

Supplement for “Understanding primary and secondary sources of ambient carbonyl compounds in Beijing using the PMF model”

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Inter-comparison of VOCs measurements

C3–C4 carbonyls, C6–C9 aromatics, isoprene and MVK+MACR were measured simultaneously by online GC-MS and PTR-MS in this study. Figure S1 shows the comparison between the PTR-MS and online GC-MS data for these species. For this comparison, the PTR-MS data have been averaged over the sampling period of online GC-MS. The blue lines in the figure show the results of an orthogonal distance regression (ODR) (de Gouw et al., 2003). Some compounds will form ions with the same m/z , and PTR-MS cannot separate them. For these compounds, the PTR-MS results were compared with the sum of the online GC-MS data.

Good agreements were found between these two systems for C3–C4 carbonyls and C6–C9 aromatics, with correlation coefficients larger than 0.90 and slopes ranging from 0.8 to 1.2 (Fig. S1(a-f)). The correlation coefficient between the PTR-MS and online GC-MS data for isoprene is only 0.78 (Fig. S1(g)). A significant intercept (about 0.2 ppb) was found for PTR-MS measured isoprene. Previous studies have reported that measurements of isoprene by PTR-MS at m/z 69 may have interferences from other species (e.g. 2-methyl-3-buten-2-ol, pentanal, methyl butanal, and pentenol) (de Gouw et al., 2003; Yuan et al., 2012). In this study, isoprene data from online GC-MS was used for PMF analysis. The correlation between the PTR-MS and online GC-MS data for MVK+MACR was reasonable ($r=0.90$), but the quantitative agreement was not well: the slope determined by the ODR analysis was

1.35 (Fig. S1(h)). MVK and MACR are two important products from isoprene oxidation, and they are detected with a different sensitivity by PTR-MS. Thus, the response factor for the PTR-MS signal at m/z 71 depends on the MVK/MACR ratio. Besides the uncertainty of response factor, several compounds include pentenes, methyl butenes, and crotonaldehyde can be detected at m/z 71 (de Gouw et al., 2003). This may explain the difference between PTR-MS and online GC-MS measurement for MVK+MACR.

Inter-comparison between PTR-MS and DNPH-HPLC method (EPA TO11A) has been done half years before our campaigns. Good agreements were found for formaldehyde and acetaldehyde (Fig. S2). After correcting the influence of humidity on formaldehyde response, a correlation coefficient of 0.93 and a slope of 1.06 were found between PTR-MS and DNPH-HPLC method.

Estimation of carbonyl loss rate coefficients

Photolysis frequencies of selected species were measured by a multi-channel spectrometer with photodiode array (CarlZeiss MicroImaging GmbH) (Yuan et al., 2013). As the photolysis frequencies of acetaldehyde and acetone were not measured, we calculated photolysis frequencies using a parameterization equation (Eq. (S1)). Z is the solar zenith angle. L , m and n are parameters for different species, which can be found in the paper of Saunders et al. (2003). The photolysis frequencies will be affected by different weather conditions, so we corrected them with the ratios between the measured J_{NO_2} and calculated J_{NO_2} (Eq. (S2)).

$$J = l \times (\cos Z)^m \exp(-n \times \sec Z) \quad (\text{S1})$$

$$J_{\text{carbonyl}} = J_{\text{carbonyl,calculated}} \times \frac{J_{\text{NO}_2,\text{measured}}}{J_{\text{NO}_2,\text{calculated}}} \quad (\text{S2})$$

To validate our calculation, we compared the calculated $J_{\text{formaldehyde}}$ with the measured $J_{\text{formaldehyde}}$, a good agreement was found with a slope of 1.14 and a correlation coefficient of 0.99.

The diurnal variations of photolysis frequencies were shown in Fig. S3, comparing with the reaction coefficients with OH. The reaction coefficients were calculated by multiplying OH concentrations by the rate constants for the reaction of

carbonyls and OH radical. As OH concentrations have not been measured in the urban region of Beijing, we used the modeled result from Liu et al. (2012) for summer. In winter, we assumed the OH concentration to be 4 times lower than in summer according to the measurements in Tokyo (Kanaya et al., 2007).

