

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 #4

Received and published: 15 November 2011

Overall:

This manuscript reported the aerosol data in terms of water soluble major ions, a few elements, and OC/EC concentrations measured over the Bay of Bengal (BOB) on a ship cruise during the north-eastern monsoon, with various aspects of discussion on atmospheric chemistry of two size-fractionated aerosol particles. However, I didn't find any exciting points (that are distinct from their earlier publication), and some results were not interpreted at all though comparison with earlier studies was made. Besides, there are a few flaws with respect to methodology and data interpretation. Surprisingly and more importantly, I found the whole data set (and also the results in part) have been published elsewhere recently (Kumar et al., 2010; Mar. Chem. 121, 167-175), along with some data on water-soluble ions published by Sarin et al. (2010; J. Atmos. C11865 Chem. 66, 1-10). I wonder if this can be allowed by this reputed, high-IF journal ACP. Overall, I don't think they can revise this manuscript to meet the standard of acceptance for publication. I have pointed out major concerns and suggestions, as below.

Response: The overall remarks made by the Referee are not in the right scientific spirit of reviewing a research article and somewhat unethical. We are appalled by the remark, “I don't think they can revise this manuscript to meet the standard of acceptance for publication”. This is more of a personal remark. We do not understand how a Referee can make this presumption and comment on our not meeting the standard of acceptance.

As pointed out in our response made to Referee # 3, it is logical to assess the impact of anthropogenic sources (in the sulphate dominated continental outflow) on aerosol chemistry in the MABL of Bay of Bengal. 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 Ca^{2+} and total-Ca content of the aerosols; (2) The acid-base displacement of chloride from NaCl by chemical reaction with $\text{H}_2\text{SO}_4/\text{HNO}_3$; 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 syntheses 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). **NOTE: See Fig. 4 as per appended set of revised Figures.**

It is also strange that on one hand the Referee had commented that some of our data set is already published; but at the same time it is stated that “there are few flaws with respect to methodology and data interpretation”. It is important to note that these results and methodology are published in high-IF journals after peer-review.

General points

Comment 1: In this work, the authors punched a piece (2 cm in diameter) of each filter for extraction with 10 ml Milli-Q water for water-soluble Fe measurement. I wonder if this small piece (3.14 cm²), only less than 1/100 of the whole filter area (20 cm * 25 cm) might have resulted in large errors, which should be estimated in the water-soluble iron concentration and the resulting iron solubility. Also I am curious why the authors didn't use an aliquot of the extract that was to be used for ionic species measurement for water-soluble iron.

Response 1: This comment from the Reviewer is rather uncalled for. We are quite well versed with the chemical and isotopic analyses of atmospheric aerosols. We had made reference to our earlier publications and standard protocol used in our Lab for more than one decade. Moreover, it is clearly stated in the text (Page 20672, lines: 9-10) that water-soluble inorganic constituents (WSICs) were measured on one-fourth portion of the filter.

Furthermore, Reviewer has commented incorrectly that “the authors punched a piece (2 cm in diameter) of each filter ----- for water-soluble Fe measurement” and thus analysing “only less than 1/100 of the whole filter area and resulting in large errors”. This is incorrect, it is clearly stated (Page 20673, lines 3-5) that 2 cm diameter “punches” were extracted (implying that more than one punch was used). Further, we wish to draw the attention of the Reviewer that “an aliquot of the water-extract for ionic species” can NOT be used for water-soluble iron. We have adopted the analytical protocol based on simple concepts in analytical chemistry. The water-soluble iron is most unstable, hydrolyses and precipitates at near neutral pH of Milli-Q water. It is, therefore, essential to acidify the water-extract immediately after the extraction step. This is unlike the protocol adopted for the extraction of water-soluble inorganic species. One can NOT acidify the water extract for measuring inorganic constituents by Ion-Chromatography. It is

also important to note that equilibrium and extraction time required for one-fourth filter in 50 ml of Milli-Q water is fairly long (~30-40 min). This is desirable for complete extraction of water-soluble inorganic constituents from one-fourth filter in relatively small proportion of water. On the contrary, water-soluble iron can precipitate during this extended extraction time; whereas inorganic constituents are highly soluble. In this context, it is relevant to state that repeat measurements starting with new filter punches for water-soluble iron have shown excellent agreement.

