

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 # 4 (Anonymous)

Comment: The main problem I see in this study is in the calibration/quantification of gases. Carbon tetrachloride mean value is reported as $0.18 \mu\text{g m}^{-3}$, which corresponds to about 30 pptv. In my opinion, this is impossible. Internationally recognized laboratories report average values that are almost 3 times this concentration (AGAGE network, CDIAC data, etc). CCl₄ has never been so low in the past many decades. No

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scientific paper can present atmospheric levels of CCl₄ so low without even pointing out this discrepancy and thoroughly discussing it.

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 ($0.18 \mu\text{g m}^{-3}$ which is equivalent to 30 pptv) than the global mean concentration (~ 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

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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). Balloon 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

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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 (~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 (~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 ($< 0.06 \mu\text{g m}^{-3}$) and $1.65 \mu\text{g m}^{-3}$. One important observation is that the data points higher than ~85 ppt i.e. CTC concentrations of higher than ~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

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(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 supportive 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 “. this is impossible” 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: Also, levels of benzene and toluene are exceptionally high. The average benzene is reported to be 81 $\mu\text{g m}^{-3}$, about 24 ppbv. As a comparison, Baker et al.,

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2008, calculated an average benzene mixing ratio of 0.5 ppbv in Los Angeles and Detroit, the two cities with the highest benzene among 28 US cities investigated in early 2000. Barletta et al., 2005 found that the highest average benzene mixing ratio among 43 Chinese cities investigated in 2001 was 10 ppbv (average benzene in Beijing was 6 ppbv or 4 times lower than in Eastern Himalaya). I find hard to believe that tourist activities over Eastern Himalaya or long range transport can increase atmospheric pollution so much. Toluene is also of concern: mean of 140 $\mu\text{g m}^{-3}$, about 36 ppbv, which is also exceptionally elevated.

Reply: Thanks to the reviewer for the concern regarding elevated concentration of Benzene and Toluene over eastern Himalaya. We would like to refer to Table 4 where we have discussed the comparison of the present VOC level with other Indian / south Asian cities. The Indian scenario in terms of vehicular populations, vehicular movement on the roads, quality of vehicular parts (engine, exhaust etc), age of the vehicles (mainly public transport), and quality of fuel used and other anthropogenic activities is different than the other developed countries. Again we feel that a comment like “I find hard to believe that tourist activities over Eastern Himalaya or long range transport can increase atmospheric pollution so much” may be contradicting the very essence of science which stresses on fact against belief.

Hoque et al., (2008) observed benzene and toluene concentrations of 97 $\mu\text{g m}^{-3}$ and 180 $\mu\text{g m}^{-3}$ over commercial areas of Delhi, India. Srivastava et al., (2005) observed 100-550 $\mu\text{g m}^{-3}$ of benzene and 150-350 $\mu\text{g m}^{-3}$ of toluene over commercial and industrial areas of Delhi, India. Srivastava et al., (2006) also observed 348 $\mu\text{g m}^{-3}$ of benzene and 303 $\mu\text{g m}^{-3}$ of toluene over Mumbai, India. Chaudhury and Kumar, (2012) observed 207 and 209 ppb of benzene and toluene respectively over a city Firozabad in India. Rekhadevi et al., (2010) observed benzene concentration of 133 $\mu\text{g m}^{-3}$ over another city Hyderabad in southern India.

In addition to Indian cities, high toluene concentrations were also observed over Manila (~170 $\mu\text{g m}^{-3}$), Bangkok (~190 $\mu\text{g m}^{-3}$) and greater Cairo, Egypt (~160 $\mu\text{g m}^{-3}$)

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(Khoder, 2007 and references therein).

However high VOC concentration over Darjeeling at eastern Himalaya in India is indeed a major concern. This high VOCs over eastern Himalaya draws serious attention from both degradation of Himalayan air quality and human health. This should be highlighted for better pollution control system over this part of India. This part of the paper (higher VOC over Darjeeling than other places) should be brought to the attention of general public of Darjeeling and other regions at eastern Himalaya and policy makers of Govt of India to initiate environmental awareness program and policy interventions immediately.

Yes, it is hard to believe, but is the fact.

