Atmos. Chem. Phys. Discuss., 10, C12138–C12144, 2011
www.atmos-chem-phys-discuss.net/10/C12138/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Continuous isotopic composition measurements of tropospheric CO_2 at Jungfraujoch (3580 m a.s.l.), Switzerland: real-time observation of regional pollution events" *by* B. Tuzson et al.

Anonymous Referee #1

Received and published: 10 January 2011

General comments:

Overall, this is a well written paper describing and interpreting carefully made measurements. The scope of the paper is somewhat narrow, but it is still very much worthy of publication in ACP because it is essentially demonstrating a new source of data and presenting some very nice interpretation.

I think some of the interpretation, especially that of the CO:CO_2 ratios and the δ^{13}C signatures can be improved by taking account of more known processes that affect them.

I have specific suggestions to that effect below. On the other hand, the interpretation of the d18O signals is excellent, and I have just one suggestion to make another estimate of the d18O of soil water from observations.

Specific comments:

24564, l4: As admitted later in the paper, it's a bit dangerous to refer to JFJ as 'free troposphere', because while this is true most of the time, it sometimes may in fact be in the PBL as shown by high pollution signals. I suppose it is an open question as to whether or not JFJ is actually in the PBL or just receiving venting from the PBL. Nonetheless, the data presented here puts at least some doubt in the statement that JFJ is 'free troposphere'.

24564, l21: The current fossil fuel emissions are above 8 GtC/yr, not 6. See http://cdiac.ornl.gov/trends/emis/tre_glob.html (this has a doi and is referenceable.)

24565, l5: The value of ~19 per mil refers only to C3 plants and doesn't account for the ~20% of plants that are C4, and have a fractionation of about 4 per mil. Overall, the global average fractionation for terrestrial plants should be more like 15 or 16 per mil. (see e.g. Scholze et al, 2003, GRL; Suits et al, 2005, GBC).

24567 l4: Insert 'a' in front of 'mid-infrared'.

24567 l 28: What is NABEL? Explain or provide a reference.

24568 l1: The units of m3/hr are quite odd. More normal is L (or dmˆ3) per minute as is later used. Additionally, it should be stated explicitly that this is an STP volume by saying so parenthetically or by using 'standard liters per minute' (or SLM).

24568 l3: 'through a 15m stainless steel tubing' should be changed to: 'through 15m of stainless steel tubing' or 'through a 15m length of stainless steel tubing'.

24568 l7: When discussing the dilution effect of water, it would be helpful to read what the requirement of drying needed to be to avoid a bias of xx ppm. E.g., in order to

keep CO_2 dilution biases below 0.1 ppm, the dewpoint of the airstream needs to be kept below about -35C. Was the water vapor measured after drying? And if so, what was the typical dewpoint of the air? I wouldn't expect a water vapor dilution effect for the isotope ratios, but what is the sensitivity to broadening?

24568 l29: Remove 'exact' here. Isotopic ratios (as stated later in the sentence) are always relative to a standard reference material, whose isotopic composition is not known to absolute accuracy.

24569 l8: The 'CO_2 converter' is more commonly referred to, in my experience, as a 'methanizer'.

24569 l25: The compromise between the actual altitude and the model surface height seems reasonable, but it would be worth it to re-run the trajectories at the actual elevation of the measurements to see if there is any difference in footprint region (these simulations are very fast in my experience). The relief around JFJ is very steep so that using the actual height also seems reasonable – in other words, treat JFJ as an extremely tall tower above Switzerland.

24570 l22: The statement that 10 minute averaging can smooth out random measurement error is odd considering the 50s minimum in the Allan variance plots mentioned earlier. It would seem that 1 minute averaging is all that is needed to smooth out measurement error. Smoothing out environmental variability, on the other hand, could benefit from longer averaging times. The actual environmental variability and instrument variability (if I am reading correctly) should not be conflated.

24570 l26: For figure 2, again, why is 2 minutes chosen for averaging, when the Allan variance suggests 1 minute can be used with equal precision. Also, Fig. 2 would benefit from ^{13}C being added. I (and possibly other readers) would be interested to see these data.

24571 l1: 'precision' should be used here instead of 'accuracy', because the 0.08 ppm

(e.g.) comes from the width of the distribution, not the deviation of the median from the assigned value of Tank B. But, in fact, it would be very nice to know what the accuracy or bias is here, by comparing the field determinations of Tank B to its calibrated or assigned value. Can this be provided?

24571 l9: The work of Turnbull et al (2010) which is cited here clearly demonstrates that one cannot assume zero biological contribution to CO_2 signals, even in winter. Furthermore many other studies (e.g. Monson et al, 2006, Nature), show that respiration can be significant even in very cold environments. However, I believe it would still be reasonable to say that biological activity during this period is likely to be smaller than in other months, minimizing but not eliminating its effects on the interpretation of pollution signals.

24571 l12: Define or reference 'Foehn events'.

24571 l14-16: Change from '... allowed to ... and determining...' to 'allowed us to ... and determine...'

