1 Instrument setup

The both Gual Pahari and Mukteshwar measurements we conducted using a Differential Mobility Particle Sizer (DMPS) coupled with a SP2 (Fig. S1). The DMPS is composed of a Differential Mobility Analyzer (DMA; medium HAUKE-type, with a bipolar radioactive (Am) neutralizer) and a Condensation Particle Counter (CPC; TSI model 3010, TSI Inc. USA). A polydisperse ambient aerosol population is dried and the charge distribution is neutralized before entering the DMA where a narrow particle size range is selected based on a voltage control (VDC) while keeping the constant flow rates (both sheath and aerosol sample: Q_a). The size-selected aerosol is then lead to the CPC, which measured the total number concentration of particles (N_{total}). The SP2 was connected in parallel to the CPC where the SP2 measures the number concentrations of all particles (N_{total}) and also those containing refractory material (N_{rBC}), which is assumed to be refractory black carbon (rBC). In addition, the SP2 measures particle sizes and the mass of refractory material (m_{rBC}) in each particle. Particle size measured by the SP2 is only used mainly as a diagnostic parameter; it should be the same as the mobility size selected by the DMA, which is used in the calculations. rBC core volume equivalent diameters (assuming a compact spherical rBC "core" with 1800 kg m^{-3} density) were calculated from the measured rBC mass; it represents the volume fraction of rBC in each absorbing particle.

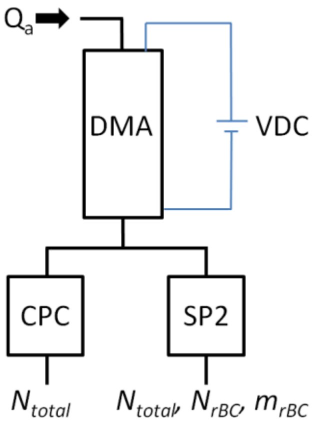

Figure S1: Schematics of the measurement setup.

The DMA voltages are changed stepwise through selected voltage range. Here 30 voltage settings were selected so that logarithmically spaced particle size bins ranged from about 20 to 650 nm (there were small fluctuations due to instrument temperature and pressure changes). The time step was initially set to 30 s, but it was later increased to 60 s to improve the SP2 counting statistics. As a result, the full scan with 60 s time step took 32 minutes.

The CPC and SP2 data were aligned visually. The CPC data is automatically saved as an average concentration for each time step, but this was done manually for the SP2 data where the relevant parameters are number concentrations for all particles and those containing rBC, and rBC core size distributions which are here represented by suitable distribution parameters. These were calculated using the standard instrument calibration and data analysis methods (see below). The first measurements showed that the rBC core size distributions are not always narrow and unimodal, which means that the commonly used number mean rBC core diameter is smaller than the corresponding mass mean diameter. For consistency with the further mass calculations, both mass and number mean diameters were saved.

1.1 SP2 calibration

The maximum incandescence and scattering signals are proportional to the refractory particle mass and the total particle size, respectively, and these dependencies are parameterized using suitable calibration reference materials. Our regular incandescence calibrations are based on size-selected Aquadag (Acheson Inc., USA) particles which masses are calculated using the density parameterization from Gysel et al. (2011). Several studies have shown that fullerene soot is the best representative of ambient rBC and its incandescence signal is about 75% of that of Aquadag with the same particle mass (Moteki and Kondo, 2010; Kondo et al., 2011; Gysel et al., 2011; Baumgardner et al., 2012; Laborde et al., 2012). Therefore, Aquadag incandescence amplitudes were multiplied by a factor of 0.75 to make it representative of the fullerene soot and ambient rBC. This fullerene soot-equivalent calibration gives ambient rBC particle mass as a function of the measured maximum incandescence signal. rBC core volume equivalent diameters (briefly: rBC core diameter) are then calculated by assuming a compact spherical “core” with 1800 kg m^{-3} density. The sizing limits for the refractory material are 0.3-380 fg for rBC mass and 70-740 nm for the rBC core diameter.

