Mass size distribution and chemical composition of aerosols at the Silent Valley, India*

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Field observational programmes were undertaken at the Silent Valley, a core zone of the Nilgiri Biosphere Reserve, in three different seasons during 1989-90 to study the mass size distributions of atmospheric aerosols and some of their water soluble components (SO₄, NO₃, K and Ca). The average concentration of total suspended particulates was 37 µg/m³ which is far below the values reported from urban and non-urban regions in the country. Atmospheric aerosols, SO₄, K and Ca showed bimodal distributions, whereas NO₃ showed unimodal distribution in all the three seasons. Although the aerosols showed bimodal distribution, the contribution of submicron particles was higher than that of coarse particles. This is the peculiarity of forest region which was not observed in other parts of the country where coarse particles dominate over the submicron particles. Another special feature observed was the mass size distribution of K aerosols which showed bimodal distribution with a prominent peak in the submicron size range. It has been observed from the mass size distributions of aerosols and some of their chemical components that most of them are in submicron size range, acidic in nature, and can cause acidification on precipitation in the region.

1 Introduction

Atmospheric aerosols, which are produced from various natural as well as anthropogenic sources, are a complex chemical entity. They interact with atmosphere, biogeoosphere and hydrosphere and thus play a crucial role in climatic processes that affect the entire global ecosystem directly or indirectly. Biogenically produced aerosols are studied scarcely due to lack of data from remote forest regions. Such studies are scanty in India.

Observation of mass size distributions of biogenic aerosols and their chemical components would be valuable for understanding the formation mechanisms of aerosols and their role in the control of many atmospheric processes like visibility, radiation balance, air pollution, cloud formation, acidification on precipitation, etc. For this purpose, measurements of total suspended particulates (TSPs) and their mass size distributions were undertaken at the Silent Valley, a tropical evergreen forest in Kerala, South India. These observations were taken during three consecutive seasons, namely, winter (December 1989), Summer (March-April 1990), and Monsoon (September-October 1990) for a period of 10 days in each season. The seasonal variation, sources and size distribution of aerosols and their influence on the acidification are discussed in this paper.

2 Location

The Silent Valley forests are located at the southwest corner of Nilgiris in the Western Ghat region of Peninsular India. This forest comes in the core zone of the Nilgiri Biosphere Reserve (NBR). The total extent of the Silent Valley forest is 8952 hectares. This is the least disturbed and one of the most precious tracts of tropical evergreen forests left in Peninsular India. The observational site is located at a height of 990 m ASL.

3 Sampling and analysis

TSPs were collected on Whatman 41 and quartz microfibre filter papers (8" x 10") using a high volume air sampler at a flow rate of 1.2 m³/min⁻¹. Daily three samples of 6-h duration each were collected in the morning (0600-1200 hrs), afternoon (1200-1800 hrs), and evening (1800-2400 hrs). The mass size distributions of aerosols were determined using Andersen Sampler Mark II (Andersen Inc., USA). These samples were collected on Whatman 41 (10 cm diam.) filter papers at a flow rate of 28.3 litres min⁻¹. To collect sufficient mass of aerosols, the sampling cycle of each observation was made for 3-4 days. Details of the procedure adopted in this regard are described elsewhere.

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All the samples of TSPs and size-distributed aerosols were then subjected to extraction. Standard extraction procedures were applied for getting the water soluble extracts. The concentrations of non-metallic components (SO₄ and NO₃) were determined using colorimetric methods. The concentrations of metallic components (K and Ca) were determined using Perkin Elmer 373, double beam atomic absorption spectrophotometer. Details of the procedure followed in this regard are given elsewhere.

### 4 Results and discussion

#### 4.1 Total suspended particulates

The average seasonal concentrations of TSPs, SO₄, NO₃, K and Ca are given in Table 1. The average concentration of TSPs was maximum during the summer season when the convective activity was highest. The minimum concentration was observed during the monsoon season due to the wash-out effects. The average concentration of TSPs was 37.0 μg/m³. The TSP values reported from the urban areas varied from 150 to 540 μg/m³ (Ref. 3). The recommended standard value of TSPs for sensitive areas in India is 100 μg/m³. Thus the concentration of TSPs in the Silent Valley is far below the recommended standard limit. Low TSP values have also been reported from other pollution free areas in India.

