# Determination of biogenic component in waste and liquid fuels by the $^{14}C$ method


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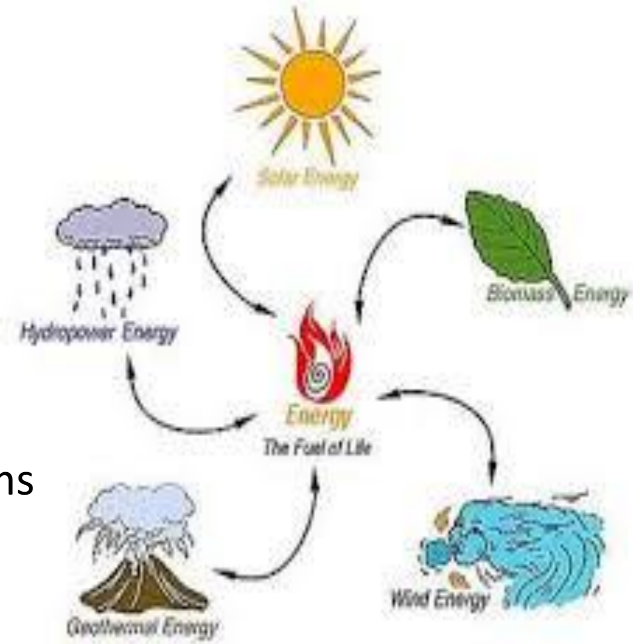
**Intensive use of fossil fuels for energy production and transport during 20th century caused an increase of $CO_2$ concentration in the atmosphere.**

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

**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 renewable energy sources - biogenic materials for energy production and/or transport

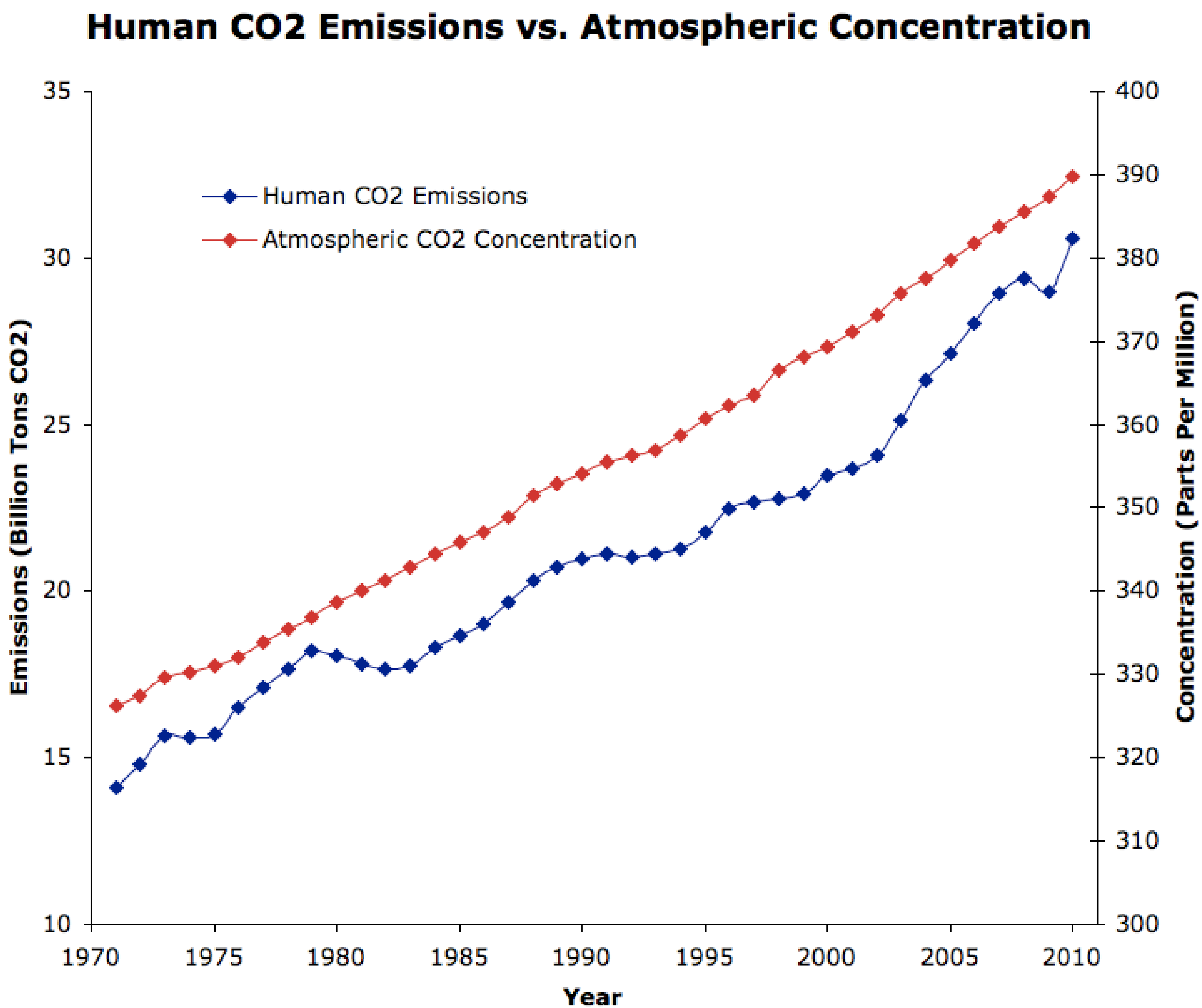
**biogenic** – produced in natural processes by living organisms but not fossilized or derived from fossil resources



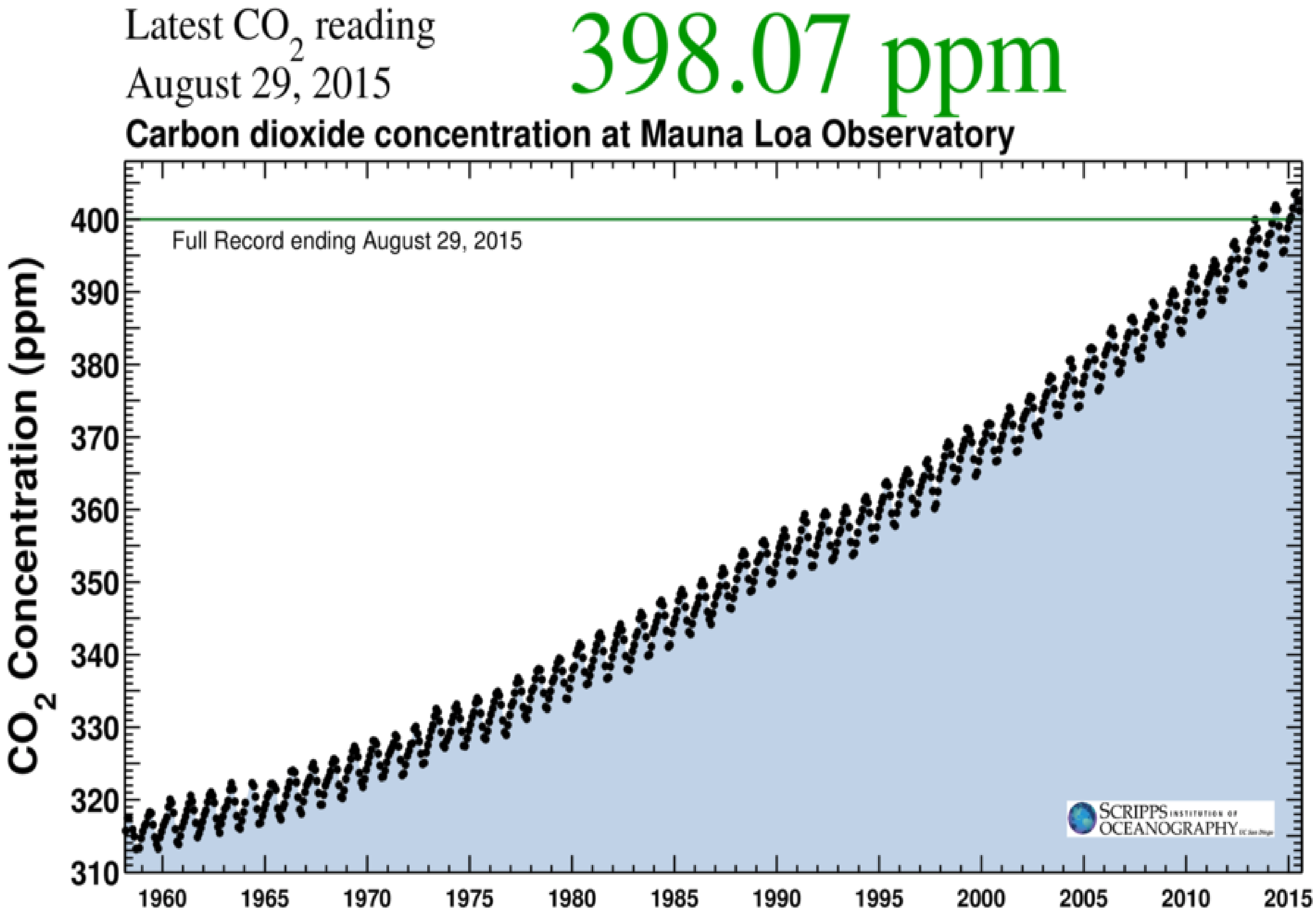

**How can we determine the biogenic fraction in any type of fuel?**

The $^{14}C$ method, which is based on different content of $^{14}C$ in biogenic and in fossil component, is a reliable method and can be used for various types of fuels.

Comparison of „human” (anthropogenic) $CO_2$ emission and atmospheric $CO_2$ concentration, 1970 – 2010

