

# Atmospheric aerosol characteristic studies at Pune and Thiruvananthapuram during INDOEX programme-1998

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Total suspended particulates (TSP) and mass size distribution of aerosols were monitored by using a high-volume air sampler and a low-volume 9-stage Anderson sampler, respectively during March–April 1998 at Pune and during 5–9 January 1998 at Thiruvananthapuram. All these samples were extracted for water- and acid-soluble components using the standard extraction method. The water-soluble extracts were analysed for Cl, SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub>, Na, K, Ca and Mg and acid-soluble extracts for Al, Fe, Mn, Cu, Zn, Pb, Cd, Ni and Sb. The concentration of TSP varied from 67 to 185 µg/m<sup>3</sup> with an average of 122 µg/m<sup>3</sup> at Pune and from 35 to 73 µg/m<sup>3</sup> with an average of 57 µg/m<sup>3</sup> at Thiruvananthapuram. The mass size distribution of aerosols showed bimodal distribution having one peak in coarse mode and the other in fine mode at both the locations. The results of the study are presented here.

ONE of the basic and useful indicators for judging the degree of air pollution is total suspended particulates (TSP) level. The airborne particulates may be caused by a variety of sources, e.g. natural sea spray or wind-blown dust, anthropogenic activities such as stationary fuel combustion, industrial processes, transportation and solid waste disposal. Chemical composition of these emissions varies widely. In order to trace down the pollution sources and determine the extent of the anthropogenic contribution, a fundamental study of the chemical composition and mass size distribution of atmospheric particulates is required. Several investigators have studied the chemical composition and mass size distribution of atmospheric aerosols both in India<sup>1–10</sup> and abroad<sup>11–13</sup>.

Knowledge of acidity of the atmospheric aerosols is important for the assessment of its role in the total deposition of acidity at the earth's surface. Acidic aerosol is common in the western countries<sup>14</sup>. In continental European aerosols, higher percentage of free acid has been reported in particles of size less than 0.1 µm radius<sup>15</sup>. Acidic ammonium sulphate has been observed in both urban<sup>16</sup> and non-urban areas<sup>17</sup>. In India, Khemani<sup>18</sup>

reported that the aerosols are, by and large, alkaline in nature and they give rise to alkaline pH of rain water here. The present study deals with, in view of the above points, the chemical composition of aerosols and their mass size distribution at Pune, an urban location, and at Thiruvananthapuram, a coastal location.

## Locations, sampling and analysis

The sampling site at Pune (18°32'N, 73°51'E, 559 m asl), an urban location, is on the terrace of the Indian Institute of Tropical Meteorology's (IITM) building which is at a height of about 12 m above the ground level. It is about 100 km inland from the west coast of India. It is located on the lee side of the Western Ghats (range of hills). Air-flow in the lower troposphere is predominantly westerly during the south-west monsoon (June–September) season. A large flux of moisture is brought inland from the Arabian Sea. The wind reverses as the monsoon withdraws from the region and easterly flow sets in during the post-monsoon (October–November) season. Continental air masses rich in nuclei of continental origin, pass over the region during this season. Normal weather conditions during the winter (December–February) season are clear sky and very low relative humidity.

The sampling site at Thiruvananthapuram (8°29'N, 76°57'E, 64 m asl) is on the terrace of the VSSC building at a height of about 4 m above the ground level. It is a coastal station and is situated on the southern tip of the Indian subcontinent. Majority of the rainfall occurs during the north-east (October–December) and southwest (June–September) monsoon seasons. Due to more rains when compared with the other parts of India, the soil here remains covered by vegetation throughout the year. There is no major industry located in the vicinity of the observational site.

The TSP samples were collected between 1100 and 1700 IST during March–April 1998 using high volume air sampler at a flow rate of 1.2 m<sup>3</sup>/min. The sampler is shielded from the top and does not collect large size dust particles falling under gravity. Around 400–450 m<sup>3</sup> of air was sampled during 6 h time. Mass size distribution of aerosol was measured by a multistage Anderson sampler,

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Mark-II (Anderson Inc., USA). To collect sufficient mass of aerosols for chemical analysis, the sampling cycle of each observation was made to be 4 to 5 days. The mass size distribution of TSP and its chemical components were obtained from the manufacturer's calibration for the Anderson sampler. All these samples were extracted for water- and acid-soluble components using a standard extraction method. The water-soluble extracts were analysed for Cl, SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub>, Na, K, Ca and Mg and acid-soluble extracts for Al, Fe, Mn, Cu, Zn, Pb, Cd, Ni and Sb. The details of sampling and analytical techniques used were described elsewhere<sup>4</sup>.