#### 4.2 Aerosol distribution

The mass size distributions of aerosols and their chemical components SO₄, NO₃, K and Ca are shown in Fig. 1. The mass size distribution of aerosols showed bimodal distribution, one peak in the coarse mode (2.1 to 3.3 μm diam.) and another peak in the submicron mode (0.43 to 0.65 μm diam.) in all the three seasons. The mass median diameters (MMDs) of aerosols were less than 2 μm in all the three seasons. It is known that the fine particles (submicron mode) are produced mainly from anthropogenic sources, and the giant particles (coarse mode) from natural sources. Although the mass size distribution of aerosols in the summer season was bimodal, the contribution of aerosols in both the modes was, by and large, equal. The high concentration of coarse particles was due to the meteorological conditions prevailing in that season. During the summer season, atmosphere generally remains unstable due to convection. Aerosols of local and land origin are continuously lifted up and they give rise to high concentrations of soil-derived elements which are in coarse size range. This can be seen from the concentrations of TSPs which are highest in the summer season. The total mass of aerosols in the submicron mode was significantly higher than that in the coarse mode during the winter and monsoon seasons. The low contribution of the particles in the coarse mode during these two seasons could be attributed to the wash-out effects due to the frequent occurrence of rainfall in SW and NE monsoon seasons.

Generally the size distributions of aerosols throughout the world are similar to that given in Fig. 1, except the difference in the percentage contributions of aerosols present in the two modes. The total mass of the aerosols in the coarse mode was reported to be higher than that in the submicron mode at a few locations in India. However, in the western countries which are highly industrialized the total mass of aerosols in the submicron mode was higher than that in the coarse mode.

The percentage contributions of the fine and coarse particles to the total aerosol mass during the three seasons are given in Table 2. The percentage contribution of fine particles in the submicron mode was higher than those of large particles in the coarse mode in the Silent Valley. This distribution is peculiar and does not agree with the distributions of aerosols reported at a few locations in India where the coarse particles dominate over the fine particles. The fine particles are mainly formed by gas-to-particle conversion processes and atmospheric pollution is the main source of these particles. The higher contribution of submicron particles in the Silent Valley does not indicate that this region is affected by the pollution sources, because the concentrations of trace gases (SO₂, NO₂, NH₃ and O₃) in this region were reported in the range of background values.

### Table 1—Seasonal variations of TSPs and their chemical components at the Silent Valley

<table>
<thead>
<tr>
<th>Concentration (μg/m³)</th>
<th>TSPs</th>
<th>SO₄</th>
<th>NO₃</th>
<th>K</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Summer</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>3.81</td>
<td>2.31</td>
<td>0.74</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td>(3.8)</td>
<td>(0.50)</td>
<td>(0.90)</td>
<td>(0.23)</td>
<td>(0.56)</td>
<td></td>
</tr>
<tr>
<td><strong>Monsoon</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1.31</td>
<td>0.52</td>
<td>0.20</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>(6.1)</td>
<td>(0.43)</td>
<td>(0.21)</td>
<td>(0.08)</td>
<td>(0.13)</td>
<td></td>
</tr>
<tr>
<td><strong>Winter</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>2.33</td>
<td>1.21</td>
<td>0.30</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>(5.8)</td>
<td>(0.85)</td>
<td>(0.39)</td>
<td>(0.14)</td>
<td>(0.25)</td>
<td></td>
</tr>
</tbody>
</table>