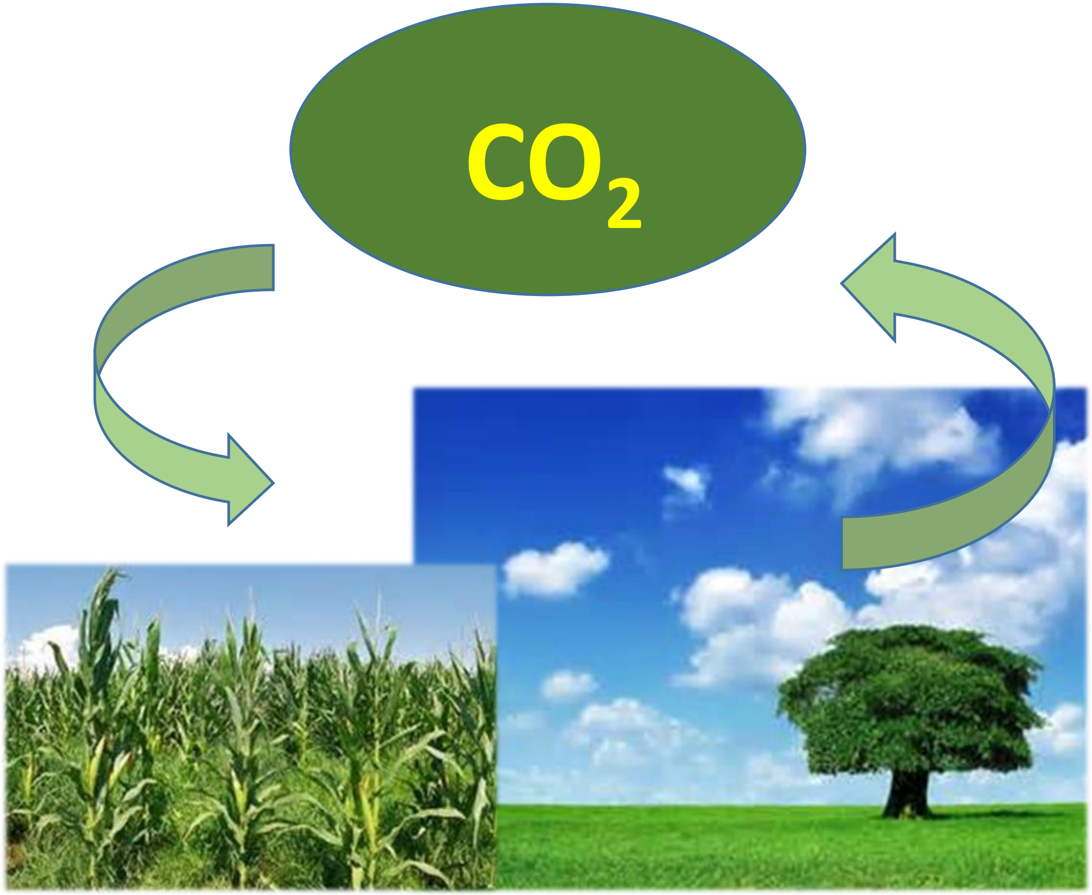



http://www.skepticalscience.com/co2-increase-is-natural-not-human-caused.htm




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

# Carbon cycle




Biogenic carbon

All carbon isotopes take part

$^{12}C$

$^{13}C$

$^{14}C$

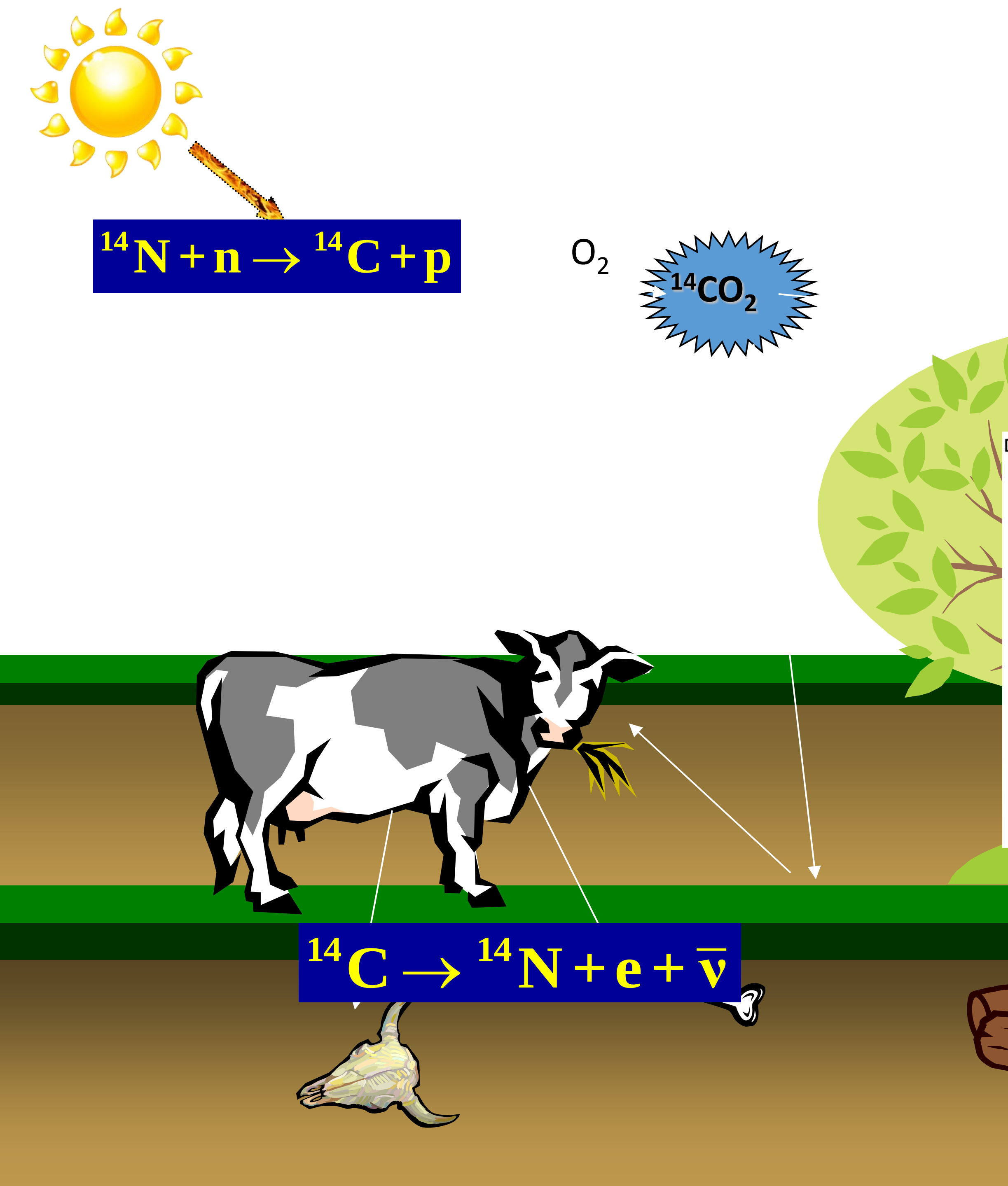
## Carbon on Earth

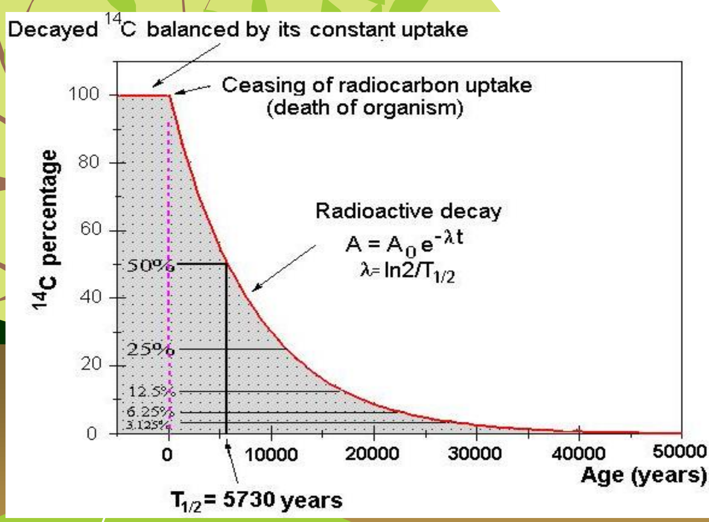
$^{12}C$: 98.89 %

$^{13}C$: 1.1 %

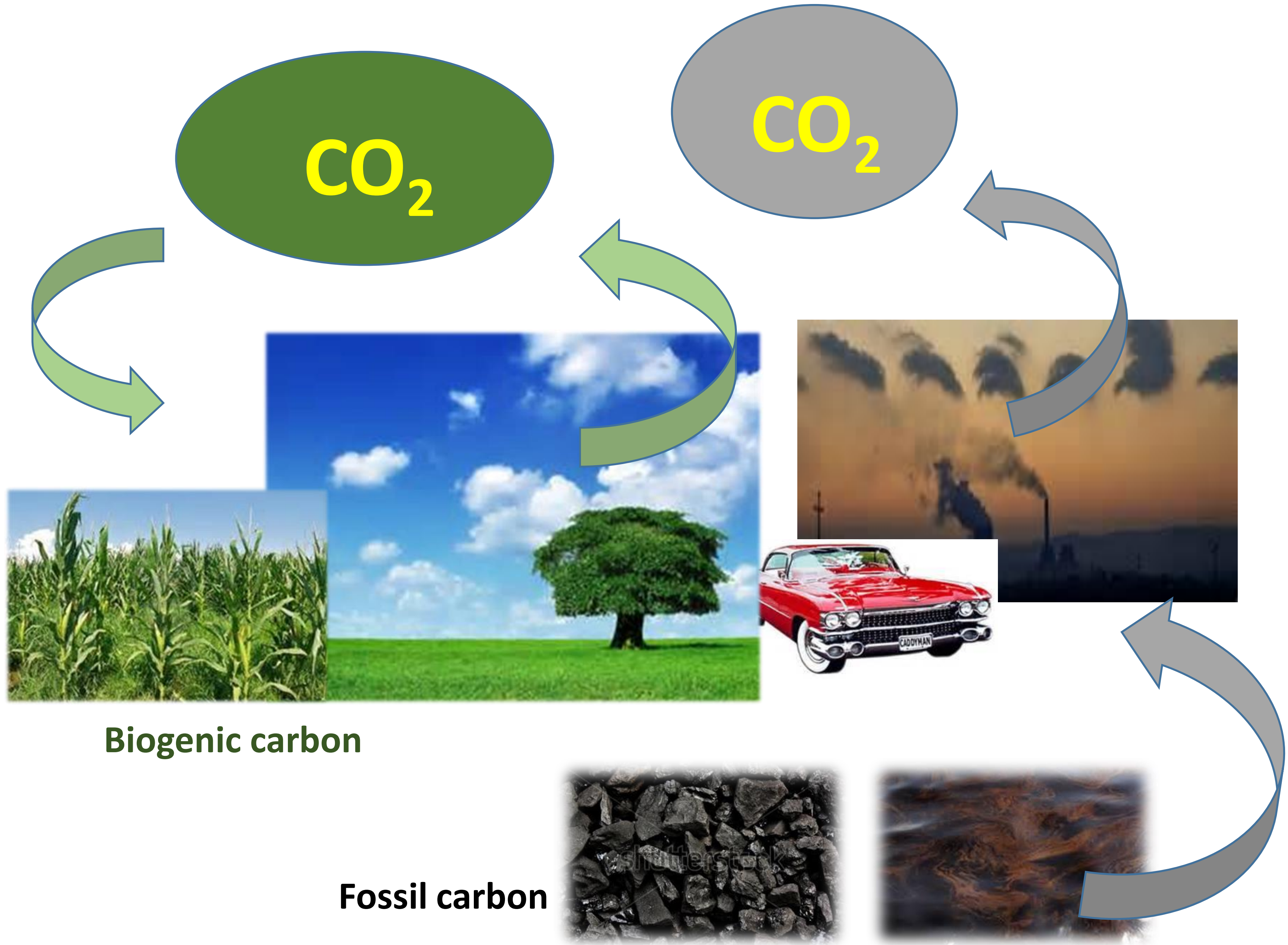
$^{14}C$: 1.18 x $10^{-10}$ %

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

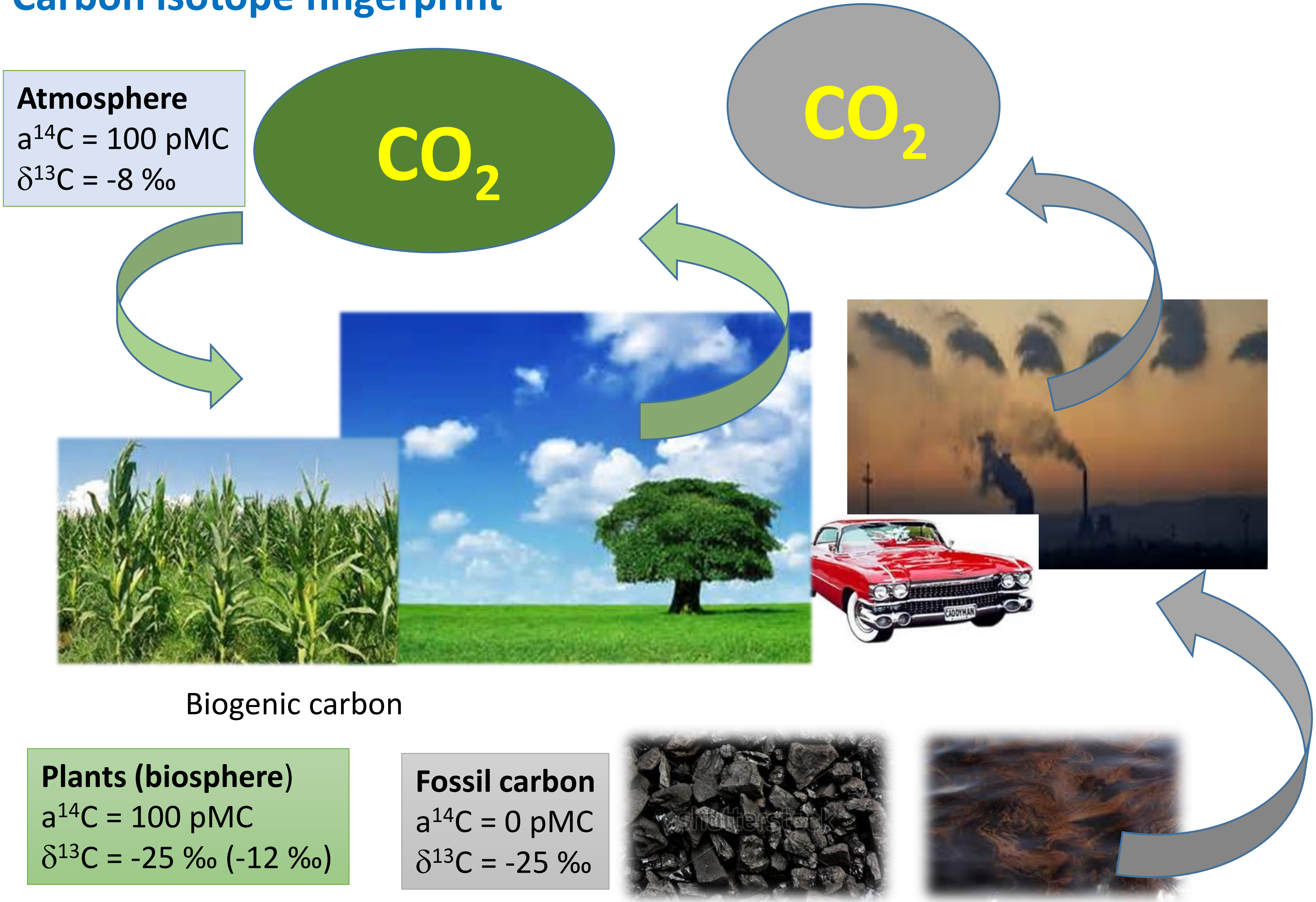


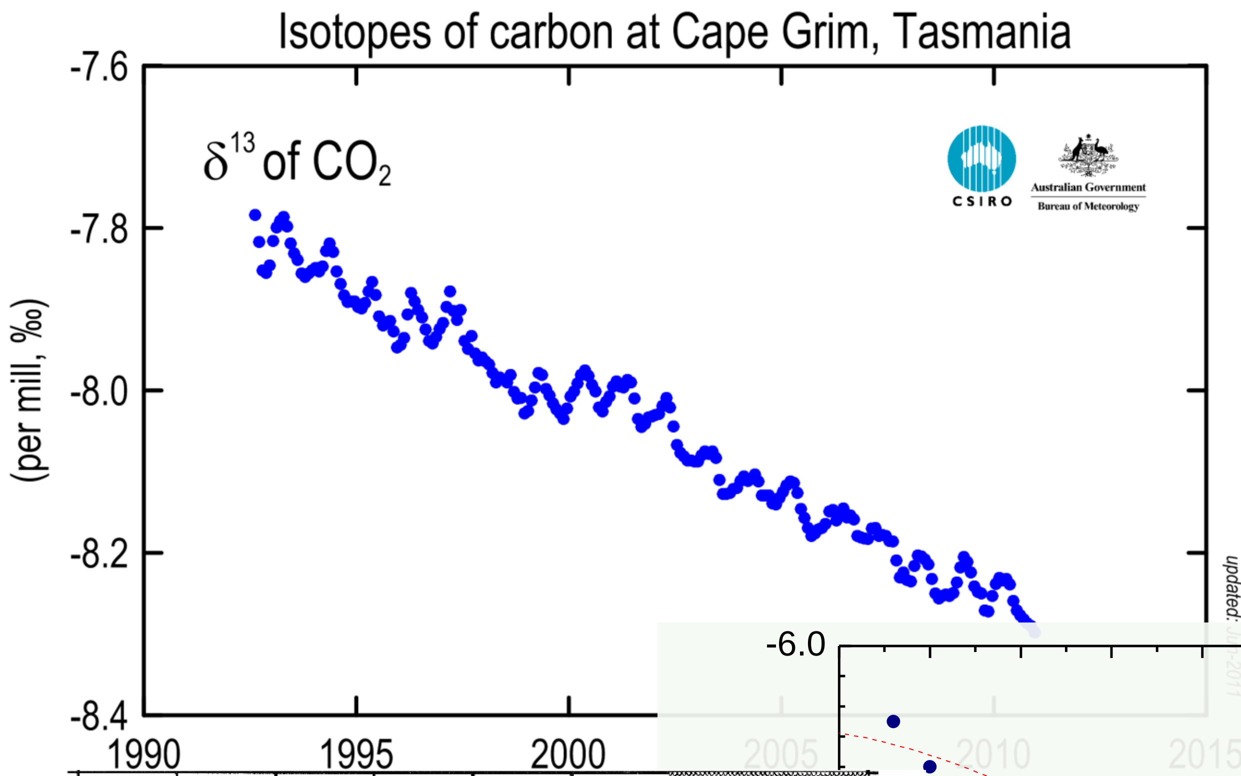




