Training event "Atmospheric standardized observations: Methods and maintenance in observatories – In-Situ." CRDS

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Ministero dell'Università e della Ricerca

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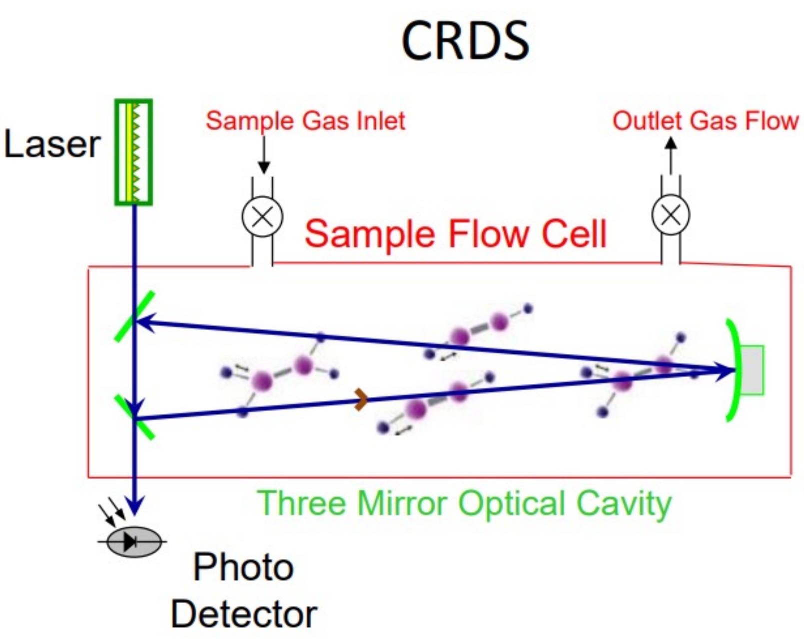
Cavity Ring Down Spectroscopy:

Technology and Applications

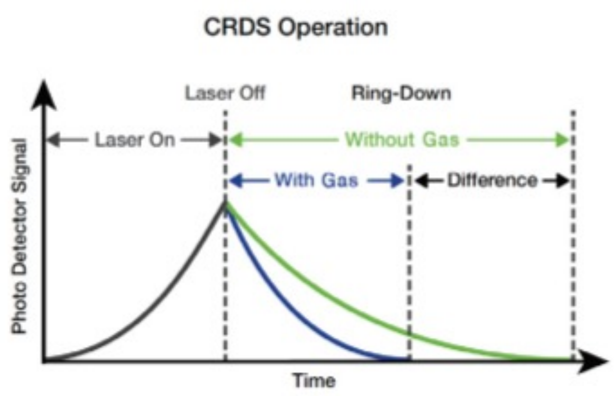
CRDS Technology

The strength of the light absorption (Absorbance) is directly proportional to the concentration of a molecule in a sample and to the distance that light travels through the sample, the pathlength. In CRDS the path is effectively increased by multiple reflections within a cavity.



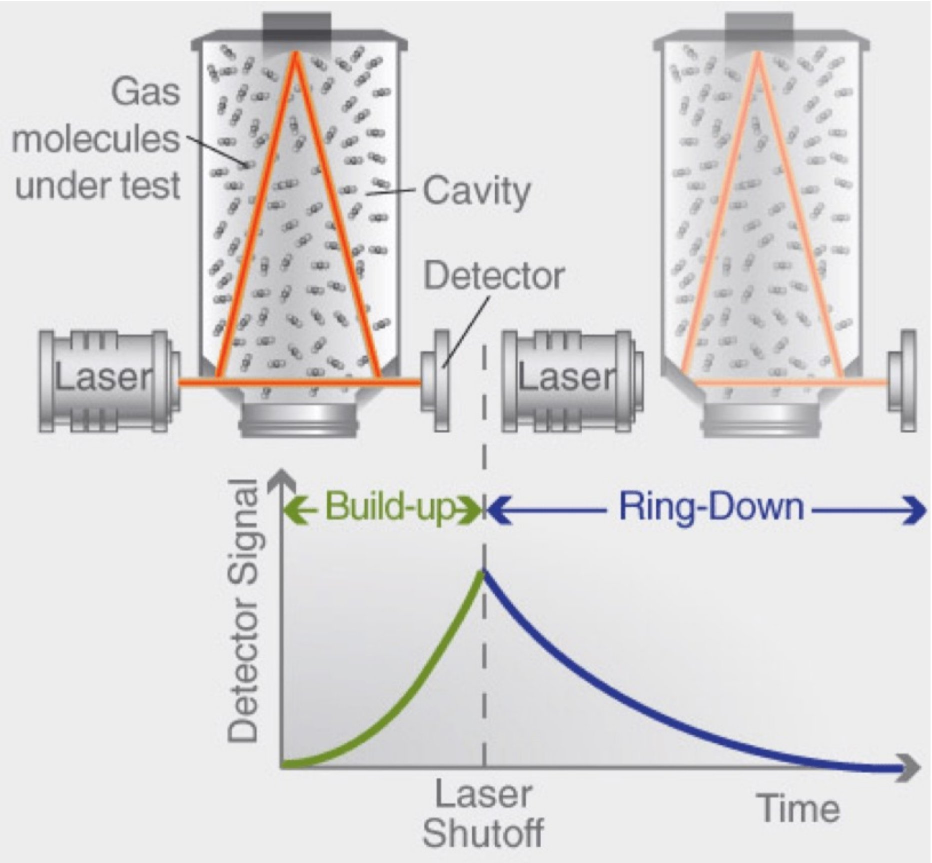
Assuming Beer-Lambert law behaviour, the decay of light within an empty cavity (ring down) occurs exponentially with time and is described by:

$$I_t = I_0 e^{-t/\tau}$$



- I_0: light intensity before the cavity
- I_t : the light intensity after the cavity
- **t**: residence time of the light within the cavity
- **τ**: ring-down time (RDT) of the cavity i.e. the time it takes for the light to decay to 1/e of its initial intensity

