

## Supplement

Table 1: Details of VOC gas standards used in the calibration experiments

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

<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%)

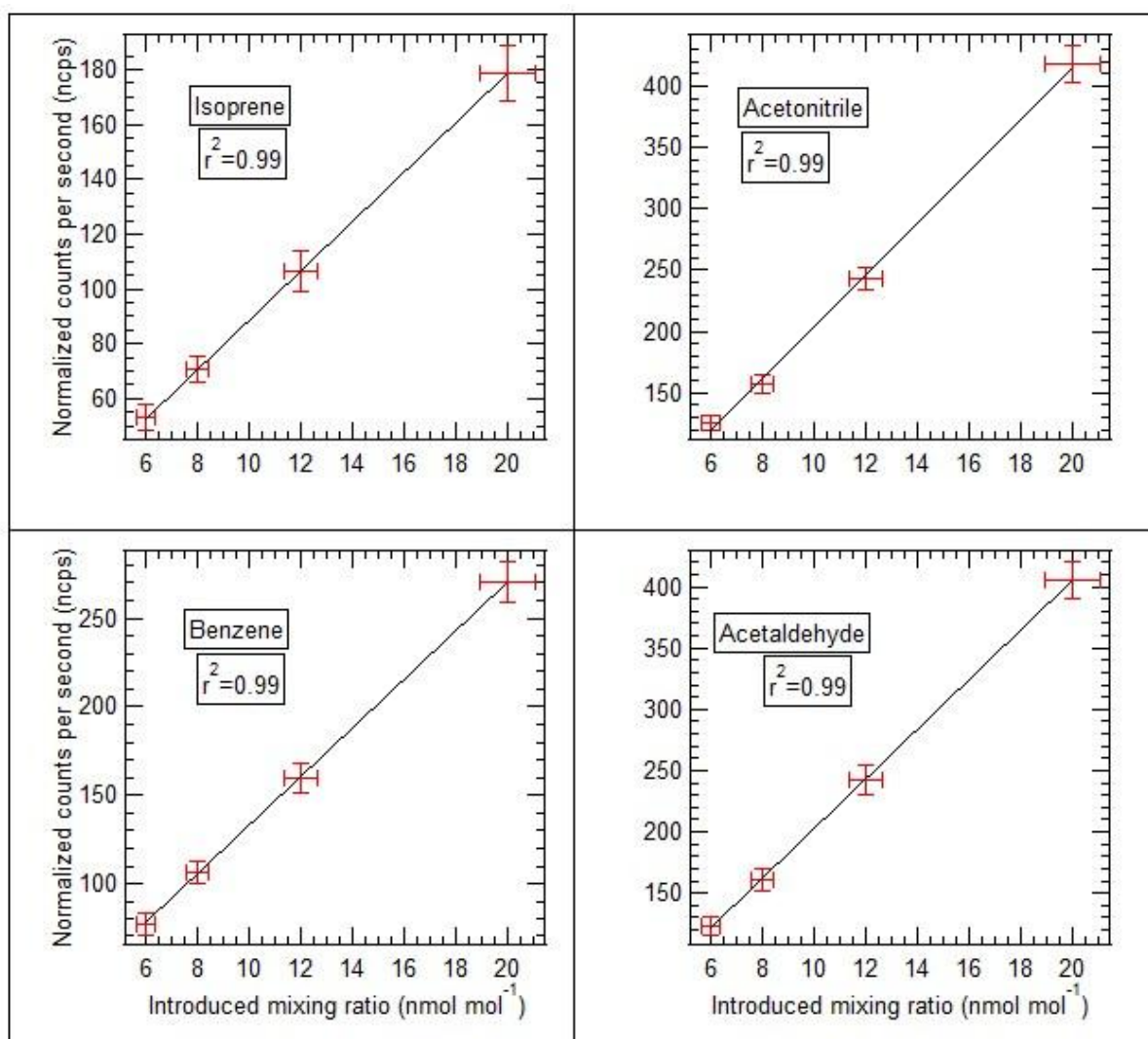


Figure 1: PTR-MS sensitivity and linearity calibrations for select VOCs in calibration experiment performed on 14.05.2013

The sensitivity of PTR-MS for isoprene, benzene, acetonitrile and acetaldehyde are shown in Figure 1. 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<sup>-1</sup> using custom ordered VOC standard 1 (Ionimed Analytik, Innsbruck, Austria). Calibration was also performed using VOC standard 2 (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 1 represent the accuracy error and the vertical error bars represent precision error. The accuracy error represents the root mean square propagation of errors due to 6% uncertainty in the VOC standard and 2% error for each of the two mass flow controllers used for calibration. The precision error was taken to be the 2 $\sigma$  variability while measuring at the given mixing ratio.

