551.574.11 (547.1)

Chemical character and probable origin of aerosols at the BARC site, Trombay

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ABSTRACT. The measurements of dustload and concentration of sodium, potassium, ammonium, calcium, magnesium, iron, aluminium, silicon, chloride and sulphate in atmospheric air at the Bhabha Atomic Research Centre premises during the period November 1971-April 1972 have been carried out. The average dustload is around 200 $\mu g/M^3$. About 50 per cent of this could be accounted for, by the present analytical estimation of the individual chemical constituents : the water-soluble fraction obtained being ~ 20 per cent and the water-insoluble fraction accounting for the rest. Marine contribution to aerosol mass, calculated on the basis of water-soluble sodium concentration indicated that the sea is a minor source of aerosols contributing to 5 per cent of the total aerosol mass. It was observed that the organic matter was about 20 per cent of the total aerosol mass. If the local soil and fly-ash are the soil contributors to water-insoluble iron and potassium in aerosols, the respective contributions by these two sources were seen to be 13 per cent and 48 per cents. If all the organics and the non-marine fraction of the water-soluble mass are of industrial origin, the man-made fraction of aerosols would constitute a maximum of 80 per cent of the dustload in the Trombay air. The remaining 20 per cent would be of natural origin, amounting to about 45 $\mu g/M^3$, a value that represents unpolluted atmospheres.

1. Introduction

It is well known that suspended particles in the air play a vital role in many atmospheric processes, such as radiation and heat balance of the atmosphere, atmospheric electricity, atmospheric chemistry (Vasudevan 1970) and nucleation of fog and cloud particles (Kuroiwa 1953). A detailed understanding of the physical properties and chemical composition of aerosols is indispensable in establishing any quantitative relation that could be existing between the aerosol matter and the atmospheric processes. Since the latter are highly complex, massive and consistent data would be called for in achieving the above purpose. The ever increasing rate of industrialisation of urban areas makes the problem still more complex by perpetually disturbing the natural balance.

In view of the above, even a semi-quantitative evaluation of the natural and man-made fractions of aerosols would be of interest to the atmospheric chemist. All the same generalization of any methods to estimate these fractions seems to be difficult since the nature and extent of air pollution varies from place to place and community to community (Cholak *et al.* 1959).

Zutshi *et al.* (1969 a) estimated atmospheric dustload and its water-soluble and organic fractions at the Bhabha Atomic Research Centre, Trombay which is located in the vicinity of a major industrial complex. The water-insoluble chemical constituents composed about 2/3 of the aerosol mass; water-soluble and organic constituents accounting for the remaining 1/3 fraction. In the work cited above only four chemical constituents, *viz.*, sulphate, chloride, nitrate and ammonium were analysed. This paper presents the results of a more elaborate chemical analysis of aerosols carried out by the authors. The location and topography of the sampling site make it ideally suited to studies on natural and man-made aerosols. On one side of this site runs a portion of the Thana Creek, while the other is flanked by a hill (highest point ~300 m) which is sparcely vegetated during the dry season. Immediately across the hill lies an industrial complex. Ten chemical constituents, *viz.*, sodium, potassium ammonium, calcium, magnesium, iron, aluminium, silicon, chloride and sulphate were chosen for the analysis, based on a reasonable assumption that these constituents make up for the major fraction of the mass of sea-salt, soil and fly-ash (Minnick 1965) which are the likely pollutants around the sampling site. Preliminary results of this analysis were reported earlier (Sequeira 1972). These results have been utilised in obtaining the following information on the aerosols :

(*i*) Basic nature of their inorganic chemical constituents.

TABLE 1

Composition and solubility characteristics of chemical constituents of aerosols at BARC, Trombay

	Dust load $\mu g/M^3$	Na	K	Ca	Mg	Fe	Al	Si	NH_4^+	Cl^-	SO_4^{2-}
					Concentration ($\mu g/M^3$)						
Max.	278	14·1	16·7	9·2	6·3	6·9	16·2	14·7	9·1	16·6	12·5
Av.	213	7·3	6·5	5·9	4·1	4·6	10·3	11·7	5·1	10·6	9·0
					Mean solubility (% total element)						
In water		45·8	61·2	67·9	29·0	2·4	0·1	7·0	—	—	—
In HCl (1:2)		31·4	9·7	29·8	34·2	55·2	28·0	51·1	—	—	—
HCl-insoluble		22·8	29·1	2·3	36·8	42·4	71·9	41·9	—	—	—

(*ii*) Total mass accountable through analysis.

(*iii*) Semi-quantitative estimates of their natural and man-made fractions.

