Atmos. Chem. Phys. Discuss., 10, C8809–C8816, 2010
www.atmos-chem-phys-discuss.net/10/C8809/2010/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ambient concentrations of aldehydes in relation to Beijing Olympic air pollution control measures" *by* J. C. Gong et al.

J. C. Gong et al.

gongj1@umdnj.edu

Received and published: 17 October 2010

1. Most if not all studies of aldehydes from urban sources are given in ppb and not μg/m3 and this needs to be changed when comparing with past studies.

A. Agreed. We present concentrations as mixing ratios (ppb) (as well as μg/m3) when comparing with results from past studies.

2. This study employs C18 cartridges without any discussion regarding the use of an ozone scrubber and/or the effects of ozone as a significant positive artifact on the formaldehyde measurements. The JGR study by Gilpin et al. (vol 102, D17, 21,161-21,188, 1997) documents this interference. The Gilpin et al. study also points to the importance of adding formaldehyde standards directly to the inlet, even when employ-

ing techniques that are calibrated by liquid phase standards, such as the present study. Unfortunately, the present study does not give any details regarding the specifics of the measurement calibration, the effects of ozone, zeroing, etc. This leads me to question the accuracy of the present formaldehyde results, particularly when ozone is changing. Can some of the present results be due to this positive artifact from ozone, and can changing ozone mask any trends the authors are trying to see due to enactment of control strategies? What is the explanation of the 115.5% collection efficiency for formaldehyde?

A. The reviewer presents a very good point on a positive artifact on formaldehyde measurement using DNPH-coated C18 cartridges to collect aldehydes. However, we did NOT use DNPH-coated C18 cartridge in our study. The method used in the current study was Dansylhydrazine (DNSH)-based, rather than DNPH-based, which was previously published in Environmental Science & Technology by Dr. Zhang (corresponding author of this paper) et al in 2000. The DNSH-based method does not have the ozone artifact problem when ozone concentration is as high as 300 ppb on collection of formaldehyde in a paper published in ES&T by Rodler et al. in 1993. And we have conducted a condition experiment to test the effect of ozone on the aldehydes recovery; and the result indicated no significant ozone effect on formaldehyde-DNSH derivatives as well (see appendix table 1).

As discussed in Zhang et al paper, the over-100% collection efficiency was perhaps due to an unknown photo chemical reaction in the DNSH coated cartridge. Therefore, during the sampling period, a black cartridge cover was used to protect the DNSHC18 substrate from direct exposure to sunlight. Under the condition of 100% darkness, the recovery of formaldehyde was 98%-104% (see appendix Table 1). We believe a recovery of 115% is acceptable, because normally, 80-120% of recovery is considered a reasonable range, given analytical errors.

Given that the DNSH- based method is not as well-known as the DNPH-based 'conventional' method, we have added additional rationale for using this method in the revised

paper. The added text reads as follows: “In this study, we used the DNSH-based method instead of the ‘conventional’ DNPH based method for the following reasons: (1) This method is not affected by ozone at concentration up to 300 ppb (Rodler et al. in 1993), (2) This method is reliable for acrolein (Herrington et al, 2005), and (3) This method uses passive sampling thus offering convenience in the field.”

3. Can the authors really claim statistically significant reduction in acetaldehyde concentration between sub-periods 1 and 2 when the standard deviations are so high and overlap? What are the median concentrations?

A. After running a two-sample assuming unequal variance t-test comparing means in two sub-periods, we got a p-value equal to 0.079 which is marginally significant. Medians for sub-period 1 and 2 were 13.20 ppb and 9.02 ppb, respectively. The t-test results and the median values are now added into the text of the revised manuscript.

4. There needs to be further explanation of the Spearman correlation coefficients on page 19745.

A. More explanation on the Spearman correlation coefficients is added in the paper.

5. On this same page of 19745 the statement that “formaldehyde and acetaldehyde concentrations in the summer time of Beijing were substantially higher than those reported for other cities during photochemical seasons” cannot be substantiated. Airborne formaldehyde concentrations in Houston, Texas, for example, attained instantaneous values greater than 30 ppb, which are higher than the average 28 ppb values reported here.

A. Good point. We replaced the sentence containing “substantially higher” with the following new sentence “Formaldehyde and acetaldehyde concentrations in the summer time of Beijing were in the high end of concentration ranges measured in other cities during photochemical seasons. And the aldehydes concentrations we reported in this paper were 24-hour averages that might be much lower than the peak concentrations

during the day time.”

6. The biggest problem I have with this paper is the inconsistency regarding the trends in the 3 aldehydes and the resulting explanations. Formaldehyde and acetaldehyde are known to both be emitted by vehicle traffic, with formaldehyde > acetaldehyde emission factors, and both are produced photochemically. Studies by Calvert in 1981 and by Sigsby in 1987 show CH2O/CH3CHO molar emission ratios in the 1.2 to 3.1 range for motor vehicles. Thus it is hard to understand how a reduction in traffic would yield a reduction in CH3CHO but not CH2O. The inconsistency in the trends is not adequately explained. If as the authors claim that Fig 4 shows common sources of the 3 aldehydes (large scatter and no regression fits), than one would expect that such a common direct source would yield the same temporal trends. Its hard to imagine that photochemistry would dominate CH2O and not the CH3CHO trends as well, when in fact both are produced from both sources. This inconsistency is compounded by the fact that nothing was given in this paper regarding the effects of boundary layer height on the concentrations. It is also very hard for me to comprehend that low correlations were observed between CH2O and CO, when every field study I have been on shows very high correlations between these two in the boundary layer. The statement on page 19748 that O3 is critical for the formation of CH2O is not quite correct. In general, O3 is produced from CH2O, which is produced from OH with various VOCs, and not the other way around. The authors note on page 19748 that VOCs play an important role in the formation of aldehydes but no measurements of VOCs were given other than the references cited and this complicates any data interpretation. The specific VOCs will have a differential effect on formaldehyde relative to acetaldehyde but nothing was given in this paper to further assess this.

