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A preliminary study of the characteristics of aerosols over Pune and Srinagar

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सार — मई महीने के दौरान पुणे और श्रीनगर में कुल प्रलंबित विविक्त द्रव्य (टी.एस.पी.एम.) प्रतिदर्शित, स्टैप्लेक्स (सं.रा.अ.) की सहायता से एअरोसोल के नमूने एकत्रित किए गए। द्रव्यमान सघनता के साथ-साथ एअरोसोल के रसायनिक अवयवों (जल विलयशील अंश) को प्राप्त किया गया और उपरोक्त मापों के परिणामों को प्रस्तुत किया गया है।

माप प्रदर्शित करते हैं कि टी.एस.पी.एम. पुणे में उनकी उत्पति औद्योगिक तथा भूपृष्ठीय (मृदा) दोनों उद्गमों से होती है। और श्रीनगर मे अधिकांशत: भूपृष्ठीय उद्गम से है, और द्रव्यमान सघनताओं दोनों स्थानों पर समान है। NH_4 और SO_4 के बीच सहसम्बन्ध और सघनताओं के अध्ययन प्रदर्शित करते है कि उपरोक्त अवयवों का अधिक अंश पुणे में $(NH_4)_2 SO_4$ के रूप में होता है दोनों ही स्थानों में अम्ल और क्षार में तुल्यमान (क्षार–अम्ल) धनात्मक या जिससे संकेत मिलता है कि दोनों ही स्थानों पर जल का pH क्षारीय परिसर के अन्दर होगा, इसकी पुष्टि वर्षाजल के pH आंकड़ों से भी की गई है जो कि पुणें और श्रीनगर के लिए उपलब्ध हैं।

ABSTRACT. Aerosol samples were collected at Pune and Srinagar during the month of May 1981 using the Staplex (USA) total suspended particulate matter (TSPM) sampler. Mass concentration as well as the various chemical constituents (water soluble fraction) of aerosols were obtained and the results of the above measurements are presented.

Measurements show that TSPM at Pune owe their origin to both industrial and crustal (soil) sources whereas at Srinagar they are mainly of crustal origin and mass concentrations at both the places are similar. Study of correlation between NH_4 and SO_4 and ratio of concentrations indicate that good fraction of the above constituents existed in the form of $(NH_4)_2 SO_4$ at Pune. At both the places, the balance between base and acid was positive (base-acid) which suggests that pH of rainwater at both the places would be in the basic range. This is substantiated also from pH data of rainwater which are available from Pune and Srinagar.

1. Introduction

Aerosols play an important role in the precipitation chemistry and study of the characteristics of aerosols can give vital information regarding the likely acidity of precipitation. Study of chemical composition of aerosols can also help in understanding the mechanism of generation of atmospheric aerosols and their role in the formation and growth of cloud drops. Due to various reasons only a few studies have been carried out on aerosols in India. Recently, Krishna Nand (1984) had pointed out the importance of aerosols in increasing the pH of precipitation samples over India. He had conjectured that high pH over Srinagar which is a hill station may be due to the presence of high cation concentrations (indicating high concentration of aerosols) which was quite effective in neutralizing the anions in precipitation. Above presumption looks a little odd in view of the fact that Srinagar is a hill station and aerosol concentrations are expected to be low. In order to verify the above presumption and also to understand the chemical characteristics of aerosols, sampling of aerosols was carried out at Srinagar (Lat. 34° 05′ N, Long. 74° 50′ E, elevation 1587 m) during May 1981. For comparison purposes aerosols sampling was also carried out at Pune simultaneously (Lat. 18° 32′ N, Long. 73° 51′E, Elev. 559 metre m.s.l.). Mass concentration of aerosols as well as the water soluble fraction regarding sulphate, nitrate, chloride, ammonium, sodium, calcium, potassium and magnesium was obtained. Analyses for sodium, calcium, potassium and magnesium were got done from Indian Institute of Tropical Meteorology, Pune. Results of the above studies are presented in this paper.

