

Interactive comment on “Influence of biomass burning and anthropogenic emissions on ozone, carbon monoxide and black carbon concentrations at the Mt. Cimone GAW-WMO global station (Italy, 2165ma.s.l.)” by P. Cristofanelli et al.

Anonymous Referee #2

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General comments:

This paper describes the observations of O₃, CO and BC at the Mt Cimone GAWWMO station and analyzes the interannual and seasonal variability observed using trajectory calculations with the FLEXPART model. More particularly, the relative contributions from biomass burning and anthropogenic emissions to the observed variability is discussed. The correlations between the observed species is also investigated.

This paper is clearly written and organized, and provides a comprehensive analysis of an important dataset, allowing the monitoring of atmospheric composition in a Mediterranean background. It is therefore interesting for the atmospheric chemistry community and I recommend publication with minor corrections/precisions, as detailed below.

AR: the authors would like to thank the referee for his important remarks that helped us to identify some weakness or obscure points in .the paper. In the following we provided point-to-point replies to the referee’s comments and we modified the manuscript basing on that .

Specific comments:

My main comment is that all source attribution is based on CO tracers simulated by the FLEXPART trajectory model. There should be more discussion about the reliability of this tool and of this approach. I think it’s a very useful approach to get a first idea, but the conclusions are subject to uncertainties due to transport errors and – probably more importantly – to emissions uncertainties. The biomass burning emissions are extremely difficult to estimate so that I think the CO_{fire} tracer should be discussed more carefully. Although the main signatures are generally correct, specific events may be strongly over or underestimated.

This needs to be discussed as possible explanations for the negative CO enhancements values for the BB events III and IV. It is long range transport so one really expects enhancements of CO. Since it has been transported over long distances, the probability that there was transport errors in the simulations is increased. Maybe the plume actually traveled a little bit North? A quick look at satellite observations may provide useful indications (MOPITT has online visualization pages at NCAR for instance, and there is also IASI CO for 2009). Diffusion of the CO plumes during long-range transport is generally overestimated in the simulations compared to “reality”. In addition to transport errors, uncertainties on the emissions may be critical. I think that the discussion of the ER for these too plumes is therefore not convincing, and should be discussed separately and with caution.

AR: The point raised by the referee is important. FLEXPART showed to be accurate in capturing long-range transport, including BB plume (e.g. Stohl et al., 1998, 2006, 2007; Forster et al., 2001; Damoah et al., 2004; Lapina et al., 2008) and has an excellent agreement with observations for a complex BB event occurred in the Mediterranean on August 2007 included in our analysis(Event II) and described in detail by Cristofanelli et al. ACP 2009. However, the simulated transport can be inaccurate in individual cases and it is therefore important to use additional data to confirm a long-range transport episode. For these reasons, we performed some additional analysis to have a qualitative assessment on the reliability of the FLEXPART analysis for the biomass burning (BB) long range transport events.

Event III

The FLEXPART simulations clearly diagnoses transport from North America jointly to CO emissions derived from active fire observations (see Fig. S3 of the submitted manuscript). CO

observations at CMN (Fig. A1) shows a CO enhancement up to 170 ppb in coincidence to the signature of BB transport by FLEXPART. Nevertheless, measurements cannot be used to unambiguously identify this event since (1) observed background CO is higher than in summer and closes to the observed peak and (2) measurement of species (i.e. terpenes, levoglucosane) that may clearly disentangle different contributions to CO were not available. Finally, despite the compactness of the air parcels transport diagnosed with FLEXPART up to 10 days prior to the observation (Fig. A2), uncertainty in transport may provide a positive false in our analysis).