As shown in Fig. S3, reactions with OH radical were the main pathway of carbonyl removal, which contributed to 69%, 99% and 87% of the 24-h averaged loss rates of formaldehyde, acetaldehyde and acetone in summer, and contributed to 67%, 99% and 91% in winter.

Comparison of o-xylene/ethylbenzene ratios between 2010 and 2011

The concentrations of NMHCs have been measured in 2010 summer with the same online GC-MS/FID system used in this study. The detailed information of that campaign has been described by Yuan et al. (2012).

The ratio between two NMHC species with common sources and evident differences in k_{OH} was often used as an indicator for the degree of photochemical processing (de Gouw et al., 2005; Yuan et al., 2012). In this study, we compared the diurnal variations of o-xylene/ethylbenzene ratios between 2010 and 2011. As the chemical reactivity of o-xylene is higher than ethylbenzene, the ratios of o-xylene to ethylbenzene will be higher in fresh air mass and lower in aged air mass.

As shown in Fig. S4, the ratios of o-xylene to ethylbenzene have similar diurnal variations in 2010 and 2011. However, the relative standard deviations of o-xylene/ethylbenzene ratios were 30% higher in 2010 than in 2011. This means the variation of photochemical processing degree is larger in 2010.

References

- de Gouw, J. A., Goldan, P. D., Warneke, C., Kuster, W. C., Roberts, J. M., Marchewka, M., Bertman, S. B., Pszenny, A. A. P., and Keene, W. C.: Validation of proton transfer reaction-mass spectrometry (PTR-MS) measurements of gas-phase organic compounds in the atmosphere during the New England Air Quality Study (NEAQS) in 2002, *J. Geophys. Res.-Atmos.*, 108, 4682, doi: 10.1029/2003jd003863, 2003.
- de Gouw, J. A., Middlebrook, A. M., Warneke, C., Goldan, P. D., Kuster, W. C., Roberts, J. M., Fehsenfeld, F. C., Worsnop, D. R., Canagaratna, M. R., Pszenny, A. A. P., Keene, W. C., Marchewka, M., Bertman, S. B., and Bates, T. S.: Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, *J. Geophys. Res.-Atmos.*, 110, D16305, doi: 10.1029/2004jd005623, 2005.
- Kanaya, Y., Cao, R., Akimoto, H., Fukuda, M., Komazaki, Y., Yokouchi, Y., Koike, M., Tanimoto, H., Takegawa, N., and Kondo, Y.: Urban photochemistry in central Tokyo: 1. Observed and modeled OH and HO₂ radical concentrations during the winter and summer of 2004, *J. Geophys. Res.-Atmos.*, 112, D21312, doi: 10.1029/2007jd008670, 2007.
- Liu, Z., Wang, Y., Gu, D., Zhao, C., Huey, L. G., Stickel, R., Liao, J., Shao, M., Zhu, T., Zeng, L., Amoroso, A., Costabile, F., Chang, C. C., and Liu, S. C.: Summertime photochemistry during CAREBeijing-2007: RO_x budgets and O₃ formation, *Atmos. Chem. Phys.*, 12, 7737-7752, doi: 10.5194/acp-12-7737-2012, 2012.
- Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, *Atmos. Chem. Phys.*, 3, 161-180, doi: 10.5194/acp-3-161-2003, 2003.
- Yuan, B., Shao, M., de Gouw, J., Parrish, D. D., Lu, S., Wang, M., Zeng, L., Zhang, Q., Song, Y., Zhang, J., and Hu, M.: Volatile organic compounds (VOCs) in urban air: How chemistry affects the interpretation of positive matrix factorization (PMF) analysis, *J. Geophys. Res.-Atmos.*, 117, D24302, doi: 10.1029/2012jd018236, 2012.
- Yuan, B., Hu, W. W., Shao, M., Wang, M., Chen, W. T., Lu, S. H., Zeng, L. M., and Hu, M.: VOC emissions, evolutions and contributions to SOA formation at a receptor site in Eastern China, *Atmos. Chem. Phys. Discuss.*, 13, 6631-6679, doi: 10.5194/acpd-13-6631-2013, 2013.