2. Details of sampling and site

Total suspended particulate matter at Srinagar and Pune was collected on Whatman No. 41 filter paper (10 cm diameter) using a high volume air sampler (Staplex, USA). The rate of sampling was about 0.7 m^3/min and the sampling period was 3 hours. Sampling was done simultaneously at both the sites in the morning (0800-1100 hr) and afternoon (1400-1700 hr).

3. Meteorological condition and pollution sources surrounding the station

Pune is about 100 km away on the leeward side from the west coast. It is an elevated station. Month of May

TABLE 1

Details of sampling of TSPM and meteorological conditions at Pune

Sample No.	Date (May 1981)	Sampling hours (IST)	Mean RH (%)	Mean Temp. (°C)	Mean wind velocity (kmph)	Wind direction	TSP ($\mu g/m^3$)
1	25	0800-1100	75	29.0	12	W	313.5
2	25	1400-1700	37	36.0	12	WNW	323.2
3	26	0805-1100	79	34.0	9	WNW	294.5
4	26	1410-1704	34	38.0	11	NW	328.8
5	27	0850-1145	75	31.0	10	NW	262.1
6	27	1405-1700	37	34.5	11	NW	318.0
7	28	0820-0935	77	29.0	9	NW	504.2
8	29	0820-1115	79	27.0	7	W	203.2
9	29	1418-1710	35	36.0	10	WNW	276.8
10	30	0820-1115	81	29.0	7	WNW	251.2

TABLE 2

Details of sampling of TSPM and meteorological conditions at Srinagar

Sample No.	Date (1981)	Sampling hours	Mean RH (%)	Mean Temp. (°C)	Mean wind velocity (kmph)	Wind direction	TSP ($\mu g/m^3$)	Remarks
1	24 May	1400-1700	29	31.0	Calm	—	320.6	
2	25 ,,	0800-1100	63	24.0	2.0	W	238.9	
3	25 ,,	1400-1700	33	31.5	Calm	—	360.3	
4	26 ,,	0800-1100	58	23.0	1	NE	390.6	
5	26 ,,	1400-1700	40	28.0	2	W	530.0	Rain
6	27 ,,	0800-1100	54	20.0	1	SE	260.8	
7	27 ,,	1400-1700	30	28.0	1	S	327.8	
8	28 ,,	0800-1100	58	22.0	1	SE	387.3	
9	28 ,,	1400-1700	37	30.0	Calm	—	299.3	
10	29 ,,	0800-1100	57	22.0	2	SE	301.0	
11	29 ,,	1400-1700	26	28.0	3	NNW	297.5	
12	30 ,,	0800-1100	82	15.0	5	S/NW	344.5	Rain
13	30 ,,	1400-1700	94	16.0	3	S	299.4	Rain
14	31 ,,	0800-1100	98	13.5	2	S	302.8	
15	31 ,,	1400-1700	92	15.0	3	W	332.0	
16	1 Jun	0800-1100	94	16.1	1	NNW	355.5	
17	1 Jun	1400-1700	75	20.0	Calm	—	402.7	

TABLE 3

Concentration of chemical constituents (water soluble fraction) of TSPM at Pune ($\mu g/m^3$)

Sample No.	SO_4	NO_3	Cl	NH_4	Ca	Na	K	Mg
1	0.90	1.48	0.45	0.38	0.61	1.12	0.22	0.29
2	1.16	0.12	0.83	0.02	0.91	1.68	0.37	0.46
3	0.76	0.06	0.98	0.07	0.77	1.50	0.43	0.43
4	1.94	1.44	1.77	0.38	0.97	2.15	0.35	0.26
5	0.65	0.59	1.42	0.15	0.47	1.69	0.23	0.38
6	4.49	1.37	1.77	1.21	0.80	1.44	0.24	0.44
7	0.56	Trace	2.62	0.11	1.10	5.44	0.54	0.81
8	0.03	0.44	1.72	0.03	0.63	2.21	0.34	0.34
9	0.65	1.87	1.23	0.78	0.73	2.14	0.37	0.44
10	0.16	0.76	1.72	—	0.74	2.61	0.60	0.37
Mean	1.08	0.81	1.45	0.35	0.77	2.20	0.37	0.42

during which sampling had been carried out is part of summer season. Surface winds at the station are mainly westerly and are fairly strong (mean >3 kmph) during May. Surface temperatures remain quite high (mean $\simeq 30°$ C). The above factors associated with low relative humidity (mean 47%) are favourable for high TSPM concentrations during May. There are number of industries in N and NW sector of the station.