Although we do not use scattering sizes measured by the SP2 (these are accurately selected by the DMA especially for absorbing particles), we calculate those for diagnostic purposes. Our regular scattering size calibrations are based on size-selected ammonium sulfate, but here we can also use size-selected ambient particles. The instrument was calibrated using ammonium sulfate before shipping to India (December 13, 2013), but not during the campaign. Scattering amplitudes from the ammonium sulfate calibration and Mukteshwar observations (February 9, 2014) are almost identical with only 3% difference in particle size. Such a small difference can be easily caused by the difference in optical properties of ammonium sulfate and ambient particles or minor changes in the instrument performance. However, significant reduction in scattering signal (equivalent to 17% increase in particle size) is observed after the instrument was moved to Gual Pahari (data from April 11, 2014). This is most likely caused by decreased laser beam intensity (Laborde et al., 2012). In order to remove this constant sizing bias, Gual Pahari scattering calibration is based on field measurements (data from April 11, 2014).

2 Data analysis

Just as in a typical DMPS data analysis, ambient size distributions need to be calculated from the raw observations of particle number versus voltage using an inversion code. This inversion depends mainly on particle charging efficiencies and the DMA transfer function. For the DMPS system we have used a standard pseudo-inverse method (see the FMI DMPS inversion description in Wiedensohler et al., 2012), but this method cannot be directly applied to the SP2 data. The main reason is that the SP2 cannot detect small particles (minimum rBC size is about 70 nm and that for scattering particles is roughly 180 nm), which means that a large fraction of the size scan particle counts are originating from multiply charged particles. To avoid problems with the data inversion, SP2 concentrations are calculated using the inversion results from DMPS. It would have been possible to convert the time and size dependent particle number concentrations measured by the SP2 (N_{SP2}) to corresponding number size distributions ($dN_{SP2}/dlogD_p$) by multiplying these with the ratio of the DMPS number size distribution ($dN_{DMPS}/dlogD_p$) to the CPC concentration (N_{CPC}). However, in order to reduce noise from the inversion and to make SP2 results less dependent on the CPC data, we have calculated the modes of the DMPS size distribution to the CPC concentration ratio for each DMA size. This method is essentially the same as taking a typical DMPS scan and calculating the inversion from that. Figure S2 shows an example of the SP2 inversion method. The blue lines and markers represent the inversion for the SP2 concentrations.

Parameters like the average rBC core diameter and scattering particle size and number fraction of absorbing particles are independent of particle concentrations, so inversion is not needed. The average parameters are just averages of those of the individual particles observed during each 30 or 60 s time step. The number fraction is calculated using the corresponding integrated number concentrations.

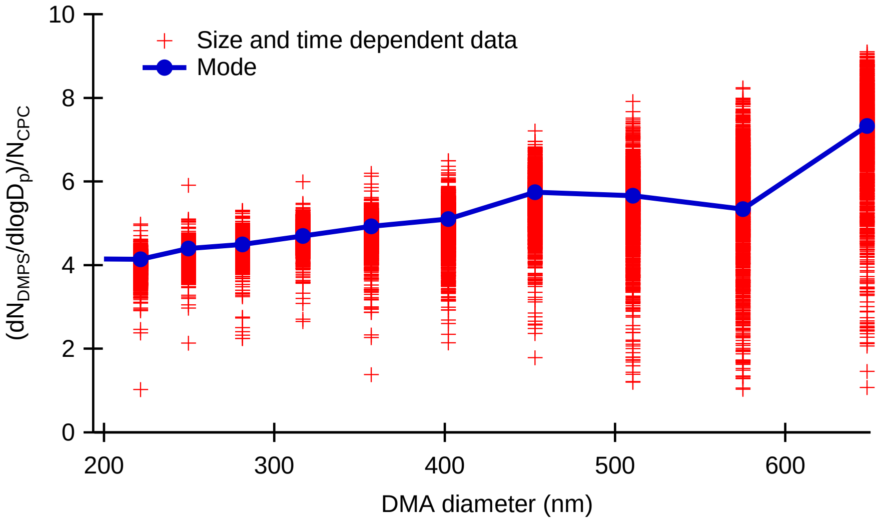

Figure S2: Size and time dependent ratios of the DMPS number size distribution ($dN_{DMPS}/dlogD_p$) to the CPC concentration (N_{CPC}) from Mukteshwar measurements. The blue line and the markers (mode for each DMA diameter) show the size dependent inversion for calculating concentration from SP2 data.