Picarro istruments use CRDS technology

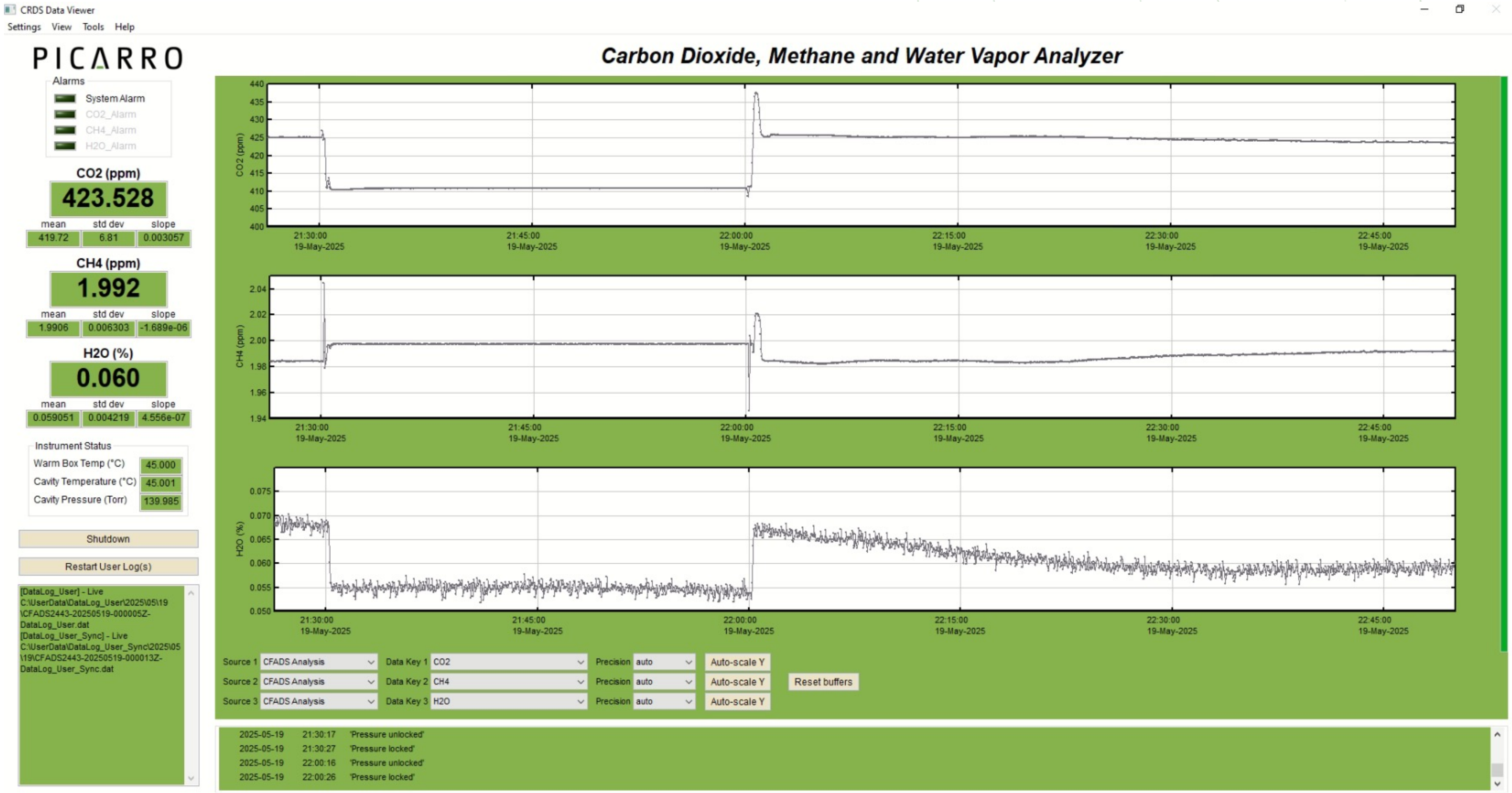


- Three mirrors inside the cavity with slightly less than 100% reflectivity (99.999%)
- For a Picarro cavity of only 25 cm in length, the effective pathlength can be over 20 kilometers
- A Picarro instrument constantly calculates and compares the ringdown time (RDT) of the cavity with and without absorption due to the target gas
- The laser is tuned to the specific wavelength of the target gas

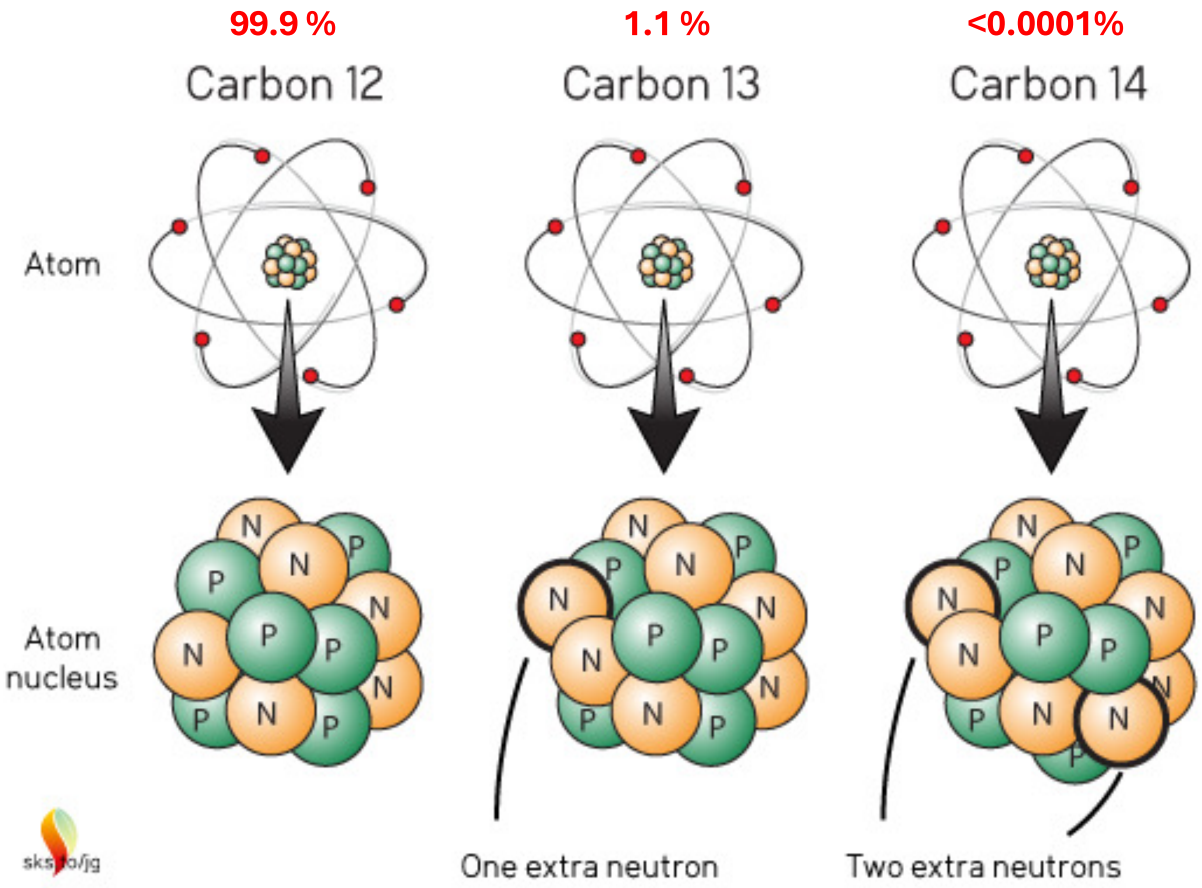
The final concentration value is very robust, because it is derived from the difference between the two RDT

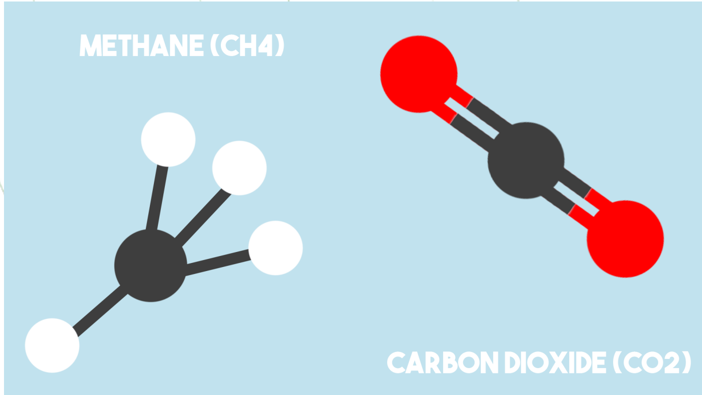
Picarro Interface - G2301

two tunable lasers: one for CH_4 and H_2O and one for CO_2



CRDS measures also isotopic ratios!

