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 #1
Received and published: 3 October 2012

The manuscript '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. characterizes CO and O3 mole fractions and black carbon concentrations measured at Mt. Cimone. The contribution of biomass burning and anthropogenic emissions is investigated using a Lagrangian particle dispersion model (FLEXPART). Five major transport events ranging from local to global scales were studied in more detail. The measurements seem to be of good quality and the methodology / model used for data interpretation is sound and provides interesting insights to the factors affecting the observed CO and O3 mole fraction and BC concentrations at Mt. Cimone.

General remarks:

The paper is well written and clearly structured. The abstract provides a good summary of the paper. The measurements as well as the methods and model used for data evaluation are scientifically sound, and the results are an interesting contribution for the readership of ACP. The paper therefore should be published after addressing the following mainly minor issues.

AR: we thank the referee for reviewing our manuscript. In the following we provide point-to-point answers and comments to the issues arisen by the referee. In compliance with referee's indications we modified our manuscript.

Specific comments:

The term 'concentration' is used throughout the manuscript to describe CO and O3 mole fractions (unit ppb) and BC (unit ng/m3). Concentration is only correct for BC; for the gaseous species, mole fraction (or mixing ratio) should be used. Consequently, 'concentration' should also be omitted in the title

AR: completely right! We fixed this point along the manuscript.

Both 'ppbv' and 'ppb' are used to describe CO and O3 mole fractions. Only 'ppb' (or nmol/mol) should be used, 'ppbv' is not correct.

AR: also this has been fixed.

Spelling: No uniform use of American / British English (e.g. both analysed and analyzed are used in the manuscript).

AR: we check throughout the manuscript for these issues. In the case, the British English has been used.

Page 21405, Lines 2-4: It is stated that the CO measurements have an accuracy of _0.5%. This seems very optimistic, since the uncertainty of standards is usually not better than 0.7% (k=2) (e.g. NOAA), and drift may also contribute to the uncertainty. Please consider revising the uncertainty budget. Furthermore, RGD detectors are often non-linear, and the use of only one working standard does not account for this appropriately. Has the non-linearity of the system been checked?

RGD detector always showed (when it was working) a slightly better precision/repeatability compared to the same FID measurements, in term of relative standard deviation (rsd) of the repeated working std runs on the same day (48 runs). As an example, the working std cylinders

used, come with an uncertainty ranging from of 0.14 to 0.37 % (k=1), in agreement with NOAA, as stated by the reviewer.
We checked all the numbers for the period considered on the paper and the typical relative standard deviation ranged from 0.24% to 7.3%; usually CO data are flagged and removed for those values with rsd higher than 5%.
For all the period, the average is 0.91 (K=1), median 0.72. So, the value reported of 0.5% has to be consider as an optimistic but valid target achieved for most of the dataset; anyway we decided to correct the value reported in the manuscript as following: "...with an accuracy, in term of daily relative standard deviation over repeated analysis of the working standard (48 runs per day) of 0.72%, total expanded uncertainty = 1.51% (k=2)"

Concerning the nonlinearity of the RGD detector, we know this problem but unfortunately we did not have a set of cylinders with different mixing ratios for having a direct assessment of this issue. Anyway we find a workaround by comparing the results from the GC-RGD and a GC-FID when the two system runs in parallel, starting from 2008, January up to 2010, January, when the RGD system was stopped. Basing on the inter-comparison between the two systems, we obtained a set of equations to partially compensate the non-linearity of the RGD. It is also stated that the non-linearity of this detector is not stable but varies during time; for this reasons different corrections was calculated for each time period characterized by different correlation between the results of the two detectors, identified and explained mainly by the change of the running working standard tanks. We have already applied the corrections to the RGD data presented in this work, by assuming that FID is not affected (or better, is less affected on the typical range of CO at Mt. Cimone) by loss of linearity. Is assumed that, for the limited range of the concentrations recorded at Mt. Cimone, the deviation is linear, so the correction is simply calculated as the regression line by the least square method. In the paper we added this sentence for clarify the point: "RGD detectors are well-known to be affected by non-linear response. At CMN, a set of calibration standards with different CO mixing ratios were unavailable. Thus, we tested the non-linearity of the GC-RGD system by inter-comparison with a GC-FID (Agilent GC6890) which was working in parallel at the measurement site since 2008, January. Even if only for the limited range of the typical mixing ratios observed at CMN, a correction function was obtained (by mean of linear correlation between the two data-sets) and applied to the data series presented in this work.