Comment 2: The methods how to derive the average percentage of each ion and the mass closure for PM_{2.5} and PM₁₀ as shown in Figures 4 and 13 should be described: that is, the mean concentrations of individual chemicals averaged from all samples divided simply by the PM mass mean concentration, or averaging the percentages of individual chemicals in each sample throughout all samples. If the latter, how to treat the samples with over 100 %, if any, should be mentioned.

Response 2: As suggested, text has been suitably corrected. The contribution of an individual ion to Σ WSIC (sum of water-soluble inorganic constituents) in each sample is first computed and then average of all samples is taken as the contribution shown in Fig 4. *[NOTE: Fig 4 is now revised by providing data from earlier cruises conducted in the Bay of Bengal]* Likewise, the percentage contribution of mineral dust, ANTH ($\text{NO}_3^- + \text{nss-SO}_4^{2-} + \text{NH}_4^+$), sea salt, EC and organic matter to PM_{2.5} and PM₁₀ mass is estimated for each sample and then average for all samples is computed. The extremely low aerosol loading in samples collected from farthest region in the south Bay of Bengal results in large error for individual components.

Comment 3: The authors discussed the relationships between ammonium and nss-sulphate by using $\text{NH}_4^+ / \text{nss-SO}_4^{2-}$ equivalent ratio as seen in the text, but, as shown in Figure 7, they putted NH_4^+ as y-axis and nss-SO_4^{2-} as x-axis. Please change them one another so that one can easily use the slope of regression line as the indicator of this ratio. Besides, the linear regression might need to be forced to the original. Additionally, they have shown that nss-sulphate and ammonium are predominantly associated with PM_{2.5}, representing.

Response 3: Contrary to the comment made by the Reviewer, we had earlier plotted NH_4^+ on the X-axis and SO_4^{2-} on the y-axis. We have now replaced Fig.7 in response to the comment made by the other Reviewer. We have now included a scatter plot between equivalent mass concentrations of $(\text{Na}^+ + \text{NH}_4^+ + \text{Ca}^{2+})$ and nss-SO_4^{2-} . It can be inferred that the excess sulphate

(nss-SO₄²⁻ after neutralization with NH₃) reacts with calcareous minerals (CaCO₃) and sea salt (NaCl).

Comment 4: As claimed by the authors (see the last paragraph of section 3.2.1), the mass ratio of NO₃⁻ and nss-SO₄²⁻ in aerosol samples has been used to assess the relative importance of emissions from stationary versus mobile sources (Wang et al., 2006; Arimoto et al., 1996; Yao et al., 2002). I do think this applicable for land based and coastal cases, but not for the remote oceans. As taken from Arimoto et al. (1996), they suggested that “Differences in the slopes for nssSO₄²⁻ to NO₃⁻ regressions at the coastal-continental stations suggest that there are regional differences in the emissions of sulfur and nitrogen compounds and possibly in their sinks.” For the remote oceans, the continental pollution outflows should be regarded as a stationary source. Eventually, I didn’t see any reasonable explanation for the observed low nitrate to nss-sulfate ratio as compared to many results observed over oceans, particularly the results of Arimoto et al.

