Atmos. Chem. Phys. Discuss., 13, C9881–C9886, 2013
www.atmos-chem-phys-discuss.net/13/C9881/2013/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Validation of emission inventories by measurements of ambient volatile organic compounds in Beijing, China" *by* M. Wang et al.

Anonymous Referee #2

Received and published: 10 December 2013

General comments

Validation of emission inventories is a relevant scientific issue and a prerequisite for air quality modelling and the implementation of emission control strategies. This work provides a robust evaluation of regional emission inventories by the use of VOC measurements at various sites in Beijing. The authors use different source-receptor approaches: one based on emission ratios relative to CO which are derived from three different methods and another one based on chemical mass balance modelling. Compared to past studies, the added value of this paper is to provide a through and temporally and spatially resolved evaluation of the emission inventories thanks to comprehen-

sive field experimental efforts at various temporal and spatial scales. It is an important point that should appear in the title for which I would suggest "A temporally and spatially resolved evaluation of emission inventories by measurements of ambient VOC in Beijing, China". The paper is of good quality. I recommend this paper for publication provided a number of revisions are provided (see below). Among requested revisions, main ones are related to a better description of the off-line sampling strategy which is not sufficient to allow a critical review of the corresponding results. Another issue is the missing discussion on the spatial variability of emission ratios. Finally, several studies with similar objectives and, for some of them, similar approaches in Western Europe have been recently published and are not reported in the paper. It is recommended to include these data and conclusions of these studies in the present paper.

Gaimoz, C., et al. (2011), Volatile organic compounds sources in Paris in spring 2007. Part II: source apportionment

VOC source appotionment using Positive Matrix Factorization and comparison to the regional emission inventory.

Borbon, A., J.B. Gilman, W. C. Kuster, N. Grand, S. Chevaillier, A.Colomb, C. Dolgorouky, V. Gros, M. Lopez, R. Sarda-Esteve, J. Holloway, J.Stutz, O. Perrussel, H. Petetin, S. McKeen, M. Beekmann, C. Warneke, D.D. Parrishand J.A. de Gouw, Emission ratios of anthropogenic VOC in northern mid-latitude megacities: observations vs. emission inventories in Los Angeles and Paris, J. Geophys. Res., 118, 2041-2057, (2013).

Many of the issues discussed in this paper are closely connected to this paper. The emission ratios were determined and reported for two northern mid-latitude megacities (Paris and Los Angeles) by the use of two independent approaches: the photochemical approach and the linear regression one on nighttime data like the ones described in this paper . The authors also discuss the consistency between ratios and other urban areas.

Boynard A., Borbon A., T.Leonardis, B. Barletta, S. Meinardi, D.R. Blake, N. Locoge, Spatial and seasonal variability of measured anthropogenic nonmethane hydrocarbons in urban atmospheres: Implication on emission ratios.Atmos. Environ. 82 258-26729, 2014.

The emission ratios from French urban areas are presented and reported on a seasonal basis.

Specific comments:

Introduction:

Page 26935, line 26: this line refers to Figure S1 which compares emission inventories for Beijing for different years. I do not agree with the interpretation of the graphs. It looks like emission inventories for the same period (90s, 2000s and mid-2000s) are consistent within the error bars. Please comment.

Page 26936, lines 6-8: the authors should moderate their statement discussing Table 1; except Bo et al (2008), other studies are quite consistent.

Page 26936: another criteria of using CO as a tracer is that it has a long atmospheric lifetime at the time scale of interest.

Page 26937, line 4 : change the sentence by De Gouw (2005) and Warneke (2007), follwed by Borbon (2013) Âż Page 26937, line 25: add Gaimoz et al. (2011) for source-receptor modelling reference.

Section 2.1.1 : offline VOC measurements

The strategy for NMHC sampling is not detailed enough to allow a critical review of CMB application and result interpretation. Missing information concerns the number of samples per site, the frequency and periods of sampling (i.e. month, time of the day). This information has to be reported in the revised manuscript (i.e. supplement material).

Section 2.2. : receptor model

Page 26941, line 19: the fitting species for CMB application only include “light” hydrocarbons that are mostly tracer of gasoline emission combustion. Please comment on the CMB results that extract a diesel factor which would not a priori be expected (see also figure 11).

