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Status report on small sample measurements with ECHoMICADAS AMS facility: 6 years of data processing and statistical results

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Introduction : In 2015, a new AMS facility, the ECHOMICADAS was installed in the Laboratoire des Sciences du Climat et de l'Environnement (LSCE). Equipped with a hybrid source, it allows the analysis of solid or gas samples for ¹⁴C measurement. Below are presented the different equipments in peripheric of the GIS (Gas Interface System), the model used to take into account the different sample contaminations, the data processing and also the results we get on standards and blanks for different measurement protocols.

Sample preparation

Sampling :

- 2 weigh stations (2 µg of precision)
- 1 automatic weigh station (EPATANT)
- ESI microdrill sampling station

Samples between 10 and 300µgC can be measured

Chemical treatment depending on sample nature:

- Wood, charcoal, vegetal (ABA treatment)
- Cellulose (bleaching treatment)
- Carbonate HNO₃ pre-treatment (on-line with the CHS2)
- Bones, (ninhydrin or collagen extraction Longin)
- Apatite
- Soil, sediment TOC (HCl treatment)
- Pollen
- DIC and DOC in water

For one sample type, different protocol possibilities :

The choice will be done taking into account the following parameters :

- Quantity of material, and carbon concentration
- Expected age
- Expected contaminant which will be added during the chemical process and the measurement

Knowing these informations (even approximately) allows to estimate, before the sample preparation, the uncertainty of the results, based on the statistic of the analysis parameters such as current, time measurement, cross and constant contamination.

Equipment description

BCA line for carbonate samples



Microline for organic matter



EDM line for water sample



CO₂ extraction line and ampoule sealing :

- lines under vacuum :
 - BCA line for carbonate samples
 - Microline for organic matter
 - Manual line for all type of sample
- lines under Helium flux and vacuum :
 - EDM line for water sample
 - active line for ¹⁴C active samples

Samples containing organic matter, with or without chemistry : Soil, collagen, charcoal, wood, cellulose, bone, pollen, vegetal, excrement...

Carbonate samples without chemistry : Biocarbonate, speleothem, stromatolith

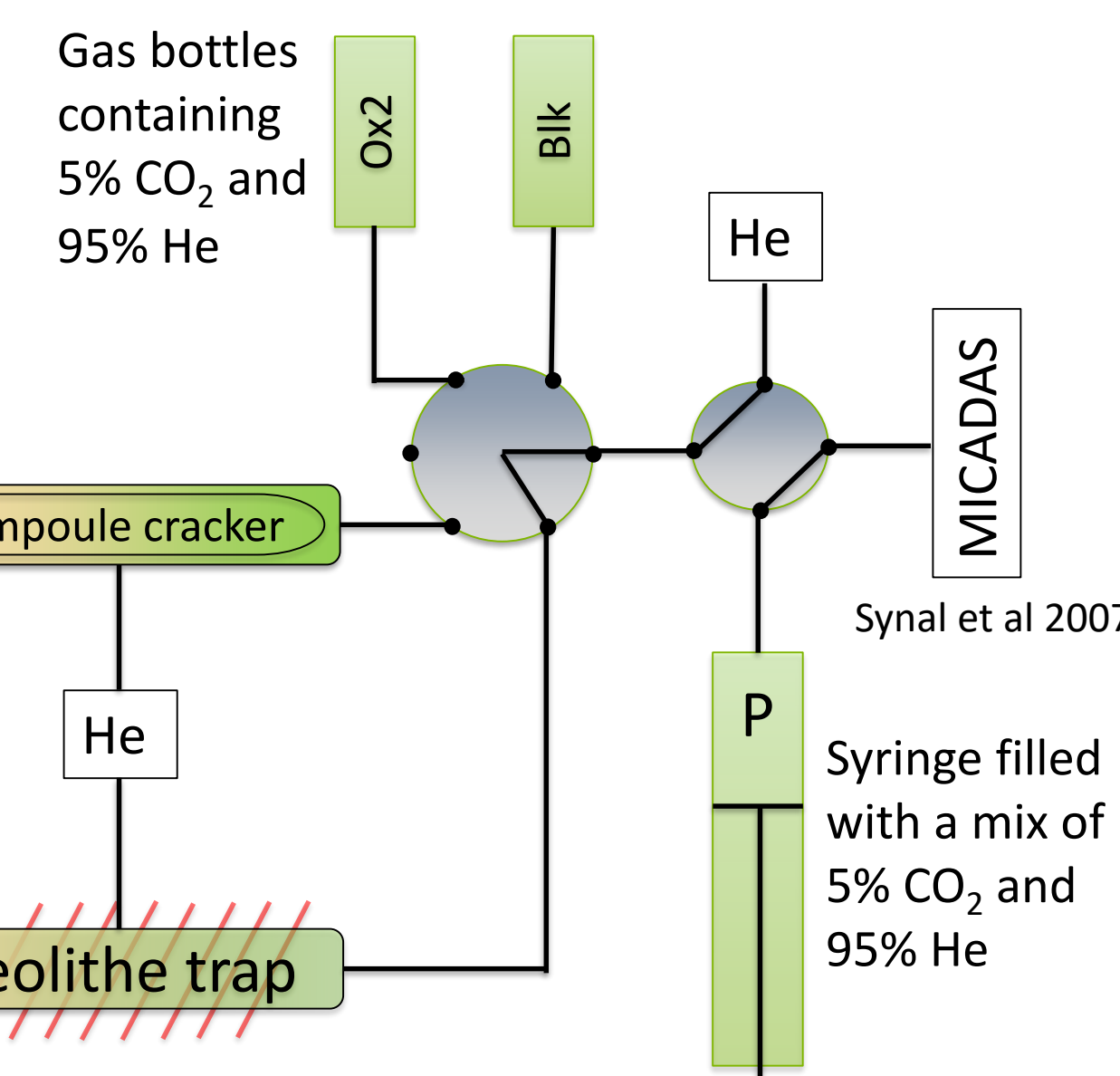
EA for direct combustion of organic matter samples (80 positions)

