MAUSAM, **56**, 1 (January 2005), 293-300

551.510.42 : 551.46.072 (267.37)

Physical and chemical characteristics of aerosols over Arabian Sea during ARMEX 2002 - 03

P. S. P. RAO, P. S. PRAVEEN, D. M. CHATE, K. ALI, P.D. SAFAI

and

G. A. MOMIN

Indian Institute of Tropical Meteorology, Pune – 411 008, India

e mail : psprao@tropmet.res.in

सार – इस शोध–पत्र में महासागर अनुसंधान पोत सागरकन्या में मानसून वर्षा ऋतु (जून – अगस्त 2002) और मानसून से पूर्व की ऋतु (फरवरी – मार्च 2003) में अरब सागर मानसून प्रयोग (आरमेक्स) अभियान के दौरान अरब सागर से कुल संस्पेंडेड पर्टिकुलेट (टी. एस. पी.) और आकार वियोजित वायुविलय एकत्रित किए गए। जल के अधिकांश विलयशील आयनिक घटकों के लिए वायुविलय के सभी नमूनों के विश्लेषण किए गए। मानसून से पूर्व की ऋतु की अपेक्षा मानसून ऋतु में टी. एस. पी. स्तर में बढ़ोतरी लगभग दोगुनी रिकार्ड की गई जो संभवतः मानसून की तेज पवनों के कारण समुद्र सतह पर वर्षा की तेज बौछारों के कारण हो सकती है। वायुविलयों के रासायनिक सम्मिश्रण से यह ज्ञात हुआ है कि मानसून ऋतु के दौरान वायुविलयों के कुल आयनिक सम्मिश्रण में समुद्री लवण (NaCl) प्रमुख रूप से सहायक हैं और मानसून से पूर्व की ऋतु के दौरान मानवोद्भव वैज्ञानिक (एंथ्रोपोजेनिक) आयनों जैसे SO_4 और NO_3 प्रमुख रूप से सहायक हैं। वायुविलयों के आकार के वर्गीकरण से उसके स्थूल आकार में अधिकतम प्रबलता वाले बाइमोडल का पता चला है। कुल 70 प्रतिशत वायुविलय समुद्र से उत्पन्न होने वाले स्थूल वायुविलयों के कारण होते हैं। वायुविलय मानसून ऋतु के दौरान एल्कालाइन प्रकृति के और मानसून से पूर्व की ऋतु में अम्लीय प्रकार के पाए जाते हैं।

ABSTRACT. Total Suspended Particulates (TSP) and size segregated aerosols were collected over Arabian Sea during Arabian Sea Monsoon Experiment (ARMEX) campaign in the monsoon season (June- August, 2002) and in the pre-monsoon season (Feb-March, 2003) onboard Ocean Research Vessel, Sagar Kanya. All the aerosol samples were analysed for major water soluble ionic components. The higher (nearly double) TSP levels in monsoon season than those in pre-monsoon season were observed which may be due to high bubble bursting activity on sea surface due to high winds in monsoon. Chemical composition of aerosols revealed that sea salt (NaCl) is the major contributor to the total ionic composition of aerosols during the monsoon season and the anthropogenic ions *i.e*., SO_4 and NO_3 are the major contributors during the pre-monsoon seasons. The size distribution of aerosols showed bimodal with a dominant peak in coarse size. 70% of the total aerosols are contributed by coarse aerosols which are originated from sea. The aerosols were found to be in alkaline nature during the monsoon season and acidic during the pre-monsoon season.

Key words – ARMEX, Aerosols, Chemical composition, Ionic balance, Size distribution, Sea salt fractionation.

1. Introduction

The impact of atmospheric aerosols (natural/ anthropogenic) on weather and climate has been one of the important research areas in recent years. The study of physico-chemical characteristics of aerosols is very much essential to understand the various atmospheric processes/ phenomena related to radiation balance, acid deposition and air quality. The climate effects of the anthropogenic aerosols have received large attention due to the magnitude and large uncertainties of their climatic effects (IPCC, 2001). In order to reduce these uncertainties measurements of the aerosol, physical and chemical properties of the aerosols are needed to trace the nature of the location and strength of the sources as well as to understand their physical and chemical transformation processes occurring in the atmosphere. Also, the study of marine aerosols helps to investigate the effects of continental and anthropogenic aerosols on background marine aerosols. Aerosol particles and gases transport over the Indian Ocean and causes for the formation of haze called Asian Brown Cloud (Ramanathan *et al*., 2001) and now called Atmospheric Brown Cloud. Also there are large emissions of soil dust from the continental areas

