

Interactive comment on “Continuous isotopic composition measurements of tropospheric CO₂ at Jungfraujoch (3580 m a.s.l.), Switzerland: real-time observation of regional pollution events” by B. Tuzson et al.

Anonymous Referee #2

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The use of a QLAS system for quasi-continuous CO₂ in air stable isotope measurements is demonstrated to work at a precision level of ± 0.05 per mill level ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$). The Jungfraujoch station has been selected to test the system in a “free troposphere” environment over 2 years. Data are presented for a limited time window of 30 days in early 2009. During this time pollution events from local sources occurred, which altered the CO₂ concentration and isotopic signature. The major advantage of the presented system is the ability to analyze stable isotope data continuously (at a rate of about 70 data points per hour). This allows to infer sources of air masses to be traced

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down to their presumed origin using a Keeling plot end-member technique. However, this can work only for two clearly distinct components (like a general C₃-derived source of CO₂ mixing into background air), but it will not allow to constrain this a lot further when several sources are involved or the sources have similar isotopic compositions. For $\delta^{18}\text{O}$ the Keeling plot technique does not provide conclusive results, owing to the decoupling between source concentration and isotopic signature.

The paper is well written and the information given is clear and concise. Publication is recommended after addressing a number of specific questions and comments:

24564, L21: The 6 GtC/yr needs updating (e.g. LeQuere et al, Nature Geoscience 2 (2009) 831; Friedlingstein et al, Nature Geoscience 3 (2010) 811)

24565, L5: the discrimination of $\delta^{13}\text{C}$ for C₃-photosynthesis only

24565, L18: except for sea-water, which is largely uniform. However, in contrast to terrestrial exchange equilibration is slow (not catalyzed by enzymes). The resulting CO₂ $\delta^{18}\text{O}$ is also a function of water temperature.

24565, L25: Please provide scale for the $\delta^{13}\text{C}$ presumably the VPDB-CO₂ scale.

24567, L7: While “simultaneous” gas calibration can also be done in series (provided the time intervals do not become excessively long), the simultaneous recording of the isotopologue absorptions is more important for stable isotope ratio precision.

24567, L24: The 50s integration time presumably applies to a complete cycle including the measurement of all 3 isotopologues. Are these measured in sequence? If so, could this be improved to a simultaneous analysis within identical time windows? How much time is spent on each absorption feature?

24568, L1: Replace ‘50 m³ h⁻¹’ with ‘833 L min⁻¹’ (use consistent units throughout the paper)

24568, L19ff: The exact way of reporting data is not clear. I assume that the short-

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term data use Tank A and the reference cell. Is Tank A then used as the longer term calibration anchor point when it is used for flushing the sample cell? What are the differences for the Tank A 'sample' against the reference cell Tank A?

24569, L4: The correct reference would be 'P Ghosh et al, Calcite-CO₂ Mixed into CO₂-free Air: A New CO₂ in-Air Stable Isotope Reference Material for the VPDB Scale, Rapid Comm. Mass Spectrom., (2005) 19: 1097-1119'

24569, L11: Please provide isotope scales information

24569, L14: ...values are better...

24571, L19: I do not understand this statement. Why is scatter "much accentuated at the permil scale" ? Compared to what? Is there another scale available for stable isotope ratios? Or do you compare to something else (mixing ratios?). Then you would compare apples with pears.

24574, L24: I do not see this as clear cut as stated. Why should the -27.4 ‰ intercept in figure 5 a be more specific for coal or biomass combustion, but not oil? It could be anything but natural gas, provided we can exclude a more complex mixture.

24576, L8: Here, the scale is misleading. +46.6 is the fractionation effect for any CO₂ equilibrated with water at 0 °C.

24576, L23: scale missing

24589ff, Fig 4 to 6: Please provide an identification with the events from Fig. 3

24587, Fig 2: The $\delta^{18}\text{O}$ stability data still exhibit a clear sinusoidal signature, which is not seen in the CO₂ mixing ratio. Where does this originate from? How can this be improved? Are these data used for correcting the $\delta^{18}\text{O}$ record?

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 24563, 2010.