

## Response to comments of Reviewer 2

### General Comments

The manuscript describes measurements of aerosol number concentrations, number size distributions, aerosol optical properties and volatility in Kathmandu Valley, Nepal. The air in the valley is very polluted as is shown by the referenced papers. The instrumentation used in the work could in principle have brought interesting new information on the aerosol physical properties in the region but there are too many strange things in the manuscript that it would bring any relevant and reliable information. You explain in section 4.4, L367 "The constraint of the experiment is that the TDD flow rate, which is restricted to 3 Lpm. Because of this we could not connect multiple instruments to maintain the TDD flow rate". This should have been mentioned much earlier, in the methodology section. And still, you could have split the 3 LPM to two instruments, for instance the CPC and the SMPS which would have made the results a bit more meaningful. Also the neph and the aethalometer could have been used at lower flow rates and then you would have had simultaneous scattering and absorption data.

### Response:

We agree with the reviewer's suggestions, but the primary objective of this study was to understand the contribution of semi-volatile fraction to ambient aerosol physical and optical properties. Initially authors set an experiment with all instruments measuring wet and dry aerosols but experiment was not able to succeed due to the constraints of TDD flow and nephelometer flow system. The blower system in the nephelometer rendered us unable to set a fixed flow rate for this kind of experiment and complicated the use of several instruments connected to single sampling line. Unlike pump with a flow sensor, blower system does not give values on air flow and also if there is no free air flow, blower system may not work efficiently. Considering these facts the authors decided to conduct individual experiments to avoid any minor biases.

As suggested by the reviewer, we have shifted the sentence into the methodology section (Line no. 127) of the modified manuscript.

**Further: why did you not run all the instruments on the non-heated branch of the inlet, it should not have any flow restrictions? Then you would at least have continuous time series of the relevant parameters in ambient conditions which would have increased the value of the work. But that is speculation, now the data are here.**

We agree with the reviewer comment and this could be an area for future study. The area of research on semi-volatile aerosols in the region is extremely sparse. The present study gives some understanding on semi-volatile aerosol properties and also presents scope for future experiments.

## Detailed comments

**1) How large is the the amount of data? It is written on L102 "a few days". This not good enough.**

**Response:** The total duration of sample collection was around 1470 hours. This includes around 490 hours of each CPC and aethalometer experiment, 470 hours of nephelometer experiment and 20 hours of SMPS experiment. As no diurnal variation was observed in the fraction of semi-volatile aerosol number, we limited the SMPS study for a few hours, which was done just to understand the variation in size distribution of semi-volatile aerosol fraction.

We have modified the text appropriately in the experimental set up section (Line no. 114-116) of the modified manuscript.

**2) How did you calibrate the nephelometer?**

**Response:** The nephelometer as well as other instruments used in this experiment were brand new ones and were used for the very first time. These instruments were all factory calibrated using CO<sub>2</sub>.

**3) There is no description of the inlet. Cutoff diameter?**

**Response:** Semi-volatile aerosol fraction contribution can occur through coating on fine or coarse mode particles. In order to capture broader size range particulate matter, we preferred to sample total suspended particulate matters for our experiments. Hence, we used a waterproof total suspended particulate assembly with debris screen for protection from insects or bugs at the inlet. The inlet was regularly cleaned and O-ring in the TSP inlet were lubricated. A picture of the same has been provided below. The inlet description has been given in the modified manuscript (Line no. 120-122).



Figure: TSP assembly with debris screen used for the experiment

**4) The length of the cycles varied: for some the temperature was kept constant during 24 hours, for some 1 hour. The results are not comparable because aerosol composition definitely varies within a day and also days are different.**

**Response:** The first set of experiments was conducted using CPC, where we were able to identify the semi-volatile aerosol number fraction. The CPC based experiments did not show any strong diurnal variation of the semi-volatile aerosol number fraction. Through all TDD set temperatures, semi-volatile fractions were observed to be consistent (as shown in Figures 3, 7, 10). In order to get additional information on aerosol size distribution, experiment with SMPS setup was undertaken for one hour duration at TDD set temperature only just to understand the particle loss due to semi-volatile fraction. This one hour experiment was also repeated few times to verify the consistency.

