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 #1

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General Comment: This paper presents the chemical (carbonaceous, inorganic ionic and trace elemental) composition of atmospheric aerosols, in two size fractions ($PM_{2.5}$ and PM_{10}), over Bay of Bengal collected in winter period (December 2008 to January 2009). The data is interesting and provides the implications for continental outflow over to Bay of Bengal and thus makes a significant contribution. However, the phrase "on chemistry" in title may be reconsidered, because this paper has mainly focused on chemical composition and spatial (N-BOB & S-BOB) distributions of chemical components rather than chemical processes. It also requires some clarification/further discussion in the text. This paper may be published in ACP after minor revision, following the comments given below.

Response: We thank the Reviewer for appreciating our data and implications to the continental outflow over the Bay of Bengal. We would like to retain the phrase "on chemistry" in the title because in this paper we have addressed to three important chemical processes: 1) Neutralization of the acidic species by NH_4^+ and mineral dust; 2) acid-base displacement of chloride from sea-salt (NaCl); and 3) fractional solubility of aerosol-Fe influenced by the chemical processing of mineral dust during long-range transport and contribution from combustion sources (biomass burning and fossil-fuel combustion).

Specific Comments: Pages 20672-20673, (i) lines 12-15: It is important to provide the details of extraction procedure adopted for ion analyses in brief, including analytical errors, instead of just stating the instrument used for the analysis. (ii) Lines 16-26: Provide the percent recovery obtained in standard analysis and reference for methodology. (iii) Lines 27-29 & 1-6: Similar to previous ones, it is important to give the analytical procedure in brief and necessary to provide the analytical errors although literature has been cited for details. (iv) What are the concentration levels of chemical components in field blanks and whether the data reported here were corrected for them or not? Field blank may contain little amount of most of the components and significant amount of OC because zip-lock bags (plastic), in which the sample filters were packed (lines 2-3), cause high contamination of organic species.

Response: We provide here the relevant and necessary experimental details, including analytical errors. The same details have been included in the revised manuscript.

For chemical analysis, sample filters were handled under clean laminar-flow bench (Class-100). For water soluble inorganic constituents (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-}), one-fourth of the filter was extracted with 50 ml of Milli-Q water (specific resistivity of 18.2 MΩ-cm) for about 35-40 min. Water extracts were analyzed for inorganic constituents on Dionex–500 Ion Chromatograph equipped with a conductivity detector (ED-50). The water soluble cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) were separated on CS-12A 4 mm column connected in line with CSRS-ULTRA®-II 4 mm cation suppressor (in the recycle mode); 20 mM methane sulphonic acid was used as a mobile phase. Anions (Cl^-, NO_3^- and SO_4^{2-}) were separated on AS-14A 4 mm column in conjunction with ASRS®-ULTRA-II 4 mm suppressor (connected in recycle mode) using carbonate-bicarbonate mixture (100 mM $NaHCO_3$ + 800 mM Na_2CO_3) as an eluant. Based on the analysis of repeat samples and standards, the analytical precession was better than 5 % for all the cations and anions (Kumar and Sarin 2010a; Kumar et al., 2010).

For trace metals (Cd and Pb) and crustal elements (Al, Fe, Ca and Mg), several filter punches (2.0 cm diameter) were digested with 0.5ml distilled HF, 5 ml distilled 8N HNO_3 and 3 ml Milli-Q water in Teflon digestion vessels (Pressure: ~ 100 bar; Temp: 210^0C) placed inside a microwave digestion system (Milestone). After digestion, sample solutions were made to suitable volume (25 ml) with Milli-Q water and stored in pre-cleaned polypropylene bottles. Subsequently, these were analyzed for Al, Fe, Ca and Mg by Inductively Coupled Plasma-Atomic Emission Spectrometer (Jobin-Yvon, ULTIMA), and for Cd and Pb on Heated Graphite Furnace- Atomic Absorption Spectrophotometer (Perkin-Elmer, Analyst 100). Along with the samples, several field blanks with filters (n = 10) were analyzed and concentrations of individual constituents were suitably corrected for blanks. Based on the repeat analysis of samples (corrected for field blanks) and reference standards (Merck® 23 trace element standard), the overall uncertainty in the measurements of (Cd, Pb) and (Al, Fe, Ca and Mg) were ±10 %. For detailed description of the analytical protocol for water soluble ionic constituents and trace metals, reference is made to our earlier publications (Kumar and Sarin, 2009; Kumar and Sarin, 2010b; Kumar et al., 2010).

