

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.

Received and published: 25 February 2009

We would like to thank reviewer 1 for carefully assessing the manuscript. We have prepared and submitted an improved manuscript based on the suggestions.

Rev 1 saw a particular value of our study in the combination of the CO/NO_x and isotope-models, but had the following comments/questions:

* Rev 1): Why restrict to 3 sources? Shouldn't industrial sources be considered?

We agree that assuming only 3 sources (wood-burning, traffic, background) is a simplification, but think that a more complex model would not be sufficiently constrained by the data. The uncertainty in the source isotope values is considerable, as discussed in

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



the manuscript, and therefore adding another source, which is not well known, would further complicate matters. We agree, however, that industrial sources could contribute to the CO load, although probably not to a very large degree at the studied sites, and therefore mentioned this point in the introduction and in the discussion.

* Rev 1): What defines the background? Is it a constant? I don't agree that the background value for NO_x is nil.

The background concentrations were determined from the lower limit of observed values and we assume that as long as only a period of a few days is investigated, the background can be considered as constant. When synoptic weather patterns are changing, the background could be different. The background influence is determined by admixture of clean air from above the inversion layer, which occurs at the valley site, e.g., by down-slope winds at night. This was discussed in "Results and Discussion".

We agree that the NO_x background may not be zero and therefore changed our equations and calculations. Equations 11, 13, and 14 were adapted for a "NO_x-Bgd" term. This makes the equations more general and complete. We recalculated and replotted Fig. 8 (CO split into different sources based on the CO/NO_x-model) and Fig. 9 (Comparison of calculated and modelled d18O) when assuming a background of 5ppb as deduced from the lower limit of observed values. Calculated proportions of CO from wood-burning were on average 1.5% higher for Roveredo and 0.9% higher for Moleno (compared to calculations for NO_x_bgd=0), while corresponding traffic-contributions were lower by the same amounts. These changes are therefore small, but were incorporated in all corresponding places in the Results and Discussion, e.g. considered also in Table 2, where a slightly lower dependence of the calculated wood-burning contribution on the emission ratios was found. Regarding the combined CO/NO_x/isotope model, the agreement between modelled and measured d18O did not change (*r* is still 0.67) after considering the NO_x-background.

* Rev 1): Regarding Fig. 1 (wood-stove experiment): When was the sampling done?

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Why is there a mixing line? What is at the other end of the mixing line?

As a response to these points, we have explained Fig. 1 in more detail in the Results section 3.1. While one fire lasted approximately 30 minutes, samples correspond to 3 minute filling time of the sample containers and were taken 3 times during each fire as apparent from Fig. 1. CO concentrations were not constant during the fires, due to different temperatures (details can be found in Weimer et al. 2008 which is listed as reference). Additionally, the mixing of the combustion gas with the dilution gas (compressed air) has to be considered. The mixing line in Fig. 1 when plotting $1/\text{CO}$ vs. $\text{d}18\text{O}$, therefore should mainly be interpreted for the y-intercept, which corresponds to the pure wood-burning $\text{d}18\text{O}$ signal according to the Keeling-plot equations, while the other end-member is determined by isotopic signal of the dilution air, which must have a relatively low $\text{d}18\text{O}$ value.

* Rev 1): The discrimination used between the wood and road traffic emissions heavily relies on the assumption that road traffic $\text{d}18\text{O}$ is restricted to the atmospheric oxygen value of 23.5per mil

This point, mentioned also by Reviewer 2, is indeed a significant issue as there are several indications from our results that the oxygen isotope ratio of the traffic emissions are not constant and could be lower than 23.5per mil. While a separate study of emissions was beyond the scope of this work, we have expanded the Discussion on this point and, in particular, have extended the sensitivity analysis (Fig. 10). While previously a fixed value of $\text{d}18\text{O}_{\text{traffic}}=23.5\text{per mil}$ has been assumed, when varying $\text{d}18\text{O}_{\text{wb}}$ and $\text{d}18\text{O}_{\text{traffic}}$ (Fig. 10 a, b, c), we have now repeated the analysis for $\text{d}18\text{O}_{\text{traffic}}=20\text{per mil}$ (a value derived from Kato et al. 1999b for an average traffic mix), which resulted in the new Figures 10 d, e, f. The results suggest that the performance of the isotope model (in terms of r , slope and offset) decreases for a traffic-value of 20per mil, but not in a very significant way. We also changed the value for traffic in Fig. 1 from 23.5per mil to a range of 20 - 23.5per mil and adapted the text at various places to emphasize more the potential range of values and associated uncertainties,

also in the Abstract. In the Introduction, e.g., we added "Regarding CO emission from cars, diesel exhausts can have a much lower oxygen isotope composition of about 11per mil compared to atmospheric O₂ (23.5per mil) due to fractionation effects, while even lower values down to 6per mil have been observed for cold gasoline engines (Kato et al., 1999b). While such differences can hamper an unambiguous source apportionment, it should be considered that a traffic mix of many cars should have a more well defined isotopic composition, determined, e.g., to be 20.7per mil +- 0.5per mil for Mainz, Germany (Kato et al., 1999b)."

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

ACPD

8, S11417–S11420, 2009

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