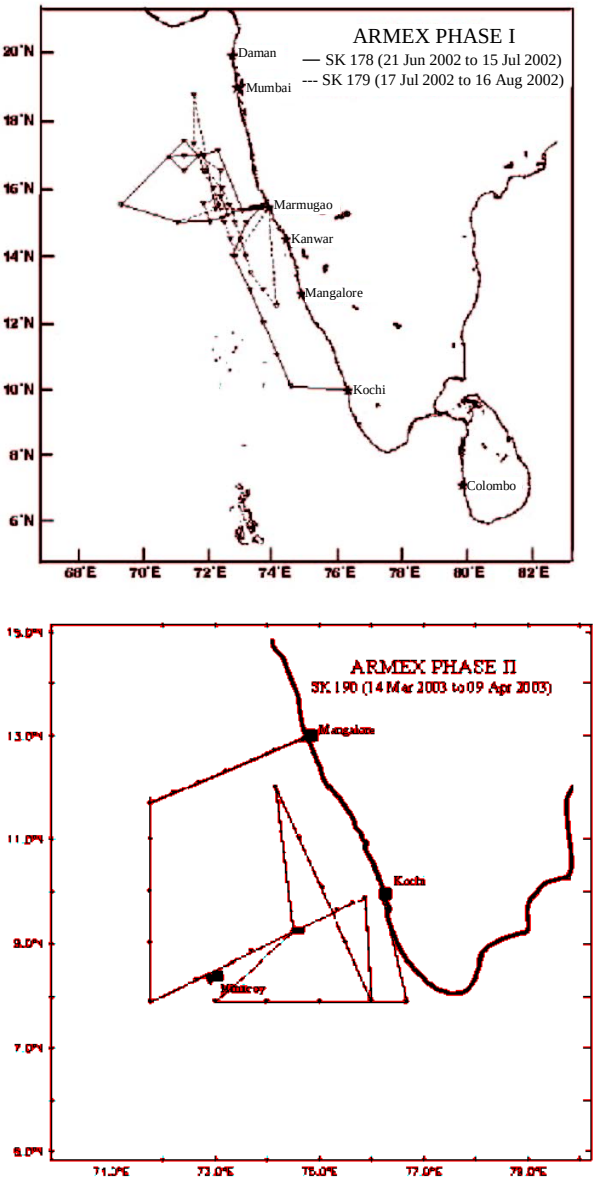

Fig. 1. Cruise tracks of Sagar Kanya during ARMEX Phase-I and II

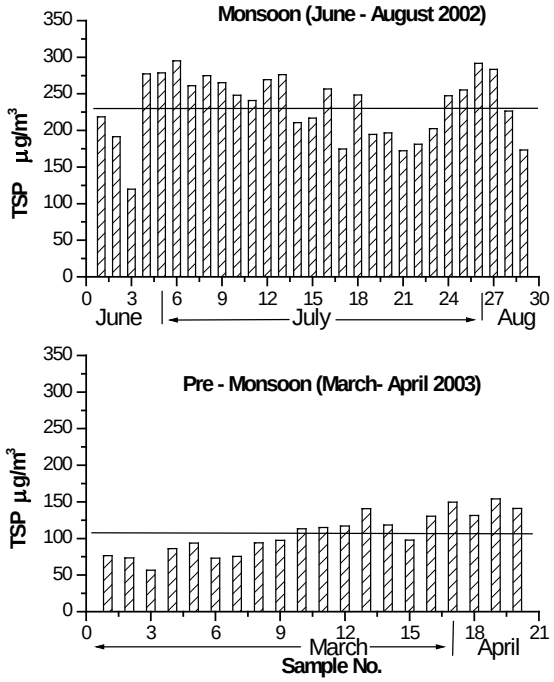

Fig. 2. Variation of TSP over Arabian Sea during ARMEX

north and northwest of the Arabian Sea (Tegen and Fung, 1994), which are subsequently advected out over the Arabian Sea. The effects of soil dust originating from the arid zones of continents, on the chemical composition of aerosols over the ocean atmosphere have been observed (Junge, 1979; Prospero *et al*., 1981; Hirose *et al*., 1983; Khemani *et al*., 1985 and Naik *et al*., 1991). Several studies have been made on the physical and chemical characteristics over the inland locations in India but such studies are very scanty over the oceans (Norman *et al*., 2002).

