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Studies of aerosols at Delhi

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सार—एंडर्सन कण सोपानी संघटक (कास्केड इम्पैक्टर) तथा जी एम डब्ल्यू उच्च आयतन सैम्पलर के उपयोग से क्रमशः वायु विलय के आकार वितरण तथा सान्द्रता को मापा गया है। धूमन अवधि की स्थिरता अवस्था, अस्थिर संवहनी अवस्थाओं (स्वतंत्र मिश्रण) तथा रात्रि की स्थिर अवधि के अनुसार नमूने एकत्रित किए गए। दिल्ली में सोडार द्वारा मापी गई ए० बी० एल० की मिश्रण ऊंचाई को ध्यान में रखते हुए इस शोध पत्र में साद्रंण, आकार वितरण तथा कणीय पदार्थ के अन्य संबंधित अध्ययनों को प्रस्तुत किया गया है।

ABSTRACT. Aerosol size distribution and concentration have been measured using Andersen particle cascade impactor and G.M.W. high volume sampler respectively. Sampling was done as per the stability conditions of fumigation period, unstable convective conditions (free mixing) and the nocturnal stable period. In the paper, concentration, size distribution and other related studies of particulate matter has been reported in the light of sodar determined stability and mixing height of the ABL at Delhi.

Key words— Aerosols, Size distribution, Concentration, Sodar, Stability, Mixing height, Atmospheric boundary layer, Enrichment factor, Correlation coefficient, Deposition velocity.

1. Introduction

The size and concentration of the particulate matter present in the atmosphere defines the extent of air pollution while the changes in the mixing height and stability determine its variability with time. For the last many years we have been studying (Singal *et al.* 1984, 1985) the diurnal, seasonal and annual variations in the mixing height and stability using acoustic sounding (sodar) of the lower atmosphere. Sodar is a remote sensing acoustic system wherein highly directional short bursts of sound waves are radiated into the atmosphere and after scattering from atmospheric inhomogeneities in temperature, wind speed and humidity are received back by a sensitive receiving system. In the back scattering mode, scattering is due to temperature inhomogeneities only and the received signal when displayed on a facsimile recorder gives information about the thermal structure of the atmosphere. Based on our investigations of the stability conditions and changes in the mixing height and turbulence through the use of sodar (Singal *et al.* 1985), we have studied the aerosol size distribution and concentration in the Atmospheric Boundary Layer (ABL) at Delhi as a function of the changes in the stability conditions and mixing height.

2. Experimental technique

The Total Suspended Particulate (TSP) samples for chemical composition and concentration studies have been collected by G.M.W. High Volume Sampler for a period of one year from April 1986 to March 1987. The sampling time covers four seasons, *i.e.*, summer (Apr-Jun), Monsoon/rain (Jul-Sep), post monsoon/fall (Oct-Nov) and winter (Dec-Mar). These samples have been collected for three distinct periods, *i.e.*, convective (1100-1700 IST), fumigation (0500-1100 IST) and stable (2300-0500 IST). Each sampling period lasted for about six hours. The total air sucked in one sampling period is 300-400 m^3. The concentration of TSP is determined from the difference in the weights of the filter paper before and after sampling divided by the volume of the air sucked. The filter papers were placed in a controlled humidity chamber for 24 hours before using.

Samples for size distribution studies have been collected by Andersen Particle Cascade Impactor for the period December 1985 to April 1987. The samples for the period December 1985 to June 1986 covering winter (Dec-Mar) and summer (Apr-Jun) have been collected for the three distinct periods, *i.e.*, convective, fumigation and stable. For the period July 1986 to April 1987, samples have been collected only for the convective period. Each sampling period has lasted for about 80 hours spread over 13-14 days for sufficient collection of material. The total volume sucked is between 120 and 150 m^3 for each sampling period.

3. Chemical analysis

The chemical analysis of TSP samples have been done for water soluble components SO_4, NO_3, NH_4, K, Na, Ca, Mg and for acid soluble components Mn, Fe, Al, Cu, Zn, Ni, Pb, Sb and Cd.

