Letter of Responses

Response to Referee #3 (Acpd-10-C2145)

The author's present NMHC data collected from 3 sites in Beijing to characterize the changes in ambient concentrations that occurred as a result of various short term pollution control measures for the 2009 summer Olympics. This is interesting work -how often does a large city perform such an experiment! The authors collected 331 air samples over a period of 3 months. Air samples were collected into fused silica lined canisters which were then analyzed for 55 species using an Entech (a US based company) preconcentration system and separation and detection using GC-MS/FID. The experimental methods are reasonably well described and referenced and the data seem to be of reasonable quality. The authors perform a chemical mass balance analysis on the data to apportion ambient concentrations to particular sources such as vehicle exhaust. The source profiles used in the CMB analysis were determined in previous work performed by these authors. The CMB analysis concludes vehicle exhaust was a significant source of NHMC at all sites contributing 57% to 69% of measured abundance.

The data are reasonably well presented and of wide interest to the atmospheric chemistry community interested in urban air quality. I have no major objections to but do have some minor suggestions for improvement. The Tables and Figures are for the most part clear and informative with the exception of Table 3. I would like a more thorough presentation of the speciated data in tabulated form for the archival literature. These points are detailed in the specific comments below.

Reply: The authors would like to thank the Referee #3 for the careful review and helpful comments to our manuscript. We have prepared responses to each of the concerns and questions, which are listed below. The referee's comments are in *italics*, followed by the authors' responses.

Specific Editorial Comments

1. *p 5573 first line; "had only 55% of mixing ratios of PKU" is an awkward, unclear statement. Do you mean on average NMHC mixing ratios were 55% lower than those measured at PKU?*

Reply: Sorry for the confusion. It has been revised into "On average, the level of NMHCs at CP site was 45% lower than those measured at PKU" (line 192-193).

It would be useful and desirable from an archival standpoint to tabulate the speciated data (as averages or medians) for the PKU site showing the decrease in mixing ratios for the 3 study periods. Such tables allow for the use of the data in later comparisons by others, as was done in Figure 2.

Reply: Accepted. Actually, to tabulate the speciated data has also been suggested by reviewer #1, and we will provide the data for PKU site in the revised manuscript (section 3.2, Table 5).

2. *p 5573 line 6. replace "of" with "in" in … difference in chemical composition…*

Reply: Accepted and fixed accordingly.

3. *p 5573 line 7. replace "source structures" with "source contributions".*

Reply: Accepted and fixed accordingly.

4. *p. 5576. It is stated that traffic counts were obtained for rush hour for 3 different ring roads and values are given in Figure 3a. For which ring road are these traffic counts for?*
Reply: Sorry for the confusion. In this study, traffic counts were obtained for rush hour for the 2nd, 3rd, and 4th ring roads in Beijing. The data presented in Figure 3a are the averaged traffic flow of the 3 ring roads, and this information has been added into the revised manuscript (section 3.2.1, page 11, line 227).

