Mausam, (1985), **36**, 3, 267-274

551.578.11 : 551.553.21 (547)

Chemical composition of rainwater during monsoon season over Pune (Maharashtra) and its relation to meteorological factors

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(*Received 18 August 1983*)

सार — 1981 की वर्षा ऋतु के दौरान पुणें में वर्षाजल के लगभग 180 नमूने भरे गए थे तथा उनमें उपस्थित विभिन्न रसायनों के लिये उनका विश्लेषण किया गया था। वर्षाजल की संरचना में योगदान करने वाले विभिन्न स्रोतों के महत्व, वर्षाजल के pH पर नियन्त्रण रखने में धनायनों तथा ऋणायनों की भूमिका तथा वर्षाजल की रसायनिक संरचना मौसम विज्ञानी परिमापकों के प्रभाव का अध्ययन करने के लिये आंकड़ों का उपयोग किया गया था।

ऐसा पाया गया है कि वर्षाजल में क्लोरीन तथा सोडियम तत्वों के लिये समुद्री वायु प्रमुख स्रोत है तथा सल्फेट अंश के लिये मानवजनिक स्रोत बहुत महत्वपूर्ण है। उपरोक्त के अतिरिक्त स्थानीय मिट्टी भी वर्षाजल में रसायनों की सान्द्रता विशेषकर धनायनों की सान्द्रता बढ़ाती है तथा नमूनों में कैल्सियम, सल्फेट तथा पोटाशियम की मात्रा काफी हो जाती है। pH मान बेसिक रेंज में रहे। H+ आयन प्रमुखतया सल्फेट धनात्मक (SO_4) तथा केल्सिमय (Ca) ऋणात्मक की अधिकता से सहसंबंधित थे। कैल्सियम तथा H+ आयनों की अधिकता के बीच ऋणात्मक संहसंबंध विलयन तथा विनिमयी अभिक्रिया की महत्ता दर्शाता है जिसमें भिन्न कणीय सामग्री (चूने वाले खनिज) जो H+ आयन खर्च करते हैं, शामिल होते हैं। ऐसा पाया गया है कि अमोनिया की सान्द्रता मृदा के तापमान पर निर्भर करती है तथा सल्फेट वायुमण्डल में सापेक्षिक आर्द्रता से भली-भांति सहसंबंधित है। अध्ययनों से यह भी पता चला है कि तड़ित् झंझा से असम्बद्ध वर्षाजल के नमूनों की तुलना में तड़ित् झंझा से संबंध वर्षाजल के नमूनों में नाइट्रेट की सान्द्रता अधिक होती है।

ABSTRACT. About 180 rainwater samples were collected at Pune during the monsoon season of 1981 and analysed for various chemical constituents. Data have been utilised to study the importance of various contributing sources to the composition of rainwater, role of cations and anions in controlling the pH of rainwater and the influence of meteorological parameters on the chemical composition.

It has been found that maritime air is the major source of Cl and Na and for SO_4, anthropogenic sources appear to be quite important. In addition to above, local soil also contributes to the concentration of constituents, specially to cations and the samples get enriched to a large extent in terms of Ca, SO_4 and K. pH values remained in basic range and H+ions were sinificantly correlated with excess SO_4 (positive) and Ca (negative). Negative correlation between excess Ca and H+ions indicates the importance of dissolution and exchange reaction involving particulate material (calcareous minerals) thereby which H+ions are consumed. Concentration of NH_4 have been found to depend on soil temperature and SO_4 correlated well with the R. H. in the atmosphere. Studies also indicate that nitrate concentrations are higher in rainwater samples associated with thunderstorms in comparison to the samples not associated with thunderstorm.

1. Introduction

Atmosphere plays an important role in the geochemical cycle of various elements. Variety of pollutants which are emitted into the atmosphere by human activities enter the natural cycles and rainfall returns these pollutants to earth where they can affect biological processes in aquatic and terrestrial ecosystems. Study of chemical composition of rainwater can, thus, help in assessing the air pollution status of different regions as well as in the study of geochemical cycle of various elements. Since, rainwater can contribute significantly to the nutrient requirement of plants, studies regarding the deposition of various constituents is of importance from agricultural point of view also. Analysis of rainwater samples for various studies were started long time ago. However, data regarding chemical composition of rainwater over India are still meagre. Recently, Maske and Krishna Nand (1982) reported the results of studies on chemical constituents of precipitation over India. The data were collected on monthly basis from a network of 10 stations in the country. Chemical composition of rainwater from a few other locations in India have been also reported by Sequeira (1976 b), Sadasivan (1979, 1980), Subramanian and Saxena (1980) and Das *et al.* (1981). The results presented here are based on the study of chemical composition of rainwater samples which were collected on an event basis at Pune (18° 32′ N, 73° 51′ E, 559 m a.m.s.l.) during the monsoon season (June to September) of 1981. Rainwater on event basis was analysed to study the importance of various contributing sources to the composition of