Srinagar is a hill station with comparatively low surface temperature (mean $\simeq 18°$ C) and wind speed (mean 4.3 kmph) but high relative humidity (mean 60%). Since rainfall at Srinagar is well distributed throughout the year, wind blown local soil dust contribution to TSPM is expected to be low. However, since the station is surrounded by a few brick kilns, they may contribute to TSPM concentrations.

TABLE 4

Concentration of chemical constituents (water soluble fraction) of TSPM at Srinagar ($\mu g/m^3$)

Sample	SO_4	NO_3	Cl	NH_4	Ca	Na	K	Mg
1	Trace	0.44	0.20	0.16	0.68	0.53	0.25	0.11
2	0.07	1.70	0.44	0.37	0.79	0.65	0.27	0.15
3	0.07	1.02	0.39	0.09	1.26	0.81	0.49	0.13
4	0.32	2.94	0.25	0.49	1.37	1.09	0.54	0.27
5	0.43	1.77	0.46	0.27	1.71	1.53	0.86	0.18
6	0.15	0.28	0.26	0.21	0.35	0.51	0.17	0.07
7	0.45	0.86	0.25	0.03	0.47	0.82	0.26	0.06
8	0.15	1.05	0.65	0.19	1.42	1.05	0.43	0.13
9	Trace	1.05	0.22	0.06	1.03	0.38	0.29	0.13
10	0.62	1.68	0.01	0.09	0.79	0.99	0.28	0.14
11	0.36	0.42	Trace	0.05	0.54	0.60	0.31	0.06
12	0.32	0.39	0.49	0.04	0.61	0.69	0.49	0.13
13	Trace	0.49	0.49	0.23	0.54	0.51	0.40	0.14
14	0.18	0.17	0.34	0.17	0.31	0.73	0.27	0.06
15	0.18	0.45	0.15	0.49	0.48	0.64	0.37	0.12
16	0.36	0.54	0.27	0.23	1.36	0.70	0.48	0.22
17	Trace	Trace	0.28	0.15	1.20	0.87	0.44	0.12
Mean	0.21	0.90	0.30	0.19	0.89	0.77	0.39	0.13

4. Analysis of TSPM samples

Water soluble extract of TSPM was analysed for chloride, sulphate, ammonium, nitrate, calcium, sodium, potassium and magnesium. Chloride, sulphate, ammonium and nitrate ion concentrations were estimated colorimetrically. Details of the analytical techniques are given elsewhere (Maske and Krishna Nand 1982). Calcium, sodium, potassium and magnesium ion concentrations were estimated using the atomic absorption spectrophotometer. Mass concentration of aerosols collected on filter papers was obtained by utilizing the following Eqn. (1) :

$$\bar{C} = \frac{W}{Q\,(t_2 - t_1)} \qquad (1)$$

where,

W = Weight of TSPM in μg.

Q = Sampling flow rate (m^3/min).

$t_2 - t_1$ = Sampling period (minutes).

5. Results of analysis

10 samples were collected at Pune from 25 to 30 May 1981 and 17 samples were collected at Srinagar from 24 May to 1 June 1981. Details regarding the date of sampling, sampling duration, wind direction and speed, relative humidity and TSPM concentrations are given in Tables 1 and 2 for Pune and Srinagar respectively. Concentration of various chemical constituents (water soluble fraction) of TSPM are given in Tables 3 and 4 for Pune and Srinagar respectively.

6. Discussions

6.1. *Concentration of TSPM and chemical constituents*

Concentrations of various chemical constituents and TSPM show large variation (Tables 1-4) at Pune and Srinagar. TSPM concentrations varied between 200 and 500 $\mu g/m^3$. In general, TSPM concentrations were lower during morning (0800-1100) in comparison to afternoon hours. Quite surprisingly, mean TSPM concentrations at Pune and Srinagar are not very different ($\simeq$ 300 $\mu g/m^3$). TSPM concentrations also appear to be independent of wind direction indicating that particulate matter are of background nature at both the places.