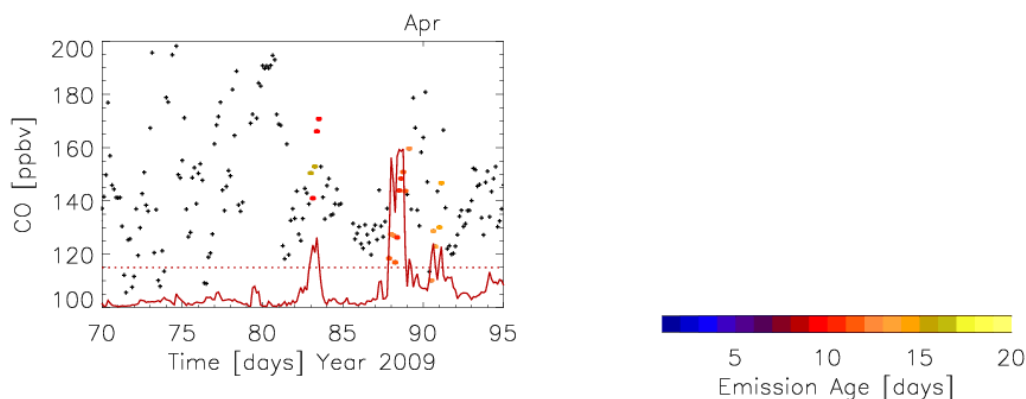


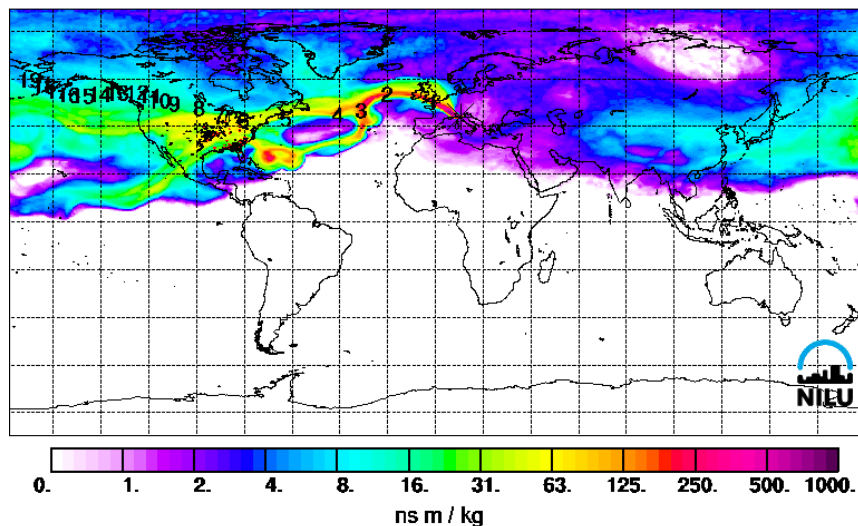
Fig A1. Time series of observed CO concentration at ICO-OV (black dots) with FLEXPART CO_{fire} (red line) for March-April 2009. Observations at ICO-OV are tagged with the FLEXPART fire emission age (colour scale). FLEXPART CO is plotted with a positive bias of 50 ppb to reduce the extent of y-axis.

Column-integrated emission sensitivity in global domain for MTC_200903

Start time of sampling 20090324. 0 End time of sampling 20090324. 30000

Lower release height 2165 m Upper release height 2165 m

Meteorological data used are from ECMWF



Maximum value 0.977E+03 ns m / kg

Fig A2: Emission sensitivity integrated over the entire atmospheric column. The numbers superimposed on the shading are the days back in time for the retroplume centroid

Satellite MOPITT CO observations provide a partial support to identify a likely role of BB emissions: from March 16 to 18 (MOPITT_CO_V2_val_20090316-18) they indicates a CO enhancement in Central North America, in concomitance with the emissions diagnosed by FLEXPART. During the following 3 days (MOPITT_CO_V2_val_20090318-21) a CO plume bulged eastward over the Atlantic Ocean. Later MOPITT observations(21-23 March 2009) still indicates a possible increase on the total CO column in Eastern North Atlantic but it cannot be unambiguously discerned over continental Europe (Fig. A3).

