

ANNUAL CYCLE OF MAJOR WATER SOLUBLE IONIC SPECIES IN AEROSOLS AT A HIGH ALTITUDE STATION, DARJEELING, INDIA (27°01'N, 88°15' E, ~2182 MASL)

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1. Introduction

Variation in the concentration of chemical species are seen over different parts of the world because of varying emission sources, the diffusion and dispersion processes caused by air parcels movements as well as removal of species from the atmosphere by reaction or deposition. Micro-pollutants are produced in the atmosphere by incomplete combustion of fossil fuels at low temperature and at low oxygen level. Because of the nature of their sources, particles in the accumulation range generally contain soluble inorganics and far more organics than the coarse particles. The salt concentration and, to some extent, size distribution depends on various micro meteorological parameters. A number of characteristics of aerosol like mass, size, chemical composition and some optical properties are responsible for their roles in atmospheric process.

Investigations from remote, sparsely inhabited regions have the importance of providing a sort of background values of such properties against which the urban impacts can be compared. In this perspective, observations from high altitude stations have a special significance as the aerosols in this region provide a 'far-field picture', quite away from potential sources and are more representative of free troposphere conditions. The rising anthropogenic interferences due to social development and population growth in the Himalayas affect not only the immediate landscape environment but also atmospheric environment. In this respect, increasing concentration of tourists and related activities in Northeastern Himalayan eco-system has resulted in severe cases of localized atmospheric pollution that ultimately adds to global pollution causing disorder to the health of world population.

Studies on the chemical composition of aerosol and precipitation in the Himalayas have been limited to date on both temporal and spatial scales. A short-term sampling program in the Nguzompa glacier basin near Mt. Everest (**Wake et al., 1994**) and another sampling at northern slope of Mt Everest (Mt Qomolangma, in Chinese) showed low ion burdens in both aerosol and snow (**Ming et al., 2007**). A 2 week sampling project in Hidden Valley in the Himalayas of western Nepal showed that temporal variations in aerosol concentrations were related to the influx of air masses by monsoon circulation (**Shrestha et al., 1997**). To understand better the aerosol loading and transportation over NE Himalayas, recently, the Darjeeling (27°01'N, 88°15' E, ~2182 masl) has been selected as aerosol and gaseous measuring station (**Sundareshwar et al., 2007**). The present work is done for Darjeeling station for data collected during 2004-2006.

2. Site

The study area Darjeeling is an important tourist destination in North Eastern Himalayas. The valley experienced tremendous growth in tourism over the last decade causing an increase in number of tourist vehicle during summer seasons. The vehicular pollution, thus produced in summer and biomass burning in winter has primarily influenced the level of air pollutants in the region of Darjeeling. As combined impact of these activities, air pollution has increased continuously since last decade and raised the concentration of respirable suspended particulate matter in the Darjeeling environment. With the establishment of a high altitude research center at Darjeeling, multidisciplinary research approach activities have been emphasized * Work was done

when author MKS was working as Research Scientist at CAPSS, Darjeeling. relating physical, chemical, biological and environmental conditions of high altitude and/or problems of regional interest.

3. Methodology

The sampling of particulates (both RSPM and PM_{2.5}) was done on weekly basis at Darjeeling with the help of high volume sampler with a constant flow rate and for a certain period for the sufficient loading of aerosol. In general, the sampling interval has been taken as 24h for sufficiency of sample required for further analyses. The concentration of RSPM and PM_{2.5} was determined gravimetrically using semi microbalance. The filter papers were desiccated properly both before and after the sampling. The major water soluble ions were analysed by sonicating the filter paper loaded with aerosol in a constant volume of de-ionised water and running in Ion chromatograph using separate columns for cations and anions. For reference measurements, similar approach is applied for blank filter paper.