Figures

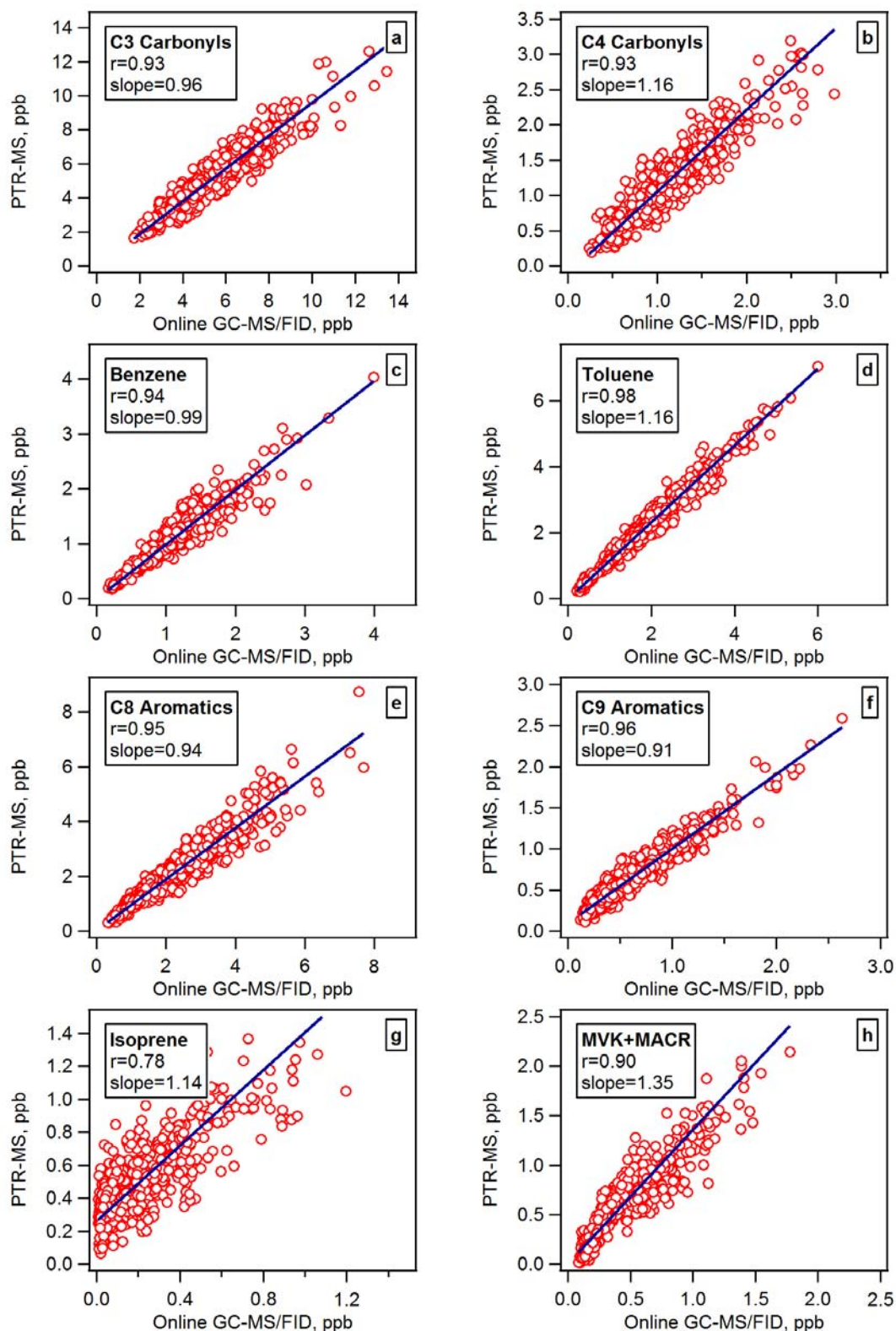


Fig. S1. Comparison between PTR-MS and online GC-MS data. The blue line gives the result of an ODR analysis.