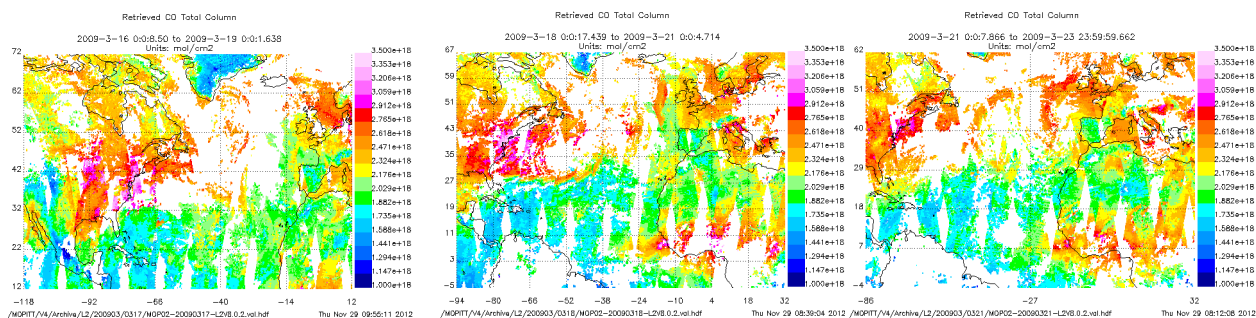


Fig A3: MOPITT CO for 16-18 March, 18-21 March and 21-23 March 2009.

Nevertheless, the role of distant CO sources due to long range transport patterns is further diagnosed by FLEXPART indicating that anthropogenic CO from American continent were enhanced from March 23 and lasted, although with minor concentrations, for the following days (http://niflheim.nilu.no/~burkhart/EUCAARI/MTC/MTC_200903/ECMWF/AGESPECTRUM_AMERI_CAN.html)

Event IV

FLEXPART column-integrated emission sensitivity (Fig. A4) indicates that transport from West Africa CO sources is plausible, due to the compactness of the air parcel cluster and that the event is related to a transport pattern that lasted from March 28 to April 1st (see below).

Column-integrated emission sensitivity in global domain for MTC_200903

Start time of sampling 20090328.210000 End time of sampling 20090329. 0

Lower release height 2165 m Upper release height 2165 m

Meteorological data used are from ECMWF

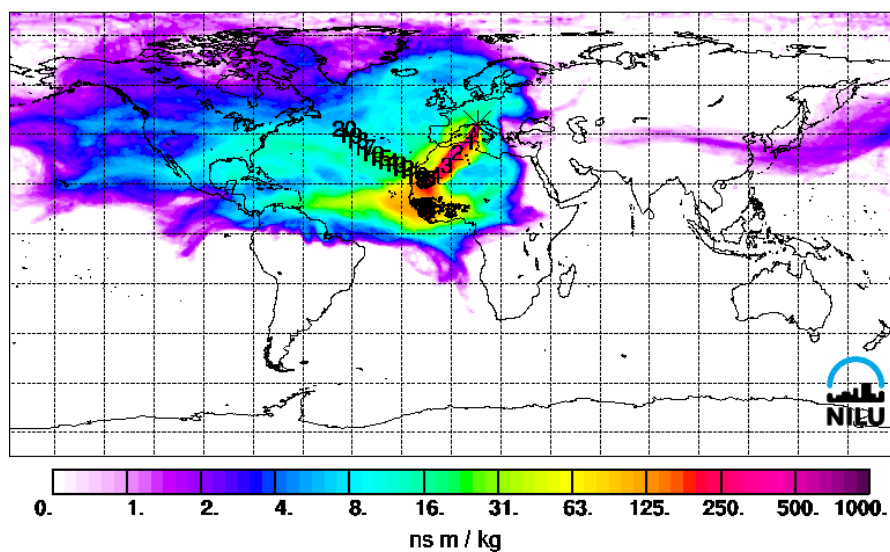


Fig A4: Emission sensitivity integrated over the entire atmospheric column. The numbers superimposed on the shading are the days back in time for the retroplume centroid. The small dots over West Africa indicated the location of MODIS hot-spot fires.

In the same period CO at CMN increased up to 160 ppbv (see Fig. A1); nevertheless should be given the same caveats of event III.

