

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

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11 **Inter-comparison of VOCs measurements**

12 C3–C4 carbonyls, C6–C9 aromatics, isoprene and MVK+MACR were measured
13 simultaneously by online GC-MS and PTR-MS in this study. Figure S1 shows the
14 comparison between the PTR-MS and online GC-MS data for these species. For this
15 comparison, the PTR-MS data were averaged over the sampling period of online
16 GC-MS. The blue lines in the figures show the results of orthogonal distance
17 regressions (ODR) (de Gouw et al., 2003). Some compounds would form ions with
18 the same m/z, and PTR-MS could not separate them. For these compounds, the
19 PTR-MS results were compared with the sum of the online GC-MS data.

20 Good agreements were found between these two systems for C3–C4 carbonyls
21 and C6–C9 aromatics, with correlation coefficients larger than 0.90 and slopes
22 ranging from 0.8 to 1.2 (Fig. S1(a-f)). The correlation coefficient between the
23 PTR-MS and online GC-MS data for isoprene was only 0.78 (Fig. S1(g)). A
24 significant intercept (about 0.2 ppb) was found for PTR-MS measured isoprene.
25 Previous studies reported that the measurements of isoprene by PTR-MS at m/z 69
26 might have interferences from other species (e.g. 2-methyl-3-buten-2-ol, pentanal,
27 methyl butanal, and pentenol) (de Gouw et al., 2003; Yuan et al., 2012). In this study,
28 isoprene data from online GC-MS was used for PMF analysis. The correlation

29 between the PTR-MS and online GC-MS data for MVK+MACR was acceptable
30 ($r=0.90$), but the quantitative agreement was not well: the slope determined by the
31 ODR analysis was 1.35 (Fig. S1(h)). MVK and MACR were two important products
32 from isoprene oxidation, and they were detected with a different sensitivity by
33 PTR-MS. Thus, the response factor for the PTR-MS signal at m/z 71 depended on the
34 MVK/MACR ratio. Besides the uncertainty of response factor, several compounds,
35 include pentenes, methyl butenes, and crotonaldehyde could be detected at m/z 71 (de
36 Gouw et al., 2003). This might explain the differences between PTR-MS and online
37 GC-MS measurement for MVK+MACR.

38 Inter-comparison between PTR-MS and DNPH-HPLC method (EPA TO11A) was
39 done half year before our campaigns at a supersite in south of China (22.71°N ,
40 112.93°E). Good agreements were found for formaldehyde and acetaldehyde (Fig.
41 S2). The ambient humidity during our inter-comparison ranged from 10.8 to 30.1
42 mmol mol^{-1} . After correcting the influence of humidity on formaldehyde response, a
43 correlation coefficient of 0.93 and a slope of 1.06 were found between PTR-MS and
44 DNPH-HPLC method. In this work, the ambient humidity in Beijing ranged from 8.1
45 to 33.6 mmol mol^{-1} in summer, and from 5.1 to 25.5 mmol mol^{-1} in winter. In these
46 two seasons, 94% and 79% of the humidity of sampled data were within the range of
47 our inter-comparison study. So we considered that the formaldehyde measurements in
48 this study could be validated by the previous inter-comparison.

49 **Estimation of carbonyl loss rate coefficients**

50 Photolysis frequencies of selected species were measured by a multi-channel
51 spectrometer with photodiode array (CarlZeiss MicroImaging GmbH) (Yuan et al.,
52 2013). As the photolysis frequencies of acetaldehyde and acetone were not measured,
53 we calculated photolysis frequencies using a parameterization equation (Eq. (S1)). Z
54 is the solar zenith angle. L , m and n are parameters for different species, which can be
55 found in the paper of Saunders et al. (2003). The photolysis frequencies would be
56 affected by different weather conditions, so we corrected them with the ratios between
57 the measured J_{NO_2} and calculated J_{NO_2} (Eq. (S2)).

58 $J = I \times (\cos Z)^m \exp(-n \times \sec Z)$ (S1)

59 $J_{\text{carbonyl}} = J_{\text{carbonyl,calculated}} \times \frac{J_{\text{NO}_2,\text{measured}}}{J_{\text{NO}_2,\text{calculated}}}$ (S2)

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

63 The diurnal variations of photolysis frequencies were shown in Fig. S3,
64 comparing with the reaction coefficients with OH. The reaction coefficients were
65 calculated by multiplying OH concentrations by the rate constants for the reactions of
66 carbonyls and OH radical. As OH concentrations have not been measured in the urban
67 region of Beijing, we used the modeled result from Liu et al. (2012) for summer. In
68 winter, we assumed the OH concentration to be 4 times lower than in summer
69 according to the measurements in Tokyo (Kanaya et al., 2007).