CO₂ extraction under helium flux

CHS2 for HNO₃ and/or H₃PO₄ acid attack for carbonate or DIC in water (64 positions)

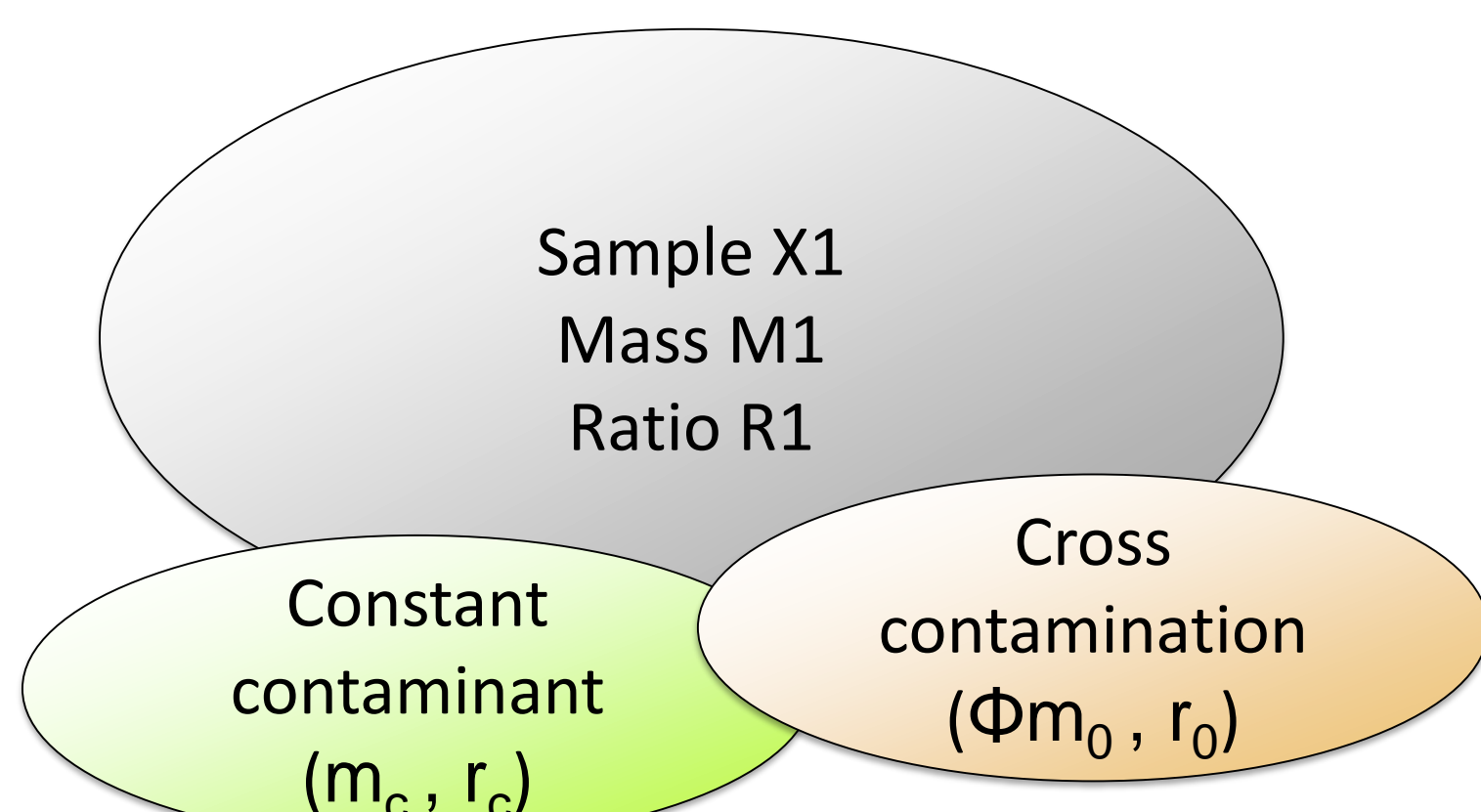
GIS (Gas Interface System) and its peripherals