Response 4: Firstly, this comment from the Reviewer re-affirms that our manuscript provides an important data set (worth reporting!!) on atmospheric chemistry within the marine atmospheric boundary layer downwind of the pollution sources. In this context, discussion on NO₃⁻/nss-SO₄²⁻ mass ratio is most relevant. The mass ratio of NO₃⁻ to nss-SO₄²⁻ in aerosols has been used to assess the relative importance of emissions from stationary versus mobile sources (Wang et al., 2006; Arimoto et al., 1996; Yao et al., 2002). In this study, NO₃⁻/nss-SO₄²⁻ ratio in PM_{2.5} varied from 0.01 to 0.18 (Av: 0.03), whereas it varied from 0.01 to 0.43 (Av: 0.10) in PM₁₀. Over the marine region, NO₃⁻ primarily exists in coarse mode due to the reaction of HNO₃ with sea salt and/or dust. However, sulphate exists in both fine and coarse mode due to the formation of (NH₄)₂SO₄, CaSO₄ and Na₂SO₄. The mass ratio of NO₃⁻/nss-SO₄²⁻, in PM_{2.5}, would decrease during long-range transport due to processes such as evaporative loss of NH₄NO₃ and the complete neutralization reaction of NH₃ with H₂SO₄. Thus, sulphate concentration far exceeds that of nitrate in the fine mode (PM_{2.5}). The lower ratio of NO₃⁻ to nss-SO₄²⁻ is not only observed in this study but also in the data from earlier cruises conducted in the Bay of Bengal; suggesting that nitrate is significantly less than the sulphate concentration. The equivalent mass ratio of NH₄⁺/nss-SO₄²⁻ (excess acid) in PM_{2.5} is far less than one, suggesting the complete neutralization of NH₄⁺. In addition, relatively high abundance of NO₃⁻ in PM₁₀, together with lower equivalent ratio of NH₄⁺/SO₄²⁻, suggests preferential association of NH₄⁺ and SO₄²⁻ in the fine mode (PM_{2.5}) and NO₃⁻ in the coarse mode. Therefore, during the long-range atmospheric transport,

preferential removal of nitrate (due to its association in coarse mode) compared to SO_4^{2-} results in significantly lower $\text{NO}_3^-/\text{nss-SO}_4^{2-}$ ratio over remote oceanic regions (south Bay of Bengal).

Comment 5: As suggested by Turpin and Lim (2001) which has been cited by the authors, the factor converting OC to POM can vary from 1.4 to 2.2. The authors may need to give convincing rationale why chose this factor.

Response 5: The conversion factor of 1.6 was used in this study to assess the POM mass from the measured concentration of OC. For typical urban aerosols, a factor of 1.4 or 1.6 is generally applicable for $\text{PM}_{2.5}$ fraction (Turpin and Lim 2001). A similar factor was also used for the INDOEX data. However, we have now revised the earlier Fig 12 by re-calculating the conversion factor based on individual components (Mineral dust, sea-salt, anthropogenic species, EC and OM) measured in this study and forcing the mass to 100 %. This approach yields a conversion factor of 2.6 (for converting OC to POM) in $\text{PM}_{2.5}$ samples. We emphasize that this approach is more appropriate to interpret our data from the MABL of Bay of Bengal in order to assess the impact of continental outflow. The calculated conversion factor of 2.6 is more realistic and representative of the data in the regional context. Accordingly, Fig 11 (earlier Fig 12) now presents data set for individual components in $\text{PM}_{2.5}$ for the North- and South-Bay of Bengal. The propagated error on the conversion factor (2.6) is within $\pm 15\%$. It has been suggested that levoglucosan can be used as a tracer for identifying the regional impact of biomass burning emission. For levoglucosan, the molecular weight to carbon weight is given as 2.3. Likewise, for aliphatic dicarboxylic acids, the ratio can vary from 1.7 to 3.8 (Turpin and Lim, 2001). The impact of biomass burning is clearly discernible from high concentrations of nss-K^+ , EC and OC; and their statistically significant linear relationship ($P < 0.05$) can, therefore, justify the conversion factor of 2.6 estimated by us based on the above rationale. These concepts are now added in the revised text and re-establish the importance of our submitted manuscript.

Comment 6: In order to applying K^+/OC ratio for estimating the relative contributions of biomass and fossil fuel combustion apart from TC/EC ratio, the authors assumed K^+/EC ratio from fossil fuel combustion aerosols to be 0. However, numerous previous investigations have observed high K (K^+) from coal combustion extensively over China (e.g., Waldman et al., 1991; AE 25, 113-120) and other locations (Wang et al., 2005; AE 39, 5865-5875; Lee et al., 2005; Terr. Atmos. Ocean. Sci. 16, 345–360). Moreover, high potassium ion has been observed extensively during the PEM-WEST and TRACE-P campaigns over the North Pacific, which has

been attributed to the Asian continental outflow dominated by coal combustion other than biomass burning. I do think this assumption inappropriate.

