

Interactive comment on “Impact of continental outflow on chemistry of atmospheric aerosols over tropical Bay of Bengal” by B. Srinivas et al. *MS Ref: acp-2011-360*

Anonymous Referee #3

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General comments: This paper presents data on chemical characterization of both soluble and insoluble fractions of PM₁₀ and PM_{2.5} over the Bay of Bengal for one month period in winter. This work evidences that transport of anthropogenic pollutants from the continent considerably affect the composition of the marine boundary layer during the late monsoon. A major concern of this paper is that most results presented have been already published in a previous paper by the same authors (Kumar et al 2010, Marine Chemistry 121, 167-175). Thus, the major conclusion of this paper is the evidence of the impact of anthropogenic sources in the MABL in the Bay of Bengal. This was already concluded by the above cited paper. Authors should clarify which is the added value of the present paper with respect to the previous one. Another concern is that, in some occasions, interpretation of the results is not adequate. Thus it is unreasonable to quantify the contribution of biomass burning based on the TC/ EC; OC/EC ratios.

Response: The primary objective of this paper is to assess the impact of continental outflow (emissions from biomass burning and fossil-fuel combustion) from the Indo-Gangetic Plain (IGP) on aerosol chemistry in the marine atmospheric boundary layer (MABL) of Bay of Bengal. The continental outflow from IGP and south-east Asia is relevant and persists over the Bay of Bengal for a short-span of about four months (late December/early January to early April). The month of April is a transition period with reversal in the winds from north easterly to south westerly. A systematic sampling of PM_{2.5} and PM₁₀ was, thus, carried out during a cruise in January 2009. Our results emphasize on the advective transport of anthropogenic species (NH₄⁺, K⁺, Ca²⁺, NO₃⁻, SO₄²⁻, OC and EC) to the Bay of Bengal. It is, therefore, logical for us to bring out and summarize the impact of anthropogenic sources (in the sulphate dominated outflow) on aerosol chemistry. In this context, we have briefly summarized and addressed to three important processes operating in the MABL. (1) The reactive uptake of acid species by mineral dust by looking at the relationship between water-soluble Ca²⁺ and total-Ca content of the aerosols; (2) The acid-base displacement of chloride from NaCl by

chemical reaction with H₂SO₄/HNO₃; and (3) enhanced fractional solubility of aerosol iron derived from chemical processing of mineral dust and/or contribution from combustion sources. These chemical processes are significantly important and merit discussion and simultaneous synthesis in one single article. Nevertheless, we have now included data from earlier cruises (Mar-April 2006, Feb 2003 and Feb-March 2001) in order to strengthen our interpretation and conclusions on the cause (due to anthropogenic sources) and effect relationship (as seen in the form of chemical processes). In addition, we have now added the concept of conversion factor to calculate POM from the measured concentration of OC. Such information is most desirable from a regional perspective, hitherto lacking in the literature. We have also performed the principle component analysis as per the suggestion by other reviewer. All experimental details regarding standards, calibration, field and filter blanks, repeat analyses of samples, and detection limits are now added in the revised version (also included in our response made to comments of Referee # 1).

Specific comments: The aim of the paper is to provide data on size dependent chemical composition of aerosols. As authors said in the introduction is necessary to provide models with “real time data ion size dependent chemical composition of atmospheric aerosols and the associated spatio-temporal variability”. However, one major limitation of this paper is the relatively short period investigated (1 month with daily resolution).

Response: In response to the Reviewer’s comment, we have now compared results from this study with the data from earlier cruises conducted during the continental outflow persisting over the Bay of Bengal from January to mid-April (see Fig 4 as per revised set of all Figures appended with this response).

Comment: Given the short duration of the sampling period a more detailed meteorological description is needed in order to interpret the source origin of particulate matter. Thus, in the first half of the sampling period background levels are similar to those recorded during the second half. However, there are two high episodes (the 2nd and the 7th of January) showing the increment of most of the PM components. What is the origin of these two episodes? It is surprising that in the previous paper, by Kumar et al., 2010, the interpretation of results is based on a more detailed meteorological interpretation, considering IGP, SEA and MAP scenarios. However in the present paper only the spatial

variation has been considered. I think it is necessary to combine both the spatial and the meteo info.