Wacker et al 2013



The quantity of sample is estimated by measuring the pressure of CO₂ obtained into the syringe (M<100µgC)

Contaminants modelling



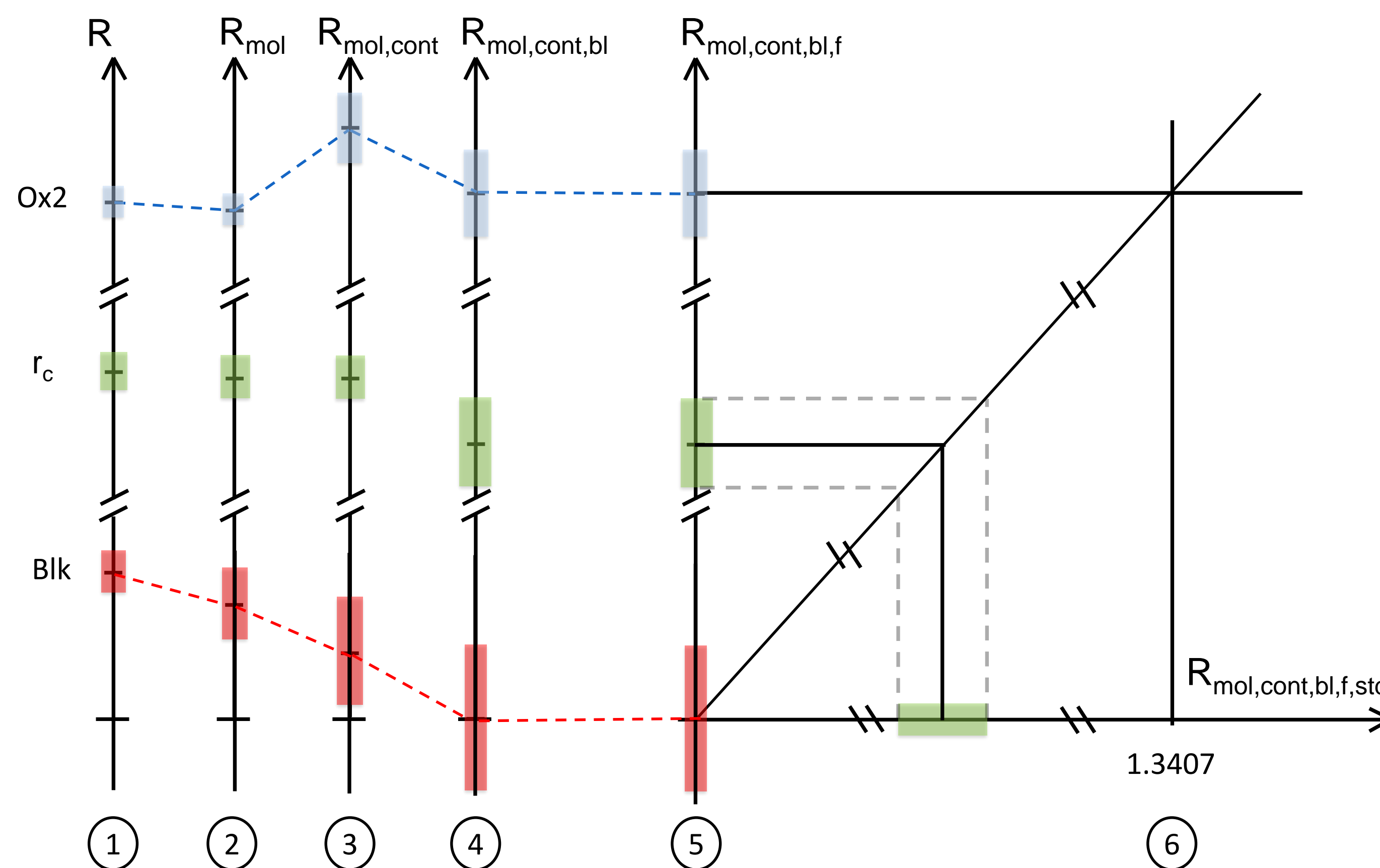
- Measured mass : m₁ = M₁ + m_c + Φm₀
- Measured ratio : r₁

