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Diurnal and seasonal variations of the atmospheric contents of sulphur dioxide, oxidants and aldehydes at BARC, Bombay during 1973

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ABSTRACT. Four-hourly average concentrations of sulphur dioxide, total oxidants (including ozone) and aldehydes (as formaldehyde) observed at the Modular Laboratory Site, BARC, Bombay during 1973 are presented. The results are compared with those of earlier years and discussed. An yearly increase of between 5-10 per cent in SO_2 (monthly average concentrations) is observed since 1969. The interaction of SO_2 with oxidants in the atmosphere, observed earlier, is confirmed.

For all the pollutants studied it is found that the corresponding four-hourly average concentrations during 1972 and 1973 are log-normally distributed.

1. Introduction

Studies of some atmospheric pollutants have been carried out at the Modular Laboratory, Bhabha Atomic Research Centre (BARC), Bombay over the past few years (Zutshi 1970, Zutshi and Mahadevan 1973 and Zutshi *et al.* 1973). With the help of the automatic multipollutant sequential sampler designed and fabricated (Zutshi and Mahadevan 1973), it has now become possible to make a more systematic, concurrent and round the clock measurements of a number of pollutants over a four-hourly averaging period.

The results of these studies during the year 1973 in respect of sulphur dioxide, total oxidants (as ozone) and aldehydes are presented in this paper. A comparison is made of the present results with those for the year 1972 (Zutshi *et al.* 1975). The observed diurnal variations of the various pollutants are discussed and the inverse correlation between the atmospheric sulphur dioxide and total oxidants observed earlier has been brought out more vividly. The concentrations of the pollutants studied during four-hourly averaging periods are found to be log-normally distributed as observed by Larsen (1971).

2. Analytical procedure

The chemical procedures adopted for the estimation of sulphur dioxide have been given elsewhere (Zutshi *et al.* 1975). Atmospheric aldehydes which mainly constitute formaldehyde, acetaldehyde and acrolein are estimated by the 3-methyl benzo 2-thiazolane hydrazone hydrochloride (3 MBTH) method (Sawicki *et al.* 1961; and Hauser and Cummins 1964) and expressed as formaldehyde. Detailed studies on their collection efficiencies and molar absorptivities have been carried out by Cohen and Altshuller (1966). It has been reported that the differences in the reactivities of formaldehyde, acetaldehyde and acrolein may not be serious since in the atmosphere it is formaldehyde which predominates over the other two (Scott and Reckner 1969).

3. Sampling procedure

The automatic multipollutant sequential sampler (Zutshi and Mahadevan 1973) has been used. An array of eighteen bubblers six each for sulphur dioxide, oxidants and aldehydes is used for every twentyfour hours of sampling. The sampling bubblers contain 25ml of the respective absorbing solutions. After the four hourly sampling is completed, the bubblers are removed from the trays of the sequential sampler and subjected to analysis for the different pollutants under study. The sampling point is located about 7-8 m above ground level in an open shaft of the Modular Laboratory.

4. Results and discussions

The four hourly monthly average concentrations at different diurnal periods during 1973, for

this is not clear. The magnitude of the potential gradient associated with a given intensity of rain is found to be always lower at Lonavla than at Mahabaleshwar (Table 2). The feature noticed is partly indicative of the elevation effect (*see* Krasnogorskaya 1965 and Reiter 1972).

5. Conclusion

An interdependence was indicated between potential gradient and rainfall at two out of the three stations where measurements were made. More extensive measurements are needed before a generalized conclusion in this regard becomes possible.

REFERENCES

Bradley, W. E. and Semonin, R. G.	1969	*J. geophys. Res.*, **74**, 1930-1940.
Chalmers, J. A.	1967	*Atmospheric Electricity*, 2nd Edition, Pergamon Press, London pp. 177.
Dvali E. R.	1965	*Studies of Clouds, Precipitation and Thunderstorm Electricity*, Amer. Met. Soc., Boston, 269-272.
Krasnogorskaya, N. V.	1965	*Studies of Clouds, Precipitation and Thunderstorm Electricity*, Amer. Met. Soc., Boston, 225-233.
Reiter, R.	1972	*Arch. Met. Geophys. Biokl.*, Ser. A., **21**, 247-272.
Selvam, M. M.	1970	India Met. Dep. Sci. Rep. , No. 121, pp. 6.
Simpson, G. C.	1949	*Geophys. Mem.*, London, 84, 1-51.
Sivaramakrishnan, M. V.	1953	*Indian J. Met. Geophys.*, **4**, 62-75.
Vonnegut, B. and Moore, C. B.	1958	*Recent Advances in Atmospheric Electricity*, pp. 317-331, Pergamon Press, New York.
Whitlock, W. S. and Chalmers, J. A.	1956	*Quart. J. R. Met. Soc.*, **82**, pp. 325-336.

