Studies of trace gases and Aitken Nuclei at inland and coastal stations – A part of INDOEX programme

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As a part of the Indian Ocean Experiment (INDOEX) programme, ground-based measurements of trace gases (SO_2, NO_2, NH_3 and O_3) and Aitken Nuclei (AN) were carried out at Pune during March–April 1998. Also, measurements of surface ozone and AN were made during 5–10 January 1998, the inter comparison campaign of various instruments at Thiruvananthapuram. The mean concentrations of SO_2, NO_2, NH_3 and O_3 at Pune were 3.75, 5.81, 3.21 and 57.8 $\mu g/m^3$ respectively and that of O_3 at Thiruvananthapuram was 44 $\mu g/m^3$. The average concentration of AN was about five times higher at Pune (19,000/cm^3) than that at Thiruvananthapuram (4,400/cm^3), indicating more pollution at Pune than at Thiruvananthapuram. The diurnal variation of surface ozone showed high concentrations during the day and low concentrations during the night at both the locations. Diurnal variation of AN at Pune showed a daytime maximum and a night-time minimum. Whereas, at Thiruvananthapuram night-time values were higher than the daytime values which can be attributed to the influence of the land and sea breeze.

ATMOSPHERIC gaseous and particulate pollutants are of great concern on account of their role in radiative forcing and effects on human health. The study of the trace gases is important for understanding the formation mechanisms of the secondary aerosols and their influence on climate change. As SO_2 and NO_2 are the major acid rain precursors, they have much importance in the acid rain studies. Aitken Nuclei (AN) play a vital role in several atmospheric studies related to atmospheric electricity, atmospheric chemistry, air pollution, cloud phenomena and radiative forcing.

As a part of the Indian Ocean experiment (INDOEX) programme, ground-based measurements of trace gases (SO_2, NO_2, NH_3 and O_3) and AN were undertaken at Pune during March–April 1998. Also, measurements of surface ozone and AN were made during the intercomparison campaign of various instruments at Thiruvananthapuram during 5–10 January 1998. The comparison of concentrations of ozone and AN at Pune, an inland location with those at Thiruvananthapuram, a coastal location and their diurnal variations are discussed here.

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Sampling locations and measurements

The sampling site at Pune (18°32′N, 73°51′E, 559 m asl), an urban location, is on the terrace of the Tropical Meteorology Institute's building, at a height of about 12 m above the ground level. It is about 100 km inland from the west coast of India and is located on the lee side of the Western Ghats (range of hills). Airflow 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 prevail during the winter (December–February) season with clear sky and very low relative humidity.

The sampling site at Thiruvananthapuram (8°29′N, 76°57′E) is on the terrace of the VSSC building, at Thumba at a height of about 5 m above the ground level. It is a coastal station, situated on the southern tip of the Indian subcontinent. The majority of rainfall occurs during the south-west (June–September) and north-east (October–December) monsoon seasons. Due to more rains in a year when compared with other parts of India, the soil remains covered here by vegetation throughout the year.

Aitken Nuclei Counter

Aitken Nuclei Counter (ANC) (Gardner Associates Inc., USA) was used to measure the total concentration of sub-micron particles (AN) in the size range 0.001 to 0.1 μm radius. This instrument works on the principle of the cloud chamber. When sub-micron particles are injected into a chamber containing saturated vapour, the vapour condenses on these particles to form droplets. In this instrument, atmospheric air is pumped into a small chamber at a pre-set pressure and slowly injected into the main

chamber containing water vapour. The vapour in this chamber is subjected to adiabatic expansion to achieve super saturation. The saturated vapour condenses on the Aitken particles present in the sampled air to form a cloud, which is illuminated by a light source. The scattered light intensity, which is proportional to the number of particles, is measured. From this, the number of droplets per unit volume or equivalently the number of AN in the sampled air is measured. It gives the direct analog display of AN in N cm^{-3}. The hourly concentrations of AN were measured.

