

Transport of Ca^{2+} and SO_4^{2-} aerosols during southwest monsoon from north African and Gulf countries towards India

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सार – अरब सागर मानसून प्रयोग (आरमेक्स) अभियान के दौरान अनुसंधान पोत सागर कन्या पर जून-अगस्त 2002 की अवधि में अरब सागर में हुई वर्षा के नमूने इकट्ठे किए गए। पी. एच. और जल में विलयशील प्रमुख आयनिक घटकों से वर्षा के जल के सभी नमूनों के विश्लेषण किए गए। वर्षा के जल का पी. एच. एल्कालाइन था तथा उनके रासायनिक संयोजन $\text{Cl}^- > \text{Na}^+ > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{Mg}^{2+} > \text{K}^+ > \text{NO}_3^- > \text{NH}_4^+$ के क्रम से है। वर्षा में समुद्री लवण के घटकों की प्रधानता (~ 90%) थी। वर्षा के नमूनों में असमुद्री लवण Ca^{2+} , SO_4^{2-} की सार्थक मात्रा तथा NO_3^- , NH_4^+ की ट्रेस मात्रा पाई गई जबकि K^+ और Mg^{2+} के मामले में असमुद्री लवण का कोई अंश नहीं पाया गया है, जिससे उनके पूर्णतया समुद्र से उत्पन्न होने का संकेत मिलता है। असमुद्री लवण घटकों के स्रोतों का पता लगाने के लिए दीर्घ अवधि अभिगमन और बैठक की पृष्ठभूमि प्रदूषण के संदर्भ में वर्षा के जल के आंकड़ों की व्याख्या की गई है। उत्तरी अफ्रीका और खाड़ी महाद्वीप से लेकर प्रेक्षण स्थल तक उत्पन्न हुई वायु राशि की विद्यमानता से बैंक प्रेक्षणों का पता चला है और उसमें संभवतः असमुद्री लवण Ca^{2+} और SO_4^{2-} एरोसॉल पाए जा सकते हैं।

ABSTRACT. Precipitation samples were collected over Arabian Sea during Arabian Sea Monsoon Experiment (ARMEX) campaign for the period June- August 2002 onboard Ocean Research vessel Sagar Kanya. All the rain water samples were analysed for pH and major water soluble ionic components. The pH of rain water was alkaline and the order of chemical composition is followed as $\text{Cl}^- > \text{Na}^+ > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{Mg}^{2+} > \text{K}^+ > \text{NO}_3^- > \text{NH}_4^+$. Sea salt components were dominant (~ 90%) in precipitation. Significant amounts of non sea salt Ca^{2+} , SO_4^{2-} and trace amounts of NO_3^- , NH_4^+ were found in precipitation samples whereas, no non sea salt fraction was observed in case of K^+ and Mg^{2+} , indicating that they were totally originated from sea. Rain water data was interpreted in terms of long range transport and back ground pollution to find out the sources of non sea salt components. Back-trajectories showed the presence of air masses originated over North African and Gulf continents towards observational point and they may possibly be carrying non sea salt Ca^{2+} and SO_4^{2-} aerosols.

Key words – Precipitation, Transport, Pollution, Trajectories.

1. Introduction

Characterisation of chemical nature of precipitation is currently under considerable investigation due to increasing concern about man's atmospheric inputs of substances and their effects on land, surface water and vegetation. Precipitation is an important process for cleaning the atmosphere of trace constituents like aerosols. Cloud and precipitation scavenges aerosols through nucleation scavenging and Brownian diffusion or impaction scavenging. Nucleation scavenging is the process where Cloud Condensation Nuclei (CCN) serve as nuclei for the cloud droplet formation, in this process hygroscopic particle plays important role. Below cloud aerosol removal occur through Impaction scavenging. The composition of wet deposition actually reflects the

composition of the atmosphere through which it falls; hence precipitation chemistry helps to study various sources of aerosols like Cloud Condensation Nuclei (CCN), soil and anthropogenic aerosol.