TABLE 1

Four-hourly monthly average concentrations (μ g/m³)

|	Hour (IST)							Night time mean	Daily mean
	06 to 10	10 to 14	14 to 18	Day time mean	18 to 22	22 to 02	02 to 06		
(a) Sulphur dioxide									
January	62	43	53	53	54	63	40	52	52
February	62	80	78	73	26	46	25	32	52
March	61	20	49	43	21	13	14	16	30
April	—	—	—	—	—	—	—	—	—
May	15	29	30	25	22	21	24	23	24
June	35	33	34	34	38	20	32	30	32
July	62	78	68	71	56	70	68	65	68
August	65	47	51	54	66	65	66	66	60
September	37	27	27	30	38	39	32	36	33
October	15	37	33	28	26	15	18	20	24
November	27	7	43	26	30	30	24	28	27
December	25	23	56	36	25	27	24	26	29
Yearly average 1973	42	39	48	43	37	37	33	36	39
Yearly average 1972	37	29	39	35	40	36	35	37	36
(b) Total oxidants (as ozone)									
January	21	41	8	23	8	12	1	11	17
February	31	38	9	26	16	13	18	16	21
March	—	23	2	12	—	—	—	—	—
April	—	—	—	—	—	—	—	—	—
May	2	3	2	2	2	2	3	2	2