4. Result & Discussion

4.1 Particulate matters and their characterization:

The average concentration of RSPM was found to be $37.7 \pm 20 \mu\text{g m}^{-3}$. The maximum value was $82 \mu\text{g m}^{-3}$ during April and the minimum $9.36 \mu\text{g m}^{-3}$ during October. The monthly variation in concentration of RSPM was found to be multimodal in nature. Apart from April, it shows a secondary peak during the month of June and then progressively decreases and showed minima during October. The values again increased during the winter months. PM_{2.5} also showed a wide monthly variation ranging between $3 \mu\text{g m}^{-3}$ during October and $67 \mu\text{g m}^{-3}$ showing peak during April with the average of $21.4 \pm 17.8 \mu\text{g m}^{-3}$. The annual average concentration of PM_{2.5} is about 1.5 times more than that of National Ambient Air Quality Standard (NAAQS), $15 \mu\text{g m}^{-3}$. It shows a significant variation ($p = 0.0$), which could be due to the thermodynamic conditions in the planetary boundary layer (PBL), that can either favor or show adverse affect to the pollutant dispersion. Weather parameters such as temperature, relative humidity, short wave radiation can also influence chemical reaction leading to secondary aerosol formation.

Figure 1 shows the monthly variation of both PM₁₀ and PM_{2.5} along with their ratio. The ratio of PM_{2.5} to PM₁₀ has been used to determine the contribution of fine particulate matter to the RSPM. The ratio varied between 0.26 and 0.81 with an average of 0.51 ± 0.16 . The ratio shows higher value during winter months and during April which is a clear indication that most of respirable aerosols are constituted by the fine particulate matter during this period. The ratio falls to 0.26 during the month of August i.e. South-West monsoon period, indicating the smaller contribution of fine range particles in RSPM due to washing out of smaller range anthropogenic particles from the atmosphere because of heavy rainfall and also due to the contribution of sea salt in the coarse mode fraction, which are probably transported from the nearby sea, the Bay-of-Bengal.

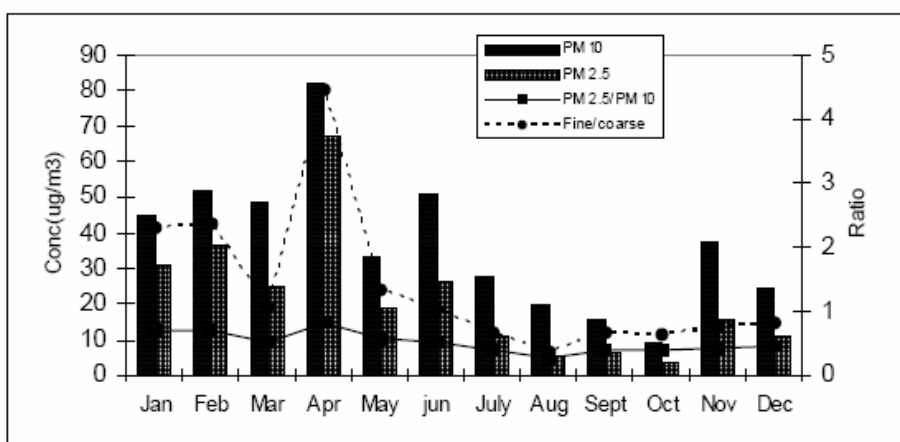


Figure 1. Monthly variation of RSPM and fine mode aerosol

4.2 Relationship amongst water soluble ions

The aerosol samples (RSPM) were analyzed for the major water-soluble inorganic ions e.g. Na^+ , NH_4^+ , K^+ , Ca^{+2} , Mg^{+2} as cations and Cl^- , NO_2^- , NO_3^- , SO_4^{-2} as anions. It was found that on an average 52% of RSPM was found to be constituted by water-soluble ions with a variation between 29% and 73%. On the basis of average concentration of water soluble ions, the abundance of the cations follows the order : $\text{Na}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Ca}^{+2} > \text{Mg}^{+2}$ whereas the same for anions follows the order : $\text{SO}_4^{-2} > \text{NO}_3^- > \text{Cl}^- > \text{NO}_2^-$. It was found that the average contribution of water soluble cations and anions to RSPM are $12.6 \pm 4.9\%$ and $40 \pm 7.4\%$ respectively. On an average 14% of RSPM and 21.3% of total water soluble ions were found to be constituted by Na^+ and Cl^- only. Also, a good correlation ($R_2=0.82$) has been observed between Na^+ and Cl^- . The correlation is found to be the best during the South-West monsoon period indicating their common marine source.

