Method to Calculate Modified Combustion Efficiency and its Uncertainty

Supplement to:

Particulate Matter, Ozone, and Nitrogen Species in Aged Wildfire Plumes Observed at the Mount Bachelor Observatory

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Enhancement ratios (ERs) are a useful tool to understand emissions and chemical transformations of plumes during transport. However, as pointed out by Yokelson et al. (2013), the calculation of ERs may be confounded by dilution from multiple background airmasses. Here we focus on the Modified Combustion Efficiency (MCE), which is similar to an ER. MCE is defined as:

$$MCE = \Delta CO_2 / (\Delta CO_2 + \Delta CO) \qquad (S1)$$

where ΔX (carbon dioxide [CO_2] or carbon monoxide [CO]) represents the in-plume enhancement, compared with the out of plume background:

$$\Delta X = X_{plume} - X_{background} \qquad (S2)$$

The MCE shows the degree of completeness for a combustion process. An MCE of 1 represents complete combustion, with all carbon in the fuel being emitted as CO_2. Typical MCE values for wildfire biomass combustion are 0.80-1.00. We have developed a method to calculate the MCE using a range of possible background mixing ratios and include an uncertainty calculation for the resulting MCE. Measurements of the plume mixing ratio of CO_2 or CO are straightforward. The challenge is to identify the correct background mixing ratio to use. In general, larger plumes exhibit smaller uncertainties, due to the fact that background variations become less important.

Our observations of wildfire plumes were made at the Mount Bachelor Observatory (MBO), located on the summit of Mount Bachelor. This site experiences strong diurnal variations in temperature, ozone (O_3), water vapor, and other parameters. Previous work has found that MBO usually experiences free tropospheric air during the night and modified (or mixed) boundary layer air during the day (Reidmiller et al., 2010; Ambrose et al., 2011; McClure et al., 2016). Fig. S1 shows the mean and median diurnal pattern of CO_2 and water vapor mixing ratios for August 2013. The figure shows that upslope air, which occurs during daytime, is more humid and lower in CO_2.

Fig. S2 shows a wildfire plume that was transported to MBO on 16 September 2012. The plume first appeared in the morning and reached a maximum around 1745 GMT (0945 local solar time [LST]). At the same time, water vapor mixing ratios were increasing, so this plume was most likely transported from the boundary layer up to the observation site. This would also be consistent with the average diurnal pattern shown in Fig. S1.

At MBO, boundary layer transport of wildfire plumes is common, but some plumes also arrive in free tropospheric airmasses. Either way, the background value is uncertain due to the transport of the plume away from its source. We consider three possible values for the background: the local minimum immediately prior to observations of the plume; the observed value at 1600 LST (0Z); and the median 0Z value for that month. Use of the 0Z values at MBO allow one to include information on the background mixing ratios in the boundary layer (where the fire plumes were formed) during the afternoon. Note that the usual procedure is to use the local minimum, but as pointed out by Yokelson et al. (2013), this may introduce a significant bias into the calculation. We then calculate $X_{background}$ (for both CO and CO_2) using the average of these three background estimates for each plume.

The uncertainty in the MCE is based on a standard "propagation of error" computation, also known as the delta method, derived from a first order Taylor series approximation of the nonlinear expression for MCE.

$$\delta M = M^* [(\delta[A+B]/[A+B])^2 + (\delta A/A)^2 - 2(\delta A^2)/(A[A+B])]^{½} \qquad (S3)$$

where M=MCE; A= ΔCO_2, B=ΔCO, and δ refers to the uncertainty (standard deviation) of the corresponding terms.

For CO_2 and CO, we do not have a true standard deviation, but assign the uncertainty to be half the range in the three background values. The final uncertainty value also includes uncertainty due to measurement error.

Table S1 shows five example plumes with a range of MCE values and uncertainties. The first (shown in Fig. S2) and the second example are both from the Pole Creek Fire, a large fire that burned over several days about 20-30 km from MBO. The large CO and CO_2 enhancements for these plumes indicate that the background variations are relatively unimportant in calculating the MCE. For the large plume on 19 September 2012 (plume #2), the CO_2 enhancement is more than 56 ppmv and the uncertainty is dominated by the instrumental/measurement uncertainty. Plumes 4 and 5 (in Table S1) both exhibit modest CO_2 enhancements; however, in the case of plume 4, the three background CO_2 mixing ratios are in good agreement and thus the overall uncertainty in MCE is relatively small. For plume 5, the CO_2 enhancements are relatively small and the variation in background is significant, so the overall uncertainty is substantial (±0.14).

In summary, we have developed a method to calculate the MCE and its associated uncertainty. The method considers multiple possible background mixing ratios, and uses these to calculate the uncertainty in the MCE. This analysis demonstrates that large, concentrated fire plumes have small uncertainties in the calculated MCE, whereas plumes with small enhancements will have much larger uncertainties.