## Results and discussion

### Variation of TSP in different environment

The average concentration of TSP and its water soluble chemical components at Pune (March–April 1998) and Thiruvananthapuram (5–9 January 1998) are given in Table 1 along with some reported values in different environments. The concentration of TSP at Pune varied from 68 to 185  $\mu\text{g}/\text{m}^3$  with an average of 122  $\mu\text{g}/\text{m}^3$ . The concentration of TSP at Thiruvananthapuram varied from 35 to 81  $\mu\text{g}/\text{m}^3$  with an average of 57  $\mu\text{g}/\text{m}^3$ . The lower concentration of TSP at Thiruvananthapuram than that at Pune may be due to the fact that Thiruvananthapuram receives more maritime air flow and also because the land at Thiruvananthapuram is mostly covered by vegetation which prevents soil erosion. The concentration of TSP is minimum (39  $\mu\text{g}/\text{m}^3$ ) over the sea area<sup>4</sup>. The second lowest concentration (31–103  $\mu\text{g}/\text{m}^3$ ) has been observed at Gurushikar, Mt. Abu, Rajasthan<sup>9</sup>, which is a hill station and is attributed not only to the absence of anthropogenic sources in the area, but also to the elevation of the station, which is about 1.7 km above the mean sea level. It is well known that the concentration of particulates decreases with height. The 24 h annual average concentration of

TSP at different locations in Bombay region varied from 108 to 570  $\mu\text{g}/\text{m}^3$  during 1989 (ref. 19). The high concentrations are attributed to the large number of industries in that area. It is well known that the atmospheric aerosols have very high loading in urban regions. The TSP levels reported for each of the ten large cities in India have varied from 200 to 800  $\mu\text{g}/\text{m}^3$  (ref. 4). Thus the TSP levels in India, in general, are more than the US primary standard which is 75  $\mu\text{g}/\text{m}^3$  for clean air. In the north-west and central India, concentration of TSP varies from 200 to 800  $\mu\text{g}/\text{m}^3$ . This is attributed to the soil in those areas, which has very poor cohesive force and does not hold the plant's roots tightly. For this reason, the land here does not remain covered by the vegetation for most of the period. The wind erodes this type of soil easily and raises a lot of dust which contributes to high levels of particulates in the atmosphere. The areas which have high levels of TSP are Delhi 426  $\mu\text{g}/\text{m}^3$  (ref. 19) and Agra 196  $\mu\text{g}/\text{m}^3$  (ref. 10).

### Chemical composition of TSP

The chemical composition of TSP at both Pune and Thiruvananthapuram is given in Table 1. The table shows that except Ca all the other chemical components of TSP showed high concentrations at Thiruvananthapuram than those at Pune. Ca being a crustal element was found to be high at Pune due to the presence of more open soil. Marine components such as Cl, Na and Mg were obviously more at Thiruvananthapuram, being a coastal location. However, high concentrations of SO<sub>4</sub>, NO<sub>3</sub>, K and NH<sub>4</sub> at Thiruvananthapuram could be mainly due to certain natural sources such as sea and vegetative emissions. The seasalt SO<sub>4</sub> was computed for both Pune and Thiruvananthapuram which clearly indicated that, at Pune, the contribution of the sea towards total SO<sub>4</sub> was only about 5% whereas, at Thiruvananthapuram it was about 50%. Vegetative emissions have been reported as

Table 1. Chemical composition of TSP at Pune and Thiruvananthapuram

Location	TSP* range– Mean	Concentration in $\text{neq.}/\text{m}^3$										
		Cl	SO <sub>4</sub>	NO <sub>3</sub>	$\Sigma^-$	NH <sub>4</sub>	Na	K	Ca	Mg	$\Sigma^+$	$\Sigma^- - \Sigma^+$
Pune (Mar.–Apr. '98)	68–185 (122)	51	62	47	160	119	21	11	125	19	295	–135
Thiruvananthapuram (5–9 Jan. '98)	35–81 (57)	85	84	60	229	204	90	18	32	35	379	–150
Bombay region <sup>19</sup>	108–570 (267)	175	249	123	547	315	277	40	259	413	1304	–757
Agra <sup>10</sup>	– (190)	191	306	135	632	362	129	64	151	102	808	–176
Nara (Japan) <sup>24</sup>	ND	32	89	34	155	94	15	8	11	2	130	25

\*TSP in  $\mu\text{g}/\text{m}^3$ ; ND = No data.

an important source for K and N containing compounds, e.g. NO, NO<sub>2</sub>, NO<sub>3</sub>, NH<sub>4</sub>, etc.<sup>20</sup>. This source could have significantly contributed towards the high concentrations of K, NO<sub>3</sub> and NH<sub>4</sub> at Thiruvananthapuram. Also, reduced sulphur emitted from certain biogenic sources like plants is reported to be a source of SO<sub>4</sub> aerosols<sup>21</sup> which could have resulted in the addition to the SO<sub>4</sub> aerosol at Thiruvananthapuram.

