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*Supplement of*

# Characteristics of wintertime VOCs in suburban and urban Beijing: concentrations, emission ratios, and festival effects

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## S1. Constraining isoprene concentration using MVK+MACR

The concentration of MVK+MACR is used to better constrain the concentration of isoprene. MVK and MACR are mainly from the photooxidation of isoprene, and they can also react with OH (Stroud et al., 2001;Roberts et al., 2006):

Isoprene + OH → 0.23 MACR + 0.33 MVK  $k_1 = 1.0 \times 10^{-10}$ $cm^3$ $molec^{-1}$ $s^{-1}$  (S1)

MACR + OH → products  $k_2 = 2.9 \times 10^{-11}$ $cm^3$ $molec^{-1}$ $s^{-1}$  (S2)

MVK + OH → products  $k_3 = 2.0 \times 10^{-11}$ $cm^3$ $molec^{-1}$ $s^{-1}$  (S3)

Combining these reactions, the MACR/Isoprene ratio can be calculated by:

$$\frac{MACR}{Isoprene} = \frac{0.23k_1}{k_2 - k_1}(1 - e^{(k_1 - k_2)[OH]t}) \quad \text{(S4)}$$

Using eq. (S4), the isoprene concentration can be constrained.

In this study, only the total concentration of MVK+MACR is measured. Fortunately, the MVK/MACR ratio is generally ~2 during daytime (Stroud et al., 2001). As a result, 1/3 of the total MVK+MACR concentration is considered to be MACR during daytime. Using the MACR concentration and an average OH concentration of $1 \times 10^6$ molec $cm^{-3}$ during winter, we estimated the daytime photochemical ages and show them in Figure S4. Three isoprene concentrations were used in this estimation: 1) all m/z 69 signal; 2) m/z 69 multiply a factor of 0.2; 3) m/z 69 signal minus an interference background. As shown in Figure S4, the daytime photochemical age changes are only ~0.2 h and ~0.6 h, when using all m/z 69 signals as isoprene and when using a factor of 0.2, which are highly unlikely. However, the daytime photochemical age change is about 5 h if a background of 0.85 ppb is applied to the m/z 69 signal, which is much more reasonable. Although uncertainties still remain in this method (e.g., using the constant background), it at least indicates that 1) most of the m/z 69 signals are not isoprene, which is similar to Valach et al. (2014); 2) the smaller reduction of m/z 69 during daytime is mainly from interferences. In addition, the interference fraction estimated using this method (84%) is similar with the fraction previous reported (78%) (Valach et al., 2014).