References

Ambrose, J.L., Reidmiller, D.R., Jaffe, D.A. (2011). Causes of high O(3) in the lower free troposphere over the Pacific Northwest as observed at the Mt. Bachelor Observatory. *Atmos. Environ.* 45: 5302-5315, doi:10.1016/j.atmosenv.2011.06.056.

McClure, C.D., Jaffe, D.A., Edgerton, E.S. (2016). Carbon dioxide in the Free Troposphere and Boundary Layer at the Mt. Bachelor Observatory. *Aerosol Air Qual Res.16, 717-728,* doi: 10.4209/aaqr.2015.05.0323.

Reidmiller, D.R., Jaffe, D.A., Fischer, E.V., Finley, B. (2010). Nitrogen oxides in the boundary layer and free troposphere at the Mt. Bachelor Observatory. *Atmos. Chem. Phys.* 10: 6043-6062, doi:10.5194/acp-10-6043-2010.

Yokelson, R.J., Andreae, M.O., Akagi, S.K. (2013). Technical Note: Pitfalls with the use of enhancement ratios or normalized excess mixing ratios measured in plumes to characterize pollution sources and aging. *Atmos. Meas. Tech.* 6: 2155-2158, doi:10.5194/amt-6-2155-2013.

Table S1. MCE calculations for five wildfire plumes.

Plume number	Plume date and time (GMT)	ΔCO_2 (ppmv)[1]	ΔCO (ppmv)[1]	Uncertainty in ΔCO_2 (ppmv)[2]	Uncertainty in ΔCO (ppmv)[2]	MCE	Absolute uncertainty[3]
1	16 Sept. 2012 1615-2155	9.04	1.51	1.96	0.03	0.86	0.04
2	19 Sept. 2012 0015-0745	56.81	8.99	2.28	0.13	0.86	0.01
3	21 Sept. 2012 0015-700	7.94	0.92	1.94	0.01	0.90	0.03
4	13 Aug. 2013 1225-1640	3.85	0.25	0.86	0.03	0.94	0.05
5	15 Aug. 2013 1200-1405	3.37	0.12	2.31	0.05	0.97	0.14

[1]The enhancements (or Δ) are calculated using the plume maximum and the average of the three background values.
[2]The uncertainty in the enhancements is assumed to be half of the range of the three background values, plus the measurement uncertainty.
[3]The absolute uncertainty in the MCE is calculated using Equation S3.