Note: Figures given in parentheses denote standard deviations.
Therefore, this region is, by and large, free from the transport of industrial pollution. Hence, the source of submicron particles is mainly vegetation and not the anthropogenic activities. This inference can be verified from the concentrations of the Aitken nuclei. The reaction products of terpenes exuded by vegetation have been considered to be one of the most important sources for the formation of Aitken nuclei. The average concentration of Aitken nuclei during the three seasons in the Silent Valley was reported to be around 1800 N cm$^{-3}$ (Ref. 8). The concentration of Aitken nuclei in the evergreen equatorial forest of southern Congo (Africa), which is free from industrial pollution, was reported to be 5000 N cm$^{-3}$ (Ref. 10). The average concentration of Aitken nuclei at the Silent Valley was about 2.7 times less than that reported at the Congo forest. This difference was attributed to the vegetation cover...
which is larger at the Congo forest than that in the Silent Valley forest. The forests are considered to be the main biogenic source of the submicron particles. The observations of mass size distribution of aerosols reported from the Congo forest indicated bimodal distribution with a prominent peak in the submicron mode. In the Congo forest, the submicron particles contributed 90% of the total mass of the aerosols\textsuperscript{10} which is more than that at the Silent Valley where the submicron particles contributed 65% of the total mass of the aerosols. This feature is attributed to the difference in vegetation cover at these two places. This indicates that the amount of the release of submicron particles depends on the extent of the vegetation cover.

4.3 Sulphate (SO\textsubscript{4})

Sulphate showed bimodal distribution in all the three seasons (Fig. 1). However, sulphate aerosols in the submicron mode were significantly higher than those in the coarse mode. During the winter season 82.5% of the total sulphate aerosols were in the submicron mode (Table 2). The MMDs of SO\textsubscript{4} were less than 1 $\mu$m in all the three seasons. Also, the SO\textsubscript{4} concentration in TSPs was highest among all the radials in all the seasons (Table 1). Highest concentration of SO\textsubscript{4} was observed during the summer season. The occurrence of forest fire during the dry season may be the reason for the production of submicron SO\textsubscript{4} particles which are released from biomass burning. The submicron SO\textsubscript{4} particles in tropical forests could be derived from gas-to-particle conversion during biomass burning or decomposition of biological material. Higher concentrations of SO\textsubscript{4} during dry periods were also reported from the tropical forest located in the Ivory Coast\textsuperscript{11}. The biogenic sulphur is the cause for low pH (5.3) in rain water in the Silent Valley\textsuperscript{8}. Slightly low pH (4.0 to 5.0) has been reported from the tropical forests like, San Carlos and Venezuela\textsuperscript{12}.

4.4 Nitrate (NO\textsubscript{3})

Nitrate has shown unimodal distributions in all the three seasons with a peak in the coarse mode (Fig. 1). Coarse size particles contributed nearly 70% to the total NO\textsubscript{3} in all the seasons (Table 2). The MMDs of NO\textsubscript{3} were also greater than 3 $\mu$m in all the three seasons. Concentrations of NO\textsubscript{3} in TSPs were high in the summer and low in the monsoon season (Table 1). Direct emissions of nitrogen gases during biomass burning in dry period and thunderstorm activities could be the sources for the formation of NO\textsubscript{3} in the summer season. It has been reported that by oxidation processes, NO\textsubscript{3} can be converted into NO\textsubscript{2} particles\textsuperscript{13-14}. By these processes, NO\textsubscript{3} should show a peak in the submicron size range, since it is formed by gas-to-particle conversion processes. However, the present study indicated that most of the mass of NO\textsubscript{3} was in the coarse mode rather than in the submicron mode. Under the normal atmospheric conditions, HNO\textsubscript{3} can initially form Aitken nuclei which will grow rapidly into the submicron size mode and react with ammonia to form ammonium nitrate. This reaction is reversible and is strongly temperature dependent\textsuperscript{15}. The formation of ammonium nitrate in the tropical countries is rare due to the persistence of higher temperature. However, HNO\textsubscript{3} can react with soil-derived particles and incorporate in the coarse aerosol mode\textsuperscript{16}. Hence, the coarse NO\textsubscript{3} in the present study appears to be a product of the reaction of airborne soil-dust with gaseous HNO\textsubscript{3}. Similar results are reported in Amazonia where approximately 70% of the total mass of NO\textsubscript{3} was in coarse mode\textsuperscript{17}.