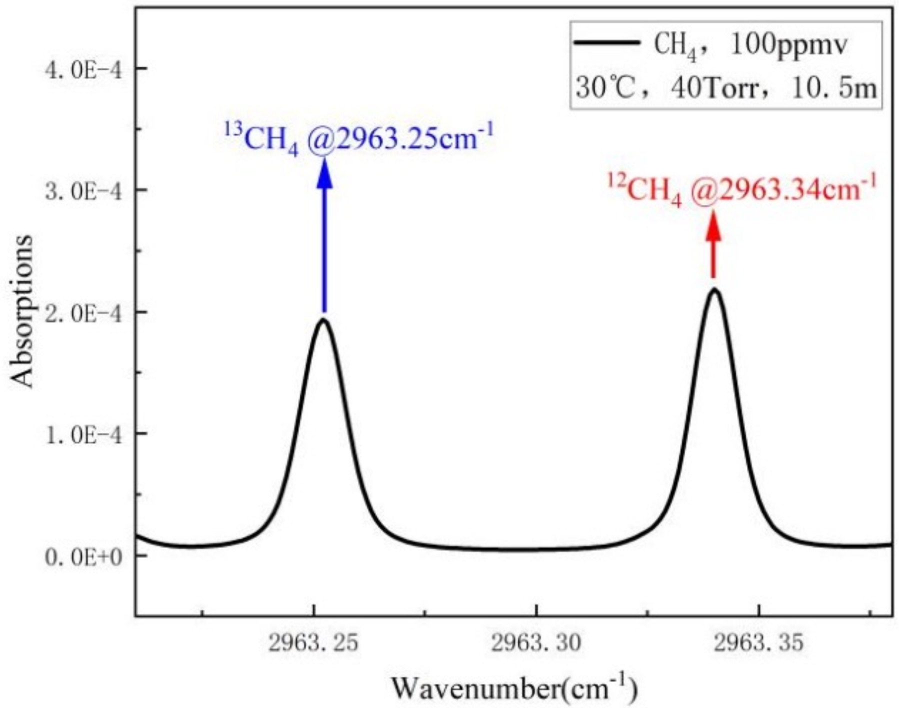




Different masses cause isotopes to behave differently in physical processes. **The bonds between lighter isotopes are weaker** due to higher vibrational energy and **easier to break**!

Also, **lighter isotopes are faster** in all physical processes (diffusion, evaporation, freezing, etc.)

Each isotope has a unique absorption spectrum



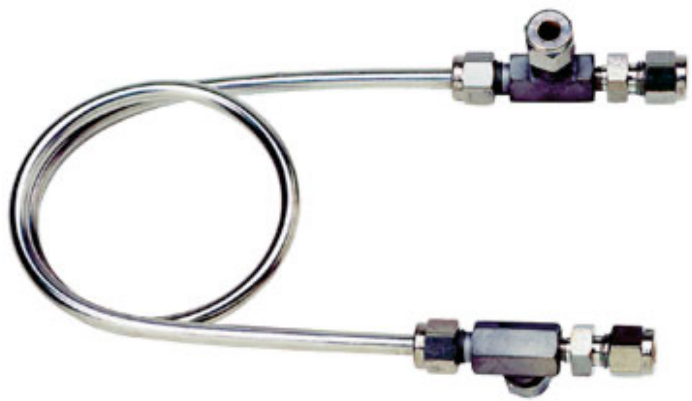
- ✓ In CRDS, the laser can be tuned to the wavelenght where the species absorb, enabling measurements of several isotopes.
- ✓ Picarro instruments measure the ratios of different isotopes within molecules like carbon dioxide (CO_2), methane (CH_4), ethane (C_2H_6), water (H_2O), and nitrous oxide (N_2O). Specifically, they can measure $\delta^{13}C$ in CO_2 and CH_4 in air samples, $\delta^{18}O$ and $\delta^{2}H$ in water samples.

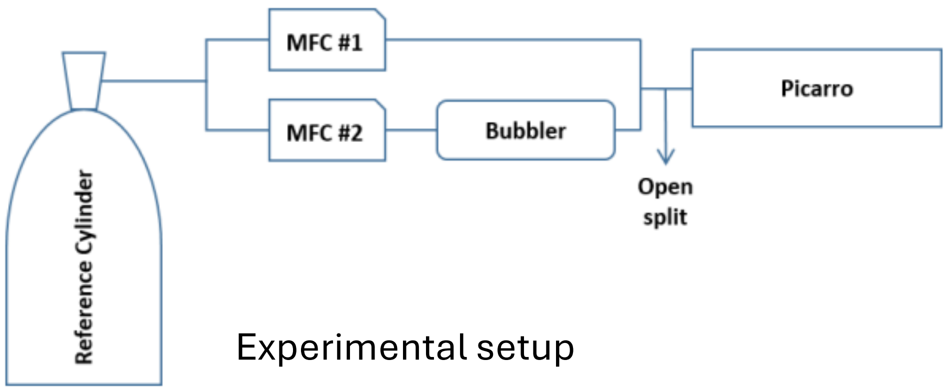
$$\partial^{13}C = \frac{R_{sample} - R_{standard}}{R_{standard}} * 1000$$

$$R = \frac{^{13}C}{^{12}C}$$

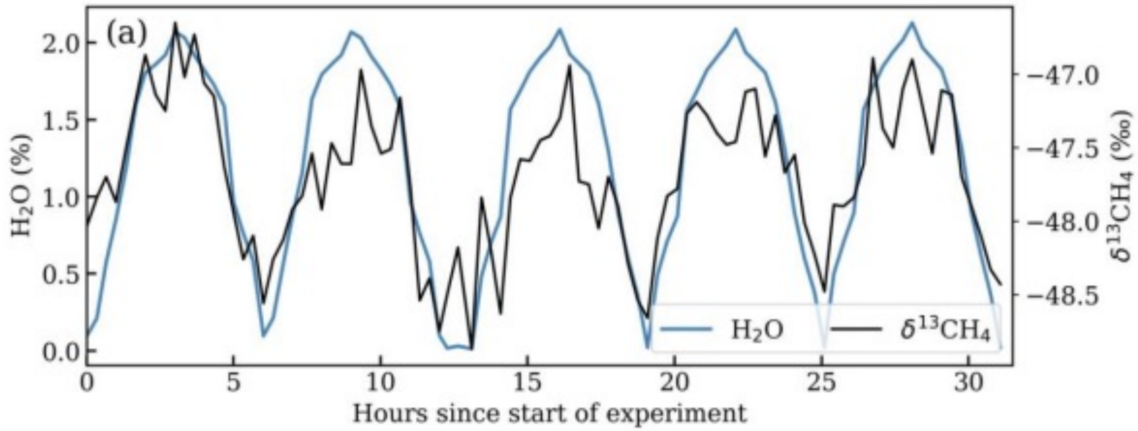
https://www.picarro.com/measurable_compounds