TABLE 1

Monthly mean values of meteorological parameters at Pune during February to September 1981

Month	Mean temp. (°C)	Rain-fall (mm)	No. of rainy days	Av. surface wind (km h^{-1})	Mean R.H. (%)	Dates of collection of rain-water samples
Feb	22.2	2.2	1	2.38	50.1	23
Mar	24.8	—	—	3.87	42.1	—
Apr	28.7	8.2	1	5.83	43.3	30
May	29.9	36.7	1	8.90	53.0	02
June	28.2	153.5	15	8.84	74.7	03, 05, 11 to 14, 18, 19, 23 to 29.
Jul	28.1	282.2	25	7.89	85.5	All days except 14, 15, 16, 27, 28, 29.
Aug	24.3	94.8	21	7.11	82.8	Except 2 3, 10, 11' 20, 26, 27' 28, 30, 31
Sep	27.3	173.0	12	3.22	79.3	6, 7, 8, 10 11, 12, 16 17, 18, 20 21, 24

rainwater, role of cations and anions in controlling the pH of rainwater and the influence of meteorological parameters on the chemical composition.

It may be emphasised here that from the analysis of monthly precipitation samples it is rather difficult to identify various sources contributing to different chemical constituents and also the influence of short term meteorological parameters on chemical constituents may be asked. It is also possible that the correlations between chemical contituents and the monthly averaged meteorological indices might not be very obvious and even many interesting results may be obscured though the chemical constituents might be strongly correlated with meteorological parameters on the shorter time scale.

2. Details of sampling and analytical methods

The location of rainwater collector station at Pune is surrounded by cropped fields. There are no industries in the immediate vicinity of the station, but various industries are located at large distances from the station. Rainwater samples were manually collected with rainwater collector and stored in polyethylene bottles. In total, 180 samples were collected during the monsoon season of 1981 for the present study. Samples were analysed for sulphate (SO_4), nitrate (NO_3), chloride (Cl), ammonium (NH_4), sodium (Na), potassium (K), calcium (Ca) and magnesium (Mg). pH and conductivity of the samples were also measured. Analytical methods for SO_4, NO_3, NH_4 Na, K, Mg, Ca, and Cl were same as those given by Maske and Krishna Nand (1982). The overall accuracy of the analytical results was $\pm 10\%$.

Rainfall at Pune mainly occurs during May to November with maximum during July. February shows minimum monthly rainfall. About 70 per cent of the annual rainfall occurs during monsoon season ($\simeq$523mm).

Monthly mean values of different meteorological parameters at Pune prior to and during the period of study are given in Table 1. It can be seen that the place was practically dry prior to the monsoon season and mean temperatures were high. These conditions were favourable for the occurrence of bare soil leading to large amount of soil dust in June.

3. Discussion

3.1. *General considerations*

Monthly average concentration of constituents of rainwater collected during the period June to September is given in Table 2. In general, it can be seen that concentrations of nitrate (NO_3) and ammonium (NH_4) were maximum during the beginning of the season and they decreased as the season progressed. Concentrations of sulphate (SO_4) broadly remained constant with minor fluctuations depending upon the rainfall amount. Concentrations of chloride (Cl) and sodium (Na) increased with increasing monsoon activity and wind speed as well as roughness of the sea. Similar observations were made by Kulkarni *et al.* (1982) during their studies at Tarapur, a site situated on the west coast of India about 100 km north of Bombay. Their concentrations decreased to quite low values during September which represents the withdrawal phase of monsoon. Almost similar pattern has been observed for calcium (Ca) and magnesium (Mg) also. One of the reasons for similar pattern is wind dependence of the concentration of these chemical constituents though they are not fully derived from single source (sources may be sea or soil).

