Biogenic and anthropogenic sources of isoprene and monoterpenes and their secondary organic aerosol in Delhi, India

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Data Processing

Identified compounds were input into the compound library in the generic form: $C_cH_hO_oN_nS_s$ (where c,h,o,n,s represent the number of carbon, hydrogen, oxygen, nitrogen and sulfur atoms respectively). Where multiple isomers were observed, each isomer was added to the library independently, based on its retention time (RT). The UHPLC/ESI-HR-MS data for each standard and ambient sample were analysed using Tracefinder general Quan software (Thermo Fisher Scientific). Blank subtractions were undertaken for all ambient samples, using a field blank. Tracefinder extracted compound peak areas from each sample based on the assigned library. The mass tolerance of the method was set to 3 ppm, with the RT window set to 10 s. The peak tailing factor was set to 2.0 and the detection algorithm used was ICIS, with a nearest RT detection strategy. Minimum signal-to-noise (S/N) for a positive identification was set to 3.0. The suitability of the peak was also assessed for a positive identification, with the peak height at which to compare symmetry of the left and right side of the peaks set to 40 % and symmetry threshold which is the minimum percentage difference considered symmetrical set to 70 %.

Matrix effects

The measured signal intensity of the standards in a blank solvent matrix were compared to the ambient aerosol matrix. A 10 µL mixture containing camphorsulfonic acid, 2-MG-OS and 2-MT-OS at 10 ppm was spiked into either 100 µL of ambient filter sample extract or into 100 µL of blank 50:50 ($MeOH:H_2O$) solvent. The samples were run as described above. The matrix effect factors were then calculated by taking the compound areas from the spiked ambient samples, subtracting the areas of compounds that were already present in the ambient sample, and then dividing by the compound areas in the blank matrix. If no matrix effect was present the ratio would equal 1. More details of the matrix effects associated with the different compound classes and quantification errors are discussed in the SI. Table S1 shows the ratios across 8 ambient samples collected during both campaigns, which represent a mixture of high and low $PM_{2.5}$ concentrations across different times of day. 2-MT-OS and 2-MG-OS showed significant matrix effects, with average ± SD matrix ratios of 0.17 ±0.06 and 0.40 ± 0.23, suggesting 83% and 60% suppressions in signal response. Camphorsulfonic acid exhibited a much smaller matrix suppression, with an average of 0.76 ± 0.16 suggesting a 24 % suppression, in line with Bryant et al., 2021. The suppression is likely due to the large numbers of co-eluting inorganic and organic species, reducing the ionisation efficiency of the marker compounds. Matrix correction factors were applied alongside calibrations to different compound classes and for compounds eluting at different times.

Table S1. Matrix effect analysis results from 5 filter samples on three different organosulfate standards (CAM-OS – Camphorsulfonic acid, MG-OS – 2-methyl glyceric acid organosulfate, MT-OS – 2-methyl tetrol organosulfate). Alongside $PM_{2.5}$ and SO_4 concentrations. The values in bold are the average ratios between a clean matrix and an ambient sample matrix.

Sample start date (dd/mm)	Time of day	Length (hour)	$PM_{2.5}$ ($\mu g\ m^{-3}$)	SO_4 ($\mu g\ m^{-3}$)	CAM-OS	MG-OS	MT-OS
16/10	13:30-14:30	1	NA	18.2	0.67	0.49	0.21
18/10	09:30-10:00	0.5	NA	25	0.60	0.58	0.23
18/10	19:00-09:30	14.5	120.2	11	0.69	0.10	0.16
30/05	17:30-08:00	14.5	134	12.8	0.84	0.22	0.06
04/06	08:30-11:30	3	124.7	19.7	1.01	0.59	0.16
Average					**0.76 ± 0.16**	**0.40 ± 0.23**	**0.17 ± 0.06**

Table S2. Average pollutant and meteorological values across the pre- and post-monsoon campaigns.

