Mausam, (1984), 35, 1, 87-90

551.578.11 : 628.17

Some observations on the chemical composition of precipitation in an industrial area and its use in air quality assessment

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(*Received 16 July 1982*)

सार–1980 में मानसून अवधि में बम्बई के प्रमुख औद्योगिक क्षेत्रों के सात स्थानों की वर्षा के नमूने एकत्रित किए गए और उनका pH,SO_4,Cl,NO_3,NH_4, एवं F-आयन, सांद्रणों के लिए विश्लेषण किया गया। एक खुले क्षेत्र की वर्षा में अम्लीयता अधिक थी, लेकिन दूसरे सभी स्थानों की वर्षा के नमूनों में क्षार अधिक पाया गया। प्राप्त आंकड़ों से पता चला है कि दो स्थान, जहां SO_2, प्रमुख स्रोत थी, SO_4 सर्वाधिक थी। स्थानीय स्रोत की वजह से चार स्थानों पर फ्लोराइड और नाइट्रेट काफी मात्रा में पाए गए। SO_4 और NH_4 की अधिकता का अनुमान उनके स्टाईकियोमीट्री अनुपातों के संदर्भ से किया गया है। उर्वरक उद्योग के आसपास वर्षण के साथ फ्लोराइड के बह जाने से फ्लोराइड के विघटन का अनुमान लगाया गया है। फिर अध्ययन के सभी परिणामों का विवेचन किया गया है।

ABSTRACT. Precipitation samples collected from seven sites situated in a major industrial region in Bombay during 1980 monsoon period were analysed for pH, SO_4, Cl, NO_3, NH_4 and F ion concentrations. Barring one site which showed predominantly acid rains, samples from other sites were found to be alkaline in nature. Data obtained suggest a predominant SO_4 excess at two of the sites where the prime source is SO_2. Higher levels of fluoride and nitrate were found at four of the sites indicating a local source. SO_4 and NH_4 excesses are estimated with reference to their stoichiometric ratios. Fluoride deposition due to precipitation washout around the fertilizer industry is assessed and the overall results of the study discussed.

1. Introduction

From an environmental point of view the magnitude of wet fallout of pollutants due to precipitation scavenging is of considerable importance as it indicates the intensity and local impact of major pollution sources. Combustion of large quantities of fossil fuels and the advent of the chemical age have spiked into rain, a number of chemical pollutants both gaseous and particulates, which supported by the complex chemical reactions have given rise to increased pollution at regional and continental levels. A number of model studies coupled with *insitu* observations have been made with reference to the washout of SO_2 (Postma 1970, Dana *et al.* 1972, Barrie 1978, Davies 1976). While acid precipitation (acid rains) (Likens and Bormann 1974) is principally associated with SO_x followed by NO_x, a few instances of HCl formation are also reported (Cogbill and Likens 1974). In our study, the chemical composition of precipitation samples collected from a major industrial region has been assessed and from the variability in their concentrations attempt has been made to identify the predominant sources. Use of this type of study in monitoring ambient air quality has been described.

2. Experimental

A small network of seven sampling stations was operated in the industrial belt of Chembur, Trombay within the Greater Bombay region (Fig. 1). The area covers a fertilizer unit, two refineries, a thermal power station and a number of chemical and pertrochemical based industries (Zutshi 1970, NEERI 1973). The rainwater samples were collected mostly on a 24 hr basis from sites 1, 2, 3, 7 and at monthly intervals from sites 4-6 during the monsoon period of June-October 1980. The prevalent wind directions during these months are westerly-southwesterly and tend to become partly northwesterly from the end of September. Polyethylene funnels and containers were used for collection and storage of samples. Sampling height was 10 metres above the ground level.

3. Analytical

The pH of the samples was measured immediately after collection and the stored samples were subjected to chemical analysis for assessing the concentration levels of SO_4, NO_3, NH_4, Cl and F. Spectropotometric and ion selective electrode techniques were employed in the analytical procedures (Zutshi *et al.* 1978).

