

Chemical composition of aerosol particles over the Arabian Sea and the Indian Ocean regions during the INDOEX (FFP-98) cruise – Preliminary results

Prabha R. Nair*, Rekha Rajan*, K. Parameswaran*, Annamma Abraham[†] and Salu Jacob[†]

*Space Physics Laboratory, [†]Analytical Spectroscopy Division, Vikram Sarabhai Space Centre, Thiruvananthapuram 695 022, India

Aerosol samples collected from the marine environment of Arabian Sea and Indian Ocean using a high volume aerosol sampler during the first field phase of the Indian Ocean Experiment (INDOEX) were analysed to study the mass concentration of cations like Na, K, Mg, Mn, Zn, Fe, Cu and Pb and anions like Cl, SO₄ and NO₃. Atomic absorption spectroscopy has been used for the estimation of cations and ion-chromatography for anions. Near the coastal regions only up to 40% of the total mass collected could be accounted by these ions whereas in the open sea including ITCZ region 50–70% of the mass could be quantified. On an average ~ 13% of total particulate concentration is contributed by sulphates and ~ 6% by nitrates. The mass concentration of sulphates varies from 0.4 to 7.2 $\mu\text{g m}^{-3}$ and that of nitrates from 0.1 to 3.7 $\mu\text{g m}^{-3}$. Ionic concentrations of Fe, K, SO₄ and NO₃ which are mostly of continental/crustal origin decrease significantly in the southern hemispheric oceanic regions. Na and Cl are found to be more abundant in the southern latitudes compared to coastal region. In the mid Arabian Sea where the concentration of sulphates and nitrates was observed to be high, the wind was directed from north-eastern regions of central Indian and West Asian regions. Major continental contributions like carbon, silicates and organic components remain unanalysed.

AEROSOL particles are introduced into the atmosphere by a variety of natural and anthropogenic activities. Because of the diversity in the sources, their concentrations and compositions show significant spatial and temporal variations. This variability makes it difficult to assess the radiative forcing by aerosols on global scale¹. A clear understanding of the chemical composition of aerosols is also important in identifying their sources and sinks. It is also known that aerosols of continental origin get transported to oceanic environments and the marine

aerosols get advected to continental regions owing to circulation systems^{2,3}. The chemical analysis of the aerosol samples collected at different regions over the oceanic environment can provide information on the advection of continental aerosols and their relative contribution^{4,5}.

The Arabian Sea and the adjoining Indian Ocean regions lie in proximity to large land masses which include arid and semi-arid areas. These land masses form significant sources of natural and anthropogenic aerosols. The major goals of the international field experiment-INDOEX (Indian Ocean Experiment) include the assessment of the role of circulation systems in the advection of aerosols and other minor constituents from the continent to oceanic environment and the subsequent transport towards the southern hemisphere during the northern hemispheric winter (when the prevailing wind over the continent is north-easterly). The Inter Tropical Convergence Zone (ITCZ), where the polluted northern hemispheric air mass and the pristine southern hemispheric air mass get mixed is a region of strong convergence and vertical updrafts⁶. The ITCZ plays significant role in the vertical transport of aerosols and other minor species from surface to higher altitudes in the troposphere. The convective activity in this convergence zone at times becomes so strong that it penetrates the tropopause and enters the stratosphere (convective cloud system). Under such conditions, the polluted tropospheric air enters the stratosphere where the horizontal transport is more effective. This polluted air entering the stratosphere gets dispersed globally and thus the regional sources become significant in the global scenario.

A series of experiments have been conducted over Arabian Sea and Indian Ocean during the First Field Phase-1998 (FFP-98) and Intense Field Phase-1999 (IFP-99) of INDOEX using ship-based, aircraft-based, satellite-based and ground-based platforms. During FFP-98, the spatial and temporal variations of the near-surface aerosol mass loading in the oceanic environments and ITCZ region have been studied in detail using a high volume aerosol sampler (HVS) and the results have been pre-

*For correspondence. (e-mail: sp1_vssc@vssc.org)

sented elsewhere⁷. Earlier studies have shown that marine aerosols comprise sea-salts, non-seasalt (nss) sulphates, mineral dust and a variety of other organic and inorganic components getting transported from remote locations^{8,9}. The chemical analysis of the aerosol samples collected over the oceanic region yields qualitative results on the advection of continental aerosols^{2,3}. During the cruise period, about 32 samples were collected from different regions of the oceanic environments over the Arabian Sea and Indian Ocean. Of these, about 15 samples were selected (considering the possible difference in air masses encountered) for the present study. These samples have been subjected to chemical analysis to quantify the ions of Na, K, Mg, Mn, Zn, Fe, Cu, Pb, Cl, SO₄ and NO₃ and their relative contribution. This paper presents the nature of the spatial variation of the different cations and anions over the different regions of Arabian Sea and Indian Ocean covering near coastal, remote oceanic, ITCZ and southern hemispheric regions.

