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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Volatile organic compounds over Eastern Himalaya, India: temporal variation and source characterization using Positive Matrix Factorization" *by* C. Sarkar et al.

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REFEREE # 1 (Anonymous)

Comments: P32135 L8: Use fewer significant figures (four is too many especially with such large error bars). Same comment elsewhere in the paper. and P32144 L25 and throughout: There are too many significant figures. Make sure the significant figures match the error bar and the measurement precision/accuracy. It seems unlikely to be able to measure these numbers to within 0.1 ug/m3. and P32152 L25: Too many

significant figures. and Table 1: The reader needs to be told the DL in order to know what BDL is. and Table 1: There are too many significant figures in Table 1: 2304.38 is not credible. Determine the correct number of significant figures based on the precision of the measurements. and Table 2: Too many significant figures here as well.

Reply: Thanks for the comments. A section "Quality assurance and quality control" has been added under "Methodology" in section 3.2. Here, we have given information related to accuracy, precision and detection limit of the analysis. The detection limit varied between 0.01 μg m-3 (1,2,4 Trimethylbenzene) and 0.08 μg m-3 (1,1 Dichloroethane). Thus, the concentration values of VOCs have been given accordingly in the text and tables so that the significant figures of concentration values matched measurement accuracy, precision and detection limit.

Comment: P32135 L14: "related mainly to tourists". Is this speculation or is there evidence for this? What percentage of vehicle emissions, biomass and coal burning, etc. are due to tourists rather than the local population? For example it is surprising that coal burning and solvent use would be mainly related to tourists.

Reply: Thanks for the comment. Darjeeling is a well known tourist destination in India. Tourist activities are increased during premonsoon and postmonsoon seasons. This is not our speculation, but fact. We have mentioned in the manuscript about a rough measurement on vehicle counts and the consumption of fossil fuel over Darjeeling over different seasons (Section: 4.2). We observed that number of vehicle counts and consumption of petrol/diesel get doubled during premonsoon and postmonsoon compared to winter and monsoon. This is due to massive influx of tourists over Darjeeling during these two seasons. A rough estimate of number of tourists from the Office of The Chairman, Indian Association of Tour Operators (Darjeeling-Sikkim) and The Secretary Office, Darjeeling Association of Travel Agents (DATA) shows that 150,000-175,000 domestic tourists and 15,000-20,000 foreigners visit Darjeeling during each of the premonsoon (March-May) and postmonsoon (Oct-Nov) seasons. However, these data have not been incorporated in the manuscript.

As a consequence of this massive tourist influx, the anthropogenic activities get increased to many folds. Vehicular emissions (due to increased number of tourist vehicles used for local tours between various tourist spots), biomass and coal burning (used in several hotels, resorts etc) get increased because of tourist activities. Bonfires are also arranged for tourist attraction. However, solvent use is not affected by the tourist activities. This has been rectified in the revised manuscript (Abstract). The sentence has been modified as: "Anthropogenic activities related mainly to tourists like diesel and gasoline emissions, biomass and coal burning and solid waste emissions were almost equal in both the seasons".

Comment: P32135 L20: Please add: "Of the measured compounds, diesel exhaust was also found" Many compounds that impact ozone formation were not measured, so the conclusions are limited to the 18 species presented here.

Reply: Thanks for the comment. The sentence has been modified as: "Of the measured compounds, diesel exhaust was also found to have the maximum potential in tropospheric ozone formation"

Comment: P32136 L4: Guo isn't really the right reference for this. Use a primary reference.

Reply: Thanks for the comment. A primary reference (Prather and Watson, 1990) has been used.

Comment: P32136 L7-10: "to form SOA by nucleation and condensation with a significant aerosol yield and thus they influence gas phase pollutants directly and particle-phase pollutants indirectly." This text is very similar to that in Saxena and Ghosh (2012), which directly quotes Brocco et al. (1997) and Odum (1997): "contribute to SOA formation by nucleation and condensation ... with a significant aerosol yield and therefore, aromatic VOCs influence gas phase pollutants directly and particle-phase pollutants indirectly." At very least the Brocco and Odum sources should be cited.

Reply: Thanks for the comment. Brocco and Odum sources have been cited.

Comment: P32136 L19: This statement isn't correct. VOC sources in Asia are highly complex have been attributed to many sources, not just vehicular emissions. The single self reference to a study of urban petrol centres in India (Srivastava et al., 2005a) is confusing because it does not capture the complexity of sources throughout Asia

Reply: Thanks for the comment. The sentence has been modified as: "High levels of VOCs have been observed in Asian countries where significant fractions of VOCs have been considered to be originating from vehicular emissions (Srivastava et al., 2005").