A. Thank you for all your valuable questions. They are very important for improving the clarity of the paper. The inconsistency among aldehydes, especially between formaldehyde and acetaldehyde may be explainable. Both formaldehyde and acetaldehyde can be contributed to primary and secondary sources. But the contribution of the

two sources to the two aldehydes may vary. Thanks to a recently published paper (Y. Li et al. 2010, Atmospheric Environment 44 2632-2639) providing equations for predicting contributions of primary and secondary sources in Beijing, we calculated the relative contributions of the primary and secondary sources and found that the primary source was more important for acetaldehyde than the secondary source in the pre-Olympic period (47.40% vs. 11.42%). In contrast, the secondary source contributed more than the primary source to ambient formaldehyde, especially in the during-Olympic period (50.27% vs. 15.36%). Since the air pollution control measures were effective to reduce primary air pollutants during the Olympic period, it was thus reasonable to observe a reduction in acetaldehyde in the mean time. Temperature and relative humidity were both as favorable as, even more than, in the pre-Olympic period, to the photochemical reactions, and the fact that typical secondary pollutant, ozone, was not reduced in the during-Olympic period may suggest less effect of air pollution control measures on secondary pollutants. Formaldehyde concentration was mainly mediated by the secondary contribution, i.e. photochemical reactions, in the during-Olympic period; therefore, it was plausible to observe no reduction in formaldehyde during the Olympic period.

At the time of our paper submission, we have not seen the paper of Li et al. In the revised version, we added a section and a new table on using the equations of Li et al to quantify primary and secondary source contributions to formaldehyde and acetaldehyde, respectively.

Yes, we observed significant correlation between formaldehyde and carbon monoxide at the significant level as 0.05. The relatively small correlation coefficient (r=0.26) between them might be due to the fact that CO was mainly from vehicle emission and formaldehyde was mainly from the photochemical reactions. We respect the reviewer's statement about high correlations between CO and formaldehyde previously observed in other places. However, it is worth noting that no places that have undergone a man-made "intervention" at such an unprecedented scale as in Beijing during the 2008

Olympics. This may have complicated the "natural" features of air pollution and we may learn many more "unconventional" findings yet to come.

One limitation of the current study was that no VOCs were measured simultaneously. Thus all we could do is a generic discussion. We wish we could have measured VOCs as well, but practical resources constraints prohibited us from doing so. On the other hand, we believe we have collected adequate amount of data and performed appropriate data analyses to support the findings and conclusions of the current study.

7. The final conclusion that the air pollution control measures adopted during the Olympics appeared to be associated with reductions in acetaldehyde but not formaldehyde and acrolein is not consistent with our understanding of these gases from both direct and photochemical sources. Since this is the fundamental topic of this paper and this inconsistency was not adequately explained by any detailed data analysis, I do not support the publication of this paper.

A: We hope that assisted with the reviewer's thoughtful comments, we have improved our explanations and discussion of our findings in the revised paper.

References: Herrington, J.; Zhang, L.; Whitaker, D.; Sheldon, L.; Zhang, J. Optimizing a dansylhydrazine (DNSH) based method for measuring airborne acrolein and other unsaturated carbonyls. Journal of Environmental Monitoring, 2005, 7, 969- 976.

Li, Y.; Shao, M.; Lu, S. H.; Chang, C. C.; Dasgupta, P. K. Variations and sources of ambient formaldehyde for the 2008 Beijing Olympic games. Atmospheric Environment, 2010, 44, 2632-2639.

Rodler, D. R.; Nondek, L.; Birks, J. W. Evaluation of Ozone and Water-Vapor Interferences in the Derivatization of Atmospheric Aldehydes with Dansylhydrazine. Environmental Science & Technology, 1993, 27, 2814-2820.

Zhang, J.; Zhang, L.; Fan, Z.; Ilacqua, V. Development of the personal aldehydes and ketones sampler based upon DNSH derivatization on solid sorbent. Environmental

Science & Technology, 2000, 34, 2601-2607.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/10/C8809/2010/acpd-10-C8809-2010-supplement.pdf

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 19737, 2010.

Table 1. Concentration measured in presence/absence of ozone

Ozone Concentration (ppb)	0	50	100	200	300		0	50	100	200	300
	Average concentration (n=4)						Standard deviation				
Formaldehyde (ppb)	42.39	37.94	39.01	39.02	38.39		1.14	2.55	2.15	3.30	4.18
Acetaldehyde (ppb)	22.23	20.12	20.12	21.01	17.89		0.25	1.30	1.07	1.66	0.94
Acrolein (ppb)	17.03	14.73	15.31	14.46	13.02		0.39	0.67	1.22	1.06	0.81

Fig. 1. Appendix Table 1.