Table 1 also shows the ionic balance in TSP at both Pune and Thiruvananthapuram. It can be seen that at both the locations, cations dominated over the anions which indicates the alkaline nature of the aerosols. Thus, even though the concentrations of acidic ions such as SO<sub>4</sub> and NO<sub>3</sub> were substantial, the overall neutralizing capacity of alkaline ions such as Ca, NH<sub>4</sub>, Na, K and Mg have kept the nature of the aerosols in the alkaline range. Besides seasalt (Cl and Na) the concentrations of SO<sub>4</sub>, NO<sub>3</sub> and Ca were quite substantial compared to K and Mg. Seasalt is considered to be neutral and will not cause the acidification of aerosol.

Table 2 indicates the chemical composition of acid-soluble fractions of TSP at Pune. It is seen that, among all the measured metals, Fe and Al showed high concentrations which again points towards the dominance of the crustal source. Concentrations of Pb, Cd and Sb were below the detection limits.

#### Mass size distribution of aerosol

Figure 1 gives the mass size distribution of aerosol and their chemical components (Cl, SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub>, Na, K, Ca and Mg) at Pune and Thiruvananthapuram. The aerosols showed bimodal distribution, with one peak in the fine size range (0.65 µm) and other peak in the coarse range (3.3 µm) at both the locations. The particles in the fine size range are produced by the gas-to-particle conversion processes and are contributed by the anthropogenic sources, whereas the particles in the coarse size range are

contributed by natural sources like sea and soil. Table 3 shows the percentage contribution of fine and coarse size modes to the total aerosol load. The contribution of coarse particles was 58% and 67% to the total mass of the aerosol at Pune and Thiruvananthapuram, respectively and the contribution of fine particles was 42% and 33%. The total mass of coarse particles was larger than that of fine particles. The coarse particles dominate in India whereas the fine particles dominate in the western countries<sup>4</sup>.

At Pune, all the ionic components of TSP showed unimodal distributions, except SO<sub>4</sub> and NH<sub>4</sub>, whereas at Thiruvananthapuram, except for the Ca and Mg, all the ionic components showed bimodal distributions. K showed unimodal mass size distribution at Pune with its peak in the coarse size range, indicating the main source of K to be the soil. On the other hand, it showed bimodal distribution at Thiruvananthapuram with a peak in the fine mode besides a coarse mode peak, indicating the presence of some other source of K, than the soil. It may be seen from Table 3, that 80% of the total mass of K aerosol is contributed by submicron particles only. Thiruvananthapuram being a coastal location in the tropics, the climate of that region is hot and humid and most parts of the region are covered with green vegetation. Hence, vegetation may be one of the major contributors for the high percentage of fine size K in the aerosol as vegetation emits K particles through its respiration. Guttation may be the cause of this emission which occurs by the transport of K from the roots to the leaves and is released through the stomata.

Table 4 shows the modal diameters (MDs) and mass median diameters (MMDs) of TSP and its chemical constituents. It is seen that at both the locations, SO<sub>4</sub> and NH<sub>4</sub> showed MMDs < 2.0 µm. At Thiruvananthapuram, NO<sub>3</sub> and K also showed MMDs < 2.0 µm. Generally the components with MMD > 2.0 µm are produced by natural sources whereas those with MMD < 2.0 µm are produced from man-made sources<sup>18</sup>. However, at Thiruvananthapuram, certain natural sources (sea, vegetation) could also be contributing towards SO<sub>4</sub>, NH<sub>4</sub>, NO<sub>3</sub> and K, along with man-made (biomass burning) sources.

Chloride showed unimodal distribution at Pune with a peak in coarse size. Whereas at Thiruvananthapuram, it showed bimodal distribution with a peak in fine and coarse mode. However, the contribution in the fine size was less. The relatively small amount of fine size Cl, could be a result of surface reactions of HCl with pre-existing aerosol, possibly K, Na and Ca in the fine size.

