PAUL SCHERRER INSTITUT

LABOR FÜR ATMOSPHÄREN-CHEMIE

$\delta^{13}C$ and $\delta^{18}O$ from Carbon Mono- and Dioxide, two proxies for tracing combustion sources

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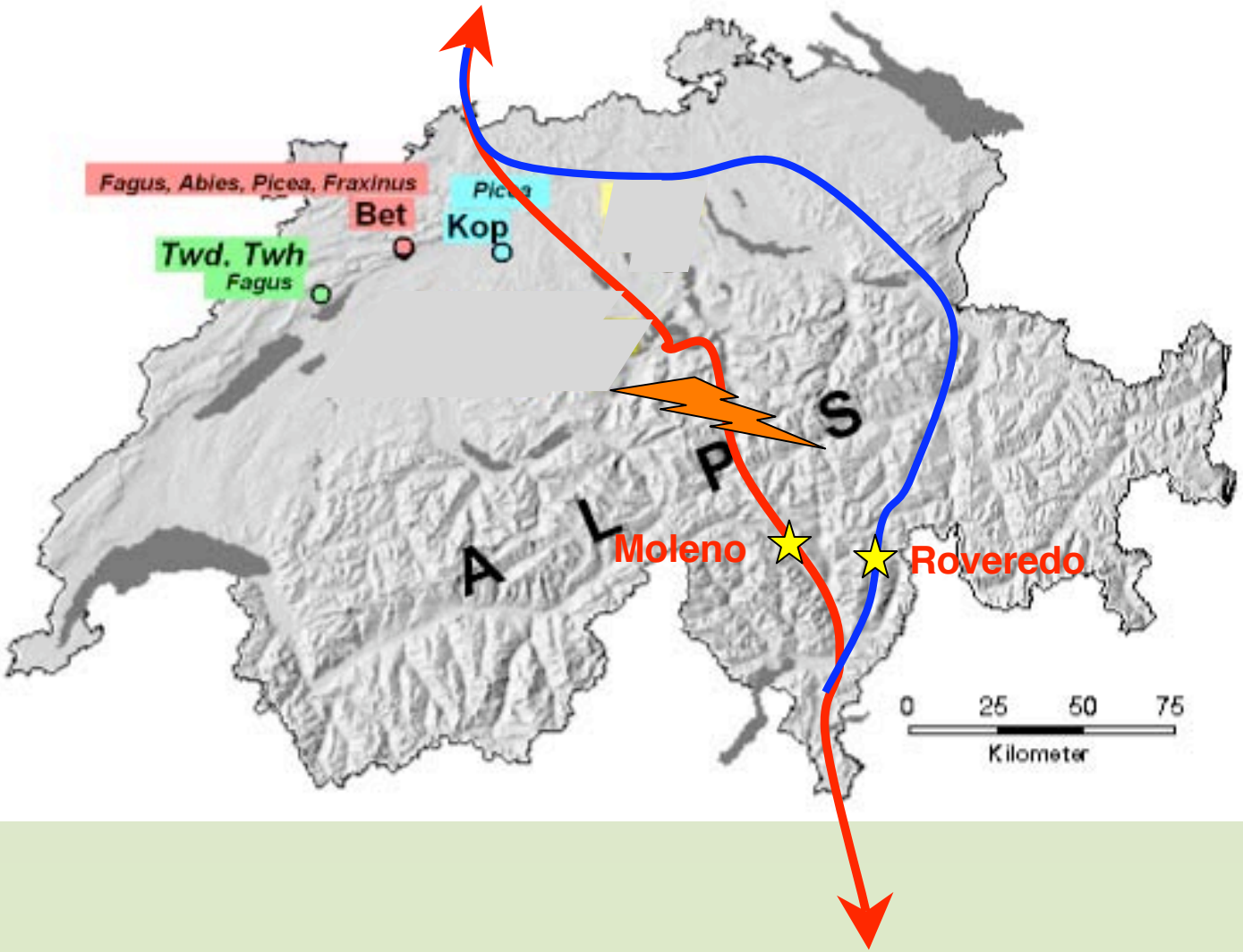
Outline

- Consequences of a traffic accident: Different sources of combustion products, a case study
- Air sampling methods
- CO or CO_2, which molecule is the better indicator in air pollution studies?
- Cars or heating with wood, what are the sources
- Outlook, further planned investigations