Comment: There is a lot of self-referencing in this paper, including 10 references to papers led by Srivastava.

Reply: Thanks for the comment. Several studies on VOCs in India have been carried out by Dr Srivastava and her groups. Dr Srivastava is a pioneer and has contributed significantly to monitoring and modelling of pollutants like VOCs, carbonyls etc in India since more than 15 years. Dr Srivastava and her group, later joined by Dr. Majumdar, are amongst the very few groups who have been taking the initiatives for VOC monitoring in Indian cities since early 2000. Thus, one should cite Srivastava's works while presenting VOC studies at least in India and from every aspect like concentrations/distributions over spatial and temporal scales, source apportionments, source strengths etc. Also, this was our first collaborative study with Dr. Majumdar and Dr. Srivastava from CSIR-NEERI, DST, Govt. of India, hence the references cited in this paper, may not be considered as "self-referencing".

Comment: P32137 L9-11: I am concerned about plagiarism in this paper. Lines 9-11 read: "Such studies over Himalayan region are of paramount interest as the ecology of the Himalaya is under serious threat from various forms of pollutants (Bostrom, 2002)." This is identical to a recent paper by Adak et al. (2014) on aerosols (many of the same coauthors): "Further, the study of aerosol over Himalayan region is of paramount interest as the ecology of the Himalaya is under serious threat from various forms

of pollutants (Bostrom, 2002)." You can also find the same sentence in Sharma et al. (2011) (different co-authors): "Further this study in the Himalayan region of Kullu-Manali is of particular interest as the ecology of the Himalaya is under serious threat from various forms of pollutants (Bostrom 2002)." The sentence should have been changed and also had some attribution to Sharma et al.

and

P32137 L11-14: The next sentence is also plagiarized. It reads: "The increase in the loading of atmospheric pollutants over the Himalaya is a matter of concern, since most of the glaciers in the region have been retreating since 1850 (Mayewski et al., 1979) with increasing melting rates." This is identical to Adak et al. (2014): "The increase in the loading of atmospheric aerosols over the Himalaya is a matter of concern, since most of the glaciers in the region have been retreating since 1850 (Mayewski et al., 1979) with increasing melting rates." Also similar to Chatterjee et al. (2010) except the topic is changed from aerosols to atmospheric pollutants: "The transport of optically active aerosol to the higher Himalayas is a matter of concern, since most of the glaciers in the region have been retreating since 1850 (5) with increasing melting rates."

and

P32137 L14-17: Same with the next sentence: "The rising anthropogenic interferences for rapid urbanization and development in the Himalaya not only affect the immediate landscape environment, but also the atmospheric environment which is becoming an increasing concern (Momin et al., 1999)." This is also identical to Adak et al. (2014): "The rising anthropogenic interferences for rapid urbanization and development in the Himalaya not only affect the immediate landscape environment, but also the atmospheric environment which is becoming an increasing concern (Momin et al., 1999)."

and

P32137 L17-21: Same with the next sentence: "The anthropogenic activities such as

increasing vehicular traffic due to increased tourism-related activities, biomass burning and fuel wood burning for cooking and heating are the causes of concern for most of the Himalayan high altitude hill stations in India which apparently look like pollution free regions as situated far away from the Indian mega-cities." This is also identical to Adak et al. (2014): "The anthropogenic activities such as increasing vehicular traffic due to increased tourism-related activities, biomass burning and fuel wood burning for cooking and heating are the causes of concern for most of the Himalayan high altitude hill stations in India which apparently look like pollution-free regions as situated far away from the Indian mega-cities." I am stopping looking for other examples at this point, but much of the introduction is essentially identical to a previous paper by many of the same co-authors in 2014, which in turn used some of the same sentences as earlier manuscripts.

Reply: Thanks for the comment and pointing out this. We are sorry for the plagiarized sentences. Most of such sentences were used to describe and provide the scenario of atmospheric pollution over Himalaya. The sentences were used in our earlier studies made on other pollutants (Black Carbon, Aerosols etc) over the same station Darjeeling and thus got plagiarized while describing Himalaya's environment in terms of air pollution. However, the plagiarized sentences have been modified and changed. Some of the sentences have been rephrased. The modified paragraph is as follows: "Where almost all the studies were conducted over several cities in India, no such study on VOCs have been ever made over high altitude stations over Indian Himalaya with both ecological and climatic importance. Mayewski et al., (1979) studied the fluctuations of Himalayan and Trans-Himalayan glaciers including Kanchenjunga at eastern Himalaya and reported that the volume and extent of these glaciers have been decreasing since 1850 which could be due to the increase in the loading of atmospheric carbonaceous pollutants. Air quality over Himalaya is deteriorating due to increased man-made activities to meet the demands related to urbanization and economic development (Momin et al., 1999; Meena et al., 2012). High altitude Himalayan hill stations especially over eastern part in India which earlier were considered as the pollution-free regions have

now become the source of huge amount of hazardous air pollutants due to the increase in various tourism-related anthropogenic activities like fossil fuel and biomass burning etc (Adak et al., 2014)."