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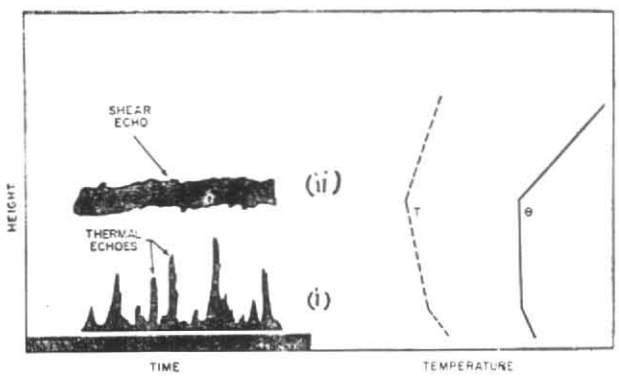


Fig. 1. Schematic representation of monostatic acoustic echoes and profiles of temperature T and potential temperature θ

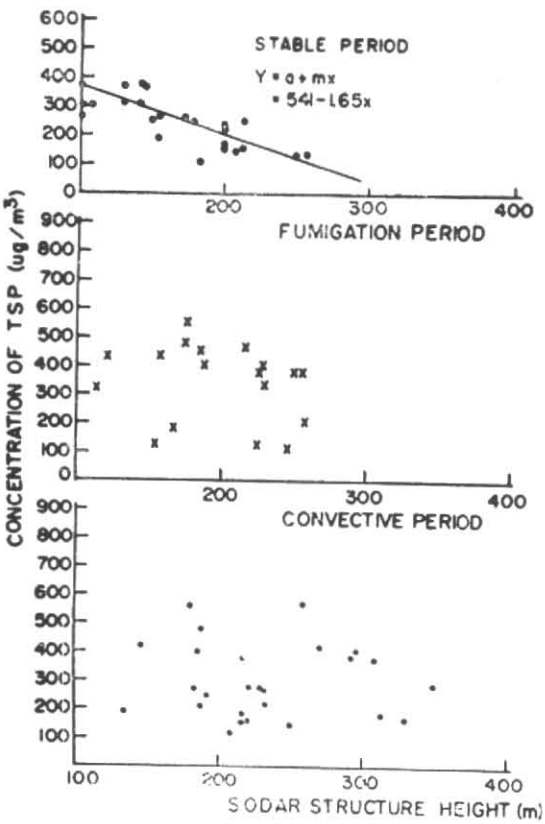


Fig. 2. Plot of concentration of TSP for three periods *versus* sodar structure height

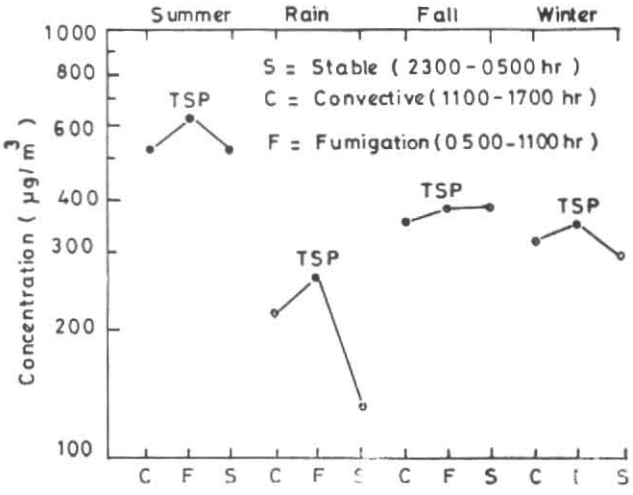


Fig. 3. Plot of concentration of TSP for three periods for fou seasons

For water soluble components, each filter paper was cut into fine pieces by stainless steel scissor and placed in the flask of the soxhlet extractor containing 30 ml of double distilled water. The solution is digested for one hour over low heat. After cooling, the solution is filtered in the beaker which is then concentrated using infrared lamps until the volume is reduced to 25 ml. The samples thus prepared, is placed in air tight polyethylene bottles previously rinsed with double distilled water for analysis for various chemical components. For acid soluble components, the filter paper is further digested for 30 minutes in 30 ml concentrated HCl at a low heat. After this operation, solution is extracted three times with water for 15 minutes each time. The acid water extracts are poured in a beaker and are evaporated to near dryness. The residue is redissolved in 10 ml HCl and 1 ml of HNO_3 solution, transferred to 25 ml volumetric flask and the volume is made to 25 ml by adding double distilled water.