Response: The continental outflow from the Indo-Gangetic Plain and south-east Asia persists over the Bay of Bengal for a short span of about four months. Therefore, meteorological information and wind speed are important only during early January to mid April. The observed two peaks in most of the PM constituents are mainly due to sampling along the northern most region (sampling along the coast). Synoptic meteorological factors have been discussed during the period of late NE-monsoon (Jan-April) when marine atmospheric boundary layer is influenced by the continental outflow.

Comment: More info about sample treatment and analysis is needed. Have the blank concentrations been subtracted from the bulk sample concentrations? Have you dissolved and analyze certified standards?

Response: All chemical constituents are corrected for blanks and method detection limits have been provided in the revised manuscript. We are quite familiar with the analytical protocol for the chemical analyses of atmospheric aerosols and have been engaged in these studies for more than one decade (as evident from number of our earlier publications). Therefore, corrections for filter and field blanks and analyses of certified standards are well built in our analytical protocol. Nevertheless, additional details are now provided with respect to analytical procedures (also stated in the response made to Referee #1.

Comment: What is the reason of the differences found out between the EC concentrations in this paper with respect to Kumar et al 2008b (page 20678) The correlation between OC and EC for PM_{2.5} shows the presented of two different groups (figure 9) of N Bo B; the same is evident for PM₁₀; however, method used for calculating R² shows a high correlation (R²= 0.87); The four values with high contents of OC and EC in N Bo B show a different ratio and can be related to a different origin (probably related to the two peak episodes reflected in Figure 8.

Response: The high concentrations of OC, EC in the above mentioned four data points were sampled along the coast and hence reflected in the OC/EC ratio and scatter plot between OC and EC. Text is edited suitably for clarity as per the suggestion by reviewer.

Comment: Ratios OC/EC >2 may be attributed to other causes than biomass burning (Page 20679; lines10-15). Thus, oxidation and ageing of VOCs, and condensation onto other particulates may increase the ratio OC/EC. Please, update the references (Plaza et al Atmospheric Environment 45, 2496-2506, 2011; Pio et al., Atmospheric Environment 45, 2496-2506, 2011.) It is not reasonable to quantify the contribution of biomass burning to the carbonaceous species based on the TC/EC and the K+/EC ratios (Page 20680). These ratios may vary considerably as a function of the biomass composition.

Response: We agree with comment made by the reviewer. The TC/EC ratio from biomass burning (from diverse vegetation and wood fuels/bio-fuels) averages around 9.1 (Andreae and Merlet, 2001) and about 2.0 from fossil-fuel combustion sources (Mayol-Bracero et al., 2002;Novakov et al., 2000). Assuming that these are representative of the two end members (viz. 2.0 for fossil fuel and 9.1 for biomass burning), the TC/EC ratio in PM₁₀ ranges from 2.2 to 7.5, suggesting contribution from biomass burning ranging from 3 to 77%. TC/EC ratio in PM_{2.5} ranges from 2.0 to 5.9 and yields 2 to 55 % contribution from biomass burning. These results are contrary to the previous study by (Sudheer and Sarin, 2008a), reporting dominant (more than 80 %) contribution from biomass burning over the Bay of Bengal during the spring inter-monsoon (March-April'06). Recent study by Gustafsson et al., (2009), has highlighted the importance of biomass burning within the IGP. It is, thus, inferred that contribution of carbonaceous species is governed by both fossil-fuel and biomass burning sources. However, these calculations can be biased due to the underlying assumption of representative TC/EC value for the two end members. More recent study by Habib et al., (2008), had shown a lower TC/EC ratio for diverse vegetation (bio-mass) burning and, hence, the contribution of biomass burning emissions towards the carbonaceous aerosols would be underestimated by this approach. Therefore, we have used the nss-K+/EC ratios for estimating the contribution of carbonaceous species from biomass burning emissions vis-à-vis fossil-fuel combustion sources.

The nss-K⁺ can be used as a marker to identify the regional impact of biomass burning. Andréa, (1983) had shown that significant linear relation between fine-K⁺ and soot carbon (EC) suggest their common source from biomass burning. However, the nss-K⁺ concentrations can vary depending on the vegetation type (viz., biomass burning;