A thermal Power Station situated in the immediate vicinity of the sampling site, is likely to be the major industrial source, since, large amount of fly-ash is released into the atmosphere at a considerable height. Some contributions to aerosols by industries other than the thermal station may be expected, though, the hills around the site are likely to dampen a considerable portion of the particle pollutants released by these industries.

The elements were determined separately, after sequential extraction in the order (*i*) water-soluble (*ii*) HCl-soluble and (*iii*) HCl-insoluble, to obtain a general idea about their chemical nature and atmospheric reactivity. Fraction (*iii*) was determined following fusion of the acid-insoluble ash of the sample with lithium fluoride-boric acid mixture, which is known to give total fusion for a variety of refractory minerals (Biskupsky 1965). However silicon could not be estimated in the above, due to the presence of fluoride. Therefore it was estimated by difference method after obtaining the total concentration of silicon, by sodium carbonate fusion of a known aliquot of the air sample.

Water soluble sodium concentration was used to calculate the sea-salt contribution to aerosol mass. Recently, Zutshi et al. (1969 b) have recommended the use of iron and potassium concentrations in air as indicators of soil and fly-ash components of aerosols. The ratio of the above elements finds use in the calculation of the relative contributions by the two sources to aerosol mass, as there are no other likely sources of iron and water-insoluble potassium around the sampling site.

2. Sampling

Air samples were collected 60-70 ft above sea level. A 'Staplex', Hi-volume air sampler and Whatman 41 filter paper were employed in sampling. Collection was made daily for 5 hours at flow rates of ~0·4m³/min and the chemical analysis was carried out on weekly or bi-weekly aggregates of daily samples, to obtain representative average concentrations.

Soil samples from the hill, and coal-ash from the nearby thermal station were analysed after sieving them through 350 mesh (equivalent to $> 45\mu m$ particle size) to almost represent their size fraction, which is likely to remain airborne (Junge 1963).

3. Analytical

Sodium was determined by flame emission spectroscopy ; potassium, calcium, magnesium and iron by atomic absorption spectrophotometry; aluminium by lake formation with hematoxylin; silicon as molybdenum blue; chloride using mercurithiocyanate in presence of ferric ion; ammonium by the Nessler method and sulphate by turbidimetry with barium chloride in the presence of glycerol-alcohol mixture. Details of the actual chemical procedures followed are described elsewhere (Sequeira 1973).

4. Results and Discussion

Total dustload and concentration of the chemical constituents obtained by analysis are presented in Table 1. The concentration of the individual chemical constituents and their solubility characteristics as given in the same table show the predominance of water-insoluble minerals in aerosols. It could be seen that Si and Al are among the predominant chemical constituents. Further, with the exception of Ca, all analysed elements have at least an appreciable acid-insoluble component—Al remaining mainly acid-insoluble.

TABLE 2

Comparison of some water-soluble fractions of aerosols determined gravimetrically and from analysis

S. No.	Water-soluble fraction (%dust)		S. No.	Water-soluble fraction (%dust)	
	by weighing	from analysis		by weighing	from analysis
1	13·4	12·8	3	26·5	28·4
2	11·9	9·6	4	27·1	26·9

TABLE 4

Calculation of mean marine and non-marine components of water-soluble aerosols

Consti-tuents	Total	Concentration (%dust)	
		Apparent from sea	Apparent excess
Na+	1·49	1·49*	Nil
K+	2·29	0·054	2·24
NH₄	2·46	Trace	2·46
Ca²+	2·23	0·056	2·17
Mg²+	0·56	0·180	0·38
Fe	0·03	Trace	0·03
Al	Trace	Trace	Trace
Si	0·34	Trace	0·34
Cl⁻	4·65	2·70	1·95
SO₄²⁻	4·48	0·37	4·11
Total	18·53	4·85	13·68

*Assuming that all Na+ is from sea

TABLE 3

Ratio of water-soluble K, Ca, Mg, Cl and SO₄ to Na in aerosols as compared to those found in sea water

	Ratio of				
	Na/K	Na/Ca	Na/Mg	Cl/Na	Na/SO₄
Max.	6·35	1·86	7·60	6·15	1·47
Av.	1·54	0·94	3·41	3·81	0·45
Min.	0·30	0·46	1·98	2·62	0·15
Sea water	27·6*	26·3*	7·8*	1·8**	4·0†

* Deduced from data of Goldberg, E. D. (1963). *The oceans as a chemical system* in M.N. Hill, ed., '*The Sea*' Int. Sci. Publ. Inc. N.Y.

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† Rankama, K. and Sahama, T. G. (1949), *Geochemistry*, Univ. of Chicago Press.