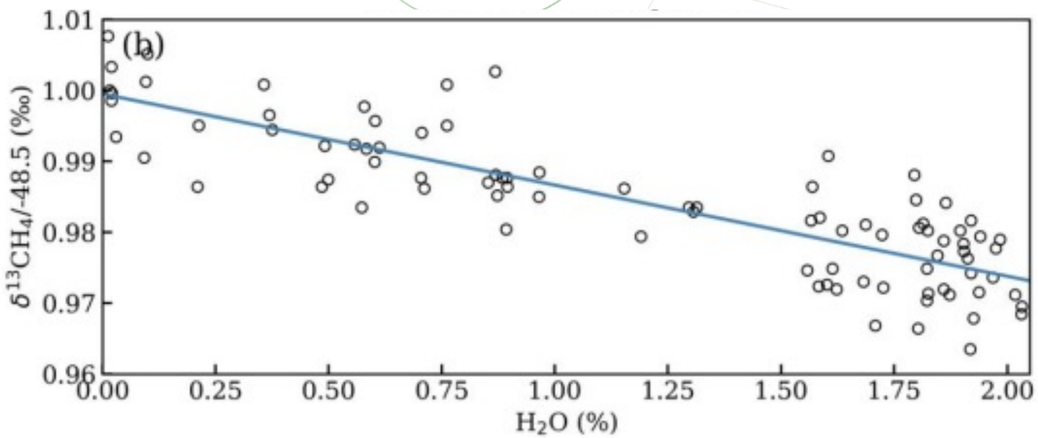
Water interference: air needs to be dried below 0.1 %





Experimental setup





Applications:
atmospheric monitoring of GHGs

Atmospheric background stations: the ICOS network

The **ICOS Atmosphere network** includes stations in 16 European countries. Each of the current **46 Atmosphere stations** measures greenhouse gas concentrations in the atmosphere, as well as meteorological parameters.

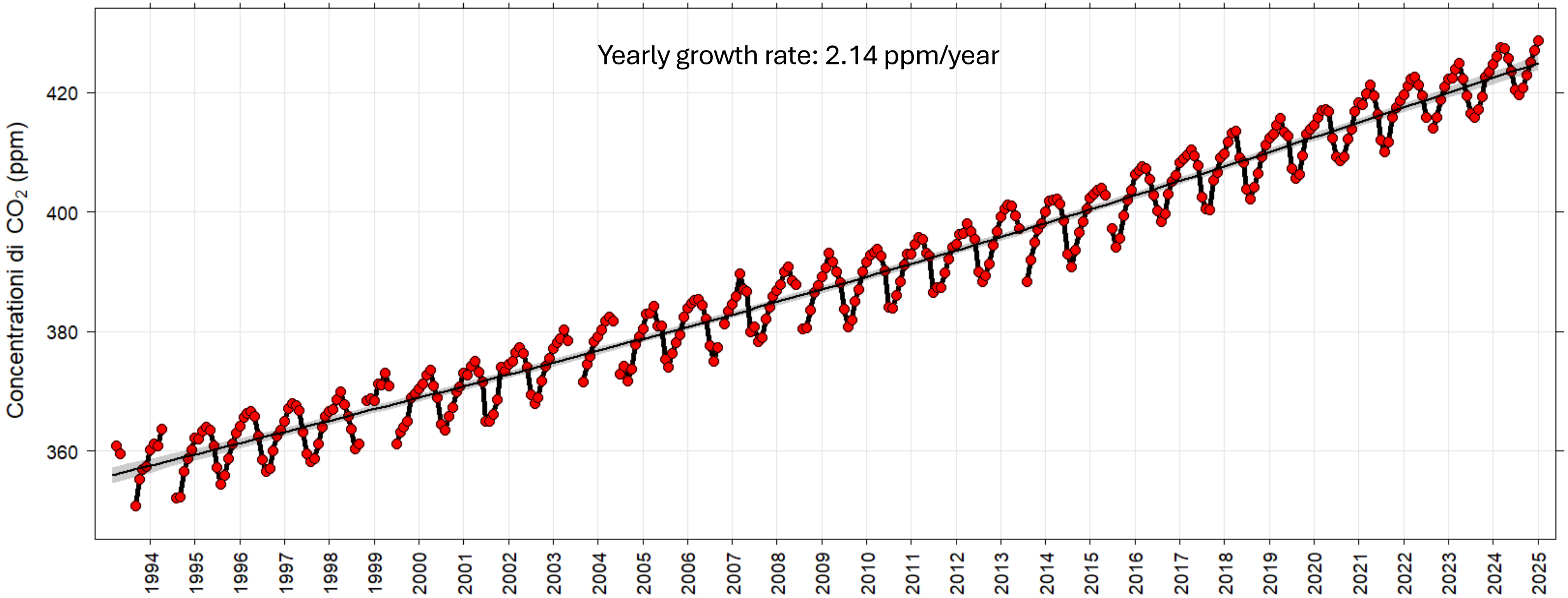
Applications:
atmospheric monitoring of GHGs

Atmospheric background stations: The Plateau Rosa station

A Picarro G2301 measures CH_4, CO_2 and H_2O concentrations

Applications:
atmospheric monitoring of GHGs

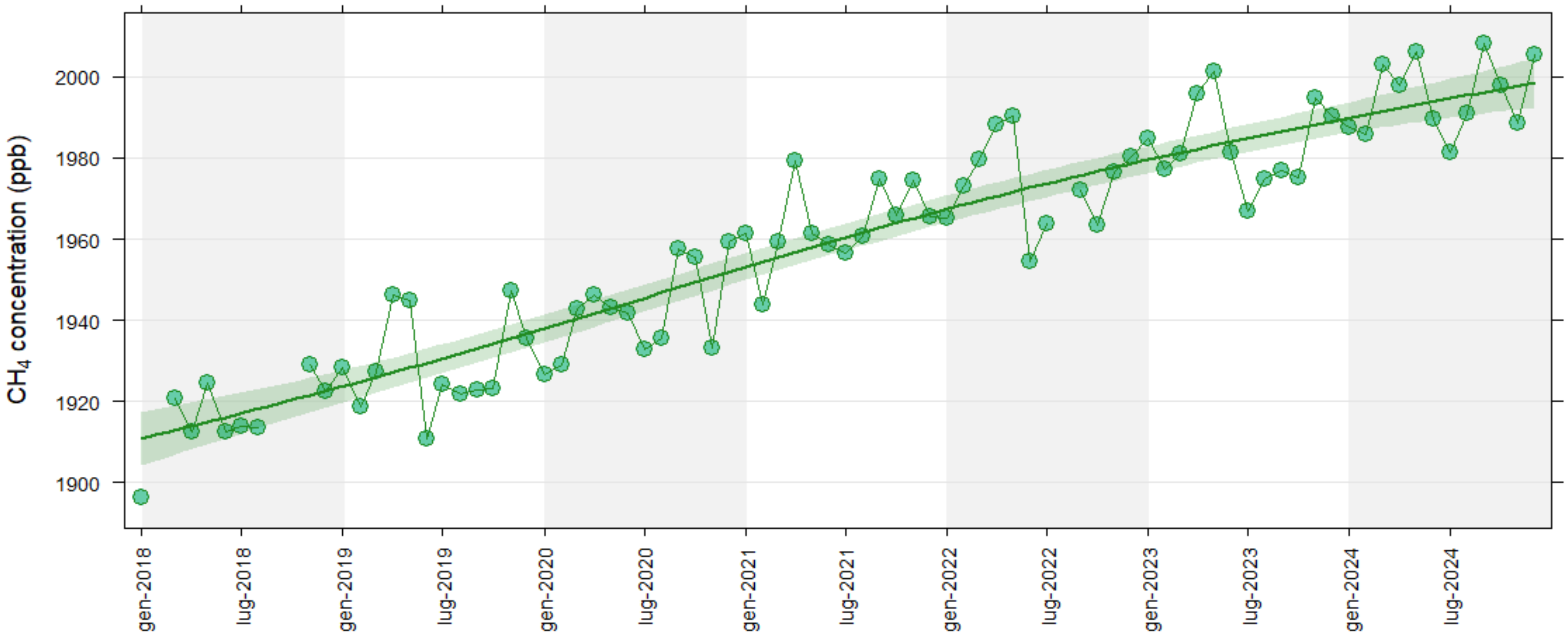
Atmospheric background stations: The Plateau Rosa station