Potassium (K) concentrations remained broadly constant during June to August with slight increase during September. pH values were more than 6.0 indicating alkaline nature of precipitation. Conductivity values were low (13 to 26 μs/cm). Minimum value was observed during September (13.5 μs/cm) which indicates the overall reduction of anions and cations in the rainwater. Maximum concentration of NH_4 during June indicates the importance of production of ammonia (NH_3) due to decomposition of organic matter in the nearby agricultural fields and biological activity in the soil. Production of NH_3 is generally maximum when soil temperature is high with just sufficient moisture. SO_4 and Cl are the predominant anions in the rain samples whereas Na and Ca predominated the cations. According to Junge (1963), for Cl and Na, sea is the main source and in the present case, Arabian Sea is the main source.

Deposition values of few significant constituents such as SO_4, Cl and Na, at Pune during the monsoon

TABLE 2

Monthly mean chemical composition of monsoon rainwater at Pune during 1981
(Concentrations are in mg/litre)

	Rain-fall (mm)	pH	Con-ducti-vity (μ s/cm)	SO_4	NO_3	Cl	NH_4	Na	Ca	K	Mg
Jun	153	6.41	25.10	1.32	—	1.55	1.52	1.08	1.31	0.17	0.43
Jul	282	6.76	25.80	1.05	0.84	1.95	0.33	1.47	1.34	0.17	0.48
Aug	95	6.72	25.80	1.44	0.71	2.00	0.26	1.92	—	0.20	0.61
Sep	173	6.12	13.50	1.20	0.58	0.45	0.26	0.37	0.49	0.27	0.16

TABLE 3

Ratios of chemical constituents of monsoon rainwater at Pune during 1981

	Cl/Na	SO_4/Na	Mg/Na	Ca/Na	K/Na
Jun	1.44	1.22	0.40	1.21	0.16
Jul	1.33	0.71	0.33	0.91	0.12
Aug	1.04	0.75	0.32	—	0.10
Sep	1.22	3.24	0.43	1.32	0.73
Combined (Jun-Sep)	1.26	1.48	0.37	1.15	0.28
Sea water	1.8	0.25	0.12	0.038	0.036

season are 8.4, 10.5 and 8.3 kg/ha respectively. SO_4 deposition values are comparable to the values reported by Eriksson (1952) from some parts of USSR (7 to 13 kg/ha) which corresponds to fairly uncontaminated air in continental areas. Chloride and sodium depositions are quite low when compared to the values reported for coastal stations. Sequeira (1976 b) had estimated the Na deposition at 54 kg/ha at Bombay. For Ceylon Cl deposition was reported as 200 kg/ha (Eriksson 1952). However, Cl depositions at Pune are comparable to the values as reported for number of locations in USSR (8 to 13 kg/ha; Eriksson 1952).

3.2. *Ratios of chemical constituents*

It is the practice to calculate the ratio of various chemical constituents with respect to Na or Cl to assess the marine influence on their concentrations. However, Na would be a better reference than Cl (Sequeira 1976 a) specially for Pune during monsoon season since atmospheric particles and cloud condensation nuclei can lose considerable amount of their original Cl due to the change in phase and separation in space. In addition to above, Cl compounds can also occur in gaseous (HCl) and other industrial compounds (Sequeira 1973). Ratios of sea salt constituents in rainwater as obtained at Pune (Table 3) have been discussed in the following paragraphs for different months.

June — Cl to Na ratio was less than the sea water value (1.8) whereas SO_4/Na, Mg/Na, Ca/Na and K/Na values were quite high.

July — SO_4/Na, Cl/Na, Ca/Na and Mg/Na values had reduced.

Decrease in the SO_4/Na and Ca/Na values was appreciable.

August — SO_4/Na value remained similar to July but Cl/Na ratio further decreased with almost constant value of K/Na and Mg/Na.

September — Values of SO_4/Na, Mg/Na and K/Na had increased. Increase in the SO_4/Na and K/Na values was appreciable.

Decrease in the Cl to Na ratio had been observed by other workers also in the past. Eriksson (1960) had attributed it to the loss of Cl from wet sea salt nuclei in the atmosphere (R.H. value $>$ 75 per cent). High ratios between SO_4, Ca, Mg and K with Na in comparison to sea water indicates that in additon to marine sources there are other continental sources also. Local soil surrounding the sampling station which are fertilized from time to time appear to contribute to the above constituents. The decrease in SO_4/Na and Ca/Na values during typical monsoon months (July and August) is mainly due to the increase in Na concentration which appears to be of marine nature.

