

Interactive comment on “Impact of continental outflow on chemistry of atmospheric aerosols over tropical Bay of Bengal” by B. Srinivas et al.

Anonymous Referee #4

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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 northeastern 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.

General points:

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.
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.
3. The authors discussed the relationships between ammonium and nss-sulfate by using NH₄⁺/nss-SO₄²⁻ equivalent ratio as seen in the text, but, as shown in Figure 7, they putted NH₄⁺ as y-axis and nss-SO₄²⁻ 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-sulfate and ammonium are predominantly associated with PM_{2.5}, representing
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

C11866

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 nssSO_4^{2-} to NO_3^- 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 the oceans, particularly the results of Arimoto et al.

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.
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.
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 $\text{PM}_{2.5}$ over the entire BoB. They concluded that “Such observation point towards

C11867

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.” (see L18-20/P20680). While applying K^+/EC ratio, they estimated that $>50\%$ of EC in both PM_{10} and $\text{PM}_{2.5}$ 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.” (see L1-3/P20681). I do think these are considerably inconsistent. In the entire paragraph, what I have seen are contrary explanations.

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.
9. Excessive SO_2 (H_2SO_4) is believed to preferentially react with carbonate mineral

C11868

particles, whereas HNO_3 would react with sea salt particles, which has been extensively observed downwind the Asian continent, the western Pacific Ocean.

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).
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.

Specific points and editing:

L2/P20670: Change “;” to “)”.

L3-4/P20677: Suggest changing to “suggest that NH_3 was inadequate and has been completely used in reaction with H_2SO_4 (and its precursor SO_2) to form fine ammonium sulfate, resulting in near —”

L5/P20678: Add a before order.

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

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

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

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.

L12/P20682: Change to suggesting.

C11869

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.

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 northeastern monsoon.

L12/P20683: This sentence is unclear.

L10/P20685: Change is compared to comparable.

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

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

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

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

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).

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

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 20667, 2011.

C11870