There are significant differences in the concentration of chemical constituents between Pune and Srinagar. In general, concentrations are higher at Pune. Quite interestingly, nitrate concentration (mean value, 0.90 $\mu g/m^3$) is higher than sulphate concentration (mean value, 0.21 $\mu g/m^3$) at Srinagar which is opposite to the trend as observed at Pune. It suggests that in precipitation, nitrate concentration would be higher than sulphate at Srinagar. This is substantiated from the measurements as carried out for the precipitation sample for the month of May 1981 ($SO_4 \simeq$ 1ppm and $NO_3 \simeq 4$ ppm). Low concentration of sulphate at Srinagar is indicative of comparatively less anthropogenic production of SO_2. Almost similar value of calcium concentration at Pune and Sringar is quite striking and it has a special significance in terms of neutralization of acidity of rainwater (Krishna Nand 1984, Stensland and Semonin 1982).

The value of the ratio Cl/Na at Pune is higher (0.69) than at Srinagar (0.40). Even though monsoon season at Pune starts from 1 June, some influence of maritime air contributing to chloride concentrations and thus increasing the Cl/Na ratio cannot be ruled out. At Pune, during monsoon, typical Cl/Na ratio may be about 1.3 (Khemani *et al.* 1983). The mole ratio of Cl/Na at Pune is about 0.45 which indicates that in the aerosols at Pune, Na and Cl are not in the form of NaCl. At Srinagar also, Na and Cl are not in form of NaCl.

Mass ratios of ammonium to sulphate at Pune (0.44) and Srinagar (1.40) are quite different. The ratio value at Srinagar is significantly different than the value (0.37) corresponding to the molecular formula $(NH_4)_2\,SO_4$. However, Pune ratio is quite close to the value corresponding to $(NH_4)_2\,SO_4$. It indicates that significant fractions of NH_4 and SO_4 are in the form of $(NH_4)_2\,SO_4$ at Pune. Khemani *et al.* (1982) had also found that during the monsoon season the molecular composition of the particulates is in the form of ammonium sulphate.

6.2. *Correlations between various chemical constituents*

TSPM correlations at Pune with Na (0.71), Ca (0.77), Mg (0.79) are significant at 1 per cent level whereas at Srinagar TSPM correlations with Na (0.83), Ca (0.76) and K(0.91) are significant at 0.1 per cent level. It suggests that correlations at Pune are less significant in

comparison to Srinagar. Same is true for cross correlations between various chemical constituents. Above observations indicate that at Pune, the chemical constituents owe their origin to both industrial and crustal (soil) sources whereas at Srinagar all the constituents appear to be of crustal (soil) origin. This is not surprising considering the fact that quite good number of industries at Pune are situated in N/NW sector of the sampling station and on number of occasions the winds during the sampling period were from NW direction.

Quite interestingly, correlations at Pune between NH_4 and SO_4(0.79) and between NH_4 and NO_3 (0.76) are significant at 1 per cent level. Significant correlation between NH_4 and SO_4 when viewed in light of its ratio at 0.44 suggests that good fraction of NH_4 and SO_4 may be in the form of $(NH_4)_2\ SO_4$.

Sulphur compounds in the TSPM at Pune could originate in a number of ways. It is possible that NH_4 and SO_4 were initially emitted in gaseous form and then converted by chemical processes in the atmosphere into particulates. This is a commonly observed pathway in comparatively polluted atmosphere where SO_2 is oxidized to H_2SO_4 and is then neutralized by ammonia gas (Cox and Penkett 1970). It is also possible that NH_4 and SO_4 were picked up by the wind in a similar manner to the rest of the constituents. However, this can be verified only if size distribution of aerosols is studied.

Khemani *et al.* (1983) had observed significant (at less than 1 per cent level) correlation between ammonium and nitrate concentrations during winter at Pune. It was conjectured that formation of nitrate may take place through the following reaction :

$$NH_3 + HNO_3 \rightarrow NH_4\ NO_3$$

It appears that the above hypothesis is valid for the present measurement also.

