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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The influence of traffic and wood combustion on the stable isotopic composition of carbon monoxide" *by* M. Saurer et al.

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The authors present some interesting data of wintertime CO, 13CO, and C18O abundances at three different sites within Switzerland. What the three sites represent are three cases; one mostly influenced by automobile exhaust, one by woodburning, and one by both. Given the fact that sampling was done during winter, when CO lifetime is long (at this latitude CO is essentially inert), d18O of CO should be a good tracer of the different combustion processes, if the source signatures don't vary much. However this does not appear to be the case. The r2 for the keeling plots of d18O vs 1/CO are low; lower than, say, that obtained in earlier studies (e.g., Mak and Kra, Chemosphere, 1999: Mak et al., JGR, 1994, I think) at continental sites. This is surprising.

I say 'appear', however, because the authors do not actually show the Keeling plots or any CO-d18O plots, but rather they show the y intercepts of the Keeing plots derived at different sampling locations (Figure 5). This is like having idiot lights in a car rather than instrument gauges. I would have much preferred seeing the range in values on the actual Keeling plots. Also, if the authors are correct in that about 30% of the total observed CO at the rural site is from background CO (Table 1), then one might expect a different y intercept on the Keeling plots as compared to the samples with higher concentration CO. Again, no plot; one can't tell.

The low r2, however, indicates either the experimentally determined source signatures are not representative of what is going on in the real world, or the d18O of background CO is varying more than thought, or there is some chemical (fractionation) process going on. In wintertime, there is probably not much removal going on (dry deposition of CO is mostly linked to biological acivity in the soil, which is nil in Switzerland in January), so one must suspect the first two possibilities. Looking at Figure 11, it appears that at the lowest CO concentrations centered around Feb 10, variation in d18O is greatest. This might be an indication that background CO (which should be around 120-140 ppb, depending on how one defines 'background') has a greater variability in d18O than assumed. It would have been nice to break down the CO-d18O relationship in different [CO] bins to see if this is the case; again, a full Keeling plot would have given an indication of this. I suspect too that the range in d18O from automobile exhaust is larger than assumed here; looking at Figure 3, showing CO near the motorway, we see [CO] up to 1800 ppb, yet d18O tops out at 20 per mil, and for the maximum CO concentration of 1800 ppb, d18O is actually lower than its maximum value by about 2 per mil. This indicates the d18O from automobile exhaust at Moleno is not 23.5 per mil, but 18 per mil or thereabouts, with a range of at least 5-6 per mil, which is twice as large as the assumed range of 2.8 per mil (page 19582). And, even though the authors state the range might be 2.7 per mil, they do not adjust their Figure 7 to reflect this. Likewise I am puzzled by the CO-d18O relationship at Roveredo (Figure 2). It is difficult to tell (again, a plot of d18O vs CO would have been nice), but looking at the first three data

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points in the time series, one sees a range in [CO] of 400-1300ppb, and a range of less than 2 per mil in d18O! And all three d18O values are quite enriched, at 17.5-19 per mil. During 11 January in particular, the CO-d18O relationship is clearly not robust. Why? The authors gloss over a potentially interesting (non)relationship. Outlying data points can give a lot of information regarding the assumptions that you are looking at a two-component relationship. In this case, they tell me that there is something else going on.

While it might be expected that CO and NOx would correlate in the wintertime if one is near a common source, and while the application of this ratio might appear to be robust, that doesn't seem to be consistent with the observations. Specifically, if I look at NOx/CO at Roveredo (Figure 4), I see a ratio varying from 0.006 to 0.04. This is far from the single value displayed in Figure 7. Secondly, the authors assert that there is a large difference in CO/NOx between wood burning and fossil burning, but the data don't support this. Taking the maximum CO value in Figure 3, at the motorway site, the CO/NOx ratio appears to be about 0.007. It would have been nice to plot the CO/NOx ratio at the motorway site (figure 3) so one could more easily compare that ratio with the one at the woodburning site. But at first glance it looks like both ratios at both locations vary by almost an order of magnitude. Therefore this makes the end members of any CO-NOx model to be so large as to have huge uncertainties associated with any conclusions attached to them. Clearly the NOx behavior is independent of CO behavior. The authors should ask what else influences NOx rather than force the hypothesis that the two should correlate, because they do not. For example, there might be large variations in the CO/NOx ratio from background CO (which is assumed to be constant in this model), which is not unreasonable, given the different lifetimes of the two species. This can be ignored if one is near a source during the winter, but certainly cannot be ignored if the CO is being transported from a great distance.

To conclude, I think the authors are stretching their interpretation a bit. They seem to assume that they should see a tight CO-d18O correlation and attempt to force the

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subsequent analysis to that assumption. I look at these data and see them telling a (possibly) different (and unresolved) story. I actually think that is the more interesting story to tell.

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