Chemical composition of rain water and rain characteristics at Delhi. II.

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ABSTRACT

Samples of rain water collected at Delhi during the period 1964–67 have been analysed for nitrate, ammonium and sulphate. The data obtained have been sub-divided and examined according to the nature of rainfall, its intensity and total seasonal rain. Smaller proportions of nitrate to ammonium and nitrate to sulphate delineated the situations of higher rainfall. Some remarks have been offered in an attempt to explain the observed feature.

1. Introduction

Study of the inter-relationships between chemical composition of rain water and characteristics of rainfall was undertaken at Delhi (28°35′ N, 77°12′ E, 714′ A.S.L) in 1963 and the study continued for a period of 5 consecutive years before it came to a close in 1967. A high power 3.2 cm radar was in operation at the site of work throughout the period. The rain water samples collected were analysed for the cations sodium, potassium, calcium and ammonium; and for the anions chloride, sulphate and nitrate.

The composition of rain water has been found to be closely associated with the characteristics of rainfall, i.e., whether the rain under question is light or intense, and whether it is from cloud systems which are dominantly warm convective, cold convective or cold layer type. The features as noticed, from the available data upto the end of 1965, in so far as sodium, potassium, calcium, chloride and sulphate are concerned have appeared (Khemani & Ramana Murty, 1968). The year of commencement for the analysis of the ionic components ammonium and nitrate was 1964. The features relating to ammonium and nitrate from the data available for the period 1964–67, which provided rainfall situations of different types, are now reported. The concomittant values obtained of sulphate have been also considered in certain contexts. Mann–Whitney test was applied for evaluating the statistical significance of the results.

2. Collection of rain water samples and analysis

Using stainless steel funnels and polythene bottles, previously rinsed with double distilled water, rain water samples were collected from the second floor terrace of the National Physical Laboratory at New Delhi. The duration of collection varied from a few minutes to about an hour depending upon how intense was the rain. Each sample collected consisted of at least 400 to 500 ml of rain water. Most of the samples were collected in the monsoon season, July to September. A few collections were also made in summer (April–June) and in winter (December–March), when the rains are infrequent.

Ammonium was analysed by Nesslerization and nitrate by using chloroform solution of brucine alkaloid and sulphuric acid. Sulphate was analysed using barium chloride. The respective concentrations, in ppm, were measured colorimetrically using Bausch and Lomb Spectronic-20 Spectrophotometer.

Table 1. *Mean concentration values, in ppm, of ionic components and their ratio values, in the monsoon season of each year*

Year	Total rain-fall (mm)	NH_4	NO_3	SO_4	NO_3/NH_4	NO_3/SO_4	NH_4/SO_4
1964	1123.1	0.32 (16)	0.47 (17)	3.39 (17)	1.47	0.14	0.09
1965	456.7	0.20 (12)	0.80 (12)	2.09 (12)	4.00	0.38	0.10
1966	351.9	0.23 (15)	1.37 (15)	2.05 (14)	5.96	0.67	0.11
1967	963.0	0.34 (17)	0.90 (18)	2.72 (14)	2.65	0.33	0.13
Mean	723.7	0.28 (60)	0.88 (62)	2.62 (57)	3.14	0.34	0.11

3. Analysis and results

a) Association with monsoon behaviour

Of the four years 1964–67 the monsoon, at Delhi, was best in 1964 and worst in 1966. The mean values, for the monsoon season, of ammonium, nitrate and sulphate are given in Table 1 for the four consecutive monsoons. The total rain received at the station during each monsoon (seasonal rain) is given. The number of days of which the given concentration value is the mean is indicated in parenthesis.

The concentration of nitrate varied within wider limits (three times) than either ammonium or sulphate (one and a half times). The ratio values of nitrate to ammonium and nitrate to sulphate were closely associated with the behaviour of the monsoon. The values were low in good monsoon and high in bad monsoon. The variations noticed in the values between the years of good and bad monsoons are, sometimes, statistically highly significant. Considering 1964 which is the best monsoon and 1966 which is the worst monsoon, the values for these years of nitrate to ammonium are 1.47 and 5.96 respectively and of nitrate to sulphate 0.14 and 0.67 respectively. These variations in the ratio values are significant at 0.0007 and 0.00003 levels respectively.

Also, the concentration of sulphate was high in the good monsoon (1964) and low in the bad monsoon (1966). The ratio value of ammonium to sulphate which varied from 0.09 to 0.13 in the four years was not closely associated with the behaviour of the monsoon.

b) Concentrations in light and heavy rain

Data were sub-divided according to the mean intensity of rainfall obtaining during the period of collection on each day when collections were made. The two categories considered are light to moderate, when the intensity ranged from <1 to 10 mm/h, and heavy when it ranged from 11 to >100 mm/h. The values of mean concentration of ammonium and nitrate during the four consecutive monsoons commencing from 1964 are presented in Table 2. The number of days of which the given concentration value is the mean is indicated in parenthesis.