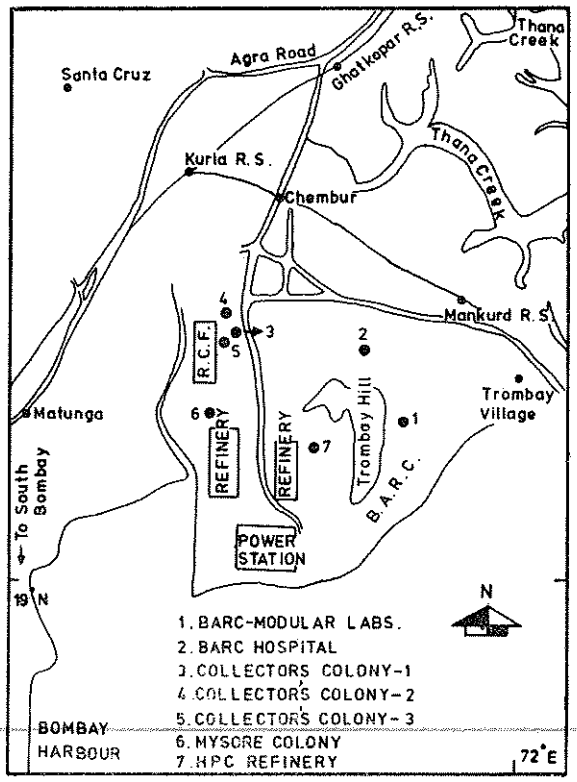

Fig. 1. The location of sampling sites

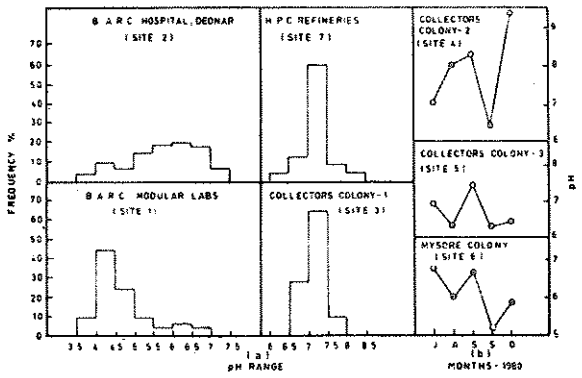

Fig. 2(a). Percentage frequency distribution as a function of observed pH

Fig. 2(b). Variation in pH of cumulative samples collected over indicated period

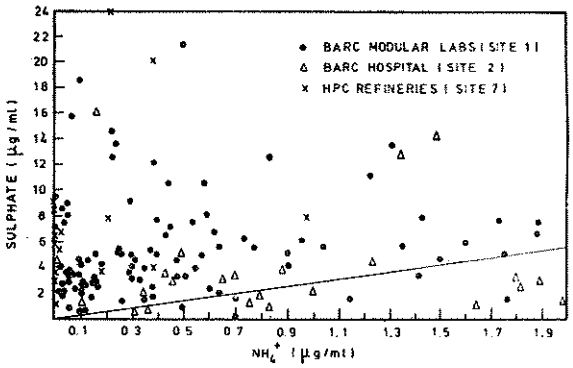

Fig. 3. Sulphate and ammonium ion concentration in relation to the ammonium sulphate stoichiometry ratio

4. Results and discussions

pH—The variation in the pH of the samples are presented in Fig. 2 as the percentage frequency distribution for sites 1-3, 7. Measured pH values for cumulative samples collected from sites 4-6 are also shown. The predominantly acidic character of rainwater at site 1 has been observed since the time we began our study in 1974 when the average one hourly SO_2 concentration during monsoon season was in the range of 100-600 μ g/m^3 and the washout SO_2 was significantly related to pH (Zutshi *et at.* 1978). The acidic trend appears to be continuing although the SO_2 levels have fallen over last two years to 50—220 μg with the reported change-over to low sulphur fuels. Probably the mechanism of SO_2 solubility in rain drops appears to be the guiding factor in determining the observed trends, although the solubility of SO_2 in liquid water is known to be high. Detailed discussion on the SO_2 washout is being presented elsewhere. The near uniform distribution of pH within the indicated range at site 2 is due to the

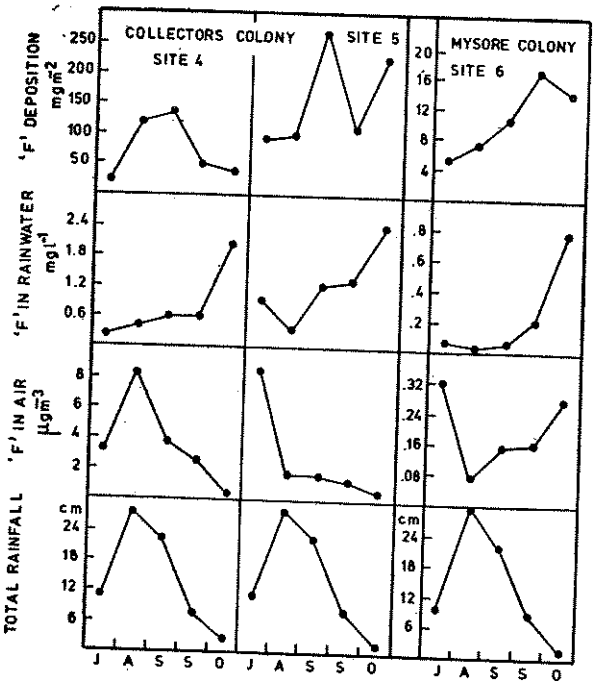

Fig. 4. Cumulative monthly mean deposition of fluoride due to precipitation washout (July-October 1980)

