

## INDIAN OCEAN EXPERIMENT

# Chemical characteristics and source apportionment of aerosols over Indian Ocean during INDOEX-1999

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During INDOEX IFP-99, the samples of aerosols were collected onboard ORV *Sagar Kanya* over Indian Ocean along the cruise track, for chemical characterization and identification of dominating sources of aerosols. The concentrations of nss-SO<sub>4</sub>, nss-Ca, nss-Mg, NO<sub>3</sub>, K, NH<sub>4</sub> and SO<sub>2</sub> were observed to be significantly higher before ITCZ in northern hemisphere than across ITCZ in southern hemisphere. In this study, variation of concentrations of nss-SO<sub>4</sub>, nss-Ca and nss-K with respect to change in latitude, wind direction, wind speed and relative humidity have been highlighted. North of ITCZ, nss-SO<sub>4</sub> varied from 2.20 to 18.31 µg/m<sup>3</sup> and south of ITCZ from 0.50 to 2.79 µg/m<sup>3</sup> while nss-Ca varied from 0.02 to 0.72 µg/m<sup>3</sup> north of ITCZ and from 0.01 to 0.14 µg/m<sup>3</sup> south of ITCZ. nss-K ranged 0.09–1.43 µg/m<sup>3</sup> and 0.07–0.60 µg/m<sup>3</sup> before ITCZ and across ITCZ respectively. nss-Ca and nss-SO<sub>4</sub> were contributed mainly by NNW and ENE winds while nss-K was observed to be contributed mainly by SSW and ENE winds. Wind speed greater than 4.5 m/s negatively influenced the concentration of nss-Ca concentrations. Correlation coefficients of nss-SO<sub>4</sub> with SO<sub>2</sub> ( $r = 0.7$ ) and RH ( $r = 0.5$ ) suggested a significant contribution of nss-SO<sub>4</sub> by aqueous phase oxidation of SO<sub>2</sub>. Using PCA, four major sources namely sea salt, biogenic combustion, secondary SO<sub>4</sub> and crustal contribution were identified over Indian Ocean during INDOEX period.

THE air pollution resulting from rapid industrialization and urbanization has prompted increased attention to its influence on the global atmospheric environment. Of particular interest has been the identification of the types and strengths of various pollutant sources in the region concerned, the transport patterns of aerosols and the chemical processes that take place in the transport<sup>1–5</sup>.

In an effort to characterize the transport processes and background levels of pollution, measurements of chemical composition of various air pollutants and meteorological parameters have been made during January–March, 1999

over Indian Ocean north and south of the Inter Tropical Convergence Zone (ITCZ) in INDOEX, IFP-99 programme. The main objective of INDOEX programme has been to assess the behaviour of aerosols in modifying the characteristics of marine boundary layer and the role of ITCZ in their transportation. The ITCZ is the region where two opposing flows, i.e. from northern and southern hemispheres, meet causing convergence due to convection. The polluted continental air overlaps the cleaner oceanic air due to the seasonal movement of the ITCZ that pollutes the oceanic air. The polluted continental air mainly contains sub-micron size aerosols, which are generated over the land by gas phase reactions of industrial and urban effluents (sulphates and soot) that contribute significantly to the air pollution over the ocean because of their long-range transport.

In this paper, we present the chemical composition of atmospheric aerosols and their dependence on various meteorological parameters over Indian Ocean before and across the ITCZ. In addition, an effort has been made to identify the possible sources over Indian Ocean by receptor modelling using Principal Component Analysis (PCA). The data are collected on board *Sagar Kanya* (SK #141) during the intensive field phase (IFP-99) experiment of INDOEX programme.

## Experimental details

### *Sampling device*

Ambient particulate matter was collected with a high volume sampler (Envirotech). This consists of a vacuum pump, a filter platform, a flow rate meter and an automatic timer. When air is sucked through the filter, particles coming in air stream settle on the filter. The collected material is referred to as total suspended particulate (TSP). The sampler was run at an average rate of 1 m<sup>3</sup>/min. In order to collect the air from desired directions, the sampler was connected with a wind vane. In general, air coming from the front side was collected to eliminate any possibility of contamination from stack of the ship.

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EPM 2000 glass fiber filters were used to collect the aerosol particles with the high volume sampler. These filters were chosen for their ability to withstand relatively high airflow rates, high efficiency without requiring impaction velocity and sensitivity to lower humidity.