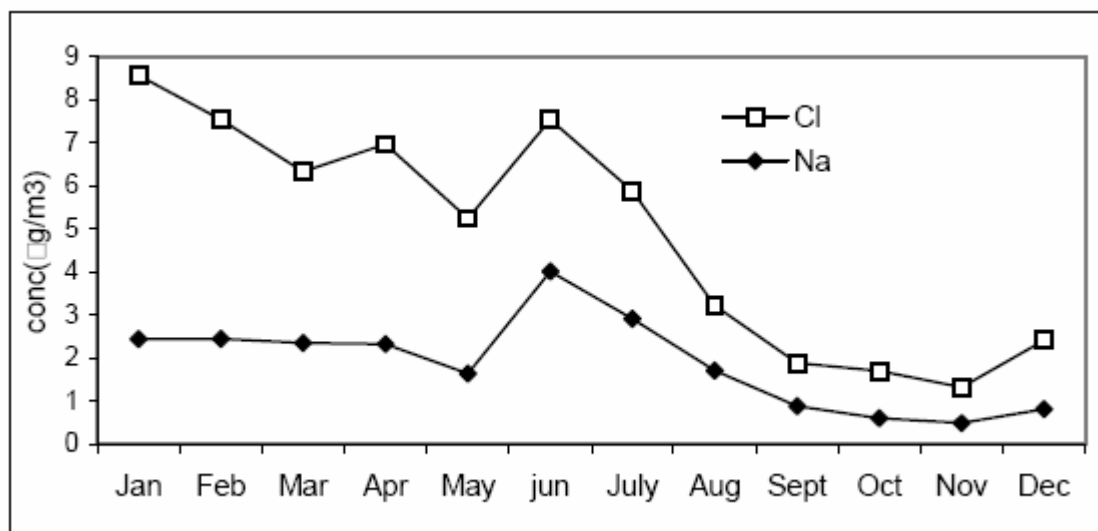


Figure 2. Monthly variation of sodium and chloride

Figure 2 shows the monthly variation in concentration of Na^+ and Cl^- giving peaks during winter months and monsoon period. During monsoon, since the incoming winds are from the sea origin, the probable source of Cl^- is due to sea-salt, also supported by the correlation between the Na^+ and Cl^- . During winters, however, the higher loading of Cl^- may be from the wood and coal burning in domestic and industrial fields in local environment around Darjeeling. The chloride of non-sea type in nature is found to be associated with coal and wood burning (Rastogi and Sarin., 2005).

Figure 3 shows the ratio of obtained Na^+ to Cl^- along with the standard value in seawater. The figure clearly indicates that during the southwest monsoon period the ratio falls below 1.17 i.e. standard ratio in sea water and in rest of the months it is quite higher than 1.17. During the monsoon the sea salt chloride transported from Bay of Bengal when interact with the anthropogenic NO_x or particulate nitrate then chloride is substituted from the sea salt particle and depletion in chloride takes place (Eldering et al., 1991, Graedel et al., 1995, Shapiro et al., 2007). This can happen if NH_4^+ is in excess after completely neutralizing NO_3^- and SO_4^{-2} and there is gaseous HCl present in the ambient air (Harrison and Pio, 1983).

About 25% of PM_{10} was found to be constituted by NO_3^- and SO_4^{-2} . The non-sea sulphate has been calculated from the standard $\text{SO}_4^{-2}/\text{Na}^+$ ratio in seawater. The ns- SO_4^{-2} varies over a wide range in Darjeeling. The average concentration of ns- SO_4^{-2} was found to be $5.68 \pm 2.8 \mu\text{g m}^{-3}$ varying variation between $1.78 \mu\text{g m}^{-3}$ and $12.13 \mu\text{g m}^{-3}$ for round the year. A good correlation was, however, obtained between ns- SO_4^{-2} and NO_3^- ($r_2=0.85$) and the slope was found to be greater than one indicating excess enrichment of ns- SO_4 over NO_3^- in Darjeeling. Several studies (Ooki et al., 2005; Tang, 2004) have shown that nitrate largely exists in coarse mode particulate range whereas SO_4^{-2} exists both in fine and coarse mode range. Wind can easily transport SO_4^{-2} to the high altitude area from low land and the consequent excess enrichment of ns- SO_4^{-2} over NO_3^- takes place. Vehicular exhaust emission and several anthropogenic activities are regarded to be the main source.