Earlier reports have indicated Ca^{2+} , SO_4^{2-} and NH_4^+ were important components in Indian monsoon rain water (Khemani *et al.*, 1985, Norman *et al.*, 2001) and also indicated that the major source of Ca^{2+} in Indian precipitation is soil dust particles emitted from earth surface and non sea salt fraction of Calcium in Indian precipitation to be, on an average 90% in coastal areas and as high as 99% in inland (Parashar *et al.*, 1996), regions. Sulfate aerosols were derived from both anthropogenic and natural sources. Largest source of sulfate is the oxidation of SO_2 , emitted from the burning of fossil fuels

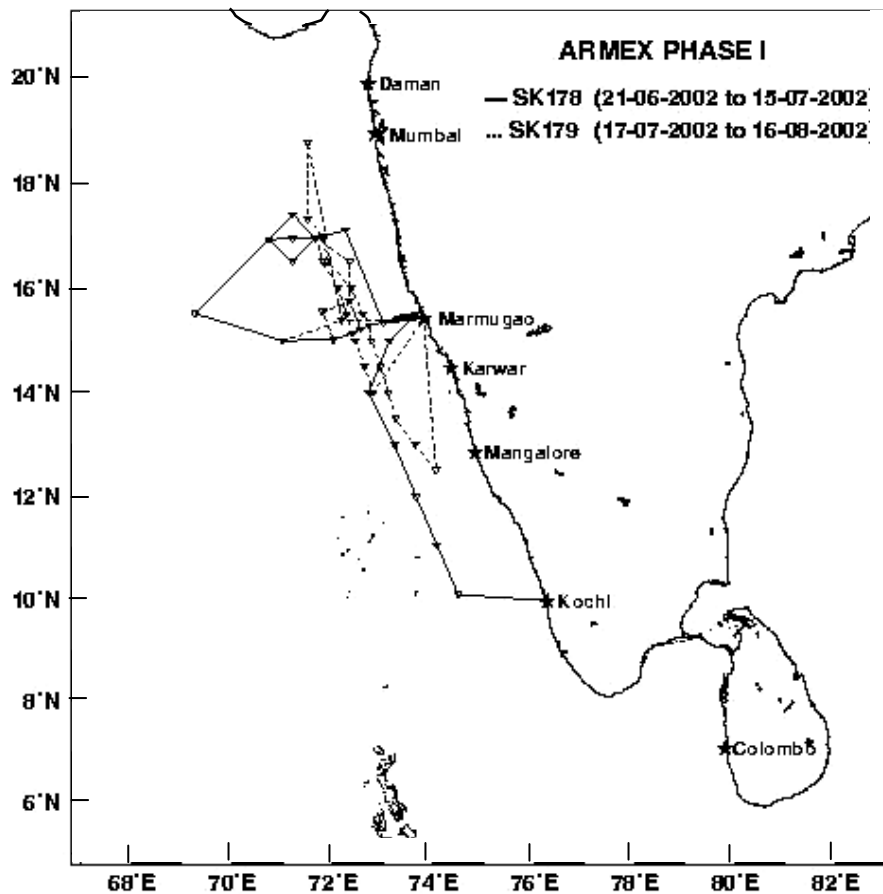


Fig. 1. Cruise track of ORV Sagar Kanya during ARMEX 2002

and biomass (Arndt *et al.*, 1997). Ammonium originates from ammonia gas (NH_3) from domestic animals, fertilizer applications to soils and burning of biomass. Bouwman *et al.*, (1997) showed that India is the second largest Ammonium emitter in the world after China. Earlier studies were more constrained to local sources and their effects on precipitation. Studies on transport of aerosols and their contribution to precipitation were lacking. In general, the precursor gases results in acid precipitation and it affects entire ecosystem. The aim of our study is to know the transport component in precipitation and contribution of Ca^{2+} , SO_4^{2-} and NH_4^+ to precipitation chemistry over marine boundary layer and understand their sources.

2. Route of the expedition

The measurements were made on research vessel Sagar Kanya from 21 June to 16th August, 2002. 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. Cruise track for Leg 1 and Leg 2 are given in Fig. 1.