Comment: These concerns about the VOC calibration are supported by the lack of info in the experimental part. The authors should add details about how the quantification/calibration was performed, what was the LOD? Precision? Accuracy? Also, concentrations are reported with too many significant figures. For instance, toluene's mean value is 140.67 $\mu\text{g m}^{-3}$: can the authors really measure it down to the second decimal?

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

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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 $\mu\text{g}/\text{m}^3$ for 1,2,4-Trimethylbenzene to 0.08 $\mu\text{g}/\text{m}^3$ for 1,1-Dichloroethane considering 70 Lit of air sample. The MDL for individual component has been given in Table 1. Thus, the concentration values have been reported as per their detection limit".

Comment: Also, the VOCs were measured with a MS, but the authors do not specify how the MS was operating: SIM or SCAN mode? How long was the sampling? The flow rate was 100 mL/min, but for how many minutes was the sample collected?

Reply: Thanks for the queries. MS was operated under SCAN mode. The sampling integration time was 11 hours for day (7 am-7 pm) and night (7 pm – 7 am) basis. This has been incorporated in the manuscript under Section 3.1.

Comment: Finally, most of the discussion is very descriptive; about what was low and what was high, I felt that the discussion was quite limited for the audience of ACP.

Reply: Discussion was made on why and how VOCs varied seasonally and between day and night. Factors have been identified which these variations depend on. We have discussed how long range transport affects the VOC loading over Darjeeling and the contributions from long distant regions have been quantified. A thorough analysis on source apportionment using PMF model was done. Major VOC sources were also investigated which played important role in tropospheric ozone formation. Thus, the discussion was not "very descriptive; about what was low and what was high". Such

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a comprehensive and first ever study on VOC over Himalaya should bring immense importance to the scientific community, as we believe.

MINOR COMMENTS:

Comment: I am not a big fan of double parenthesis: abstract L5; section 3.1 L24

Reply: Thanks for the comment. It has been rectified as:

“A total of 18 VOCs consisting of mono aromatics-BTEX (Benzene, Toluene, Ethylbenzene, Xylene), non-BTEX substituted aromatics and halocarbon have been measured over Darjeeling (27.01 °N, 88.15 °E, 2200 m asl) in the eastern Himalaya in India during the period of July, 2011 – June, 2012.”

Comment: Page 32136, L3, please replace “they also have the potential towards...” with “Some of them also have the potential...”

Reply: Thanks for the comment. It has been rectified

Comment:page 32137, L20. I am not sure what “apparently” means in this contest.

Reply: Thanks for the comment. The sentence has been rephrased as:

“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: Page 32141, L23: change “get increased”

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

Comment: Page 21141, L24: “... remain same in these...” change to “....remain the same in these....”

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

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Comment: Page 32142, L12. I am not sure how the info about the transport of carbonaceous compounds fits here, particularly because at the end it seems like the main source is attributed to tourist activities, not biomass burning.

Reply: Thanks for the comment. Other than the local sources, one major possibility is the transport of biomass burning plume over Darjeeling during postmonsoon. As we observed highest VOC concentration in postmonsoon season, we have discussed all the possibilities regarding VOC sources whether local or transported. This transport of biomass burning plume could enhance VOC over Darjeeling in postmonsoon. However, we have apportioned the sources of VOC based on the data of all the seasons i.e. on annual scale, where we have found that vehicular activities are the major source of VOC over Darjeeling. Thus, transport of carbonaceous compounds could contribute to VOC over Darjeeling to some extent and in a particular season and does not play major role as a significant VOC source over the year as observed from PMF model.

Comment: Section 4.3 is particularly descriptive with no conclusions. Also, the high levels at night compared to the daytime could also be the result of the shallower BL. I am surprise that the author don't mention this possibility.

Reply: Thanks for the comments. This section discussed on how VOC varied between day and night times over different seasons with the help of night to day ratio values. The ratio values were determined and day versus night time VOC was explained based on the anthropogenic and meteorological influences.

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

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and hence the night to day ratio. 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: Figure 3 is very hard to read, please increase the font in the figure.

Reply: Thanks for the suggestion. It has been changed (Figure 5).

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/14/C13385/2015/acpd-14-C13385-2015-supplement.pdf>

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