Furthermore, lower dispersion during the winter month lead to higher loading in the atmosphere. Higher density of tourist vehicles during the summer months and biomass burning could be considered as the major source for nitrate and sulphate. The higher concentration of NO_x from vehicular emission in Darjeeling enhances the production of nitrate and their subsequent reaction with the ammonium ion to form

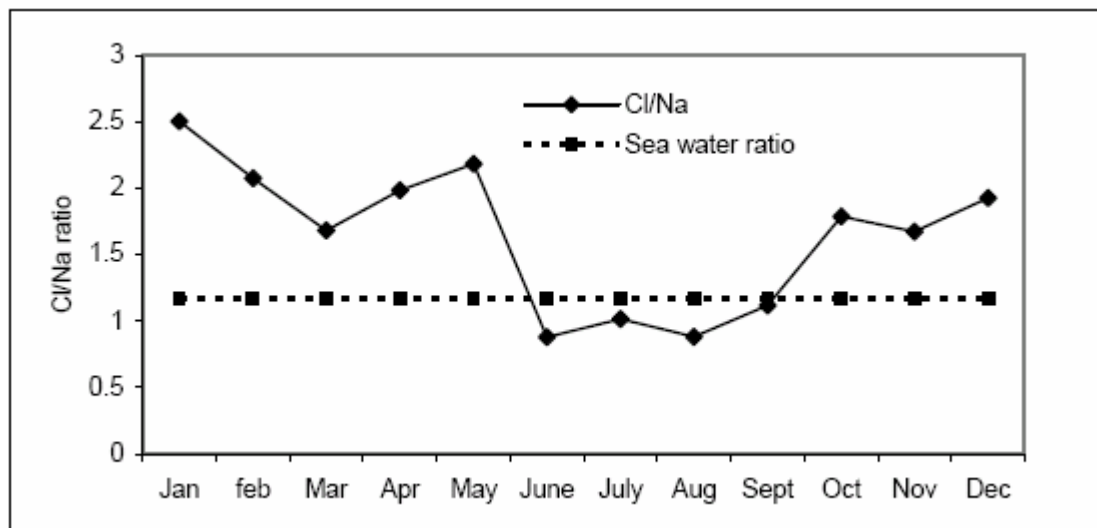


Figure 3. The month wise variation of ratio of chloride to sodium in RSPM

NH₄NO₃ in the atmosphere. Especially in cold weather, the partition of NO₃⁻ between HNO₃ and NH₄NO₃ is driven towards aerosol nitrate. Generally SO₄²⁻/NO₃⁻ ratio has been used by several research studies (Yao et al., 2002) as an indicator of the relative dominance of stationary (coal combustion, biomass burning etc) vs. mobile (vehicular emission) sources of sulphur and nitrogen in the atmosphere.

Figure 5 shows the monthly variation of the ratio of ns-SO₄²⁻ to NO₃⁻, showing the higher value throughout the year. This indicates that the stationary sources are more dominating over the mobile sources. K⁺, Ca²⁺ and Mg²⁺ were found to be present in RSPM, but in fewer amount (4.1%), on an average and show a peak during winter month and before the onset of South-West monsoon. Wind blown soil dust particles are the main source of these ions. Based on the study, Figure 6 shows the percentage contribution of aerosol from natural and anthropogenic sources.