UV photometric O_3 analyser

The UV Photometric O_3 analyser (Thermo Environmental Instruments Inc., USA) was used to measure the surface ozone concentration. It determines ozone concentration by measuring the attenuation of light due to ozone in the absorption cell, at a wavelength of 254 nm. The instrument's precision is ± 1 ppb. It is a continuous O_3 monitor, connected to a data logger which prints hourly average concentration in ppb. It is calibrated frequently with a built-in ozonator (i.e. ozone generator) against pure zero grade air. The hourly average concentrations were used in the present study.

Trace gases (SO_2, NO_2 and NH_3)

These gases were measured by wet-scrubbing method and analysed by analytical techniques[1]. The methods of detection for SO_2, NO_2 and NH_3 are due to West and Gaeke[2]; Saltzman[3] and Weatherburn[4], respectively. Daily two samples of trace gases of 3 h duration each in the morning (0900–1200 h) and afternoon (1400–1700 h) were collected at Pune, during March–April 1998.

Results and discussion

Trace gases and AN at Pune

Table 1 presents the mean concentration of trace gases, viz. SO_2, NO_2, O_3 and NH_3 measured at Pune during March–April 1998. Also, their range of variation and the world background range of the above trace gases have been presented. It may be seen from the table that the mean concentration of SO_2 is 3.75 μg/m^3 ranging between less than 1 and 8.83 μg/m^3. The value is found to be within the world background range of 0.1 to 10 μg/m^3. The mean concentration occurring on the lower side of the range indicates that on a maximum number of occasions the concentration of SO_2 has been low. The mean value of SO_2 concentration, as reported, ranges from about 1 to 3 μg/m^3 for clean air and 10 to 443 μg/m^3 for heavily polluted air[5].

Mean concentration of NO_2 is found to be 5.81 μg/m^3 which appears to exhibit a higher value but within the range of the world background. On some occasions it has exceeded the world background range also. The minimum and the maximum values of NO_2 were 2.83 and 11.7 μg/m^3, respectively. The mean value of NO_2 concentration, as reported, ranges from about 2.1 to 2.9 μg/m^3 for clean air and 2.1 to 89 μg/m^3 for heavily polluted air[5].

The mean value of ozone (57.8 μg/m^3) lies at the midway of the world background range. The range of variation (3.9–141.1 μg/m^3) during the period of observation has been found to be much greater than the world background range (20–100 μg/m^3).

The concentration of NH_3 is in the world background range of 0.1 to 10 μg/m^3. The mean value is 3.21 μg/m^3. The mean values of NH_3 concentration, as reported, range from 2.5 to 5.1 μg/m^3 for clean air and 4.9 to 20.5 μg/m^3 for heavily polluted air[5].

Overall, results indicate that SO_2 and NH_3 have never crossed their world background values whereas NO_2 has crossed it on some occasions and O_3, on several occasions.

Smaller values of SO_2 and NH_3 are indicative of both the absence of their major local sources as well as their influx from long-range transport. On the other hand, continuously growing vehicular traffic close to the observational site may be one of the reasons for increase of NO_2 on some occasions. Very large variation in O_3 is thought to be caused mainly due to its diurnal variation.

During daytime, the production of ozone dominates and at night the destruction of ozone dominates to cause such a lower concentration of 3.9 μg/m^3.

Table 1. Trace gases and AN at Pune during March–April 1998

	Trace gases (μg/m^3)			
	SO_2	NO_2	O_3	NH_3
Minimum	< 1.00	2.83	3.9	1.00
Maximum	8.83	11.70	141.1	6.24
Mean	3.75	5.81	57.8	3.21
World background*	0.1–10	0.2–10	20–100	0.1–10

*Meszaros[9].