$$^{14}C \rightarrow {}^{14}N + e + \overline{\nu}$$

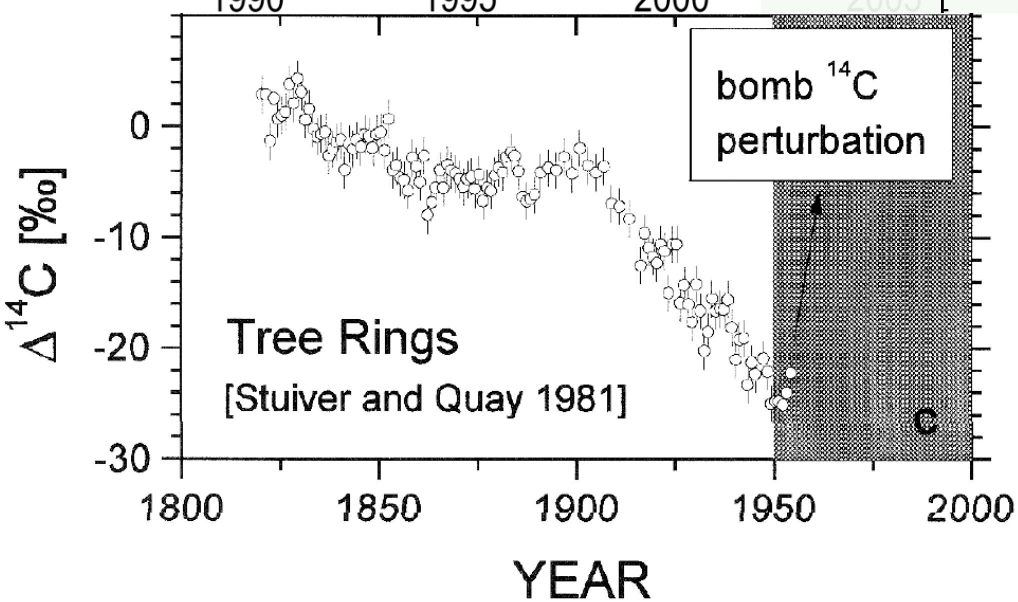

$CO_2$
$CO_2$
Biogenic carbon
Fossil carbon

# Carbon isotope fingerprint

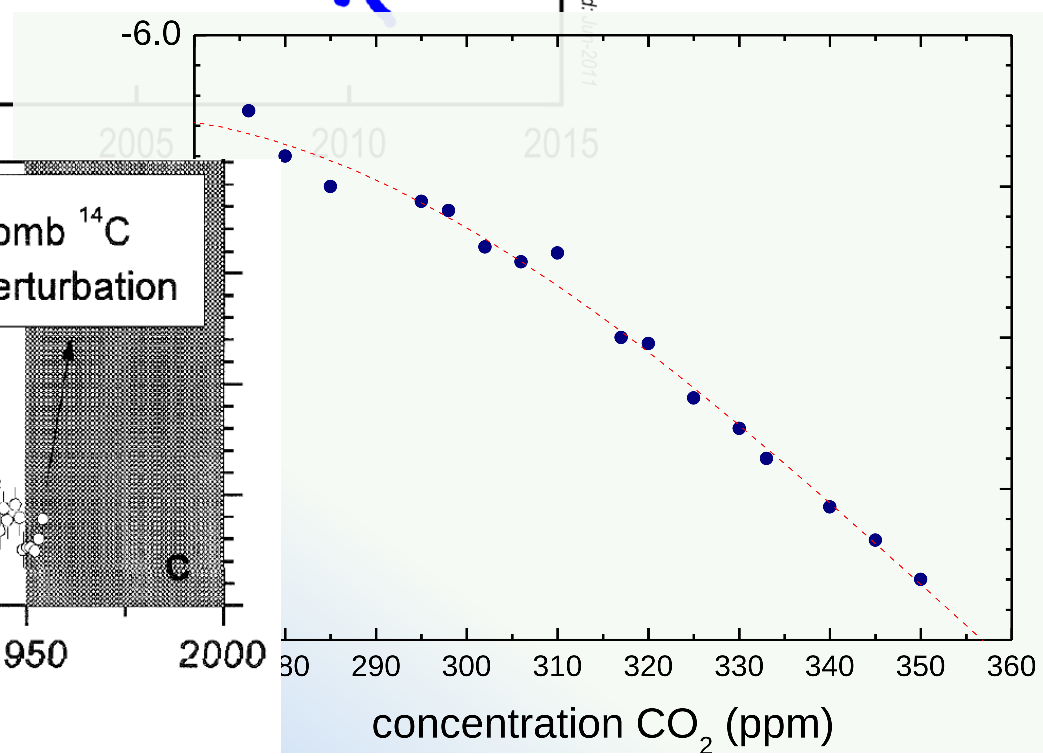




Isotopes of carbon at Cape Grim, Tasmania
$\delta^{13}$ of $CO_2$
(per mill, ‰)
-7.6
-7.8
-8.0
-8.2
-8.4
1990
1995
2000
2005
2010
2015
CSIRO
Australian Government
Bureau of Meteorology

$\Delta^{14}C$ [‰]
0
-10
-20
-30
bomb $^{14}C$ perturbation
Tree Rings
[Stuiver and Quay 1981]
c
1800
1850
1900
1950
2000
YEAR

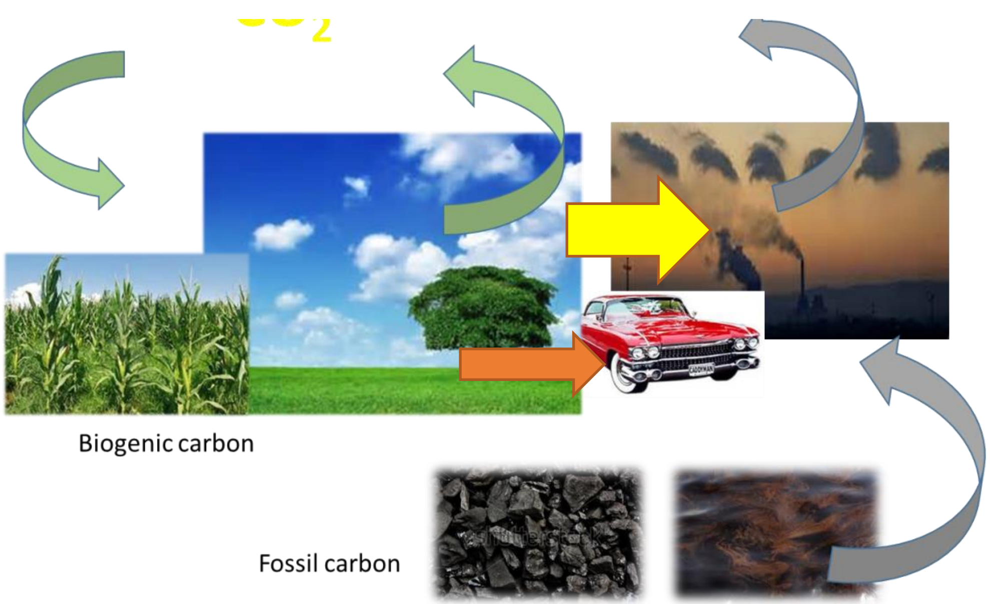



-6.0
290
300
310
320
330
340
350
360
concentration $CO_2$ (ppm)