	Pre-				Post-			
Pollutant	**Mean**	**Median**	**SD**	**Max**	**Mean**	**Median**	**SD**	**Max**
NO (ppbv)	17.8	1.65	66.1	474	176	71.8	223	871
NO_2 (ppbv)	30.8	25	17.9	109	41.7	38.1	21.1	169
NO_X (ppbv)	48.7	27.2	77.3	548	218	123	221	900
SO_2 (ppbv)	5.29	3.55	15.8	431	5.41	4.72	3.95	69.6
O_3 (ppbv)	50.8	46.8	30.6	182	22.4	5.91	29.4	285
$PM_{2.5}$ (µg m^{-3})	141	125	66.2	672	182	170	93.9	695
Inorg SO_4 (µg m^{-3})	16.9	17.7	4.56	26.7	16.5	16.2	3.38	26.4
Org SO_4 (µg m^{-3})	7.5	7.3	1.78	13.2	5.55	5.16	2.68	14.2
Organics (µg m^{-3})	19.8	15.8	13.7	114	48.7	37.8	35.4	221
Nitrate (µg m^{-3})	1.58	1.13	1.36	8.01	5.83	4.68	4.18	28.8
PBLH (m)	891	508	879	4064	412	84.9	601	2722
ws (ms^{-1})	3.81	4.1	1.44	8.23	1.71	1.8	1.33	5.4
Temp (^{o}C)	35.8	35.5	4.53	46.5	24.7	24.5	4.56	35
RH (%)	39.4	39.3	13.6	70.6	57.3	58.1	16.6	90.1
Isoprene (ppbv)	1.22	0.51	1.28	4.62	0.93	0.79	0.65	6.67
limonene (ppbv)	0.0095	0.0065	0.017	0.19	0.42	0.19	0.51	2.12
α-pinene (ppbv)	0.034	0.034	0.011	0.078	0.1	0.052	0.11	0.56