Page 21406, Line 20: ': :emissions with age less than 20 days and thus still not mixed within the atmospheric background': Would it not be better to say 'still not fully mixed'? Mixing of emissions with background air is a process, and it starts immediately after emission.
AR: we completely agree and we modified the text of the manuscript.

Figures 6 and 7 are too small and hard to read in the printer friendly version of the manuscript.
AR: the original version of these figures was larger, in fact (A4 at 300X300 dpi). We suppose that this was an issue related to the small format of pages in the printer friendly version

Page 21410, Line 2: 'BB transport at ICO-OV accounted for a total of 21 days over the three years.' It should also be mentioned here that only events with a contribution of larger than 10 ppb were considered (if I understood correctly).
AR: In compliance with the referee observation, we rephrased as following: ". By considering only the period with COfire exceeding 10 ppb, 16 events with a duration ranging from 12 to 72 hours were identified, for a total of 21 days over the three years."

A general concern on the methodology for the detection of BB events is the difference between the 21-day running mean and the 3 hourly averages. The variability of other potential contributions to the CO mole fractions at ICO-OV are neglected; however, they may significantly influence the 21-day running mean, and detection of BB enhanced CO might become somewhat difficult / arbitrary.
AR: Actually, the BB events has been identified by using FLEXPART outputs, without considering any constraint to observed data: this led to the identification of the 16 events. We realized that this point was not so much clear in the first version of the manuscript. Thus we rephrased as following:

"To identify at ICO-OV the presence of BB plumes, we considered the time periods for which FLEXPART COfire continuously exceeded 10 ppb for more than 12 hours. Figure 3 reports CO observed at ICO-OV (black points) together with calculated FLEXPART COfire (red line): time periods for which the selection criterion is fulfilled. are highlighted with coloured dots, scaled on the fire emission age deduced by FLEXPART outputs."
Finally, we note that we used the "21-day running mean of CO", just to provide a "measure" of the possible impact of BB emissions to the typical seasonal CO variability at CMN without a-priori assumption on the type of sources (e.g. anthropogenic versus natural) that determine this variability.

Page 21410, Line 10: Are only 5 of total 16 events associated with increased CO mole fractions at ICO-OV? If yes: Why do you see no enhancement during the other events?
If no: Based on which criteria were these 5 events selected?
AR: We thanks the referee for arising this point that allowed us to clarify another part of the manuscript that, actually, appeared a little bit obscure! The 5 events we decided to show in details, have been selected with the aim of presenting a set of representative (or text-book) example about different cases of BB transport at Mt. Cimone. In this perspective, the selection certainly have a degree of arbitrariness, but these events covered the whole range of transport scales (from "local" to "global" as defined by FLEXPART analyses) and they present conditions for which both CO increases or decreases (expressed as ⊿CO) were observed at CMN. In fact, over the 16 events detected by FLEXPART, those having a local source were for the greatest part characterised by ⊿CO increases (5/8), those having global sources were characterised by negative or non-significant ⊿CO (7/7) and only one event was attributed to emission occurring at "regional" scale (positive ⊿CO).
Now these points have been better highlighted in the manuscript along the Section 6

The summary (Section 6) comprises many repetitions of the findings described in the previous sections. It should be considered to shorten the summary and integrate the parts which are new into the previous section. The paper could than end with a new section 'Conclusions' (instead of Summary), which describes very briefly the major findings of the work together with concluding remarks and an outlook.
AR: OK, we rearranged the paper following the referee suggestions.

Technical remarks:
AR: all the technical remarks were fixed!
Page 21404, Line 24: mercury vapour, not vapours
Page 21406, Line 28: 'showed' instead of 'presented'?
Page 21407, Line 15: 'thoseat' should be 'those at'
Section 3.1.2 and 3.1.3: refer also to Figure 1, since O3 and BC are also shown.
Page 21410, Line 3: 'Basing' should be 'Based'.
Page 21413, Line 4: GDAS-NCEP abbreviation needs to be spelled out.
Page 21413, Line 25/26: no commas after that and after FLEXPART
Figure S4: The numbers are difficult to read.