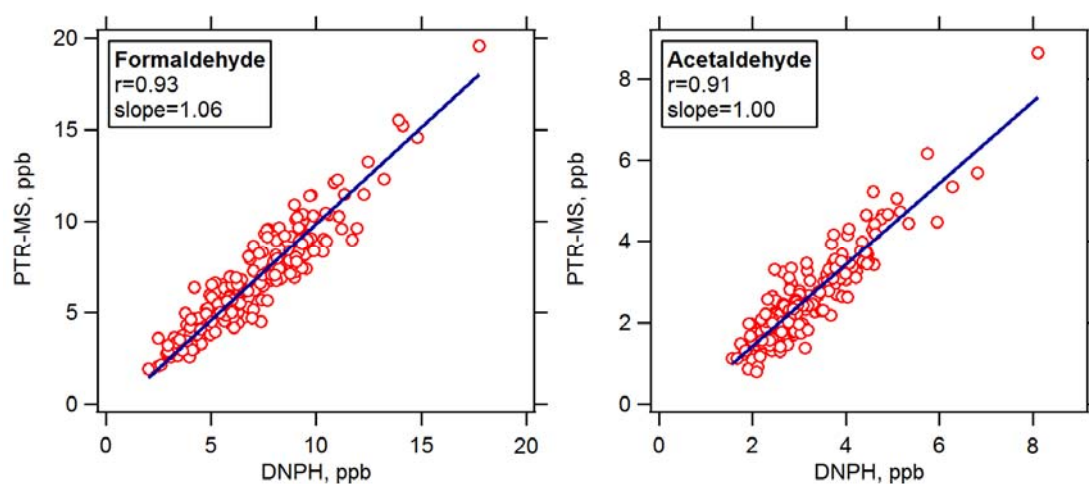


Fig. S2. Comparison between PTR-MS and DNPH data. The blue line gives the result of an ODR analysis.