3 Consistency tests

Since this is a new method, tests were made to confirm the validity of the results. First of all, CPC and SP2 total (absorbing + non-absorbing particles including those that saturate the detectors) number concentrations (used without inversion) should be equal for all DMA sizes larger than about 200 nm, which is the SP2 detection limit for scattering particles. Secondly, the DMA-selected and non-absorbing particle mean diameters should be almost identical. Any fluctuation in concentration or size could mean fluctuations in SP2 performance; the DMA and CPC could have problems too, but these are generally highly stable instruments. Finally, the total rBC mass concentrations are compared with equivalent black carbon (eBC) measured by a 7-wavelength Aethalometer in Mukteshwar.

3.1 Number concentrations

Figure S3 shows the ratio of CPC and SP2 total (scattering + absorbing) number concentrations as a function of DMA size. The DMA size was limited to 200-420 nm size range, because scattering particle detection limit is close to 200 nm and low particle counts increase noise at sizes larger than 450 nm. Although the number concentrations are correlated, there seems to be a constant bias between CPC readings and total concentrations from SP2. The CPC readings are consistently about 82 % of those of the SP2 at both sites. Because CPC is a commonly used and robust instrument, it is expected that the SP2 over counts possibly due to a higher flow rate than expected. Therefore, all SP2 mass and number concentration values are here multiplied by a factor of 0.82. With this correction CPC and SP2 results become practically identical.

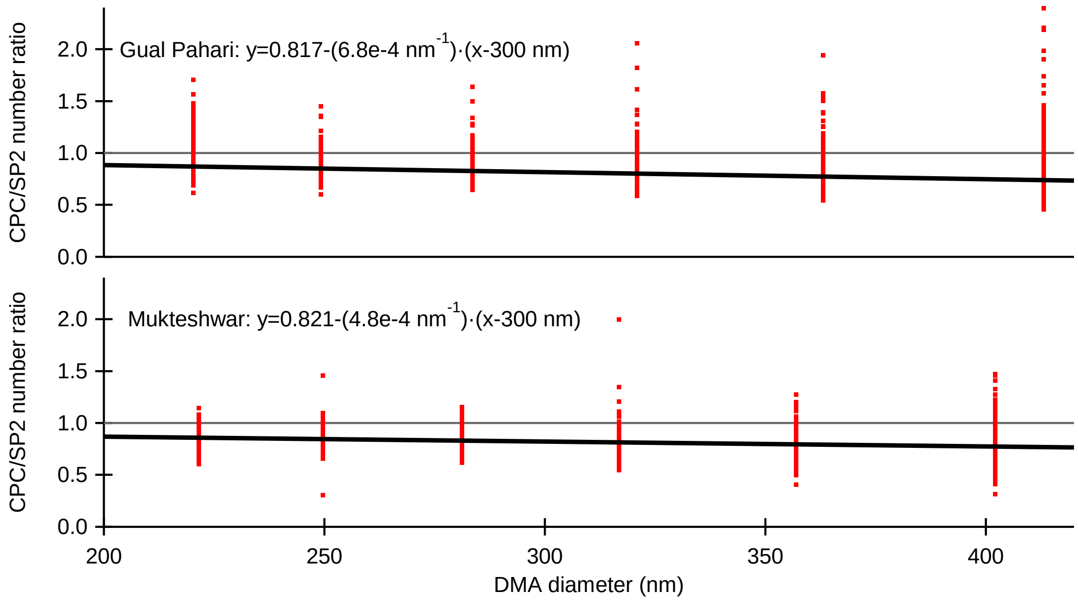

Figure S3: The CPC to total number concentration ratios as a function of DMA size for both Gual Pahari and Mukteshwar. Also shown are the linear fits to the data. The highest number ratios (about 4 for Gual Pahari) are not shown.

The figure above shows that there is some variability in the ratios, but a closer look shows that much of this variability is actually time-dependent. Furthermore, these time-dependent variations correlate with the SP2 chamber temperature. Figure S4 shows the number ratio for about 285 nm DMA diameter as a function of chamber temperature from both measurements campaigns. SP2 chamber temperature depends strongly on the temperature of the air-conditioned measurement building, but less on the ambient temperature. This indicates that the difference in particle number concentration is most likely caused by the SP2. Although temperature dependent bias correction could be applied to SP2 concentrations, a constant correction is considered to be more robust. The remaining temperature dependent bias introduces some additional noise to the mass and number concentrations, but there is no systematic error since SP2 temperature variations are not following a frequent cycle. Specifically, if the SP2 temperature would have been following the ambient temperature, the observed diurnal cycles would have been affected.