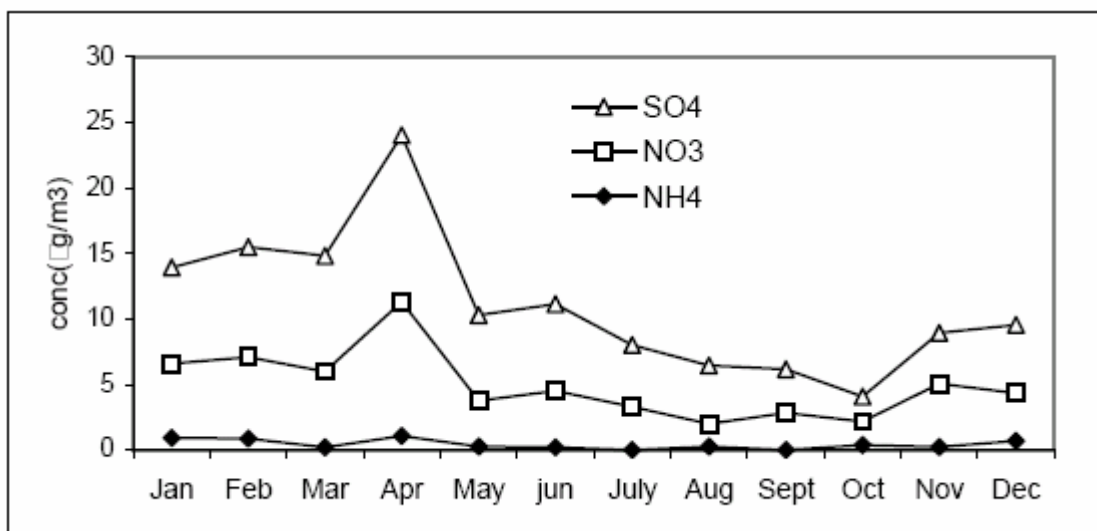


Figure 4. Monthly variation of components of anthropogenic sources

4.3 Acidity of aerosol:

The average pH of respirable aerosol sample was found to be 5.74 ± 0.4 ranging between 5.26 and 6.5. Figure 7 shows the comparison between the ratio of Σ_+ (sum of cation) to Σ_- (sum of anion) and pH. Both of them showed the similar trend. The higher enrichment of SO_4^{2-} , NO_3^- and Cl^- in the atmosphere in Darjeeling due to vehicular emission, biomass burning and also from sea salt chloride could not be neutralized by NH_4^+ , Ca^{+2} and Mg^{+2} lead to the aerosol somewhat acidic in nature.

5. Conclusion

The results obtained by the preliminary analyses for the data obtained are presented here. The water soluble ionic species are dominated by anthropogenic and sea salt aerosol. The sea salt aerosol was found to be dominated during south-west monsoon whereas contribution from anthropogenic sources was relatively high during the summer (April-May) and during the winter months (Dec-Feb).