## 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.

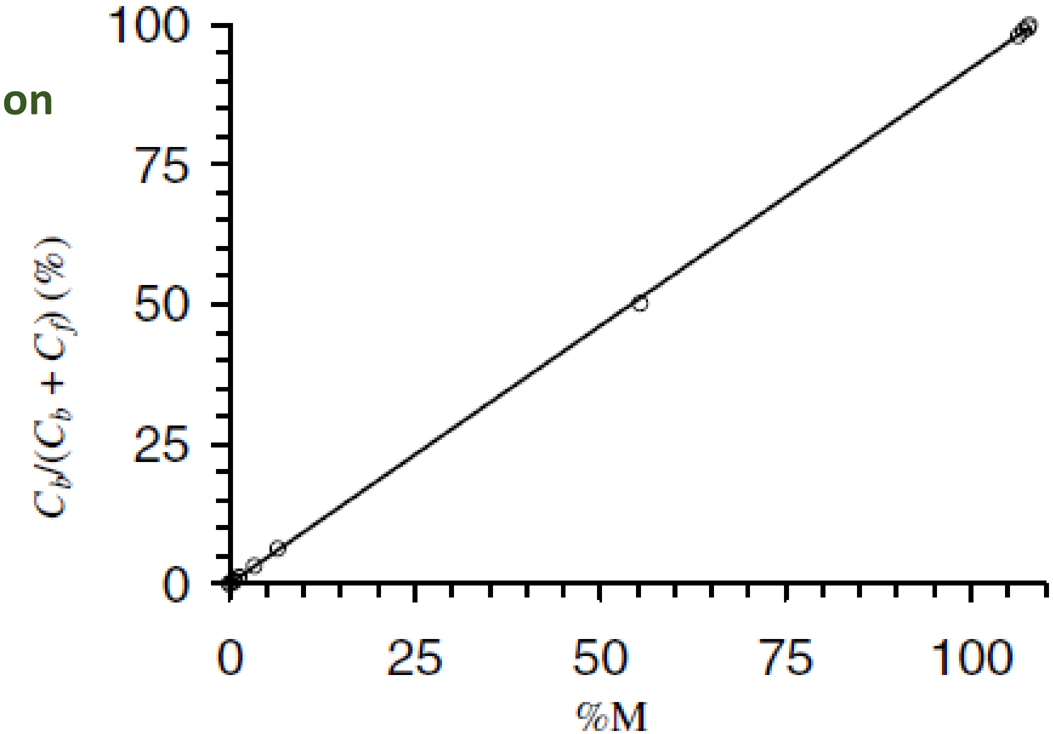
**$^{14}C$ method** is based on different content of $^{14}C$ in biogenic and in fossil component: while the biogenic component reflects the modern atmospheric $^{14}C$ activity, no $^{14}C$ is present in fossil fuels.

**$^{14}C$ method** is suitable for samples of all types of fuel

"Problems" or limitations: i) the measurement of $^{14}C$ content requires highly specialized instruments and personnel (this standard gives a number of about 100 radiometric and 40 AMS laboratories on the global scale!),
ii) $^{14}C$ releases in the 1950's ("bomb-peak") has diminished the accuracy of the $^{14}C$ method in some cases

A pure biogenic material reflects the modern atmospheric $^{14}C$ activity, while no $^{14}C$ is present in fossil fuels (oil, coal). Therefore, a biogenic fraction of any material of interest is proportional to its $^{14}C$ content .

**biogenic fraction**




**$^{14}C$ content**

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, $R^2 = 0.9999$.

RADIOCARBON, Vol 48, Nr 3, 2006, p 315–323


**QUANTITATIVE DETERMINATION BY $^{14}C$ ANALYSIS OF THE BIOLOGICAL COMPONENT IN FUELS**

Ivo J Dijs[1,2] • Eric van der Windt[1] • Lauri Kaihola[3] • Klaas van der Borg[4]

**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…)

G.A. Norton and S.L. Devlin. Determining the modern carbon content of biobased products using radiocarbon analysis. *Bioresource Technology* 97 (2006) 2084–2090.

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

J. Mohn, S. Szidat, J. Fellner, H. Rechberger, R. Quartier, B. Buchmann, L. Emmenegger. Determination of biogenic and fossil fuel $CO_2$ emitted by waste incineration based on $^{14}CO_2$ and mass balances. *Bioresource Technology* 99 (2008) 6471–6479

G.K.P Muir, S. Hayward, B.G. Tripney, G.T. Cook, P. Naysmith, B.M.J. Herbert, M.H. Garnet, M. Wilkinskon. Determining the biomass fraction of mixed waste fuels: A comparison of existing industry and $^{14}C$-based methodologies. *Waste management* 35 (2015) 293-300.

## How to determine biogenic fraction

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:

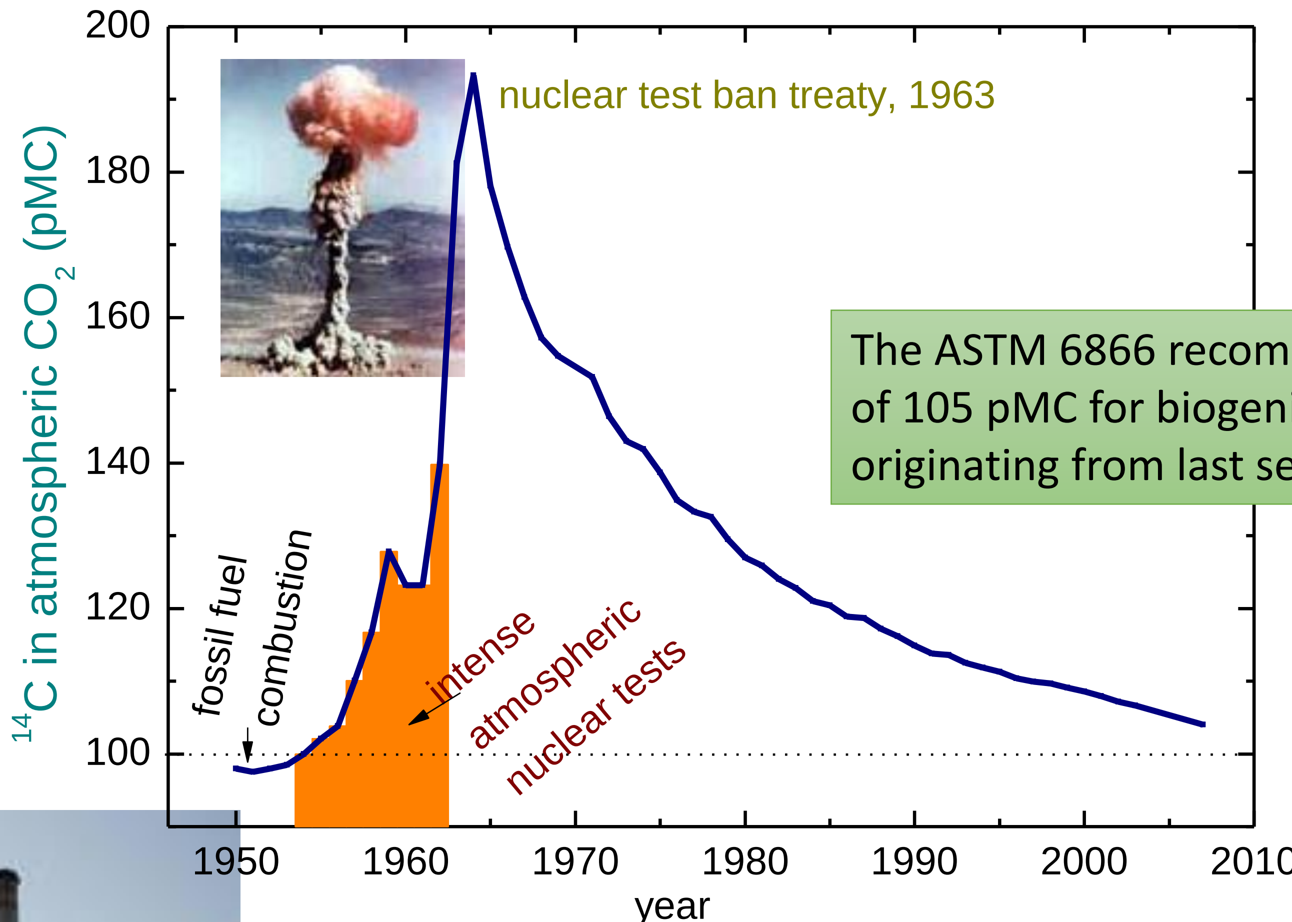
$$a^{14}C_{mix} = f_f \, a^{14}C_f + f_{bio} \, a^{14}C_{bio}$$

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

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

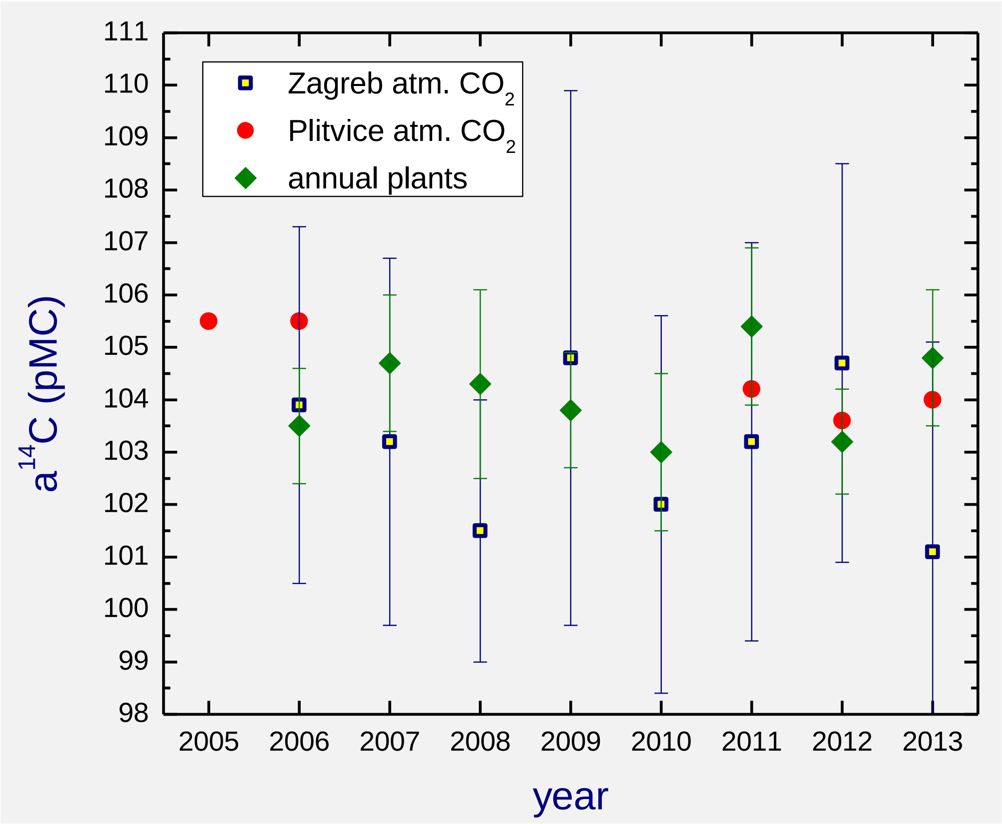
# Anthropogenic activities

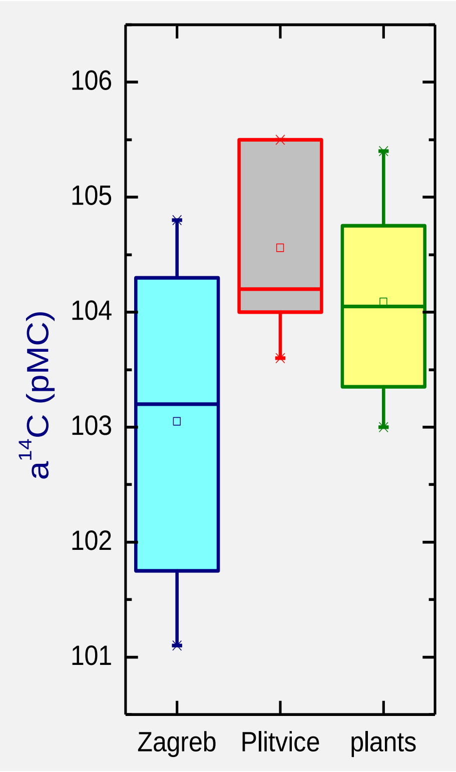
## $^{14}C$ in atmospheric $CO_2$ on the Northern Hemisphere




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/ADSM 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 20$^{th}$ 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 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-$CO_2$ #** | 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

## $^{14}C$ activity of used car tyres

Certain industries use end-of-life-tyres as fuel to reduce the consumption of traditional fuels and also to reduce their energy bills. The cement industry uses more scrap tyre fuels than any other industry.