The same has been modified in section 4.2 line no. 279-283. “Our experimental setup using SMPS was different from other instrumental setups. In first experiment using CPC, we identified that semi-volatile aerosol number fraction which did not show any strong diurnal variation. From this point, we wanted to understand particle size loss due to the semi-volatile aerosol fraction rather than diurnal variability. Hence, we operated identical SMPSs (as described in the instrument setup section), but changed the TDD set temperature every hour. We readily acknowledge that this decision also reveals a limitation of our study.”

**5) In the manuscript "dry sample" refers to measurements carried out with instruments coupled with TDD. Well, if you heat it to 50°C or more, it is dry. But if the denuder is at room temp the sample air is just as humid as the one without the TDD.**

**Response:** The TDD itself is filled with activated carbon that acts like a desiccant and hence, while air passes through it at TDD set room temperature, the experiment is considered as dry. Previous research also reports that thermodenuder creates thermophoretic and diffusional losses creating dryer conditions which will lead to particle loss. Our experiment conducted at room temperature is not assumed as “wet sample” because we observed around 12% particle loss using TDD set room temperature experiment. Hence we consider TDD at room temperature experiment also as dry one.

The same has also been explained with proper references in the text (Line no. 206-213) in the modified manuscript.

**6) L317 it is written "If we assume BC mixing state absorption affects is similar at 370nm and 880nm wavelengths, then the difference between 370nm to 880nm wavelength absorption is contributed by brown carbon" Well, the effect of coating depends on wavelength so definitely at wavelengths so far from each other the effect is very different. It is not possible to calculate the contribution of BrC this way.**

**Response:** Agreeing with the reviewer, changes in absorption at different wavelengths can be due to intrinsic properties, different size distribution of the aerosols, mixing state and partly by brown carbon, which needs further investigation and is presently out of the scope of this study. The sentence is modified in line no. 342-344. “If we assume BC mixing state absorption affects is similar at 370nm and 880nm wavelengths, then the difference between 370nm to 880nm wavelength absorption may be contributed to changes in intrinsic properties of the semi-volatile aerosol, size of aerosols, mixing state or the Brown Carbon (BrC), which is unknown at present.”

7) L346 - 348 it is written: "Dry absorption was deducted from wet absorption values to compute the semi-volatile aerosol absorption. Then semi volatile aerosol absorption values were used to compute AAE for the semi-volatile fraction. We computed AAE over the range of wavelengths 370nm-970nm for wet, dry and semi-volatile aerosols individually". From the wet absorption, How can you deduce dry absorption at different temperatures?? Deduction: the process of reaching a decision or answer by thinking about the known facts. Linked to this, in Table 3 there are the AAE values of wet, dry and semi-volatile aerosols at different temperatures of the thermodenuder. What is this: wet aerosol at the temperature of 300°C? It is not wet then anymore. The same applies to Table 4.

**Response:** As mentioned in the original manuscript, 'wet' sample always represents ambient aerosol and 'dry' sample represents ambient air passing through TDD. For better clarification, how we computed AAE and SAE, we provide below text as additional supplementary material.

The semi-volatile aerosol fraction contribution to ambient aerosol properties were measured through the difference between wet and dry aerosol properties.

$$SV_{AP} = WA_{AP} - DA_{AP}$$

Where,

$SV_{AP}$  = Semi-Volatile aerosol fraction contribution which can be number, scattering or absorption

$WA_{AP}$  = Wet aerosol property which is ambient aerosol number, scattering or absorption

$DA_{AP}$  = Dry aerosol property which is TDD derived aerosol number, scattering or absorption at different TDD set temperatures

For example semi-volatile aerosol fraction absorption contribution was calculated from the below formula.

$$SV_{Abs_{\lambda}} = WA_{Abs_{\lambda}} - DA_{Abs_{\lambda}}$$

Where,

$SV_{Abs_{\lambda}}$  = Semi-Volatile aerosol fraction absorption at wavelength  $\lambda$