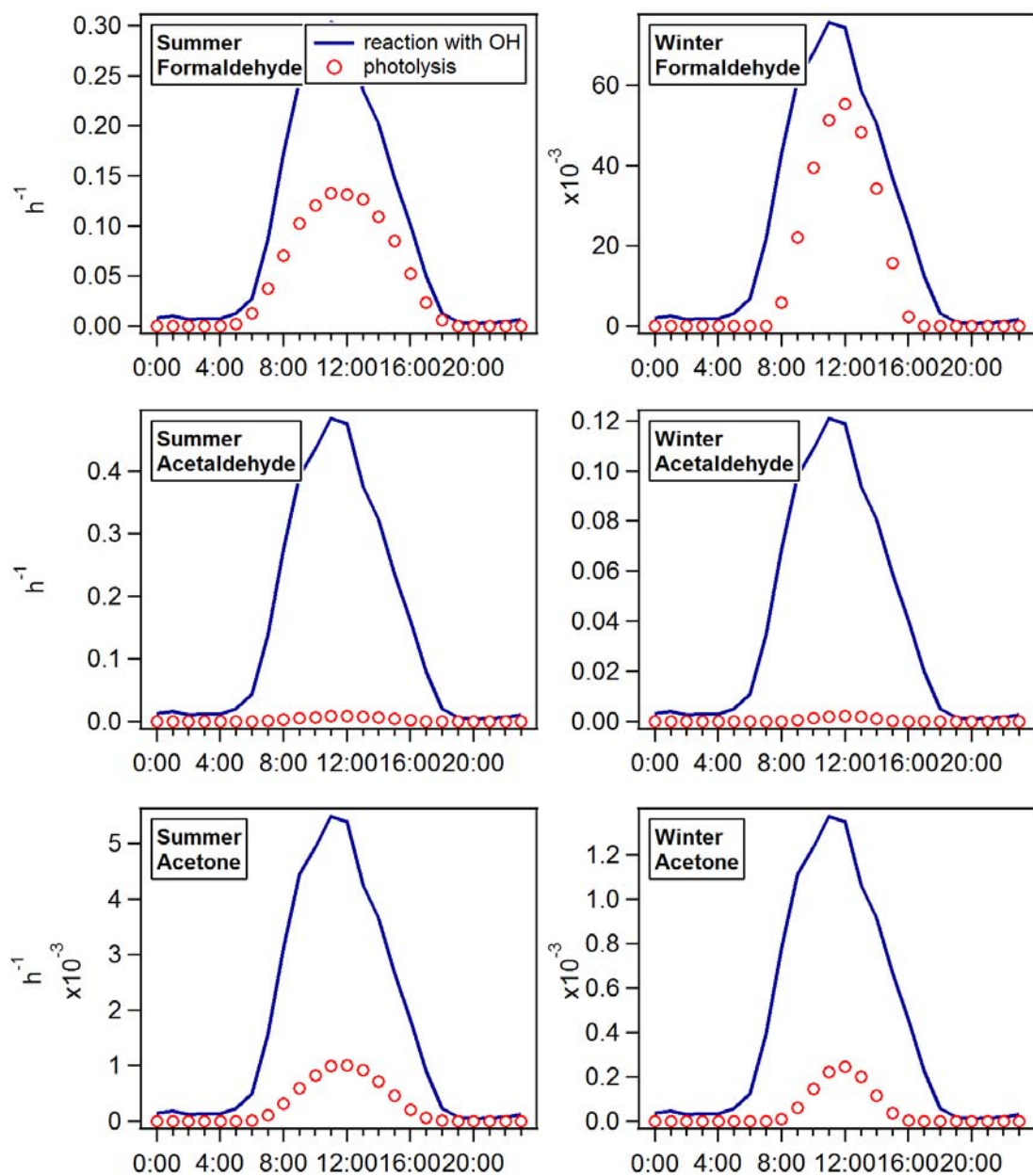


Fig. S3. Carbonyl loss rate coefficients in Beijing

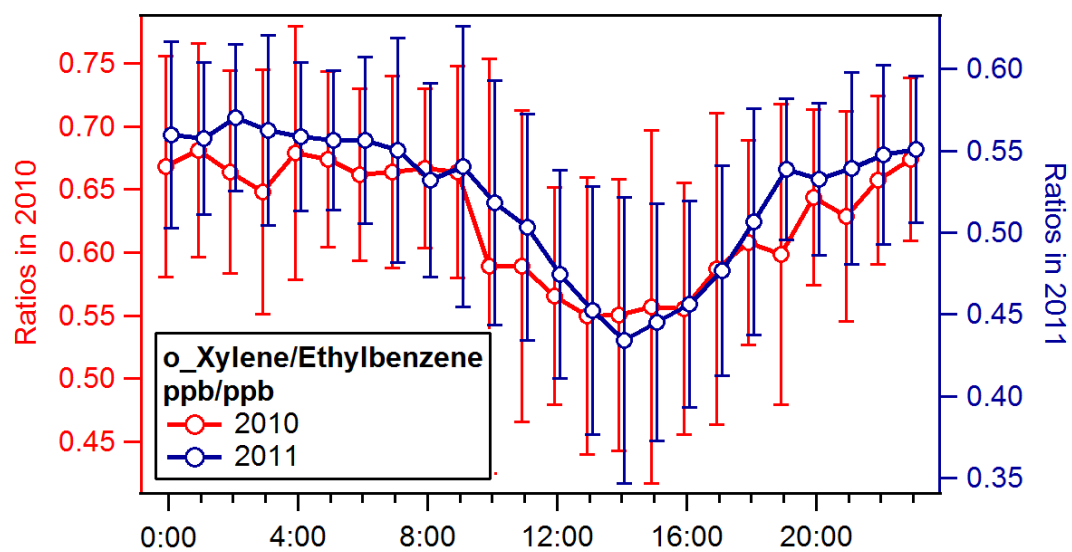


Fig. S4. Diurnal variations of o-xylene/ethylbenzene ratios in 2010 and 2011