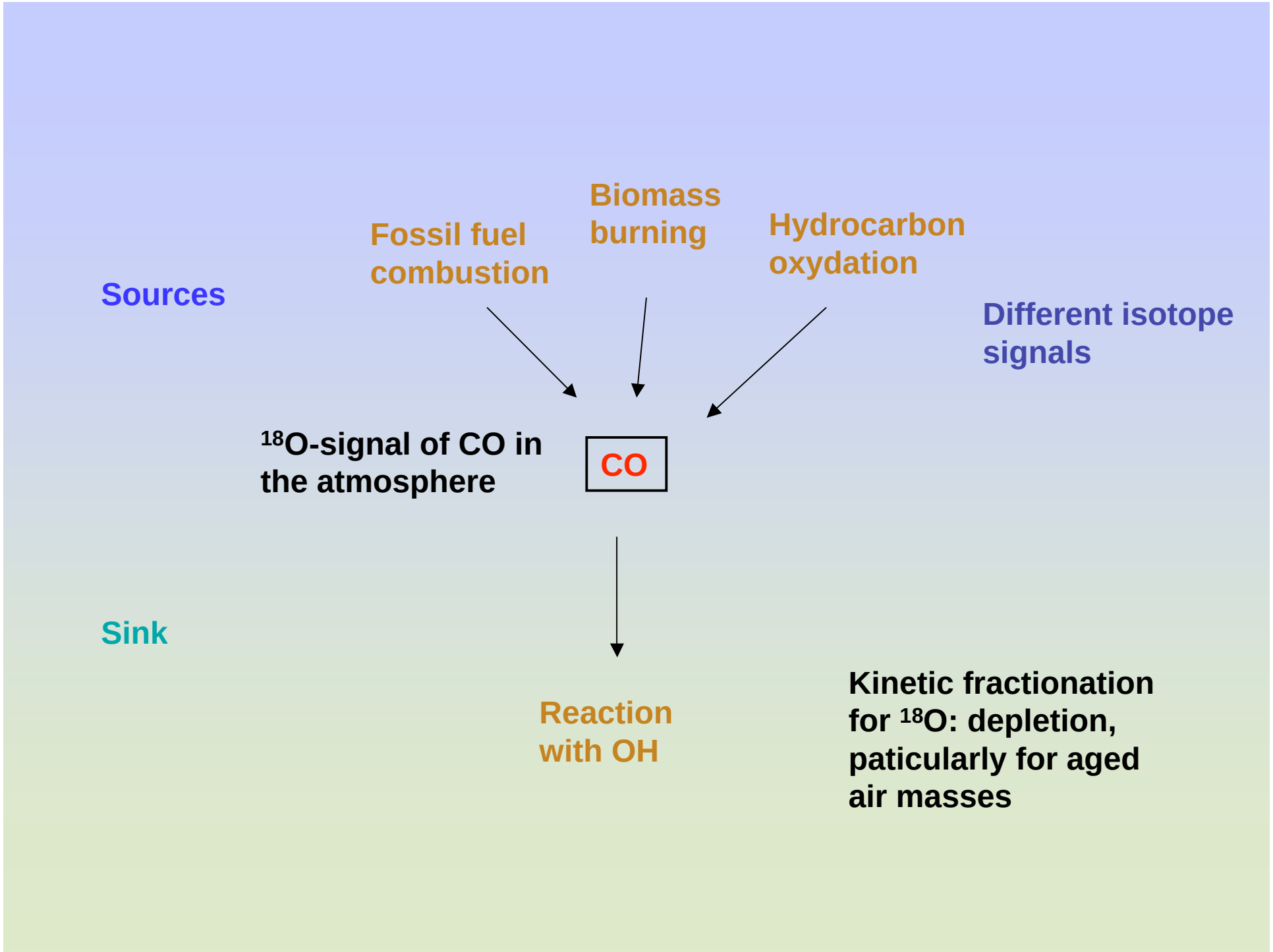
A Changed North - South - Transit Route



AEROWOOD: Aerosol from Wood Burning versus Other Sources

- Many parameters measured:
- Aethalometer, ^{14}C, Levoglucosan, OC/EC, AMS, …

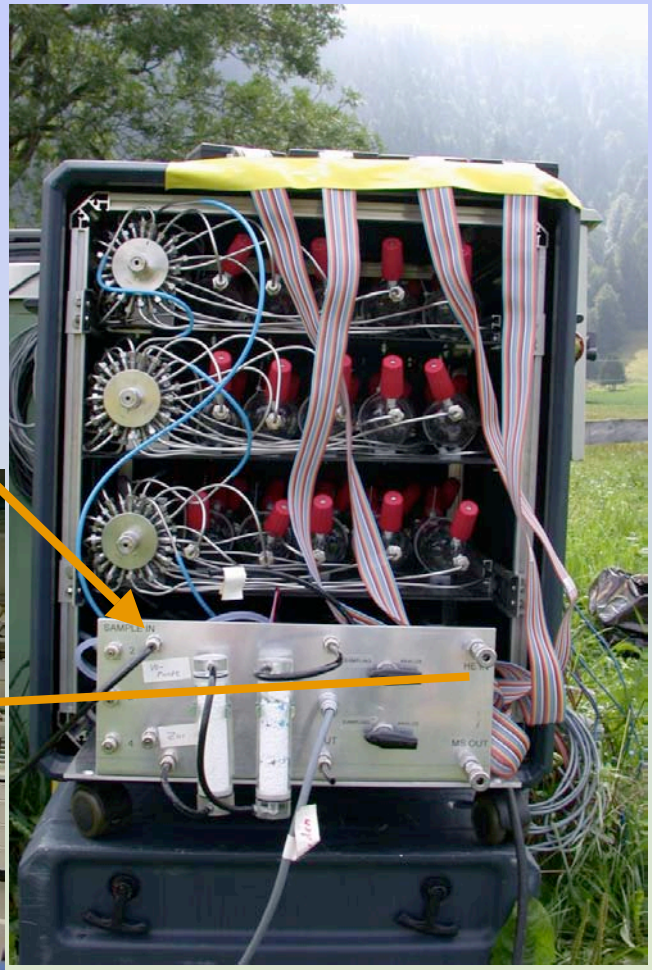
- Exposed to traffic and wood burning: Roveredo
- Exposed to traffic (Gotthard Autobahn): Moleno


Sources
Fossil fuel combustion
Biomass burning
Hydrocarbon oxydation
Different isotope signals
^{18}O-signal of CO in the atmosphere
CO
Sink
Reaction with OH
Kinetic fractionation for ^{18}O: depletion, paticularly for aged air masses

Air Sampling for stable isotope analysis

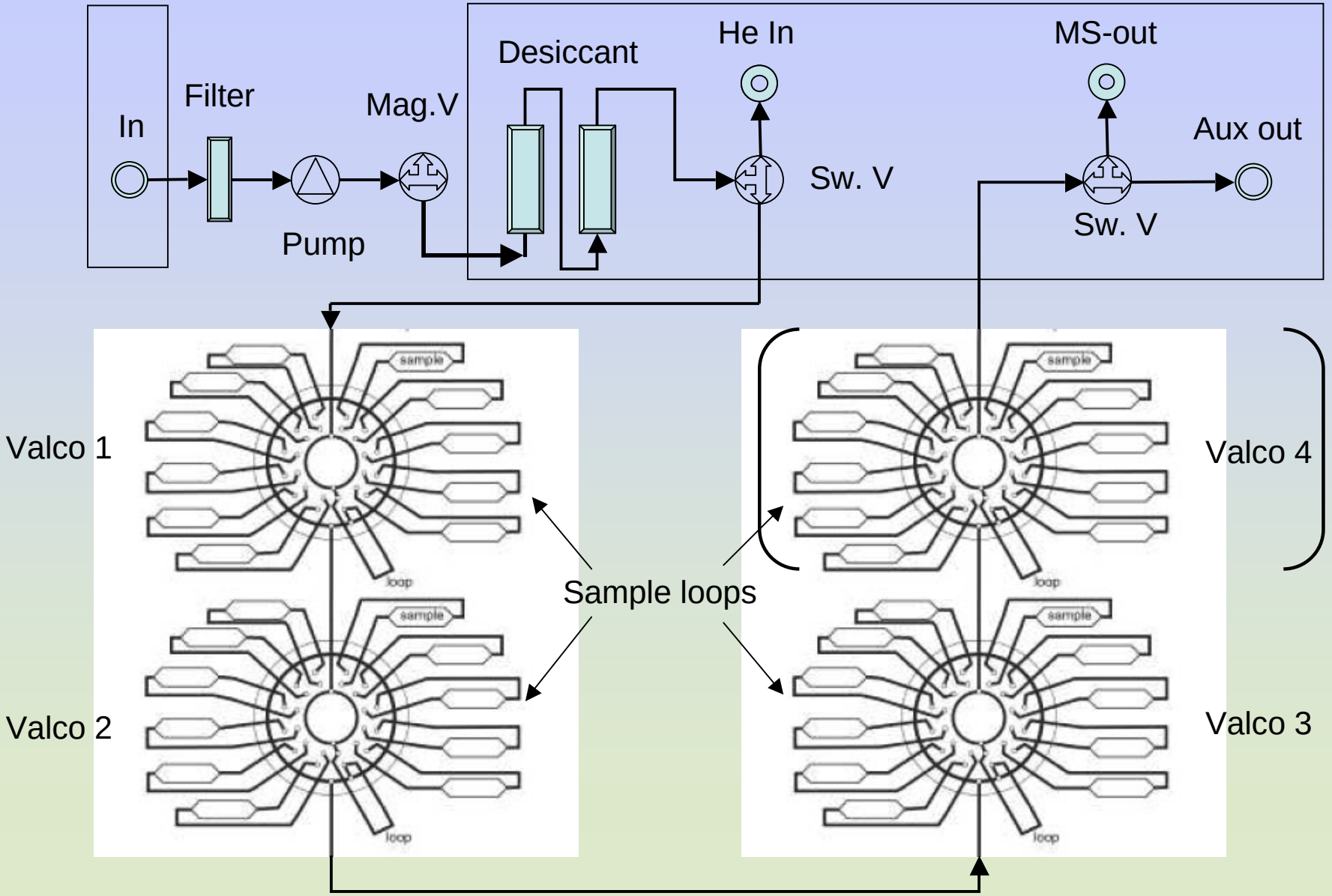
Concentration measurements

In the lab: Determination of Stable C and O isotope ratios with an IR mass spectrometer