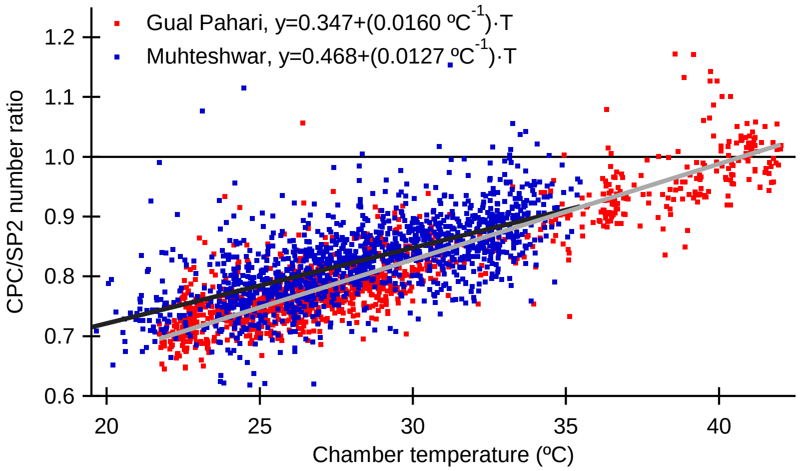

Figure S4: CPC to SP2 total number concentration ratios for 285 nm DMA size for both Gual Pahari and Mukteshwar. Also shown are the linear fits to the data.

3.2 Particle sizes

Figure S5 shows the ratio of DMA selected size to those measured by the SP2 as a function of DMA size. The SP2 derived particle sizes are geometric mean diameters of the observed non-absorbing particle distributions (determined by fitting a log-normal size distribution to the observed size distributions). Because scattering calibration is based on ambient particles, the average sizing bias is only about 1%.

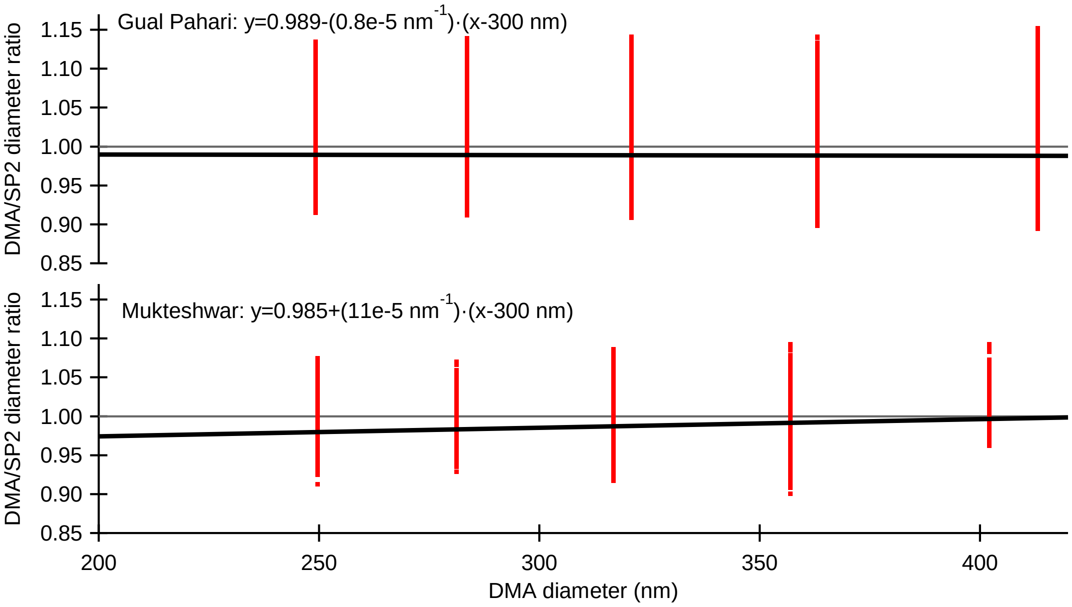

Figure S5: The DMA to scattering diameter ratios as a function of DMA size for both Gual Pahari and Mukteshwar. Also shown are the linear fits to the data.