The sulphate, ammonium and nitrate ion concentrations have been determined calorimetrically (spectronic 20) using barium iodate method (Klockow and Roniche 1973), Berthelot colour reaction procedure (Weatherburn 1967) and the burcine method (Jenkins and Nedsben 1964) respectively. The concentrations of metallic components (K, Ca, Mg, Al, Fe, Mn, Cu, Ni, Zn, Pb, Cd and Sb) have been determined using Perkin Elmer 373 double beam atomic absorption spectrophotometer with air acetylene and nitrous oxide acetylene flame. Calibration curves for different chemical components have been obtained by preparing standard solutions using analar grade chemicals. The calculations are periodically repeated to check accuracy. The analytical errors are within $\pm 10\%$ (Khemani 1985).

4. Sodar structure

Thermal structure as seen on the facsimile sodar echograms is broadly of two types (Fig. 1), (*i*) thermal echoes which are stalagmite like structures rising from the ground and are caused by turbulence in the unstable, super adiabatic layer of the atmosphere (potential temperature decreasing with height). They occur when the surface is appreciably warmer than the air aloft. The intermittent groups of thermal echoes mark individual rising convective cells called thermals and the echo free regions between thermals represent neutral or adiabatically descending air; (*ii*) shear echoes which

tend to be horizontal and are caused by turbulence in regions of static stability (potential temperature increasing with height). These basic sodar echograms or structures can be linked in one form or another to all observed prevailing meteorological conditions in the atmosphere.

In the morning, solar heating erodes the surface based stable layer forming ground based thermal plumes with the stable layer rising above them. These structures pertain to fumigation period. With continued solar heating, the stable layer rises sufficiently to go beyond the detection range and thermal plumes dominate all over on the sodar echograms. Height and rate of occurrence of these thermal plumes have been observed to reach a maximum by the afternoon after which they start decreasing in line with the fall in solar heat flux. These structures represent convective period. During night time, under slight or no wind conditions, strong short range echoes having an abrupt and an almost uniform upper limit exhibit a nearly flat top layer. Surface winds bring in mixing within the stable layer resulting in a random spiky structure at the top. Sometimes stratified/multi-layer or layer with oscillatory behaviour and an elevated layer over and above the ground based layer may also be seen. These structures pertain to stable period.

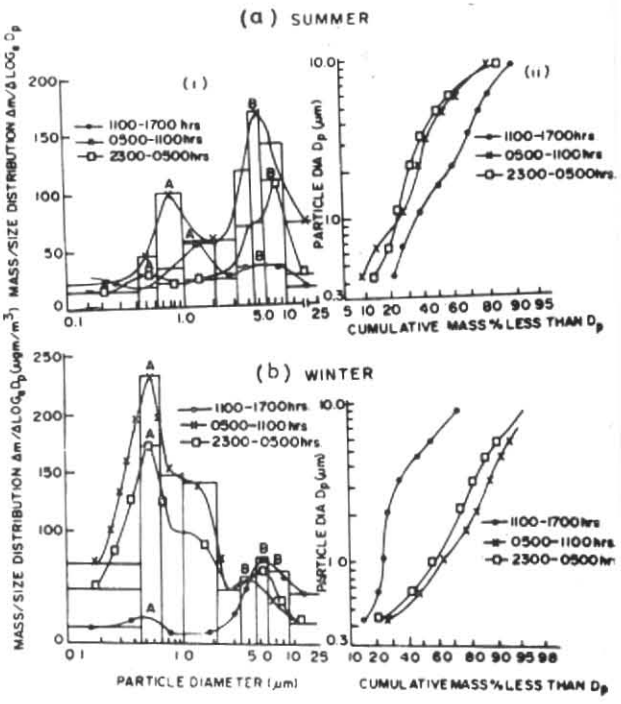
5. Results and discussion

Fig. 2 is a plot of the concentration of TSP *versus* sodar structure height for the three stability periods over the year. It may be seen from this plot that the concentration is inversely proportional to the sodar structure height for the stable period while for the fumigation and convective periods, there is no trend of this kind.

Fig. 3 further shows the variations of concentrations of the total aerosols for the three stability periods for all the four different seasons of the year. It may be seen that the concentration of aerosols is maximum for the fumigation period for all the seasons while in the post monsoon/fall period it is comparable in the stable and fumigation hours.