Tyres provide a heat output equivalent to that of petroleum coke and coal, but also make it possible to reduce fossil $CO_2$ emissions due to combustion significantly because of their biomass fraction of 18.3 % and 29.1 % in passenger car tyres and truck tyres, respectively.

C. Clauzade. Using used tyres as an alternative source of fuel: Reference values and characterisation protocols. Reference document. ALIAPUR, R/D Department. 2009.

Car and truck tyres represent a **heterogeneous material**, and the sampling is a critical step of the complete process of determination of the biogenic fraction in tyres by the $^{14}C$ method.

Radiocarbon laboratory of the RBI: car tyre samples obtained from cement industries. non-homogeneous bulk samples of ~1 kg consisted of several types of material

Pre-treatment: acid-base-acid method usually applied in radiocarbon dating laboratories for removal of impurities

About 90 g of homogenized tyre scraps was carbonized for 15 min at 400 °C followed by 15 min at 600 °C.


An aliquot of 7.5 g (out of ~30 g obtained after the carbonization) was taken for combustion if benzene synthesis followed, while for the $CO_2$-absorption technique an aliquot of ~5 g produced enough $CO_2$ to prepare duplicate $CO_2$-cocktails. Ones the $CO_2$ was obtained, further preparation and measurement procedure was the same as for any other sample.

For AMS, about 14 mg of pre-treated and homogenized tyre scraps was taken for combustion and subsequent graphite synthesis

## $^{14}C$ activities of several car tyre samples obtained by different measurement techniques, as well as the fraction of biogenic component

AMS gave the smallest and LSC-$CO_2$ the highest measurement uncertainties
the AMS subsample (14 mg) may not represent a perfectly homogenized mixture of various types of material in a composed sample which may cause somewhat different $a^{14}C$ value from that obtained by the LSC method.
All techniques gave consistent results.
Generally, all obtained $f_{bio}$ fractions are lower than the global average of biomass fraction of car tyres (18 – 29 %).

| | AMS | | LSC-benzene | | LSC-$CO_2$ | |
|---|---|---|---|---|---|---|
| Sample | $a^{14}C$ (pMC) | $f_{bio}$ (%) | $a^{14}C$ (pMC) | $f_{bio}$ (%) | $a^{14}C$ (pMC) | $f_{bio}$ (%) |
| A | 4.32 ± 0.05 | 4.11 ± 0.05 | | | 8.3 ± 1.5 | 7.9 ± 1.4 |
| B | | | | | 8.7 ± 0.9 | 8.3 ± 0.9 |
| C | | | | | 6.2 ± 1.0 | 5.9 ± 1.0 |
| D | | | 5.8 ± 0.2 | 5.5 ± 0.2 | | |
| E | | | | | 6.0 ± 0.9 | 5.7 ± 0.9 |
| F | | | 4.3 ± 0.1 | 4.1 ± 0.2 | | |

# 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) 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

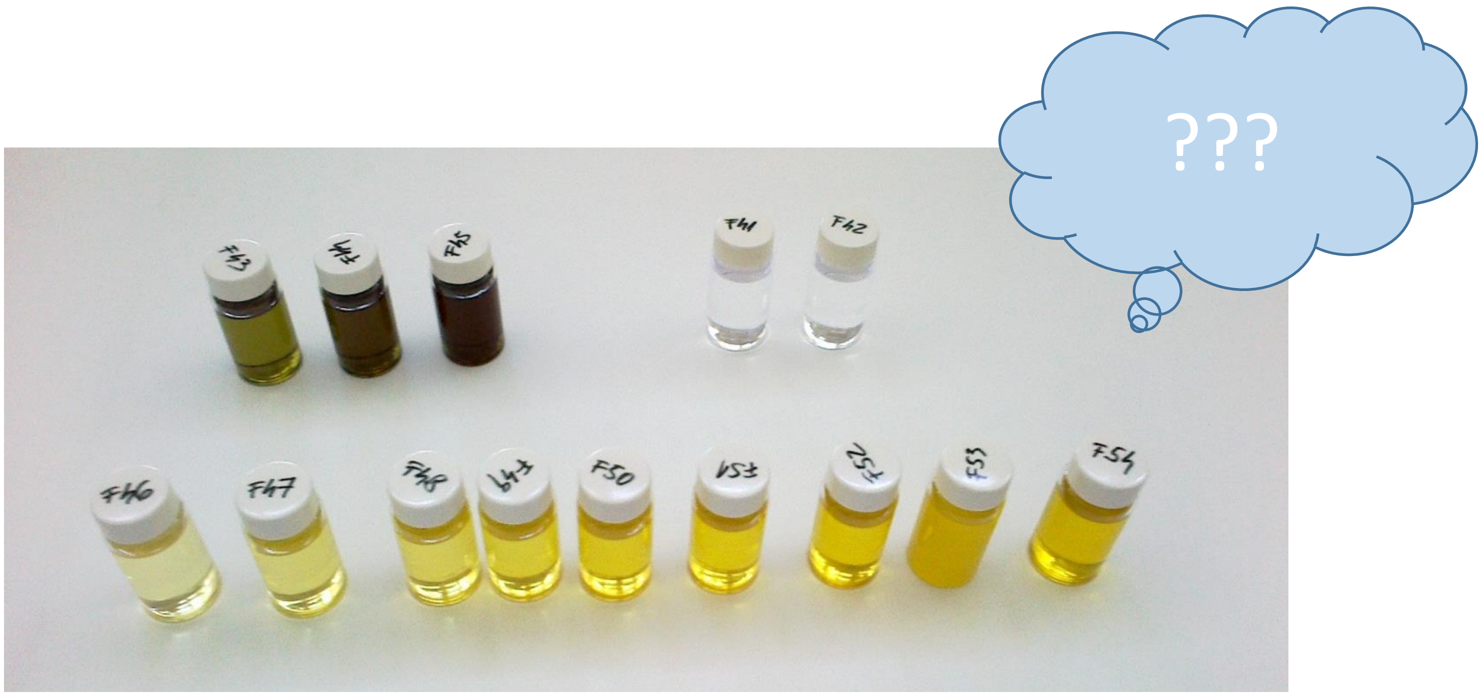
A large variety of mixtures
fossil matrix + biogenic blend

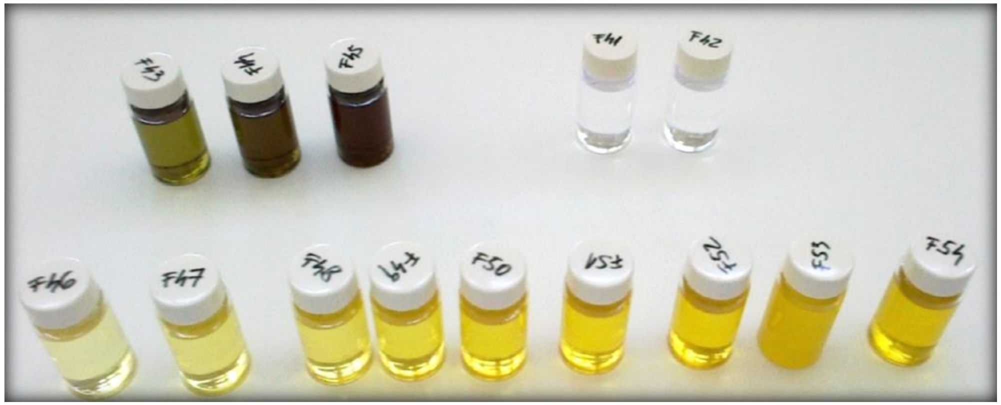
Various colors of fuels cause different counting properties (SQP - quenching, counting efficiency)

Various methods have been suggested to overcome this problem

- Different quenching curves for various combinations of the fossil matrix and biogenic blends by using $^{14}C$ spikes
- Various methods of decolorization - bleaching
- Different evaluation techniques of the LSC spectra for different combinations f.f. + b.b.

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



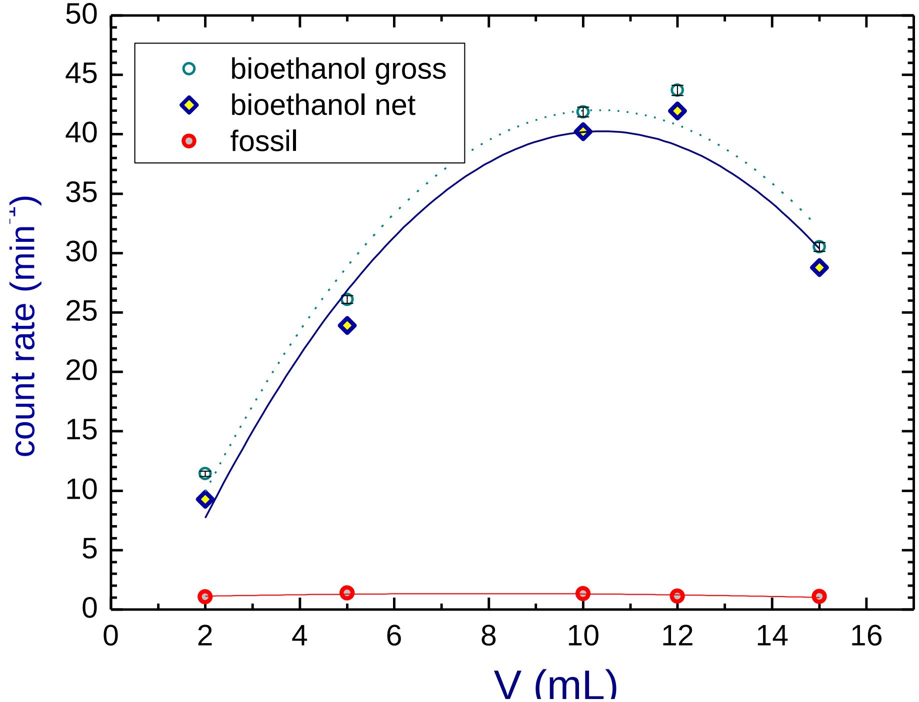


## Idea!

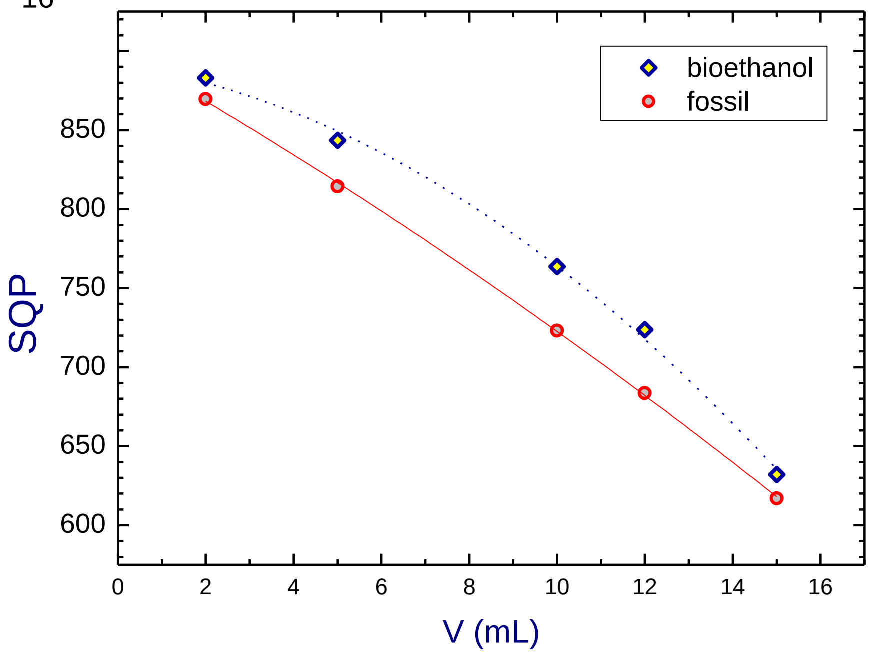
Convert the problem/main drawback to the advantage - **quenching parameter of various samples use as the calibration parameter**!