*Sampling site*

Aerosol samples were collected at B-deck of ship *Sagar Kanya* which was about 16 m above the sea surface. The sampling was carried out from 8 to 24 h during the cruise period.

*Sample preparation*

Before and after sampling, the filters were desiccated to eliminate the effect of humidity (RH < 50%)<sup>6</sup>. The water-soluble fraction of aerosols was extracted using an ultrasonic extractor. For estimation, 4 squares of 1" x 1" were cut from the EPM 2000 filters. The extraction was made in 50 ml of deionized water for 5 min. This duration was

found sufficient to extract 99.9% of water-soluble fraction. The extract was then filtered through Whatman 41 filters and kept at low temperature in the prewashed polypropylene bottles for the analysis of anions Cl, NO<sub>3</sub> and SO<sub>4</sub> and cations Ca, Na, K, Mg and NH<sub>4</sub>.

*Analysis*

The cations (Na, K, Ca, and Mg) were determined by atomic absorption spectrophotometer (AAS) (Model Perkin Elmer 5000). Ammonium was estimated by indophenol blue method<sup>7</sup> by using a spectrophotometer (Perkin Elmer Lambda 3A). Anions (Cl, NO<sub>3</sub> and SO<sub>4</sub>) were determined by capillary electrophoresis (The Prince Technology, The Netherlands, Model 460) at ICT, Hyderabad.

**Results and discussion**

During INDOEX IFP-99 (SK cruise #141), ship covered the region from 15°N to 20°S latitude and 57°E to 77°E longitude. According to meteorological observations

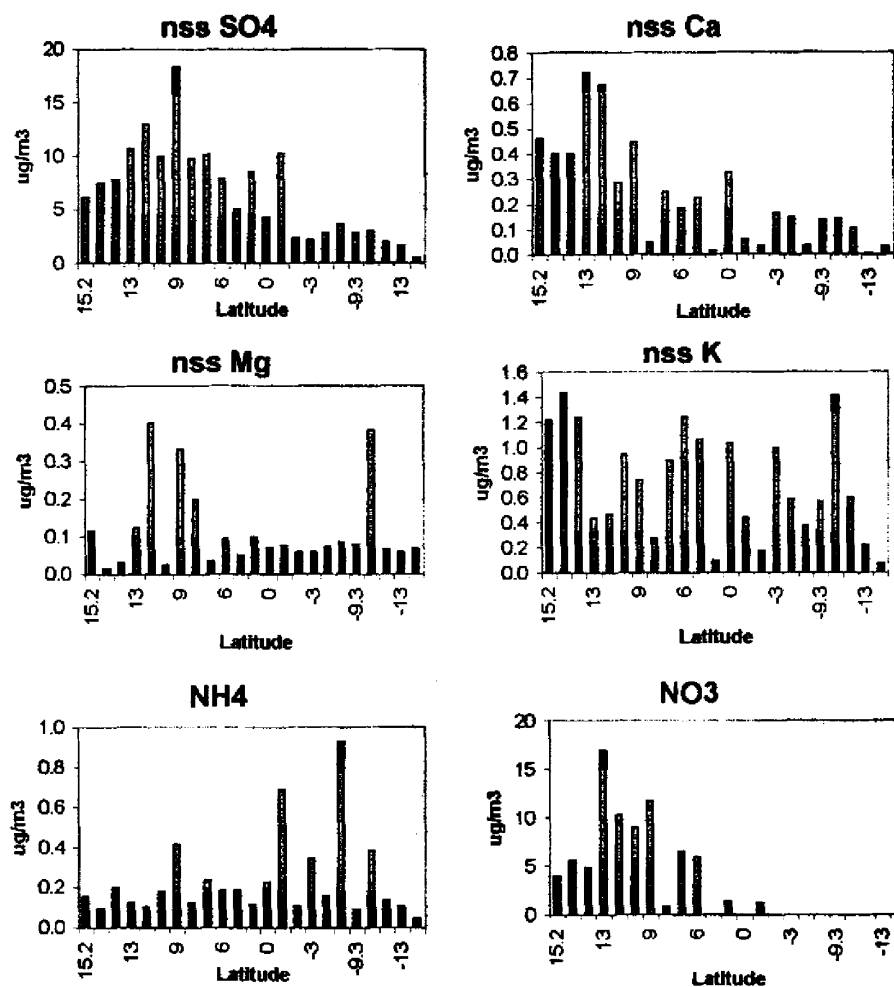


Figure 1. Latitudinal variation of major chemical components of aerosols.