The various types of particulate matter can have the earth's crust as their source or they have a anthropogenic source or any other source since aerosols collected near the earth's surface are expected to have the crust as their major source. It will be appropriate to compare the composition of the crust in order to get a first hand idea of the origin of the aerosols. This comparison is conveniently done by calculating the Enrichment Factor (EF) for the various elements in the aerosols which can be defined as

$$EF = \frac{(X/Fe)\,air}{(X/Fe)\,crust}$$



Figs. 4 (a & b). Plots of mass/size distribution and mass median diameter (mmd) of total aerosols (TSP) for three respective periods for : (a) winter, and (b) summer

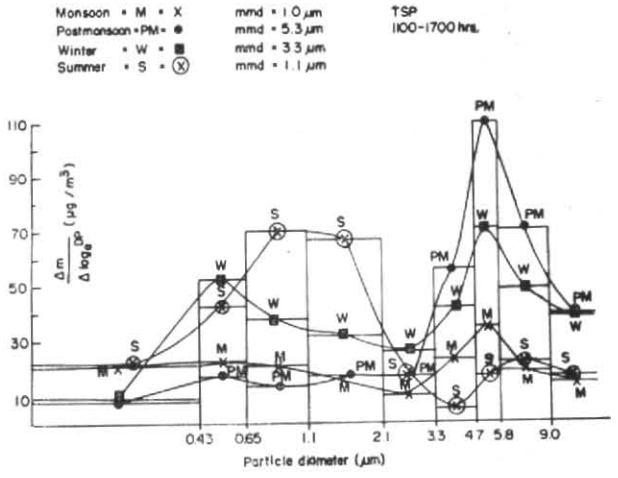


Fig. 5. Mass/size distribution plot of TSP for four seasons

TABLE 1

Monthly average concentration and enrichment factors (EFS) for TSP and trace elements for the fumigation period (0500-1100 IST) at Delhi

Months	No. of sample	Conc ($\mu g/m^3$) EF	TSP	Cu	Zn	Ni	Pb	Cd	Mn	Al	K
Apr	4	Conc	623.54	0.08	0.01	0.05	0.13	0.003	0.18	6.77	1.05
		EF		(35)	(5)	(15)	(201)	(400)	(4)	(2)	(1)
May	5	Conc	543.13	0.04	0.01	0.14	0.12	0.03	0.14	1.36	1.07
		EF		(20)	(3)	(45)	(201)	(3100)	(4)	(1)	(1)
Jun	3	Conc	777.17	0.06	0.01	0.05	0.10	0.01	0.30	7.65	1.14
		EF		(24)	(3)	(15)	(151)	(3000)	(7)	(2)	(1)
Jul	4	Conc	231.88	0.03	0.01	0.03	0.08	0.01	0.12	5.03	0.27
		EF		(20)	(6)	(16)	(189)	(1100)	(4)	(2)	(1)
Aug	3	Conc	173.36	0.04	0.01	0.03	0.15	0.01	0.06	5.99	0.35
		EF		(26)	(6)	(14)	(318)	(800)	(2)	(2)	(1)
Sep	4	Conc	371.22	0.05	0.01	0.03	0.15	0.01	0.06	4.99	0.35
		EF		(22)	(5)	(10)	(292)	(1200)	(3)	(1)	(1)
Oct	5	Conc	207.87	0.05	0.02	0.07	0.17	0.01	0.05	7.13	0.09
		EF		(60)	(6)	(11)	(197)	(1500)	(2)	(2)	(1)
Nov	2	Conc	657.72	0.17	0.02	0.04	0.16	0.02	0.14	6.66	1.71
		EF		(60)	(6)	(11)	(197)	(1503)	(2)	(2)	(1)
Feb	4	Conc	380.92	0.08	0.02	0.02	0.17	0.01	0.06	2.92	1.86
		EF		(36)	(5)	(7)	(28)	(1200)	(2)	(1)	(2)
Mar	4	Conc	334.98	0.07	0.01	0.02	0.22	0.02	0.05	1.62	1.72
		EF		(35)	(5)	(7)	(403)	(3200)	(2)	(1)	(2)

where, X stands for concentration of element X and Fe stands for Iron as average crustal rock reference. The numerator refers to the air borne concentrations of the elements X and Fe while the denominator refers to the average concentration of X and Fe in the earth's crust. Low values of EF's (non-enriched) of the elements suggest that the source is crust while higher values of EF's (enriched) may hint at anthropogenic sources or other non-crustal sources (Milford and Davidson 1985).

