**Supplement of**

**Chemical composition of pre-monsoon air in the Indo-Gangetic Plain measured using a new air quality facility and PTR-MS: high surface ozone and strong influence of biomass burning**

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## Table S1: Details of VOC gas standards used in the calibration experiments

<table>
<thead>
<tr>
<th>Assigned VOC identity</th>
<th>Nominal protonated m/z (Th)</th>
<th>Proton affinity (kJ/mol)</th>
<th>Concentration in VOC standard 1 (ppbV)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Concentration in VOC standard 2 (ppbV)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>33</td>
<td>180.3</td>
<td>–</td>
<td>1050</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>42</td>
<td>186.2</td>
<td>516</td>
<td>1060</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>45</td>
<td>183.8</td>
<td>501</td>
<td>1040</td>
</tr>
<tr>
<td>Acetone</td>
<td>59</td>
<td>194.1</td>
<td>510</td>
<td>990</td>
</tr>
<tr>
<td>Isoprene</td>
<td>69</td>
<td>200.4</td>
<td>482</td>
<td>940</td>
</tr>
<tr>
<td>Benzene</td>
<td>79</td>
<td>181.3</td>
<td>509</td>
<td>990</td>
</tr>
<tr>
<td>Toluene</td>
<td>93</td>
<td>189.8</td>
<td>508</td>
<td>930</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>107</td>
<td>190</td>
<td>511</td>
<td>970</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>121</td>
<td>199.9</td>
<td>510</td>
<td>–</td>
</tr>
</tbody>
</table>

<sup>a</sup> Apel-Riemer Environmental, Inc., Colorado, USA; Stated accuracy: 5%

<sup>b</sup> Ionimed Analytik, Innsbruck, Austria; Stated accuracy: 5% (except acetonitrile, benzene and toluene; for which the stated accuracy was 6%)
Figure S1: Sensitivity and linearity of selected VOCs in the calibration experiment (PTR-MS) performed on 14.05.2013.

The sensitivity of PTR-MS for isoprene, benzene, acetonitrile and acetaldehyde are shown in Figure S1. The data is shown for the calibration performed on 14.05.2012 at 75% relative humidity (RH) in the range of 6 - 20 nmol mol$^{-1}$ using a custom ordered VOC standard (Ionimed Analytik, Innsbruck, Austria). Calibration was also performed using another VOC standard (Apel-Riemer Environmental, Inc., Colorado, USA) at 75% relative humidity in the range of 3ppbV and 10 ppbV on 06.05.2012. The standard gas flow was dynamically diluted with 1000 sccm synthetic air (99.999% purity; Sigma gases, New Delhi), for obtaining the desired mixing ratios of VOCs. As added precaution, the synthetic air flow was further cleaned off VOCs by passing over a Supelco activated charcoal tube and VOC scrubber catalyst (Gas calibration unit; Ionimed Analytik, Innsbruck, Austria). The horizontal error bars in Figure S1 represent the root mean square propagation of errors due 6% uncertainty in the VOC standard and 2% error for each of the two mass flow controllers used for calibration. The vertical error bars represent 2σ instrumental precision error while sampling the standard gas at each dilution mixing ratio.
Figure S2 shows representative five point calibration plots obtained using the O₃, SO₂, CO and NOₓ analyzers. These calibrations were performed on 19.05.2012, 30.04.2013, 08.11.2012 and 31.10.2012, respectively. Calibrations of SO₂, CO and NO were performed using custom ordered gas standards (Chemtron Science Laboratories Pvt. Ltd., Mumbai), whereas the calibration of O₃ was performed using U.V. Photometric Ozone (O₃) Primary Source Calibrator (Model 49iPS; Thermo Fischer Scientific, USA, NIST traceable). The mixing ratios of SO₂, CO and NO in the gas standard cylinders were 5 ppmv, 22 ppmv and 6 ppmv respectively in nitrogen. The horizontal error bars in the calibration plots in Figure S2 represent the accuracy error which includes the 2% uncertainty due to each of the two mass flow controllers used during the calibration, and 5% uncertainty in the external standard for SO₂, CO and NO and 1% uncertainty for the O₃ primary standard. The vertical error bars represent 2σ instrumental precision error while sampling the standard gas at each dilution mixing ratio.

![Calibration Plots](image)

*Figure S2: Linearity of trace gas analyzers during calibrations*
Figure S3: Map of India showing fire activity (at confidence interval > 80%) detected by MODIS (red dots) on 11th, 15th and 31st of May 2012. 72 hours back trajectories arriving at the receptor site at 20 m above ground level on 11th May 20:30 local time (green), 16th May 05:30 local time (yellow) and 31st May 19:30 local time (blue) respectively are also shown.
Figure S4: Correlation plot of acetonitrile and C8- aromatics with NO₃ (top panel); correlation plot of methanol, acetaldehyde, acetone and isoprene with acetonitrile (bottom panel) (individual points are the 1 minute temporal resolution night-time data).
Figure S5: Diel box and whisker plot of a) C-8 aromatics, b) C-9 aromatics, c) acetone + propanal, d) PM2.5 and e) PM10 derived from all measurements (n > 14300 for each species) in May 2012.