p. 5577. Emission ratios and Figure 4. It would be better to show the vehicle emissions ratio from the Shao et al. 2009 tunnel study for these species rather than the fits to the data. The data seem quite scattered which would indicate: 1) that other sources contribute to ambient mixing ratios rather than just vehicle exhaust 2) analytical precision problems or 3) differences in atmospheric lifetime between the plotted pairs. It would be prudent to show species that are have very similar lifetimes to highlight the differences between analytical precision and true variability in the data (i.e. hexane vs. 2-methylpentane ; i-butane vs. n-butane, i-pentane vs. n-penatne). Your T-2-butene vs C-2-butene plot Figure 4a shows good correlation and indicates good precision of the measurements and presumably one dominant source since the ratio is invariant. Some explanation of why the ratios are considered constant is warranted given the scatter in Figure 4 since you state "… the ratios are constant …" between the periods. The figure is useful but I think a stronger argument can be made that the vehicle emissions are a dominant source of many of these VOCs based on correlations, low degree of scatter, and fit to tunnel data.
Reply: Accepted, the data of the tunnel study have been added into Figure 5, as well as the linear correlation coefficients of the NMHC pairs. Actually, in this study, the NMHC pairs are selected according to the methods of Parrish et al. (2009). The pairs are benzene vs. acetylene, trans-2-butene vs. cis-2-butene, ethylene vs. toluene, and n-hexane vs. toluene. These species are among those observed at higher concentrations, and our QA/QC results showed that the precisions of the measurements are generally lower than 4%. Both species of each selected pair have similar atmospheric lifetimes with respect to photochemical reaction with hydroxyl radical, implying that the ratio of the measured ambient concentrations should be very close to the emission ratio. As shown in the revised Figure 5, the linear fits from June to September of the 2008 campaign were not varied apparently and very close to those of the tunnel study, and the linear correlation coefficients are generally greater than 0.7.
The authors agree with the reviewer that these selected species (except for T-2-butene and C-2-butene) may also be from non-vehicle sources as stated in the manuscript (section 3.2.1), and this has also been suggested by Parrish et al. (2009). As shown by our CMB calculations, the non-vehicle sources contributed 31-43% of the measured NMHCs. Thus, the relatively smaller correlation coefficients between these species and the scatter may be resulted by emissions from these non-vehicle sources. However, this will not hurt the conclusion that vehicle emission is the dominant source, since the ambient ratios were very close to the tunnel data. The corresponding parts of section 3.2.2 have been modified accordingly.

5. *p. 5581. The MIR values used should be noted or at least a reference to the source of MIR values used.*

Reply: Accepted. As also recommend in comments (5) by reviewer #1, the authors have added a reference to the source of MIR values used into the revised manuscript (section 3.4, page 15, line 405-407).

Table 3 is not very informative. The 10th and 90th percentile ranges for characterizing the similarity of wind direction conditions for the 4 sites is not a good metric in my view. What were the typical conditions?

Reply: Actually, the table is designed to show the common conditions of meteorology in each of the 4 periods during the 2008 campaign, which have excluded the 20% extreme conditions. Additionally, another aim for presenting this table is to show the second criterion for data selection, with respect to temperature, relative humidity, and pressure. Actually, the criterion for selecting data by wind directions and wind speeds is not the range between 10^{th} and 90^{th} percentiles, but wind directions of 315^{o}-360^{o} and wind speeds lower than 2 m/s. As shown by the rose plots of wind directions and speeds below, this criterion stands for the typical conditions from June to September, and the low wind speed indicate local emissions could be most important factor influencing the ambient mixing ratios of NMHCs which favors the discussion on the effectiveness of the air quality controls. The authors feel sorry for the typo in stating the criterion of wind directions, and thanks for noting it. Section 2.4 has been revised accordingly.