In this case MOPITT (Fig. A5) observations still confirm the presence of a CO plume on 24 – 26 March 2009 over West Africa (where FLEXPART diagnosed BB emissions, see Fig. S4 of the submitted manuscript), with a tongue of air-mass rich in CO is present offshore of the African coastlines. During the following days (particularly during 30 March – 1 April, 2009), a stream with high CO is detected by MOPITT extending from North Africa to the Mediterranean basin and North Italy, as well. However, it should be noted that the retroplume centroid is shifted northward in

respect to the MODIS fire location. Nevertheless a large fraction of simulated air particle travelled over the BB areas (see, http://niflheim.nilu.no/~burkhart/EUCAARI/MTC/MTC_200903/ECMWF/global_retroplume/MTC_200903.global_retroplume_224.html). Thus, contributions from fires are likely for this case, even if mixing with air-masses from Atlantic Ocean is also possible. Finally it should be noted (Fig. A1) that Event IV is also characterized by an enhancement in CO that occurs 24 hours after the arrival of the BB potential contribution (which contribute to the $\Delta\text{CO} < 0$ ppb observed during the BB event). Even if possible error in the timing of the plume arrival at CMN cannot be ruled out, nevertheless no clear BB signature can be seen in O₃ and BC data for this latter CO increase (not shown).

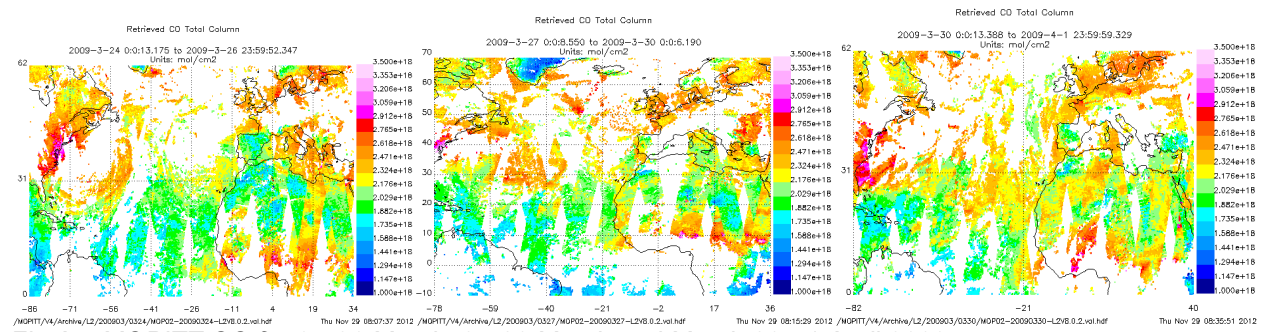


Fig A5: MOPITT CO for 24-26 March, 27-30 March and March 30 - 1 April 2009.

Also basing on these evidences, we discuss the Events III and IV separately as suggested by the referee and by highlighting a caveat on the possible uncertainties modifying the discussion in section 3 and Conclusions. We prefer to limit the inclusion of all additional material presented here to avoid to smear out the results of this paper that, in any case, indicates that biomass burning have an overall small contribution to the CO budget at CMN.

In particular, in the Section 3, we added the following sentences: “FLEXPART showed to be accurate in capturing long-range transport, including BB plume (e.g. Stohl et al., 1998, 2006, 2007; Forster et al., 2001; Damoah et al., 2004; Lapina et al., 2008). However, the simulated transport can be inaccurate in individual cases and it is therefore important to use additional data to confirm a long-range transport episode. For these reasons, we performed some additional analysis to have a qualitative assessment on the reliability of the FLEXPART analysis for these BB long range transport events. As shown by Figure 3bis, Event III is characterized by an increase of CO up to 170 ppbv. Nevertheless, due to the relatively high CO values occurring before and after the event, ΔCO was negative. Event IV is also characterized by CO up to 160 ppb. However, a further enhancement in CO occurred 24 hours after the possible arrival of the BB plume. Even if possible error in the timing of the plume arrival at CMN cannot be ruled out, nevertheless no clear BB signature can be seen in O₃ and BC data for this latter CO increase (not shown). It is not possible to disentangle the role of uncertainty in air parcel position and timing related with transport simulation, that may induce an erroneous attribution, and the limits in detectability of the event from observations, due to a highly variable background that may hide CO increase related with BB emissions. Nevertheless, even if it is difficult to provide a definitive attribution of those events, the arguments supporting a realistic impact of BB emissions for these two events are (1) the compactness of the FLEXPART retroplume that indicates a persistent and robust transport pattern; (2) the biomass burning emission based on fire observations, further supported by satellite CO observations (MOPITT instrument on board of on NASA's EOS Terra spacecraft) showing enhanced CO in the BB source regions identified by FLEXPART (not shown here).”