**Table 1.** Concentration ranges ( $\mu\text{g}/\text{m}^3$ ) of different components north and south of ITCZ

Region		nss-SO <sub>4</sub>	nss-Ca	nss-K	nss-Mg	NH <sub>4</sub>	NO <sub>3</sub>	SO <sub>2</sub>	Wind speed	RH	Wind direction
North of ITCZ	Min.	2.20	0.02	0.09	0.01	0.09	nd	0.76	0.5	62	NNE,
	Max.	18.31	0.72	1.43	0.40	0.93	16.85	6.00	6.7	81	NNW
South of ITCZ	Min.	0.50	0.01	0.07	0.06	0.04	nd	0.48	4.0	60	SSE
	Max.	2.79	0.14	0.60	0.08	0.13	nd	2.23	5.9	78	

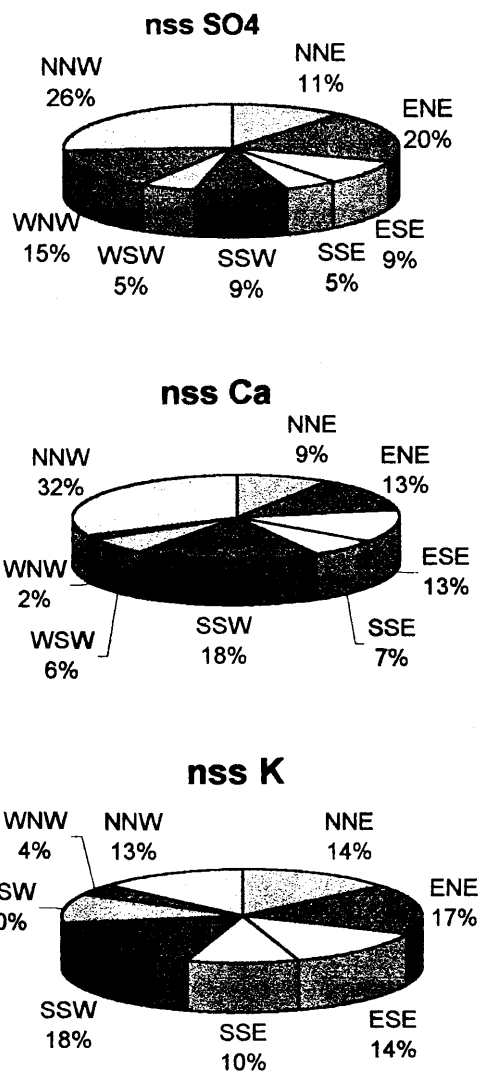
nd, not detectable.

onboard, during onward leg, the ITCZ was located 11–13°S while during return leg, it was located 7–9°S. A total of 23 samples were collected, out of which 19 samples were collected north of ITCZ. Due to unfavourable wind direction (wind coming from ship’s chimney side), only four samples were collected south of ITCZ. During the cruise, synoptic observations were taken for wind speed, wind direction and relative humidity. The variation of non sea-salt (nss) concentrations of nss-SO<sub>4</sub>, nss-Ca and nss-K with respect to meteorological parameters has been discussed below. The nss concentrations of components have been calculated assuming that all Na is contributed by sea-salts.

*Latitudinal variation of chemical constituents*

Figure 1 shows the latitudinal variation of nss-SO<sub>4</sub>, nss-Ca, nss-K, nss-Mg, NH<sub>4</sub> and NO<sub>3</sub> starting from Goa to Mauritius and back (SK cruise #141). It is clear from the figure that the concentrations of nss-SO<sub>4</sub>, nss-Ca, nss-Mg and nss-NO<sub>3</sub> are higher in northern hemisphere and decrease towards southern hemisphere. The concentrations of nss-K and nss-NH<sub>4</sub> do not show any latitudinal variation. Table 1 gives the range of concentrations of components in north and south of ITCZ. The concentrations of all the components have been observed to be significantly higher before ITCZ in the northern hemisphere than across ITCZ in the southern hemisphere. This indicates the abundance of pollutants in the air masses of northern hemisphere. In the north of ITCZ, nss-SO<sub>4</sub> varied from 2.20 to 18.31  $\mu\text{g}/\text{m}^3$  and 0.50 to 2.79  $\mu\text{g}/\text{m}^3$  in the south of ITCZ. The range for nss-Ca ranged between 0.02 to 0.72  $\mu\text{g}/\text{m}^3$  and 0.01 to 0.14  $\mu\text{g}/\text{m}^3$  in the north and south of ITCZ respectively. Very high nss-SO<sub>4</sub> concentrations are supposed to be the cause for acid rain occurrence over Indian Ocean during various campaigns of INDOEX<sup>9</sup>. Across ITCZ in southern hemisphere, the NO<sub>3</sub> concentrations were found almost below detection limit.