70 As shown in Fig. S3, reactions with OH radical were the main pathway of
71 carbonyl removal, which contributed to 69%, 99% and 87% of the 24-h averaged loss
72 rates of formaldehyde, acetaldehyde and acetone in summer, and contributed to 67%,
73 99% and 91% in winter.

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

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

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

84 As shown in Fig. S4, the ratios of o-xylene to ethylbenzene had similar diurnal
85 variations in 2010 and 2011. However, the relative standard deviations of
86 o-xylene/ethylbenzene ratios were 30% higher in 2010 than in 2011. This means the

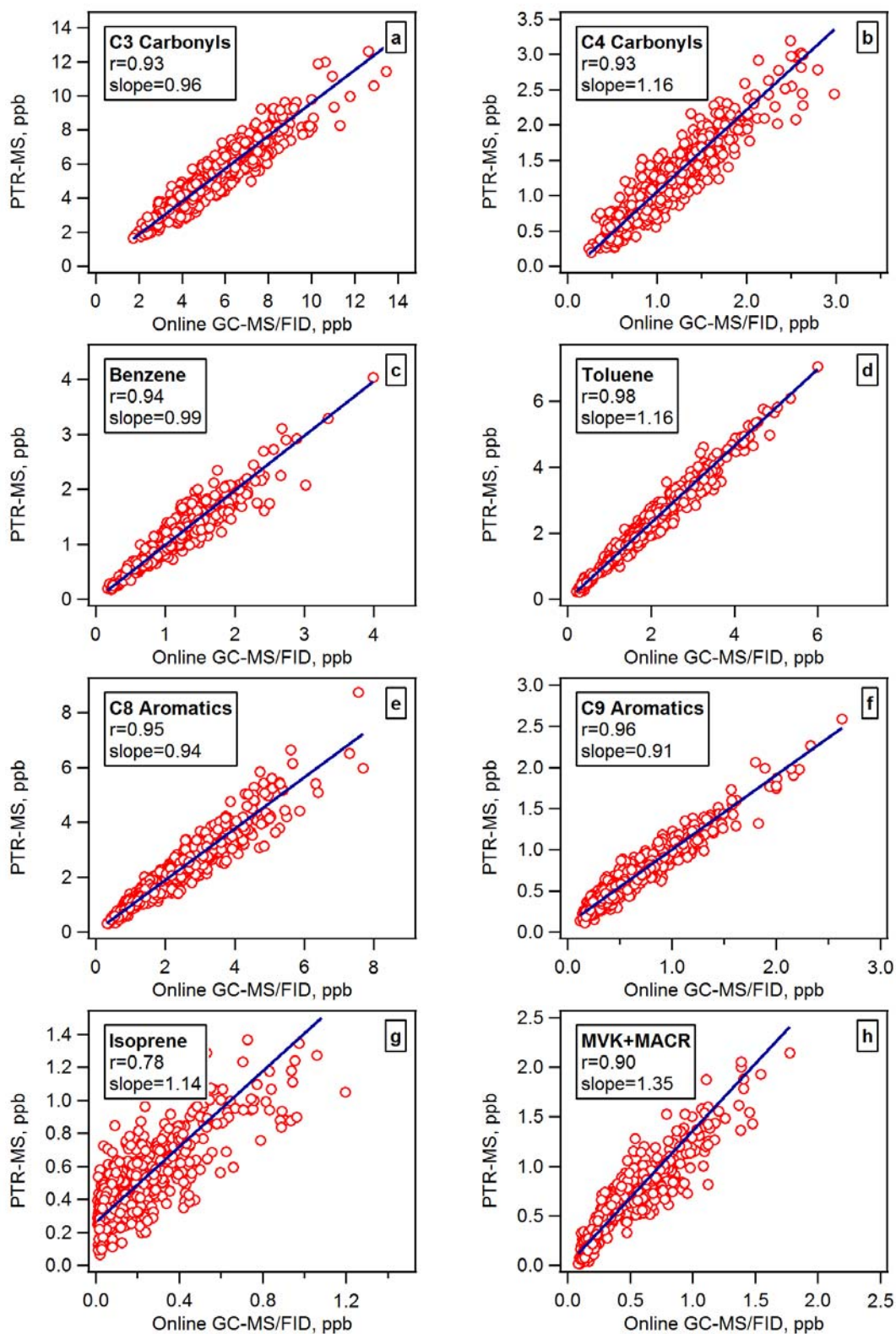
87 variation of photochemical processing degree is larger in 2010.