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

# Determine the ratio of the liquid fuel and scintillator

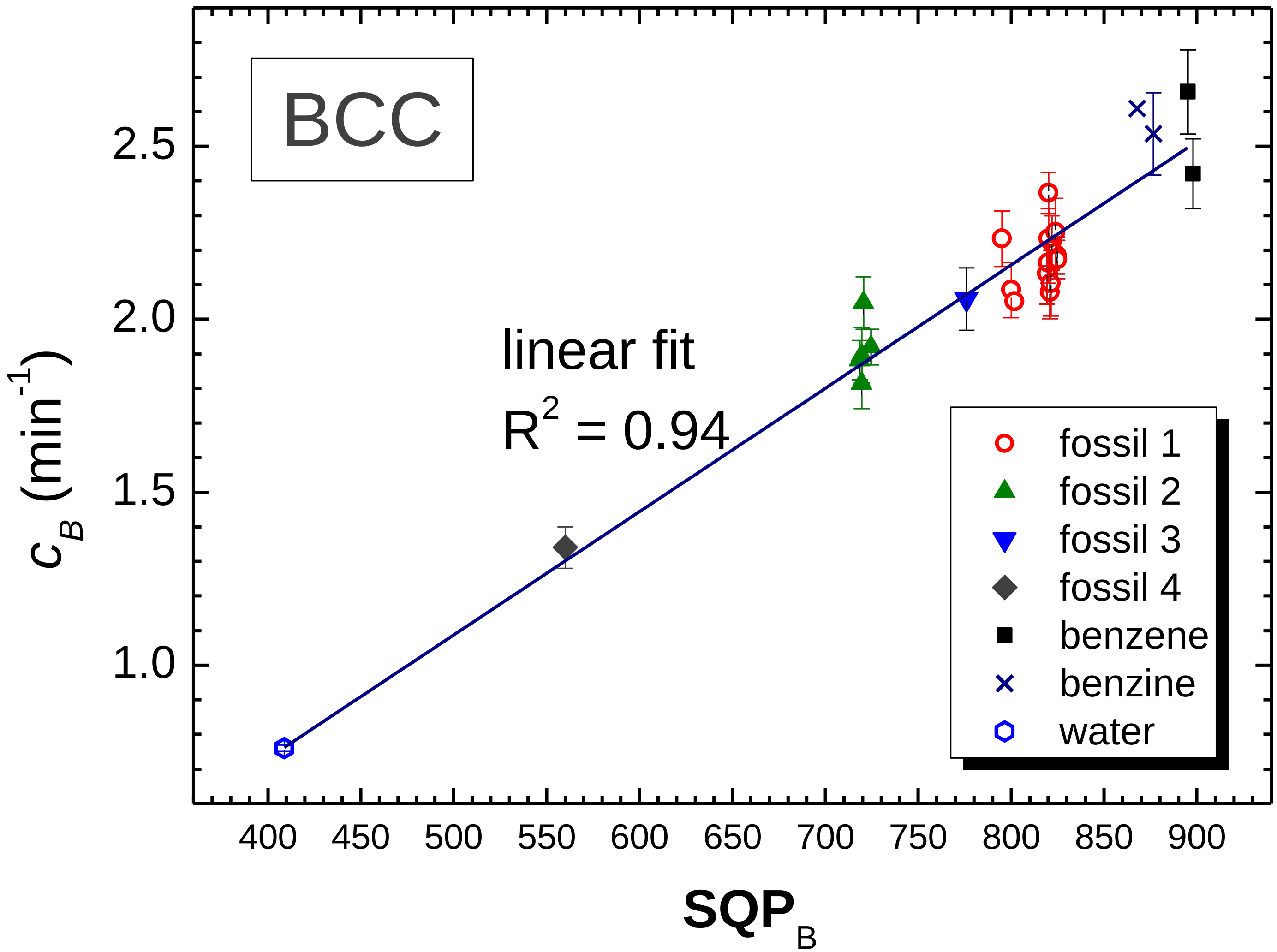



UltimaGold F
20 mL  glass vials
cocktail volume 20 mL
LSC Quantulus
ROI 145 – 570 ch

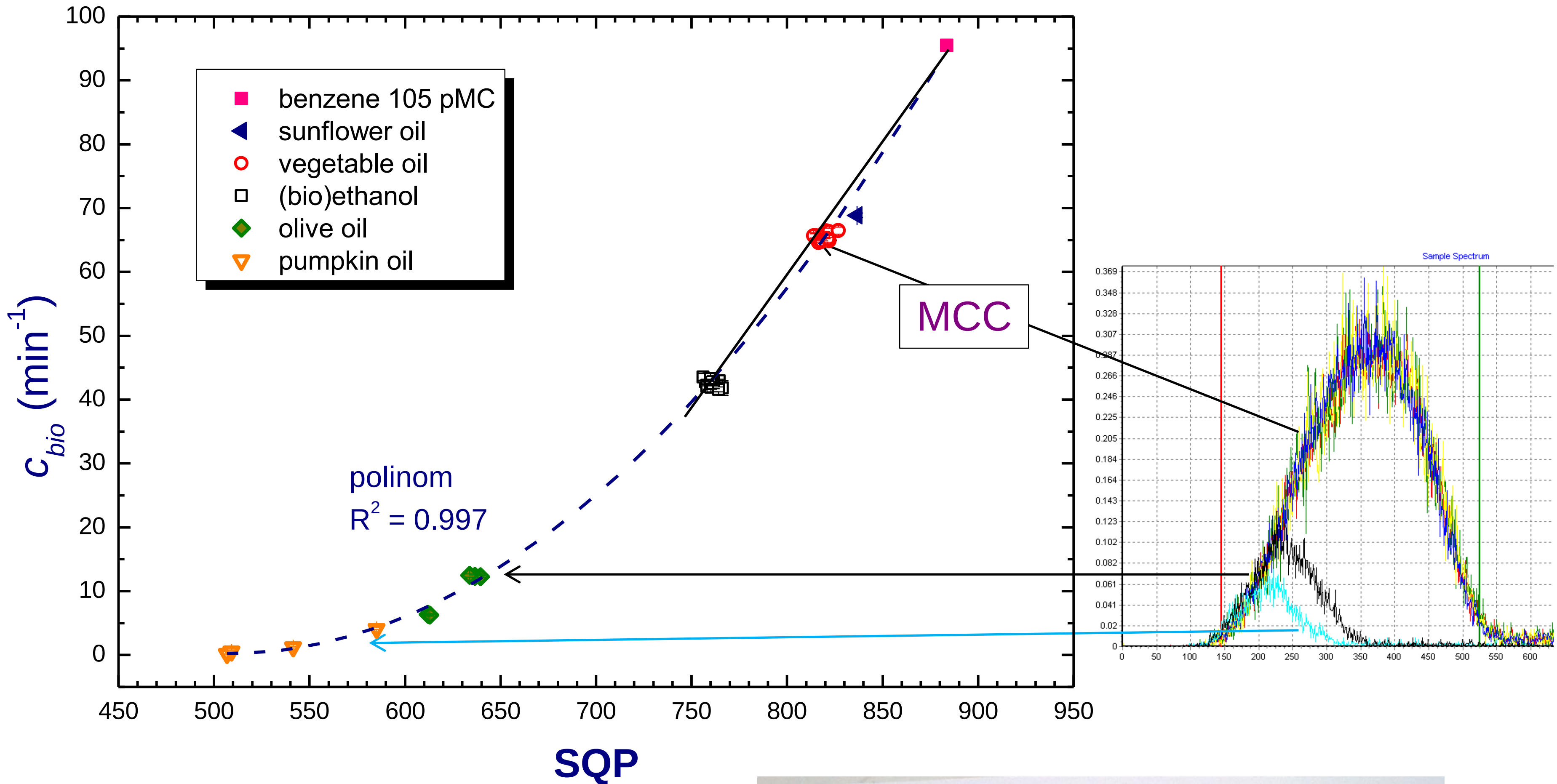


# Background calibration curve (BCC)

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 channels

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

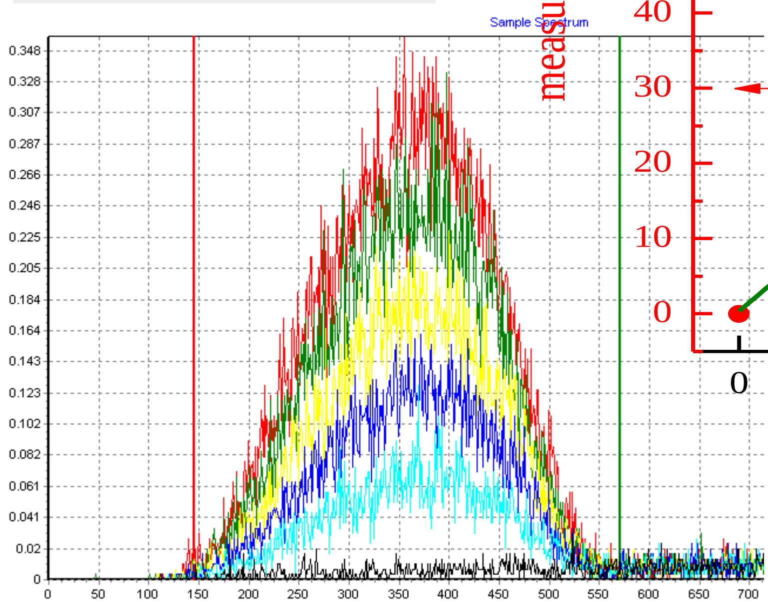
In all cases, the calculated biogenic fraction agreed well with the nominal fraction.

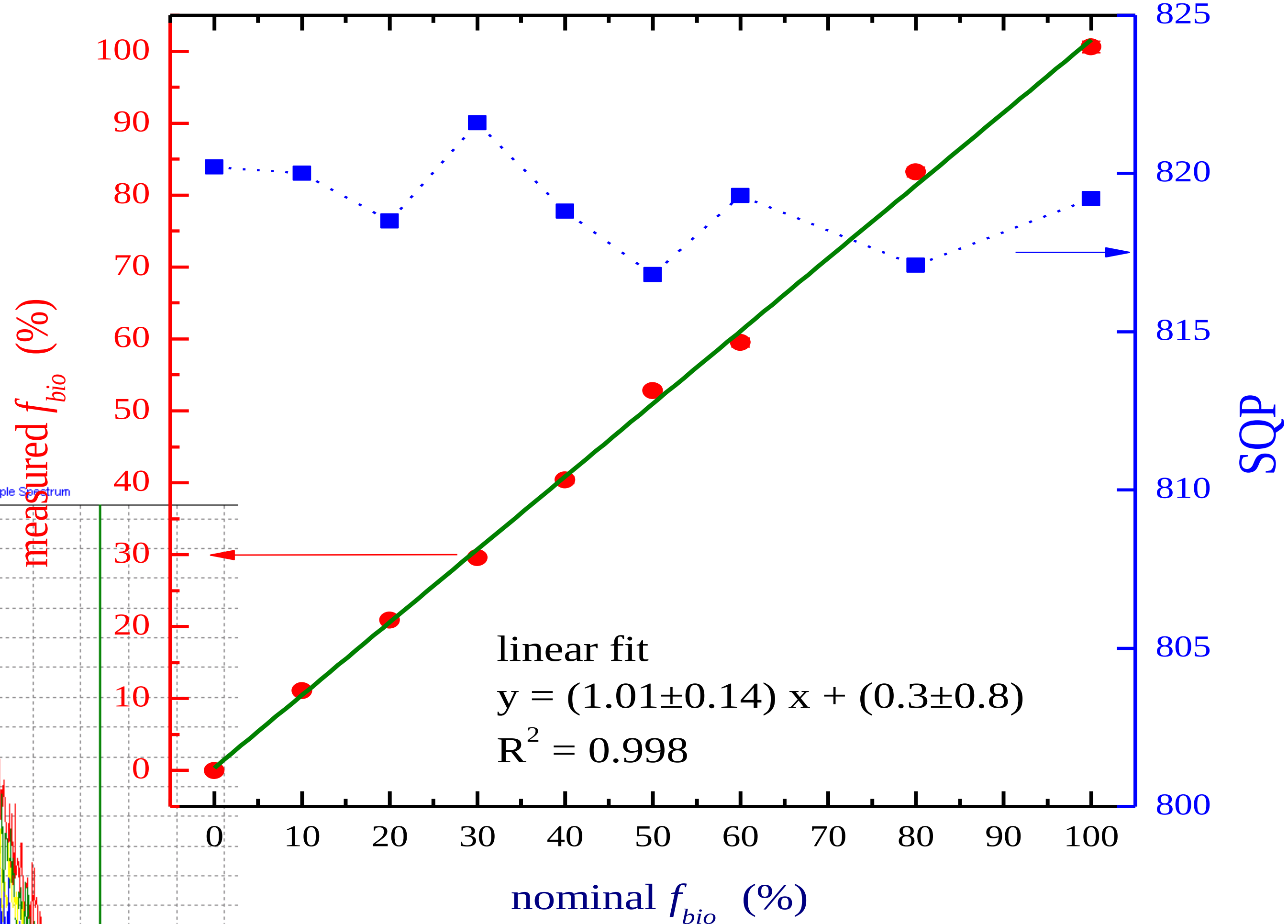
- mixtures of two different biogenic liquids (vegetable oil and bioethanol, vegetable oil and olive oil) having different SQP