Figure 2 shows representative five point calibration curves obtained using the O<sub>3</sub>, SO<sub>2</sub>, CO and NO<sub>x</sub> analyzers. These calibrations were performed on 19.05.2012, 30.04.2013, 08.11.2012 and 31.10.2012, respectively. Calibrations of SO<sub>2</sub>, CO and NO were performed using custom ordered gas standards (Chemtron Science Laboratories Pvt. Ltd., Mumbai), whereas the calibration of O<sub>3</sub> was performed using U.V. Photometric Ozone (O<sub>3</sub>) Primary Source Calibrator (Model 49iPS; Thermo Fischer Scientific, USA, NIST traceable). The mixing ratios of SO<sub>2</sub>, 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 2 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 SO<sub>2</sub>, CO and NO and 1% uncertainty for the O<sub>3</sub> primary standard. The vertical error bars represent 2σ instrumental precision error while sampling the standard gas at each dilution mixing ratio.

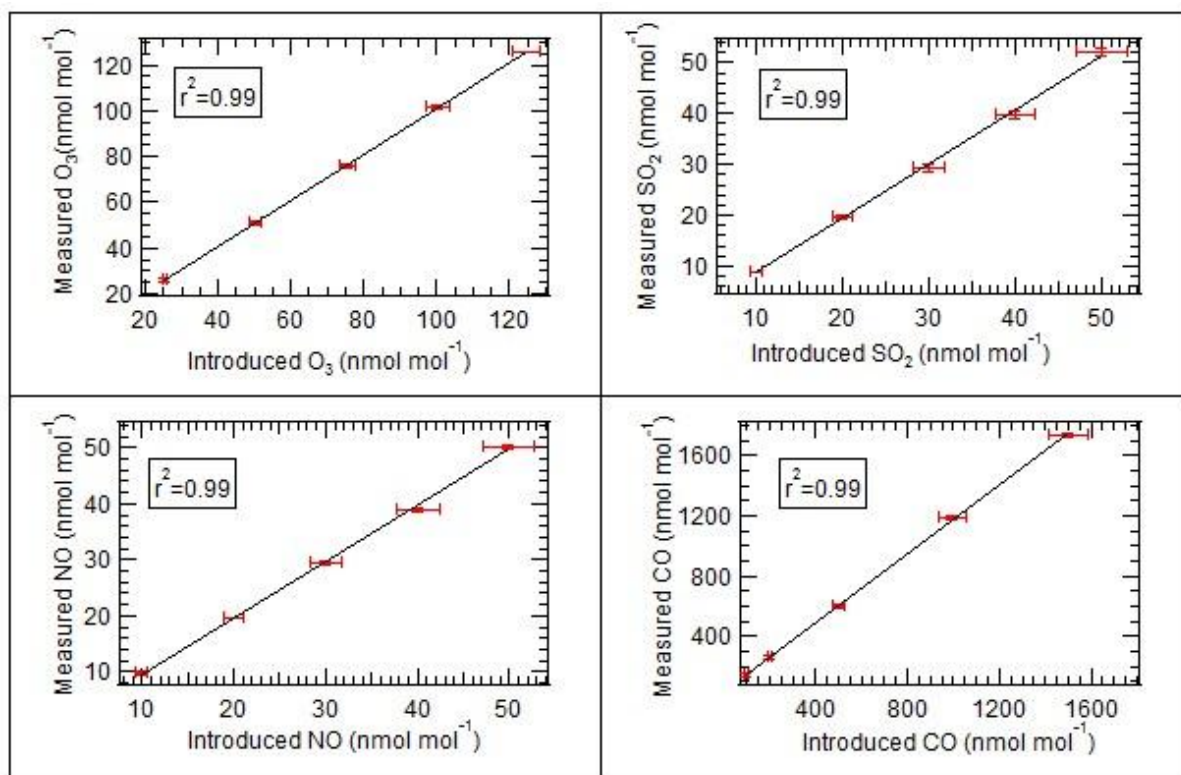


Figure 1: Calibration curve showing linearity of trace gas analyzers during calibration