INDOEX FFP-98 cruise and aerosol sampling

The cruise path of ORV *Sagar Kanya* (cruise no: #133) dedicated to FFP-98 of INDOEX is shown in Figure 1. The onward journey (upleg) of the ship started from Goa on 17 February 1998 and reached Mauritius on 12 March 1998. The return voyage (downleg) started on 17 March 1998 reaching Goa on 30 March 1998. The cruise track had a latitudinal coverage of ~15°N to 20°S with a narrow longitudinal span of ~10° (64°E to 74°E) travelling a distance of ~6000 km in 42 days. The cruise track was organized such that during the upleg it travelled along the west-coast from Goa to Trivandrum and to Male via Minicoy. After a short halt at Male, the ship proceeded to Mauritius. The return voyage was almost direct through the oceanic environment without going near to any landmass. During the upleg, the ship encountered ITCZ in the latitudinal belt ~12°S and during downleg it travelled through the ITCZ in the region 8°S to 10°S, when the ITCZ was rather dynamic and diffuse⁷.

The high volume aerosol sampler-Model GH 2000 of Grassby Andersen, USA was operated on the scientific cruise of *Sagar Kanya* during the FFP-98 to collect aerosol samples from different locations in the marine environment. The HVS is a portable, compact, single stage instrument designed for the collection of aerosols in the size range 0.01 to 10 µm. The sampler consists of a blower fitted with a stainless steel filter holder. A 4" diameter quartz fibre filter was used as the collection substrate for the aerosols. A variable orifice meter with pressure taps located at the throat of the filter holder measures the flow rate of air through the filter. The sampling rate of HVS is ~20 CFM, which is verified in laboratory before taking on the cruise using the calibration system associated with the instrument.

The collection substrates were preconditioned by first heating to ~100°C and then desiccating. The preconditioned substrates are tare-weighted using a Mettler Microbalance (sensitivity of ±2 µg) and kept in separate polythene bags, sealed and taken to ship, along with the sampler. The sampler was installed at the front end of the ship deck (~10 m above sea level) which enables the sampling of marine air from the front uncontaminated by the ship exhaust. Aerosol samples were collected on the preconditioned substrates on almost everyday of the cruise during day time. Intense care was taken to avoid unfavourable smoke and other contamination from the chimney of the ship. The aerosol samples collected on the substrates were sealed individually and brought to laboratory for analysis. Of the 32 samples collected during the cruise, 15 samples were selected for chemical analysis, each representing distinct locations during the cruise (shown by open circles in Figure 1).

Sample preparation and analysis

One half of the collection substrate along with the deposits was digested in 50 ml of de-ionized water containing 1 ml of concentrated HNO₃. The solution was filtered and analysed for soluble components using atomic absorption spectroscopy. The atomic absorption spectrometer-Model Varian Spectr AA250 Plus was used for the mass determination of cations Na, K, Mg, Mn, Zn, Fe, Cu and Pb. Calibration standards were prepared from stock solution in de-ionized water. Nitrous oxide-acetylene flame was

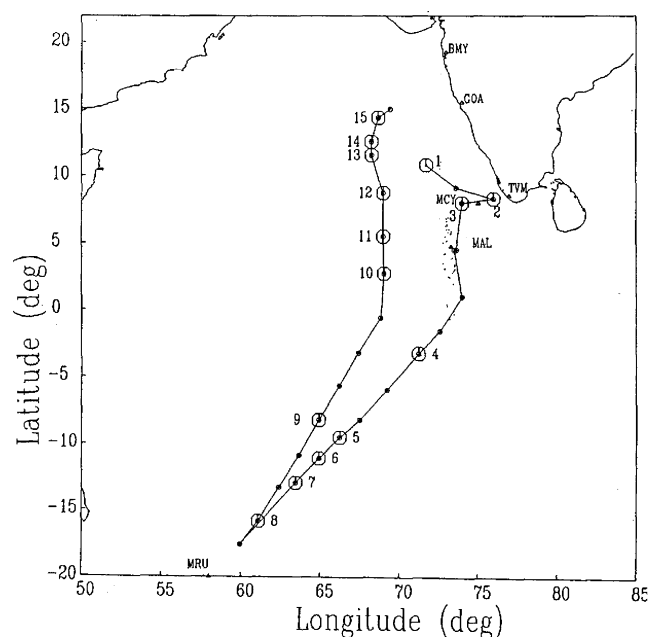


Figure 1. Cruise track of ORV *Sagar Kanya* (solid line) for FFP-98 of INDOEX. Solid circles indicate the positions of ship from which aerosol samples were collected and open circles denote the samples for which chemical analysis carried out.