The ratio of nitrate to ammonium varied widely (upto about four times) under both the categories of rain from year to year but in all the years considered, the value of the ratio in light to moderate rain was more than that in

Table 2. *Mean concentration values, in ppm, of ionic components and their ratio values in situations of light to moderate and heavy rain in the monsoon season of each year*

Year	Light to moderate rain			Heavy rain		
	NH_4	NO_3	NO_3/NH_4	NH_4	NO_3	NO_3/NH_4
1964	0.23 (10)	0.41 (11)	1.78	0.33 (5)	0.44 (5)	1.33
1965	0.19 (8)	0.94 (8)	4.94	0.21 (4)	0.53 (4)	2.52
1966	0.23 (7)	1.61 (7)	7.00	0.24 (8)	1.15 (8)	4.79
1967	0.23 (7)	0.74 (7)	3.21	0.42 (10)	0.99 (11)	2.35
Mean	0.22 (32)	0.86 (33)	3.91	0.32 (27)	0.87 (28)	2.72

Table 3. *Mean concentration values, in ppm, of ionic components and their ratio values, season-wise in two years*

Year	Season	Total rain-fall (mm)	NH_4	NO_3	SO_4	NO_3/NH_4	NO_3/SO_4
1966	Summer	205.6	0.20 (5)	3.66 (5)	5.30 (4)	18.30	0.69
	Monsoon	351.9	0.23 (15)	1.37 (15)	2.05 (14)	5.96	0.67
	Winter	69.2	0.34 (5)	3.30 (5)	4.24 (5)	9.71	0.78
1967	Summer	35.4	0.10 (3)	1.10 (4)	6.17 (3)	11.00	0.18
	Monsoon	963.0	0.34 (17)	0.90 (18)	2.72 (14)	2.65	0.33
	Winter	116.2	0.93 (7)	1.96 (7)	9.16 (7)	2.11	0.21

heavy rain, by about 50 %. Also, the lowest and the highest values of the NO_3/NH_4 ratio in both light to moderate and heavy rains are observed in the years 1964 and 1966 which corresponded to the best and the worst monsoon respectively. The variation noticed in the ratio value between the two categories of rain is not statistically significant.

c) *Variation with season*

The total number of rainy days sampled in each season other than in the monsoon is generally few in each year. In 1964 and 65, the number sometimes was even zero. It is only in the years 1966 and 1967 that the number in none of the seasons was zero. Hence, the data of these latter two years only are considered. The values of the mean concentration of ammonium, nitrate and sulphate for each of the three seasons in the two years are shown in Table 3. The number of rainy days sampled in each season is given in parenthesis. The total rain received at the station in each season is also given.

The values of all the three constituents are conspicuously higher in winter than in monsoon. The values for nitrate and sulphate are the least in monsson. The ratio values of nitrate to ammonium and nitrate to sulphate are very different in the corresponding seasons in the two years, these being conspicuously less in 1967, which is the year of higher rainfall, than in 1966.

d) *Association with type of rainfall*

The rain occasions sampled in all the four years were classified, in the manner as reported earlier (Khemani & Ramana Murty, 1968), into three categories, warm convective, cold convective and cold layer type, with the help of information as obtained by radar of the height of the echo top and the presence of the bright band. The mean ionic concentrations in rain water evaluated for the three categories of rain are shown in Table 4. The figures given in brackets denote the values of standard deviation.

The value of ammonium, which remained essentially the same in warm and cold convective types of rain, was higher in the layer type rain. But, the value of nitrate, which showed variation with the type of rain, was minimum in the cold layer type. Thus, the ratio of nitrate to ammonium was minimum in the cold layer type rain. The variations noticed in the ratio value with the type of rain are not, however, statistically significant.

e) *Ice nucleus concentration in the air and ionic concentrations in rain water under similar meteorological situations*

A non-continuous programme of work on ice-nucleus measurement by the millipore technique was in progress at Delhi up to the end of 1966. The concentrations of ice nuclei, effective at $-15°C$, are available from that programme for a number of rainy days during 1965–66, which were all calssified into the three categories already mentioned according to the information obtained by the radar. The value of the mean concentration of ice nuclei corresponding to each category of the rain situation is given under the last column of Table 4 in which the ratio values of nitrate to ammonium, for the rain situations of the three categories during the four year's period 1964–67, have been tabulated. The values of sulphate and the ratio values of ammonium to sulphate are also given in columns 5 and 7 of the same table. The fol-

Table 4. *Mean concentration values, in ppm, of ionic components and their ratio values, and the mean concentration values of ice nuclei, in number per m³, in the three different rain situations mentioned*