Air Sampling

Schematics of the ASA: Pneumatic Design

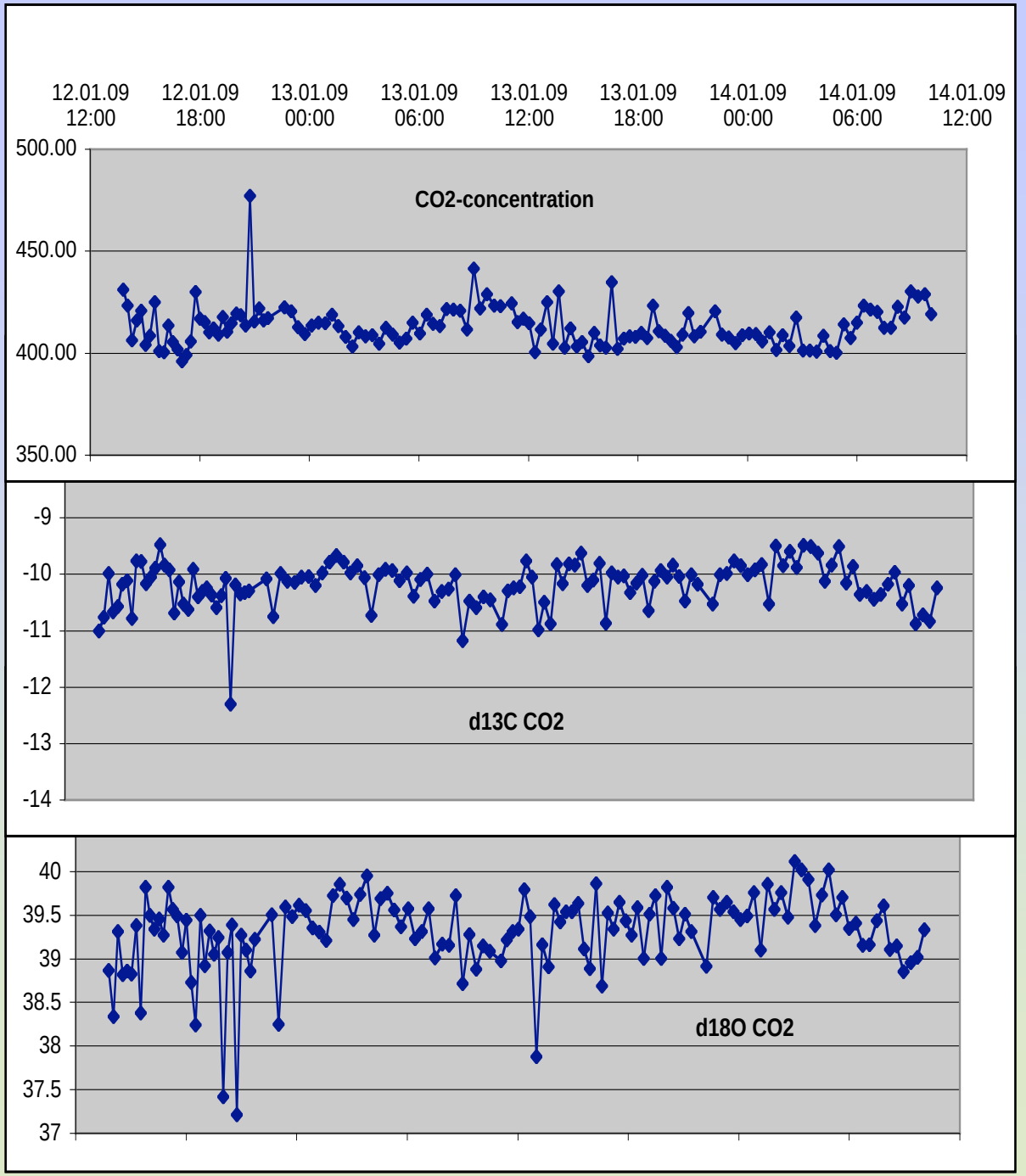


ROVEREDO

Diurnal course of CO_2

$\delta^{13}C$

$\delta^{18}O$



CO_2- isotopes: The Keeling-plot approach

$$\delta^{13}C_{air} * C_{air} = \delta^{13}C_{pollutant} * C_{pollutant} + \delta^{13}C_{background} * C_{background}$$

$$C_{air} = C_{pollutant} + C_{background}$$

...

$$\delta^{13}C_{air} = \delta^{13}C_{pollutant} - (\delta^{13}C_{pollutant} - \delta^{13}C_{background}) * C_{background} / C_{air}$$

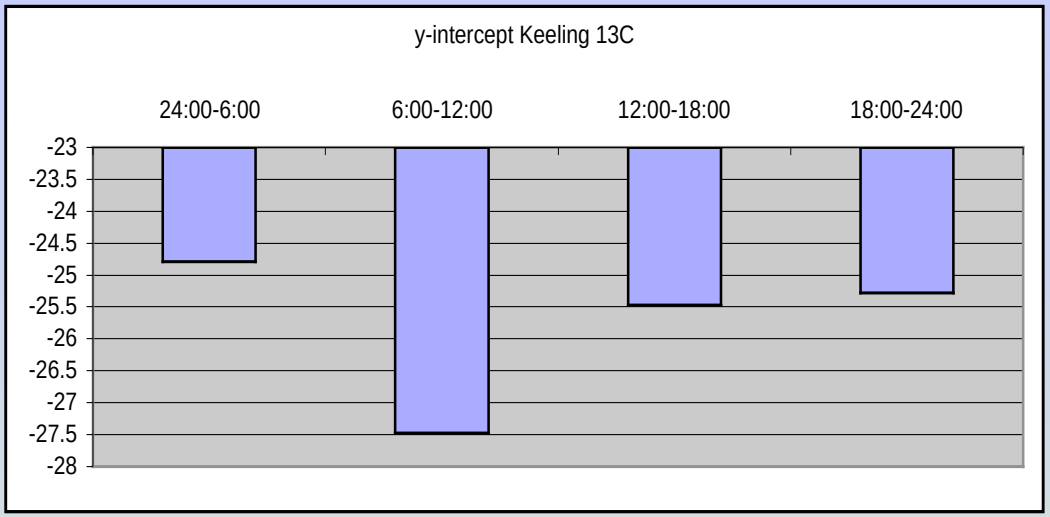
⟶ Linear in $1/C_{air}$ with y-intercept δ^{13}C-pollutant