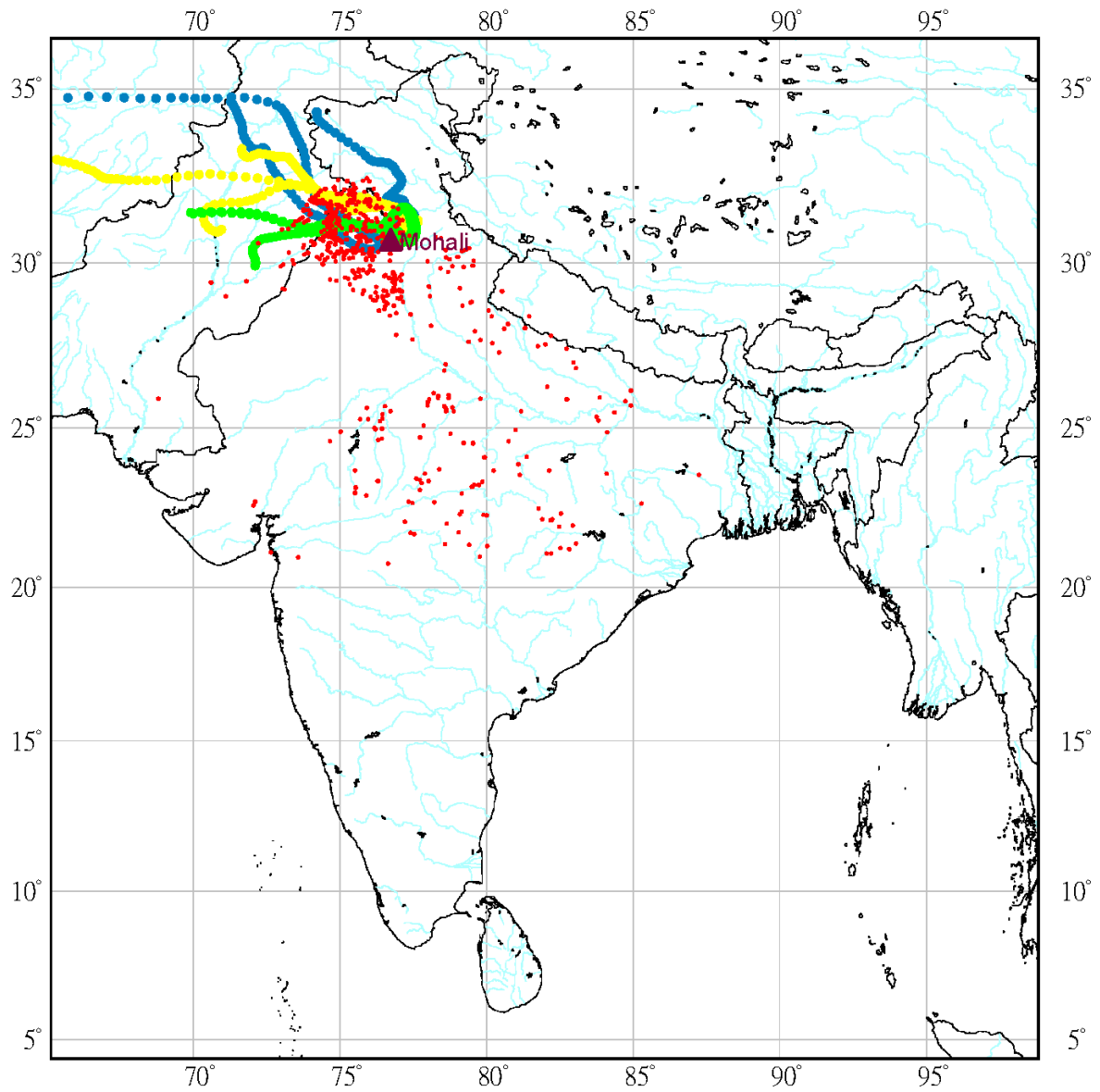


Figure 2: Map of India showing fire activity (confidence > 80%) detected by MODIS (red dots) on 11<sup>th</sup>, 15<sup>th</sup> and 31<sup>st</sup> of May 2013. 72 hours back trajectories arriving at the receptor site at 20 m above ground level on 11<sup>th</sup> may 20:30 local time (green), 16<sup>th</sup> may 05:30 local time (yellow) and 31<sup>st</sup> may 19:30 local time (blue) respectively are also shown.