The EF's of Cu, Zn, Ni, Pb, Cd, Mn, Al and K for fumigation period are given in Table 1. It can be seen that K, Al and Mn have low enrichment factors and so they may have crustal origin while Zn, Ni, Cu, Pb and Cd have high EF's and they may thus belong to anthropogenic or non-crustal sources.

Complimentary information with regard to aerosol origin can also be obtained by computing correlations between the elements defined by the correlation co-efficient γ as follows :

$$\gamma = \frac{U_{11}}{\sigma_X \sigma_Y}$$

where,

$$U_{11} = \frac{1}{n} \sum \left(X_i - \bar{X} \right) \left(Y_i - \bar{Y} \right)$$

$$\sigma_X = \sqrt{\frac{1}{n} \sum \left(X_i - \bar{X} \right)^2}$$

$$\sigma_Y = \sqrt{\frac{1}{n} \sum \left(Y_i - \bar{Y} \right)^2}$$

and

n — No. of observations,

X_i — Concentration of element X,

$\bar{X}$ — Average concentration of element X,

Y_i — Concentration of element Y, and

$\bar{Y}$ — Average concentration of element Y.

The values of correlation co-efficient γ between the TSP and the elements are given in Table 2. Based on this table the elements can be divided into two groups. The first group is the one with high correlation with TSP as also with its own members. The elements

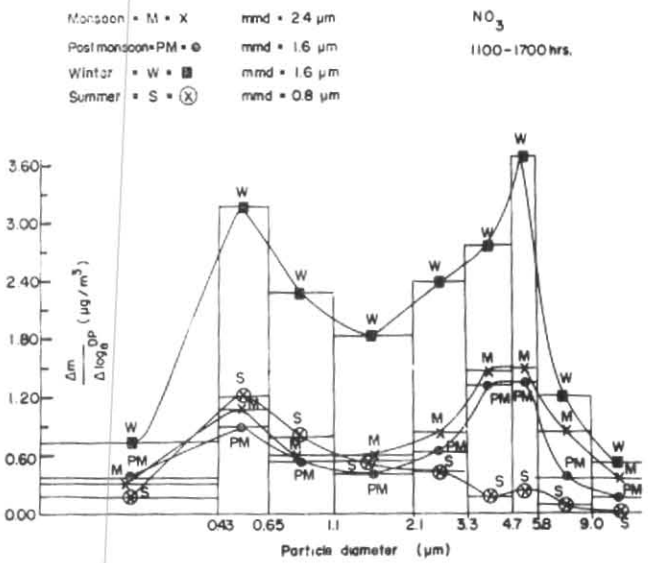


Fig. 6. Mass/ size distribution plot of Nitrate for four seasons

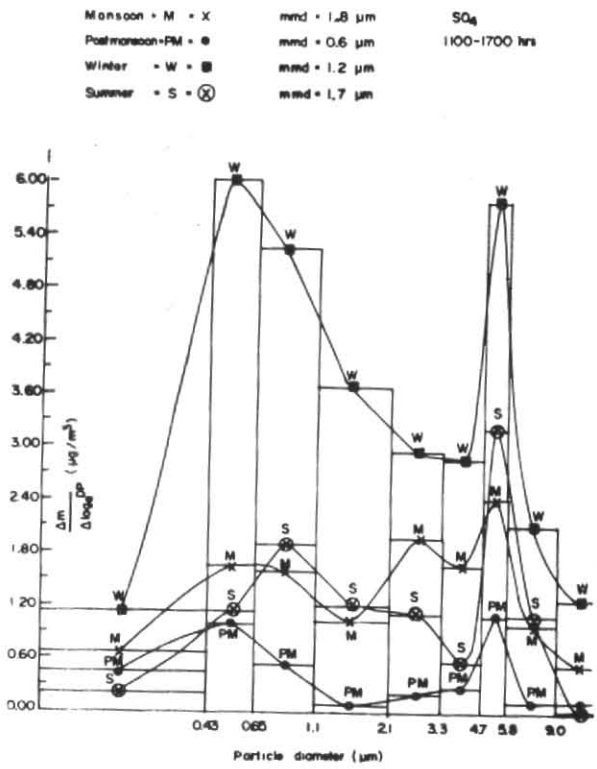


Fig. 7. Mass/size distribution plot of Sulphate for four seasons

TABLE 2

Correlation factors between trace elements and TSP for the fumigation period (0500-1100 IST) at Delhi