During September which represents the withdrawal phase of monsoon, surface wind speeds are reduced and predominant winds which are mainly westerly/southwesterly during June, July and August, change and components from N/NNW, NW and WNW are added. These factors are favourable for transport of less marine salt to Pune and thus the ratios of constituents which have significant continental sources with sodium (which is mainly of marine origin during monsoon period) increase significantly. Particulate matter from NW sector of the station where a few industries are situated also influence the concentrations of Ca, Mg and K.

Complete monsoon season — Comparison of mean ratios of various constituents for the complete monsoon

TABLE 4

Ratios of mean concentrations in rainwater sample

Ratio	Sea water	Average soil (Vinogradov 1959)	Average soil surrounding Pune station	Present work (Jun to Sep)	Delhi (Khemani and Ramanamurty 1968)	Calcutta (Handa 1969)	Bombay (Colaba) Sadasivan 1979)	Pune (Khemani 1974)
Ca/Na	0.038	2.17	2.40	1.15	4.60	3.27	0.40	1.37
K/Na	0.036	2.60	0.46	0.28	0.63	0.37	0.07	0.31
Mg/Na	0.12	1.00	0.41	0.37	—	0.50	0.12	—
Ca/K	1.00	1.00	6.40	5.80	7.30	8.80	5.60	3.70

season (SO_4/Na=1.48, Cl/Na=1.26, Ca/Na=1.15, K/Na=0.28 and Mg/Na=0.37) with seawater ratios (Table 3) suggest that rainwater samples at Pune get enriched to a large extent interms of Ca, SO_4 and K. Enrichment for Mg is also high. Enrichment, E, is defined as $E=(X/\text{Na})$ atm/(X/Na) S.W.-1 where (X/Na) atm is the weight ratio in the sample of element X to sodium and (X/Na) seawater (S.W.) is the same element weight ratio in seawater. Maximum enrichment has been observed for Ca (29.26). Enrichment in various constituents over Pune had been also reported by Murty and Ramanamurty (1969). Depletion of Cl as observed in the present studies have been reported by other workers also. (Khemani and Ramanamurty 1968; Murty and Ramanamurty 1969 and Sequeira 1976 b).

A comparison between the mean ratios as obtained from present measurements has been made with the ratios in monsoon rainwater samples from 3 other cities in India (Bombay, Calcutta and Delhi) and are given in Table 4.

Results show that enrichment of Ca at Pune is significantly higher than the coastal station (Bombay) but is quite low when compared with an inland station (Delhi). Enrichment of Mg is also high at Pune in comparison to costal station but is not that spectacular. Enrichment in K is in between the above two values. Handa (1969) had attributed the excesses of Ca, K and Mg in rainwater at Calcutta to soil origin particles. This appears to be applicable for Pune samples also.

An interesting observation regarding Ca/K ratio is that its value at Pune and Bombay is almost similar and is only slightly lower than Delhi. Further, a large Ca/K (6.40) ratio in the soil at Pune in comparison to average soil ratio of 1.0 indicates that average soil value may not be truly representative for soil samples over Pune and other parts of India. In the Table 4, ratios as obtained by Khemani (1974) at Pune during the monsoon season of 1972 are also given. The ratios as obtained at Pune in 1972 and 1981 are quite close.

3.3. *pH and ionic balance*

pH values exhibit large variation. However, the values are between 6 and 7. One of the reasons suggested by various workers for high pH (>5.6) is the acid base neutralization reactions in the presence of particulate matter in the atmosphere. A study of the ionic balance and its correlation with pH (individual samples) indicated that with increasing excess of cations, pH values also increased. However, the linear correlation coefficient between the above two parameters is not significant, but simple correlation between excess of calcium with H^+ ion concentration (-0.17) and also between excess of sulphate (after subtracting the contribution from sea) and H^+ ion concentration (0.20) is significant at 5 per cent and 1 per cent level, respectively. It indicates that excess sulphate and calcium are able to influence the pH values to a large extent at Pune during monsoon season and other constituents are not that imporant.

It is interesting to mention here that linear correlation between H^+ ion and SO_4 concentration is quite low (0.11) and with nitrate it is negative (insignificant). It indicates that pH at Pune is not controlled by HNO_3. However, H_2SO_4 may play an important role in controlling the pH alongwith HCO_3.