$WA_{Abs_{\lambda}}$  = Wet aerosol absorption at wavelength  $\lambda$

$DA_{Abs_{\lambda}}$  = Dry aerosol absorption at wavelength  $\lambda$

Wet and dry aerosol absorption were measured using identical aethalometers (AE-33) at seven different wavelengths. We derived semi-volatile aerosol fraction absorption at seven different wavelengths from above equation and aethalometer's (wet and dry) absorption data.

$$AE = - \frac{\log \frac{E_{\lambda_1}}{E_{\lambda_2}}}{\log \frac{\lambda_1}{\lambda_2}}$$

AE= Angstrom Exponent

$E_{\lambda_1}$ = Absorption/Scattering/Extinction coefficient at wavelength  $\lambda_1$

$E_{\lambda_2}$ = Absorption/Scattering/Extinction coefficient at wavelength  $\lambda_2$

From the above equation we derived wet, dry and semi-volatile aerosol fraction absorption/scattering angstrom exponent.

**Table 3.** Summary of influence of volatility on absorption at various temperatures.

TDD set temp. in °C	Loss of absorption at 370nm (%)	Loss of absorption at 880 nm (%)	Absorption due to intrinsic properties or BrC	Average absorption angstrom coefficient of wet aerosol * (Avg±SD)	Average absorption angstrom coefficient of dry aerosol (Avg±SD)	Average absorption angstrom coefficient of semi-volatile aerosol fraction (Avg±SD)
Room temp.	16	16	0	1.02±0.24	1.01±0.24	1.12±0.47
50	23	20	3	1.08±0.17	1.08±0.18	1.10±0.43
100	19	18	1	1.01±0.23	0.98±0.23	1.12±0.38
150	25	21	4	0.97±0.27	0.92±0.30	1.19±0.41
200	31	27	4	0.97±0.19	0.92±0.18	1.13±0.43
250	35	28	7	1.03±0.20	0.99±0.22	1.12±0.30
300	37	28	9	1.30±0.30	1.24±0.30	1.43±0.33

\*Average absorption Angstrom coefficient of wet aerosols (ambient aerosol) while the simultaneous dry experiment was being conducted at TDD set temperatures.

**Table 4.** Summary of influence of volatility on scattering at various temperatures.

TDD set temp. in °C	Loss of scattering at 450nm (%)	Loss of scattering at 550nm (%)	Loss of scattering at 700nm (%)	Average scattering Angstrom coefficient of wet aerosol * (Avg±SD)	Average scattering Angstrom coefficient of dry aerosol (Avg±SD)	Average scattering Angstrom coefficient of semi-volatile aerosol fraction (Avg±SD)
Room temp.	18	15	8	1.94±0.45	1.68±0.45	4.35±2.46
50	17	13	8	1.76±0.38	1.47±0.34	5.52±2.01
100	29	27	20	1.92±0.42	1.69±0.39	2.85±0.32
150	39	38	32	1.96±0.44	1.70±0.44	2.69±0.71
200	48	46	40	1.93±0.42	1.59±0.40	2.65±0.64
250	62	59	52	1.94±0.44	1.45±0.41	2.61±0.46
300	71	70	66	1.99±0.46	1.49±0.41	2.47±0.80

\*Average absorption Angstrom coefficient of wet aerosols (ambient aerosol) while the simultaneous dry experiment was being conducted at TDD set temperatures.

8) The scattering Ångström exponent (SAE) of the semivolatile aerosol in Table 4 reaches values like  $5.5 \pm 2.0$ . This is another indication that there is something seriously wrong with the method. The authors obviously do not know that SAE depends very strongly on particle size and for the smallest realistic light scatterers in the atmosphere, the gas molecules,  $SAE = 4$ . It is called Rayleigh scattering.

Response: The scattering loss observed in Table 3 was comparable with particle loss in Table 2.

In comparison with the repeated experiments conducted for particle number and absorption (with CPC and aethalometer) experiments, scattering loss (measured by nephelometer) at higher wavelength (700nm) was observed to be less (~8%). Whereas, at lower wavelengths scattering loss was observed to be ~15% at lower TDD set temperatures. Nephelometer's first set of experiments was analyzed and it showed high semi-volatile aerosol fraction SAE at lower TDD set temperatures. We repeated the same experiments several times to cross-check the SAE values and observed a consistent trend (Representative figure given below from few experiment days). Thus we don't suspect any errors in the experimental procedures. However, this low scattering loss at 700nm, indicates the necessity for significant in-depth future studies. The scattering contribution at 700nm wavelength may be representing bigger particles and they may have less contribution of highly volatile aerosols. This and other possibilities can be an area of future study.