Many researchers have found nitrate mass size distribution to be bimodal with one peak in submicron mode and another in coarse mode. Whereas some studies have reported that most of the mass of nitrate was in the submicron mode\textsuperscript{18-19}, others have reported it to be more in the coarse mode\textsuperscript{1-2-20}. But the chemical nature of the coarse continental NO\textsubscript{3} is unknown.

4.5 Potassium (K)

Normally the K aerosols show unimodal distribution with its peak in the coarse size range. Generally, soil is considered to be the main source of K. The bimodal distribution as observed in Fig. 1 indicates that there is another source for K in submicron size. Also, the submicron aerosols of K contributed 70% to the total mass of K aerosol during the summer and winter seasons. In addition, the MMDs of K particles in these two seasons were less than 1 $\mu$m, indicating that K aerosols in the Silent Valley are present in the submicron mode. Many researchers have attributed vegetation as the another source of K particles of submicron size in the forest areas\textsuperscript{10-21}. The plants emit submicron K particles through the respiration mechanism. Guttation may be the cause of this emission which occurs by the transport of potassium from roots to leaves and is released through stomata. This phenomenon has already been noticed by phylogist, and seems to take place under hot and humid conditions\textsuperscript{22}. Potassium has shown bimodal distribution at Trivandrum\textsuperscript{23} and unimodal distribution with a peak in the coarse size at Pune, Raichur\textsuperscript{4} and Chembur, Bombay (unpublished results). It has been observed for the first time in India that submicron particles of K aerosols are also released by vegetation.
However, the MMD of K aerosol was 2.3 μm in the monsoon season which is higher than those in the remaining two seasons. Soil is considered as the source of coarse K aerosols. Vegetation might be the source of coarse size K particles which probably might have been produced by mechanical processes like breakdown of epicuticular waxes of plant leaves.

4.6 Calcium (Ca)

The mass size distribution of Ca has shown bimodal distributions during the summer and winter seasons and unimodal distribution during the monsoon season (Fig. 1). The coarse size particles of Ca have contributed maximum to the total mass of Ca aerosol in all the seasons (Table 2). The submicron size particles of Ca have contributed about 40%, 28.5% and 15.0% respectively to the total mass of Ca aerosol during the winter, monsoon and summer seasons. The MMDs of Ca were greater than 2.5 μm in all the three seasons. The higher MMDs of Ca indicate that major part of Ca is present in the coarse mode.

Calcium aerosols in the atmosphere are mainly released from the soil and have shown unimodal distribution in other parts of the country. It is surprising to note bimodal distributions of Ca in the forest region. Although the contribution of coarse size particles in the winter season is about 60%, yet the contribution of submicron particles is about 40% which is substantial and needs explanation. At present, the authors have no direct evidence about the source of submicron Ca particles. However, it has been assumed that the submicron size particles of Ca might have been originated from the biomass burning. Similar source has been reported for the submicron size Ca particles over the Venezuelan Savannah. Also, it is suggested that plant wax constituents observed in aerosols can carry trace amounts of Ca particles. If we consider biomass burning as the source of submicron Ca particles, then the submicron SO₄ particles should also have been released from the biomass burning. Percentage contribution of SO₄ particles in the submicron mode in the summer and winter seasons (Table 2) give some indication, where the percentage contribution of submicron SO₄ particles was 75.5% and 82.5% respectively as compared to the monsoon period where it was slightly less. However, further studies are required for ascertaining the source of submicron Ca particles in forest areas.

5 Conclusion

The mass size distribution of aerosols in the Silent Valley, a core zone of the Nilgiri Biosphere Reserve, has shown different features as compared to those found in other parts of the country. The contribution of submicron particles to the total mass of the aerosol has been found to be higher in the forest area as compared to other urban and non-urban areas in the country. Vegetation has been found to be the prominent source of potassium aerosols in the forest area. Thus biogenic aerosols play a vital role in the biogeochemical cycles of various elements in the forest region. At present the man-made sources have not perturbed the ecology of this forest region. But the dominance of submicron size aerosols indicated that atmospheric aerosols in this area are acidic in nature and can cause marginal acidification in rain-water. Aerosol characteristics suggest that this area is sensitive to acidification and care should be taken to avoid installation of major industrial complexes in this region.

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References

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