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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.

M. Saurer et al.

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We would like to thank reviewer 2 for carefully assessing the manuscript. We have prepared and submitted an improved manuscript based on the suggestions.

The concerns of Rev 2 centred on 1) the use of Keeling plots (or lack of showing them) and on 2) the application of the CO/NOx model and assumed distinct emissions ratios for wood-burning and traffic. Specific comments are:

* Rev 2): The r2 for the Keeling plots of d18O vs. 1/CO are lower than obtained in other studies. The authors do not actually show the Keeling plots.

We removed Figure 5, which showed only the y-intercepts of Keeling plots, and re-

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placed it with a Figure (also Fig. 5) showing the actual data plotted as d18O vs. 1/CO for Roveredo and Moleno, as well as the rural site PSI. We have shown these values separately for day and night values, and calculated all corresponding regression equations. We would like to stress that the classical Keeling-plot is based on a two end-member mixing model that only works (i.e. produces a linear relationship) for two (and not more) sources. These two sources are often considered to be 1) the background and 2) an additional source (see e.g. Pataki et al. 2003), as described also in Section 2.3.2. We therefore are convinced that in situation with more than one pollutant, as is the case in our study, the use of Keeling plots can only give a limited insight, while our isotope source separation model with 3 sources is more appropriate. Nevertheless, we agree that it is important to show the Keeling plots for the data visualization and help in interpretation. The low r2 that is apparent from Fig. 5 actually clearly indicates that a 2-source-model is not applicable. The influence of wood-burning with relatively low d18O compared to traffic results in the scatter in the plot, because the mixture of these two pollutants is not constant over the course of a day. Based on this new Fig. 5, the section 3.4 has been completely re-written, but we want to emphasize that we are proposing our model to be used instead of the simple Keeling plots and therefore do not rely on their interpretation only. The corresponding part in the "Results and Discussion" was also re-written, e.g.: "The correlation coefficients are lower than in other published studies (Brenninkmeijer et al., 1999), reflecting the fact that there are more than two components to be considered at the studied sites. As we have shown, there are large diurnal variations in the contribution of wood-burning and traffic to the CO load and accordingly there does not exist a unique y-intercept, i.e. source isotope signal, which results in the scatter observed in Figure 5." etc. The Keeling plot for the rural plot PSI (shown now in Figure 5, lower panel) shows a much tighter relationship, both for day and night values. We believe that this is due the a less variable mixture of pollutants reaching this location, which is farther away from emissions. The corresponding parts in the Results (3.8) and Discussion and Conclusions were re-written.

* Rev 2): The d18O of the background is varying more than thought, the range in d18O

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from automobile is larger than assumed here

We agree that the isotopic composition of the different sources can vary considerably. Firstly, we have considered this point as explained in more detail in the answer for Reviewer 1. We expanded the sensitivity analysis and included also the case of d18O-traffic=20.0 per mil. The performance of the model was tested for a range of d18O-wood-burning and d18O background for this different traffic value resulting in the new Figures 10 d, e, f. It is apparent that the model is relative insensitive towards changes in d18O-traffic, but in general lower r, slope and higher offset are found for d18O-traffic=20.0 per mil, indicating a better model performance for a traffic value of 23.5 per mil.

On the other hand, as a response to this point, we indicate and discuss on multiple places in the manuscript that source uncertainties are significant. For instance, in Results 3.7: "Besides the uncertainty in the CO/NOx separation due to uncertain emission ratios, the agreement between modelled and measured values depends strongly on the assumed isotope values for the different sources." And at the beginning of "Results and Discussion": "Regarding traffic CO emissions, values could be close to the value of atmospheric O2 under ideal combustion conditions (hot engine) and in the absence of fractionations. A range of values was, however, reported for car emissions,..." and the following sentences. And towards the end of the manuscript: "More studies with better definition of the source isotope values would clearly be helpful to verify the approach. This could be done with the help of Keeling-plot analyses in situations where one pollutant dominates. Once the source values are better characterized the isotope mass balance equation may be more widely applied."

* Rev 2): 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, 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

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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.

As a response to this point, we have included a graph of the time course of CO/NOx in Roverdo and Moleno (Figs. 2 and 3), shown together with CO and NOx (we removed PM10 instead from these figures). The level and diurnal course of CO/NOx at the two locations is very instructive in our opinion and indeed helps a lot in understanding the different emission ratios of wood-burning and traffic and therefore helps demonstrating and justifying the use of the CO/NOx model: The CO/NOx ratios in Roveredo show much increased values during the night, compared to the day (up to 0.04), obviously due to the influence of wood-burning, whereas there is only a small diurnal cycle of CO/NOx at the motorway site and much lower values throughout ($<$0.01). Corresponding changes in the Text were made, e.g. in 3.2.: "CO/NOx ratios were strongly enriched during the night, when traffic was minimal. It is known that due to a lower combustion temperature, much more CO and less NOx is emitted by wood combustion compared to traffic (Johansson et al., 2004; Kirchstetter et al., 1999). Therefore, the ratio of CO/NOx can be used as an indicator of the relative emission strength of wood burning and traffic. Qualitatively, it seems obvious that the low d18O values and high CO/NOx in Roveredo at night reflect the influence of wood burning." We would also like to mention that values displayed in Fig. 7 are well compatible with the CO/NOx ratios shown in Fig. 2 for Roveredo. We have made reference to the changed Figures in the text. We also removed the CO/NOx values from Fig. 4 and changed the corresponding text. Furthermore, we provide independent evidence for the influence of wood-burning with the aethalometer results and therefore can confirm that CO/NOx ratios very likely are an indicator of wood-burning vs. traffic, which would not possible in a study with CO and NOx measurements only. We are convinced that the combination of different methods that we provide (isotopes, CO/NOx, aethalometer) results in a high degree

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of confidence about the relative source contributions. We agree with reviewer 1 who considers the combination of the CO/NOx- and isotope models as a strength of the manuscript.

* Rev 2): The authors seem to assume that they should see a tight CO-d18O correlation

We think that our conclusions are valid based on the presented evidence. We actually do not presume a linear relationship between 1/CO and d18O for ambient samples, but rather think that a 3-source model as presented is more appropriate.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 19561, 2008.

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