Applications:

atmospheric monitoring of GHGs

Atmospheric background stations: The Plateau Rosa station

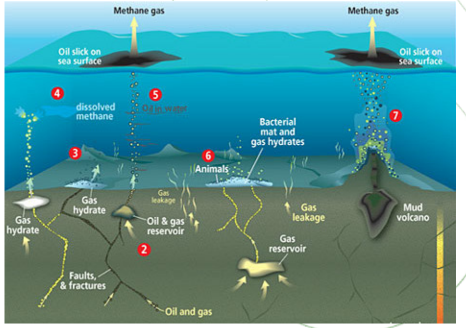


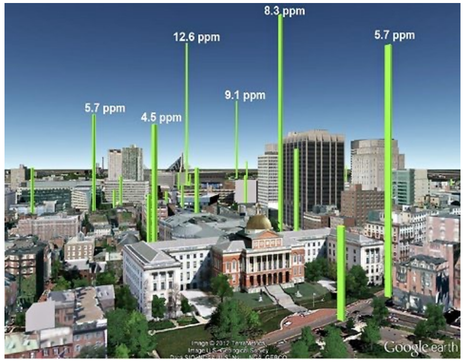
Isotopes are good tracers of different sources

The methane (CH_4) example

Microbial Methane Sources: light sources
(lower ratio $^{13}C/^{12}C$)

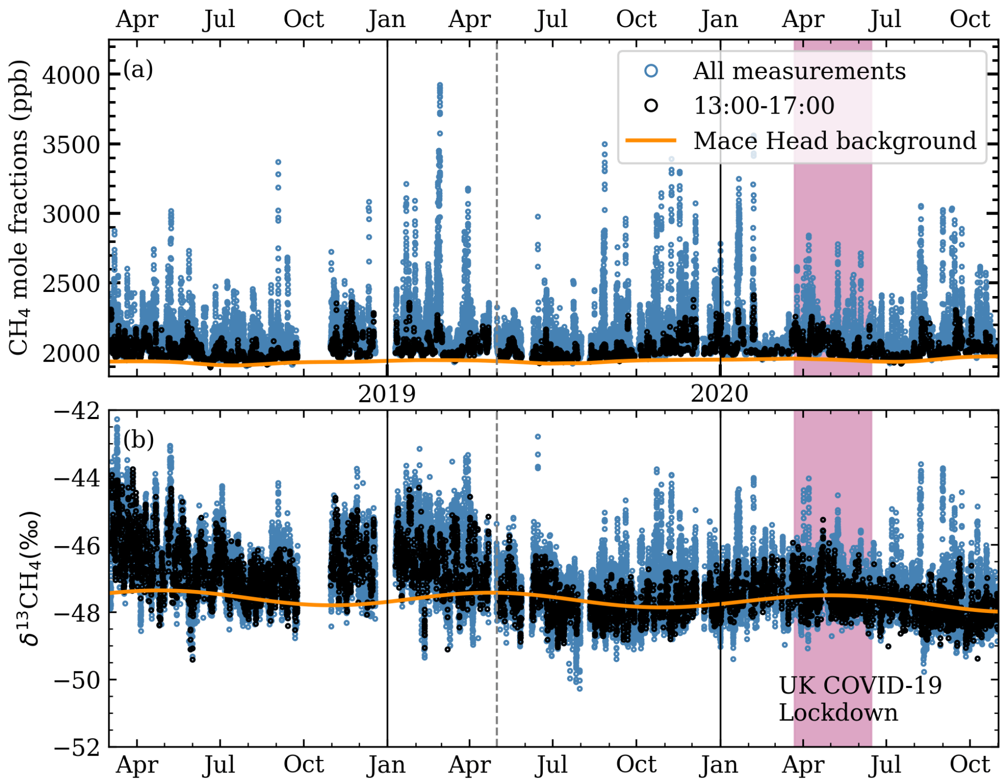
Fossil Methane Sources: heavy sources
(higher ratio $^{13}C/^{12}C$)





Applications:
atmospheric monitoring of GHGs

Atmospheric stations in cities for pollution studies



Picarro G2201-i analyser

Saboya et al. 2022

Applications:
atmospheric monitoring of GHGs

London produces up to a third more methane than estimates suggest

by Hayley Dunning
17 February 2022

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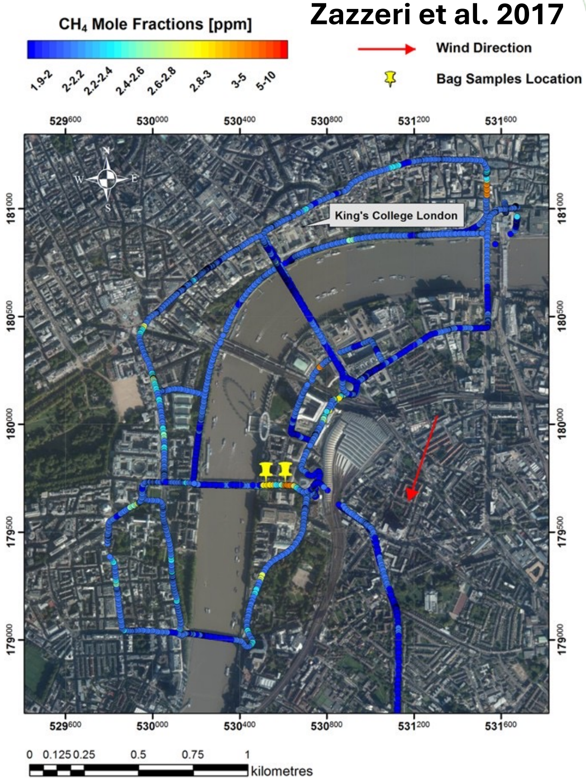
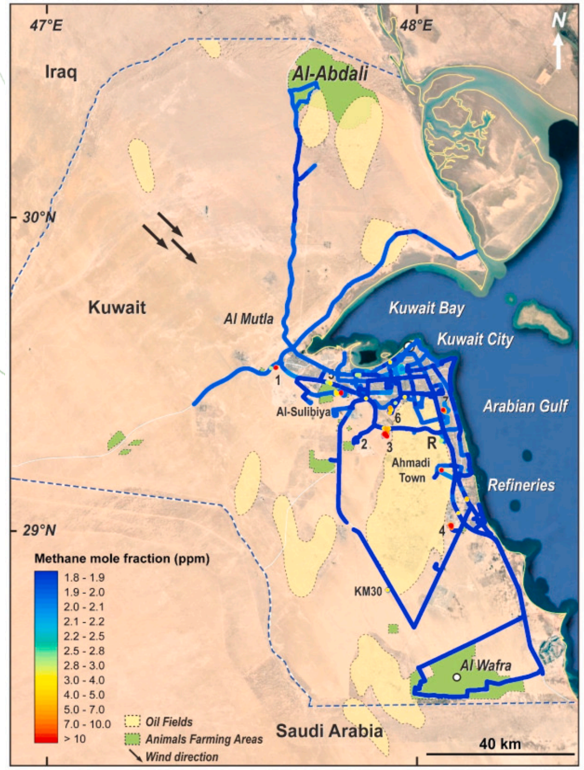
Applications:
identification of sources