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121 **Figures**

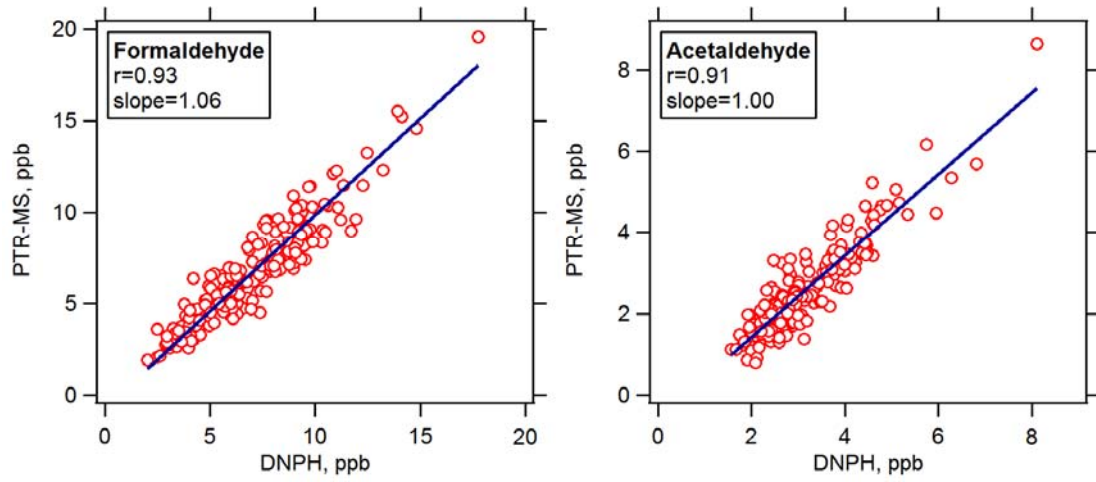


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123 Fig. S1. Comparison between PTR-MS and online GC-MS data. The blue line gives

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the result of an ODR analysis.