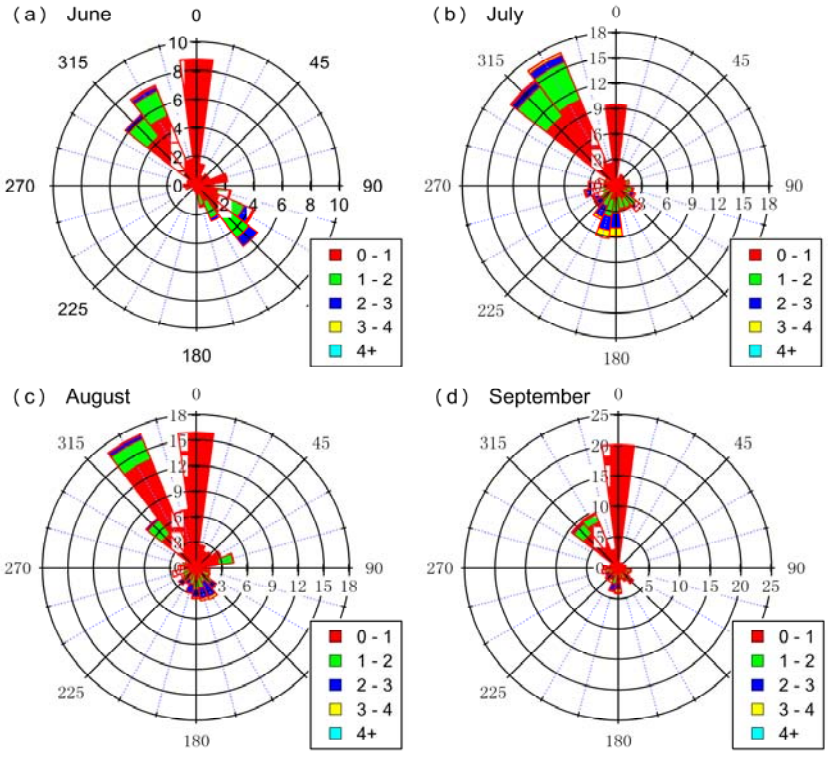

Figure 1. Rose plots of wind directions and wind speeds at PKU site in (a) June, (b) July, (c) August, and (d) September. Different colors indicate the wind speed (m/s).

Table 5. A dividing line between the alkenes and aromatics data would be a useful edit to the table.

Reply: Accepted and the dividing line has been added accordingly. After tabulating the speciated

data, this table is now Table 6 in the revised manuscript.

Figure 2. Typo in figure caption (b) Propene not Propane? Why are averages being plotted? These data likely have log-normal distributions. Can median values be shown instead?

Reply: Yes, it's propene, and sorry for the typo. The reasons for plotting averages are (1) to compare with the results reported by previous studies in Beijing (Lu et al, 2007; Shao et al, 2009), and (2) also provide a basis for researchers to do comparisons with other measurements around the world (Velasco et al., 2007; Barletta et al, 2009; Parrish et al., 2009; Sauvage et al., 2009; etc.), in which the averages were reported. The medians of the data are presented by the table below. Actually, the medians and the averages are very close to each other for this study.

Table 1. The averages and medians of propane, propene, and toluene from June to September at PKU site (Unit: ppbv).

	propane		propene		toluene	
	averages	medians	averages	medians	averages	medians
June	2.85	2.66	0.88	0.89	2.53	2.44
July	2.77	2.53	0.69	0.62	1.95	1.57
August	2.46	2.43	0.55	0.49	1.36	1.25
September	3.21	3.01	0.53	0.48	1.01	0.94

References:

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2. Shao M., Lu S., Liu Y., Xie X., Chang C., Huang S., and Chen, Z.: Volatile organic compounds measured in summer in Beijing and their role in ground-level ozone formation, J. Geophys. Res. 114, D00G06, 2009.

3. Velasco, E., Lamb, B., Westberg, H., Allwine1, E., Sosa, G., Arriaga-Colina, J.L., Jobson, B.T., Alexander, M.L., Prazeller, P., Knighton, W.B., Rogers, T.M., Grutter, M., Herndon, S.C., Kolb, C. E., Zavala, M., de Foy, B., Volkamer, R., Molina, L.T., and Molina, M.J.: Distribution, magnitudes, reactivities, ratios and diurnal patterns of volatile organic compounds in the Valley of Mexico during the MCMA 2002 & 2003 field campaigns. Atmos. Chem. Phys., 7, 329–353, 2007.

4. Barletta, B., Meinardi, S., Simpson, I.J., Atlas, E.L., Beyersdorf, A.J., Baker, A.K., Blake, N.J., Yang, M., Midyett, J.R., Novak, B.J., McKeachie, R.J., Fuelberg, H.E., Sachse, G.W., Avery, M.A., Campos, T., Weinheimer, A.J., Rowland, F.S., and Blake, D.R.: Characterization of volatile organic compounds (VOCs) in Asian and north American pollution plumes during INTEX-B: identification of specific Chinese air mass tracers. Atmos. Chem. Phys., 9, 5371–5388, 2009.

5. Parrish, D.D., Kuster, W.C., Shao, M., Yokouchi, Y., Kondo, Y., Goldan, P.D., de Gouw, J.A., Koike, M., Shirai, T.: Comparison of air pollutant emissions among mega-cities. Atmos. Environ., 43, 6435–6441, 2009.

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