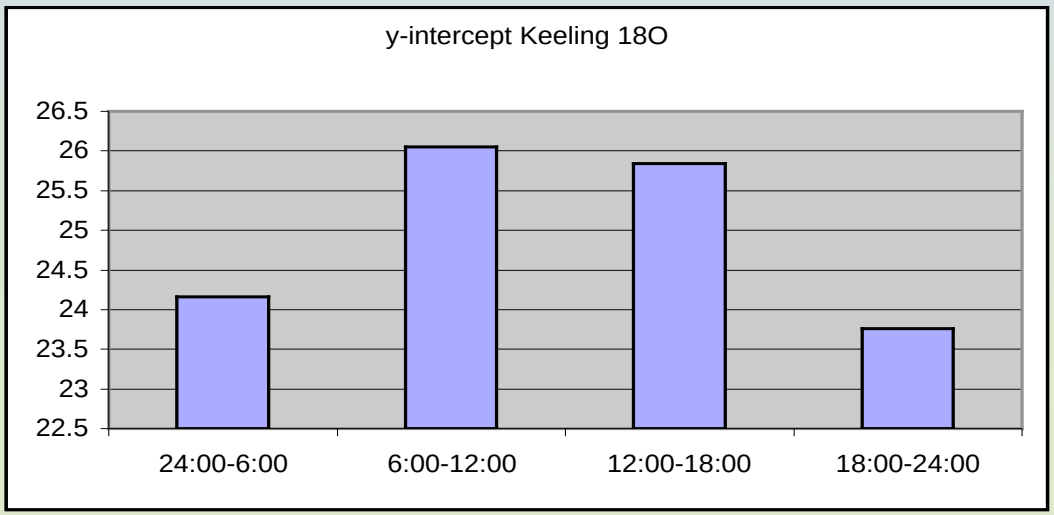
Table 1
Measured and inferred isotopic composition for the main sources of CO (see Brenninkmeijer et al., 1999 for references) and estimated uncertainties

	$\delta^{13}C$ (‰) V-PDB	$\delta^{18}O$ (‰) V-SMOW
Fossil fuel combustion	-27.5^{a}	23.5^{a}
Biomass burning	-22.9^{b}	17.15^{b}
CH_4 oxidation	-52.6^{b}	0^{c}
NMHC oxidation	-32^{b}	0^{c}

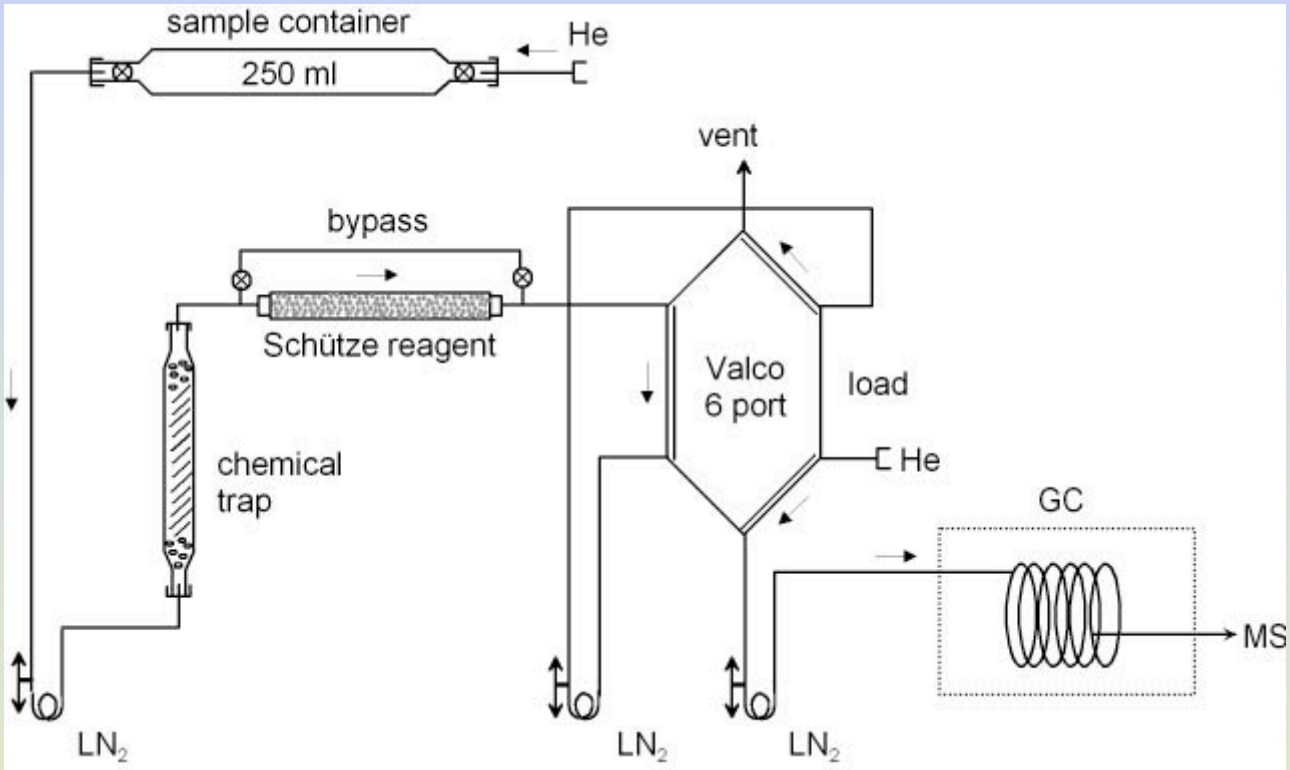
V. Gross et al. Atmospheric Environment (2002)