Comment: P32138 L16: A map still needs to be shown here (this paper needs to stand alone). You could even use Figure 3.

Reply: A map of study area is given as Figure 1. The description of the study area has also been re-written in section 2 under "Study site" which is as follows:

"The study has been carried out at a high altitude hill station Darjeeling at eastern Himalaya in India. A map showing the geographical position of Darjeeling and its adjacent regions is given in figure 1. The sampling site (27° 01'N, 88°15'E) in Darjeeling is situated at the elevation of 2200 from mean sea level at eastern Himalaya. The site is located at an elevation of 200 m from the main town centre which is populated mainly by several hotels and resorts, offices, shopping malls, bus and car stands, schools and colleges. The National Highway (NH55) with high vehicular density connects Darjeeling with the city called Siliguri at the foothill of Himalaya. Darjeeling Himalayan Railway (also known as "Toy Train"), is a narrow gauge railway which runs by coal and diesel for the tourists and a world heritage site, too. The site in Darjeeling represents a typical urban atmosphere with major anthropogenic sources like vehicular emissions, biomass burning, agricultural activities etc. The description of the study site has been given in detail in our earlier studies (Chatterjee et al., 2010, 2012, Adak et al., 2014)."

Comment: P32139 L2: Rainfall amount has too many significant figures.

Reply: Thanks for the comment. It has been modified.

Comment: P32139 L9: What was the sample integration time? Is it 12 hours?

Reply: Thanks for the questions. The sample integration time was 11 hrs for both day (7 a.m. to 7 p.m.) and night (7 p.m. to 7 a.m.) time. Usually, daytime samples were collected during 7 am – 6 pm and night-time samples were collected during 7 pm – 6

am. It has been incorporated in the manuscript.

Comment: P32139 L10: Two samples collected once a week for a year should give about 100 samples: why are there only 90?

Reply: Thanks for the questions. Samples were not collected on some days (winter and monsoon) due to the adverse weather conditions and power supply issues.

Comment: P32139 L11: What tests have you done to ensure that the custom-made glass sampling tube is appropriate for VOC measurements? Have you done sensitivity tests to see whether VOCs might interact with the surface or whether concentrations in the tubes change with time? How soon after sample collection was the analysis done?

Reply: We are sorry but have to say here that the above comments regarding sampling method using glass tubes surprised us. Glass tubes are widely used for sampling of VOCs as glass is inert towards VOCs. The analysis was done by following USEPA TO-17 compendium method. The method is well known and widely used for the sampling of VOCs. All the researchers who work on VOCs and collect VOC samples are quite familiar to this internationally accepted method. Kindly refer to the following sections of the reference USEPA 1997.

Page: 17-5, Section 5.3: "Sorbent Tube (Also referred to as 'tube' and 'sample tube')-stainless steel, glass or glass lined (or fused silica lined) stainless steel tube, typically 1/4 inch (6 mm) O.D. . . . . ..used to concentrate VOCs from air."

Page: 17-11, Section 7.1.3.2: "Once retained on a sorbent tube, chemically stable VOCs, loaded in laboratory conditions, have been shown to give good recoveries, even under high ozone concentrations for storage of a year or more."

Page 17-12, Section 7.5.3. "Air movement is not a factor indoors or outdoors at wind speeds below 10 miles per hour (< 20 km per hour)."

Please refer to the following links: (http://www.restek.com/pdfs/EVFL1065.pdf, http://www.epa.gov/solidwaste/hazard/testmethods/sw846/pdfs/0031.pdf).

However the analysis was done within a week after sampling of VOCs to get the best analytical results.

Comment: P32139 L20: Are the CPCB references accessible to the general reader?

Reply: Thanks for the queries. CPCB 2010 is accessible from the following link: http://cpcb.nic.in/upload/NewItems/NewItem_160_cups.pdf CPCB 2007 is accessible from CPCB, India on request basis.