3. Sampling

Precipitation samples were collected using one wet-only and two bulk collectors. All of these three collectors are consisting of polypropylene funnels and bottles. The wet only collector was of MISU (Department of Meteorology, Stockholm University, Sweden) design. Wet-only and one bulk collector were placed on front side of bridge deck nearly 20 m a.s.l. Wet-only collector was operated using a remote control, to remove possible contamination from ship exhaust and it was operated only in clean air condition. The second bulk collector was placed near Balloon deck (deck below the bridge) at 17 m a.s.l. These three collectors were cleaned with deionised water twice a day once each in morning and evening to remove possible contamination from sea spray. Samples were collected in 100 ml polypropylene bottles which were washed thoroughly with deionised water. Samples were weighed immediately after collection using

TABLE 1

Average pH and concentration of major ionic components ($\mu\text{eq/l}$)

Collector	Cl	SO ₄	NO ₃	NH ₄	Na	K	Ca	Mg	pH
Wet-only	337	48.5	1.2	0.55	290	6.7	71	44.6	6.43
Bulk	459	77.9	2.0	0.59	398	9.9	108	67.2	6.40

TABLE 2

Average equivalent ratios of various ionic species to Na and f_{ns} of Ca, SO₄

Collector	Cl/Na	SO ₄ /Na	K/Na	Ca/Na	Mg/Na	f_{ns} Ca	f_{ns} SO ₄
Wet-only	1.20	0.20	0.024	0.30	0.21	0.81	0.34
Bulk	1.18	0.22	0.024	0.34	0.21	0.84	0.38
Sea water	1.16	0.125	0.0218	0.0439	0.227	-	-

electronic balance and then sealed. Samples were cold stored, preservative (Thymol) was added to avoid biological degradation.

4. Analysis & quality check

Rain water samples were analysed for major cations and anions. Na⁺, K⁺, Ca²⁺, Mg²⁺ were determined by Atomic Absorption Spectrophotometer (Perkin- Elmer 373). Cl⁻, SO₄²⁻ and NO₃⁻ were measured by Ion Chromatograph (DIONEX 100) using Analytical column- AS4A – SC 4mm; eluent- 1.8 mM Na₂CO₃/1.7 mM NaHCO₃; regenerant- triple distilled water and Anion Micro-Membrane Suppressor. NH₄ was measured by colorimetric method using UV-Visible Spectrophotometer. pH was measured by using Digital pH meter with an accuracy of ± 0.01 . Analytical quality check was done for instruments using different standards and external reference samples. Deviation was found to be nearly 1% to 2% between the reference samples. Even though, precautions were taken during observation period, later in Laboratory samples were selected after considering ship heading and wind direction, in most of the cases ship heading and wind direction was almost opposite to each other, during which sampling location comes under upwind of the ship exhaust. So in such cases, there will not be any contamination from ship exhaust on rain water composition. Out of total collected 114 samples, 72 samples were considered for the present study after considering all precautions and removing the contaminated samples.

5. Results & discussion

The average concentration of major chemical components in $\mu\text{eq/l}$ along with pH are given in Table 1.

The average pH value was 6.41 which represents alkaline precipitation. Na⁺ and Cl⁻ were main chemical components contributing nearly 80% of total chemical composition. During the observation period, surface winds were strong (about 10m/s). Sea salt aerosol production was due to high bubble bursting caused by high wind speeds (Blanchard, 1963). Trace amount of NH₃ and NO₃⁻ were observed, representing less polluted air. Moderate concentrations of Ca²⁺, K⁺, Mg²⁺ and SO₄²⁻ were also found in rain water samples. Non sea salt components of Ca²⁺, K⁺, Mg²⁺ and SO₄²⁻ in rain water were calculated by assuming that total Na⁺ in rain water is from sea salt (Keene *et al.*, 1986) and from standard sea salt ratios. Non sea salt fractions were calculated as follows:

$$f_{\text{ns}} = \frac{[X] - [Na] * r}{[X]}$$

Where f_{ns} is the non sea salt fraction,

[X] Indicates the concentration of the ion X,

r Indicates standard sea water ratios (Table 2).