Although the average sizing bias is negligible (about 1 %) and the bias is independent of particle size (slope in the order of 10^{-5} nm^{-1}), there is some variability in the calculated scattering sizes (about ±10 % difference from the DMA-selected size). Again, it seems that the variability in scattering size is related to the variability of the SP2 chamber temperature (Fig. S6), but the dependency is weaker than in the case of concentrations (Fig. S4). In general, this about 10 % sizing uncertainty is within the typically reported sizing uncertainty limits (e.g. Laborde et al., 2012).

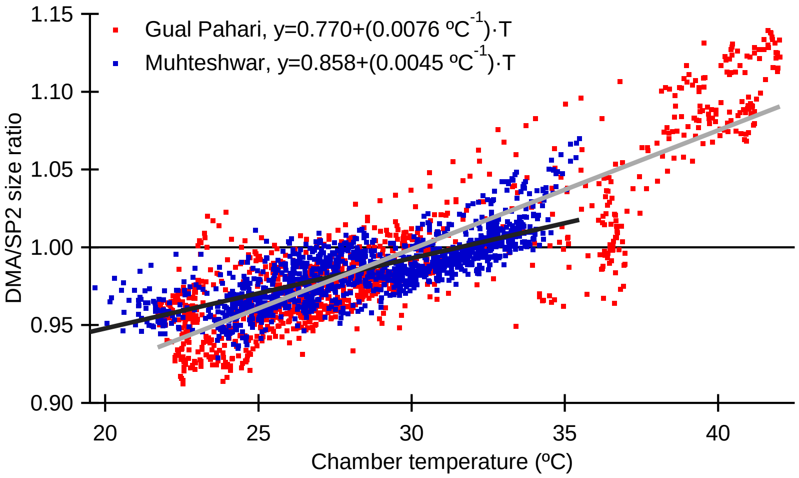

Figure S6: DMA to scattering diameter ratios for 285 nm DMA size for both Gual Pahari and Mukteshwar. Also shown are the linear fits to the data.

3.3 Refractory and equivalent Black Carbon

The Aethalometer collects particles to a filter and measures the change in light attenuation due to the accumulated absorbing aerosol mass (Hansen et al., 1984). The mass concentration of the absorbing aerosol is then calculated from the attenuation and is reported as an equivalent black carbon (eBC). Since this is only a consistency test, the Aethalometer data, which is available for Mukteshwar only (Hyvärinen et al., 2009), is used without typical corrections (e.g. Weingartner et al. 2003). Figure S7 shows that eBC and rBC are in excellent agreement considering their different measurement methods. Figure S8 also shows that the eBC/rBC ratio is independent of SP2 temperature. This supports the decision that temperature dependent correction is not needed for SP2.

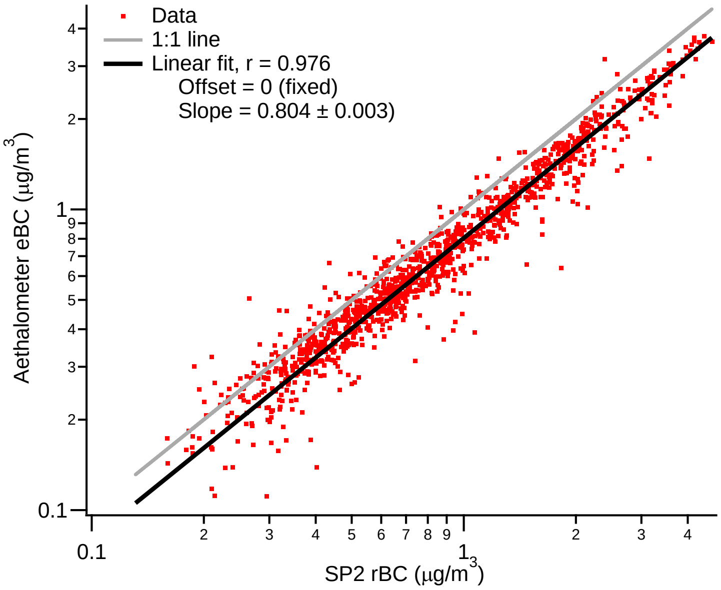

Figure S7: Aethalometer eBC as a function of SP2 rBC and linear fit to data (clear outliers not shown).