## 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.

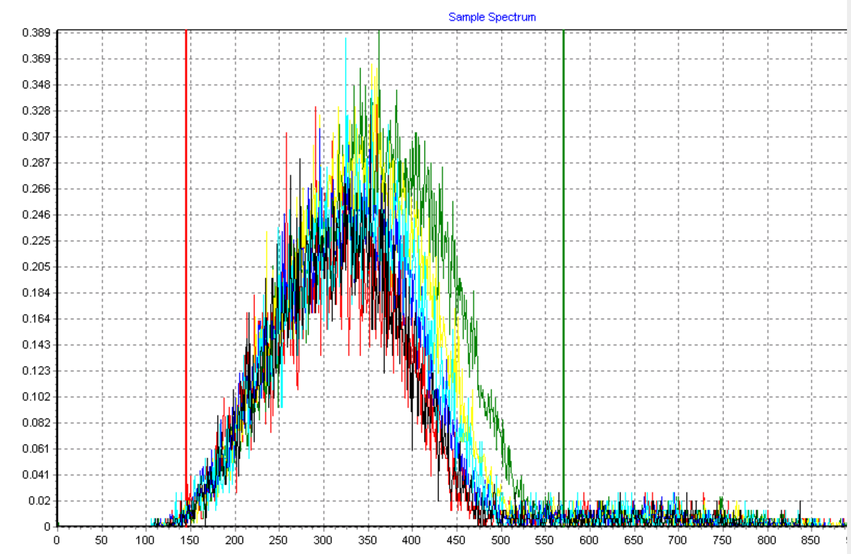
100% vegetable oil
80% oil + 20% fossil
60% oil + 40% fos..
40% oil + 60% fos.
20% oil + 80% fos.
100% fossil

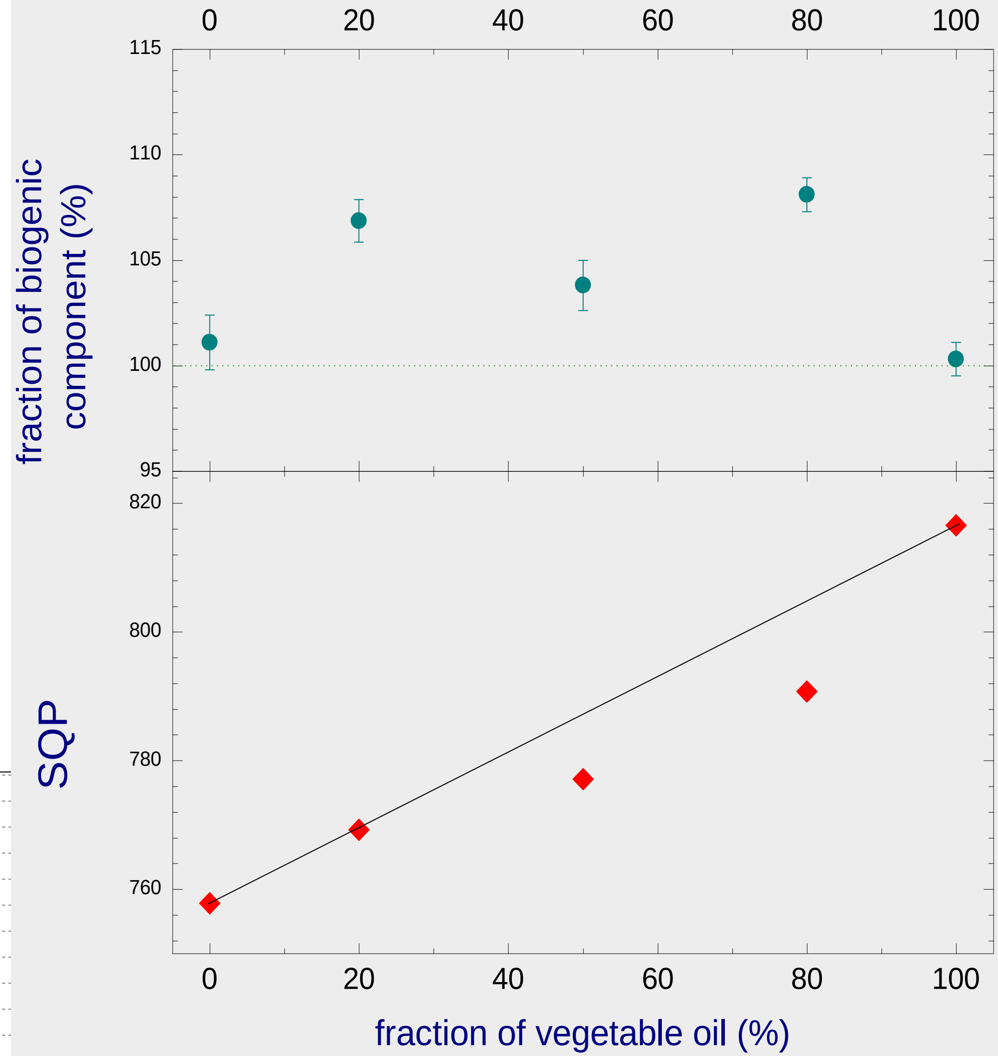


# Mixtures of two 100%-biogenic liquids with different SQP:
vegetable oil and (bio)ethanol

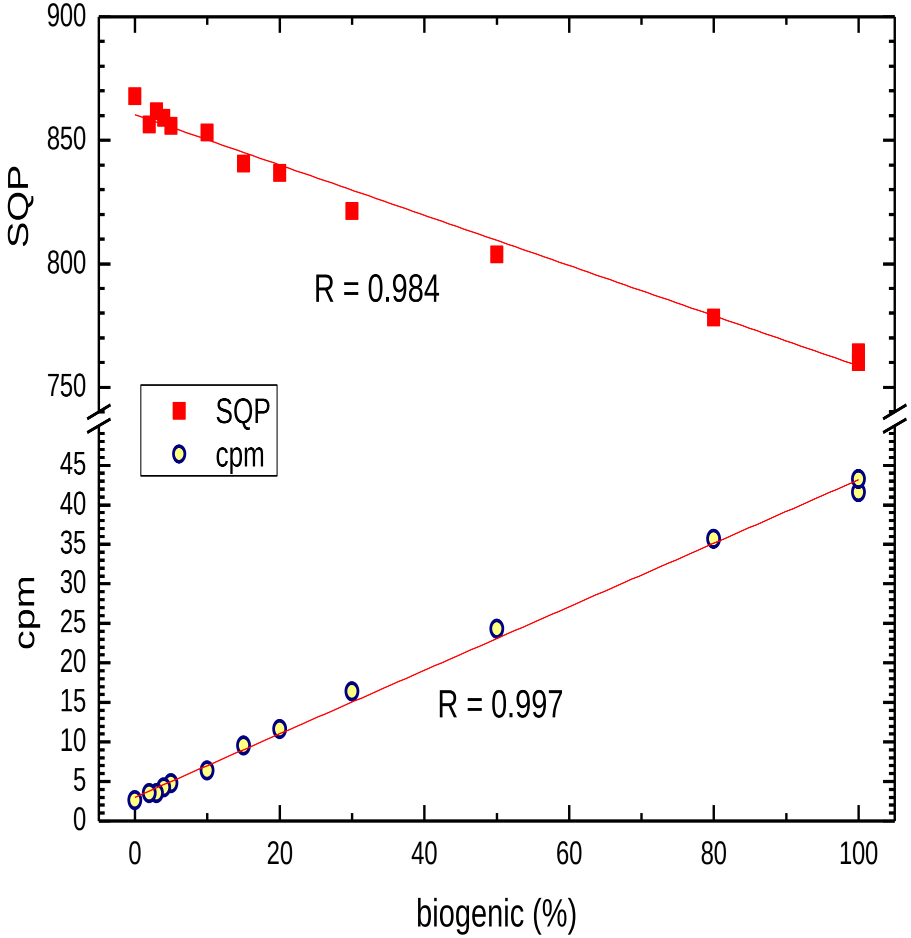
100% vegetable oil
80% oil + 20% bioeth.
50% oil + 50% bioeth.
20% oil + 80% bioeth.
100% bioeth.
100% bioeth. (earlier pr.).



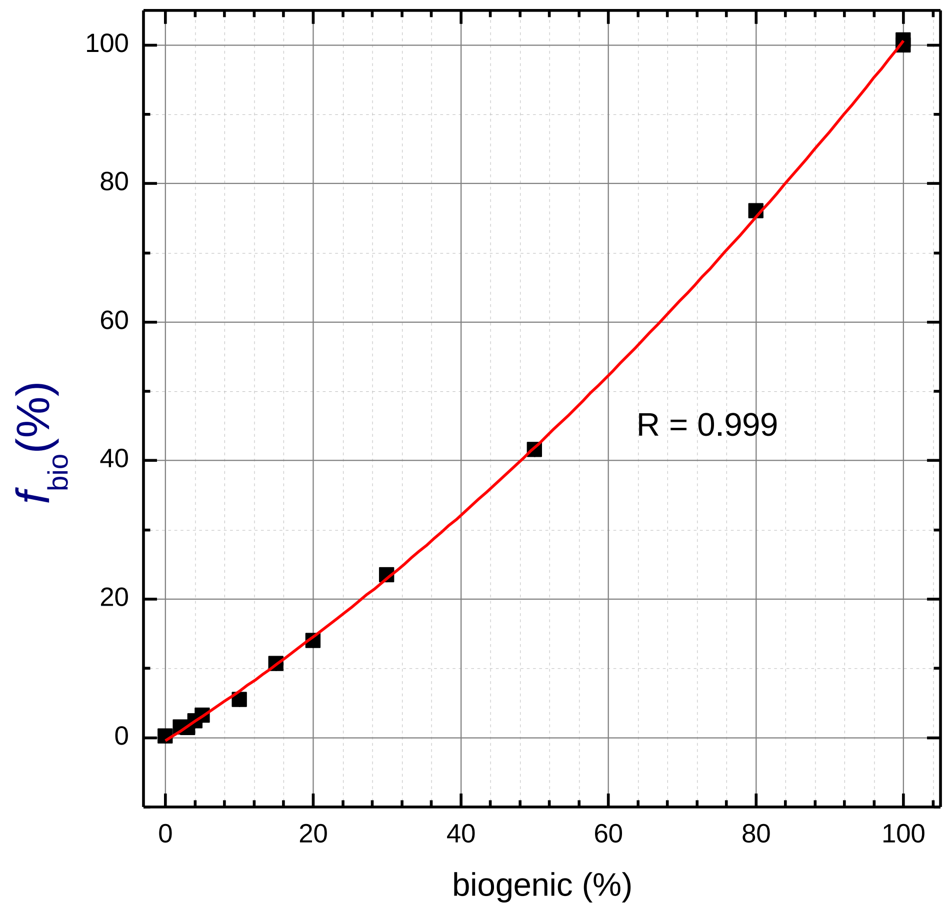




SQP values and count rates changed continuously as the mixture composition changed.
The measured biogenic fraction ranged from 97 % to >100 %. The results indicate: the method should be improved, specially for low SQP.