Aerosols were collected onboard ship "ORV Sagar Kanya" during both the cruises of ARMEX *i.e*., monsoon season (23 June – 16 August, 2002) and pre-monsoon season (14 March – 9 April, 2003). The physical and chemical characteristics of marine aerosols over the Arabian Sea and their seasonal variations are discussed in this paper.

2. Route of the cruise

During ARMEX the measurements were made on research vessel Sagar Kanya during different seasons *i.e*., monsoon and pre- monsoon. Monsoon observations were conducted from 21 June to 16 August, 2002. During Monsoon, the Sagar Kanya cruise was divided into two legs. Leg 1 (SK178) started from Kochi port (Lat. 9.57°N, Long. 76.16° E) on 21st June and ended at Goa port (Lat. 15.24° N, Long. 73.47° E) on 15th July. Leg 2 (SK179) started from Goa port on 17th July and ended at Goa port on 16th August, 2002. The pre-monsoon campaign had only one leg (SK190), it started from Mangalore port (Lat. 12.59° N, Long. 74.48° E) on 14th March and ended at Kochi port (Lat. 9.57° N, Long. 76.16° E) on 9th April, 2003. Cruise tracks for both the seasons are given in Fig. 1.

3. Sampling and analyses

Total Suspended Particulates (TSP) were collected on Whatman-41 filter papers using High Volume Air

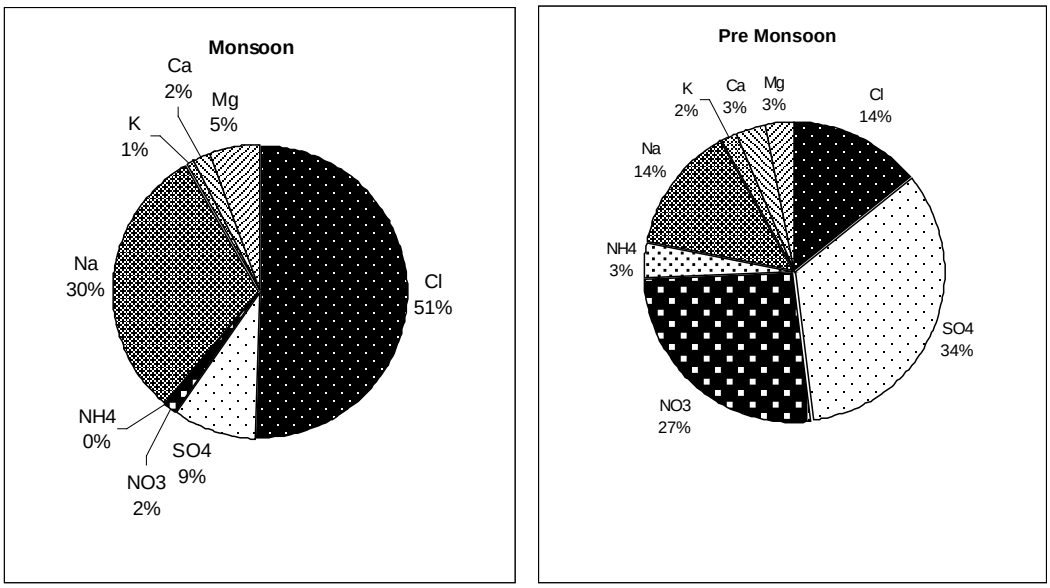

Fig. 3. Percentage contribution of various ions to the total ionic composition of TSP during ARMEX

Sampler at a flow rate of 1.1 m^3/min. and Mass size distributions were obtained by using 9 stage Low Volume Andersen Sampler at a flow rate of 0.03 m^3/min. The samplers were mounted on the front side upper deck of the ship at a height of about 12 m above the sea level to avoid the contamination from the sea spray and ship's exhaust. The sampling duration of each TSP sample was 12 hours. The sampling duration for one set of mass size distribution was about 120 hours. All the samples of TSP and the size segregated aerosols were extracted for chemical analyses using standard extraction method. All the extracted samples were analysed for major ionic components (Cl, SO_4, NO_3, NH_4, Na, K, Ca and Mg). The Cl, SO_4 and NO_3 were analysed by using Ion Chromatograph (DIONEX 100) and metallic components by using Atomic Absorption Spectrophotometer. NH_4 was measured by colorimetric method using UV-Visible Spectrophotometer.

4. Results and discussion

4.1. *Total suspended particulates (TSP)*

The concentrations of TSP during the monsoon and pre-monsoon seasons during ARMEX cruises are shown in Fig. 2. During the monsoon season TSP varied from 120 to 295 μg/m^3 with an average of 234 μg/m^3, whereas, during the pre-monsoon season, it varied from 56 to 154 μg/m^3 with an average of 107 μg/m^3. The higher (nearly double) TSP levels in monsoon season than those in pre-monsoon season may be due to high bubble bursting activity on sea surface due to high wind speeds in monsoon.