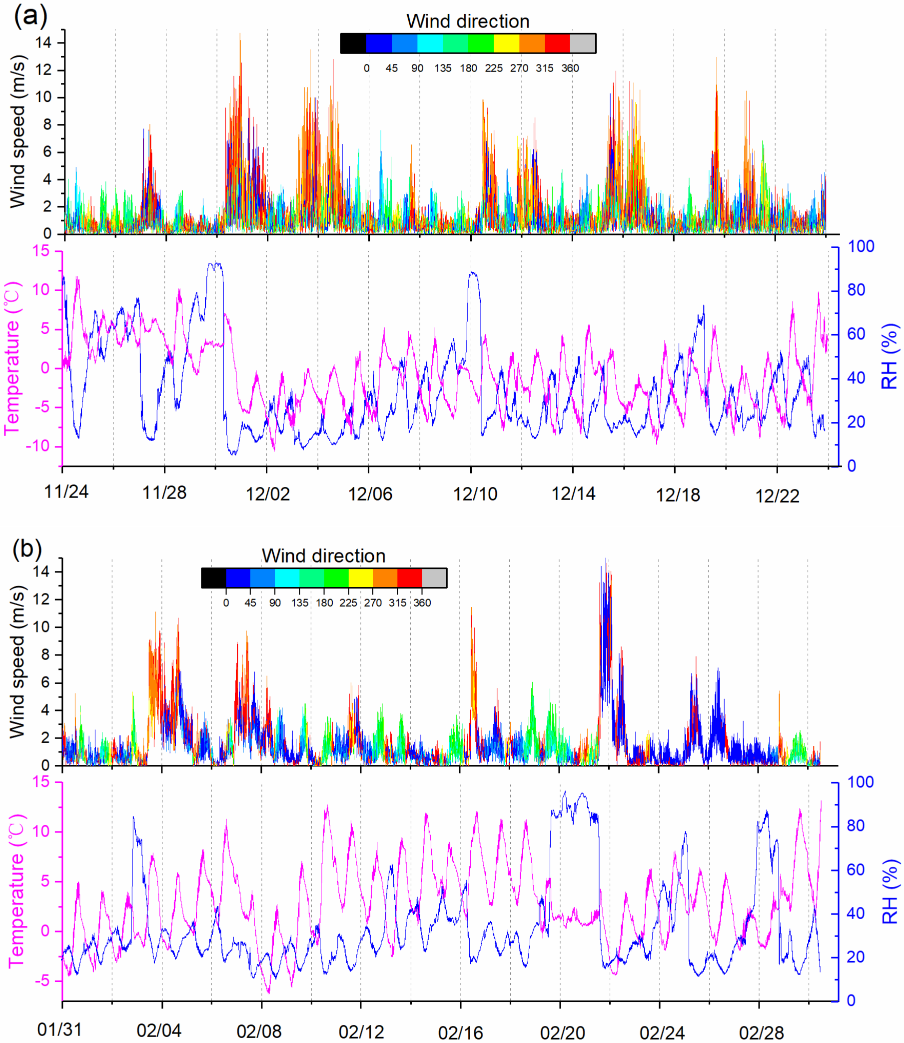


Figure S1. Time series of wind speed, wind direction, temperature, and relative humidity (RH) at the suburban site (a) and the urban site (b).