For water-soluble iron (Fe_{ws}), separate filter punches (2.0 cm diameter) were extracted with 10 ml of Milli-Q water. The water-extract was filtered through 0.45μm PTFE filter-cartridge, acidified to pH ~ 2 with quartz-distilled HNO_3, and subsequently analyzed by GF-AAS for soluble iron. Relevant details on the extraction procedure are given in earlier publication (Kumar and Sarin, 2010b; Kumar et al., 2010). Owing to uncertainties in the measurement of Fe_{ws} (±10 %) and Fe_{Tot} (±5 %)), a relative uncertainty of ~11% is associated with the fractional solubility of aerosol iron (defined as $Fe_{ws}\% = Fe_{ws}/Fe_{Tot} *100$; where Fe_{ws} = water soluble-Fe; Fe_{Tot} = total aerosol-Fe). The method detection limits (MDL) are defined as three times the standard deviation of field (filter) blanks, normalized to the volume of air filtered (~1400 m^3). The MDL for Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}, Fe, Al, Ca, Mg, Cd, Pb, and Fe_{ws} are 11.3, 6.8, 6.5, 0.8, 3.0, 15.2, 8.0, 30, 11, 80, 15, 11, 0.04, 0.15 and 0.13, respectively. The non-sea-salt (nss) components of K^+, Mg^{2+}, Ca^{2+} and SO_4^{2-} are calculated using the following equations : $nss-K^+ = K^+ - 0.037 * Na^+$; $nss-Ca^{2+} = Ca^{2+} - 0.038 * Ca^{2+}$; $nss-Mg^{2+} = Mg^{2+} - 0.12 * Na^+$; $nss-SO_4^{2-} = SO_4^{2-} - 0.25 * Na^+$; where 0.037, 0.038, 0.12, 0.25 are weight ratios of K^+, Ca^{2+}, Mg^{2+} and SO_4^{2-} to Na^+ in seawater, and as a reference element for sea-salt contribution (Keene et al., 1986).

Elemental carbon (EC) and organic carbon (OC) were assayed on EC-OC Thermo-optical Analyzer (Sunset Laboratory, USA) using NIOSH protocol (National Institute for Occupational Safety and Health, Birch and Cary, 1996). As used in our Laboratory for the past couple of years, relevant details of analytical procedure are provided in earlier publications (Rengarajan et al., 2007; Sudheer and Sarin, 2008a; Ram et al., 2008). The MDL for EC and OC are 50 and 100 ng m^{-3}, respectively. ***NOTE: Soon after their collection, filters were wrapped in Al-foils and then packed in zip-lock bags in order to avoid any contamination of organic species.***

Comment: Page 20673-20674: (i) As air mass trajectories and mass concentration belongs to different categories, it is better to divide the sub-Sect. 3.1 into two sub-sections.

Response: The temporal variability in the mass concentrations of $PM_{2.5}$ and PM_{10} associated with different wind regimes over North Bay of Bengal (N-BoB) and South Bay of Bengal (S-BoB) are separately stated in two sub-sections in the earlier version of the manuscript.

Comment: Page 20673-20674: (ii) Lines 19-26: Define acronyms; SEA, MAP, N-BoB and S-BoB, at appropriate places.

Response: Page 20673-20674: All acronyms, SEA (south-east Asian outflow), MAP (Marine Air Parcel), N-BoB (North Bay of Bengal) and S-BoB (South Bay of Bengal) are defined at appropriate places.

Comment: Page 20673-20674: (iii) as the range and temporal and spatial variability in mass concentration of PM_{10} and $PM_{2.5}$ has already been reported in Kumar et al. (2010), it is necessary to note that in the text or to cite the reference in Table 1. Similarly, the same reference should be cited in the cases of $nss-SO_4^{2-}$, $NO_3^-/nss-SO_4^{2-}$ ratios and OC/EC ratios as well as metal species in other sections of the text (or Table/Fig), as they have also been used in Kumar et al. (2010).

Response: The reference of (Kumar et al., 2010) is cited at appropriate places in the text as per the suggestion.

Comment: Page 20673-20674: (iv) Lines 10-15: The higher (2-3 times) PM_{10} concentration observed in this study than the TSP reported previously needs to be explained further, probably relating to the seasonal differences in meteorology.

Response: Yes! The temporal shift in the wind regimes is responsible for higher PM_{10} concentration during Jan'09 compared to intermonsoon period (March-April'06). In addition, seasonal change in the source strength of biomass burning emissions in the Indo-Gangetic Plain is also a likely cause for lower TSP concentration in March-April. Text is suitably edited for clarity.

Comment: Page 20675, (i) Line 7: —ionic composition (WSIC; Does it 'composition (or) content'? (ii) Lines 9-14: —— northern Bay of Bengal. —— N-BoB and S-BoB. Use either full-name or acronym through out the text consistently. (iii) Lines 21-22: Replace 'dot' mark with 'cross' symbol to indicate the multiplication in all equations, and also in other sections of the text.

Response: **(i)** In order to avoid confusion, we now refer to water-soluble inorganic constituents (WSIC); (ii) we have now consistently used acronym (N-BoB, S-BoB) throughout the text. (iii) 'Dot' mark is replaced by cross symbol in all equations.