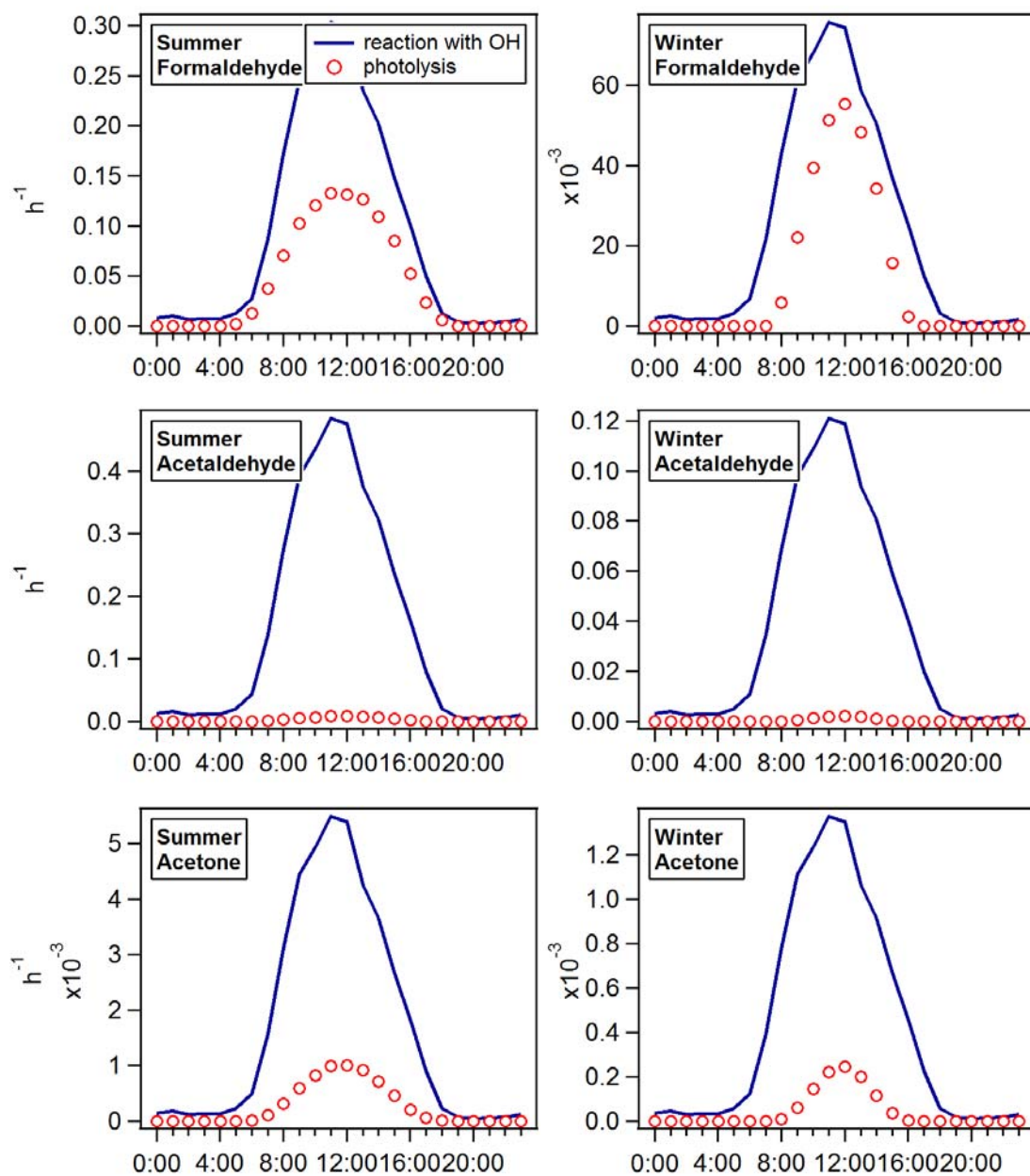


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126 Fig. S2. Comparison between PTR-MS and DNP data. The blue line gives the result

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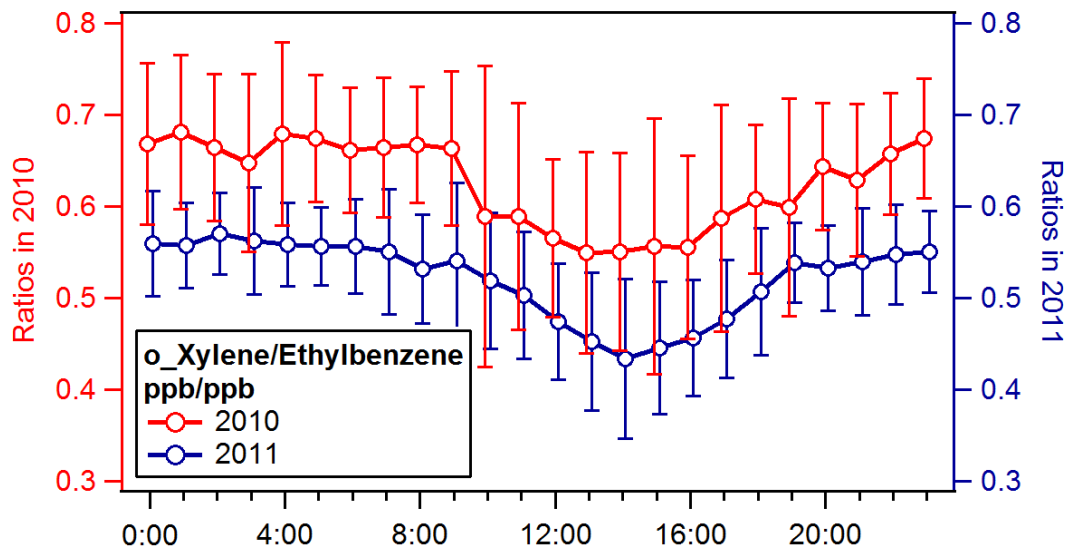
of an ODR analysis.



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Fig. S3. Carbonyl loss rate coefficients in Beijing



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