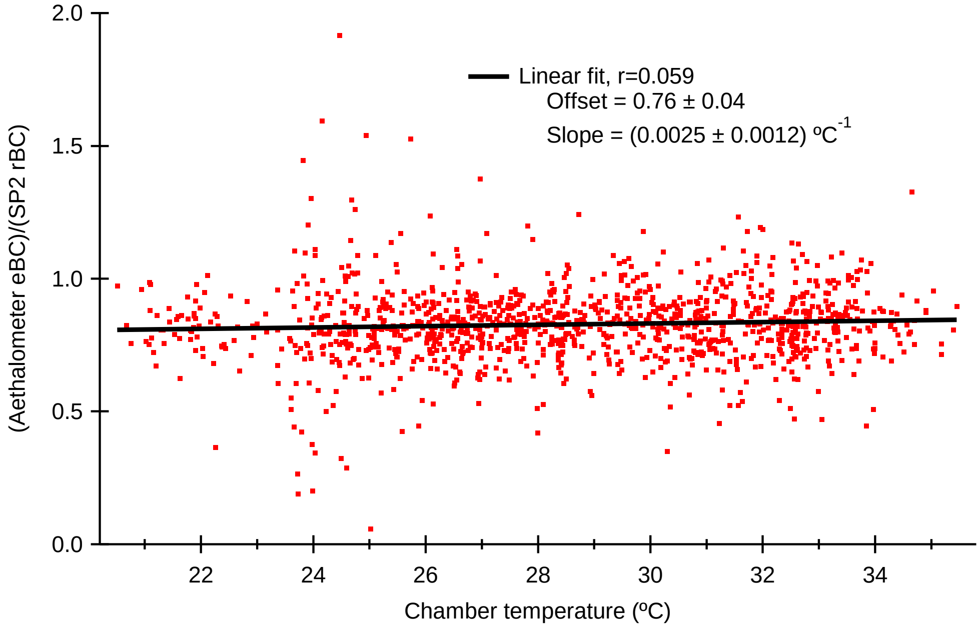

Figure S8: The ratio of Aethalometer eBC to SP2 rBC as a function of SP2 chamber temperature (outliers not shown). Also shown is a linear fit to the data.

4 Supplementary figures

Refractory black carbon size mass and number distributions as a function of rBC core volume equivalent diameter are shown in the main text (Fig. 4). Figure S9 shows rBC and total particle number and mass size distributions measured by the SP2 and DMPS as a function of the DMA-selected mobility diameter.