The ocean is a major source of aerosols and gases for the overlying atmospheric boundary layer. Bubbles produced by breaking waves burst after rising back to the air-sea interface and produce sea salt aerosols (Blanchard 1963), while photochemical and/or marine biological processes in near-surface water may lead to significant evasion of halogen and sulfur containing gases (Andreae and Raemdonck, 1983). Because precipitation scavenges these constituents of atmosphere, the chemistry of precipitation over the ocean is typically dominated by a marine component.

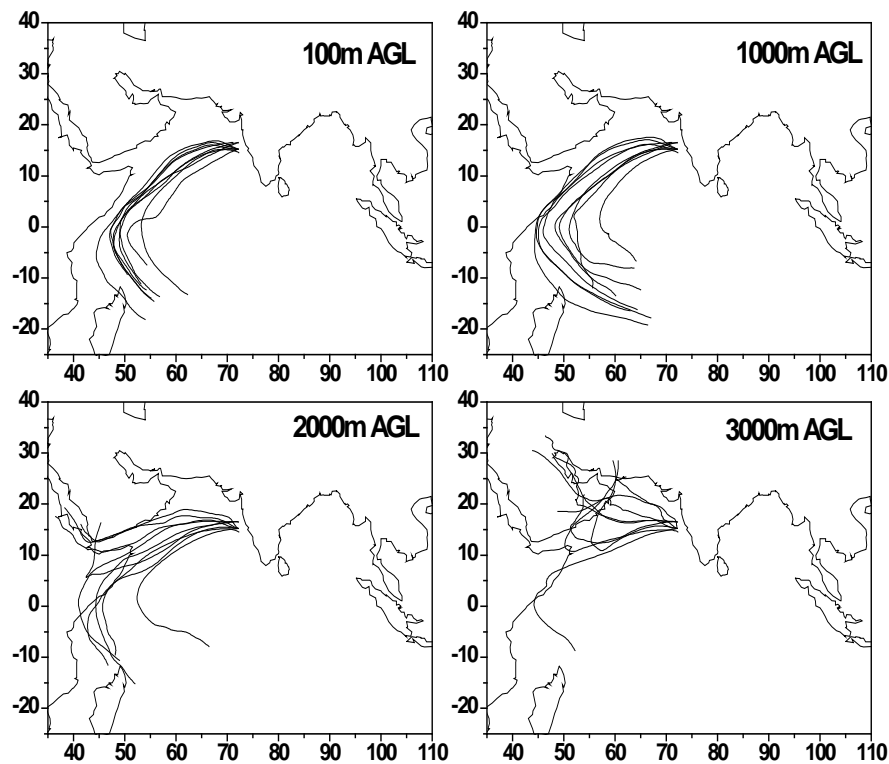


Fig. 2. Back trajectories at observational points for major rain events at 100, 1000, 2000, 3000 m a.g.l. (Above Ground Level)

The accurate calculation of non-sea-salt, or excess, concentrations of chemical constituents is essential for quantifying the influence of natural terrestrial, non sea salt, marine and anthropogenic sources on marine aerosol and precipitation chemistry. Reference species such as Na^+ or Mg^{2+} are commonly used to estimate the sea salt fractions. The average equivalent concentration ratios of Ca^{2+} , K^+ , Mg^{2+} and SO_4^{2-} with Na^+ and standard sea salt ratios were given in Table 2. Results were indicating presence of good amount of non sea salt Ca^{2+} and SO_4^{2-} since their ratios with Na in rain water were higher when compared with standard sea water ratios, whereas K^+ and Mg^{2+} matching with sea salt fractions with less deviation ± 0.03 to ± 0.01 indicating they were originated from sea. Non sea salt fractions for Ca^{2+} and SO_4^{2-} were given in Table 2 representing nearly 80% of total Ca^{2+} and 36% of total SO_4^{2-} were found as non sea salt components.