-Weighed average ratio, where r₁ is the measured ratio:
m₁ r₁ = M₁ R₁ + m_c r_c + Φm₀ r₀

$$R_1 = \frac{m_1 r_1 - m_c r_c - \Phi m_0 r_0}{m_1 - m_c - \Phi m_0} \quad (1)$$

Salazar et al 2015

Data processing



Step 1 : raw ratio ¹⁴C/¹²C. The uncertainty is linked to the ¹⁴C counting.

Step 2 : the molecular current ¹³CH correction impacts more old sample than young one.

Step 3 : this correction is based on the formula (1). It impacts more the ratio when this one is far from the contaminant ratio and when the sample mass is closed to the contaminant. For ratios closed to the contaminant, the correction has no effect.

Step 4 : the same blank ratio is subtracted to all ratios. This subtraction has a greater impact on old samples. Generally only big blank (>80µgC) are taken into account.

Step 5 : the ratio is corrected from the mass fractionation. This fractionation is calculated with the ¹³C/¹²C of the sample compared to the ¹³C/¹²C of the standard.

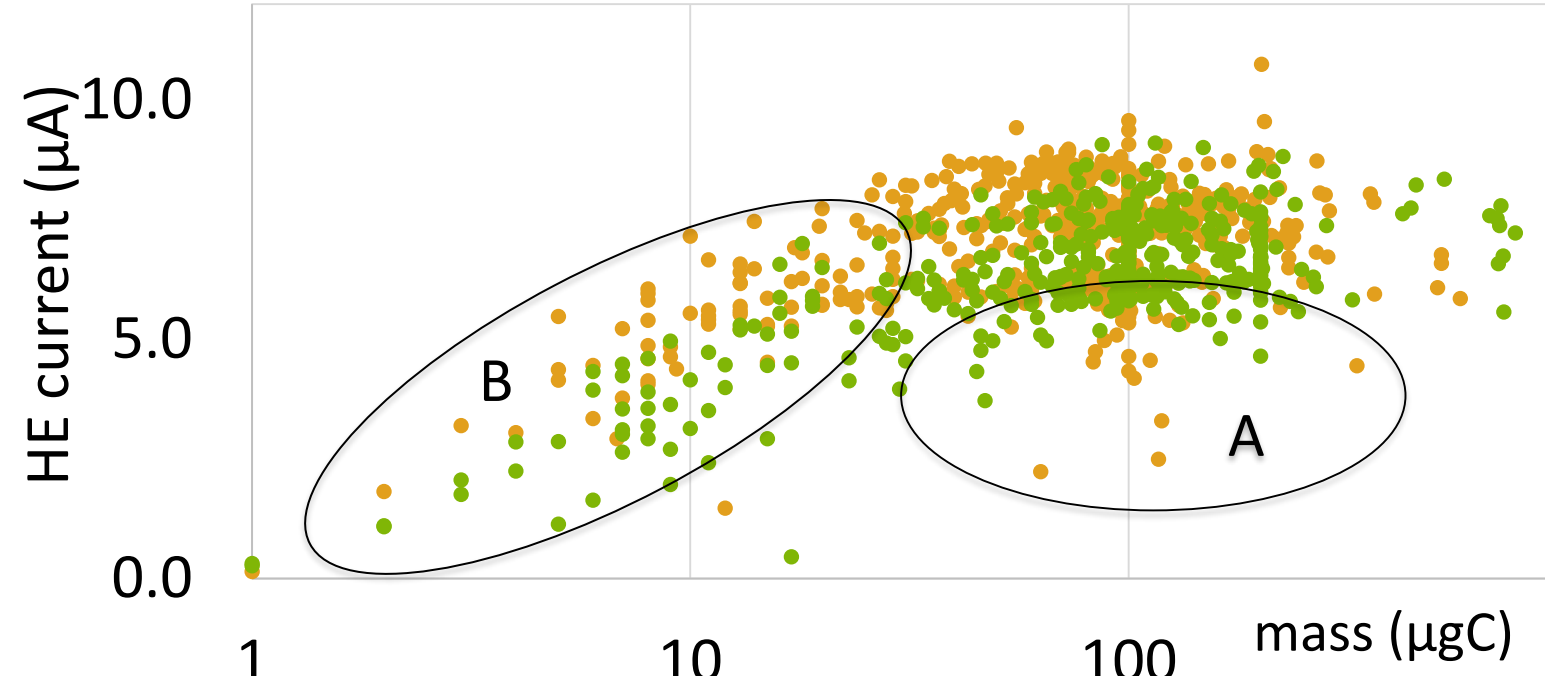
Step 6 : Weighed average of the ox2 ratio allows to normalize all ratio values. Generally, only « big » ox2 are taken (>80µgC)