Table 1. Concentrations ($\mu\text{g m}^{-3}$) of cations

Sample no.	Date	Lat. (°)	Long. (°)	Na	K	Mg	Mn	Zn	Fe	Cu	Pb
1	20.02.98	10.82 N	71.73 E	1.40	0.16	0.33	0.01	0.02	0.26	0.12	0.10
2	22.02.98	8.32 N	76.00 E	1.55	0.39	0.43	0.01	0.01	0.60	0.15	0.04
3	23.02.98	8.01 N	74.00 E	1.50	0.35	0.72	0.01	0	0.59	0.10	0.04
4	04.03.98	3.23 S	71.26 E	3.19	0.32	0.48	0.02	–	0.16	0.10	0
5	07.03.98	9.50 S	66.23 E	3.36	0.26	0.41	0	–	0.11	0.15	0
6	08.03.98	11.09 S	64.91 E	3.71	0.26	0.66	0	0	0.05	0.12	0.03
7	09.03.98	12.93 S	63.44 E	1.13	0.27	0.27	0	0.04	0.03	0.19	0.05
8	17.03.98	15.85 S	61.07 E	0	0.14	0.42	0	0	0.07	0.77	0.07
9	20.03.98	8.20 S	64.90 E	0.55	0.09	0.15	0	0.01	0.02	0.31	0.36
10	24.03.98	2.75 N	69.05 E	0.89	0.25	0.08	0.01	0.02	0.50	0.14	0.12
11	25.03.98	5.53 N	69.00 E	0.25	0.37	0.20	0.01	–	0.40	0.06	0.02
12	26.03.98	8.75 N	69.00 E	0.30	0.36	0.30	0.02	0.60	0.60	0.08	0.01
13	27.03.98	11.56 N	68.27 E	1.84	0.70	0.61	0.03	0.02	1.22	0.08	0.12
14	28.03.98	12.59 N	68.26 E	0.90	0.72	0.72	0.02	–	0.96	0.09	0.04
15	28.03.98	14.97 N	69.45 E	2.18	0.98	0.68	0.02	0.03	1.16	0.37	0.10

used for estimation of Ca and air-acetylene flame for all other elements.

The solutions prepared by dissolving the other half of the quartz fibre collection substrate in de-ionized water were analysed for anions of SO_4 , NO_3 and Cl by using ion-chromatography. A Dionex model DX100 ion-chromatograph equipped with AS4A separator column, AG4A guard column and AMMS II suppressor column was used.

The estimated mass of sulphates includes seasalt components and the non-seasalt (nss) sulphates, which represent the anthropogenic component transported from near-by continents. From the estimated concentration of sulphates (M_s) the mass concentration of nss sulphates (M_{nss}) was calculated using the relation⁸,

$$M_{\text{nss}} = M_s - 0.2517 \times \text{concentration of } N_a,$$

where the factor 0.2517 represents the SO_4/N_a mass ratio in sea-water.

Results and discussion

All the 15 samples were analysed and the mass concentrations ($\mu\text{g m}^{-3}$) estimated for eight cations (Na, K, Mg, Mn, Zn, Fe, Cu and Pb) and three anions (Cl, NO_3 and SO_4). Table 1 lists the mass concentration of the eight cations as obtained from the present analysis along with the sample number (as marked in Figure 1) date on which the sample was collected, mean latitude and longitude of the position of the ship. Table 2 shows the corresponding mass concentrations for anions of Cl, NO_3 , SO_4 and nss-sulphate. Sample 1 was taken near Goa, 2 taken near Trivandrum and 3 near Minicoy. The selected samples include representatives free from continental influence (samples 4 to 7, 11 and 12), from the ITCZ region during upleg and downleg (samples 8 and 10 respectively) and from the coastal region of Mauritius (sample 9). Central Arabian