June	2	3	2	2	3	2	1	2	2
July	2	1	0	1	1	1	1	1	1
August	1	3	1	2	1	1	1	1	1
September	2	4	1	2	1	0	0	0	1
October	6	15	1	7	2	2	3	2	5
November	8	21	1	10	2	2	7	4	7
December	10	20	2	10	3	4	7	5	8
Yearly average (1973)	8	16	3	9	4	4	5	4	6
(c) Aldehydes as formaldehyde									
January	13	17	15	15	9	10	9	9	12
February	14	19	15	16	10	10	10	10	14
March	2	6	7	5	5	8	16	10	7
April	—	—	—	—	—	—	—	—	—
May	13	11	11	12	10	8	8	9	10
June	14	16	13	14	13	12	12	12	13
July	10	10	11	10	8	8	9	8	9
August	9	12	12	11	7	6	6	6	9
September	7	11	10	9	7	9	7	8	8
October	9	13	10	11	6	4	5	5	8
November	9	13	11	11	5	6	5	5	8
December	10	12	11	11	5	6	6	6	9
Yearly average (1973)	10	13	11	11	8	8	8	8	10
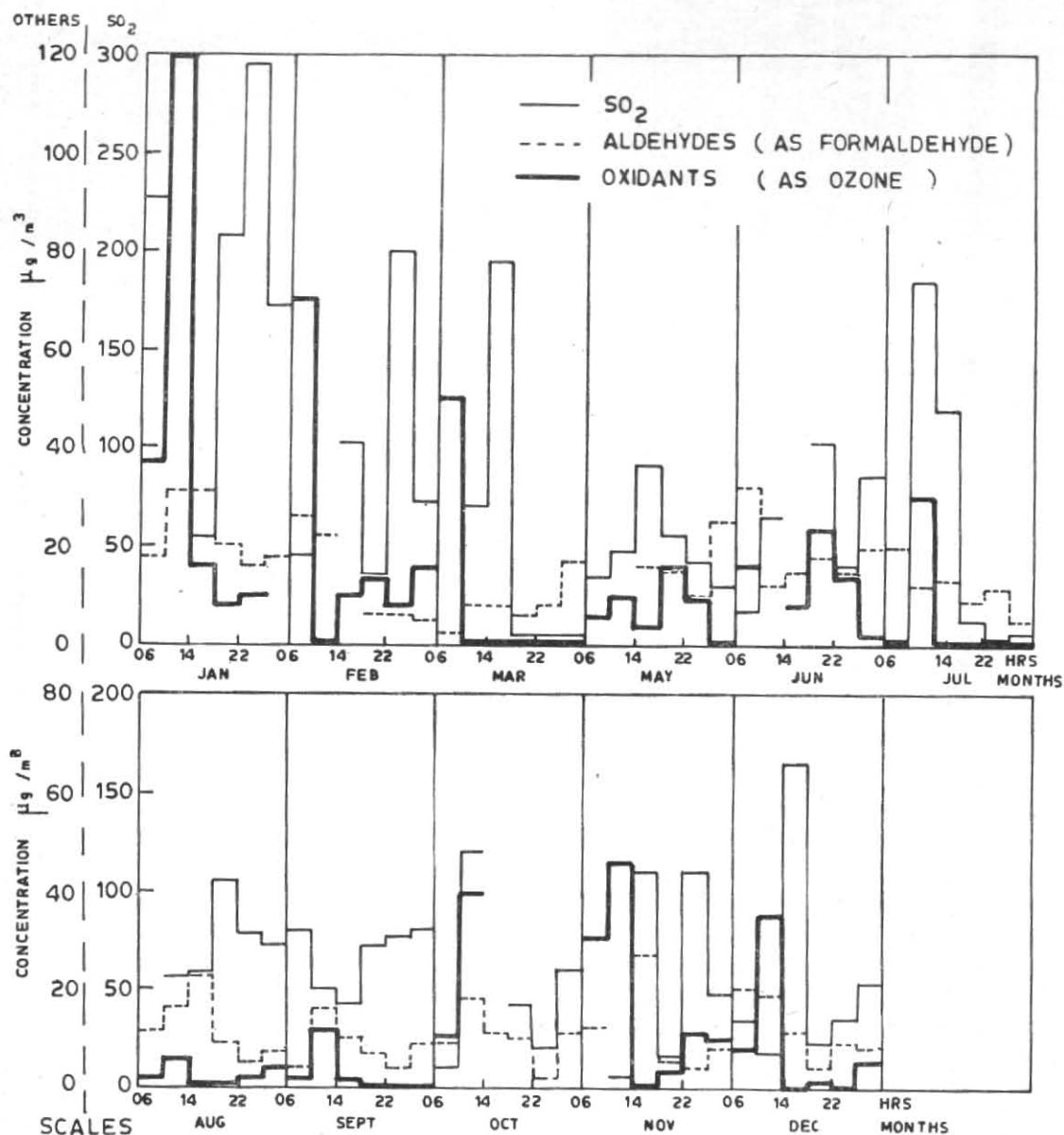
Fig. 1. Four-hourly average concentrations of sulphur dioxide, aldehydes (as formaldehyde) and oxidants (as ozone) on the respective days of observed maxima during each month of 1973