3.4. *Correlation studies between various chemical constituents*

(*a*) *Monthwise* — During the month of June, highest correlation has been observed between Cl and Na (0.96) as expected. High corrlations have been observed between Na, K, Ca and Mg. Quite interestingly SO_4 is also well correlated with Na, Ca and K and NO_3 with Ca. Significant correlation between NO_3, SO_4 and Ca indicates that NO_3 and SO_4 are being contributed from continental sources also. However, insignificant correlation coefficient between SO_4 and NO_3 indicates that both are not being derived exclusively from single source.

The general pattern of correlation during July, August and September remained broadly similar to that of

June. However, lowering of correlation coefficients between Cl and K, K and Mg are observed during July which indicates that source of K and Mg are not same druing this month. One of the reasons could be that the influence of local soil sources contributing to K and Mg has reduced due to wetting of ground and growth of grass due to rains. Quite interestingly, significant positive correlation has been observed between NH_4 and NO_3 during August indicating that a common source for both these constituents was prevalent during the above month. The exact reason for this is not very clear. Soil and decomposition of organic material can contribute significantly to the NH_4 concentration but, this is expected to be low during August. During the month of September correlation between Cl and Na reduces significantly suggesting that both are not being drawn from single source. This indicates that the influence of sea which was a major source for Cl and Na during June to August reduced during September.

(*b*) *June-September* — Correlations for the combined period, in general, are similar to that of June, July and August as expected (since number of samples for the month of September are comparatively small, *i.e.* 28). However, significant correlations between NH_4 and SO_4 (significant at 1 per cent) and between NH_4 and NO_3 (significant at 1 per cent) have been also observed. Most interesting correlation has been the positive correlation between excess SO_4 and $H+$ (0.20) and negative correlation between excess Ca and $H+$ (—0.17). It indicates that SO_4 probably in the form of H_2SO_4 influences the lowering of pH. Negative correlation between Ca and H+ion indicates the importance of dissolution and exchange reaction involving particulate matter by which H+ions are consumed. Low correlation between K and Mg confirms that both are not primarily derived from the same source.

3.5. *Chenical composition and meteorological parametres*

3.5.1. *Variation of concentration with rainfall*

The chemical composition of rainwater reaching ground level is governed by various physical processes such as formation and growth of raindrops, rainout and washout of the pollutants and on the intergap between two rainfall events. Concentration generally varies inversely with the amount of rainfall. Inverse relationship was attributed by Junge (1963) to droplet evaporation, amount of liquid water content in cloud and the contribution of a washout. Mukherjee (1980) also showed that there is an inbuilt inverse relationship of concentration of washed out material with the intensity of rainfall. The variation in concentration of Na with rainfall amount is shown in Fig. 1. It can be seen that concentration decreased with increasing rainfall amount. The variation of other constituents (Ca, Mg, K, Cl) is broadly similar to Na. The data set, in Fig.1 has been fitted by a curve of the form $Y=AR^{-B}$ where Y is the concentration of Na (mg/litre), A and B are constants and R is the rainfall (mm). Constants have been estimated as $A=0.92$ and $B=0.81$. The decrease in concentration with increasing rainfall is generally believed to be due to the increasing droplet diameter as well as increasing liquid water content of the precipitation cloud. As observed by Junge (1963) and Georgii & Weber (1960) the concentratons for Pune samples also showed large increase for low rain fall.

3.5.2. *Variation of NH_4 concentration with soil temperature*

Linear correlations between various constituents in rainwater and soil temperature were studied. Significant positive correlation (0.29) was obtained between concentration of NH_4 and soil temperature (measured close to surface). Soil temperature can be taken as representative of the biological activity. Positive correlation with NH_4 indicates that over Pune the amount of NH_4 deposited through rainfall is controlled by its rate of release from the soil by biological activity during decomposition of soil organic matter. High concentration of NH_4 during June substantiates the above positive correlation. However, some contribution to NH_4 concentration from the fertilizers which are put in the surrounding agricultural fields cannot be ruled out

3.5.3. *Variation of concentration with relative humidity (R.H.)*

Significant positive correlation between SO_4 and R.H. (average values preceding the rainfall event) at 1 per cent level (0.20) has been obtained. It indicates that SO_2 released from various sources get oxidized to SO_4 in presence of sufficient humidity in the atmosphere. This is in agreement with the results of other workers also. It also suggests that sulphates in rainwater over Pune may not be only derived from marine sources and soil. Positive correlation between NH_4 and R.H. (0.14) significant at 5 per cent level has been also obtained. It has to be viewed alongwith positive correlation with soil temperature. For production of NH_3 from soil (biological activity) alongwith high temperature some moisture is also required. However, the quantity of mositure required is quite critical. Very high moisture content may actually retard the production of NH_3 (Yaalon 1964).