Comparison of AN and surface ozone at Pune and Thiruvananthapuram

Table 2 shows the concentration of AN and surface ozone at Pune and Thiruvananthapuram. It may be seen from the table that the minimum, the maximum and the mean values of AN are much lower at Thiruvananthapuram than the respective values at Pune. This indicates that the pollution levels are higher at Pune than those at Thiruvananthapuram. Khemani *et al.*[6] reported that the average concentration of AN at Delhi was 40,000/cm^3 and those over the Arabian Sea and Bay of Bengal were 460/cm^3 and 730/cm^3, respectively.

The range of variation of ozone at Pune is greater than that at Thiruvananthapuram. The maximum ozone value was found to be very high at Pune than that at Thiruvananthapuram and it was vice-versa in case of the minimum ozone value. This indicates that both the production and destruction of ozone were higher at Pune than those at Thiruvananthapuram. However, its average concentration at Pune is 29 ppb which is slightly higher than its mean value (22 ppb) at Thiruvananthapuram.

Diurnal variation of AN at Pune and Thiruvananthapuram

Figure 1 shows variation of the number density of AN observed during the period from 0900 h to 2400 h at Pune and Thiruvananthapuram. It is clear from the figure that throughout the period of observation the number density of AN at a particular time is always less at Thiruvananthapuram than that at Pune. At Pune, the AN concentration was found to be higher during the daytime than those during the night-time. Whereas at Thiruvananthapuram, the AN were found to be lower during the daytime than those during the night-time. The higher concentration of AN during the night-time may be due to the land breeze which sets-in around 2000 h. Since the sea breeze prevails during the daytime, low concentrations of AN were noticed.

Diurnal variation of ozone at Pune and Thiruvaananthapuram

Figure 2 shows the diurnal variation of surface ozone at Pune and Thiruvananthapuram. From the figure it can be seen that except at two hours, i.e. 0700 h and 0800 h, the concentration of ozone at Pune was found to be higher than that at Thiruvananthapuram. The concentration of ozone was high during the daytime and low during the night-time at both the locations. This feature is attributed to the photochemical production of ozone during the daytime. Diurnal variations with afternoon ozone maxima have been observed at many sites influenced by local pollution sources[7]. After sunrise, with the onset of mixing, the stable surface layer established during the night breaks up. This process of the formation of convective boundary layer increases to its upper limit by the afternoon and

Table 2. Comparison of AN and surface ozone at Pune and Thiruvananthapuram

	AN (N/cm^3)		Ozone (ppb)	
	Pune	Thiruvananthapuram	Pune	Thiruvananthapuram
Minimum	5,000	900	2	6
Maximum	91,000	23,000	70	42
Mean	19,000	4,400	29	22

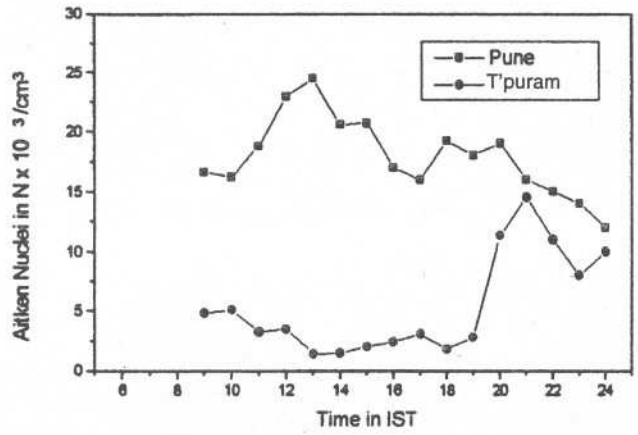

Figure 1. Diurnal variation of Aitken nuclei at Pune and Thiruvananthapuram.