Comment: P32140 L1: More information needs to be given about the quality of the measurements. What is the detection limit? What is the precision? What is the accuracy? How has this been demonstrated? I have not heard of the German company; are they synced to internationally recognized calibration scales? Some reference or website needs to be provided for this company.

and

P32140 L2: 'For estimation of the target compounds external five point calibration curve was prepared in triplicate using VOC mix 20 by Dr. Ehrenstorfer GmbH, Germany.' As discussed in the comment below, the CCl4 concentrations presented here are not plausible in today's atmosphere. Therefore the five point calibration curve in triplicate appears to have been ineffective for CCl4, leading to concern about the quality of the remaining VOC measurements.

Reply: A section has been added under methodology addressing the issues.

"Quality assurance and quality control

Breakthrough for air sampling procedure value was estimated by connecting two tubes in series and it was considered that breakthrough occurred when the backup tube had concentration more than 10% of the total concentration. Breakthrough has been observed after passing 70 Lit of air sample in ambient condition. As soon as the air pump was turned off, the sorbent tubes were removed, capped tightly and sealed in plastic bags and stored at four degree centigrade. Blank cartridges were also stored in

identical conditions.

Percentage accuracy for observation has been determined as a relative difference of measured concentration and spiked concentration for each component. Also mean response factor and percent relative standard deviation for all target compounds has been calculated. For determination of Relative Standard Deviation (RSD) we performed five runs of the same concentration of mixed standard. For the lowest concentration of 0.005 μg of each target compound the RSD varied between 3-10%. Method detection limit (MDL) has been established by making seven replicated measurements of 0.005 μg of each target compound. The standard deviation for these replicated concentrations multiplied by student's t value for 99% confidence for seven values gives the MDL. The MDL varied from 0.01 μg/m3 for 1,2,4-Trimethylbenzene to 0.08 μg/m3 for 1,1-Dichloroethane considering 70 Lit of air sample. The MDL for individual component has been given in Table 1."

The credentials of M/s Dr. Ehrenstorfer Standards can be confirmed from their website: http://www.lgcstandards.com

Comment: P32140L2: Table 1 gives a mean CCl4 concentration of 0.18 ug/m3. The molecular weight of CCl4 is 153.82 g/mol, so this translates to about 30 ppt. CCl4 is long-lived and very well mixed in the atmosphere, with global concentrations in 2011-2012 of about 85 ppt, without much inter hemispheric difference (http://cdiac.ornl.gov/oceans/new_atmCFC.html). CCl4 concentrations have not been as low as 30 ppt since the 1940s, and there is nowhere on Earth today where you can find a reading this low. This is also not a question of altitude (the measurements from this paper were taken at an altitude of 2200 m) as demonstrated by aircraft measurements of CCl4 throughout the troposphere. I am concerned both at the quality of the CCl4 measurements (and therefore of the other VOC measurements), and that the authors did not recognize that this concentration is not possible in today's atmosphere.

Reply: We would like to thank the reviewer for the comment and showing concern

about the concentration of CTC.

First of all, we would like to say here that our study mainly focused on the total VOC (TVOC) concentrations and its temporal variations over eastern part of Himalaya. The present study is the first ever ground based study made over eastern Himalaya in India where our primary objective was to focus on TVOC and NOT on individual VOC components. However, CTC concentration over eastern Himalaya with such low value (30 ppt) should have been recognized. It has been done in the revised manuscript. The incorporated part is as follows:

"An important observation is that the concentration of carbon tetrachloride (CTC) over Darjeeling was found to be much lower (0.18 μg m-3 which is equivalent to 30 pptv) than the global mean concentration ($\sim$ 85 pptv during 2011-2012; http://cdiac.ornl.gov/oceans/new_atmCFC.html). Studies on global distribution of CTC were made using model-based simulation studies (Liang et al., 2014), occultation measurement studies (Allen et al., 2009) etc. But, very few ground-based observations on CTC were made in India where no such studies exist over eastern part of this country. However, the concentration of CTC was found to have wide spatial variation. Srivastava et al., (2006) observed CTC concentration of 55 pptv over an industrial region of Mumbai whereas very high CTC concentration of 560-800 pptv was observed over an industrial region of Delhi (Srivastava et al., 2005). Glavas and Moschonas (2002) observed very low CTC concentration of 40 pptv over Athens, Greece during summer in 2000. There is no industries exist in and around Darjeeling which could result to such low CTC concentration"

Response to the reviewer regarding CTC concentration over Darjeeling

Global distributions/concentrations of CTC have been obtained by simulation based studies, satellite based observations, balloon flight measurements etc. Liang et al., (2014) conducted simulation studies on CTC using GEOSCCM (Geos Chemistry Climate Model) where they run five simulations using geographically resolved emissions.

