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Chemical composition of aerosols over Bay of Bengal during pre-monsoon: Dominance of anthropogenic sources

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ABSTRACT

Total suspended particulates were collected from the marine boundary layer of Bay of Bengal (BoB) as part of the Integrated Campaign for Aerosols gases & Radiation Budget (ICARB) conducted under the Geosphere Biosphere Programme of Indian Space Research Organisation during pre-monsoon period. These samples were analyzed to quantify various chemical species and to bring out a comprehensive and quantitative picture of the chemical composition of aerosols in the marine environment of Bay of Bengal. Almost all the species showed highest mass concentration over north/head BoB. On the other hand, their mass fractions were high over mid/south BoB which has implications on the radiative forcing in this region. The source characteristics of various species were identified using specific chemical components as tracers. Presence of significant amount of non-sea-salt aerosols (~7–8 times of sea-salt) and several trace species like Ni, Pb, Zn, etc were observed in this marine environment indicating significant continental/anthropogenic influence. An approximate estimate of the contributions of anthropogenic and natural aerosols to the total aerosol mass loading showed prominence of anthropogenic component over mid and south BoB also. Based on this study first-cut aerosol chemical models were evolved for BoB region.

1. Introduction

Aerosols in the marine environment consist of in situ generated sea-salt particles, produced by the action of wind on the sea surface (Blanchard and Woodcock, 1980; Exton et al., 1985), and non sea-salt particles, formed either as a result of oceanic biogenic activities (Charlson et al., 1987; Savoie et al., 1989) or through transport of continental aerosols from nearby/far-off land masses (Nair et al., 2004; Ramanathan et al., 2001). Continental aerosols can be of either natural or anthropogenic origin. Ships sailing over the oceans form another source of non sea-salt aerosols polluting the pristine marine environment (Fridell et al., 2008). In the present scenario, increase in anthropogenic contribution of aerosols over the oceans has become a serious issue. The impact of continental advection is assessed by systematic observations through cruise-based campaigns or through fixed point observations from island locations. Several cruise experiments have been conducted during the last two decades in different oceanic environments as a part of various investigative programmes (Andreae et al., 2000; Arimoto et al., 1996; Bates, 2004; Huebert et al., 1998; Raes et al., 2000; Ramanathan et al., 2001; Verver et al., 2000). The international field campaign INDOEX (Indian Ocean Experiment) conducted in 1998–1999 was a unique attempt bringing out observational evidence of long-range transport of continental aerosols over to Arabian Sea (AS) and Indian Ocean (IO) (Lelieveld, 2001; Nair et al., 2004; Ramanathan et al., 2001; Satheesh et al., 1999). Cruises conducted as a part of the Arabian Sea Monsoon Experiment (ARMEX) (Moorthy et al., 2005; Rao et al., 2005), and a few other cruises (Satheesh et al., 2006; Vinoj et al., 2004) also, revealed significant intrusion of continental aerosols over to the AS and IO. However, most of the above studies are focused on the physical characteristics of aerosols and mostly confined to AS/IO and the marine environment of Bay of Bengal (BoB) remained more or less unexplored in terms of the chemical composition of aerosols. Lawrence and Lelieveld (2010) have published an extensive review on the outflow of pollutants from Asian landmass to the surrounding oceans based on all the available measurements.

With the main objective of mapping the physical and chemical characteristics of aerosols over Indian landmass and adjoining oceanic environments a major field campaign – Integrated Campaign for Aerosols gases & Radiation Budget (ICARB) – has been conducted under the Geosphere Biosphere Programme of Indian Space Research Organisation. During ICARB, ship-borne measurements on aerosol properties were carried out over BoB and AS

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during the summer/pre-monsoon period of March–May, 2006, on board the Oceanic Research Vessel (ORV) *Sagar Kanya*. Several results on the physical and chemical characteristics of aerosols and their radiative impacts have been published (Kumar et al., 2008; Moorthy et al., 2008, 2009; Nair et al., 2008, 2010; Sudheer and Sarin, 2008). The present study focuses on the spatial variation of various chemical species in aerosols over BoB with a view to identify the major sources of aerosols over this wide oceanic environment, the pathways and mechanisms leading to the observed spatial distribution and to delineate the natural and anthropogenic contributions. It is also attempted to evolve a chemical model for the BoB region.

2. Experimental techniques and data

Aerosol samples were collected using a single stage High Volume Sampler (HVS, model GH2000 of Graseby Anderson, USA) which samples the total suspended particulates (TSP). Quartz fibre filters (10.1 cm dia) are used as the collection medium. The sampler was operated at the front deck and front end of the ship in order to avoid contamination from the chimney of the ship. Moreover, extreme care was taken to avoid contamination, by constantly monitoring the wind direction from the Automatic Weather Station (AWS) on board and under unfavorable wind direction, the sampler was switched off. The sampling point was ~10 m from sea surface and the sampler was operated only when the ship was moving. The collection substrates were preconditioned (heated to 100 °C for 2 h and desiccated for 24 h at RH of 45%), tare-weighed using a microbalance (AT 20 of Metler, Switzerland) having resolution of 2 μg and taken in glass petri dishes sealed with teflon tape for the cruise. About 38 samples were collected from the BoB region along the crack. The sampling duration was ~3 h which corresponds to a distance of ~50–60 km. After sampling the collection substrates were again sealed in petri dishes and preserved in refrigerator. The samples were brought back to laboratory, desiccated for 24 h and weighed again. The measurements were carried out in the laboratory under low humidity condition (~50%) to avoid artifacts of hygroscopic growth of particles. The aerosol mass loading (M_L) in ($\mu g\ m^{-3}$) corresponding to each sample was measured gravimetrically. The sample-laden substrates were later subjected to chemical analysis for identifying and quantifying various chemical species as reported by Nair et al., (2006); George et al., (2008).