4.2. *Chemical composition of aerosols*

Chemical composition of aerosols indicated that sea salt (NaCl) is the major contributor to the total ionic composition of aerosols during the monsoon season and the anthropogenic ions *i.e.*, SO_4 and NO_3 are the major contributors during the pre-monsoon seasons. The total percentage contribution of all the major measured ions in the TSP during monsoon season is 44% whereas in the pre-monsoon season it is about 22%. This indicates that the major contributor to the aerosols is sea during monsoon season.

The percentage contributions of ionic species to the total ions of TSP collected during the monsoon and pre-monsoon seasons are shown in Fig. 3. The sea salt (NaCl) contribution was found to be very high in monsoon (81%) than that in pre-monsoon (28%). This higher contribution of sea salt in the monsoon season is due to higher bubble bursting activity by higher wind speeds as well as the prevailing wind direction being from the west blowing towards the sampling location.

The higher contributions of anthropogenic ions *i.e.*, SO_4 and NO_3 were found to be higher in pre-monsoon season (SO_4–34%, NO_3–27%) than those in monsoon season (SO_4–9%, NO_3–2%). The higher contributions of SO_4 and NO_3 in pre-monsoon season are due to the influence of continental aerosols brought over the Arabian Sea by the prevailing northerly winds. Whereas, during the monsoon season, the prevailing SW winds bring the

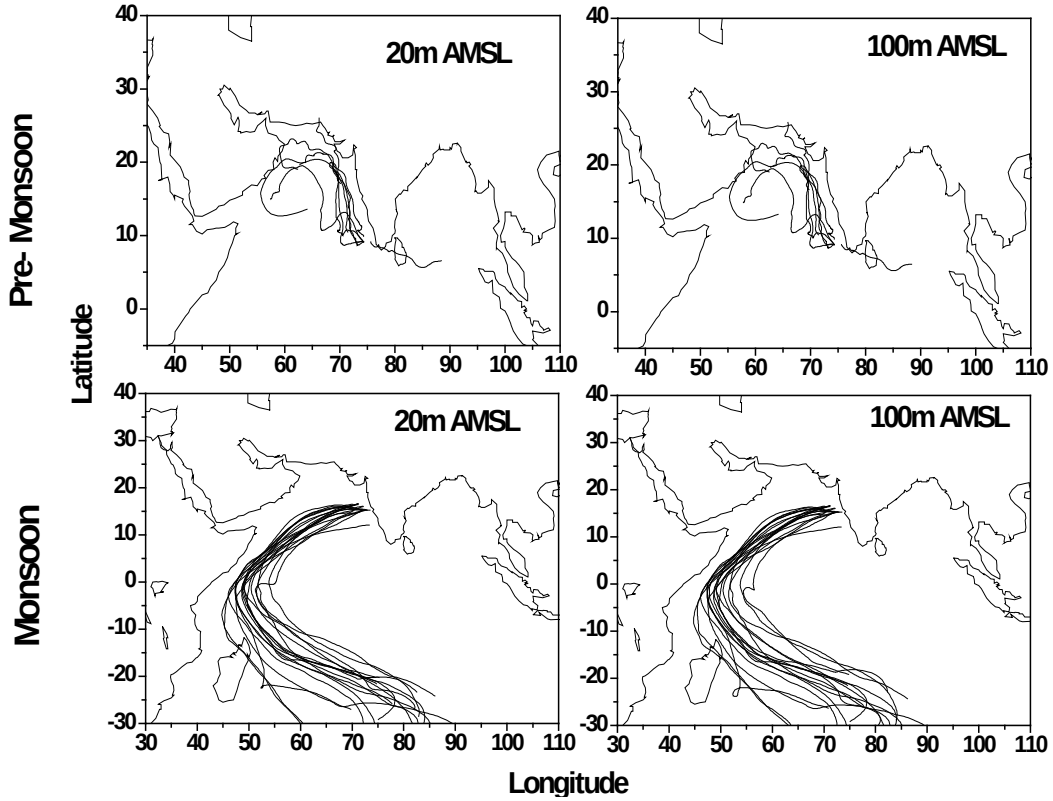

Fig. 4. Back trajectories at observational points at 20, 100 m amsl (above mean sea level)

prestine marine air masses to the sampling site over the Arabian Sea. Ca, K and NH_4 have followed the pattern similar to SO_4 and NO_3; Whereas, Mg followed the pattern of NaCl as one of its major sources is sea.