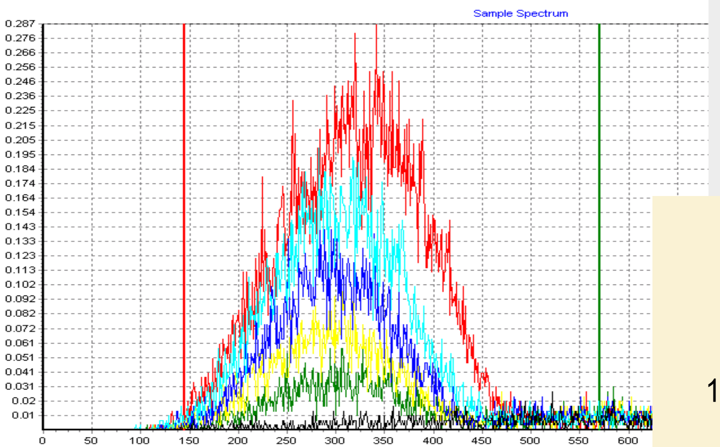
# Bioethanol and benzine p.a. mixtures (different SQP)



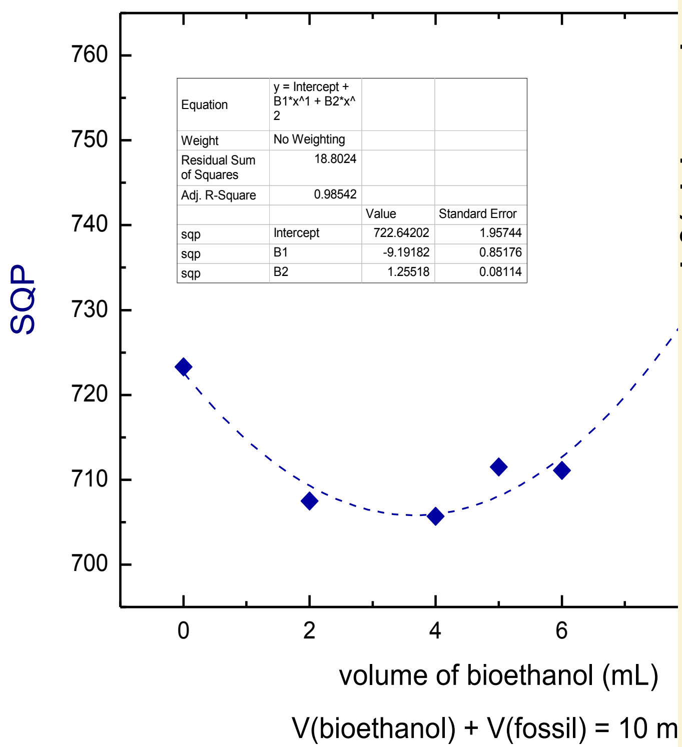

benzine + bioethanol



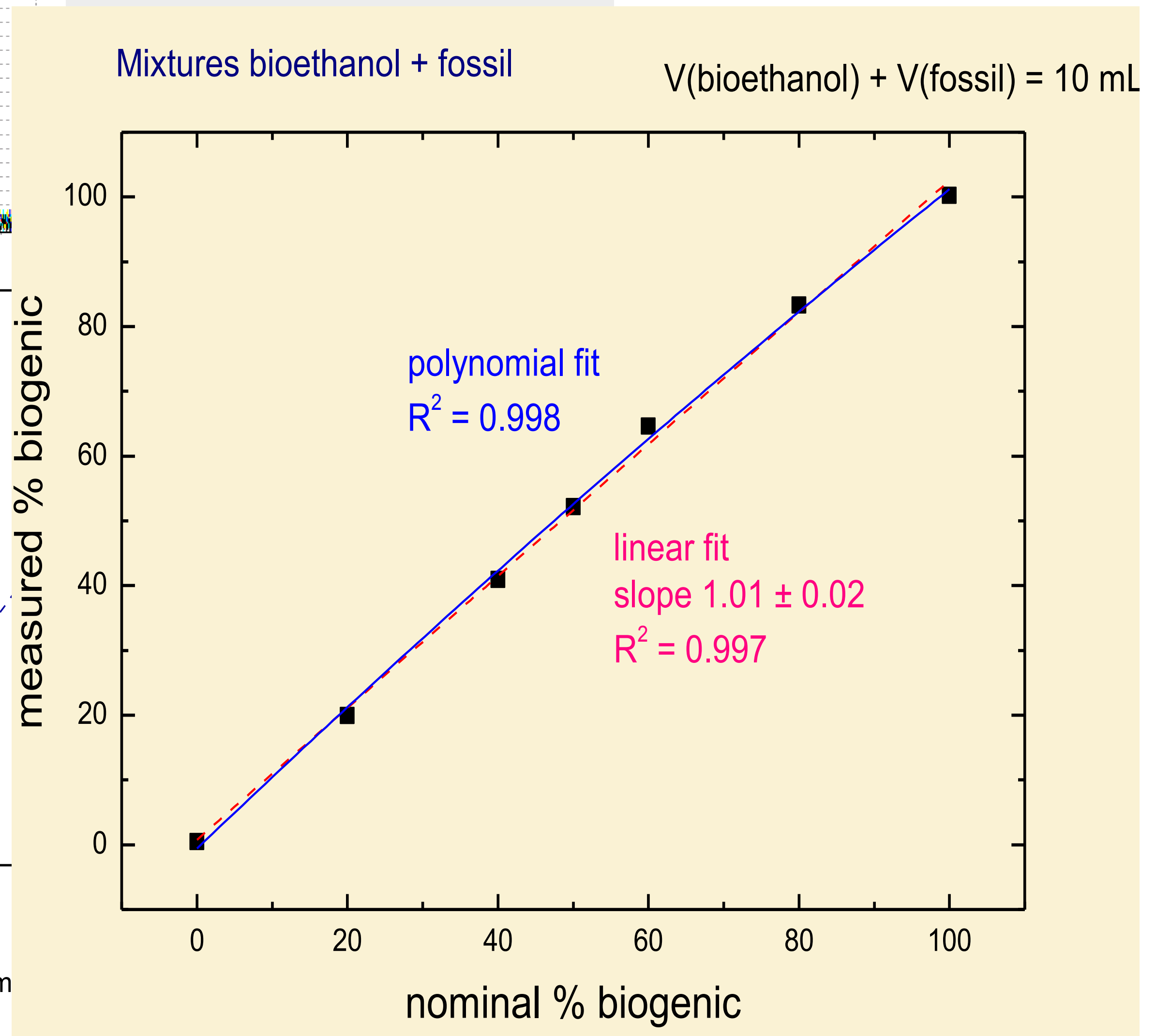
# Bioethanol and fossil fuel mixtures of different SQP



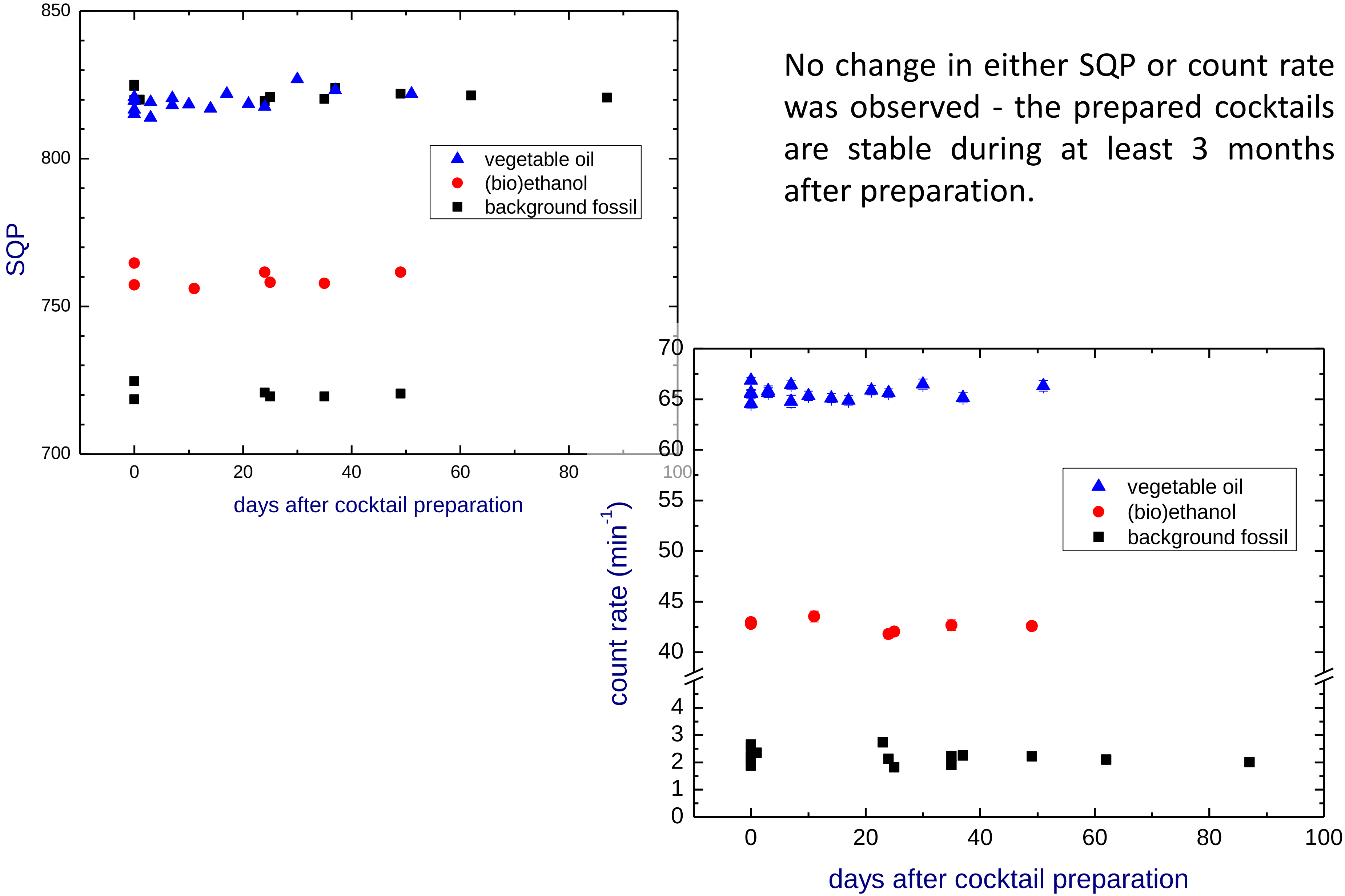

100% bioethanol
80% bioeth. + 20% fossil
60% bioeth. + 40% fos.




| | | | |
|---|---|---|---|
| Equation | y = Intercept + B1*x^1 + B2*x^2 | | |
| Weight | No Weighting | | |
| Residual Sum of Squares | 18.8024 | | |
| Adj. R-Square | 0.98542 | | |
| | | Value | Standard Error |
| sqp | Intercept | 722.64202 | 1.95744 |
| sqp | B1 | -9.19182 | 0.85176 |
| sqp | B2 | 1.25518 | 0.08114 |



# 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.

## Intercomparison

The obtained results were in good agreement with those obtained by different evaluation technique, both for the benzine 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** | benzine | 841.6 | 0.1 ± 0.1 (< 0.5) | 838.9 | 0.26 ± 0.19 (< 0.57) |
| **7** | benzine | 790.7 | 3.1 ± 0.2 | 790.6 | 5.22 ± 0.57 |
| **8** | benzine | 823.4 | 3.4 ± 0.2 | 828.4 | 4.44 ± 0.43 |

# Conclusion

Determination of the biogenic fraction in various materials 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 lower the increase of atmospheric $CO_2$ conc. of fossil origin.

The $^{14}C$ method is a very powerful method for determination of the biogenic fraction.

Different measurement techniques (developed for the radiocarbon dating application) can be successfully applied also for the purpose of biogenic fraction determination. Methods differ in complexity and the required mass of a sample, precision and costs.

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 method still needs some improvements, especially for highly quenched liquids, but it gives comparable results with other data evaluation techniques.