Nitrate showed significantly high contribution in the coarse size (~80%) at Pune which indicated crustal source. According to Wolff<sup>23</sup>, the coarse continental nitrate could result from the absorption of HNO<sub>3</sub> vapours on coarse crustal elements like Ca, Al or Fe.

Table 2. Chemical composition of acid-soluble fraction of aerosol at Pune during March–April 1998

Component	Concentration (ng/m <sup>3</sup> )			
	Min.	Max.	Ave.	S.D.
Cu	53	550	230	144
Zn	9	76	45	20
Mn	29	106	53	16
Fe	1980	5430	3340	790
Al	1330	4890	2810	870
Ni	0.4	7.1	1.2	1.2
Pb	BDL	BDL	BDL	–
Cd	BDL	BDL	BDL	–
Sb	BDL	BDL	BDL	–

BDL – Below detection limits.

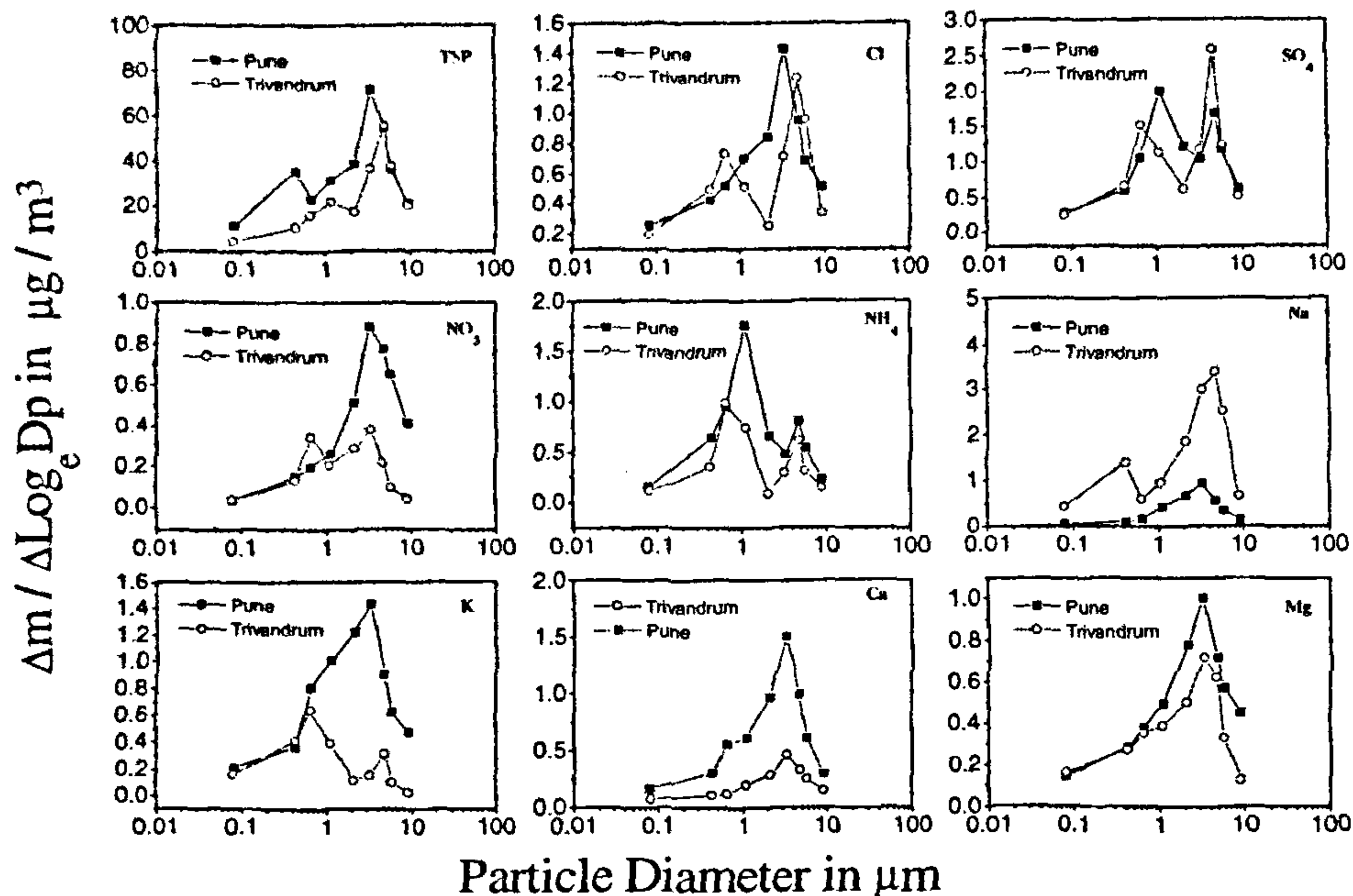


Figure 1. Size distribution of TSP and its chemical components.