The air mass back trajectories at the observational location at 20 and 100 m above sea level during monsoon and pre-monsoon season are shown in Fig. 4. Trajectories showed that during the monsoon season the air masses, reached to the sampling site are originated from SW direction and bringing the pristine marine air; whereas during the pre-monsoon season the air masses originated from N direction bringing continental pollution to the sampling site. Also, it can be seen that the air masses traveled a very long distances during monsoon season due to high wind speeds compared to that during the pre-monsoon season.

In order to study the possible sources of water soluble components of TSP, a comparison of the ratios of these components was made with the corresponding ratios in sea water (Table 1). It can be seen from the table that the ionic ratios in TSP during the monsoon season are nearly equal to those in the sea water indicating that the sea is the major source of these elements. Whereas, during the pre-monsoon season the ionic ratios for SO_4, Ca, K and Mg in TSP were very much higher than the sea water ratios indicating that they have sources other than sea. This indicates that these components are transported from land regions. The lower Cl/Na ratio than the sea water ratio during the pre-monsoon season suggests the reaction of sea-salt with either H_2SO_4 or HNO_3 and forms HCl (Green, 1972).

TABLE 1

Equivalent ionic ratios of TSP during ARMEX observations

	Cl/Na	SO_4/Na	Ca/Na	K/Na	NO_3/SO_4
Monsoon	1.06	0.142	0.074	0.015	0.013
Pre-monsoon	0.69	1.485	0.383	0.090	0.715
Sea-water	1.16	0.125	0.048	0.028	-

The loss of chloride has been observed in the sub-μm particles of sea-salt from the analysis of size segregated aerosols obtained from the Andersen sampler. The Cl/Na ratio in coarse aerosols (> 2.1 μm dia) was 1.75 which is equal to that of sea water; in fine aerosols (< 2.1 μm dia) it was 0.97 which is nearly half of the sea water ratio; and in very fine particles (< 0.4 μm dia) in Back-up Filter was 0.43 which is very less than the sea water

TABLE 2

Mass ionic ratios of size segregated aerosols during the monsoon season

	Cl/Na	SO_4/Na	Ca/Na	NO_3/Na
Coarse	1.748	0.220	0.138	0.077
Fine	0.966	0.966	0.067	0.123
Back filter	0.426	1.275	0.082	0.044
Sea water	1.800	0.250	0.038	-

TABLE 3

Percentage contribution of non sea salt (nss) SO_4, Ca and K

	SO_4	Ca	K
Monsoon	16.5	35.2	Nil
Pre- monsoon	86.8	78.7	67.9

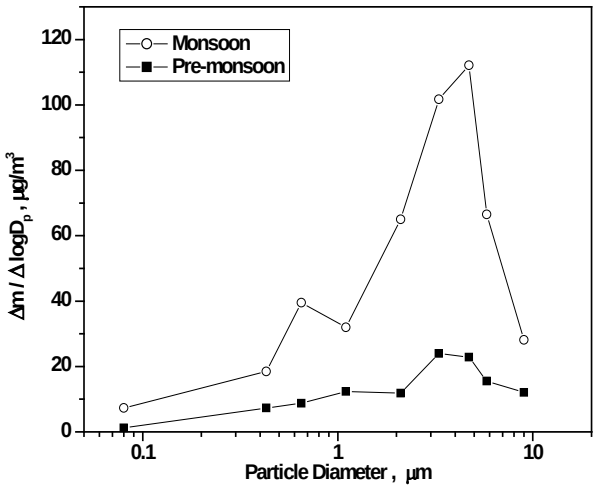

Fig. 5. Mass size distribution of aerosol over Arabian Sea during ARMEX : 2002-03

ratio (Table 2). Several investigators have reported the loss of Cl in the fine particles (Wilkniss and Bressan, 1972; Martens *et al*., 1973; Sadasivan, 1978 and Khemani *et al*., 1985).