sulphur dioxide, oxidants and aldehydes are presented in Tables 1 and their diurnal variations (four-hourly) on the days of their respective maxima in each month are given in Fig. 1. From these tables and figures it can be seen that :

(1) There are large seasonal variations of the oxidant concentrations. The concentrations being minimum during the monsoon months and maximum during winter. They are, in general, significantly higher during the earlier parts of the day, confirming to their origin in the lower atmosphere from the interaction of the solar radiation with nitrogen dioxide and unsaturated hydrocarbons largely released from auto vehicles and to some extent from other operations involving fossil fuel combustion.

(2) Sulphur dioxide concentrations are significantly higher during the intense monsoon period and the winter. In general, these concentrations show a dip during the noon periods which can also be observed in their yearly average values for the years 1972 and 1973 (Table 1).

TABLE 2

Maxima, arithmatic means (A.M.) and standard deviations (S.D.) of concentrations (μg/m³) of SO₂, oxidants and aldehydes for the indicated periods

(Total number of four-hourly samples for the three constituents being 797, 798 and 791 respectively during the year 1973)

	Sulphur dioxide			Oxidants			Aldehydes		
	Max.	A.M.	S.D.	Max.	A.M.	S.D.	Max.	A.M.	S.D.
January	290	52	55	120	17	18	31	12	5·5
February	200	52	54	90	21	20	26	14	5·2
March	194	30	38	50	12	16	17	7	3·0
April	—	—	—	—	—	—	—	—	—
May	91	24	19	16	2	3·8	25	10	4·6
June	150	32	29	24	2	4·4	32	13	5·1
July	186	68	49	30	1·5	3·5	21	9	3·5
August	136	60	33	10	1·5	1·9	23	9	4·4
September	128	33	27	12	1·5	2·2	31	8	4·6
October	120	24	22	40	5	6·6	18	8	3·4
November	111	27	25	46	7	9·0	27	8	4·8
December	165	29	25	35	8	8·2	20	8	4·2
Year (1973)	290	36	39	120	6	11	31	10	4·9

NOT —The minimum observed concentrations for all the three constituents during each month were between 0—3 μg/m³

(3) The aldehydes show a lesser diurnal and seasonal variability. This is confirmed by their standard deviations presented in Table 2.

The entire concurrent concentration data as four-hourly averages for the three constituents studied during 1973 have been presented in Table 2 on a monthly basis giving only the observed maximum values, the arithmatic means and the standard deviations.

These results, while confirming the earlier observations, visually bring out the negative correlation between the sulphur dioxide and oxidant concentrations. It has also been observed that while the SO₂ peaks could occur at any time, the oxidant peaks are observed during the early or mid-day periods only. The observed inverse correlation between SO₂ and the oxidants is also substantiated by mathematical correlation studies between their concentrations. Since interaction between SO₂ and oxidants, if it does take place—the correlation between the SO₂ and oxidant concentrations, which arise from different sources—can perhaps be better studied by correlating the concentrations of one (say SO₂) with the corresponding ratios of the two (oxidants/SO₂). Since both are initially independent variables, the trend of their relative concentrations rather than their absolute

values, to our mind, will be a better measure of their interaction, if any. If there is no interaction between them, their relative concentrations with respect to the concentrations of anyone of them shall bear no correlation as the two originate independently of each other.

As such, we have calculated the correlation coefficients between the SO₂ concentrations and the corresponding ratios of oxidants to SO₂ from the Karl Pearson's formula. The calculations are made under three different conditions —

(1) Taking all the observations into account.

(2) Taking into account only those sets of observations where both the constituents are not simultaneously less than their geometric means (Figs. 2 and 3). That is, where SO₂ and oxidants are not simultaneously less than 33 μg/m³ and 9 μg/m³ respectively.

(3) Neglecting all observations where SO₂ and oxidant concentrations are simultaneously less than 50 μg/m³, and 20 μg/m³ respectively.

We find that although the correlation coefficient in all the three cases works out negative, it is insignificant in the first case. In the second

case the average for various months is $-0.45\pm$ 0.09 and for the third case the calculated values along with errors are presented in Table 3. No sampling was done during the month of April. The number of pairs of observations falling in this category during the months of March, May, October and November being individually fewer, we have clubbed together the observations of March with those of May and the observations of October with those of November. It may be observed (Table 5) that on the average the value of the correlation coefficient is -0.62 and in each case its magnitude is more than five times the probable error. Therefore, the observed negative correlation is significant.

From the above it follows that either the interaction between the two constituents is more pronounced at higher concentrations or the errors of measurement of the relatively large number of lower concentrations mask the affects of interaction between them.

4.1. *Monthly and yearly averages*

The monthly average concentrations, during different four-hourly diurnal periods, for the three constituents studied here, are presented in Table 1 along with their yearly average values during the corresponding periods. For comparison, the corresponding yearly average values of SO_2 for the year 1972 are also included in the Table 1.

It can be seen from Table 1 that although there are wide fluctuations in the monthly average concentrations during the six diurnal periods from month to month, the yearly averages during the corresponding periods are remarkable even both during 1972 and 1973.

The usual mid-day dip in the SO_2 concentration when oxidant concentrations are usually higher can also be noticed in the yearly averages, similar to one observed during 1972, although these have been made less prominent by the inclusion of a larger fraction of data during which the midday oxidant concentrations were sufficiently low to cause an appreciable dip. The data for oxidants (Table 1 b) and aldehydes (Table 1 c) confirm the earlier observations.

The overall (four-hourly) yearly average concentration of sulphur dioxide was $41\,\mu g/m^3$ during 1973 and $35.5\,\mu g/m^3$ during 1972. Even after allowing for errors, there is an average increase of about 5-10 per cent during 1973 over the previous year. Yearly increases of about the same order of magnitude have been observed earlier from 1968 to 1971 (Zutshi et al. 1973).