The higher concentrations of components like nss-SO<sub>4</sub>, nss-Ca, nss-Mg and nss-NO<sub>3</sub> may be due to contribution from continental activities, thereby generating pollutants that are transported by NE winds up to ITCZ. From north of ITCZ to south of ITCZ, the decrease in concentrations of K and NH<sub>4</sub> is not remarkable compared to Ca and SO<sub>4</sub>, suggesting their contribution due to biomass burning in Australia and Africa.



**Figure 2.** Variation of nss-SO<sub>4</sub>, nss-Ca and nss-K with wind direction.

*Variation of nss-SO<sub>4</sub>, nss-Ca and nss-K with wind direction*

The concentrations of nss-SO<sub>4</sub>, nss-Ca, nss-K have been shown as a function of wind direction in Figure 2. From the figure, it is clear that more than 50% nss-SO<sub>4</sub> is contributed by northerly winds (NW/NE). Similarly, nss-Ca is also contributed by frequent NW and NE winds. Small

fraction of nss-Ca is contributed by SSW winds. Interestingly, nss-K is contributed by frequent SW and SE winds and to some extent ENE winds. As shown in Figure 1, higher nss-SO<sub>4</sub> and nss-Ca in northern hemisphere are contributed by northerly winds while nss-K may be contributed both by northerly and southerly winds. The concentration of K has been observed low S of ITCZ but not negligible (Table 1).

*Variation of nss-SO<sub>4</sub>, nss-Ca and nss-K with wind speed*

The concentrations of nss-SO<sub>4</sub>, nss-Ca and nss-K with respect to wind speed have been plotted in Figure 3. It shows that the concentrations of nss-Ca are greatly affected by higher wind speed. The effect of wind speed on nss-SO<sub>4</sub> concentrations is not so much critical. This may be due to the reason that SO<sub>4</sub> aerosols are present in the sub-micron size range which have negligible effect of wind speed. nss-K has moderate influence of wind speed while nss-Ca has significant influence of wind speed. High wind speed may have higher influence on coarser particles as a result they become settled easily. K in relatively fine mode has been affected less by wind speed. The wind speeds above 4.5 m/s influence Ca, probably because nss-Ca is mainly of crustal origin having coarse mode abundance which gets settled by means of impaction,

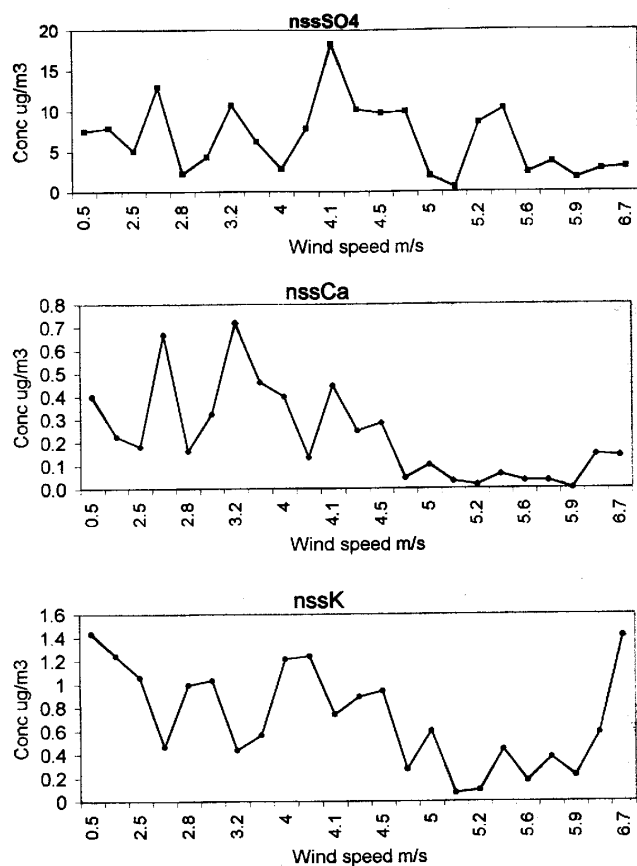


Figure 3. Variation of nss-SO<sub>4</sub>, nss-Ca and nss-K with wind speed.

while nss-SO<sub>4</sub> and nss-K are not very much affected, suggesting that they are in more fine mode. It is reported that fine mode K is emitted by biogenic combustion having less effect of wind speed<sup>8</sup>.