forest fires, bio-fuel burning etc.). According to Andréa and Merlet (2001), the K^+/EC ratio in the biomass burning emission spreads between 0.1 to 0.63. The observed ratio over Bay of Bengal, in $PM_{2.5}$ and PM_{10} , averages around 0.35 ± 0.10 and 0.39 ± 0.15 respectively; suggesting significant contribution of K^+ and carbonaceous aerosols from biomass burning (fossil-fuel combustion is a insignificant source of K^+). In order to quantify the relative contribution of carbonaceous species from two sources we assumed that K^+/EC ratio from fossil-fuel combustion sources is zero (Park et al., 2007; Andrea., 1983) and that from biomass burning sources is 0.63. Based on the average K^+/EC ratio, contribution towards EC from biomass burning is more than 50% in $PM_{2.5}$ and PM_{10} . It is also noteworthy that the nss- K^+/EC ratios are relatively high over S-BoB (0.39 ± 0.09 for $PM_{2.5}$ and 0.47 ± 0.15 for PM_{10}) as compared to N-BoB (0.29 ± 0.09 for $PM_{2.5}$ and 0.29 ± 0.08 for PM_{10}). This comparison suggests dominant contribution of biomass burning emissions during SEA outflow over S-BoB. Earlier studies during INDOEX had concluded the dominant contribution of carbonaceous species from fossil-fuel combustion based on the BC/TC ratio (Novakov et al, 2000; Mayol-Bracero et al., 2002; Salam et al., 2003). In contrast, based on the presence of nss- K^+ , acetonitrile, BC/CO ratio and also based on the correlations of aerosol optical depth with the fire count data (Lawrence and Lelieveld, 2011 and references there in), it was concluded that the primary source of BC is from biomass burning emissions. The study by Guazzoti et al., (2003) suggests that for the air mass sampled from India, biofuel and biomass burning is the dominant source. In addition, regional and global emission inventories suggest major contribution of carbonaceous aerosols from biomass and bio-fuel burning (Venkataraman, 2005; Lawrence and Lelieveld, 2010 and references therein). Based on C^{14} measurement of aerosol particle collected from the west coast of India, Gustafsson et al., (2009) have concluded dominant contribution of carbonaceous aerosols from biomass and bio-fuel burning. In this study, high concentrations of nss- K^+ and EC in $PM_{2.5}$ aerosols provide better evidence for the dominant contribution from biomass burning sources.

Comment: Section 3.2.3. (Page 20682). This section is obscure. It is not clear if a desert dust outbreak was sampled during the study period. Ratios of Al/Ca or Al/Fe may vary considerably with respect to the crustal ratio as a function of the source origin. In addition, these components may be emitted by a number of anthropogenic sources such as traffic

resuspension, industrial activities, or construction, with a different chemical signature and finer size distribution with respect to the naturally originated. As deduced from Figure 8, crustal related elements show a high correlation with anthropogenic elements; therefore an anthropogenic origin for these elements could not be discarded. For the above reasons, the estimation of crustal load from Al is not adequate; mainly if the crustal ratio is applied for the PM_{2.5} fraction. It would help for interpretation a correlation analysis or a single principal component analysis (PCA).

Response: Principal component analysis is performed for both PM₁₀ and PM_{2.5} fractions. We have discussed various factors contributing to the chemical composition in the revised text.

Comment: In section 3.2.1, about water soluble ionic composition, a clear correlation between coarse nitrate and Na is evidenced showing the interaction between nitric acid and marine sodium chloride. However in section 3.3.1 an interaction between sulfate and Na is suggested (although not evidences are presented). These two sections should be combined and clarified.

Response: Text is edited for clarity as per the suggestions by Reviewer.

Comment: Section 3.3.2. This paragraph is not connected to the MS. Sections 3.3.3 and 3.3.4. Results are a summary of results previously published in Kumar et al., 2010. Thus, subsection 3.3.3 on “Anthropogenic sources on aerosol iron solubility”, showing the enhancement of Fe solubility by the interaction with anthropogenic pollutants, is mainly based on results presented in the above mentioned paper. This subsection should be eliminated. These results could be summarized and presented as support of the results presented in this paper but the statement on iron solubility should be eliminated from the abstract, given that these conclusions were obtained in the previous paper.

Response: Text is suitably edited as per the suggestion. For fractional solubility of aerosol iron, we have compared data from this study with the samples collected during Mar-April 2006.

Comment: Technical corrections 20676 - L6; is 20682- 121- “where the dust levels were significantly low.” Please include equations and regression coefficients in Figures 7 and 9 to 12 Figures 6 and 8; quality can be improved; these Figures are very similar to Figures presented in Kumar et al 2010.

Table 1. Include number of samples.

Response: Text is suitably edited as per the suggestion by reviewer. The relevant Figures have been modified and/or replaced with new ones.