The contributions of sea to various ions in TSP were estimated by assuming that the total Na in aerosols is from sea and using the standard sea water ratios. Then non-sea salt (nss) percentage contributions of Ca, K, Mg and SO_4 in aerosols were calculated by subtracting the sea salt contribution from the total concentration of a particular ion (Keene *et al*. 1986) as follows:

$$\text{nss\%} = \frac{[X]-[\text{Na}]*r}{[X]}*100$$

Where nss% is the non sea salt percentage,

$[X]$ indicates the concentration of the ion X

r indicates standard sea water ratios (X/Na)

The non sea salt (nss) percentage contributions of SO_4, Ca and K in TSP during monsoon and pre-monsoon seasons are given in Table 3. The SO_4 contribution from sea was found to be 83% during monsoon and only 13% during pre-monsoon season. The concentration of nss SO_4 was 1.6 μg/m^3 in monsoon and 8.13 μg/m^3 in pre-monsoon season. The SO_4 concentration in pre-monsoon season is found to be nearly equal to that (7 μg/m^3) reported over the north Indian Ocean during the INDOEX (Ramanathan *et al*., 2001). The percentage contribution of nss SO_4 during the pre-monsoon season in the present study (87%) is in good agreement with that reported (90%) during INDOEX by Ramanathan *et al*., 2000. Ca contribution from sea was 65% during monsoon and 21% during pre-monsoon season. In case of K, sea contributions were 99 and 22% in monsoon and pre-monsoon seasons respectively. This indicates that the land influence is very less on marine aerosols during monsoon than that in pre-monsoon season.

4.3. *Nature of aerosols through ionic balance in TSP*

In order to see the nature of aerosols, ionic balance was studied. The difference between the cations and anions suggests the nature of the aerosols *i.e*., alkaline or acidic. If the difference between the sum of anions and cations is positive (*i.e*., excess anions), the aerosols are said to be in acidic nature. Or, if the difference is negative (*i.e*., excess cations), the aerosols are said to be in basic nature. In the present study, the cations were found be excess (279 μeq/l) during the monsoon season indicating the alkaline nature of aerosols, whereas, during the pre-monsoon season, the anions were found to be excess (70 μeq/l) indicating the acidic nature of aerosols. From the reported data on chemical composition of aerosols during the INDOEX, it was found that the anions were found to be higher than the cations which suggests the acidic nature of aerosols (Granat *et al*., 2002). Also, Granat *et al*., reported that the rain water was acidic (pH ranging from 4.8 to 5.4) during the INDOEX *i.e*., January – March, 1999. This acidic pH was attributed to high concentration of nss SO_4. During the ARMEX also, authors found that the rain water was found to be acidic during pre-monsoon season and alkaline during the monsoon season.

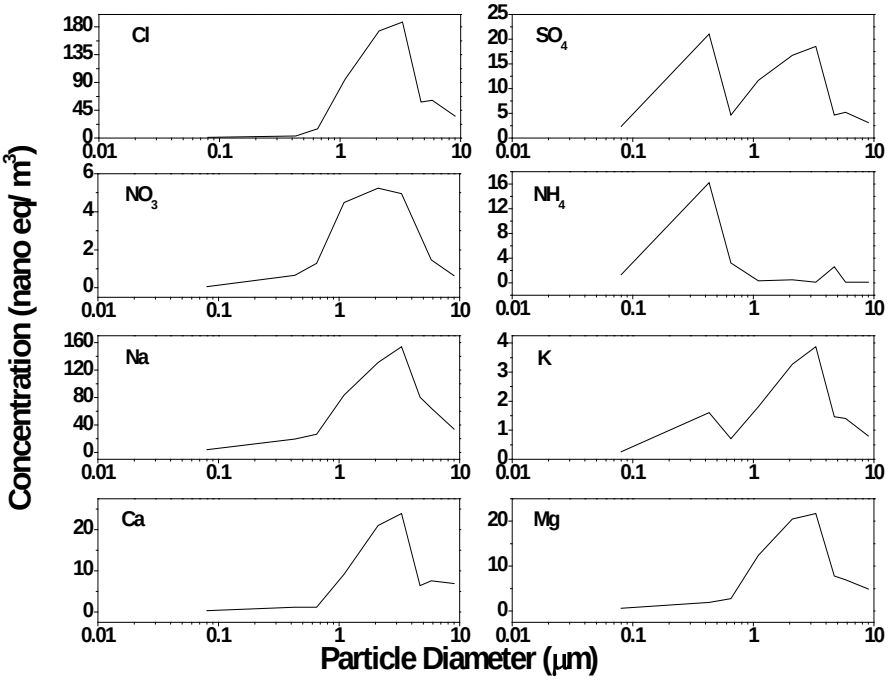

Fig. 6. Size distribution of major ionic components of aerosols during ARMEX in monsoon season