Table 2. Concentrations ($\mu\text{g m}^{-3}$) of anions

Sample no.	Date	Lat. (°)	Long. (°)	Cl	NO_3	SO_4	nss SO_4
1	20.02.98	10.82 N	71.73 E	2.60	2.39	3.06	2.71
2	22.02.98	8.32 N	76.00 E	0.25	3.62	–	–
3	23.02.98	8.01 N	74.00 E	2.33	3.17	3.40	2.56
4	04.03.98	3.23 S	71.26 E	11.20	2.40	6.76	5.96
5	07.03.98	9.50 S	66.23 E	10.10	0.52	3.50	2.64
6	08.03.98	11.09 S	64.91 E	0.23	0.72	1.81	0.90
7	09.03.98	12.93 S	63.44 E	1.61	0.09	0.59	0.31
8	17.03.98	15.85 S	61.07 E	3.90	0.17	1.10	–
9	20.03.98	8.20 S	64.90 E	0.71	0.21	0.42	0.28
10	24.03.98	2.75 N	69.05 E	1.16	0.14	4.01	3.79
11	25.03.98	5.53 N	69.00 E	0.31	1.36	7.20	7.14
12	26.03.98	8.75 N	69.00 E	–	1.25	3.42	3.34
13	27.03.98	11.56 N	68.27 E	1.22	3.91	5.05	4.59
14	28.03.98	12.59 N	68.26 E	1.80	4.56	6.70	6.47
15	28.03.98	14.97 N	69.45 E	2.41	3.69	3.56	3.01

Sea and close to Mumbai/Goa are represented by sample 13, 14 and 15.

The concentration of Na varied between $0.25 \mu\text{g m}^{-3}$ and $3.7 \mu\text{g m}^{-3}$ and was found to be most abundant component in all the samples irrespective of the region. However, the maximum concentration of Na occurs in the southern latitudes of 3°S to 11°S . On the other hand, Fe, Mg and K showed higher concentration towards the mid-Arabian Sea near to Mumbai/Goa coast (11°N to 15°N). The concentrations of these ionic components were low in the ITCZ region. Observed concentrations of Zn, Mn and Pb were relatively low being one order less than the other cations. Zn and Mn did not show any significant variation over the cruise track whereas Pb showed high values near the coastal regions and also in the ITCZ region encountered during the upleg. In general, the mass concentration of almost all other ions exhibited rather low values in the ITCZ region.

The concentrations of SO_4 and NO_3 are generally high in the northern latitudes (near land mass) and lower concentrations for these constituents are encountered in the

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central Arabian Sea. On an average ~ 13% of total mass concentration was contributed by sulphates and 6% by nitrates. On the other hand, Cl, which is mainly of oceanic region is found to be highest in the remote oceanic environments in the southern latitudes. Low concentrations of SO₄ and NO₃ are observed in the ITCZ region. The spatial pattern of non-sea salt sulphate and total sulphate concentrations were almost similar indicating the dominance of anthropogenic component in the total sulphate loading. The sea-salt component of SO₄ was only a minor fraction of the total sulphate. The estimated concentrations of NO₃ and SO₄ are significantly higher than their corresponding background values (0.1 μg m⁻³ for NO₃ and 0.3–0.7 μg m⁻³ for nss-SO₄)⁸.

Table 3 lists the total mass loading M_L in μg m⁻³ estimated for each sample along with approximate location of the ship, latitude, longitude and percentage of mass concentration accounted by the present analysis.

Near the coastal regions and central Arabian Sea (samples 1 to 3, 13 to 15) where high mass concentrations were observed, only 20–40% of the total mass could be accounted by the ionic components estimated by the present analysis, indicating the presence of more unidentified ions in these regions. In the remote oceanic environments (represented by samples 5 to 11) in general 50–70% of the mass collected could be accounted by the estimated mass of ions.

Ions like Na, Mg and Cl arise mainly from sea-salt and are considered to represent oceanic aerosols whereas ions like Fe, K, Cu, Zn, Pb, SO₄ and NO₃ are mainly of crustal/anthropogenic origin and represent continental aerosols^{10,11}. In the marine environment, the aerosol concentration is determined mainly by wind-driven *in situ* production or by transport. The dominance of ions like Fe, Cu, SO₄ and NO₃ closer to the subcontinent and the decrease of concentrations with increase in distance from

Table 3. Total mass concentration and percentage of the analysed component at different locations