Keeling intercepts from CO_2 data





Isotope analysis of Carbon monoxide in small air samples

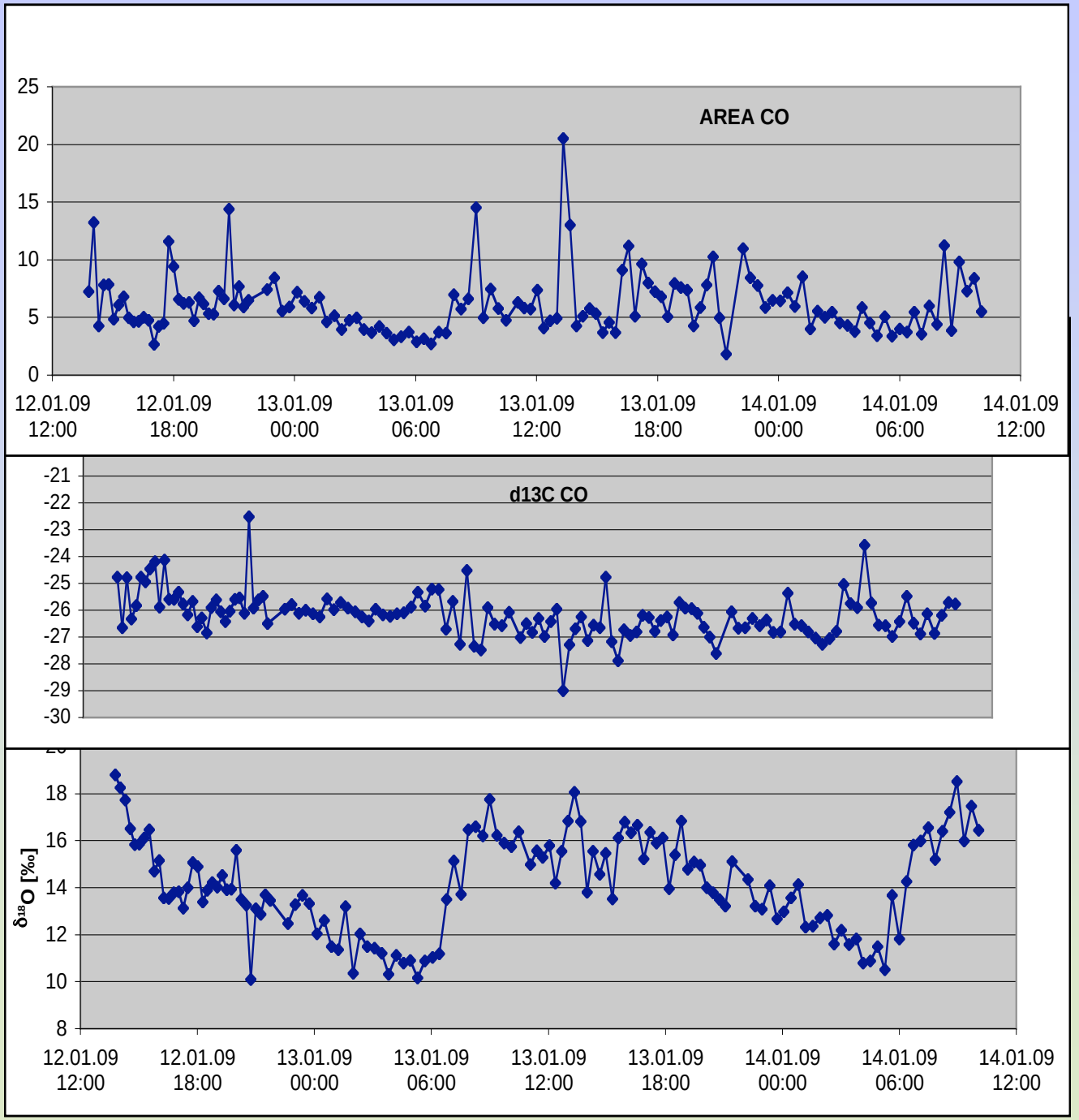


Diurnal Course of

CO

$\delta^{13}C$

$\delta^{18}O$



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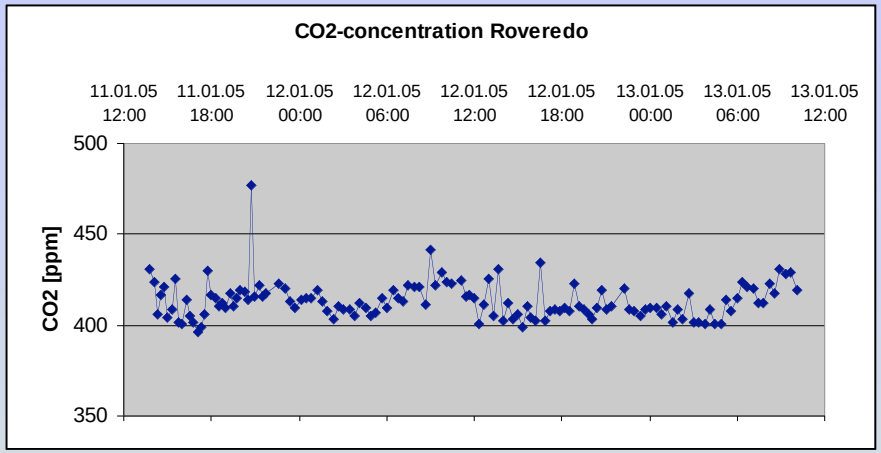
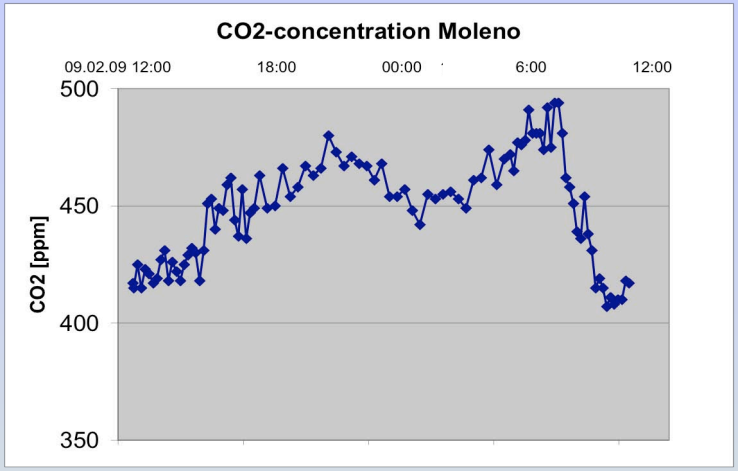
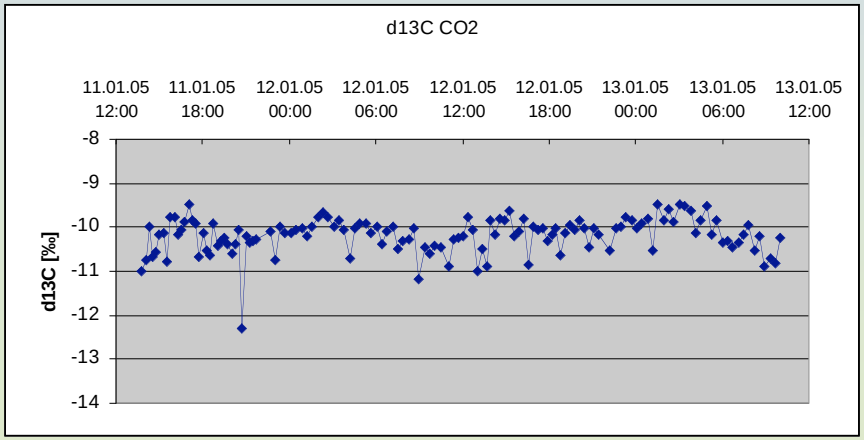
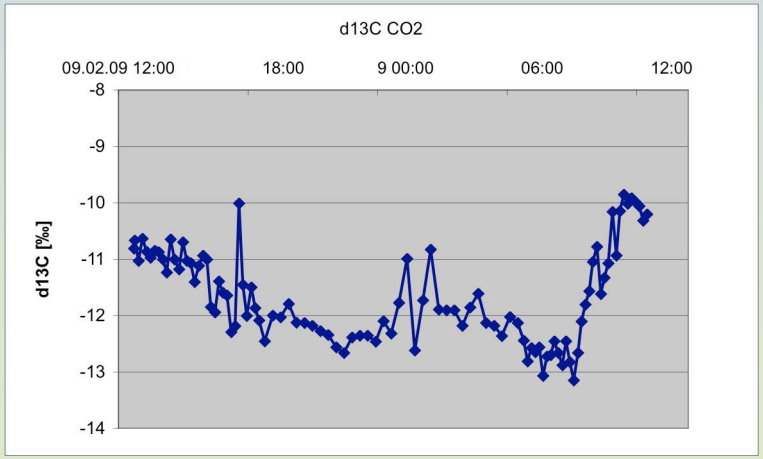
Roveredo CO_2 Moleno