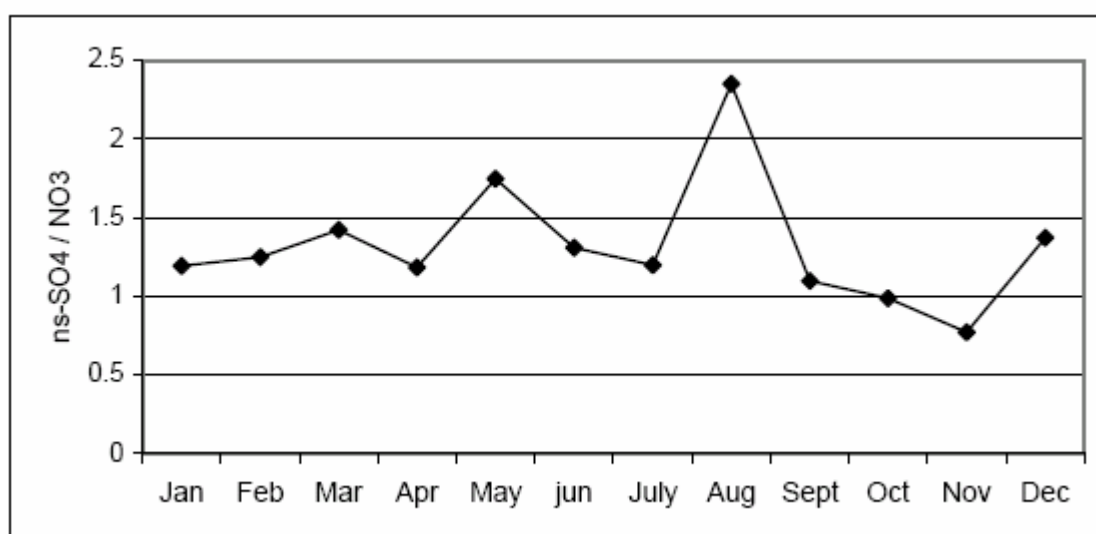


Figure 5. Monthly variation of the ratio of non-sea sulphate to nitrate

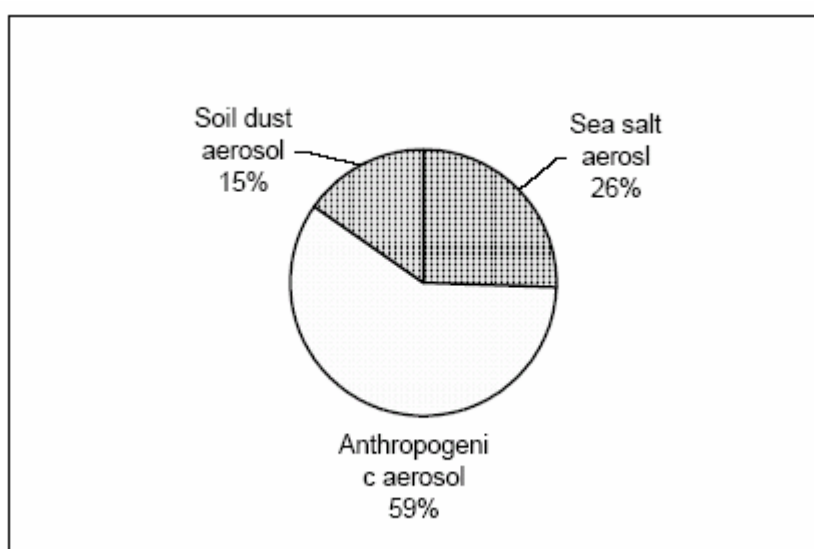


Figure 6. Total aerosol mass source apportionment

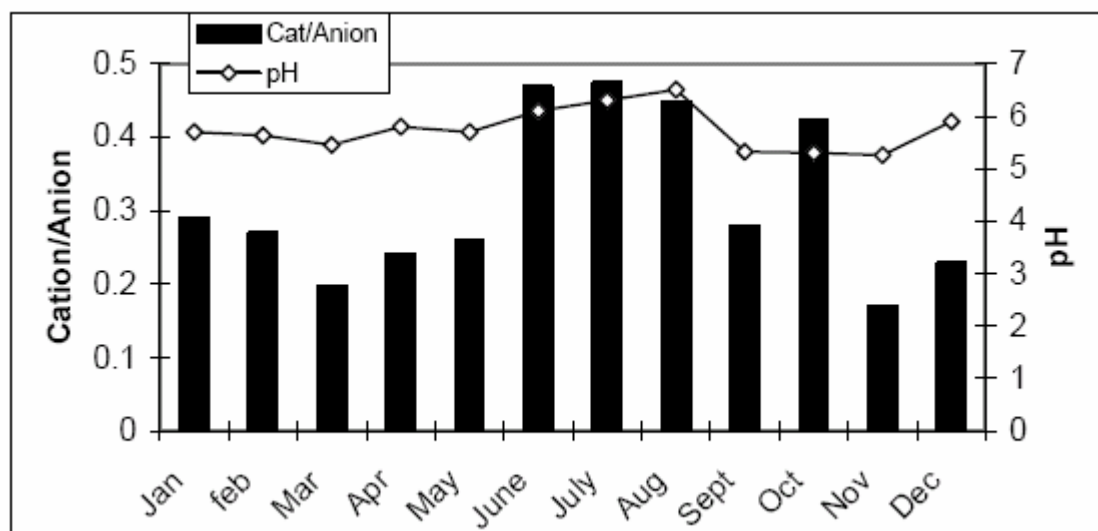


Figure 7. Monthly variation of Σ^+/Σ^- with pH of aerosol

During the monsoon period chloride depletion was found to be taken place due to the interaction of sea salt aerosol with anthropogenic constituents from the continental origin. Amongst the anthropogenic sources, the stationary sources i.e. emission of chloride and sulphate due to the biomass burning was found to be dominated over the mobile sources i.e. emission of particulate nitrate by “gas-to-particle” conversion process from the NO_x originated from the vehicular emission. The aerosol on average was found to be acidic in nature which may be due to the incomplete neutralization of highly enriched non sea sulphate and nitrate. Further analyses, however, is being performed and final results will be presented at a later stage.

6. Acknowledgements

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