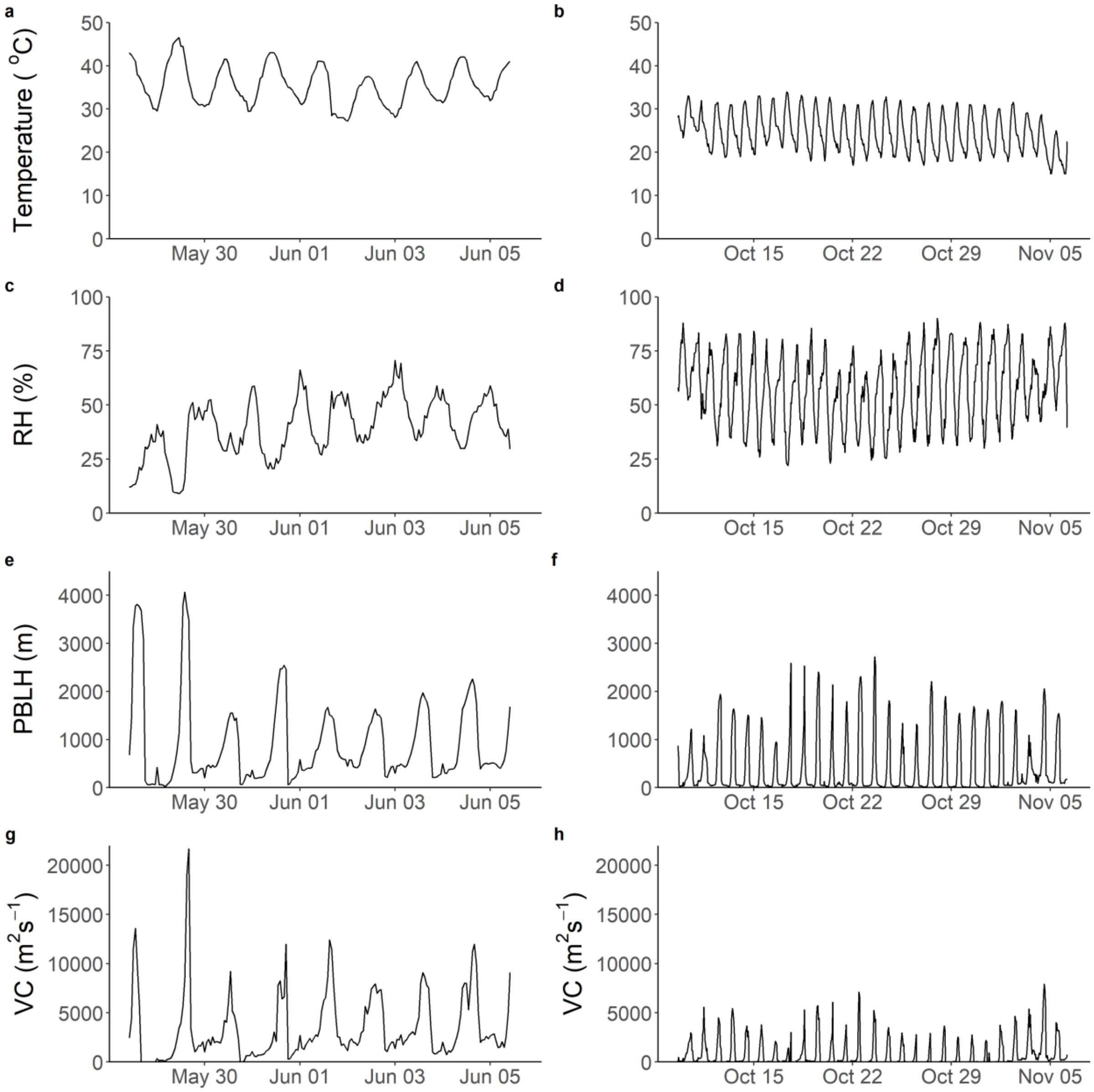

Figure S1. Time series variations of measured temperature, planetary boundary layer height (PBLH), relative humidity (RH) and ventilation coefficient (VC, PBLH x wind speed) across pre- (left, a, c, e, g) and post- (right, b, d, f, h) monsoon.

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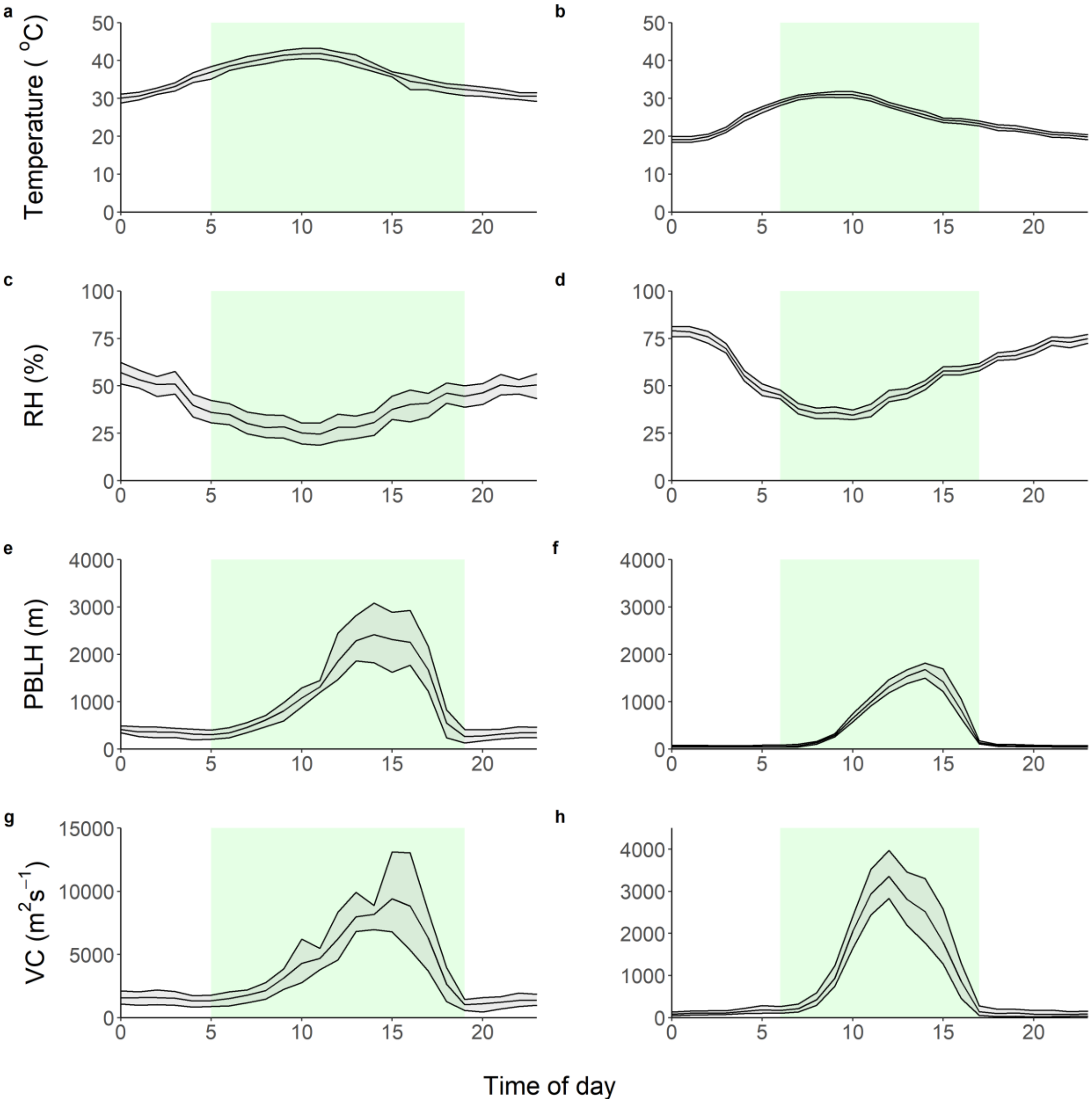