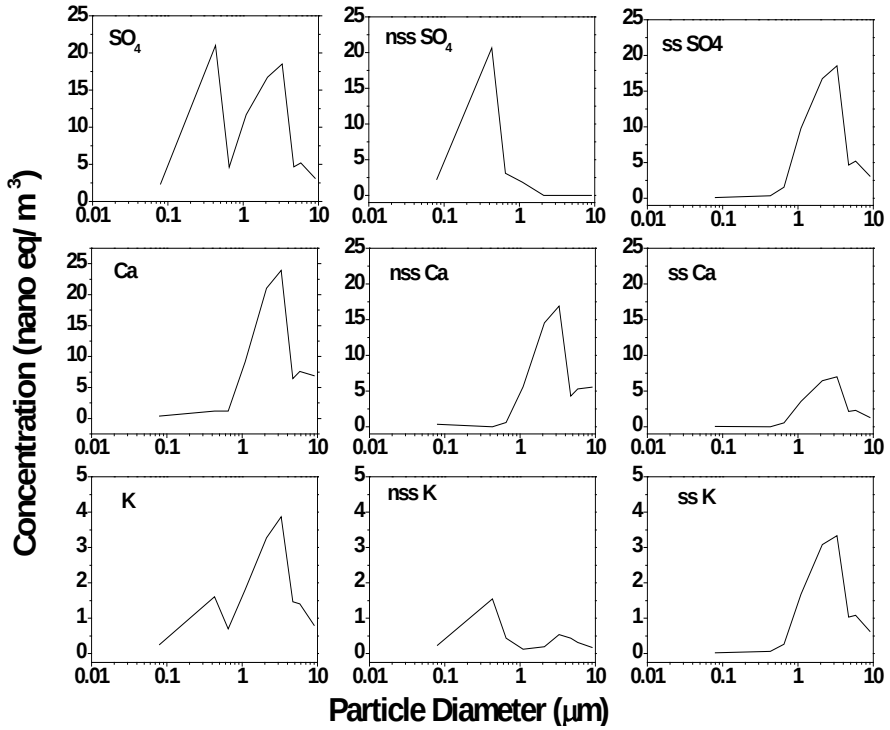

Fig. 7. Size distribution of non sea salt and sea salt components of SO_4, Ca and K aerosols during ARMEX in monsoon season

4.4. *Mass size distribution of aerosols and their chemical components*

The average mass size distributions of aerosols during monsoon and pre-monsoon seasons are shown in Fig. 5. Aerosols showed bimodal distribution with one peak in fine size range (0.65 1.1 μm dia.) and the other peak in coarse size range (3.3 – 4.7 μm dia.).The magnitude of aerosols in all the stages is very high (about 4 times) during monsoon season as compared to that during pre-monsoon season. This result is similar to that observed in case of TSP. During the pre-monsoon season, the fine size aerosols were amounted to 15 μg/ m^3 which was very close to the reported value of 17 μg/ m^3 over the north Indian Ocean during INDOEX (Ramanathan *et al*., 2001).

Except SO_4, NH_4 and K, all the ionic components of size segregated aerosols, collected during the monsoon season, showed unimodal distribution with a peak in coarse size range (Fig. 6). This indicates that their source is natural *i.e*., sea. Whereas, SO_4, NH_4 and K showed bimodal with one peak in coarse and another in fine size. The fine size peak for SO_4 may be due to the DMS emissions from sea. The fine size NH_4 and K may be originating from the inland regions. Size distributions of non sea salt and sea salt components of SO_4, Ca and K are shown in Fig. 7. Nss SO_4 showed peak in fine size indicating its source as other than sea and sea salt (ss) SO_4 showed peak in coarse size indicating the natural source *i.e*., sea. Both nss and ss Ca showed peak in coarse size indicating a natural sources *i.e*., soil and sea. Nss K showed bimodal indicating two sources *i.e*., biomass burning (cooking, forest fires, crop-waste burn etc., from Indian sub-continent) for fine size and soil for coarse size particles; whereas, ss K showed unimodal with peak in coarse mode indicating sea as a source.

5. Conclusions

The aerosol (TSP) load over the Arabian Sea is higher during monsoon season than that during pre-monsoon season. Sea salt is the major contributor to total aerosols during the monsoon season, whereas, the acidic components (SO_4 and NO_3) are the major contributors during the pre-monsoon season. During the monsoon season, the prevailing winds are southwesterly which brings clean marine air masses, whereas, during the pre-monsoon season, the prevailing winds are mostly north and northeasterly which brings polluted continental air masses from the Indian subcontinent. The size distribution of aerosols showed bimodal with a dominant peak in coarse size. 70% of the total aerosols are contributed by coarse aerosols which are originated from sea. The aerosols were found to be in alkaline nature during the monsoon season and acidic during the pre-monsoon season.