3.5.4. *Variation of concentration with wind speed*

Positive correlations, though not significant, between Cl, Na, Ca, K, Mg and wind speed have been obtained. Minimum correlation coefficient (0.05) is between K and wind speed. Correlation coefficients between Cl, Na, Ca, Mg and wind are almost similar (0.09 to 0.12). One of the reasons for the above correlations is that contributions from sea and soil for various constituents increase with wind speed.

3.5.5. *Variation of nitrate concentration with thunderstorm activity*

Variation of nitrate (Y_1 in mg/l) with rainfall (R in mm) for the samples collected during thunderstorms and without thunderstorm have been examined separately and the data have fitted by a curve of the form $Y_1 = A_1R^{-B_1}$ where, A_1 and B_1 as obtained for two data sets are as follows :

$$\left.\begin{array}{l} A_1=1.83 \\ B_1=0.49 \end{array}\right\} \text{Data set associated with thunderstorms.}$$

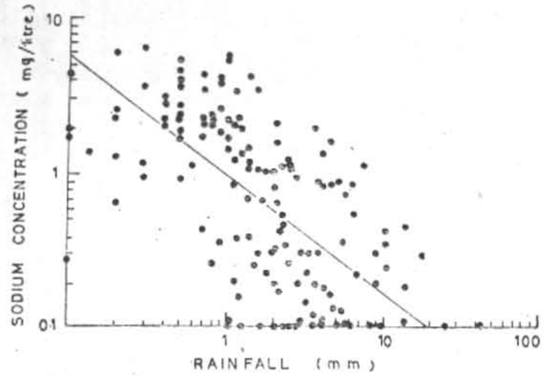

Fig. 1. Variation in sodium concentration with rainfall amount in rainwater samples

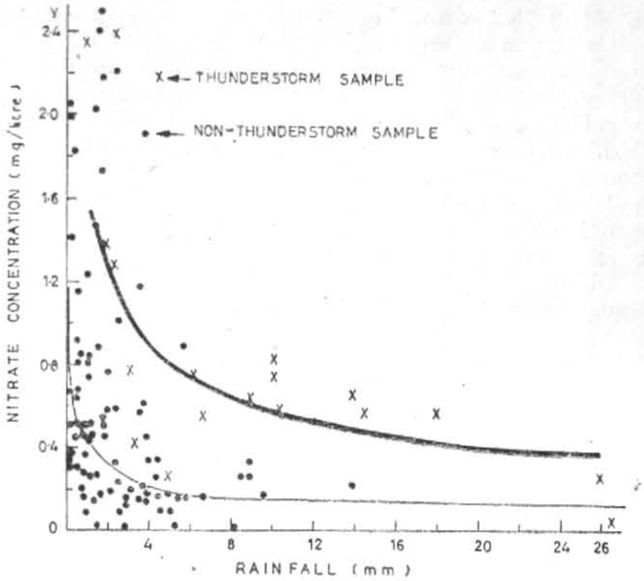

Fig. 2. Variation in nitrate concentration with rainfall amount in rainwater samples

$A_1=0.40$, $B_1=0.46$ } Data set not associated with thunderstorms.

It can be seen that values of B_1 are almost similar but the values of A_1 are quite different. In Fig. 2 variation of nitrate concentration with rainfall amount is shown for the events with thunderstorm and without thunderstorm separately. Least square lines fitted to the data sets are also shown in Fig. 2, and they indicate large scatter in the data points. Hutchinson (1944) had studied in detail the subject of thunderstorm and fixation of nitrogen in rain and had summarised the various processes by which fixation of nitrogen takes place in the atmosphere. Hutchinson (1944) had inferred that, in general, the major part of nitrate falling in rain may not be derived from the direct oxidation of N_2 in the atmosphere during thunderstorms. Angstrom and Hogberg [1952, (a, b)] from their observations in different parts of Sweden and Mukherjee (1955) from his studies over Sylhet and Bombay had concluded that in the ower atmosphere, electrical spark discharge may have some effect but it is not primarily responsible for the formation of nitrates in rainwater. Similar inference had been drawn by Gambell and Fisher (1964), Viemeister (1960) and Vissar (1964) also. However, Pratt (1977) suggested that perhaps 10 to 20 MT of nitrogen are fixed per year by lightning. Delwiche (1970) had also made similar estimates. Pratt (1977) had finaly summarised that there is seeming agreement that most of the nitrate—nitrogen in rainwater is of terrestrial origin, but there is sufficient evidence from differences in ratio of nitrate to ammonium and of other constituents of rainwater over tropical and temperate regions to justify an estimate of 10 MT of nitrogen fixed annually by lightning and other electrical discharge phenomena in the atmosphere. This is just four per cent of the total nitrogen fixed in the atmosphere by various processes.