24571 l 29: change 'with partly' to 'partly with'

24572 l9: Using data from Spivakovsky, JGR, 2000 and the JPL rate constant data indicate that at 44 N in Jan in the lower half of the atmosphere, the lifetime of CO with respect to OH averages more 12 months. This doesn't significantly change your point, but I would change 'several months' to 'about a year'

24572 l9: While CO can be used as a tracer for fossil fuel, it is only quantitative if the flux-weighted average of all the emission ratios are known and there is no biological contribution. And, as several of the studies you cite show, (especially those using ^{14}C), the emission ratio can not simply be assumed from inventory data. I think 'quantitative' should be stricken; it's enough to say that it is a tracer.

24572 l13-14: Change: 'ratios are indicative for' to 'ratios indicate'

24572 l18: Were the regressions calculated using a 'model-II' regression (see Pataki,

2003 GBC and Miller, 2003, Tellus) which is necessary to avoid biases in these kinds of plots?

24572 l23-24: While it might appear that one could count on the background taking out the influence of the biosphere, I think this is unlikely. The enhanced pollution events seen at JFJ are coming from the surface, and this is exactly the location where biospheric respiration contributions are coming from as well. So, anytime pollution enhancements are seen, these are likely to be accompanied by respiration enhancements as well. One nice way to look at this would be using ^{14}C. (n.b. While Ingeborg Levin's group collects samples ^{14}C at JFJ, these are unfortunately two-week integrated samples from which the background and the pollution events cannot be disentangled.)

24573 l3: Unfortunately, high correlations are not necessarily an indication that CO:CO_2 emission ratios are well constrained. As shown in Turnbull et al, 2010, (and as explained in the comment directly above), biological CO_2 can be co-transported with fossil CO_2 and fossil CO preserving tight correlations, but giving biased apparent emission ratios.

While the ratios for event II III and IV may correspond well to the Swiss tunnel study cited, an examination of the footprints in Fig. 7 shows that only for event IV, is the footprint more Swiss than of any other nation. Events II and III show a much stronger influence from Italy and France, respectively, than Switzerland. This is significant because other studies give higher auto emission ratios: e.g. close to 0.020 ppm/ppm for Germany (as cited in Vogel et al, 2010, Tellus). I do not know if Switzerland stands out as having exceptionally clean burning cars within Europe, but given that JFJ is receiving air from all over Europe, the observed CO:CO_2 slopes of $\sim$0.010 ppm/ppm could also be indicative of higher fossil fuel emission ratios then diluted by a biological contribution. Similarly, the hypothesis of wood burning in event I is highly speculative, without knowing the emission ratios for cars and other industrial sources in central Italy.

I think the conclusions presented here are premature without considering emission

ratios throughout the regions of influence: not just Switzerland, and not just for cars. In terms of this paper, I do not insist on such an analysis (though it would be interesting to see), but rather that the authors not ascribe the apparent emission ratios (i.e. slopes) to Swiss auto emissions and acknowledge these other factors.

Finally, the analysis of 18O later in the paper is consistent with the presence of a significant amount of biological CO_2 reaching JFJ. Briefly, in order to explain the source signatures for 18O, the authors conclude that air must have had a significant residence time near the surface for invasion to have occurred. While invasion is an abiotic process, it requires liquid, not frozen, water to occur – the same conditions that are required for soil respiration.

24573 l8: What is the parenthetical (3) after 0.008? If an uncertainty, please write as 0.008+/- 0.003.

24573 l24-25. The $>$75 ppm range necessary for good statistics on Keeling plots is actually a function of the analytical precision. This range doesn't apply to the very nice precision of the QCL system in question here and this repeated statement from Pataki et al is a bit misleading and unnecessary.

24574 5-17: The interpretation here is a bit simplistic. The range of isotopic signatures across events could represent geographic variability in fuel mixtures, likely a variable amount of natural gas combustion (which is isotopically depleted relative to coal and oil). The number given by Andres et al (2000), is, I believe (I don't have access to the reference) a global number and is not specific to W. Europe, where natural gas usage is higher than the global average (see fuel type consumption in the cdiac reference given above). Along these lines, just because European emissions have not changed much, it does not mean the mix has been stable. In fact, looking at Switzerland (http://cdiac.ornl.gov/trends/emis/swi.html), we see a stable total masking a big rise in natural gas usage over the past 20 years.

Furthermore, for the same reasons that the CO:CO_2 ratios probably reflect a combi-

nation of fossil and biological sources, so to do these Keeling plot intercepts. These complexities should be acknowledged in the discussion – not merely as complications, but as opportunities to leverage the footprint information to gain insight into potential regional differences in combustion processes.

24575 l27: While the regression approach seems reasonable, I would also check the IAEA isotope hydrology data to see if it agrees with the current approach. Overall, I think the 18O analysis is very good.

24577 l12: Capitalize Foehn here.

24577 l20: As mentioned earlier about the regional δ^{13}C of fuels, the Netherlands and Belgium use about 30-40% natural gas (compared to Switzerland about 16%), which could help explain the -30 per mil signature from this event.

24580 l1: 'illustrates' to 'illustrate'

Fig2. Change Date (tt.mm.yyy) to Date (dd.mm.yyyy)

Fig 4. Explain more clearly (if this is the case) that the number in parentheses refers to the uncertainty in the last digit.

Fig5 and 6. Here the uncertainties are presented differently. I suggest choosing a uniform presentation.

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