TABLE 3

Correlation coefficients (C.C.) between sulphur dioxide concentrations and the ratios of the concentrations of oxidants to those of SO_2 of individual four hourly concurrent samples for the year 1973

For these calculations samples for which the SO_2 and oxidants concentrations are simultaneously less than 50 and 20 $\mu g/m^3$ respectively have not been taken into account.

Period	No. of samples	C. C.	Probable error
January	46	—0.41	0.082
February	24	—0.69	0.072
March and May	19	—0.68	0.083
June	20	—0.56	0.103
July	56	—0.89	0.019
August and September*			
October and November	30	—0.58	0.082
December	21	—0.55	0.103
Total	216		

*Oxidants were almost nil throughout the period

The observed diurnal variations of sulphur dioxide concentrations, as reflected in their monthly averages as well, are apparently due to the daily and seasonal variations of the meteorological parameters (Zutshi et al. 1975), since the known major sources of sulphur dioxide are fixed in space and their diurnal emissions are more or less uniform (Zutshi 1970). While the gradually increasing fossil fuel consumption in metropolitan Bombay is causing a slow but consistent yearly increase in the atmospheric SO_2 concentration, the remarkable uniformity of the yearly average diurnal concentrations over different periods confirms that the emissions from sources are more or less uniformly distributed in time*. Further, at our sampling site the diurnal and seasonal variations of the meteorological parameters appear to get smoothed out when the concentrations are averaged over the entire year, except for a minor dip during the mid-day period.

Whether the yearly average concentrations of SO_2 over the same averaging period at other sampling points around the city will be the same as reported here and whether the meteorological parameters shall similarly be evened out over the year at other places are mute points for which, there is no evidence either way, as yet.

5. Mathematical formulation

Although there are no national or state standards for various atmospheric pollutants for this country so far, there exist various international standards, most of which are expressed as concentrations of a specific pollutant linked to the duration of exposure to that pollutant. However,

*Since data on fossil fuel consumption during 1968-73 are not available for Bombay, a quantitative comparison could not be made between them and observed SO_2 increases.

the growing number of air pollution study groups in this country, sample and estimate various pollutants over different averaging time periods. As such comparison of their data with the standards, which correspond to other exposure periods, is not justified. Attempts have, therefore, been made to develop a mathematical model for the atmospheric concentrations of the various pollutants, so that it may be possible to mathematically calculate the concentrations of a given pollutant over any averaging period from observations of its concentrations over a given averaging period (Larsen 1971). For example, from concentration frequency distribution of four-hourly averaging period observations given here it should be possible to calculate concentration frequency distribution curves for 10-min or 1 month averaging periods. This is exactly what has been worked out by Larsen (*loc. cit.*). The following characteristic is the corner stone of the above mathematical model, *viz.*, 'Pollutant concentrations are lognormally distributed for all averaging times'.

An attempt has been made to check the validity of the above statement for results presented here. Cumulative frequency distribution curves were prepared (Figs. 2 to 4) for our data for the sulphur dioxide, oxidants and aldehydes respectively. The terminology used therein is after Larsen (1971) and is as follows.

m_g is the geometric mean,

S_g is the standard geometric deviation,

C_{max} is the likely maximum concentration in 1 out of 100 observations of the given averaging period.

The graphs are drawn on log-probability graph papers and the abscissae of the three curves represent the cumulative percentage frequency of samples above the indicated concentrations of the various pollutants.

It is clearly seen from Figs. 2 to 4 that the present data as well as that for the year 1972 (Zutshi *et al.* 1975) fits in a straight line pattern in each case, particularly so at higher concentrations which are more important from the air pollution stand point, since the main purpose is to know what are the maximum concentrations of a given pollutant that are likely to be encountered over different averaging periods of time.