Response 6: The air-mass back trajectory cluster computed for arrival height at 100, 500 and 1000 m during the sampling period in Jan 2009 clearly indicate downwind transport of pollutants from the Indo-Gangetic Plain (IGP) and south-east Asia (SEA). Several recent studies have shown that the biomass burning emission is a dominant source in the IGP (Badarinath et al., 2006; Venkatraman et al., 2006; Sudheer and Sarin, 2008). A recent study by Gustaffson et al, (2010), has also shown that emission inventories in the Indo-Gangetic Plain are dominated by the biomass burning. In addition, relatively high concentrations of K^+ are observed in aerosols from the forest-fires over the Amazonian region and over the Western Africa during ground-based and aircraft sampling (Guzzaroti et al., 1993; Paris et al., 2010). Likewise, higher abundance of K^+ is observed during agricultural crop-waste residue burning in the IGP (Rishi Pal, 2008; Ram et al., 2008). Therefore, we argue that the high abundance of $nss-K^+$ in fine mode aerosols ($PM_{2.5}$) is derived from biomass burning emissions and hence, $nss-K^+/EC$ in $PM_{2.5}$ can be used to assess the relative contribution from biomass burning source versus fossil-fuel combustion. Earlier study by Andreae (1983) had suggested that the correlation between excess fine mode- K^+ and EC can be used identify the impact of biomass burning emissions in the long-range transport. Further, the transmission electron microscope images of the aerosol samples collected over the African savannah fires, suggest that potassium is embedded in the carbon spherules. Text has been suitably edited to incorporate the above stated concept.

Comment 7: By using the TC/EC ratio, the authors estimated that the relative contributions are 35% from biomass burning and 65% from fossil fuel combustion in PM_{10} , and 20% from the biomass burning and 80% from the fossil fuel combustion in $PM_{2.5}$ over the entire BoB. They concluded that “Such observation point towards mixed contribution from both sources contrary to the previous study by (Sudheer and Sarin, 2008b), reporting the dominant (more than 80 %) contribution from biomass burning over Bay of Bengal during spring inter-monsoon.” While applying K^+/EC ratio, they estimated that >50% of EC in both PM_{10} and $PM_{2.5}$ is from biomass burning. Then they concluded that “This further supports our inference of mixed contribution from both (fossil fuel and biomass burning) sources towards carbonaceous aerosols over Bay of Bengal.” I do think these are considerably inconsistent. In the entire paragraph, what I have seen are contrary explanations.

Response 7: Although we have used TC/EC ratio to decipher the relative contribution of biomass source versus fossil-fuel combustion, this ratio may not represent the source signature due to the partitioning of OC viz., evaporative loss of VOCs away from the source region and their oxidative loss during long-range atmospheric transport. EC is refractory and inert in nature, and does not undergo chemical reactions unlike OC (Lim et al., 2003). Therefore, we have used the $nss-K^+/EC$ ratio to assess the relative contribution of biomass source and fossil-fuel combustion. Recent study by Gustaffson et al., 2010, has suggested that emission inventories of carbonaceous aerosols are dominated by biomass burning rather than fossil-fuel combustion. From our study, using $nss-K^+/EC$ ratio in fine mode (PM_{2.5}) aerosols (Andreae, 1983; Guzzoriti et al., 1993; Park et al., 2007), we suggest that >50% of EC in PM₁₀ and PM_{2.5} is from biomass burning.

Comment 8: As seen in Taylor and McLennan (1985), the Fe/Al mass ratio is equal to 0.84, with Fe abundance 7.06% and Al 8.4%, not 0.43 (see L16/P20681). Also, the ratios Ca/Al (0.37) and Mg/Al (0.17) ratios given here are incorrect (should be 0.63 and 0.38, respectively). I do believe the ratios (relative to Al) among major elements when compared to average crust must be carefully used particularly for aiming to identifying the sources and even evaluating their relative contributions as it is well known the average crust (shale and surface soils) that is used as the reference crustal material can vary within a certain range. That is why when using Enrichment Factor (EF) values for exploring the abundance anomalies of aerosol elements ten (10) is often adopted for differentiating which natural and anthropogenic sources are dominated. Moreover, the Fe/Al ratios in difference dust sources taken from the literature for comparison and especially for explaining the observed low Fe/Al ratios have wrongly used or overlooked some information. For example, Buck et al. (2010) haven't dealt with Asian dust (should be Saharan dust), and also given in their study is the molar ratio, rather than mass ratio. The Fe/Al ratios for Chinese desert and loess dust given in Zhang et al. (1997) range from 0.25 to 1.2; when these Chinese dust sources are classified into three major sources, as seen in that paper, the ratios are 0.44, 0.65, and 0.83, respectively.

