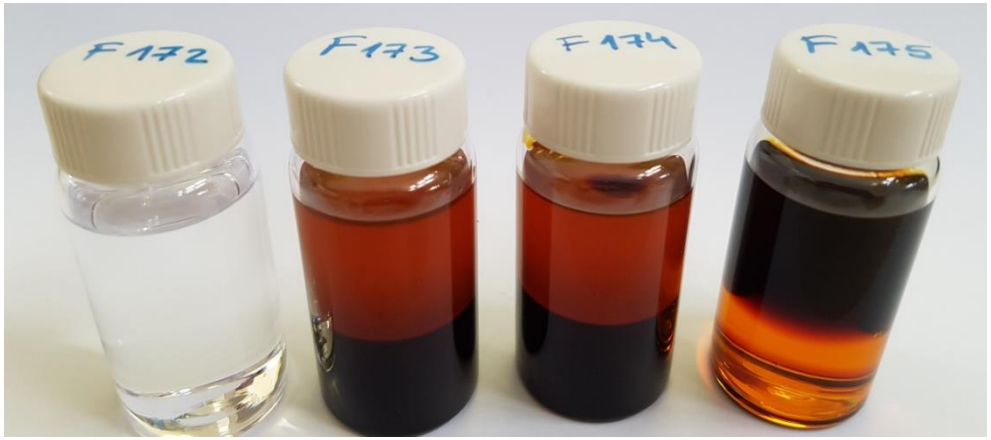
The limit when the count rates of the biogenic and the fossil samples become close to each other or indistinguishable is set to SQP ≈ 700. The method gives comparable results with other data evaluation techniques, and the results are very good for SQP > 700. Qualitative results obtained for 600 < SQP < 700. Below SQP ≈ 600 this value the obtained results for biogenic fractions are not reliable and other techniques should be used.

Next to study

- Influence of aging of both original mixtures and prepared scintillation cocktails on SQP and count rate will be studied



- Bio-pyrolytic oils – dark, not dissolvable in custom organic solvents – application of AMS



Thank you