It is, thus, evident that nitrate concentration in rainwater samples depends on various parameters and it may be difficult to separate out the contribution of atmospheric electric discharges unless other factors have been well isolated during the collection of the rainwater samples itself. Quite good number of the earlier studies suffered on this account.

Similar values of B_1 as obtained in the present study (during thunderstorm and non-thunderstorm events) which determines the shape of the decay curve suggest that the physical processes relating to the nitrate concentrations and rainfall amount were similar in both the cases at Pune. However, quite high value of A_1 for the data set with thunderstorms indicate that nitrate concentrations were higher in comparison with the rainfall events not associated with thunderstorm. A visual inspection of the least square curves fitted to the two data sets (Fig. 2) also indicates the same. The increase in nitrate concentration can be attributed to the fact that discharge of electrical energy in the lightning stroke causes free nitrogen to be oxidized into rainwater and brought to ground as nitrate. However, the large scatter indicates that for further quantific studies additional data are essential and it may be also desirable to quantify the thunderstorm activity. Nevertheless, the results from Pune are quite signficant even though the explained variance is only about 7 per cent considering the fact that the scatter in nitrate concentration is generally quite high as it depends on many factors.

4. Conclusions

Based on the sudy of rainwater chemistry data from Pune during the monsoon season of 1981, following conclusions can be drawn :

Maritime air is the major source of Cl and Na at Pune. For SO_4, anthropogenic sources appear to be quite important. Local soil also appear to contribute to the concentration of cations.

Desposition values of chloride and sodium are quite low when compared with coastal stations in India as well as in other countries, but they are comparable to the values as reported for number of locations in USSR. SO_4 depositions are also comparable to USSR. values reported from two continental areas representing fairly uncontaminated air over the area.

Study of ratios between various constituents and a comparison with sea water ratios suggest that rainwater samples at Pune get enriched to a large extent in terms of Ca, SO_4 and K. Enrichment for Mg is also high. Studies also show depletion of chloride at Pune as observed by other workers.

pH values exhibited large variation but the values remained in basic range (between 6 and 7). Correlation studies indicate that excess of SO_4 and Ca are able to influence the pH values significantly. Insignificant negative correlation between NO_3 and H^+ ion concentration indicates that pH at Pune is not controlled by HNO_3. H_2SO_4 may play an important role in lowering the pH. Negative correlation between excess Ca and H^+ ions indicates the importance of dissolution and exchange reaction involving particulate material (calcareous minerals) by which H^+ ions are consumed.

An inverse relation of form $Y=AR^{-B}$ between the trace constituent and rainfall has been found. B value for sodium has been estimated as 0.81.

Concentration of NH_4 has been found to depend on soil temperature which represents the biological activity. Significant positive correlation has been found between SO_4 and relative humidity, indicating that SO_2 released from various sources get oxidized to SO_4 in presence of sufficient humidity in the atmosphere. Positive correlation though not significant between Cl, Na, Ca, K, Mg and wind speed have been also obtained. One of the reasons of the above positive correlations is that contributions from sea and soil for various constituents increase with wind speed.

Study of variation of nitrate concentration for events with and without thunderstorm indicates that nitrate concentrations were higher for events with thunderstorms in comparison to the events not associated with thunderstorm. The above result is quite significant even though the explained variance is only about 7 per cent considering the fact that scatter in the nitrate concentration is generally quite high as it depends on many factors.

Acknowledgements

Authors are thankful to Dr. Bh. V. Ramanamurty, Director, Indian Institute of Tropical Meteorology, Pune for the facilities extended for the analysis of rainwater samples in his laboratory for Calcium, Potessium, Sodium and Magnesium. Thanks are also due to S/Shri S.D. Kachare and S.G. Ghanekar for the help rendered in the analysis of rainwater samples and to Mr. Ismail-Magdum for typing the manuscript.

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