Figure S2. Diurnal variations of temperature, relative humidity (RH), planetary boundary layer height (PBLH) and ventilation coefficient (VC, PBLH * wind speed) across the pre- (left, a, c, e, g) and post-monsoon (right, b, d, f, h) campaigns. The grey shaded area represents the 95 % confidence interval. The green shaded area represents the times driven by biogenic emissions, as defined by the isoprene diurnals (Figure 3).

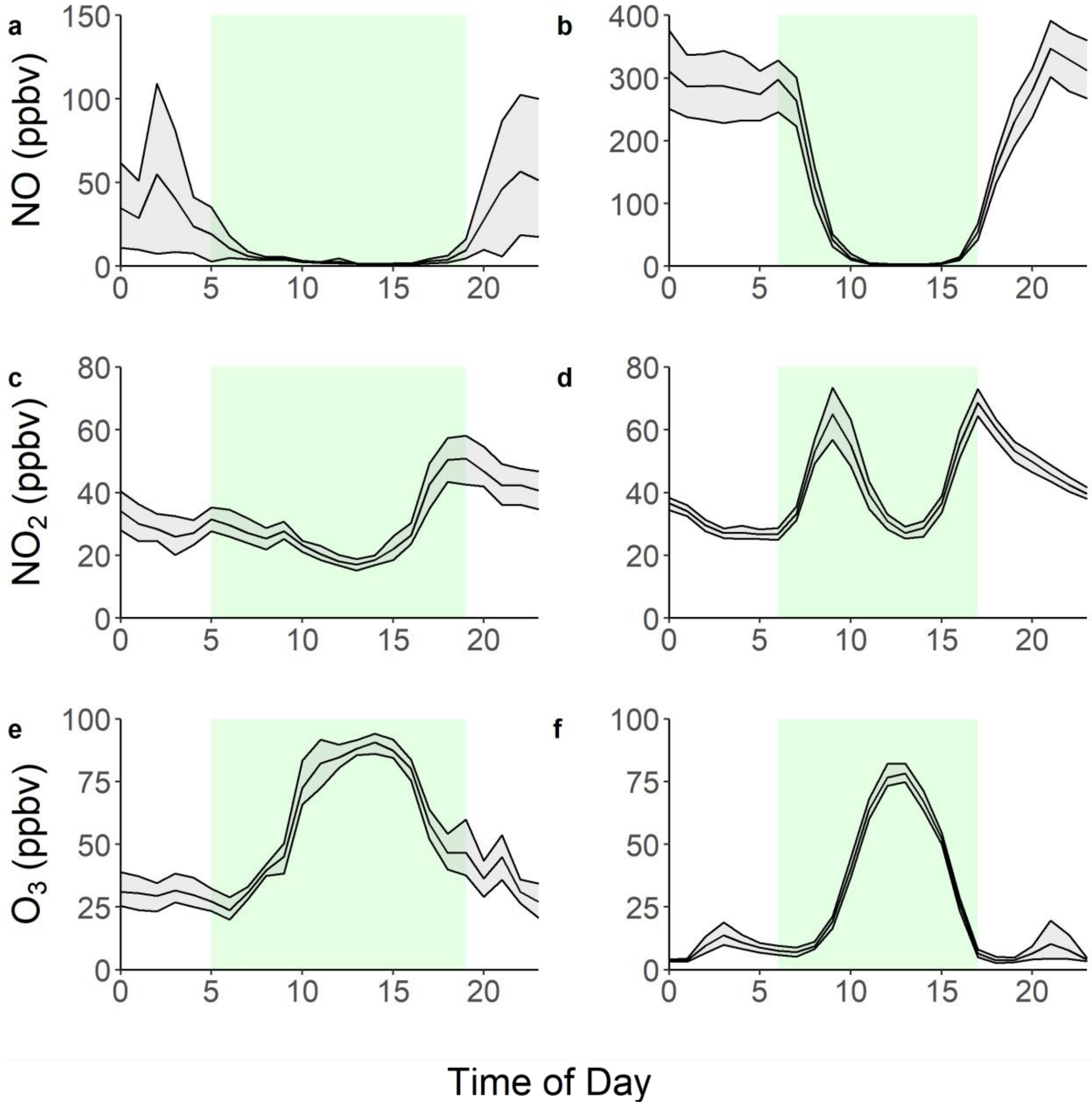

Figure S3. Diurnal variations of NO, NO_2 and O_3 across the pre (left, a,c,e) and post-monsoon (right, b,d,f) campaigns. The grey shaded area represents the 95 % confidence interval. The green shaded area represents the times driven by biogenic emissions, as defined by the isoprene diurnals (Figure 3).

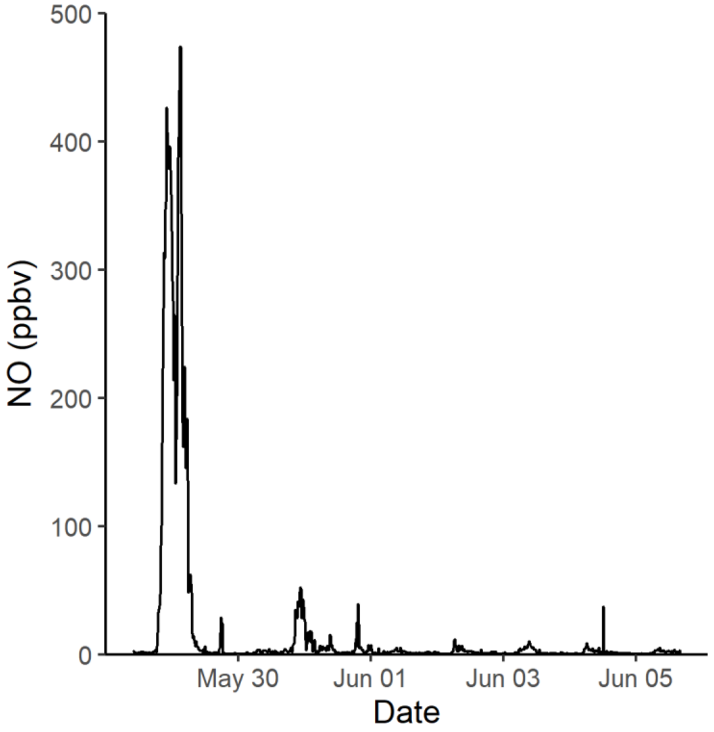

Figure S4. Full time series of NO concentrations during the pre-monsoon campaign.