Comment: Page 20678, lines 3-5, 9-11 & 21-23: Does the meteorology is a driving force for the differences in concentrations observed in the present study and previous report(s)?

Response: Yes! The prevailing meteorology (wind regimes) is a driving force for the differences in concentrations of EC, POM observed in the present study (Jan'09) and previous report (Mar-

April'06). As explained above; source strength of the biomass burning emissions also decreases in March-April.

Comment: Page 20680, lines 9-21 & page 20681, line 1: Quantification of source (biomass & fossil-fuel combustion) contribution based only on TC/EC ratios is not appropriate, because EC concentrations in particles emitted from biomass burning are highly depend on type of biomass (or biofuel) and burn rate (Habib et al., Environ. Sci. Technol. 42, 2008; Stone et al., J. Geophys. Res. 115, 2010). Further, based on recent evidences (e.g. Gustafsson et al., Science 323, 2009), the contribution of 80% of aerosol carbon from fossil fuel combustion in South Asia is unbelievable, although such contribution has been reported earlier over northern Indian Ocean. Hence, it is more reasonable to state qualitatively (mixed sources) rather quantitatively (percent contribution).

Response: Text is suitably corrected as per the suggestion. 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 PM_{10} 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: Page 20682, lines 7-9: Discuss the comparability (and differences) of metal ratios observed in this study with those of literature values in the text instead of just providing the data in Table 3. In fact, Ca/Al and Mg/Al as well as mean Fe/Al ratios reported in all sites, Arabian

Sea and Bay of Bengal, respectively (Table 3), are quite different to those observed in the present study.

Response: The observed differences in the elemental ratios of Ca/Al, Mg/Al and Fe/Al from the present study (Jan'09) to that in Mar-April'06 (Bay of Bengal), April-May'06 (Arabian Sea) can be explained due to differences in the type of mineral dust during the two sampling period (Dec-Feb; Mar-May). During winter months, Bay of Bengal receives mineral dust (depleted in Ca) from the Indo-Gangetic Plain (as inferred from AMBTs) and hence, can explain the lower ratios of Ca/Al and Mg/Al. However, during the intermonsoon (March-April), with seasonal shift in the winds, AMBTs suggest that mineral dust is transported from Thar Desert (Rajasthan, India). These mineral aerosols are enriched in Ca as reported by earlier studies (Kumar et al., 2008a; Kumar and Sarin, 2010; Rajamani et al., 2008) and hence, can explain the observed high elemental ratio of Ca/Al and Mg/Al. It is also important that significant contribution of Ca can be derived from biomass burning emissions as evident by comparing $nss-Ca^{2+}/nss-K^+$ ratio for the two seasons (Jan'09: 0.3 ± 0.1; Mar-April'06: 3.0 ± 0.9).

Comment: Page 20683, lines 12-14: —— are in well agreement ——. Provide the percent differences between measured and weighed mass in the text.

Response: For PM_{10}, difference between measured and weighed mass over N-BoB and S-BoB is 11 and 15 % respectively; whereas, the difference in $PM_{2.5}$ is 14 and 18 % over N-BoB and S-BoB respectively. Text is suitably edited as per the suggestions.

Comment: Page 20685-20686, sub-Sect. 3.3.3: As aerosol iron solubility over BoB has been reported in Kumar et al. (2010), it is not appropriate to discuss it again here under separate sub-section. So delete sub-Sect. 3.3.3 and include its essence in sub-Sect. 3.3.4.

Response: Text is suitably corrected as per the suggestion.

Comment: Page 20686, lines 15-18: Where the scatter plot and linear correlations are shown? The origins and transport of Cd and Pb needs to be better explained based on spatial variability linking with air mass trajectories in order to show the impact of anthropogenic sources on chemical components of aerosols over BoB.

Response: Text is suitably edited as per the suggestion.

Comment: Technical Errors/Typos: Citation of literature in the text is not appropriate at certain places; for example: page 20672, lines 11-12: "—— described in (Kumar et al., 2010; Kumar and

Sarin, 2010)". It should be "—- described in Kumar et al. (2010) and Kumar and Sarin (2010)". Look for similar kind of error throughout the text.

Response: References are suitably corrected as per the suggestion.

Comment: Page 20683, (i) lines 22-23: As PM_{10} contains $PM_{2.5}$ particles too, it is not correct to use the phrase 'size-segregated aerosols' in the text. Rather it may be termed as 'two size fractions of aerosols'.

Response: Yes! Text is suitably corrected as per the suggestion.

Comment: (ii) Lines 24-26: —— over the north Indian Ocean ——. Does it north Indian Ocean (or) Bay of Bengal? If it is north Indian Ocean, how does this study emphasize —-! I feel that this concluding statement is not necessary here.

Response: Text is suitably corrected as per the suggestion.