Response 8: As commented by the reviewer, we have checked the calculation of Fe/Al ratio in UCC. Taylor and McLennan (1985) had reported Al₂O₃ and FeO abundances as 15.17 % and 4.49 % (weight percent). Therefore, the mass ratio of Fe/Al is close to 0.44, as used in the present study. Likewise, the Ca/Al and Mg/Al ratios are 0.38 and 0.17 (CaO: 4.19 % and MgO:

2.2 %) respectively. Reviewer has stated that the crustal abundances of these elements vary considerably. However, the estimated crustal enrichment factors of Fe, Ca and Mg are less than 10 over the study region (Bay of Bengal). Hence, these are considered as non-enriched elements (Chester et al., 2002) derived from the upper crust, and not from anthropogenic sources. Buck et al., 2010 reference has been corrected for addressing the source from Saharan desert dust. Although, Zhang et al (1997) have identified Chinese dust sources from three regions and have reported the average elemental ratio as 0.44, 0.65 and 0.83. The Fe/Al ratio in their study varies from 0.25 to 1.2. Here we are not comparing the average Fe/Al from Zhang et al., (1997) with the present study. The observed low Fe/Al ratio in the south Bay of Bengal (where the AMBTs at 1500 m and above show their origin from these dust sources) is attributed to the dust transport from the Chinese and African desert dust regions. The lower range is reported for Chinese dust sources by Zhang et al., (1997) and similarly by other studies (Buck et al., 2010a, Reid et al., 2003) for the African desert dust sources. *A comparison of elemental ratios from the Bay of Bengal and the Arabian Sea has been now included in the revised version (Fig 10). A set of new Figures are appended with this response.*

Comment 9: Excessive SO₂ (H₂SO₄) is believed to preferentially react with carbonate mineral particles, whereas HNO₃ would react with sea salt particles, which has been extensively observed downwind the Asian continent, the western Pacific Ocean.

Response 9: Text is suitably edited as per the suggestion.

Comment 10: Most of the contents, particularly the whole two sections Cl-deficit and Fe solubility, have been published elsewhere (Kumar et al., 201; Sarin et al. 2010).

Response 10: Although part of the data is published in Kumar et al., 2010 and Sarin et al., 2010, the main emphasis of this manuscript is to explain the chemical composition of two size fractions (PM_{2.5}, PM₁₀), collected from the MABL during the continental outflow. In Kumar et al., (2010), we have mainly explained the enhanced fractional solubility of aerosol iron, suggesting the importance of combustion sources and chemical processing of alluvial dust. Likewise, in Sarin et al., (2010), we explained the impact of continental outflow on the chloride depletion from sea salt aerosols in the MABL. This manuscript primarily focuses on controlling factors and, hence, we have summarized the impact (effect) on chemical reactions occurring in the MABL.

Comment 11: Good correlations between two aerosol chemicals measured in the remote oceans don't necessary to demonstrate them being of same origins, likely being triggered by the same carrying agent. They cannot serve as convincing evidence.

Response 11: Text is suitably corrected as per the suggestion by the Reviewer. Nevertheless, multiple linear regression analysis to infer common sources is still relevant within or near to the source region.

Specific points and editing:

Comment 12: L2/P20670: Change “;” to “)”.

Response 12: Text is suitably edited.

Comment 13: L3-4/P20677: Suggest changing to “suggest that NH₃ was inadequate and has been completely used in reaction with H₂SO₄ (and its precursor SO₂) to form fine ammonium sulfate, resulting in near —”

Response 13: Text is suitably edited.