*Variation of nss-SO<sub>4</sub> with relative humidity*

Figure 4 is the plot of nss-SO<sub>4</sub> vs RH. A significant correlation has been observed between nss-SO<sub>4</sub> and RH ( $r = 0.5$ ) at 0.01 significant level which suggest that SO<sub>4</sub> is formed by heterogeneous in-situ oxidation of SO<sub>2</sub> over the ocean. Our earlier observations on precipitation chemistry over Indian Ocean also suggest that the occurrence of acid rain is due to high concentrations of nss-SO<sub>4</sub> in rain water<sup>9</sup>.

Figure 5 also corroborates the above hypothesis indicating that most of nss-SO<sub>4</sub> is contributed by the oxidation of SO<sub>2</sub> over the ocean. The correlation coefficients of nss-SO<sub>4</sub> with SO<sub>2</sub> ( $r = 0.7$ ) and RH ( $r = 0.5$ ) further suggest that in high RH conditions, SO<sub>2</sub> gets oxidized giving rise to SO<sub>4</sub> aerosols over the ocean. The source of SO<sub>2</sub> could be Indian subcontinent or other NE regions.

*Source apportionment using principal component analysis*

In order to identify the probable sources of pollutants

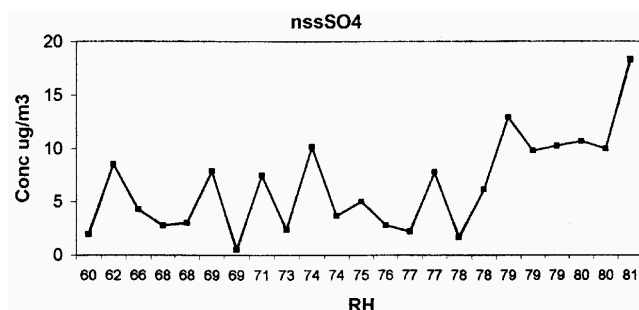


Figure 4. Variation of nss-SO<sub>4</sub> with relative humidity.

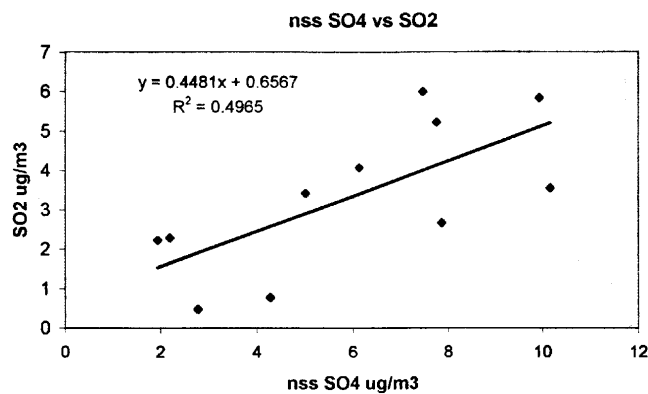


Figure 5. Regression plot of nss SO<sub>4</sub> vs SO<sub>2</sub>.

**Table 2.** Varimax factor matrix of INDOEX aerosol samples

Variable	PC1	PC2	PC3	PC4	Communality
Cl	0.9373	-0.2836	0.0717	-0.1384	0.9833
SO <sub>4</sub>	-0.0017	0.0171	0.9485	0.1752	0.9308
Na	0.9302	-0.3066	0.0627	-0.1470	0.9850
K	-0.1300	0.9572	-0.0104	-0.0042	0.9333
Ca	-0.4085	0.1944	0.2586	0.8314	0.9628
Mg	0.9238	-0.3501	0.0654	-0.0552	0.9834
NH <sub>4</sub>	0.1312	-0.1071	0.5662	-0.4158	0.5222
nss-SO <sub>4</sub>	-0.1447	0.0599	0.9340	0.1757	0.9277
nss-K	-0.2822	0.9291	-0.0176	0.0195	0.9437
nss-Ca	-0.6628	0.2531	0.1666	0.6727	0.9838
nss-Mg	0.2948	-0.4767	0.0176	0.6919	0.7934
SO <sub>2</sub>	-0.3910	0.7404	0.2130	-0.3159	0.8463
Wind speed	0.1238	-0.8056	0.1105	-0.3788	0.8200
RH	-0.6765	-0.0797	0.3978	-0.0491	0.6247
Eigenvalue	6.0748	2.6464	2.0234	1.4961	
% variance	43.4	18.9	14.5	10.7	
Cumulative variance	43.4	62.3	76.7	87.4	
	Sea salt	Combustion	Secondary SO <sub>4</sub>	Crustal	