No.	Element	K	Ca	Mg	Cu	Zn	Mn	Pb	Cd	Ni	Al	Sb	Fe
42	TSP	0.31	0.32	0.52	0.56	—0.22	0.86	—0.06	+0.11	0.28	0.22	0.16	0.69
	K		0.69	0.75	0.45	+0.13	+0.06	0.44	—0.31	—0.13	—0.32	0.01	0.63
	Ca			0.74	0.45	0.21	+0.11	0.26	0.13	—0.10	—0.01	—0.05	0.47
	Mg				0.55	0.19	+0.32	0.27	0.16	0.02	0.02	+0.03	0.70
	Cu					0.37	+0.36	0.17	0.30	—0.08	0.19	—0.13	0.55
	Zn						—0.25	0.28	—0.08	0.28	—0.30	0.33	0.04
	Mn							0.19	—0.04	+0.27	+0.35	0.10	0.58
	Pb								+0.32	—0.24	—0.15	—0.14	0.20
	Cd									0.29	—0.27	0.46	0.15
	Ni										—0.01	0.71	0.04
	Al											—0.35	—0.06

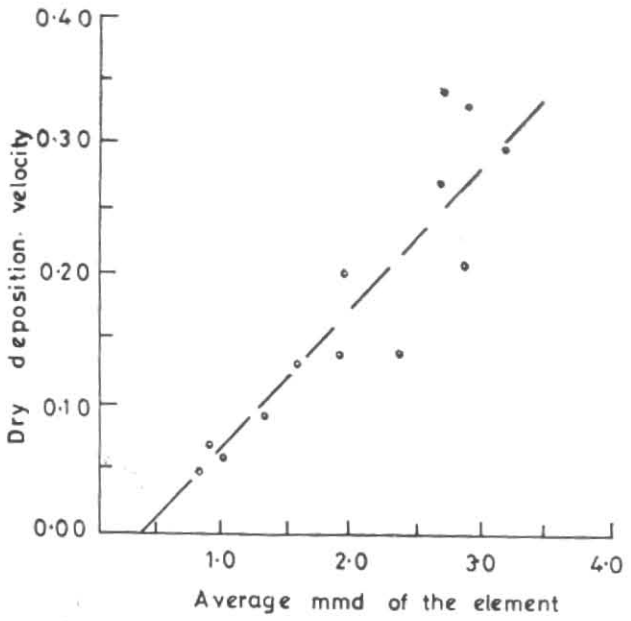


Fig. 8. The plot of dry deposition velocity *vs* mmd of TSP and its constituents

TABLE 3

Dry deposition velocity of TSP and its various constituents based on the model of Davidson et al. (1982)

Constituent	Average mmd (μm)	Dry deposition velocity (cm/s)
TSP	2.67	0.21
Cl	2.38	0.14
SO_4	1.29	0.09
NO_3	1.59	0.13
NH_4	0.93	0.07
Na	1.88	0.14
K	0.84	0.05
Ca	1.92	0.20
Mg	3.17	0.30
Cu	2.85	0.21
Zn	2.90	0.33
Mn	2.70	0.34
Fe	1.00	0.06

K, Ca, Mg, Mn, Ni, Cu, Al and Fe fall under this group. These elements are non-enriched. The high correlation within the group are indicative that the elements are primarily from the same source which is crustal in origin (Munger 1982). These elements contribute maximum to the TSP levels. The second group is the one with low correlation with TSP but with high correlation within its own members. The elements Zn, Cd and Sb fall under this group. These elements are enriched and are of industrial origin. Also these elements have good correlation with the elements of the first group. Hence, they owe their origin to both industrial and crustal sources. The element Pb, however, does not show significant correlation with any of the elements in the two groups, its source may be thus in vehicular traffic.

In order to see the effect of stability over size distribution of aerosols, data have been analysed for the three specific periods for two seasons, winter (Dec–Mar) and summer (Apr-Jun). For this purpose (following Kadowaki 1976) a term mass median diameter (mmd) has been defined which is the particle diameter up to/ which 50% of cumulative mass is collected. The mass/ size distribution and mmd plots of total aerosols for the two seasons (a) winter and (b) summer thus obtained are shown in Figs. 4 (a & b). Herein smaller particles of sub-micron size represent A mode while coarser particles of super micron size represent B mode, (Khemani *et al.* 1982).