Four of the five simulation runs, top-down emission estimates of CTC derived from global one-box model were used as the global annual emissions. It was observed that the decline in CTC concentrations matched with the in-situ measurements and flux data of GMD (Global Monitoring Division) observations. But, in one of the five simulation runs, when they used global emissions of CTC of 35 Gg/yr (for 1995-2012) and lifetime of 26 years, the rate of decrease in CTC concentration was found to be double (2.2 ppt/yr) of the observed rate. Based on this particular simulation run (with low emissions and lifetime of 26 years), the global mean emission of CTC comes around 72 ppt in 2012. Their simulation study showed global trend inconsistent with the observations under the condition of low emission and lifetime of 26 years.

Advanced Global Atmospheric Gases Experiment (AGAGE) has made in-situ CTC observations from clean sea air at five locations (Prinn et al., 2000). Airborne measurement campaigns were conducted by NASA over the Pacific in 1991, 1994 and 2001 (Blake et al., 1996, 2003). In-situ measurements were carried out on board the ER-2 aircraft (Romashkin et al., 2000). Ballon flight measurements were carried out between 7 degree South and 67 degree North during 1996-2000 (Moore et al., 2003). ATLAS-3 Space Shuttle Mission in November 1994 determined the volume mixing ratio of CTC between 30 degree North to 51 degree North using Fourier Transform Spectrometer (Chang et al., 1996). Satellite based observation of global CTC distribution was carried out by Allen et al, (2009) from ACE occultation measurements.

While several satellite-based observations, simulation studies have been conducted for CTC distributions, the number of ground-based observation in east and south-east Asia is very few. In India, most of the ground-based observations were carried out in mega-cities like Mumbai, Kolkata, Delhi etc where hardly CTC concentration was reported. As far as the Himalaya is concerned, the present study is the first ever study made over eastern part of Himalaya in India or even eastern India as a whole.

In India, a wide spatial variation in CTC concentration was observed. Srivastava et al., (2006) reported very low CTC concentration ($\sim$55 ppt) over an Industrial region in

Mumbai during their study period of 2001-02 which was well below the global mean values during the said period. They observed such low CTC concentration even under the influence of huge industrial activities in a mega city like Mumbai in India. Again, very high CTC concentration (560-800 pptv) was observed over a commercial and industrial region of Delhi in India as reported by Srivastava et al., (2005). Thus CTC concentration over a region could be governed by industrial and other anthropogenic activities over that region.

Glavas and Moschonas (2002) reported mean CTC concentration of 60 ppt over an urban atmosphere at the foothill of Hymettos Mountain in Athens, Greece in summer, 2000. The concentration of CTC observed over Athens, was well below the global average ($\sim$100 ppt) during the period. They even observed the CTC concentration of as low as 40 ppt in the month of August. According to the authors "Since no chemical or major metal industry is located in the Athens basin, it is reasonable to expect very low carbon tetrachloride concentrations." This indicates that the local and regional sources also play the important role in regulating the CTC concentration over a region.

In the present study, we have analyzed CTC data over Darjeeling where it was found that it varied between BDL (< 0.06 μg m-3) and 1.65 μg m-3. One important observation is that the data points higher than $\sim$85 ppt i.e. CTC concentrations of higher than $\sim$85 ppt were all associated with the air masses arrived only from W/NW and S/SE directions. The air masses arriving from highly populated industrial regions over Indo-Gangetic Plain (IGP) and Nepal (W/NW) and over Kolkata, India and Bangladesh (S/SE) could be the reason for higher CTC concentration for those days. On the other hand, no industries exist in and around Darjeeling which could contribute to CTC over Darjeeling. This strongly suggests that a source-receptor relationship holds good for CTC. Glavas and Moschonas (2002) also observed variability in CTC concentration (though lower than that observed over Darjeeling) with types of air masses.

Thus, as per internationally accepted practice, for better understanding of the effect of local and regional sources on CTC concentration over a region we need support-

ive ground-based observations vis-à-vis the satellite-based observations, model-based simulation studies and other remote sensing observations. This will in turn help us to better understand and minimize the uncertainties used in the models. At very least, such ground-based observations have much importance over ecologically and geographically important regions like Himalaya to better understand the source-receptor relationship. Among the Asian countries, India is the second largest contributor to the emission of non-methane VOCs (Kurokawa et al., 2013). But unfortunately, very few data has been generated for CTC in India where no study has reported CTC concentration at the eastern part of this country to the best of our knowledge.