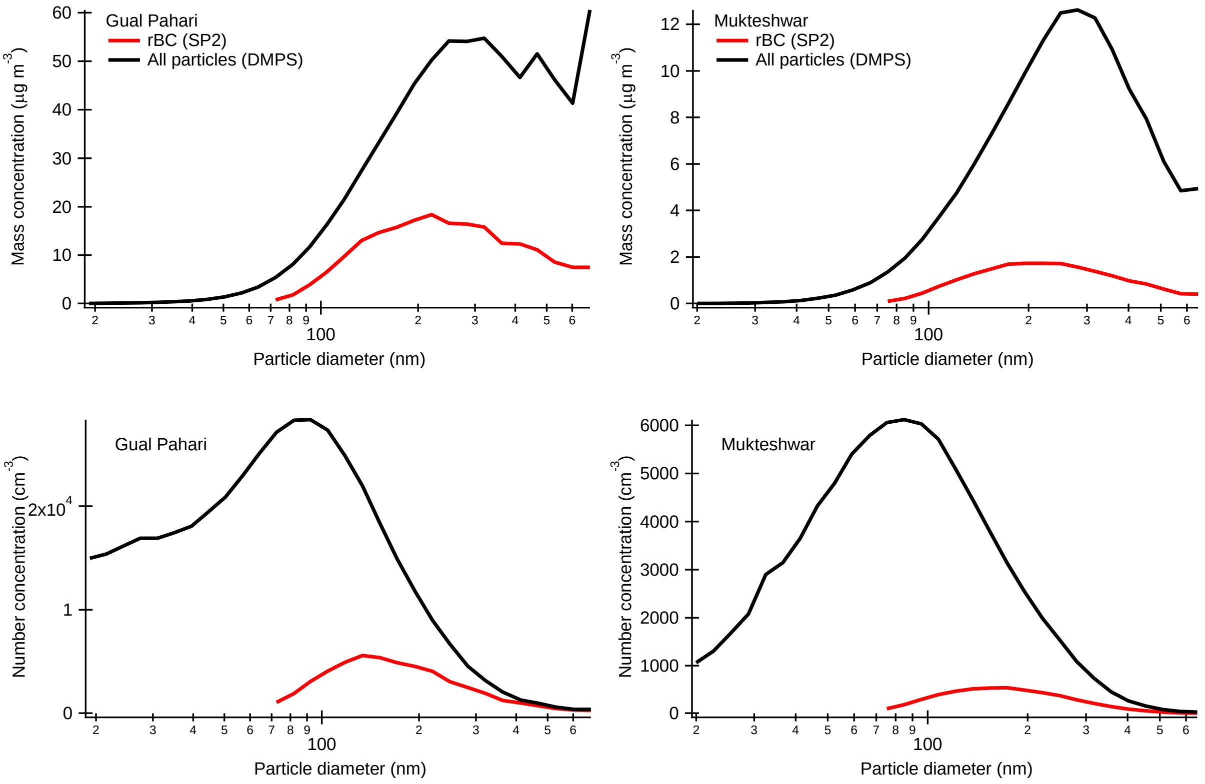

Figure S9: Total and rBC mass and number size distributions measured by the DMPS and SP2 for Gual Pahari and Mukteshwar. The volume distributions measured by the DMPS have been converted to mass by using 1000 kg m^{-3} particle density.

In addition to the average rBC mass size distributions (total mass and geometric mass mean diameter and standard deviation) and mixing state (number and volume mean core diameters, those normalized by the mobility size, and number fraction of particles containing rBC) parameters for the 360 nm mobility size bins given in the main text (Table 1), figures S10 and S11 show the time series of these parameters (except number and volume mean core diameters as these are proportional to the normalized values).