We can, therefore, conclude that these observations also suggest that pollutant concentrations are log-normally distributed. Calculations based on this premise shall be presented elsewhere.
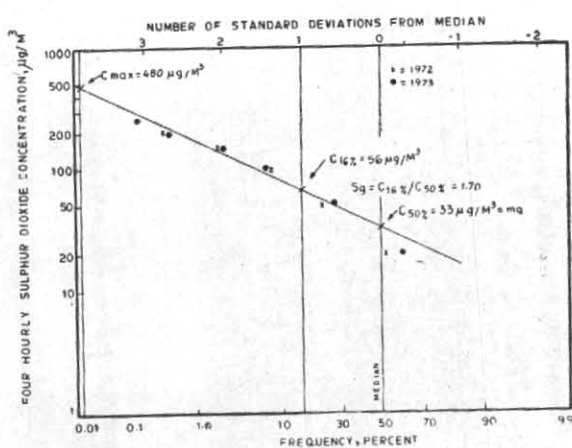

Fig. 2. Cumulative frequency distribution of SO_2 concentrations (averaging period : four hours)
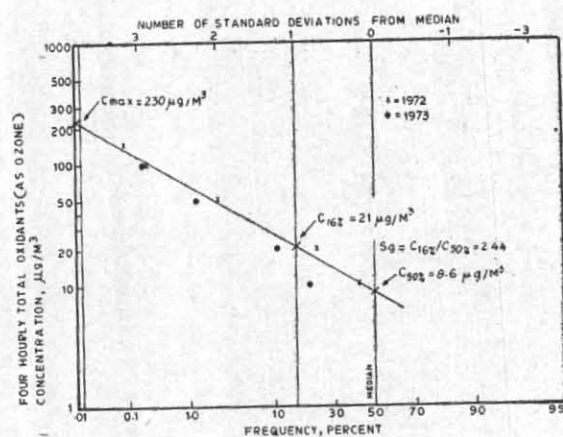

Fig. 3. Cumulative frequency distribution of total oxidant concentrations (averaging period : four hours)
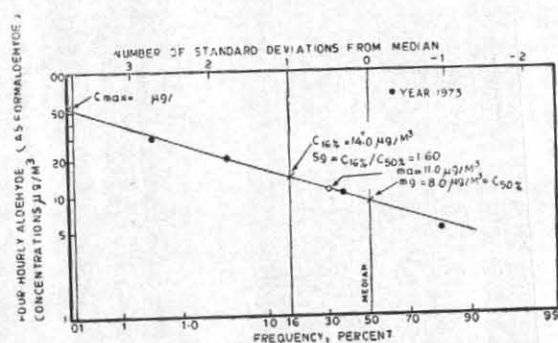

Fig. 4. Cumulative frequency distribution of aldehydes (as formaldehyde) concentrations (averaging period : four hours)

6. Conclusions

Based on the data presented here, the following conclusions have been drawn :

(1) The yearly average sulphur dioxide concentrations are found to be increasing by about 5-10 per cent per annum from the year 1969 onwards.

(2) There is a well defined inverse correlation between sulphur dioxide and total oxidant concentrations, indicating a relatively fast and destructive chemical or photo-chemical interaction between the two.

(3) Aldehydes in the atmosphere appear to be higher in the presence of oxidants.

This is plausible since it is known that formaldehyde is also a product of photochemical interaction in the atmosphere involving free radicals (Heuss and Glasson 1968).

(4) Four-hourly average data for sulphur dioxide, oxidants and aldehydes confirm the observation that the pollutant concentrations for various averaging time periods are lognormally distributed.

Acknowledgement

REFERENCES

Cohen, I. R. and Altshuller, A. P.	1966	*Anal. Chem.*, **38**, p. 1418.
Hauser, T. R. and Cummins, R. L.	1964	*Ibid.*, **36**, p. 93.
Heuss, J. M. and Glasson, W. A.	1968	*Environ. Sci. Tech.* **2**, p. 1109.
Larsen, R. I.	1971	U. S. Environ. Protection Agency, Publ. No.AP-89.
Sawicki, E., Hauser, T.R., Stanley, T.W., and Elbert, W.	1961	*Anal. Chem.*, **33**, p. 93.
Scott, W.E. and Rechner, R. L.	1969	Scott. Res. Lab. Rep. APRAC Project, CAPA 7, 68.
Zutshi, P. K.	1970	BARC-Rep. 461.
Zutshi, P. K. and Mahadevan, T. N.	1973	*Indian J. Tech.* **11**, p. 230.
Zutshi, P. K. Mahadevan, T. N. Banerjee, (Kum) Topoti	1973	*Indian J. Met. Geophys.*, **24** p. 61.
Zutshi, P K. Mahadevan, T. N. and Sathe, A.P.	1975	*Indian J. Environ. Health*, **17**, 4, p. 323.