Therefore, "Global Distributions" of CTC (or any species) based only on model-based simulation studies or satellite-based observations remain futile without confirming with ground based observations. Local and regional factors have to be taken into account through ground-based observations which will contribute to the LOW and HIGH values across the globe for resulting in to a Global MEAN. We can therefore be able to indicate the factors which make the data well deviate from the Global Mean values derived from model-based studies.

Thus, the comment "..... there is nowhere on Earth today where you can find a reading this low" made by the reviewer may not be true at least over Darjeeling, eastern Himalaya in India where no industrial activities or any other sources of CTC are observed historically. In the eastern part of India, very few VOC studies were made and no CTC data is available; while this may be debatable and more ground based study is required to draw any proper inference, we feel that a firm statement like "30 ppt CTC over Darjeeling is not possible" is against the basic essences of science. The air quality over this part of Himalaya is still being explored.

Comment: P32140 L20: Of the xylenes is appears that only m-xylene and o-xylene are measured (not p-xylene). How does this therefore affect comparisons with other cities (Table 4), given that one of the components of BTEX is missing?

Reply: Thanks for pointing out this. The reported concentration of m-xylene is actually the combined concentration of m-xylene and p-xylene as these two compounds could not be separated under the given analytical conditions. So we reported the value as a combined concentration of these compounds. The manuscript, the tables and figures are rectified accordingly.

Comment: P32142 L11: What evidence is there that VOC emissions remained comparable during pre- and post-monsoon?

Reply: Thanks for the comment. As stated earlier (in response to earlier comment) that premonsoon and postmonsoon seasons are the peak tourist seasons over Darjeeling. The tourist activities remain almost same with comparable numbers of vehicles and tourists in these two seasons. We have mentioned in the manuscript about a rough measurement on vehicle counts and the consumption of fossil fuel over Darjeeling over different seasons (Section: 4.2). We observed that number of vehicle counts and consumption of petrol/diesel get doubled during premonsoon and postmonsoon compared to winter and monsoon. This is due to massive influx of tourists over Darjeeling during these two seasons. We received a rough estimate of number of tourists from the Office of The Chairman, Indian Association of Tour Operators (Darjeeling-Sikkim) and The Secretary Office, Darjeeling Association of Travel Agents (DATA). The estimate shows that roughly 150,000-175,000 domestic tourists and 15,000-20,000 foreigners visit Darjeeling during each of the premonsoon (March-May) and postmonsoon (Oct-Nov) seasons. Thus, number of vehicles, consumption of fuel and overall the number of tourists remain more or less same during premonsoon and postmonsoon seasons. However, these data have not been incorporated in the manuscript. Hence, we could expect the comparable emission sources/source strengths of VOCs related to anthropogenic (mainly tourist related) activities in these seasons.

Comment: P32143 L1 and elsewhere: Given that meteorology is being used to explain much of the seasonality in concentrations, it would help to show plots of weekly temperature and insolation, so the reader can see how this relates to seasonal variability.

Likewise it would help to show the individual data points with time, rather than seasonal averages, to see if the correlations make sense.

Reply: Thanks for the suggestions. The plot is given as Figure 4. It shows that TVOC increased as the temperature increased favouring the evaporation of some VOCs during monsoon. On the other hand, TVOC was found to decrease with the increase in solar radiation favouring the photo-decomposition of VOCs during premonsoon. This has been incorporated in the discussion part (Section 4.2) as follows:

“In order to better establish the fact of the dependence of TVOC with meteorological parameters, we have investigated the day-to-day variations of TVOC with temperature and solar radiation during the entire study period and shown in Figure 4.. It shows well correlation between TVOC and solar radiation during premonsoon. TVOC was found to decrease with the increase in radiation. Thus, we can say that solar radiation played key role in atmospheric clean-up and degradation of VOCs during premonsoon. On the other hand, correlation was also observed between TVOC and temperature during monsoon. We observed increase in TVOC with the increase in temperature favouring evaporative emissions during monsoon”.

Comments: P32143 L25: Please provide a more in-depth statistical analysis, rather than ‘greater than 1.0’.

and

Section 4.3: While they may be correct, the arguments in this section all seem speculative. Please provide more concrete arguments.

Reply: Thanks for the comment and suggestions. The ratio was determined to check the dominance of VOC concentrations between day and night time. The ratio alone, could well explain the fact. Thorough explanations towards the variations in the ratio values have been given. We would therefore request the reviewer to suggest and specify the statistical analysis which could explain the fact better, if any.