Regarding the calculations, the average aerosol scattering coefficients (in  $Mm^{-1}$ ) at 450, 550 and 700nm at  $50^{\circ}C$  were observed to be  $7.1E-05$ ,  $5.0E-05$  and  $3.1E-05$  for wet (ambient) and  $6.0E-05$ ,  $4.4E-05$  and  $3.0E-05$  for dry. The averaged difference between wet and dry aerosol scattering found to be  $1.1E-05$ ,  $6.1E-06$  and  $8.5E-07$ , which is nothing but semi-volatile aerosol fraction contribution at the set TDD temperature. This semi-volatile aerosol fraction scattering angstrom exponent is 5.82. Similarly, at room temperature average aerosol scattering coefficients at 450, 550 and 700nm were observed to be  $4.7E-05$ ,  $3.2E-05$  and  $1.9E-05$  for wet,  $4E-05$ ,  $2.8E-05$  and  $1.9E-05$  for dry while  $7.2E-06$ ,  $4E-06$  and  $9.47E-07$  for semi-volatile aerosol fraction contribution. These lead to subsequent scattering angstrom exponent of 4.65. After thorough cross-check of the dataset we observed consistency in high semi-volatile aerosol fraction SAE which was due to less scattering contribution at 700nm wavelength. Above explanation has been added accordingly in the manuscript at line no. (404-407).

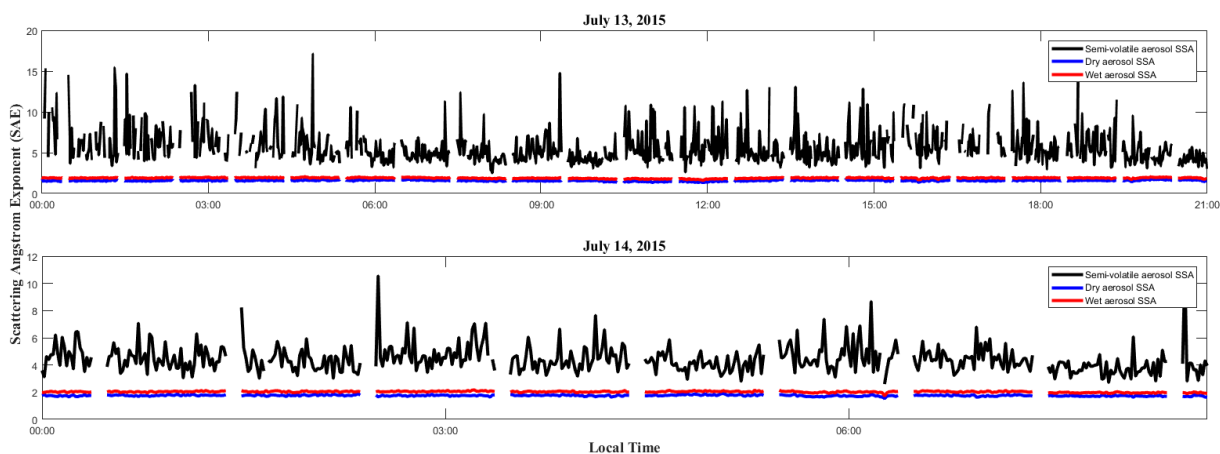


Figure: Change in scattering Ångström exponent on different days of experiments



9) The way single-scattering albedo is calculated and discussed (section 4.5) makes no sense. The nephelometer and the aethalometer were used in different days. And then you derive somehow the SSA of the semivolatile aerosol fraction at different temperatures. Even when both an aethalometer and a nephelometer are used correctly connected simultaneously to an inlet, SSA has high uncertainties. And even then, after heating sample air and volatilizing the shell of particles you would be able to get the SSA of the core but not that of the semivolatile particles. The semivolatile material is very probably as a shell on an absorbing core, not as externally mixed semivolatile particles. By heating the particle also its size changes which then changes the whole optics.