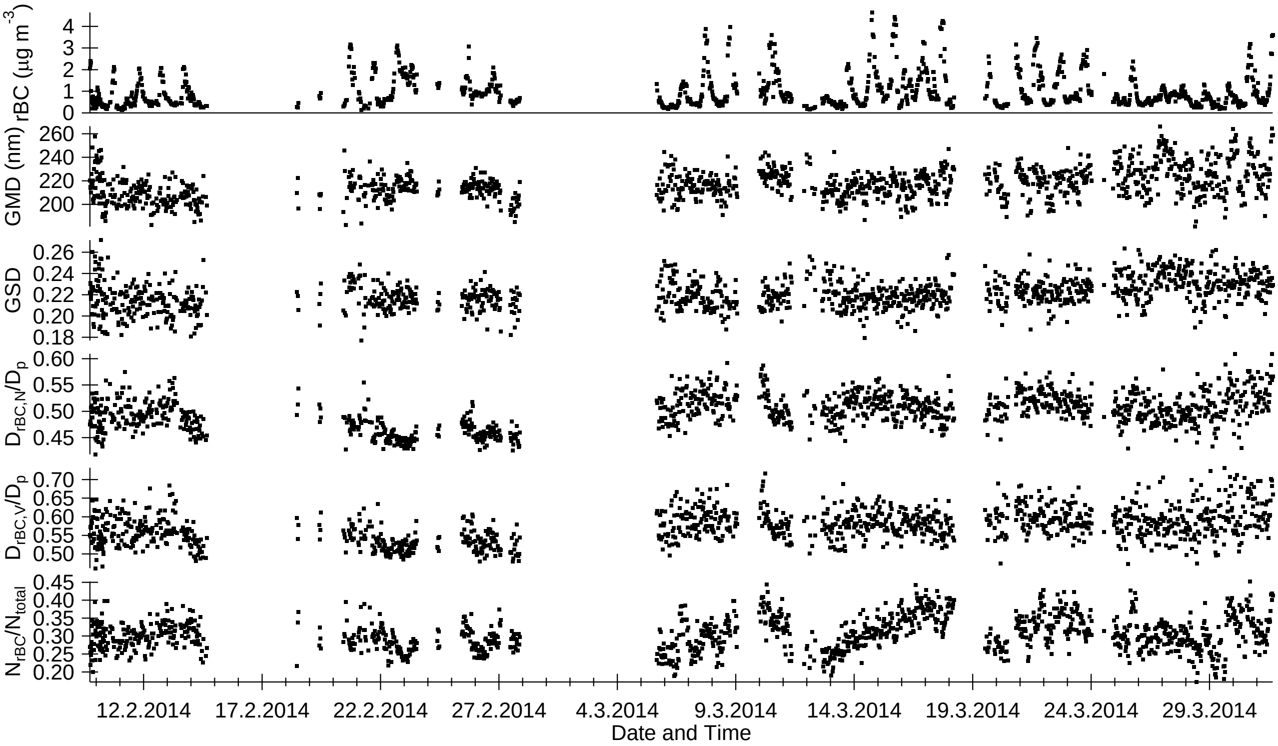

Figure S10: Time series of the measured rBC mass size distribution parameters (total rBC concentration and geometric mass mean diameter and standard deviation) and mixing state parameters (rBC core volume equivalent diameter (both number and volume averages) to particle diameter ratio and number fraction of particles containing rBC) for Mukteshwar.

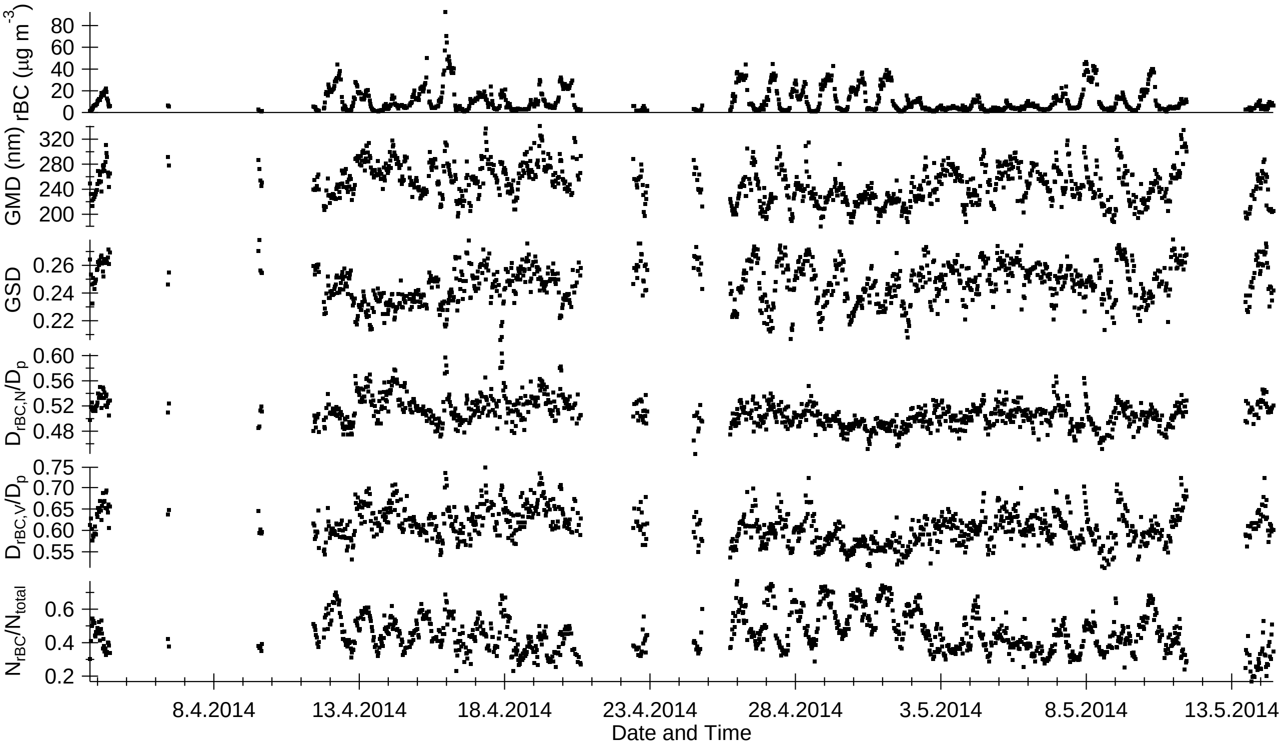

Figure S11: Same as Fig. S10, but for Gual Pahari

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