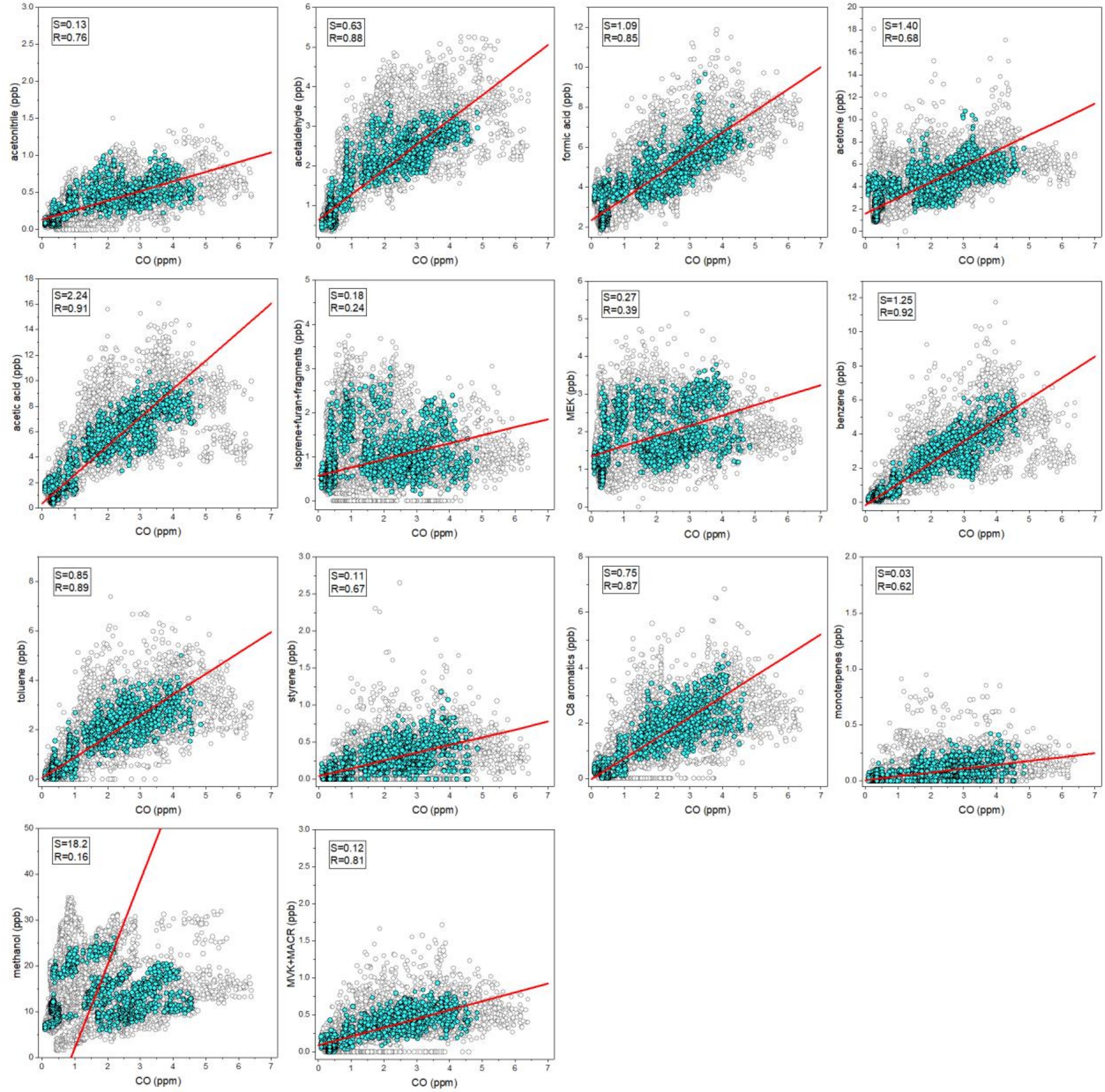


Figure S2. Scatter plots of VOCs over CO at the urban site (Period I only). The colored circles are the 0:00-4:00 LT data, while the grey circles are the all-day data. The slope (S, i.e., emission ratio) and correlation coefficient (R) are also shown in each panel.