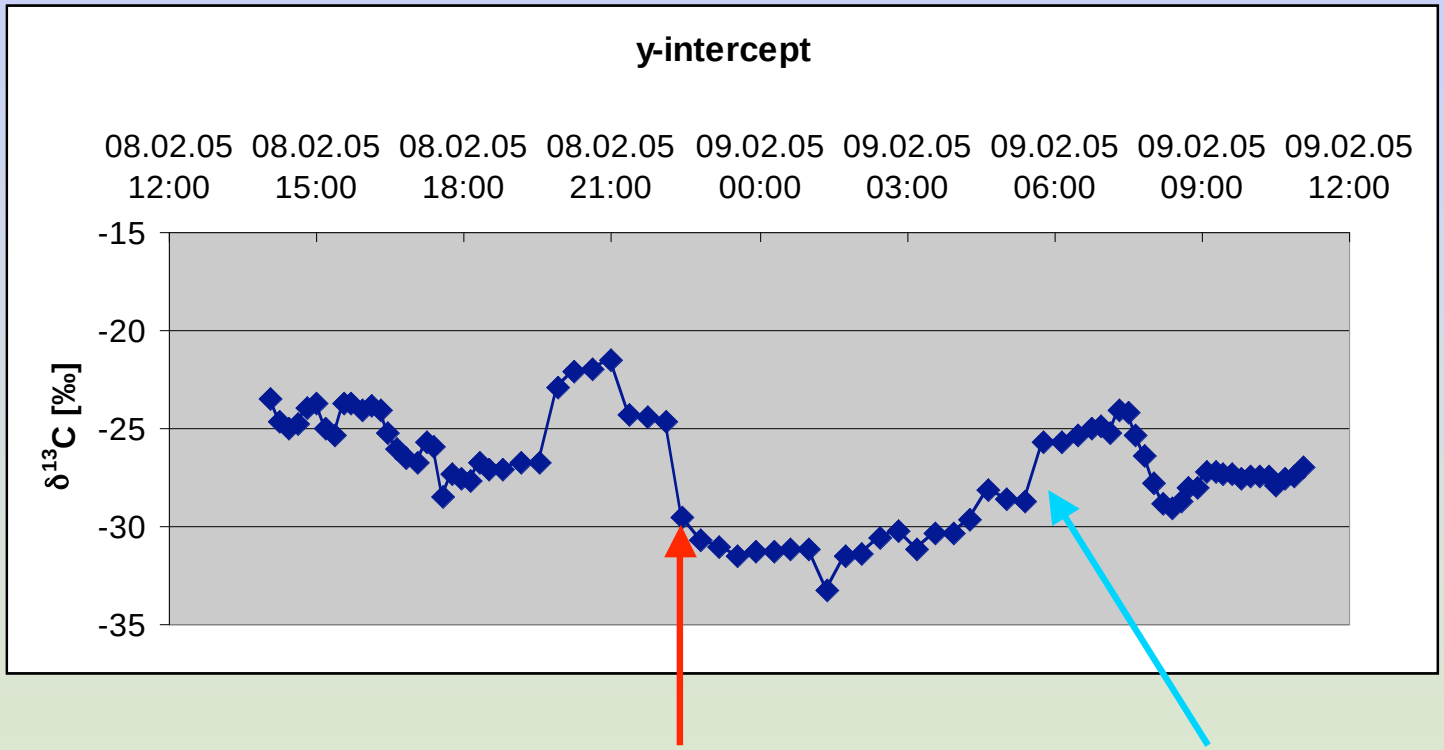






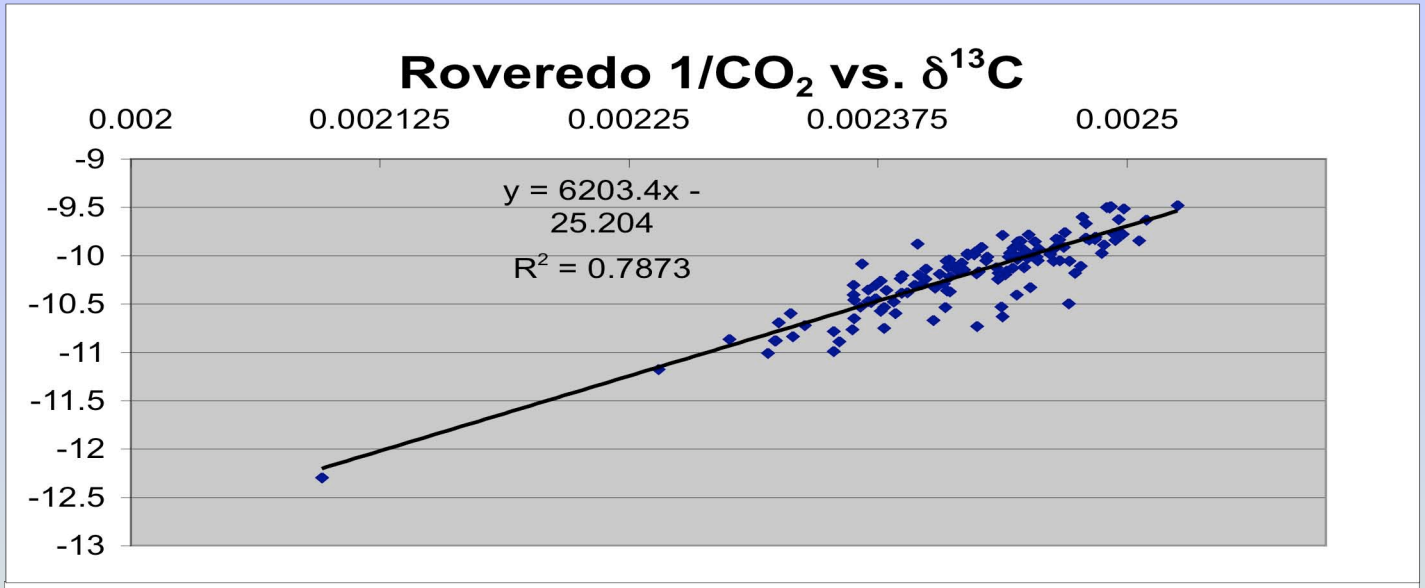


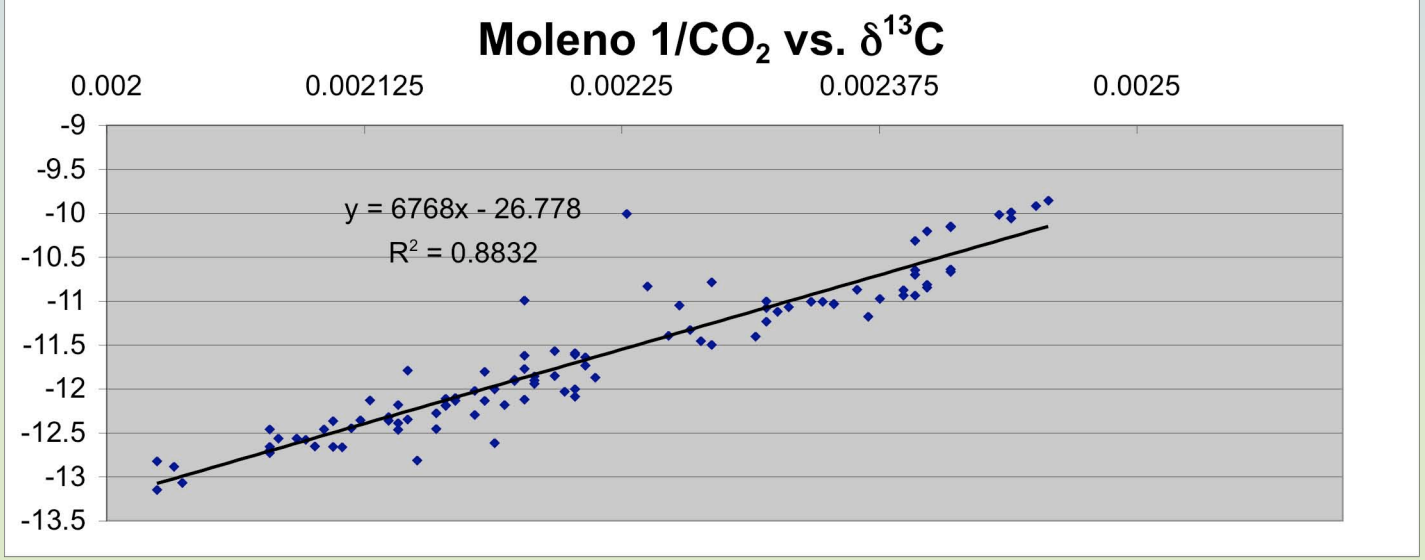
Signal of „combustion-$\delta^{13}C$“ of CO_2 in the course of the day in Moleno