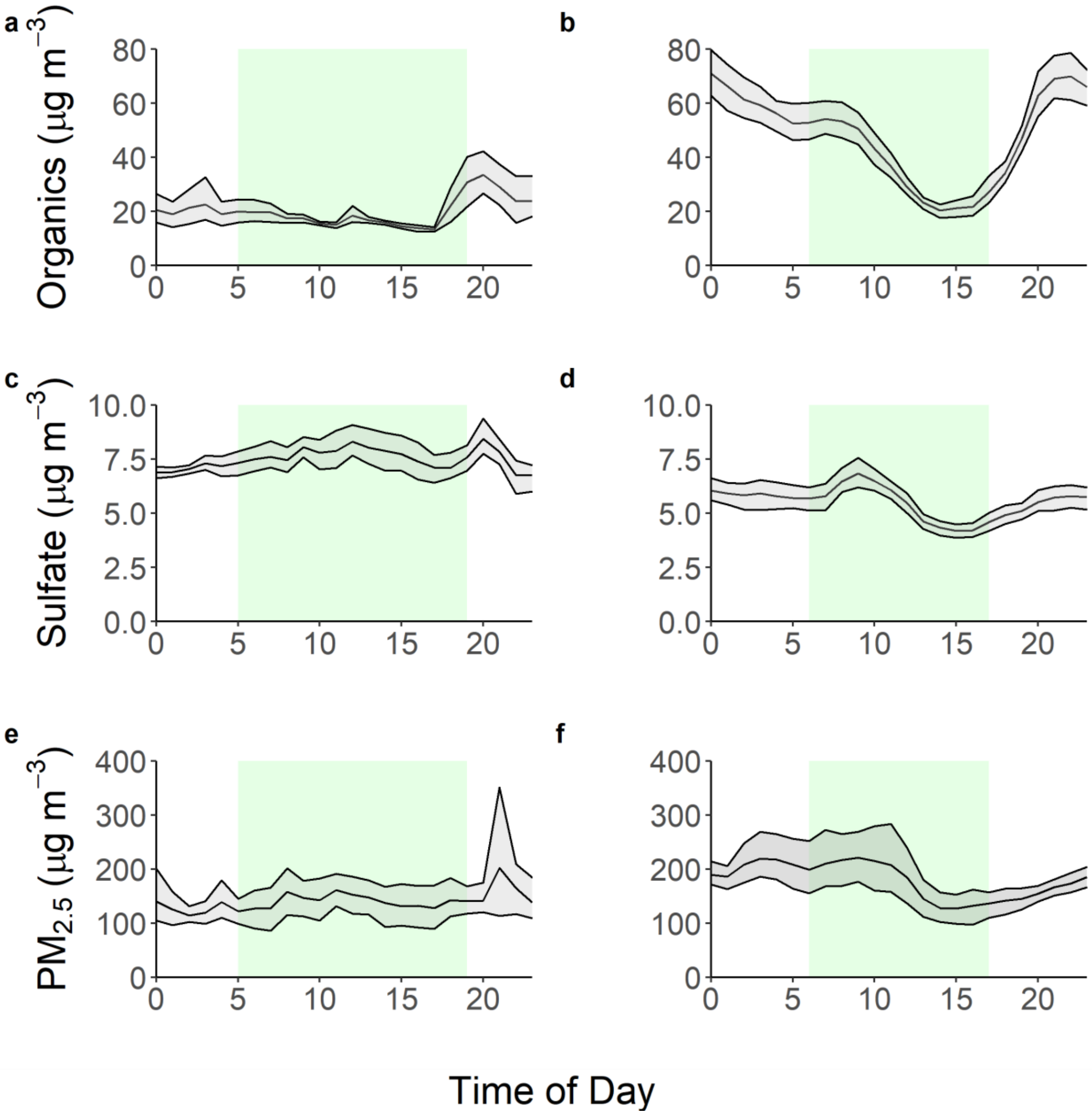

Figure S5. Mean diurnal variations for the aerosol chemical species, sulfate and total organics and $PM_{2.5}$ concentrations across the pre-mosnoon (left, a,c,e) and post-monsoon (right, b,d,f). The 95 % confidence interval is given in grey. The green sections highlight the daytime hours as defined by the isoprene diurnal.

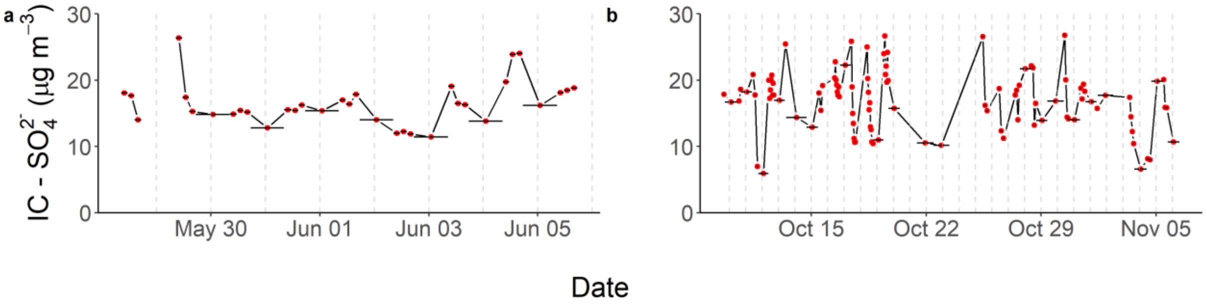

Figure S6. Time series across the pre- (left,a) and post-monsoon (right,b) campaigns of inorganic sulfate quantified by ion chromatography. The vertical dotted lines represent midnight for each day. Only species identified in more than 40 % of the samples for each campaign were included.