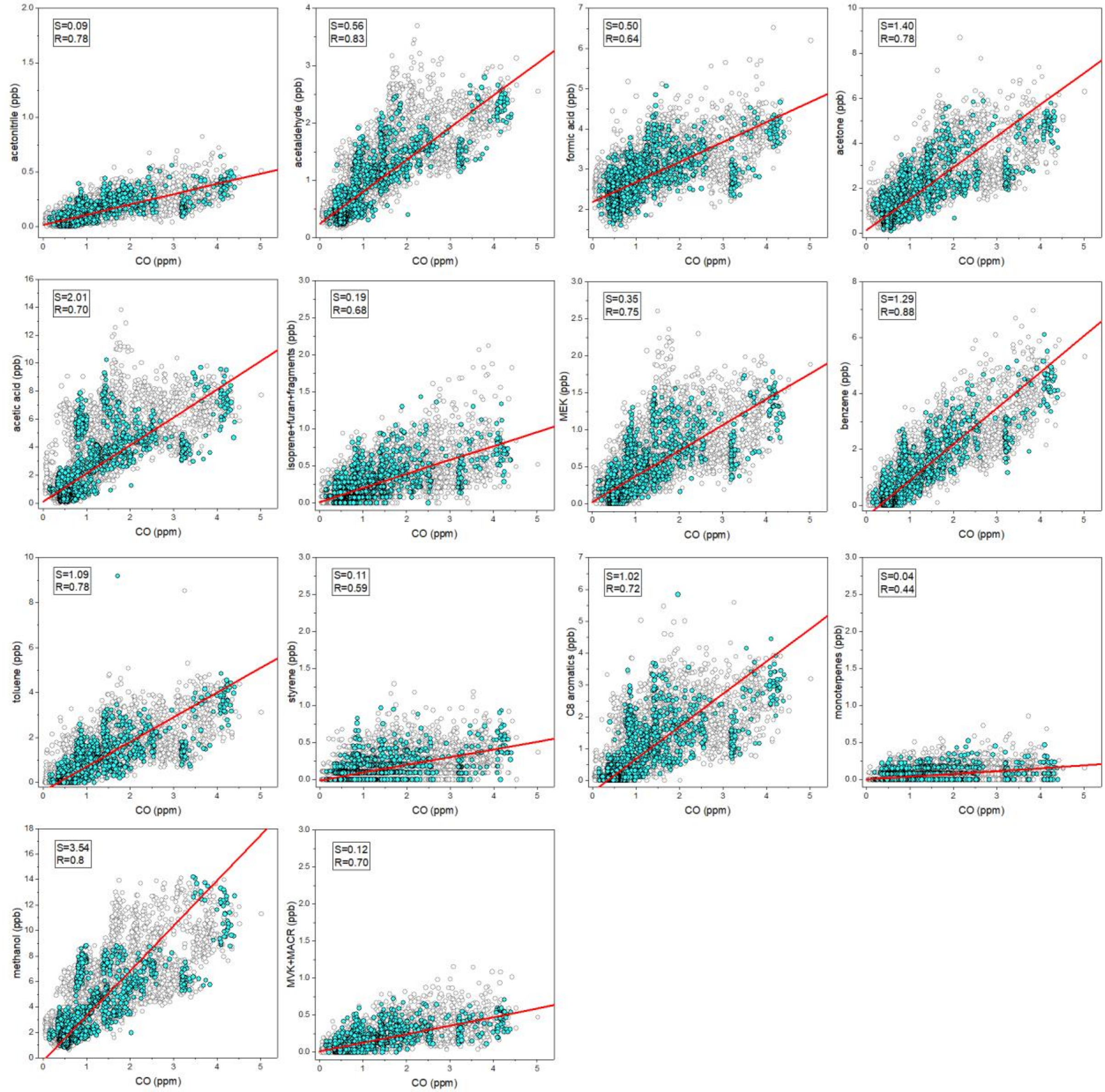


Figure S3. Same as Figure S2 but for the suburban site.

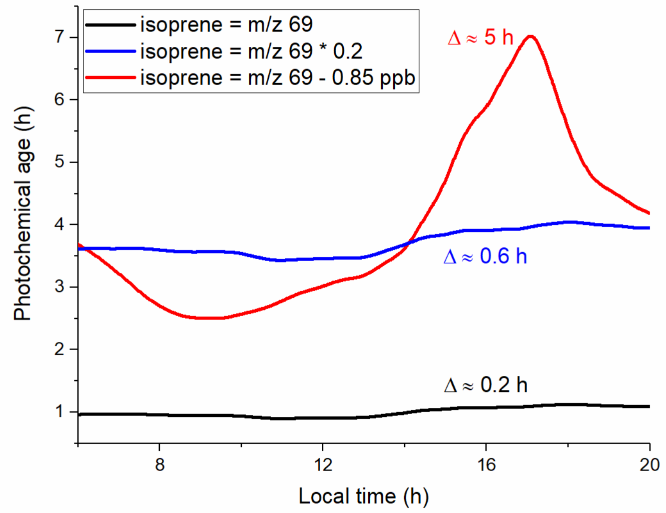


Figure S4. Daytime photochemical age estimated by MACR and isoprene concentrations.

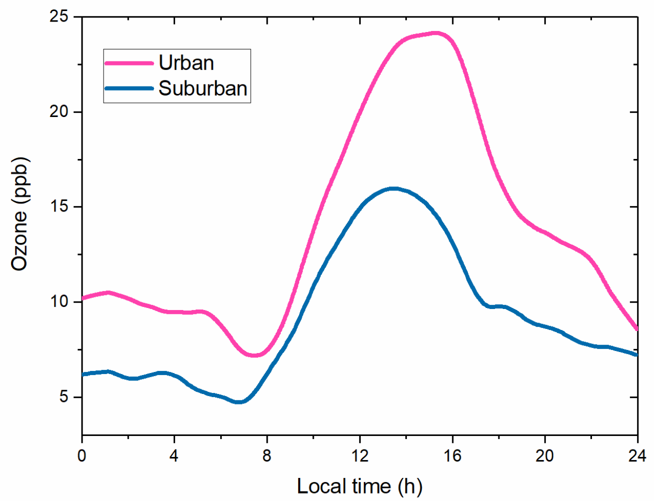


Figure S5. Diurnal variations of ozone in urban (Period I only) and suburban sites.

## References


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