**Response:** Our objective is to understand the semi-volatile aerosol fraction **contribution** to ambient aerosol optical properties rather than to determine semi-volatile aerosol properties. This study is trying to explain what could be the semi-volatile fraction influence on SSA.

There is a constant fraction contribution of semi-volatile aerosol physical-optical properties in our experiments (figure 3, 7 and 10). Linear regression and correlation coefficients indicated that the average absorption and scattering losses at each temperature were almost consistent for a particular TDD set temperature with very little variation in the slope. Taking this into account, the linear slopes were used to derive the semi-volatile fraction contribution for wet (ambient) aerosol absorption and scattering. Same fractions were used to understand semi-volatile aerosol fraction contribution for given wet aerosols SSA. This will give important information on the nature of semi-volatile aerosol contribution to aerosol radiative forcing. Below we explain how we have calculated SSA values.

Single scattering albedo (SSA) is defined as the ratio of scattering to total extinction due to atmospheric aerosols as suggested in the equation below.

$$SSA = \frac{Scattering}{(Scattering + Absorption)} \quad (1)$$

Assuming wet aerosol SSA = 0.9 and scattering = 100, we derived the absorption using the above equation;

$$0.9 = \frac{100}{(Absorption + 100)} \quad (2)$$

$$\Rightarrow \text{Absorption} = \frac{100-90}{0.9} \quad (3)$$

So, wet aerosol absorption = 11.11

Similarly, when we consider wet aerosol SSA = 0.95 and scattering = 100, absorption = 5.2

The semi-volatile aerosol fraction contribution derived from regression slopes were used in below equations.

$$\text{Semi-volatile aerosol scattering} = \text{wet aerosol scattering} * (\% \text{ contribution of semi-volatile}) \quad (4)$$

$$\text{Semi-volatile aerosol absorption} = \text{wet aerosol absorption} * (\% \text{ contribution of semi-volatile}) \quad (5)$$

For wet aerosols scattering =100 and absorption=11.11

Semi-volatile aerosol scattering from equn. 4 = 24.58 (Table R1 Column 3, given below) (for TDD set temperature 50°C while absorption = ((11.11\*17)/100)) (Table R1 Column 2, given below)

$$SSA = \frac{\text{Semi-volatile aerosol scattering}}{\text{Semi-volatile aerosol scattering} + \text{Semi-volatile aerosol absorption}} \quad (6)$$

Semi-volatile SSA at 50°C = (24.58/(24.58+2.73))

=0.861595 (Table R1 Column 4) (for TDD set temperature 50°C)

Where;

Scattering (%) = Loss of scattering at  $T_i$

Absorption (%) = Loss of absorption at  $T_i$

$T_i$  = TDD set temperature

Table R1: Table for wavelength interpolation

		Absorption fraction	Scattering Fraction	SSA of semi-volatile fraction assuming wet SSA=0.9	SSA of semi-volatile fraction assuming wet SSA=0.95
At 450nm	TDD temp				
	Room Temp	16.57	18	0.907291	0.954318
	50	24.58	17	0.861703	0.930072
	100	19.15	29	0.931707	0.966802
	150	23.05	39	0.938435	0.970183
	200	27.96	48	0.939269	0.970601
	250	30.36	62	0.948448	0.975169
	300	31.73	71	0.952738	0.977289
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At 550nm					
	Room Temp	14.7	15	0.901892	0.951511
	50	23.59	13	0.832347	0.913776
	100	18.32	27	0.92996	0.965919
	150	22.02	38	0.939566	0.970749
	200	27.04	46	0.938748	0.97034
	250	29.13	59	0.948044	0.974969
	300	30.33	70	0.954112	0.977966
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At 700nm					
	Room Temp	12.73	8	0.849886	0.923578
	50	20	8	0.782779	0.884956
	100	14.89	20	0.923668	0.962729
	150	18.33	32	0.940219	0.971075
	200	23.73	40	0.938218	0.970074
	250	25.64	52	0.948109	0.975001
	300	26.79	66	0.956887	0.979329