Table 3. Percentage contribution of aerosols and their chemical components in fine and coarse modes

Location	Mode	Aerosol	Cl	SO <sub>4</sub>	NO <sub>3</sub>	NH <sub>4</sub>	Na	K	Ca	Mg
Pune	Fine (< 2 μm)	42	41	52	21	65	31	44	37	36
	Coarse (> 2 μm)	58	59	48	79	35	69	56	63	64
Thiruvananthapuram	Fine	33	48	52	52	70	34	80	38	48
	Coarse	67	52	48	48	30	66	20	62	52

Table 4. Modal diameters and mass median diameters of aerosols

Chemical components	Pune		Thiruvananthapuram	
	MD (μm)	MMD (μm)	MD (μm)	MMD (μm)
TSP	0.43, 3.30	2.91	1.10, 3.70	4.08
Cl	3.30	2.94	0.65, 4.70	2.62
SO <sub>4</sub>	1.10, 4.70	1.98	0.65, 4.70	2.62
NO <sub>3</sub>	3.30	4.22	0.65, 3.30	1.92
NH <sub>4</sub>	1.10, 4.70	1.55	0.65, 4.70	1.24
Na	3.30	3.22	0.43, 4.70	3.53
K	3.30	2.47	0.65, 4.70	0.85
Ca	3.30	3.30	3.30	2.94
Mg	3.30	3.20	3.30	2.16

Table 5. Aerosol factor loadings at Pune

Element	Factor 1	Factor 2	Factor 3	Factor 4
TSP	0.605			
Cl				0.631
SO <sub>4</sub>			0.620	
NO <sub>3</sub>	0.564			
NH <sub>4</sub>			0.803	
Na				0.671
K		0.920		
Ca	0.647			
Mg				0.562
Zn		0.700		
Mn	0.881			
Fe	0.850			
Al	0.708			
Eigenvalue	3.750	2.590	2.160	1.170
% Variance	30.80	21.500	18.40	10.4
Cumuli. % variance	30.80	52.3	70.70	81.1

*Source apportionment of aerosols*

The information about source identification of aerosols at the sampling location (Pune) was obtained through varimax rotated factor analysis. The factor loadings of elements in aerosols are given in Table 5. There are 4 factors with eigenvalues cut-off at unity. The eigenvalues and the percentage variance indicated the strength of the source. The 4 factors explained about 81% of the total variance indicating that the 4-factor model is satisfactory at Pune. As the number of samples collected at Thiruvananthapuram was limited, the factor analysis was not carried out. The first factor shows high loadings for TSP, Al, Fe, Mn and Ca, indicating the crustal source. The second factor shows significant loadings for K, Zn and NO<sub>3</sub> and may be attributed to the biomass and refuse burning. The third factor shows high loadings for SO<sub>4</sub> and NH<sub>4</sub>, indicating a common source for both, which again confirms that they could be in the molecular form (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The fourth factor shows high loadings for Cl, Na and Mg, indicating a marine source.

**Conclusions**

The study of the total suspended particles and mass size distribution of aerosols at Pune and Thiruvananthapuram during INDOEX Intercomparison Programme revealed the following:

1. The average concentration of TSP at Thiruvananthapuram (57 µg/m<sup>3</sup>) was found to be lower than at Pune (122 µg/m<sup>3</sup>). This may be attributed to more vegetative cover at Thiruvananthapuram which prevents soil erosion.
2. The chemical composition of TSP showed that the cations dominated the anions at both the locations. This feature indicates that the aerosols are alkaline in nature.
3. The mass size distribution of aerosols were found to be bimodal at both the locations with the dominance of coarse particles over the fine particles. This suggests that the natural sources contributed more than the man-made sources to the total aerosol loading.
4. The maximum percentage contribution of K in fine size at Thiruvananthapuram may be due to vegetative emissions. High concentration of NO<sub>3</sub> in the coarse size at Pune indicates that it could be originating from the crustal source. Besides the pronounced peak in the coarse size, the additional peak of Cl in the fine size at Thiruvananthapuram could be attributed to the surface reaction of HCl possibly with K, Na or Ca.

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