Sample no.	Type of ocean region	Date	Lat. (°)	Long. (°)	M_L (μg m ⁻³)	Total (%)
1	Near Goa	20.02.98	10.82 N	71.73 E	25.9	40
2	Near Trivandrum	22.02.98	8.32 N	76.00 E	23.7	30
3	Near Minicoy	23.02.98	8.01 N	74.00 E	42.4	24
4	Open sea (Indian Ocean)	04.03.98	3.23 S	71.26 E	33.8	73
5	Open sea	07.03.98	9.50 S	66.23 E	21.0	88
6	Open sea	08.03.98	11.09 S	64.91 E	19.3	39
7	ITCZ (Indian Ocean)	09.03.98	12.93 S	63.44 E	08.4	44
8	Near Mauritius	17.03.98	15.85 S	61.07 E	14.5	46
9	ITCZ (Indian Ocean)	20.03.98	8.20 S	64.90 E	04.7	54
10	Enters Arabian Sea	24.03.98	2.75 N	69.05 E	14.1	60
11	Mid Arabian Sea	25.03.98	5.53 N	69.00 E	18.7	55
12	Mid Arabian Sea	26.03.98	8.75 N	69.00 E	30.3	21
13	Mid Arabian Sea	27.03.98	11.56 N	68.27 E	51.0	30
14	North of Goa	28.03.98	12.59 N	68.26 E	43.5	38
15	North of Goa	28.03.98	14.97 N	69.45 E	49.6	30

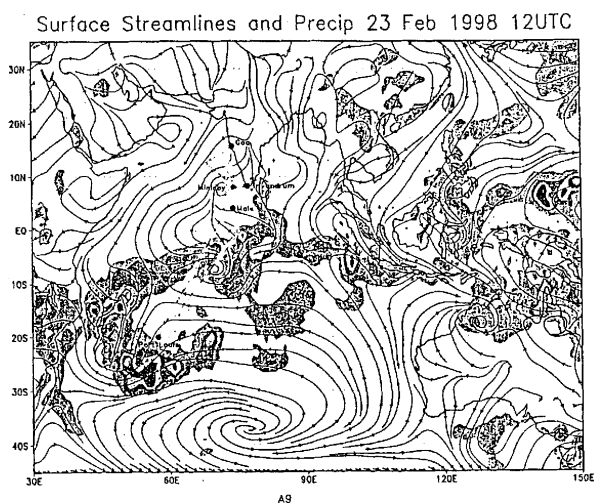


Figure 2. Surface streamlines over the cruise track on 23 February 1998.

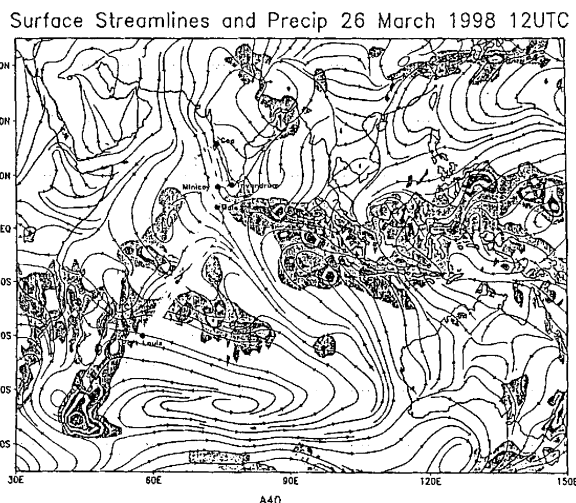


Figure 3. Surface streamlines over the cruise track on 26 March 1998.

land suggest that the aerosol properties over the marine boundary layer are governed by transport. Figure 2 shows the nature of typical surface streamlines when samples 1 to 5 were collected. It can be seen that during this period, winds from southern peninsular India intercepted the cruise and there is a general decrease in the concentration of Fe, K, Cu, etc. as the ship advanced towards southern latitudes. When the samples 6, 7, 11 and 12 were collected, the cruise track encountered pristine Southern Hemisphere air. These samples show low concentrations of SO₄, NO₃, Fe, etc. Figure 3 shows the surface streamlines when the ship was sailing along the mid-Arabian Sea (samples 13, 14 and 15). During this period, the ship received air mass from the north-western side of central India and West Asian countries. The winds from these arid and polluted regions enhance the anthropogenic pollutants like SO₄ and NO₃ and the mineral components like Fe, Cu and K in the central Arabian Sea regions during this period. The sulphates and nitrates are found to be less towards the coastal region of western India compared to central Arabian Sea. The decrease of mineral components from northern to southern latitudes observed during the upleg of the cruise shows the influence of landmass in enhancing these components. A cross examination of Table 3 shows that only 20–30% of total aerosol collected from these regions could be quantified by these (analysed) constituents. The major portion of the

aerosol mass remained unanalysed. This unanalysed part can possibly be constituted of silica, carbonaceous and other organic aerosols that are not investigated in the present analysis. However, the observed significant increase in the concentration of sulphates and nitrates indicates that significant amount of anthropogenic (industrial by-products) aerosols from the continents are being advected over the oceanic environment in this region.

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