One quarter of the sample-laden substrate was cut out and ultrasonically extracted with de-ionized water (Milli-Q water with 18.2 M Ω resistivity) for analyzing the water-soluble fractions of F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+}. NH_4^+ being a highly volatile species, the sample was extracted using de-ionized water by rigorous shaking only. The samples for the acid-soluble components were prepared by extracting one half of the collection substrate with 3 ml of suprapure HNO_3 (65% of Merck) and 50 ml de-ionized water. Ion chromatograph model DX-120 of Dionex, USA was used for the quantification of the water soluble species. Solution with 3.5 mM Na_2CO_3 and 1 mM $NaHCO_3$ was used as eluent for anions and a 20 mM solution of methane sulfonic acid is used as the cation eluent. Atomic absorption spectroscopy (AAS) (model Varian SpectrAA 250 plus) was employed for the analysis of Na and K and other metallic species, viz., Al, Ca, Cu, Fe, Mg, Mn, Pb, Ti, Zn, etc. were analyzed using ICP-AES (model Perkin Elmer Optima 4300V). Calibration of the instrument was done prior to and in between analysis, using calibration standards from Merck for ion chromatography and those from Perkin Elmer for ICP-AES and AAS with appropriate dilution. In addition, blank filters (about 1 blank for each set of 5 samples) extracted in the same manner as those of the samples were analyzed to obtain the blank values. The black carbon measurements using aethalometer reported by Nair et al., (2008) also have been used in the present study. The corrections for the uncertainties arising due to the multiple scattering effect (C factor) and shadowing effect (R factor) have been done while analyzing the data (Weingartner et al., 2003). The meteorological parameters were also continuously monitored and recorded onboard the ship by the AWS. Fig. 1 shows the day-to-day variation of daily mean wind speed (corrected by using the data on ship speed and ship-head angle available through global positioning system), air temperature and RH recorded on board, during the cruise period along with the standard deviation.

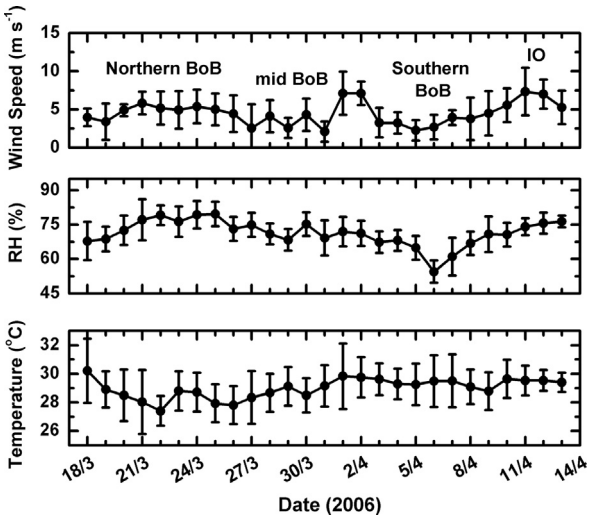

Fig. 1. Day-to-day variation of wind speed, RH and air temperature over BoB during the cruise period.

The regions in which the ship was sailing during different periods are also indicated in Fig. 1. The mean temperature varied in the range 27–30 °C while the variation of RH was in the range 55–80%. It may also be noted that RH is relatively low over the southern part compared to that in the north. The daily mean wind speed, which was ~5 m s^{-1} when the ship was traversing the northern BoB, showed a decrease in the mid BoB region and increase in south BoB. Very high wind speeds were encountered on April 1 and 2. Columnar content of water vapour was also measured using Microtops II Sunphotometer (Solar light Co USA). The measurement of ground reaching solar radiation at 940 nm and 1020 nm were used for the estimation of column water content. The technical details and retrieval methodology of the instrument are described elsewhere (Morys et al., 1996). The error in the estimation of column water using this instrument arises due to inaccuracy in sun pointing, not cleaning the windows, contamination from thin, invisible clouds, lack of calibration, etc among which errors due to lack of calibration is most important. Microtops were operated on board ship at ~30 min interval, during day time, under extremely clear sky conditions, by trained persons. Each measurement is the average of 3–4 consecutive measurements to avoid error in sun pointing. A detailed study on the performance of Microtops by Ichoku et al., (2002) showed that the error in water column reduces to ~0.1 cm in a newly calibrated instrument whereas it is 0.8 cm in an instrument without calibration. Even though absolute calibration of instrument was not done, the measurements were compared with simultaneous measurement using a newly calibrated Microtops (available with another team onboard the ship) which matched fairly well (deviation < 2%).