TABLE 1
Average and maximum concentration levels of SO_4, NH_4, NO_3, Cl and F ions in precipitation samples

Site No.	Location	Concentration µg/ml									
		Sulphate		Ammonium		Nitrate		Chloride		Fluoride	
		Av.	Max.	Av.	Max.	Av.	Max.	Av.	Max.	Av.	Max.
1	B.A.R.C. Mod. Labs.	4.8	21.3	0.36	2.4	0.88	4.8	2.7	11.2	0.05	0.19
2	B.A.R.C. Hospital	3.6	16.1	1.20	4.1	0.93	5.0	4.0	10.8	0.06	0.24
3	Collector's Colony-1	4.1	12.3	7.0	26.7	29.0	17.0	13.9	31.0	2.67	12.0
4	Collector's Colony-2	2.6	4.4	0.76	1.4	5.2	12.0	10.9	30.2	0.92	2.8
5	Collector's Colony-3	3.6	7.4	0.73	1.1	4.2	10.5	5.4	11.2	1.23	2.4
6	Mysore Colony	2.2	3.7	0.70	2.5	3.0	11.0	4.7	8.5	0.22	0.78
7	Hindustan Petroleum Refineres	6.2	24.8	0.15	0.69	0.67	4.7	9.1	16.6	0.03	0.06

fact that it lies a little farther away on the down-wind direction of a number of contributing emission sources. The alkaline pH at sites 3-6 is evidently due to the proximity of the fertilizer industry manufacturing ammonia. The observed trends at site 7 need to be investigated further, since they tend to be alkaline even while recording sulphate excesses and low ammonium ion concentrations.

5. Composition of negative ions

The most abundant ions found in rainwater are SO_4, NO_3, NH_4 and F (in a few sites), related to local sources and Cl mainly of maritime origin. Table 1 gives the mean and maximum values of these ions for the individual sites.

Specific ion excesses can be clearly seen with sharp demarcation, in their variabilities which is site oriented. SO_4 excesses was found at sites 1 and and NH_4, NO_3 F excesses in site 3-6 Results for site 2 indicate a mixed trend with reference to all these ions. Since the aerosol samples normally showed a near stoichiometric ratio for $(NH_4)_2 SO_4$ at site 1 (Zutshi *et al.* 1980). their relative affinity in rain was ascertained by plotting the variabilities in concentration as shown in Fig 3. A dominant SO_4 concentration at site 1 and 7 can only originate from the washout of

SO_2 by precipitation. Site 2 samples follow the stoichiometry line with SO_4 excesses in a few samples, which could be possibily originating from SO_2 washout as shown in Fig. 3. Site 3 being closer to the fertiliser industry clearly dominates in the NH_4 concentration for 24-hr samples but for cumulative collection over a month (sites 4-6) the levels tend to get equilibrated, with the free ammonia getting volatalised from the liquid phase. Perhaps the levels of free acid associated with NO_3 and Cl ions is not significant to neutralise the ammonia and form ammonium compounds.

A significant correlation between NO_3 and F concentrations has been observed at sites 3-6 indicating a common source for both these ions.

6. Fluoride washout by precipitation

The monthly average fluoride concentration in precipation for sites 4-6 where cumulative samples were collected are shown in Fig. 4. Although monthly means may not represent the conditions prevalent during rainfall, the values presented give an average index of the impact on the receiving system. The total rainfall and the fluoride concentration in air and its deposition for the corresponding period are also presented in Fig. 4. There is inverse relationship, in general, between rainfall intensity and washout with a few exceptions. The fluoride deposition on the ground is directly related to rainfall within the fluctuations in washout concentrations. The atmospheric fluoride concentrations as estimated by the lead dioxide method (Meenakshy *et al.* 1981) for the corresponding period has semblance with the washout curve only at site 6 which comes in the shadow and away from the source giving enough time for the air concentrations to equilibrate with the prevalent wind conditions. For sites 4 and 5 which are very near the source such a relationship is not seen either because of plume fluctuations or the variations in the gaseous and particulate emissions. Hence the vertical column of air containing fluoride through which the precipitation falls guides the concentration level in washout as rainout is relatively unimportant. However, short term fluoride measurements in air along with showerwise rainfall collection may provide more conclusive results as seen for SO_2.

7. Conclusions

The present work highlights the importance of precipitation analysis for gross assessment of air quality in an industrial region with reference to specific pollutants using conventional analytical techniques. The observed variations in the concentration levels necessitates the use of an extensive sampling network in order to assess the impact of pollutants which get deposited on soil, plants and aquifers. The study also aids in evaluating the local and long range transport of contaminants. These effects can however, be exemplified better with more extensive surveys.

Acknowledgements

The authors thank Dr. U. C. Mishra, Head, Air Monitoring Section for his keen interest and useful suggestions.

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