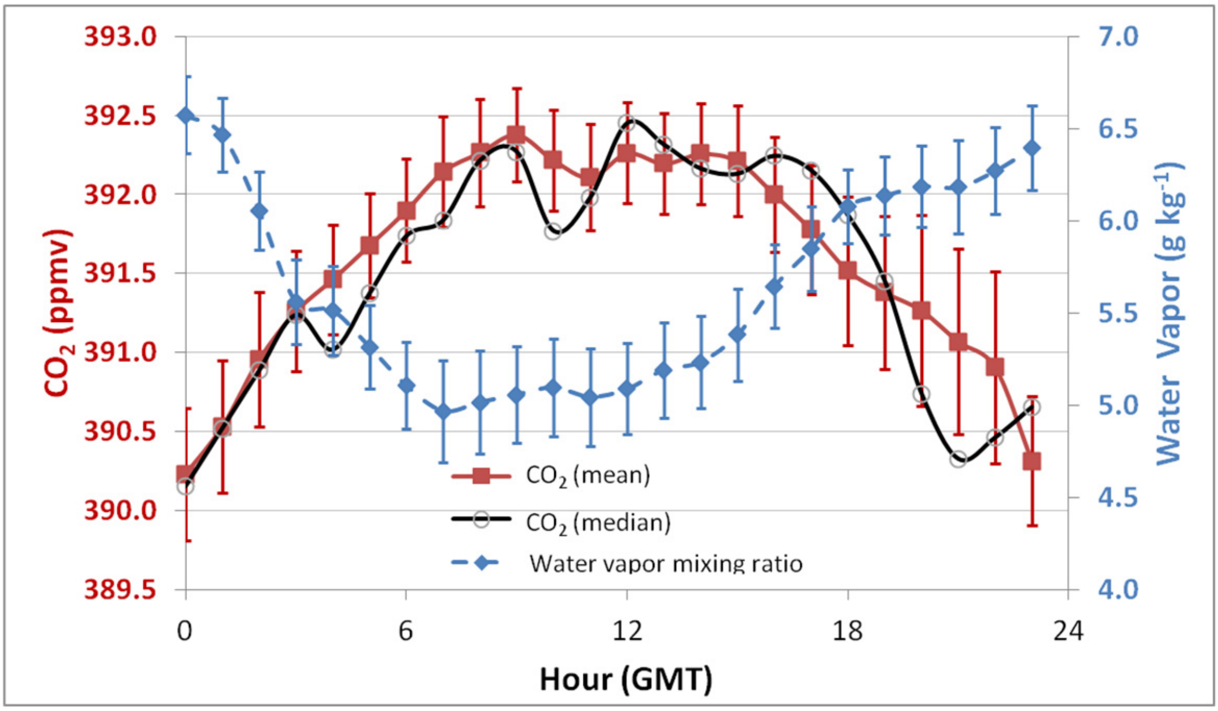

Fig. S1. Mean and median CO_2 mixing ratios measured at MBO in ppmv for August 2013 vs. hour (GMT). The error bars show the standard error of the mean. Also shown is the water vapor mixing ratio in g kg^{-1}. The downslope free tropospheric air occurs at night between hours 0400-1600 GMT (2000-0800 local time). This air is drier and higher in CO_2. The upslope air is more humid and lower in CO_2 (1600-0200 GMT, 0800-1800 local time).

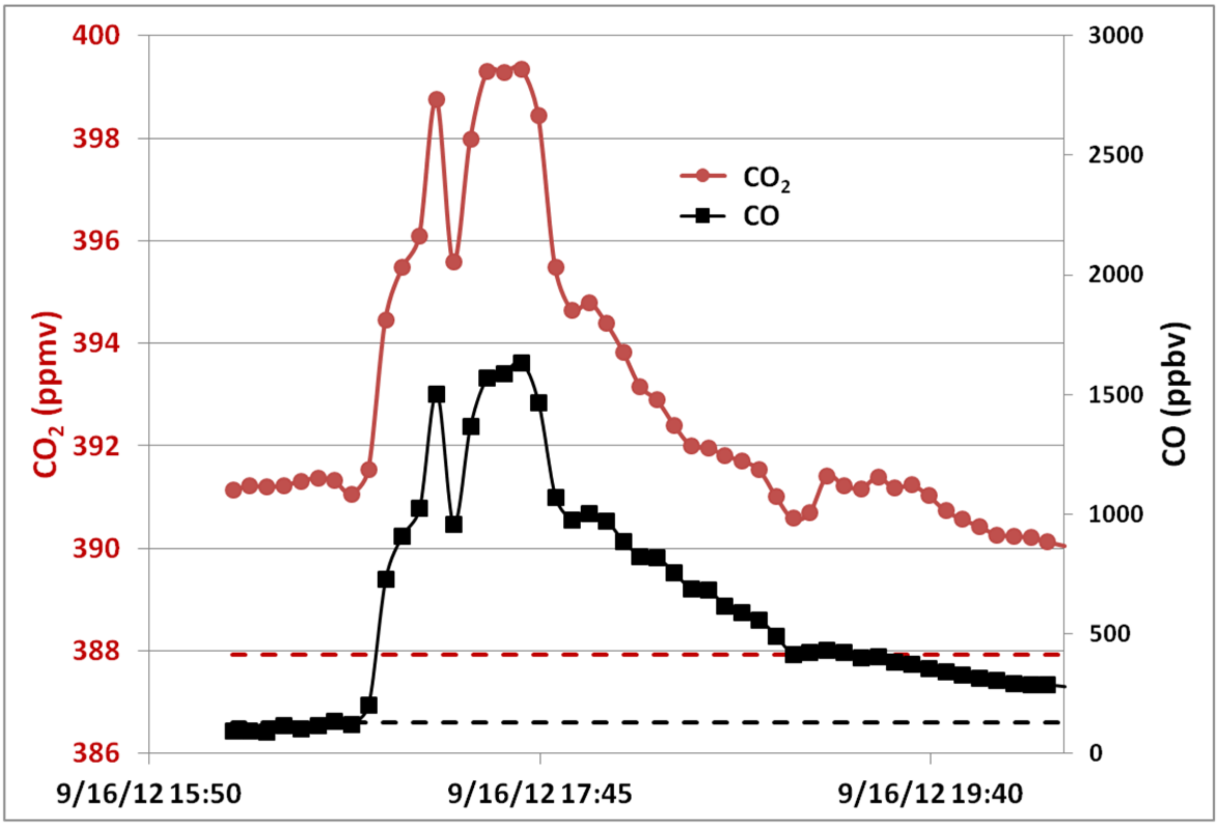

Fig. S2. CO_2 (left axis) and CO (right axis) mixing ratios in a wildfire plume observed at MBO on 16 September 2012. Back-trajectories and other data indicated that the source was the Pole Creek fire in central Oregon (Baylon et al., 2014). The dashed lines show the 0Z median values for the same month, as observed at MBO.