Statistics on analytical parameters

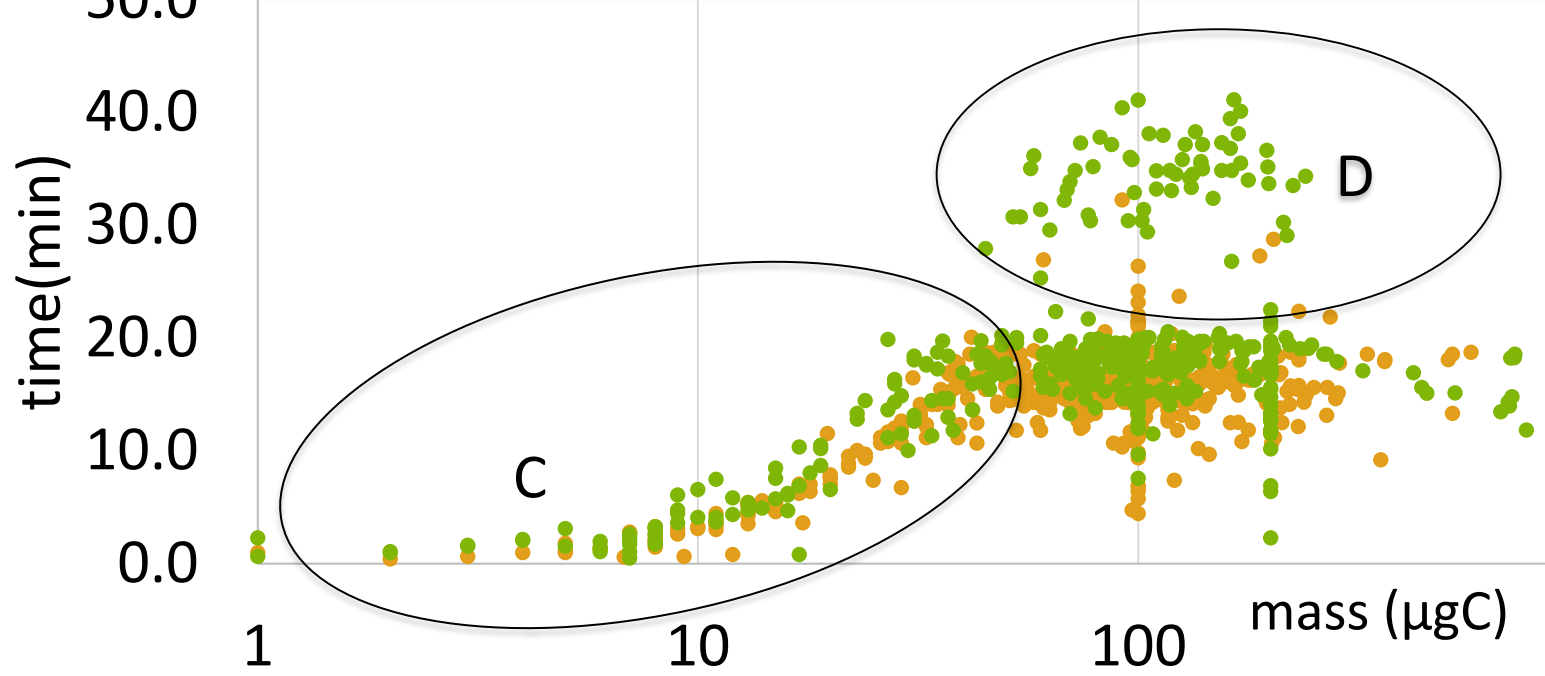
Current and analysis time are two key parameters directly linked to the ¹⁴C counting and consequently to the precision of the measurement.