Ground base measurements

Zazzeri et al. 2017



Al-Shalan et al. 2022



Applications:
identification of sources

Ground base measurements

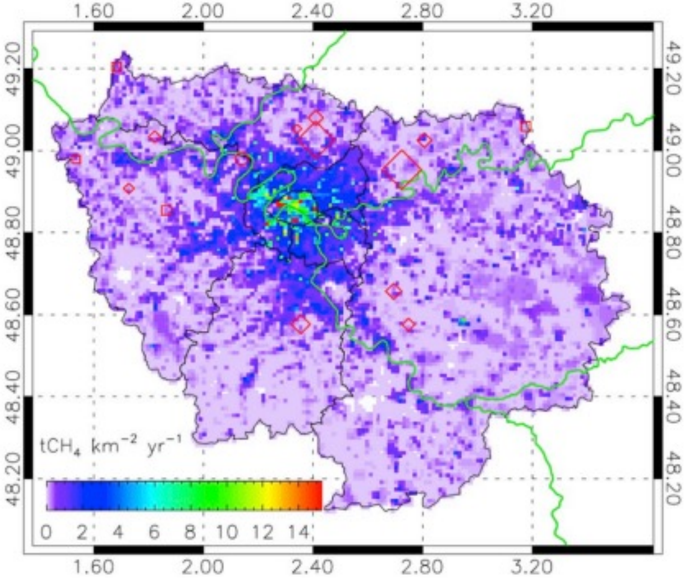
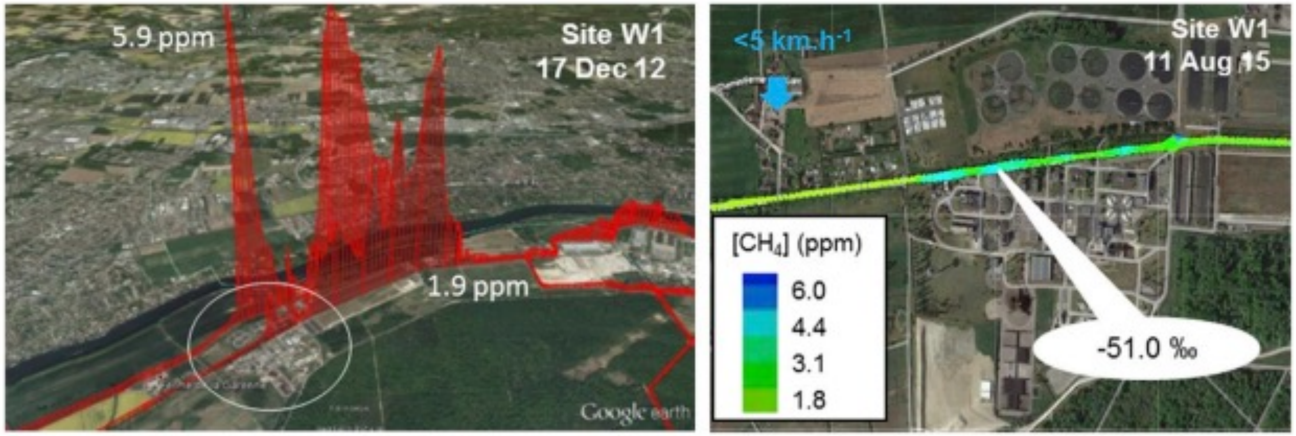


Fig. 2. Methane emissions in IDF according to the AIRPARIF 2013 emissions inventory. Losanges indicate the positions of landfills, squares the ones of the gas storage sites and the circle the one of the Achères waste water treatment facility, that were all surveyed in the framework of this study. Another gas storage site located out of IDF further in the North was also surveyed (see Table 2).The symbol size is calibrated to the emissions given by AIRPARIF inventory.

Xueref-Remy at al., 2020



- ~ 40 methane plumes were detected in the Paris city
- Regional emissions inventory could underestimate methane emissions from wastewater treatment

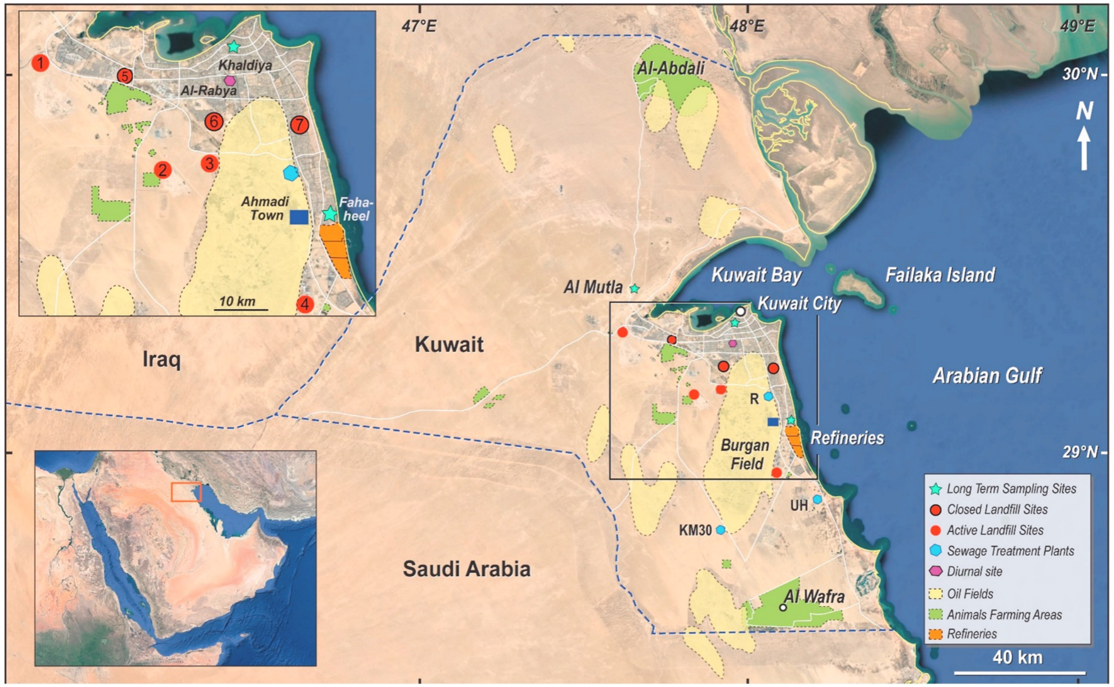
Applications:
identification of sources

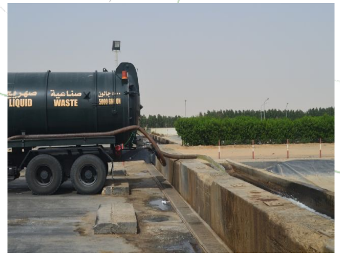
Identification of sources not accounted in the inventories