In the Conclusions, we mentioned that: “FLEXPART showed to be accurate in capturing long-range transport, including BB plume (e.g. Stohl et al., 1998, 2006, 2007; Forster et al., 2001; Damoah et al., 2004; Lapina et al., 2008). Especially for individual events of long-range BB transport, some uncertainties can affect the identification of the BB transport event at CMN, due to air-mass transport simulation, identification of fires and estimate of emissions. However, as also shown by MOPITT satellite measurements for two case studies of long-range BB transport, FLEXPART seems to be able in describing the impact of BB emissions.”

For the discussion of the ER in the BB plumes, it would be very interesting to link the slopes with the age of the plumes. A link to the source region and type of vegetation burnt would also be extremely useful in order to better understand the information available in these observations.

AR: our estimated emission age of the BB plumes are already reported in the Table 1 together with enhancement ratios (i.e. slope of the linear fit) of O₃ and BC in respect to CO for the 5 “representative” events. However, following the referee suggestions and with the aim of providing a more “robust” assessment, we discussed the ERs calculated for all the 16 BB events detected by the FLEXPART model. In particular, we added (on Section 4) the following sentences: “To provide a more robust characterization of the O₃/CO and BC/CO ER as a function of the BB plume ages, we considered the 16 BB events identified by FLEXPART (Fig. 5). By excluding event IV (as discussed before) and a further very old BB event (representative emission age: 273 hours), we observed for O₃ a good qualitative agreement with previous investigations showing a general increase of ER values with the ageing of BB plumes (e.g. Pfister et al., 2006; Val Martin et al., 2006; Real et al., 2007; Cristofanelli et al., 2009), probably indicating the role of PAN, HNO₃ and organic nitrates, which favour the photochemical formation of O₃. On the other side a general decrease of ERs with increasing emission age has been observed for BC, possibly related to a more efficient scavenging of aerosol particles during long atmospheric transport.”

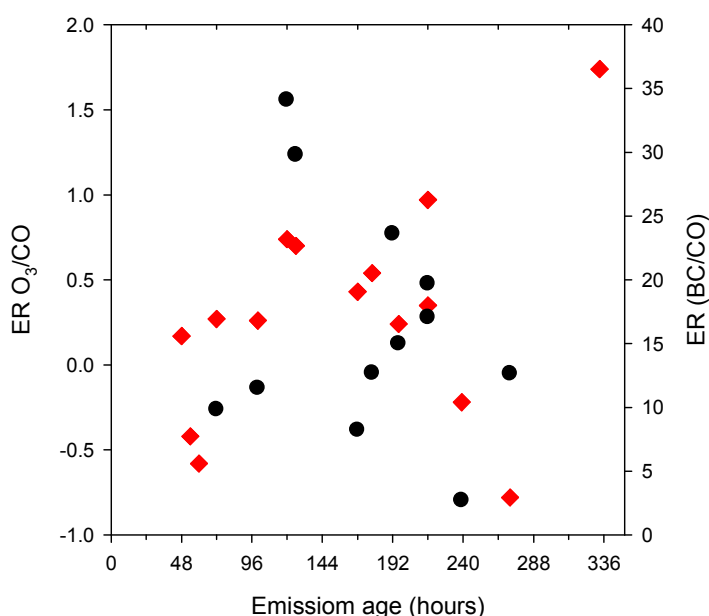


Figure 5. ERs of O₃ (red) and BC (black) relative to CO observed for the 16 BB events detected at CMN by FLEXPART.

We also tried to relate the calculated ERs with source region and type of vegetation burnt but we did not obtain any robust relationship between these parameters. We commented this point in the manuscript as following: “On the other side we did not obtain a clear relationship between the type of vegetation burnt or the different source regions with the ERs. This could indicate that the plume aging is the main parameters for determining ERs in relatively aged (i.e. older than 2 days) BB plume. However, a number of uncertainties related with the actual type of combustion (e.g. smoldering vs. flaming), actual composition of the fuel, its moisture and structure (see Andrae and Merlet, 2001) can affect our results.”