The low day-time VOC (high night to day-time ratio) concentration during premonsoon has been explained in terms of high day-time wind speed favouring dispersion of pollutants and high solar radiation favouring photo-decomposition. Although the boundary layer measurement was beyond our scope, the height of the boundary layer could not be as high as 2200 m during winter nights and thus remained well below the observational site. This could favour the accumulation of pollutants generated during winter nights well below Darjeeling. This in turn reduced the night-time VOC concentrations and hence the night to day ratio. The seasonal variation of micro-meteorological parameters has been shown in figure 2. Thus, the arguments made in the section were based on the meteorological observations. The explanation for premonsoon and winter has been modified slightly. However, authors will welcome further suggestions if the fact could be explained better.

The modified part is as follows:

"The highest ratio in premonsoon could be due to the removal of VOCs by efficient and faster photo-degradation by very high solar insolation and higher wind speed favouring dispersion of pollutants during day time leading to lower day-time VOC concentrations compared to the other seasons. However, the minimum value of the ratio in winter could be due to minimum night-time VOC emissions due to subdued anthropogenic activities (except biomass burning) in colder nights. Another possibility is that the boundary layer could remain well below the observational site (2200 m asl) during winter nights and hence pollutants could be accumulated below Darjeeling leading to lower night-time VOC concentration."

Comment: P32145 L1: Because the error bars on the concentrations are large, also use error bars for the factors of 7 and 1.5.

Reply: Thanks for the suggestion. The range has been mentioned as 5.5-8 times and 1.3-1.8 times rather than 7 and 1.5 times respectively.

Comment: P32146 L10-24: This is introductory/methods material, not results.

Reply: Thanks for the comment. Yes, this is introductory/methods material and not results. But, the background of the relationship and the description of the fit parameters need to be given for the general reader. Otherwise, the explanation for the results obtained would not be well understood by the readers that why and how the fit parameters describes the influence of source contributions on the variability-lifetime relation.

Comment: P32147 L26: All readers might not be familiar with PMF. Describe the 'decay adjustment problem' in more detail. On P32148 L3 describe 'stable Q values'.

Reply: Thanks for the suggestions. The following sentences have been added in section 4.6 to describe decay adjustment problem and stable Q values.

"PMF does not require any priori knowledge on the exact VOC emission profiles, and it can be used to apportion source contributions solely based on observations at the receptor site, thus avoiding VOC decay adjustment problem i.e. quick loss of some reactive VOC species in the path between source and receptor. However, very high reactive species could be excluded from the model run provided they are not marker or tracer of any VOC source. In this study, we have measured 18 VOC species which are major and abundant in the atmosphere and can not be considered as highly reactive and have been included in PMF model run by earlier studies, too. More details about the PMF method were described by several studies (Paatero and Tapper, 1994; Paatero, 1997; Reff et al., 2007).

Q is a typical parameter in PMF which is the measure of goodness of fit parameters. Q (true) is calculated including all data points where Q (robust) is calculated excluding data points not fit by the model. The difference between Q (true) and Q (robust) is the measure of the impact of data points with high scaled residuals whereas high uncertainties result in similar Q values. Q (robust) is used to choose the optimal run from the multiple runs. If the number of sources is estimated properly, Q (robust) will have little variability between the runs and thus we get stable Q. The variability of Q (robust) is the indication of the variability of initial base run results."

Comment: P32148 L7: Provide some literature that shows the typical B/T ratio in gasoline exhaust and gasoline evaporation. How does it compare to the B/T ratio measured here?

Reply: Thanks for the suggestions. Literatures have been provided in the text (Section 4.6) "Several earlier studies showed the ratio values near 1.0 (1.0 over Kolkata, India by Som et al., 2007; $\sim$ 1.0 over Mumbai, India by Srivastava et al., 2004; $\sim$ 1.0 over Ganga Mountain, China by Zhang et al., 2013; 0.8 over Hongkong, China by Lau et al., 2007; 0.7 over Sanghai, China by Cai et al., 2010) attributing to gasoline emissions."

Comment: P32149 L17: Do back-trajectories confirm any history of travel over lowland townships and cities?

Reply: Thanks for the comment. Two representative trajectory plots are given here which show that they are originating from low land regions like IGP or eastern Indian states where many cities and townships exist. The altitude of the trajectories confirms their travel over those low land regions.

Comment: P32149 L23: Provide more detail of the 'various environments'.