It may be seen from Fig. 4 (a) which is for the winter season that during the convective period mass collected is small and it has a mmd of 5.0 μm. Further the super-micron B mode predominates over submicron A mode. For the fumigation period, mass collected is large and it has a mmd of 0.8 μm and further A mode predominates over B mode. For the stable period mass collected is less than that of the fumigation period but the mmd is again 0.8 μm and A mode is predominating over B mode.

Similarly from Fig. 4 (b) which is for the summer season, it may be seen that mass collected is greater in the fumigation period than that of the other two periods. The mmd's of the total aerosols for all the periods are in the super-micron region and are 1.5 μm, 4.1 μm and 4.4 μm for convective, fumigation and stable periods respectively. There is a predominance of coarser particles in all the periods.

Size distribution has also been studied for the Total Particulate Matter (TSP) and its constituents sulphates (SO_4) and Nitrates (NO_3) for the different seasons of the year. Figs. 5-7 show the corresponding mass/ size distribution plots of TSP, NO_3 and SO_4 at Delhi. The following can be seen from these plots :

* The size distribution of total aerosols, nitrates and sulphates (Figs. 5–7) has bimodal distribution during all the four seasons.

* The TSP mass is higher in the coarse size range than that in the submicron size range in all the seasons.

* The mmd for TSP has varied from 1.0 to 5.3 μm.

* The total mass of nitrates during winter period is the highest in both the modes.

* Nitrates have a higher mmd during winter, *i.e.*, coarser particulates are present more in number than that in summer.

From size distribution details (Milford and Davidson 1985) the elements can be traced to their sources. For example, those with mmd smaller than about 2 μm are commonly associated with high temperature anthropogenic processes. In contrast, elements with mmd greater than 2 μm are emitted mainly by natural processes such as crustal erosion. Of course some anthropogenic activities may also contribute to air borne concentrations of large particles on a local scale. (Lee and Ven Lehmden 1973, Davidson *et al.* 1974, Lee *et al.* 1975, Duce *et al.* 1975). Further from the sodar observations, Singal *et al.* (1985) have reported that mixing height is low during winter. This means that high concentration of nitrates during winter season is associated with the low mixing heights. Since nitrate from vehicular sources is formed in the atmosphere by gas to particle conversion process, it is expected that nitrate should show a unimodal distribution with a peak in the sub-micron size range. This is not true as analysed above which means that erosion from the earth's crust, *i.e.*, soil may be mainly contributing to the presence of nitrates in Delhi.

In the above context, we may also look at the following observations reported in literature. Milford and Davidson (1987) have reported that in temperate regions NO_3 aerosols have been found in both sub-micron and coarse size particles. Wolff (1984) has reported that large amount of fine NH_4NO_3 is only formed in areas with relatively low ambient temperatures, high concentration of atmospheric NH_3 and with NO_x emissions exceeding SO_2 emissions. Bessett and Seinfeld (1984) have reported that in the presence of H_2SO_4, nitrate will tend to evaporate from small particles and deposit on giant marine and soil derived particles. It is presumed that at Delhi with high ambient temperature, HNO_3 may be mainly reacting with coarse particles to give high concentrations of nitrates in the coarse size range.

The utility of the size distribution data is in the calculation of the deposition velocities from size dependent distributions. In our case dry deposition velocities have been calculated using the model of Davidson *et al.* (1982). The equation

$$V_d = \sum v_{di} \triangle C_i \Big/ \sum \triangle C_i$$

has been used to calculate dry deposition velocities where V_d is the overall deposition velocity, v_{di} is the deposition velocity corresponding to particle size range i and $\triangle C_i$ is the mass concentration in size range i. Averages of three distributions for monsoon, two distributions for post monsoon, three distribution for winter and one distribution for summer have been taken for each individual constituent for calculation of v_{di}. The plot of overall deposition velocities and average mmd of TSP and its constituents is shown in Fig. 8 while the results are summarised in Table 3. It is seen that as the mmd of the constituent increases, the deposition velocity also increases and the relationship is linear.

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