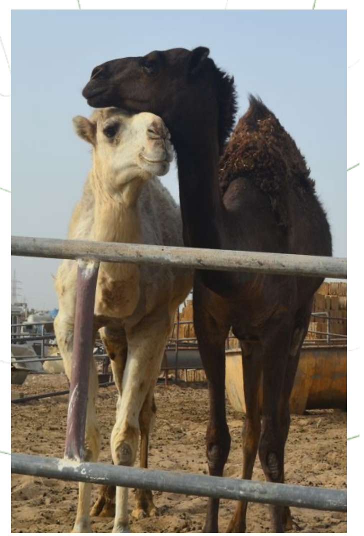
FARADAY GIVING HIS CARD TO FATHER THAMES;
And we hope the Dirty Fellow will consult the learned Professor.

Applications:
identification of sources

Which is the main source sector?







CH_4 concentrations were measured continuosly while driving. When a peak was detected, a sample for the isotopic analysis was collected.

Applications:
identification of sources

Which is the main source sector?

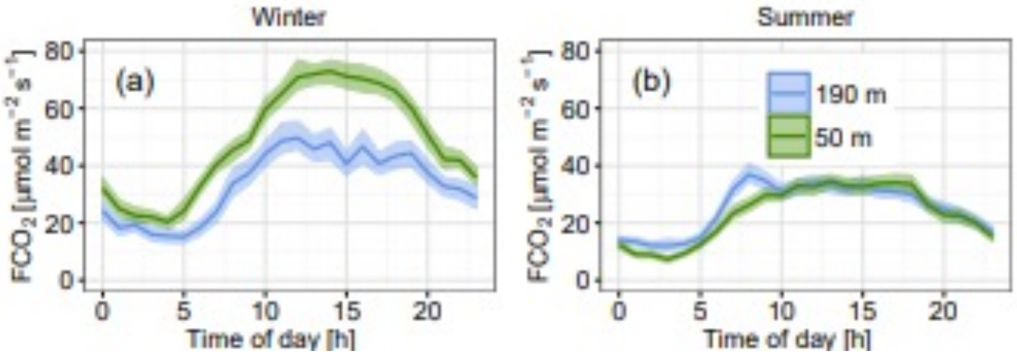
Applications: Flux towers

Eddy Covariance Method

It measures the covariance between the concentration of interest and vertical wind speed.

$$F \approx \overline{\rho}_d \overline{w's'}$$

Helfter et al., 2016
Fluxes measured at KCL (50 m) and BT tower (190 m)



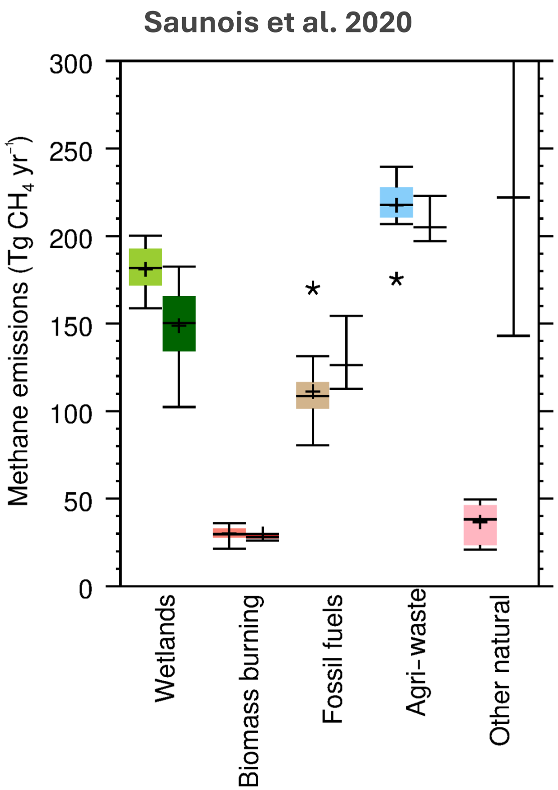
Picarro cavity ring-down spectrometer and calibration tank.

Continuous measurements of GHG

Applications:

verification of inventories using observations and modelling

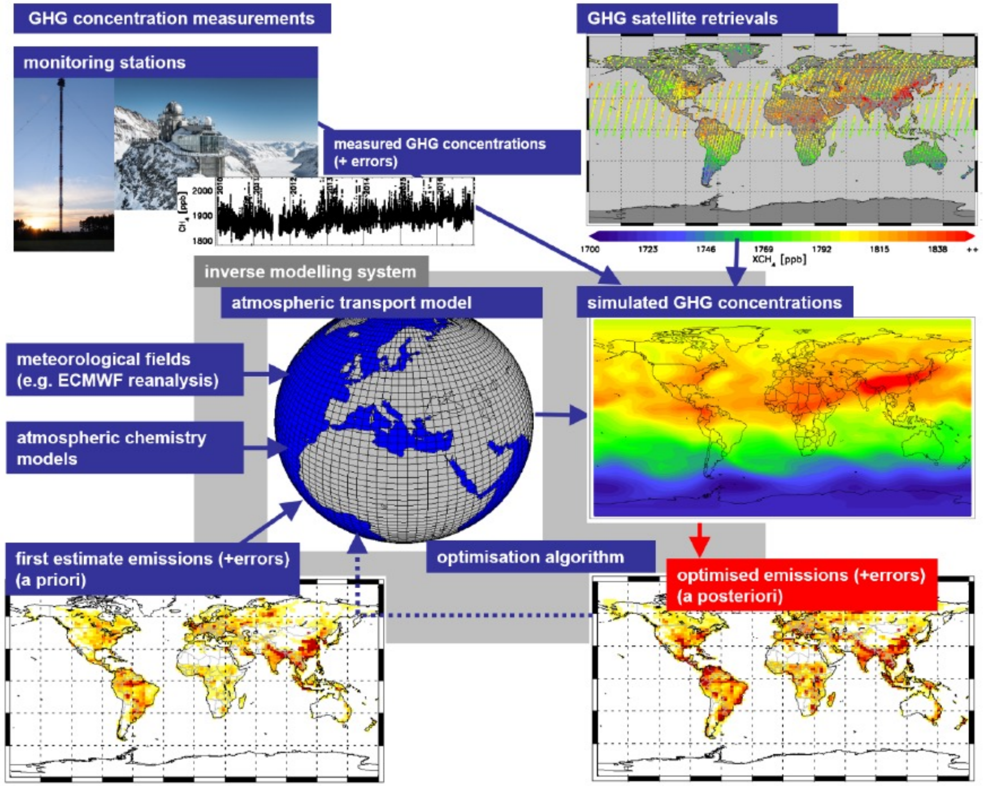
TOP DOWN (measurements) ≠ BOTTOM UP (statistics x emission factors)



- What about unpredictable events? E.g. gas leakages
- Emission factors are country specific.