Reply: Thanks for the suggestion. It has been given in detail.

"Kuntasal (2005) found X/E ratio to be varied between 3.8- 4.4 in fresh emissions at gasoline station, underground garage and a tunnel."

Comment: P32150 L15-17: General comment: This study provides a limited range of VOCs, so concluding that the major source of VOCs in Darjeeling is vehicular exhaust only applies to these 18 VOCs. A wider range of compounds would have given different results. Please discuss this further.

Reply: Thanks for the suggestion. We have specified the number and types of VOCs measured over Darjeeling.

"Thus it can be concluded that the major source of 18 VOCs (BTEX, non-BTEX aromat-

ics and halocarbons) measured over Darjeeling is gasoline and diesel driven vehicular activities which contributed by more than 60 %."

Comment: P32151 L9-11: Again, this conclusion is based on only 18 VOCs, plus does not factor in the role NOx might play.

Reply: Thanks for the comment. We have mentioned that although NOx plays important role in tropospheric ozone formation, the measurement of NOx was beyond our study and hence, we have limited our investigation of ozone formation potential to VOCs only. We have also mentioned that amongst the 18 measured VOCs, those emitted from vehicular emissions and solvents, played important role in ozone formation. The modified sentences are:

"Although it is well known that tropospheric NOx plays important role in tropospheric ozone formation, the measurement of NOx was beyond our scope during the study period. Hence, in this study, the investigation of ozone formation potential (OFP) was limited to VOCs only. To find out the potential of various VOC sources (as derived from PMF model) to the tropospheric ozone formation over Darjeeling, we have computed OFP of each source using the Maximum Incremental Reactivity (MIR) values derived by Carter (2008)."

Comment: Figure 4 needs labelling to show which data points correspond to which VOCs.

Reply: Thanks for the suggestion. The data points have been labelled in the modified figure (Figure 6).

Comment: Figure 4: The number of significant figures needs to be reduced to a more reasonable number.

Reply: Thanks for the suggestion. The changes have been made (Figure 6).

Comment: Figure 5: After the discussion in the introduction about vehicles and biomass burning, I'm surprised that biomass burning isn't one of the factors (differ-

ent from coal burning). For example benzene is a general combustion tracer. Please discuss.

Reply: Thanks for the comment. Benzene is a general combustion tracer but it cannot be used as marker of biomass burning. Benzene is emitted from combustion of coal burning, biomass burning and fossil fuel burning. Acetonitrile and methyl chloride are well known biomass burning tracers (Wang et al 2007). But it was beyond our scope to analyze those in our study. Thus we were unable to separate biomass burning from coal burning due to lack of biomass burning tracers.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/14/C13359/2015/acpd-14-C13359-2015-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 32133, 2014.

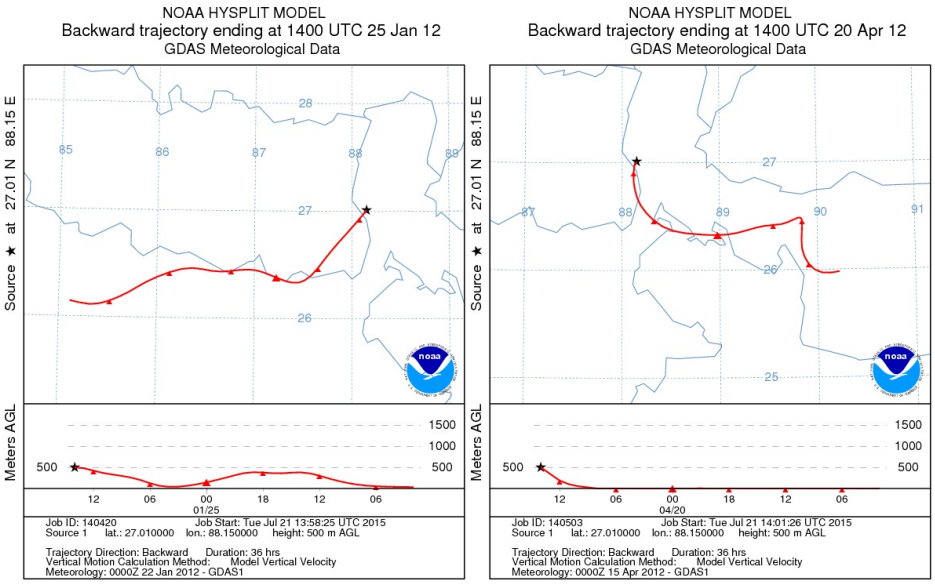

Fig. 1. Trajectory plots