TABLE 5

Mean concentrations and acid-solubilities of water-insoluble iron and potassium in local coal-ash, hill-soil and aerosols at the BARC, Trombay

	Water-soluble fraction of elements				
	Iron		Potassium		
	Total (%dust)	HCl-soluble (%water-insoluble)	Total (%dust)	HCl-soluble (%water-insoluble)	Fe/K
Coal-ash	1·6 (1-2)	25	1·0 (0·5-1·5)	42	1·60
Soil	2·6 (1·5-3·0)	1	0·08 (0·04-0·15)	70	32·0
Aerosols	2·3	25	0·91	60	2·53

Average values of Fe and K in soil and fly-ash are used to calculate the natural and man-made fractions of water-insoluble aerosols. The variations are shown in parenthesis.

Water-soluble fraction

A comparison of the gross water-soluble fraction of aerosols obtained by direct weighing and by summation of the concentration of the analysed constituents, shows good agreement as indicated in Table 2 — suggesting the completeness of the chemical analysis envisaged. Total water-soluble fraction of the aerosols obtained as above, amounted to about 19 per cent of the aerosol mass.

Ratios of water-soluble potassium, calcium magnesium, chloride and sulphate to sodium as obtained by analysis, and their corresponding values in sea-water are given in Table 3. The marine fraction of the individual water-soluble constituents was calculated on the basis of the sodium values, assuming that the latter constituent is of sea-origin. Table 4 gives the marine component of the different constituents. One finds that the sea-salt contributes to only 5 per cent *of the total aerosol mass*. Nevertheless, this corres-

ponds to about $10 \mu g/M^3$, a reasonable value for a coastal station (Junge 1963).

HCl-soluble and HCl-insoluble fraction of aerosols

If one expresses the HCl-soluble and HCl-insoluble fraction of the elements as oxides, 32 per cent of the aerosol mass could be accounted for. These and the water-soluble fraction therefore account for 50 per cent of the aerosol mass. Results of the analysis showed that the total water-insoluble fraction of elements is equally distributed as HCl-soluble and HCl-insoluble. The latter could be considered as the chemically 'inert" fraction of the aerosols.

Calculation of soil and fly-ash contributions

The average concentrations of water-insoluble Fe and K and the acid-solubility of the two elements in soil, coal-ash and aerosols are presented in Table 5. These results strongly indicate that the local fly-ash is a more important source of aerosols than the soil. It is interesting to find that the ratio of

water-insoluble iron-to-potassium is widely different for the soil and the coal-ash. Fig. 1 gives the relation between the calculated values of iron-to-potassium ratio and the fly-ash fraction of water-insoluble aerosols, on the assumption that soil and fly-ash are the sole contributors to water-insoluble iron and potassium. The values of this ratio in aerosols, as obtained experimentally are also plotted in the same figure. These values lie in a region which correspond to contributions of 58-98 per cent from fly-ash to the water-insoluble fraction of aerosols, the average value being 78 per cent, leaving behind 22 per cent as contribution from soil.

Estimates of natural and man-made fraction of aerosols

Average estimated value of the organics was found to be 20 per cent of the total aerosol mass. The analytically accounted inorganic fraction and the organic fraction obtained above add up to ~ 70 per cent. The remaining 30 per cent may be due to other constituents such as water-insoluble carbonates, sulphates and phosphates. The above results show a soil contribution of 13 per cent which, along with the sea-salt would make 18 per cent of the total mass of aerosols. Thus, it can be seen that the estimated natural fraction amounts to $\sim 45\mu g/M^3$, a value very near to that for unpolluted atmospheres. The results, therefore, indicate that for the sampling location, man-made contribution could be as high as 80 per cent of the dust load.
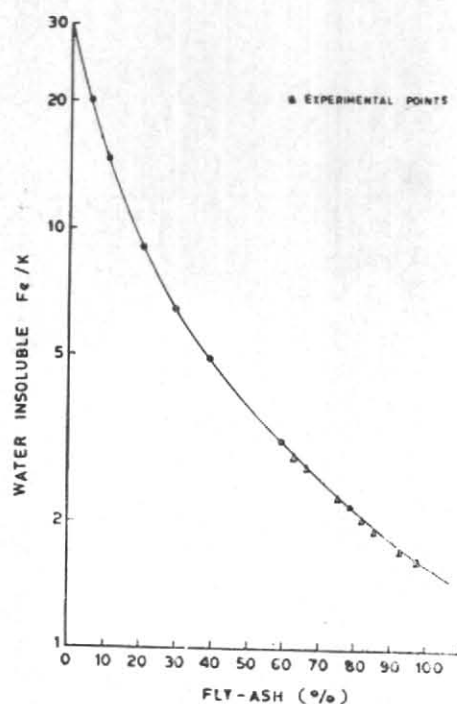

Fig. 1. Variation in fly-ash contribution to water-insoluble aerosols with iron to potassium ratio

Acknowledgements

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