- . > 20µgC : > 5µA and analysis time > 5 min => comfortable for precision.
- . Zone A : low current due to CO₂ impurities
- . Zone B : small sample size -> bad CO₂/He ratio
- . Zone C : analysis time proportional to sample mass.
- . Zone D : 2 targets on a same gas -> extra analysis time

¹²C HE-current vs mass

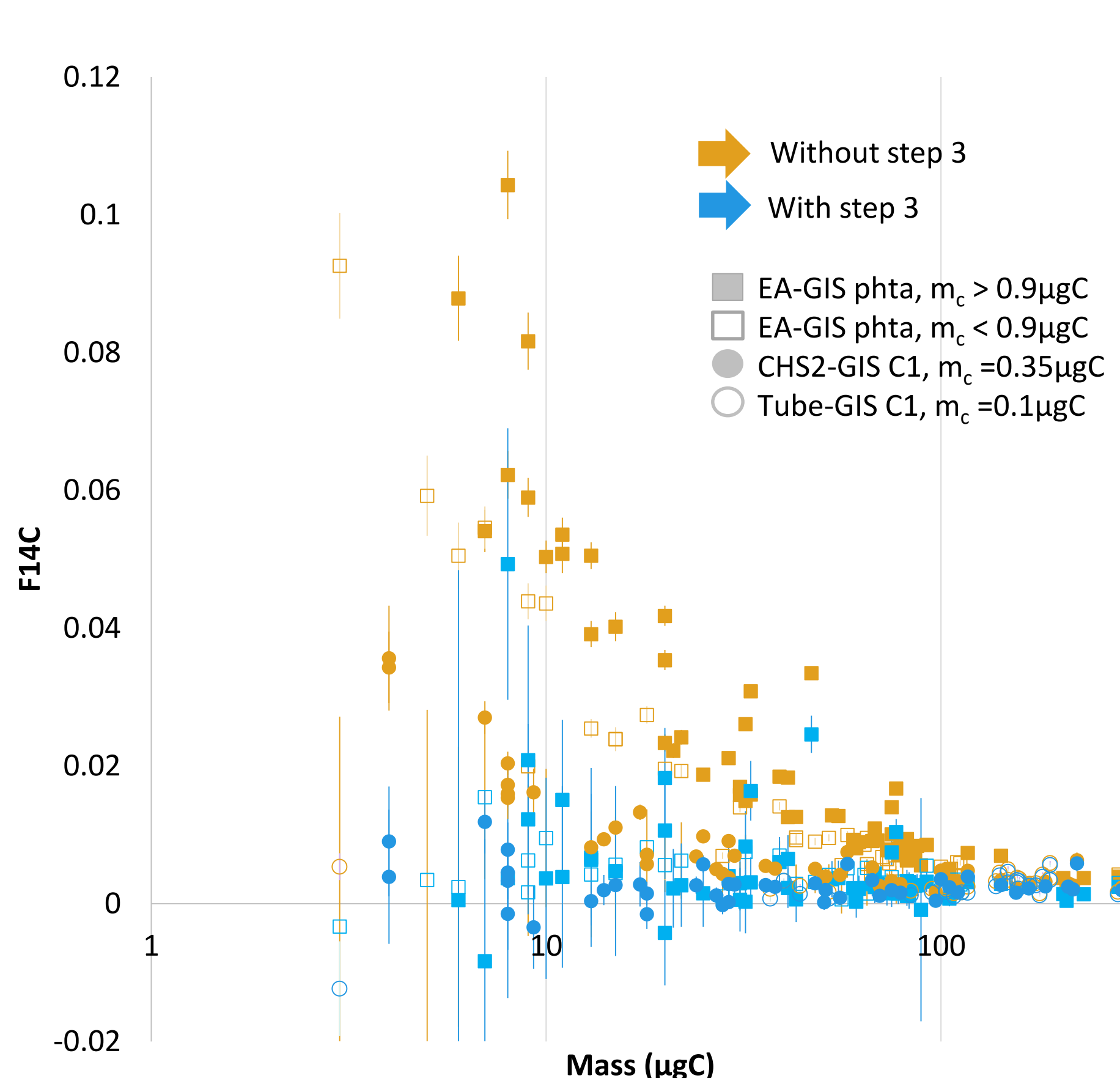


Analysis time vs mass

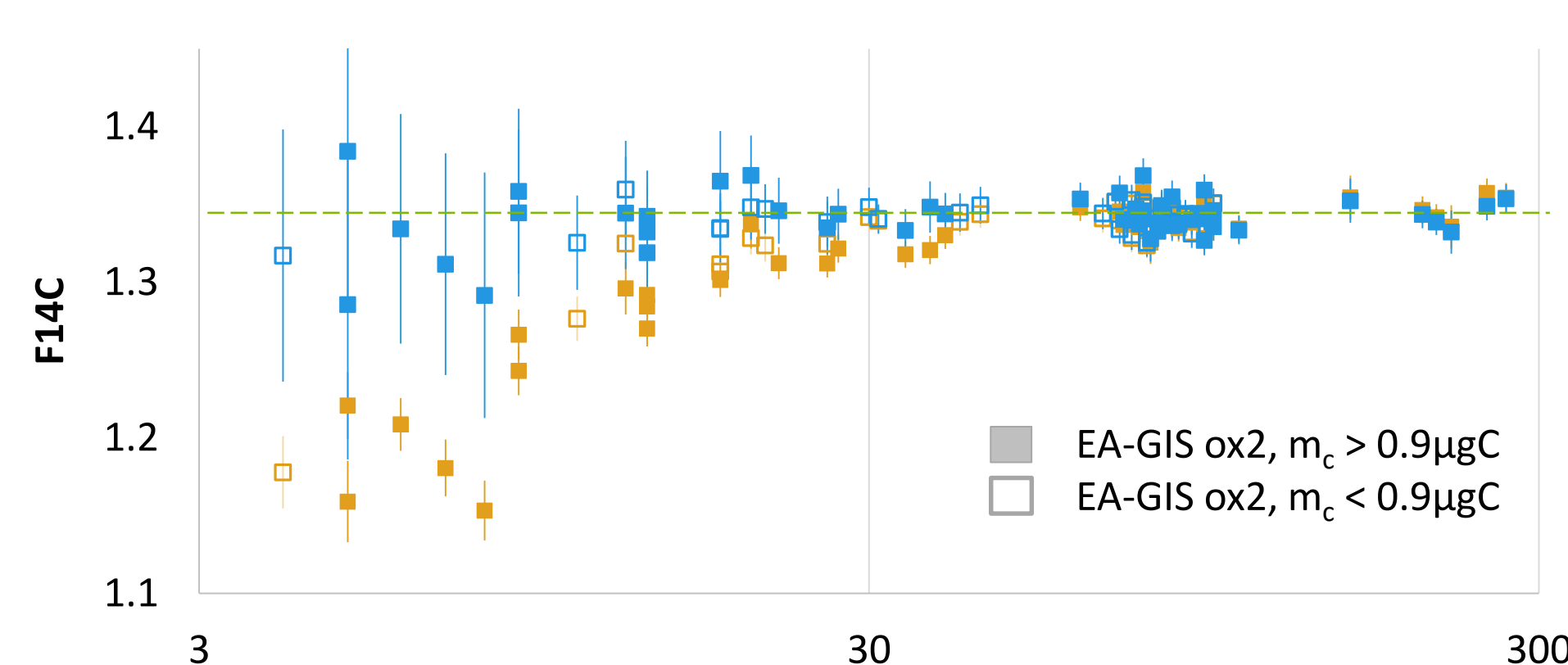


Some blank and standard results

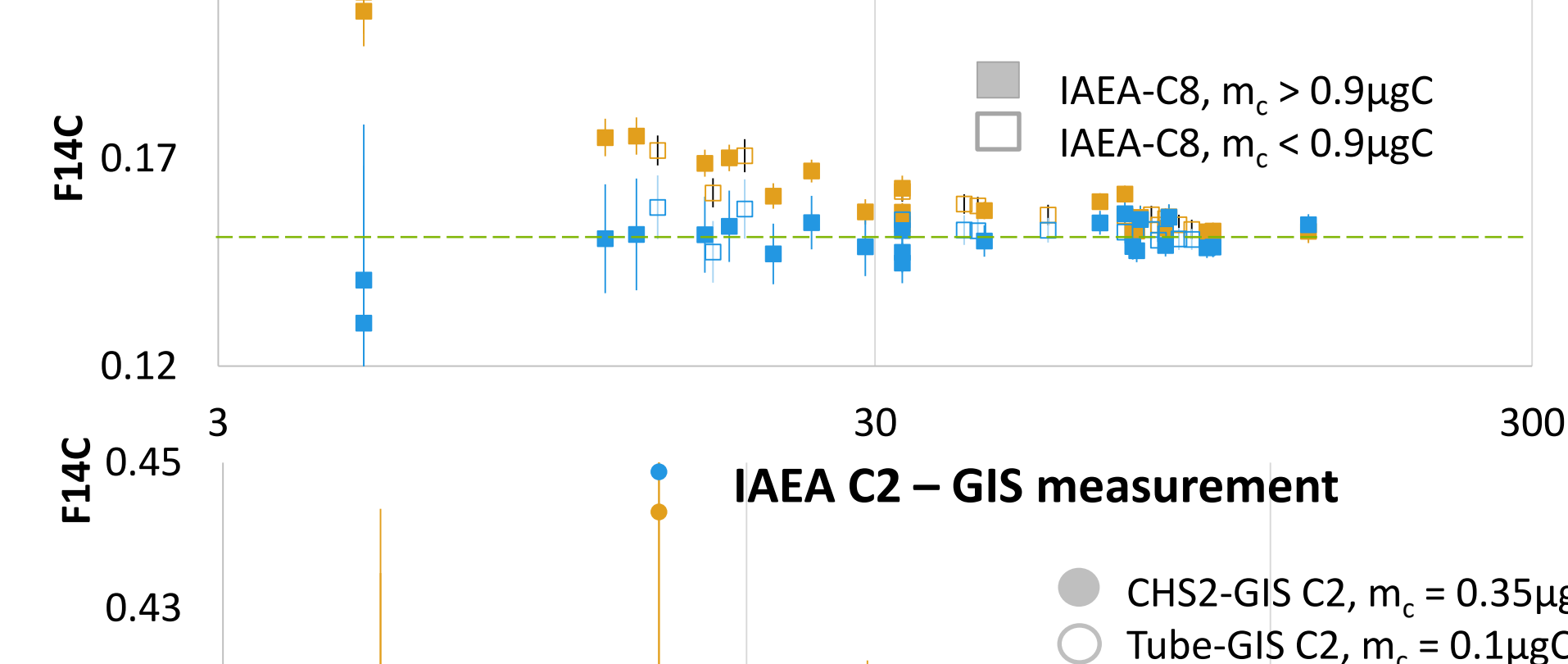