Acknowledgements

Authors are thankful to Director, IITM for his encouragement for undertaking this work. Authors are also thankful to Department of Science and Technology for providing financial support to carry out measurements on board ship Sagar Kanya during the ARMEX cruises.

References

Green, W. D., 1972, "Maritime and mixed maritime continental aerosols along the coast of Southern California", *J. Geophys. Res*., **77**, 5152-5160.

Granat, L., Norman, M., Leck, C., Kulshrestha, U. C. and Rodhe, H., 2002, "Wet scavenging of sulfur compounds and other constituents during the Indian Ocean Experiment (INDOEX)", *J. Geophys. Res*., **107**, INX2 24 1-10.

Hirose, K., Dokiya, Y. and Sugimura, Y., 1983, "Effect of the continental dust over the North Pacific Ocean: time variation of chemical components in maritime aerosol particles in spring season", *J. Met. Soc*., Japan, **61**, 670-677.

IPCC, (Intergovernmental Panel on Climate Change), 2001, "The scientific basis", J. T. Hougthon, Y. Ding, D. J. Griggs, M. Noguer, P. J. van der Linden and D. Ziaosu (eds.), Cambridge University Press, Cambridge, UK, 2001.

Junge, C. E., 1979, "The importance of mineral dust as an atmospheric constituent", In: Saharan Dust (editor: Morales C.), 49-60. John Wiley, New York.

Keene, W. C., Pszenny, A. P., Galloway, J. N. and Hawley, M. E., 1986, "Sea salt corrections and interpretations of constituent ratios in marine precipitation", *J. Geophys. Res*., **91**, 6647-6658.

Khemani, L. T., Momin, G. A., Naik, M. S., Rao, P. S. P., Kumar, R. and Murty, Ramana Bh. V., 1985, "Trace elements and sea salt aerosols over the sea areas around the Indian sub-continent", *Atmos. Environ*., **19**, 277-284.

Martens, C. S., Wesalowski, J. J., Harriss, R. C. and Kaifer, R., 1973, "Chlorine loss from Puerto Rican and San Francisco Bay area marine aerosols", *J. Geophys, Res*., **78**, 8778-8792.

Naik, M. S., Khemani, L. T., Momin, G. A., Rao, P. S. P and Safai, P. D., 1991, "Origin of calcium in marine aerosol over the Arabian Sea near the west coast of India", *J. of Aerosol Science*, **22**, 365-372.

Norman, M., Leck C. and Rodhe, H., 2002, "Interhemispheric differences in the chemical characteristics of the Indian Ocean aerosol during INDOEX", Atmospheric Chemistry and Physics Discussions, Vol. 2.

Prospero, J. M., Glaccum, R. A. and Nees, T. R., 1981, "Atmospheric transport of soil dust from Africa to South America", *Nature*, **289**, 570-572.

Ramanathan, V., Crutzen, P. J., Leileveld, J., Mitra, A. P., Althausen, D., Anderson, J., Andreae, M. O., Cantrell, W., Grass, G. R., Chung, C. E., Clarke, A. D., Coakley, J. A., Collins, W. D., Conant, W. C., Dulac, F., Heintzenberg, J., Heymsfield, A. J., Holben, B., Gowell, S., Hudson, J. A., Jayaraman, A., Kiehl, J. T., Krishnamurti, T. N., Lubin, D., McFarquhar, G., Novakov, T., Ogren, J. O., Podgorny, I. A., Prather, K., Priestley, K. Prospero, J. M., Quinn, P. K., Rajeev, K., Rasch, P., Rupert, S., Sadourny, R., Satheesh, S. K., Shaw, G. E., Sheridan, P. and Valero, F. P. J., 2001, "Indian Ocean Experiment: An integrated analysis of the climate forcing and effect of the great Indo-Asian haze", *J. Geophys. Res*., **106**, 28,371-28,398.

Sadasivan, S., 1978, "Trace elements in size separated aerosols over sea", *Atmos. Environ*., **12**, 1677-1683.

Tegen, I. and Fung, I., 1994, "Modelling of mineral dust in the atmosphere: Sources, transport and optical thickness", *J. Geophys. Res*., **99**, 22,897-22,914.

Wilkniss, P. E. and Bressan, D. J., 1972, " Fractionation of the elements F, Cl, Na and K at the sea-air interface", *J. Geophys.. Res*., **77**, 5307-5315.