In the discussion of the anthropogenic contributions, it would be interesting to indicate the region of origin in the case of aged plumes/long-range transport.

AR: With the aim of answering to this point, we performed a new analysis of FLEXPART outputs. In particular, we calculated the average contribution to the total CO_{ant} at Mt. Cimone for the

different source regions “tagged” by FLEXPART (i.e. Europe, Asia, North America and other continents). The result of this elaboration is reported in Section 5, Figure 7.

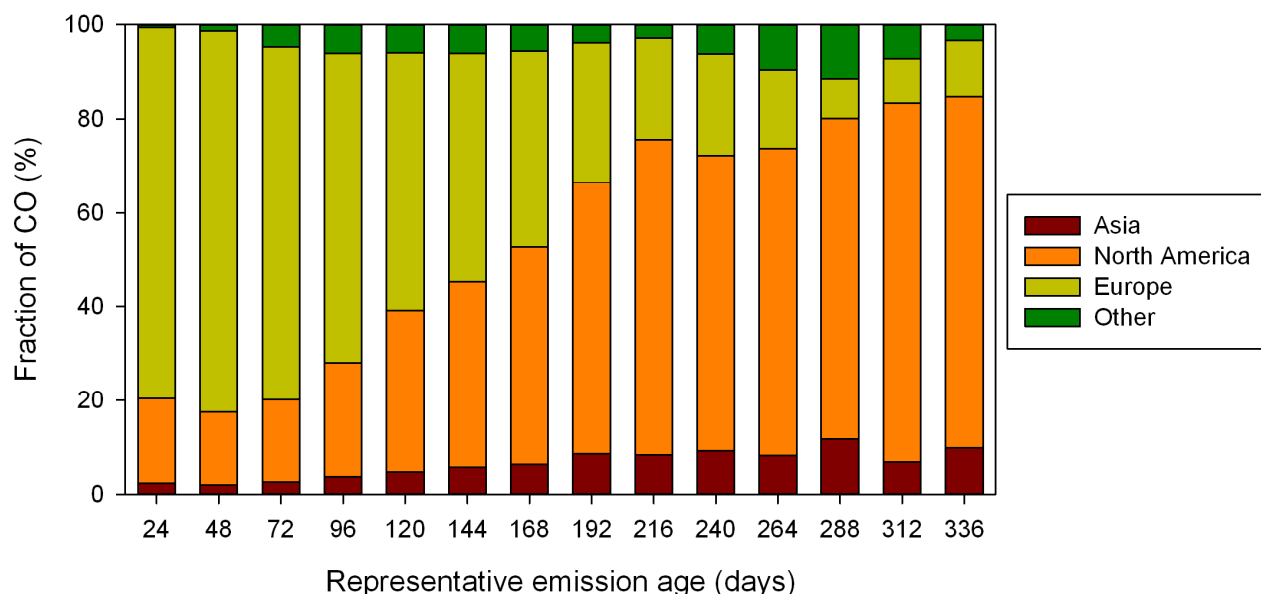


Figure 7. Fraction of CO_{ant} at CMN (y-axis) as a function of source regions (stacked coloured bars) and representative emission age (x-axis)

We added the following sentences to the manuscript: “With the aim of systematically investigate the source regions of CO_{ant} as a function of the representative emission ages, we calculated the average contribution to the total CO_{ant} at Mt. Cimone for different source regions tagged back by FLEXPART (i.e. Europe, Asia, North America and other continents). This analysis (see Fig. 6) suggests that the contributions related to the long-range transport from outside Europe became predominant for emission ages larger than 120 hours. In particular, anthropogenic emissions from North America appeared to play a predominant role when the CO_{ant} emission age exceeded 192 hours. For emission ages older than 120 days not negligible contributions were also tagged to emissions from Asia (ranging from 4.7 to 11.7%, as a function of emission age) as well as from other continents (ranging from 3.9 to 11.5%), with predominant contribution related with transport of anthropogenic emission from Africa.”

Technical comments:

- p. 21407, l.15: “those at”
- p. 21410, l.3: “Based on the FLEXPART...”
- p. 21410, l.20: “with respect to”
- p. 21412, l.5: “this could possibly...”

AR: all the technical comments have been fixed.