GIS Blank 2021 and 2022



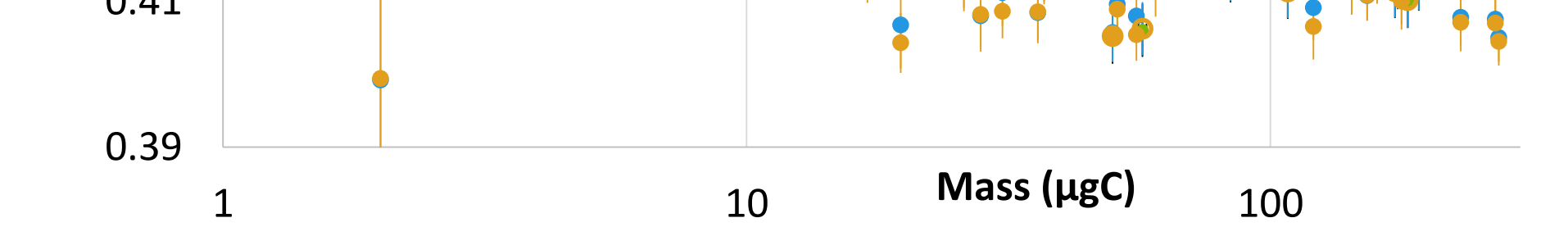
Oxa 2 - EA-GIS measurement



IAEA C8 - EA-GIS measurement



IAEA C2 - GIS measurement



Conclusion : Since 2016, more than 5600 gas targets have been analysed with the GIS. Measurements of blanks and standards allow to characterize the contamination level for each type of sample and each chemical process. The EA-GIS constant contamination is regularly evaluated and varies between 0.9 and 1.4µgC with a F¹⁴C of 0.4 – 0.8. For the CHS2-GIS, R_c is between 0.25 and 0.4µgC with a F¹⁴C around 0.4. For tube cracker system, the contaminant is even lower (less than 0.15µgC, and F¹⁴C around 0.6).

This makes it possible to estimate the age uncertainty even before we consider the sample for chemistry. It is useful to take decisions on amount of material for the sampling and protocol to be applied, regarding the preciosity of some samples and the analytical feasibility.

Acknowledgments :

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