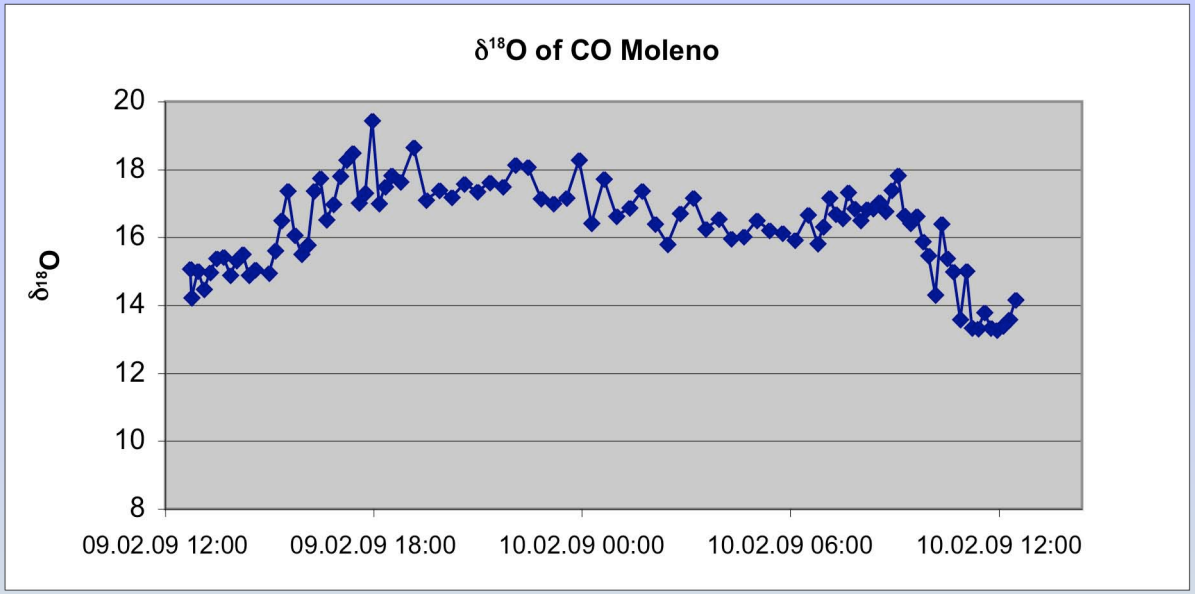


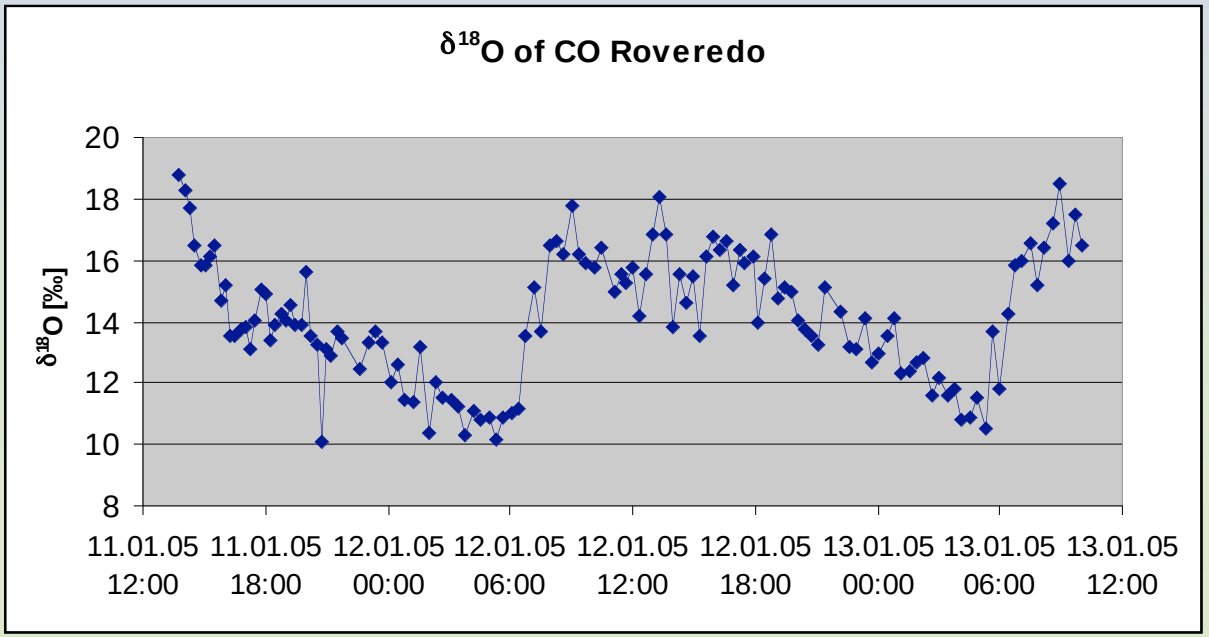
A strong decrease in $\delta^{13}C$ at 10pm and an increase at 6 am is observed

An example from Ticino Feb 2005:



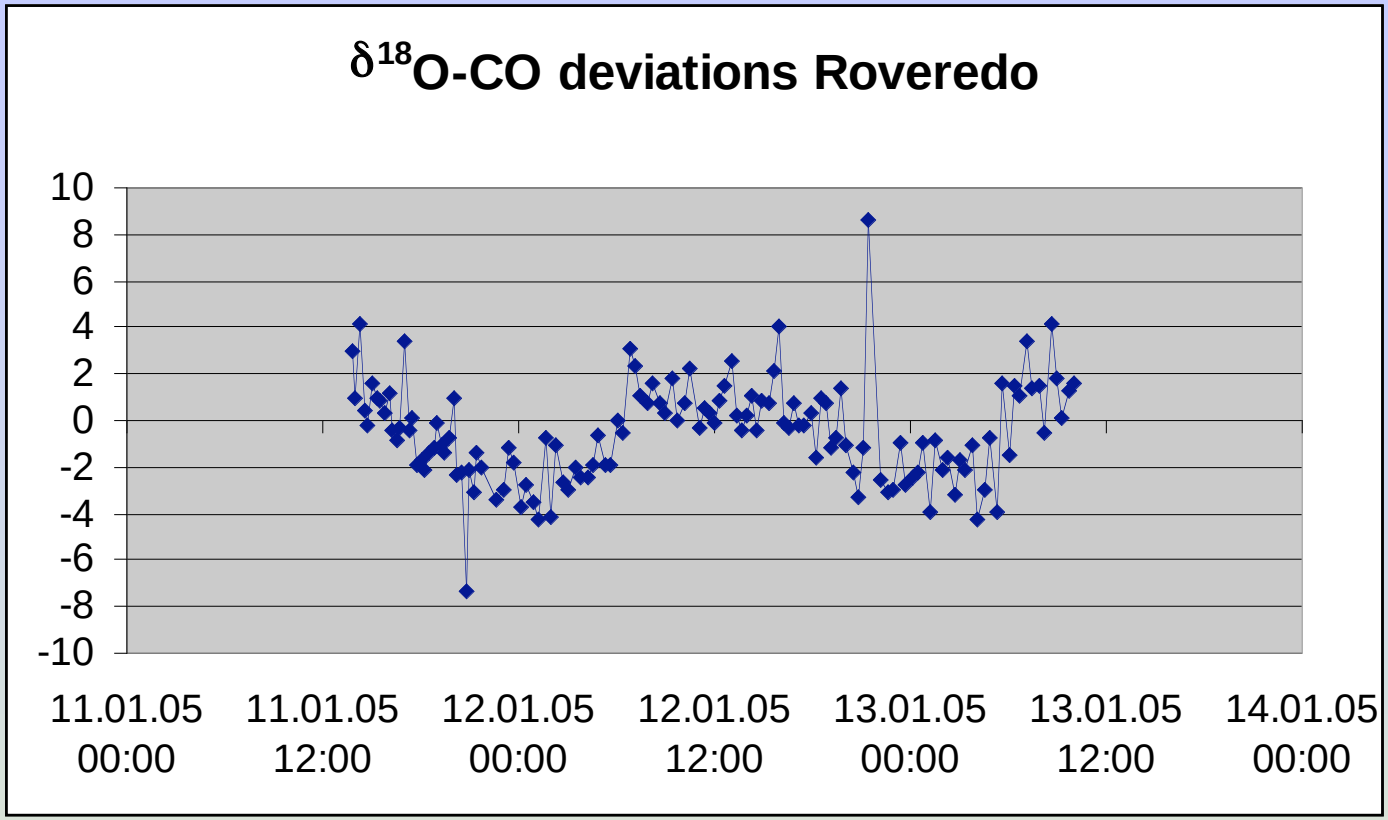






Contrasting diurnal course in Roveredo and Moleno

Why…?



Moleno is taken as pure traffic signal -> Deviations from this line in Roveredo due to wood burning

Next steps:

Combine all information to disentangle the influence of

1) wood burning

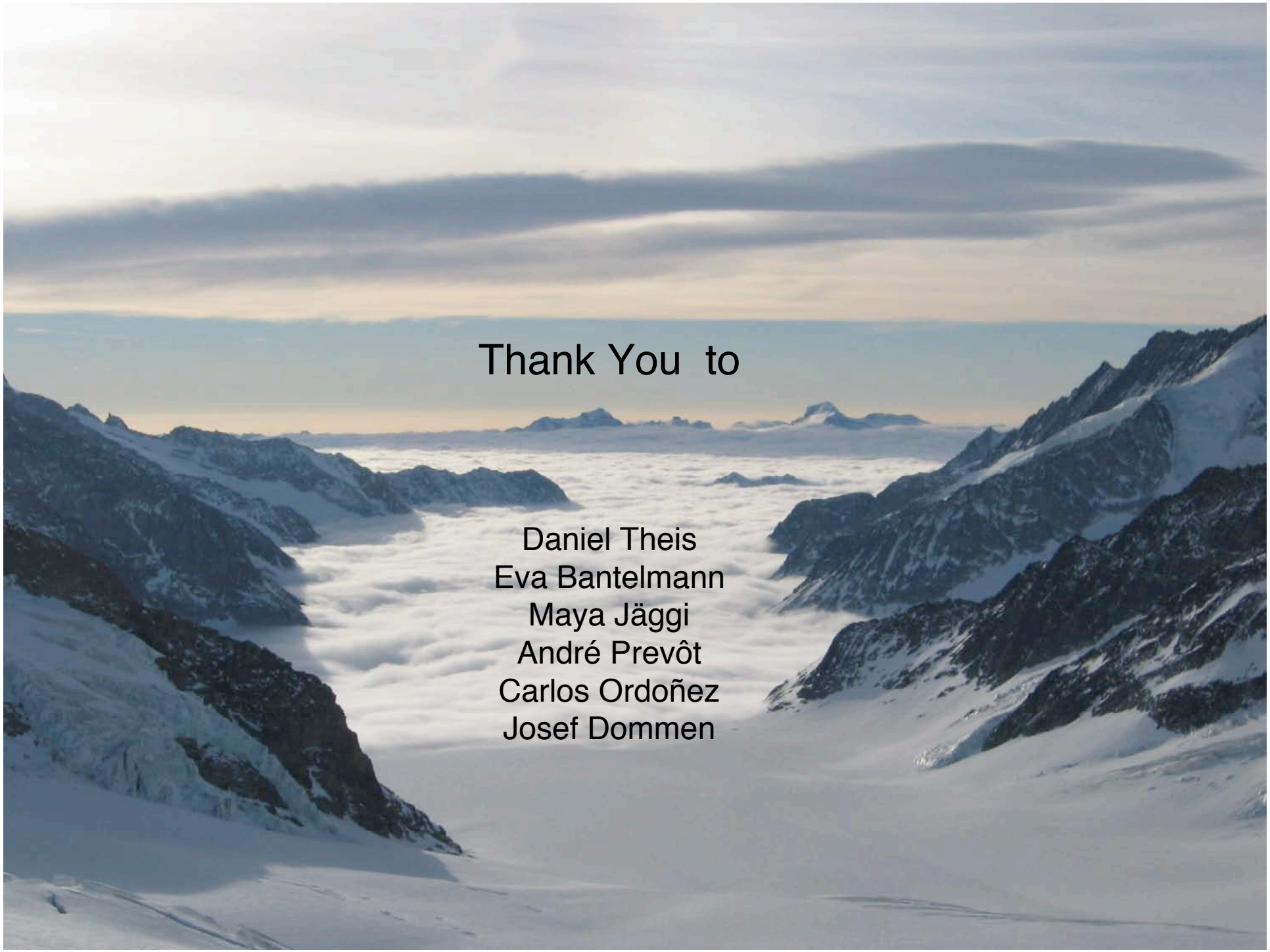
2) traffic

3) background (clean) air

using the 6 time-series δ^{13}C-CO, δ^{18}O-CO, CO-conc., δ^{13}C-CO_2, δ^{18}O-CO_2, CO_2-conc.

So far we can state that ....

- **Isotopes of CO provide specific, high-resolution data-set carrying a specific source signal**
- **Combination of isotopes and concentrations of CO and CO_2 provide 6 (partly) interrelated parameters**
- **Calibration with other tracers are required for understanding the isotope signal**


Thank You to
Daniel Theis
Eva Bantelmann
Maya Jäggi
André Prevôt
Carlos Ordoñez
Josef Dommen