Applications:
verification of inventories using observations and modelling

- **Inverse modelling:** it links emissions with atmospheric concentrations using atmospheric transport (and chemistry) models.



'A priori' emissions is fed into a model

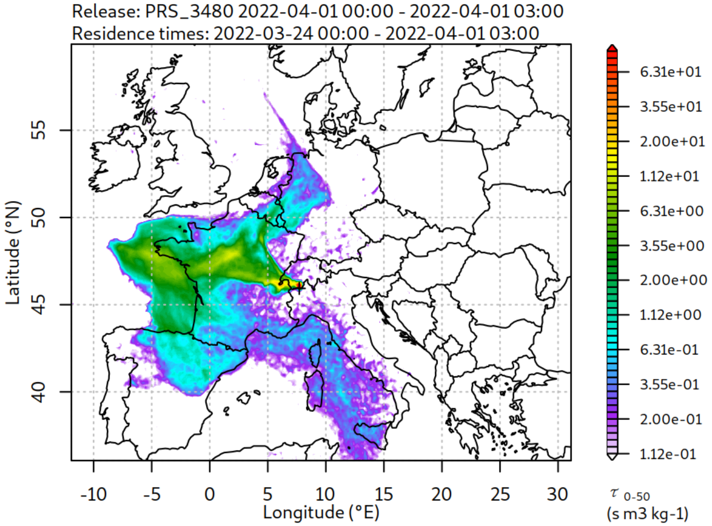
Simulated observations are produced

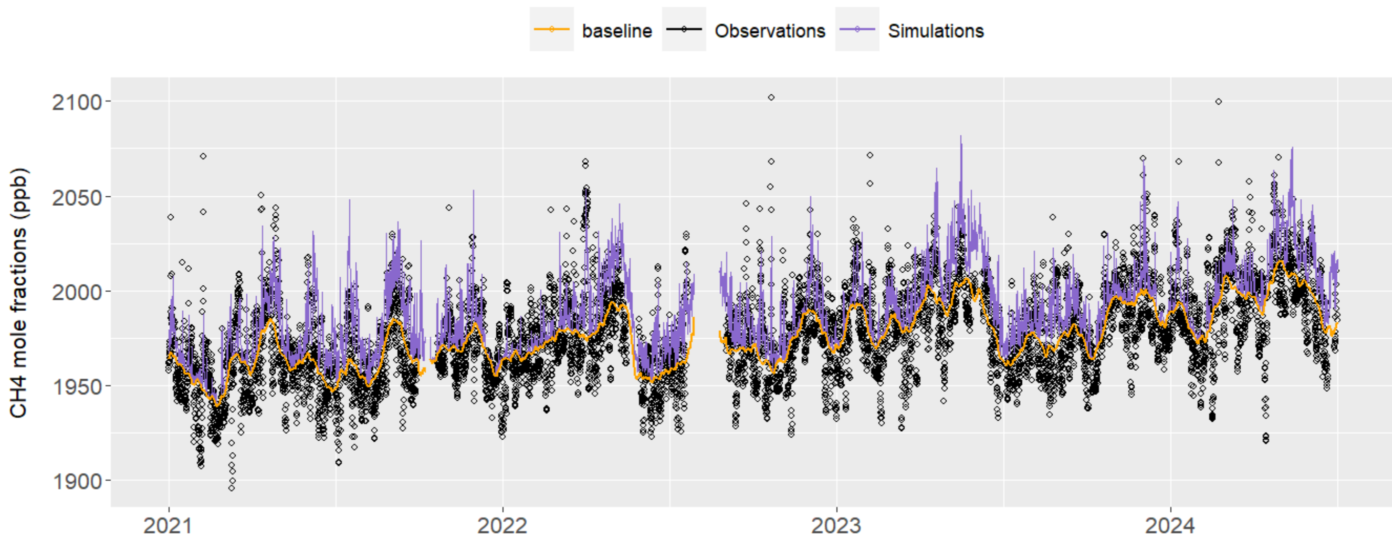
The model system optimises the emissions map to minimise the discrepancies between the actual GHG measurements and the modelled GHG values

Bergamaschi, P. et al. 2018
doi:10.2760/759928, JRC111789

Applications:
verification of inventories using observations and modelling

- The transport model produces footprints, i.e. source–receptor relationship between potential emission sources and the change in concentration at the measurement station.
- Footprint x emission inventories = simulated concentrations





Summary of Applications

- Atmospheric monitoring: background and urban stations
- Mobile measurements for identification of sources
- Use of isotopes for characterization of sources and identification of the main sources sector
- Continuous flux measurements
- Verification of inventories

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THANKS!

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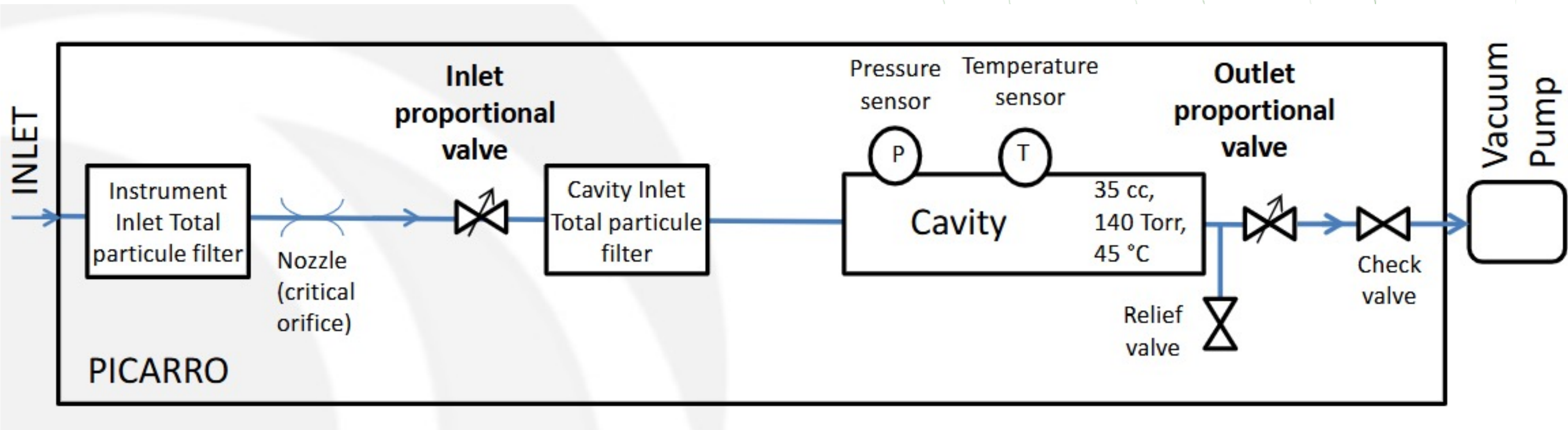
Picarro Plumbing Design



- The flow rate is fixed by the Nozzle (around 250 cc/min) if the pressure drop is sufficient