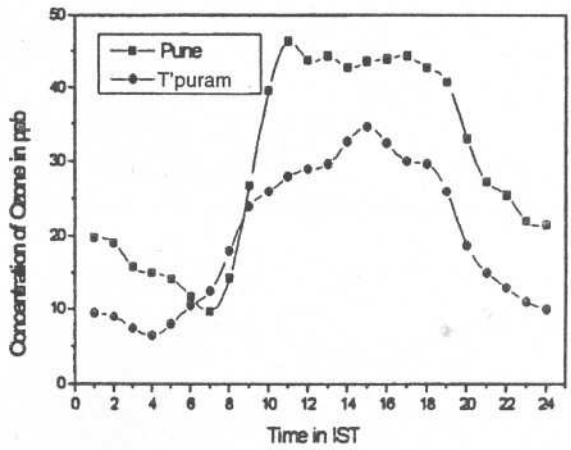

Figure 2. Diurnal variation of ozone at Pune and Thiruvananthapuram.

Table 3. Inter comparison of Aitken Nuclei Counter and Electrical Aerosol Analyser

	8 January 1998												
Time	10	11	12	13	14	15	16	17	18	19	20	21	22
ANC $\times 10^3$ cm^{-3}	2.0	4.7	5.0	1.5	1.5	3.5	5.0	7.2	2.0	2.5	23	20	11
EAA $\times 10^3$ cm^{-3}	3.7	4.7	4.1	4.0	1.8	2.1	3.1	2.6	2.6	3.2	23	22	17

ozone-rich air is being added continuously from the higher levels. Thus, in the time interval between sunrise and noon, ozone from higher levels is mixed into the mixing layer and high concentration is observed during the afternoon. Also, photochemistry of the pollutants give rise to production and build-up of ozone during the daytime. On subsidence of this mixing layer ozone concentration goes on decreasing because no more ozone-rich air is added. The diurnal variation of surface ozone closely follows the diurnal variation of surface temperature[8]. The peak is observed at 1100 h at Pune and at 1500 h at Thiruvananthapuram. The concentration of ozone started rising at 0700 h in Pune and 0400 h in Thiruvananthapuram. This may be due to the differences in meteorological conditions, such as mixing height, sunrise, humidity, etc. that prevailed during the sampling period at both the locations.

Intercomparison of ANC and Electrical Aerosol Analyser

The AN concentration measured at Thiruvananthapuram on 8 January 1998 using the ANC are compared (Table 3) with those particles with a similar size range measured by another instrument, electrical aerosol analyser (EAA) at the same location by another group from the Indian Institute of Tropical Meteorology (IITM). The EAA measures the aerosols of 7 different size ranges for which the mid values are 0.012, 0.021, 0.038, 0.067, 0.118, 0.211 and 0.38 μm radius. The total of the first 4 size ranges are given in Table 3. It may be noted that ANC measurements are almost instantaneous, whereas EAA measurements are the averages of 5 samples obtained every half an hour. Significant deviation is observed at 1300, 1600, 1700 h; and the agreement is very good at 1100, 1400, 2000 and 2100 h. At the other timings, the agreement is satisfactory. Thus, in general, there is a satisfactory agreement between the values measured by the two instruments considering the error bars (limitation as size range and averaging time).

Conclusions

Measurements of trace gases such as SO_2, NO_2, O_3 and NH_3 at Pune during March–April 1998 and at Thiruvananthapuram during 5–10 January 1998 revealed the following:

The concentration of Aitken Nuclei was five times less at Thiruvananthapuram (4,400/cm^3) than that at Pune (19,000/cm^3). This indicates that the pollution levels are higher at Pune than those at Thiruvananthapuram. The average concentrations of trace gases SO_2, NO_2, O_3 and NH_3 were found to be in the order of world background values. However, on some occasions, the concentrations of O_3 and NO_2 exceeded the background values. The average surface ozone concentration was slightly less at Thiruvananthapuram (22 ppb) than that at Pune (29 ppb). The diurnal variation of surface ozone revealed high concentrations during day time and low concentrations during night-time at both the locations. This feature is attributed to the photochemical production of ozone.

The diurnal variation of AN showed day time maximum and night-time minimum at Pune. Whereas, at Thiruvananthapuram night-time values of AN were higher than those at day time which could be attributed to land breeze which sets in during night-time.

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