Comment 14: L5/P20678: Add a before order.

Response 14: Text is suitably edited.

Comment 15: L27/P20678: The good correlation may also suggest that they are driven by the same transport processes by winds along with their similar sources.

Response 15: Text is suitably edited.

Comment 16: L23/P20679: Suggest changing from is more to would be longer.

Response 16: Text is suitably edited.

Comment 17: L4/P20682: Change to 2010, not 2010a (unless adding to cite another reference of Buck et al.)

Response 17: Text is suitably edited.

Comment 18: L5-6/P20682: Large variability in Ca/Al, Fe/Al, and Mg/Al was attributed to low dust concentrations. I wonder why low dust resulted in large variability of these ratios. That what I can image is due to relatively large uncertainties in chemical analyses because of their low raw concentrations. If so, the authors just face that.

Response 18: Text is suitably edited. During the cruise, we have sampled the entire Bay of Bengal which is influenced by the continental outflow from the IGP and SEA. However, the samples collected in the northern Bay of Bengal show characteristic high aerosol loading than the southern Bay region. This is reflected in the chemical composition of water soluble ions,

mineral dust and carbonaceous aerosols. The high particulate loading in the northern Bay region is attributed to the proximity of continental sources. Since, the Al abundance is used to estimate the mineral dust concentration, we have observed a progressive decrease in the concentration of dust from north to south Bay of Bengal. The large spatio-temporal variability reported in the present study could largely arise due to varying proportion (mass fraction) of dust to the total aerosol mass with parallel increase in the contribution of Ca^{2+} from biomass burning source, and thus affecting the Ca/Al ratio.

Comment 19: L12/P20682: Change to suggesting.

Response 19: Text is suitably edited for clarity as per the suggestion by reviewer.

Comment 20: L13/P20682: I think some water-soluble Ca^{2+} concentrations might be higher than total Ca, and then the authors treated them as same for the two fractions. If so, the authors might need to describe clearly.

Response 20: In all PM_{10} samples, the aerosol Ca concentrations are relatively high compared to its water-soluble Ca^{2+} . However, due to very low concentrations of total aerosol Ca in $\text{PM}_{2.5}$ samples, the solubility approaches near 100 % in most of the samples.

Comment 21: L18-19/P20682: The authors attributed the good correlations between Ca and nitrate to acid uptake by mineral aerosols. However, I think nitric acid may preferentially react with sea salt particles, thus leading to the observed high chloride depletion. The good correlation might be due to the transport of dust and pollutant driven by the same north-eastern monsoon.

Response 21: As stated in the response to earlier comment, NO_3^- is significantly lower than that of SO_4^{2-} . Therefore, chloride depletion is mainly influenced by reaction of NaCl with SO_4^{2-} . Nevertheless, there are studies reported in literature (based on laboratory experiments) suggest that HNO_3 is preferentially react with carbonate minerals (References)

Text is suitably edited for clarity as per the suggestion by reviewer.

Comment 22: L12/P20683: This sentence is unclear.

Response 22: Text is suitably edited.

Comment 23: L10/P20685: Change is compared to comparable.

Response 23: Text is suitably edited.

Comment 24: Table 1: Please give the method detection limit (MDL) for each species, particularly those with BDL. Change Stdev to S.D.

Response 24: Text is suitably edited.

Comment 25: Table 2: please clearly specify mass ratio, and change Std. Dev. to S.D.

Response 25: Text is suitably edited.

Comment 26: Table 3: The authors may consider showing the whole range of these ratios for Chinese dust, rather than specific areas.

Response 26: Text is suitably edited.

Comment 27: Figure 3: This seems to be not needed; just describe in the text.

Response 27: Figure 3 is deleted.

Comment 28: Figure 5: Also this figure could be removed; otherwise, the data other than this cruise conducted in this study could be removed, as they have reported elsewhere (Sarin et al, 2010).

Response 28: Text is suitably edited.

Comment 29: Figures 7, 9, and 10: Suggest performing the linear regression forced to original and showing the slopes.

Response 29: Figures are suitably corrected and/or replaced with new Figures (as detailed in the covering letter to the Editor).