Section 3.2: Temporal variations in VOC species

Page 26943, line 9: “the chemical composition of ambient VOCs can be affected by their emission, their photochemical removal or formation and dilution”. Please add the third term dilution to the sentence. Page 26943, line 24: add Borbon et al. (2001) who first clearly showed the anthropogenic origin of isoprene in urban areas.

Page 26944, line 25: please add Warneke, 2007 and Borbon, 2013 that showed the effect of chemistry has to be taken into account when determining emission ratios

Page 26945, line 3: the authors state that to estimate the emission, ratios of target species have to be affect by photochemical processing. It is surprising after showing the necessity to exclude chemistry effect. Please comment or provide more details.

Page 26945, line 18: please provide value of the uncertainty on CO emissions.

Page 26945, line 23: it is surprising to see a good correlation between ethane and propane, two tracers of natural gas and LPG emissions, and CO. Please comment.

Lines 19 to line 4 (page 26946): this part is not very useful

Section 3.3.2 Page 29946: To strengthen the choice of time-of-the-day filters to determine emission ratios I would suggest to add two figures (fig 4c and 4d) to figure 4 (same as fig 4a and 4b) color-coded by the time of the day on order to show that low ozone values correspond to early morning period 03:00-07:00 AM. In her paper (2013) for Los Angeles, Borbon et al. used a larger nighttime filter (10:00 PM to 05:00 AM). I am wondering why time-of-the-day filter here is smaller. Line 13: please add Borbon et al. (2013) reference that used the same approach and showed that emission composition between day and night is not different.

Page 26948: explain the reason of choosing o-xylene to ethylbenzene ratios to estimate OH time exposure.

Section 3.3.3: Temporal variations in VOC emission ratios

The results presented here should be also discussed by comparing to Boynard et al. (2014) emission ratios determined on a seasonal basis in French urban areas. The seasonal differences in emission ratios should be also addressed regarding CO emission variations which are not discussed here.

Page 26950, line 1: please change the sentence by “these results suggest a similarity between VOC emission composition”

Section 3.3.4: Comparison with other VOC emission ratios The comparison here should include the most recent results by Borbon et al (2013). While it is not always clear in the text, the emission ratios were determined in Beijing not only from the PTU dataset but also from the regional measurements. Therefore it would be more appropriate to calculate an average emission ratio from all measurement sites and associate a standard deviation to this averaged emission ratios. Indeed the spatial variability of emission ratios is not discussed in the paper and one can wonder how much the PKU ratios are representative of the urban mixture of VOC anthropogenic emissions. It might be the case but this has to be addressed. Calculating a standard deviation will also be useful when comparing to emission ratios from emission inventories in order to test whether a factor of 2 is significant or not. Finally, no discussion is provided to explain the observed differences in Figure 9.

Section 3.3.5: Estimation of VOC emissions in Beijing

The comparison to emission inventories is not always straightforward because emission database usually lump VOCs according to their atmospheric reactivity (see also Borbon et al. 2013). One can wonder if this is the case here. Please comment.

Section 3.4: VOC source apportionment

The way CMB model is applied to data is missing (which observed data ? which sites? Which periods?). Also explain the statistical indicators used to test the quality of CMB modeling (lines 15-20 page 26954). Comparing CMB results to calculated emission ratios would be an added value and a good way to test the consistency of both methods and the potential effect of chemistry which is assumed to be negligible by the choice of non reactive fitting species in CMB modelling. From CMB modelling results one can derive the total concentration explained by the model for different VOC, divide it by CO and compare to the emission ratios determined in previous sections. Finally if CMB modelling is applied to each measuring station dataset it would be interested to discuss the influence of the site typology on the results.

Figures: Figure 6: the linear regression slope does not appear on Figure 6b. Figures 1, 8 and 13 are hard to read (axis and colorcode labels especially) Figure 2: [. . .] Error bars represent standard deviation from the mean calculated at the 27 measuring sites” Please add “calculated at the 27 measuring sites”. Figure 4: ozone is used as an indicator of photochemistry. Usually it is more appropriate to use the sum of oxidants ozone+NO2 in order to take into account the titration of ozone by NO in urban areas (Veres et al., 2011, GRL). Figure 10: for figure 10a, precise it is Beijing measurements. Figure 13: “Spatial distribution of the relative contribution (in %) [. . .]”. Please add “in %” to the caption of the figure

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/13/C9881/2013/acpd-13-C9881-2013-supplement.pdf

---

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 26933, 2013.