Significant correlation (at 1 per cent level) between Cl and Na (0.80) at Pune indicates the influence of maritime air during the month of May.

6.3. *Influence of meteorological factors on TSPM*

In general, insignificant correlations between meteorological parameters such as wind speed, temperature and humidity and TSPM have been observed at both the places. However, the correlations are in right direction. For example, negative correlation with humidity is physically correct, similarly positive correlations with temperature and wind speed are in right sense. In addition to above, various chemical constituents have also not been found to be significantly correlated with meteorological parameters.

6.4. *Acid/base potential of TSPM*

Study of the acid/base potential of aerosol is quite important from the point of acidity of rainwater. In India, pH of rainwater is in general in basic range (Krishna Nand 1984). Acid/base potential of the TSPM at Pune and Srinagar have been compared. Bases taken for the study are Na, Ca, K, Mg and NH_4 whereas, acids are Cl, NO_3 and SO_4 (in terms of micro eq./m^3). It is interesting to note that at both the places the balance is positive (base/acid); mean values 0.10 and 0.08 at Pune and Srinagar, respectively. It indicates that pH of rainwater at both the places would be in the basic range. Further, the base concentration at Pune is dominated by Na. It is, therefore, expected that pH at Pune would be lower than Srinagar since a fraction of Na is expected to be in the neutral form which may not take part in neutralization reactions. In addition to above, direct dissolution of gases like SO_2 and NOx in raindrops inside the cloud (Mukherjee 1979) and while falling through the atmosphere at Pune which is somewhat more polluted than Srinagar can also decrease the pH to some extent. Above inferences are substantiated from the pH observations of rainwater samples at Pune (6.40) and Srinagar (6.70). pH values are annual mean for the year 1981.

7. Conclusions

(1) Mean concentration of TSPM at Pune and Srinagar was similar ($\simeq$300 μg/m^3). However, the source of such high concentration of TSPM at Srinagar is not clearly evident. There are significant differences in the chemical constituents (water soluble fraction) of TSPM at Pune and Srinagar. In general, concentrations are higher at Pune.

(2) Nitrate concentration is higher than sulphate at Srinagar which is opposite to that observed at Pune. High value of NO_3 in comparison to SO_4 as observed in monthly rainwater sample for May 1981 at Srinagar substantiates the above observation.

(3) At Pune, concentrations of NH_4 are well correlated with SO_4 and NO_3 and the ratio of NH_4 to SO_4 concentration was about 0.44. Above observations indicate that good fraction of the above constituents existed in the form $(NH_4)_2SO_4$ and NH_4NO_3.

(4) TSPM concentrations at Srinagar are well correlated with Na, Ca and K suggesting that probably all the above constituents are of crustal origin (soil derived). At Pune, chemical constituents owe their origin to both industrial and soil sources.

(5) At both the places, the balance between base and acid is positive (base-acid) which suggests that pH of rainwater at both the places would be in the basic range. This is substantiated also from pH data of rainwater which are available from Pune and Srinagar.

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References

Cox, R.A. and Penkett, S.A., 1970, 'The photo-oxidation of sulphur dioxide in sunlight', *Atmos. Environ.*, **4**, 425.

Khemani, L.T., Momin, G.A., Naik, M.S., Vijaykumar, R. and Ramanamurty. Bh. V., 1983, 'Chemical composition and size distribution of atmospheric aerosols over the Deccan Plateau, India', *Tellus*, **34**, 2, 151-158.

Krishna Nand, 1984, 'Prospects of Acid rain over India', *Mausam*, **35**, 2, pp. 225-232.

Maske, S.J. and Krishna Nand, 1982, 'Studies on Chemical Constituents of precipitation over India', *Mausam*, **33**, 2, pp. 241-246.

Mukherjee, A.K., 1979, 'Dissolution of gases in rain', communication a la VIII eme conference internationale sur la Physique des nuages, Clermont-Ferrand, France, pp. 169-172.

Stensland, G.J. and Semonin, R.G., 1982, 'Another interpretation of the pH trend in the United States', *Bull. Am. met. Soc.*, **63**, 11.