The regional patterns of NO_3^- and NH_4^+ deposition reflect emission sources and atmospheric-transport processes. Fossil-fuel combustion is a known source of NO and NO_2 , which are oxidized in the atmosphere to form HNO_3 vapor and particulate NO_3^- . Although HNO_3 vapor has a high deposition velocity and a relatively short

residence time, it can react with other pollutants such as NH_3 and NaCl to form particles with low deposition velocities that can be transported hundreds of miles. Particulate NO_3^- also tends to have a low deposition velocity that facilitates long-range transport. Wet and dry deposition of NH_4^+ has generally been attributed to NH_3 emissions from high concentrations of livestock and nitrogen fertilization of croplands. Emissions from automobiles can also contribute atmospheric NH_3 . Unlike the NO and NO_2 released from fossil-fuel combustion, NH_3 in the atmosphere is highly water-soluble and its deposition velocities are high.

6. Sources and transport of non sea salt components

To find out the sources of excess Ca^{2+} and SO_4^{2-} , back trajectories were plotted for 200, 1000, 2000 and 3000 m a.g.l. (Above Ground Level) as shown in Fig. 2. Back trajectories indicated up to 1000 m height, winds were passing over Indian Ocean and originated from southern hemisphere with southeasterly winds crossing equator and becoming southwesterly. Above 1000 m winds were originated from land mainly crossing North African and Gulf countries. This result indicated two

potential sources for excess Ca^{2+} and SO_4^{2-} in precipitation, one is air mass originated from southern hemisphere and second one air mass from North African and Gulf countries.

Influence of air mass originated from southern hemisphere was studied using INDOEX observations. Observations during INDOEX helped to study the main differences of air mass qualities like pollution levels and aerosols characters over northern and southern hemispheres (Norman *et al.*, 2002, Granat *et al.*, 2002). During this period, northern and southern hemispheric winds were separated by Inter Tropical Convergence Zone (ITCZ). During INDOEX campaign, precipitation and aerosol observations were carried in both northern and southern hemispheres. Concentration of chemical constituents was much higher in the precipitation collected over northern hemisphere than those over the southern hemisphere. Over southern hemisphere, concentrations of nss SO_4^{2-} , NH_4^+ , nss K, NO_3^- and DMS were very less; also their variation in concentrations was attributed to variation in the marine biogenic sources (Norman and Leck, 2002). Non sea salt Ca was found to be about 10% of total amount. Above results indicated that potential sources for nss Ca^{2+} and SO_4^{2-} from southern hemispheres were negligible.

Earlier studies have shown that oxidation of SO_2 in presence of ozone in sea-salt-bound condensed water contributes to the major part of nss SO_4^{2-} (Sievering *et al.*, 1991). Chameides and Stelson (1992) showed that, O_3 oxidation of SO_2 proceeds in the sea-salt water until its pH drops to 6; while at a pH of 6 or less, O_3 oxidation is quenched. The magnitude of nss SO_4^{2-} produced by this mechanism should equal to the alkalinity present in the sea-salt-bound condensed water. Hydrogen peroxide oxidation of SO_2 contributes in a minor way, when its pH = 6 or less (Chameides and Stelson, 1992). The halogen release mechanism proposed by Vogt *et al.*, (1996) and discussed further by Keene *et al.* (1998) may also contribute to the large amount of nss SO_4^{2-} found internally mixed with sea-salt particles. On the assumption that the excess calcium was present as CaCO_3 when sea salt particles were emitted from the sea surface, the buffering capacity of sea salt particles is roughly doubled. The sum of alkalinity and calcium excess buffering capacity is sufficient to attribute 70-90% of the super-micrometer nss SO_4^{2-} production, than the other mechanism of the high-pH O_3 oxidation of SO_2 pathway (Sievering *et al.*, 1999). Hence, nss SO_4^{2-} can directly relate to SO_2 gas available in MBL. A significant correlation between Ca^{2+} and SO_4^{2-} (0.86) was observed indicating the above mechanism play major role.

7. Conclusions

Ca and SO_4 aerosols were transported during south west monsoon from north African and Gulf countries towards India. Precipitation chemistry showed less NH_4 and NO_3 indicating less polluted air moving towards India. Above results indicated that in Indian monsoon precipitation, total NH_4 and NO_3 was originated from local (India) source, whereas for Ca and SO_4 , some contribution was from transport of aerosols from North African and Gulf countries.

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