over Indian Ocean, principal component analysis (PCA) has been applied to whole data set. The results of PCA are shown in Table 2. In total, four PCs have been detected. These four PCs explain 87.4% variance with very high communality for most of the components. Meteorological parameters like wind speed and relative humidity have also been included in PCA.

PC1 explains 43.4% variance of the data. In this principal component, Cl, Na and Mg have high loadings of sea-salt. This PC may be attributed to marine contribution, as sea salts are major fractions of ambient aerosols over the ocean.

PC2 has high loadings of K with negative high loadings of wind speed. It suggests that concentrations of K may be affected negatively by wind speed. As shown in Figure 3, K has moderate influence of wind speed. It suggests that K is coming from some combustion process in the form of plume or K rich air masses which gets diluted whenever there is high wind. As nss-K is said to be a good tracer for biomass combustion, this PC may be associated with combustion process. In addition, the moderate loadings of SO<sub>2</sub> also suggest that this PC may be related with combustion sources. This PC explains 18.9% of total variance in the data set.

PC3 is having high loadings of SO<sub>4</sub> and nss-SO<sub>4</sub> and moderate loadings of NH<sub>4</sub> which suggest that SO<sub>4</sub> is formed by the oxidation of SO<sub>2</sub> forming H<sub>2</sub>SO<sub>4</sub> which further react with NH<sub>4</sub> to form (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Hence, this PC may be called as secondary SO<sub>4</sub> which explains 14.5% of total variance in data set.

PC4 explains 10.7% of variance in data set. It can be attributed to crustal contribution as it has high loadings of Ca, nss-Ca, nss-Mg which are crustal components.

### Comparison of SO<sub>4</sub> and Ca concentrations with other INDOEX cruises

During INDOEX first pre-campaign in 1995-96 (SK cruise #109), SO<sub>4</sub> varied from 0.34 to 8.49 µg/m<sup>3</sup> while Ca varied from 0.04 to 1.02 µg/m<sup>3</sup>. nss-SO<sub>4</sub> and nss-Ca were 84% and 81% of the total SO<sub>4</sub> and Ca concentrations respectively. During this period, all observations were taken in the N of ITCZ only as this cruise covered a region from 15°N to 5°S latitude and 60°E to 76°E longitude which was very near to Indian coast. The contribution by continental activities may be the reason for higher nss concentrations of SO<sub>4</sub> and Ca during cruise #109. The cruise of INDOEX FFP-98 (SK cruise #133) covered a region from 15°N to 20°S latitude and 57°E to 74°E longitude which touched Goa, Male and Mauritius. In this cruise, the fine aerosol concentration (dia < 0.9 µm) of Ca was observed 10 times higher north of ITCZ than south of ITCZ while SO<sub>4</sub> concentration was observed 20 times higher in north of ITCZ than south of ITCZ. During IFP-99 (SK cruise #141), at an average, around 81% of total SO<sub>4</sub> was nss-SO<sub>4</sub> in the north of ITCZ, while it was 47% in the south of ITCZ. Similarly, around 60% and 24% of the total Ca was nss-Ca in the north and south of ITCZ respectively. These observations suggest that nss-SO<sub>4</sub> and nss-Ca concentrations decreased as we moved from northern hemisphere to southern hemisphere, indicating a gradual weakening of the influence of Indian continent towards south.

### Conclusion

The study suggests that meteorology plays a very important role in aerosol studies. All components have been

observed abundant in northern hemisphere before ITCZ which are contributed mostly by northerly winds. In southern hemisphere across ITCZ, the concentrations of nss-K and nss-NH<sub>4</sub> are not as low as expected which may be due to significant biomass burning possibly coming from Australia and Africa. Most of the nss-SO<sub>4</sub> is formed by the oxidation of SO<sub>2</sub> over the ocean giving rise to SO<sub>4</sub> which is responsible for atmospheric acidity as well as for radiative forcing. In an attempt, the PCA revealed that sea salt, biogenic combustion, secondary SO<sub>4</sub> and crustal contribution are the four major sources which dominate over the ocean during INDOEX period.

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