Rain situation	No. of occasions when rain samples collected during 1964–67	NH_4	NO_3	SO_4	NO_3/NH_4	NH_4/SO_4	No. of occasions when ice nuclei measurements made during 1965–66	Concentration of ice nuclei
Warm convective	9	0.25 (0.141)	1.24 (0.944)	4.00	4.96	0.06	10	16.4
Cold convective	19	0.26 (0.183)	0.85 (0.526)	2.72	3.27	0.10	15	24.7
Cold layer	16	0.33 (0.258)	0.76 (0.435)	1.76	2.30	0.19	25	45.5

lowing interesting points are revealed. Warm convective type situation is associated with minimum concentration of ice nuclei in surface air layers (16.4/m³), and maximum ratio value of nitrate to ammonium in rain water (4.96). Cold layer type situation is associated with maximum concentration of ice nuclei in surface air layers (45.5/m³), and minimum ratio value of nitrate to ammonium in rain water (2.30). The ratio of ammonium to sulphate was minimum in warm convective type situation (0.06) and maximum in cold layer type (0.19).

f) *Thunder versus non-thunder rain*

The rainy days which are sampled in each monsoon season were classified into two categories, thunder and non-thunder, depending upon whether thundering was heard or not heard in the course of sampling. The criterion laid down for classifying the days in this manner is subjective. From the mean values of ammonium and nitrate as obtained under the two categories, thunder and non-thunder, the following points were noticed. The value of ammonium in rain water did not vary between thunder and non-thunder days. The value of nitrate, on thunder as against non-thunder days, showed noticeable increase (about double) in one season (1965), but also noticeable decrease (about half) in the following season (1966), suggesting no specific relation of the nitrate with thunder activity. Divergent views have been expressed in the literature about the relation of nitrate with thunder activity (Hutchinson, 1954; Gambell & Fisher, 1964).

4. Discussion

The features noticed suggest that the chemical state of the air in the region (the chemical composition of rain water is a good index of the chemical state of the air within the troposphere) and the precipitation activity are closely associated, although they do not reveal which is the cause and which is the effect. If the chemical state of the air in which clouds are formed is to influence the precipitation activity of those clouds, the question which arises is whether there is physical basis for considering that the presence of relatively more ammonium and sulphate than nitrate in the cloud-air would help facilitate more rainfall. While the question cannot be answered at this stage, the following preliminary remarks are offered. Laboratory studies recently made (Ramachandra Murty & Ramana Murty, 1972) have shown that supercooled water drops freeze more readily when they contain sulphates than when they do not. Also, the drops containing higher concentration of sulphates are found to freeze at warmer temperatures. Of the sulphates tested, ammonium sulphate is found to facilitate freezing with considerable fastness. Also, ice-nucleating substances like silver iodide have been found to improve in their activity in the presence of sulphates. These findings suggest that the presence in the cloud air of higher concentration of sulphates in general and of ammonium sulphate in particular would help facilitate development of ice-phase in clouds in situations where cloud build-ups extending beyond 0°C level are favoured. As prospects of rainfall improve in such situations, the above feature leads to the inference that higher contents, in cloud-air, of sulphates in general, and ammonium sulphate in particular, could lead to higher rainfall activity. This is partly corroborated by the fact that of the three types of cloud situation analysed, it is in the cold layer type cloud (the bright band noticed in such cloud ensures development of ice-phase in it), that the concentration of ammonium in rain water, in contrast with the other ionic components, was maximum (vide figures in column 3 of Table 4). Also, it is only under such situation (cold layer type) that the concentration of the ice-forming nuclei in the air was found to be maximum.

The ratio of ammonium to sulphate from year to year varied within the range 0.09 to 0.13. This value is considerably small as compared to what was found in west Germany by Georgii & Weber (1960) according to whom the ratio of ammonium to sulphate in the rain water was close to the value 0.37 which corresponds to that of ammonium sulphate. The low value for the ratio noticed in the present study agrees with what was found by Herman & Gorham (1957) in a predominantly agricultural area (0.1). The low value noticed at Delhi points out that sulphates are present there in the air in sizable concentration in forms other than ammonium sulphate.

The mean ratio value noticed in the present study for nitrate to ammonium for the four monsoon seasons is 3.14 (vide Table 1). This is higher than the value reported (about 2) for the Scandinavian region (Ångström & Högberg, 1952*a*, *b*) and for the British Isles (Stevenson, 1968) and much higher than the value noticeable (0.86–1.44) for regions in USSR (vide Table 2 of Petrenchuk & Selezneva, 1970).

5. Conclusion

At Delhi, the chemical state of the air (ratios of nitrate to ammonium and nitrate to sulphate), as indicated by the composition of rain water, has been found to vary markedly during contrasting rainy periods as of (1) light versus heavy rain, (2) warm versus cold rain, and (3) good monsoon versus bad monsoon. The variations noticed may be characteristic of the geographical region in which Delhi is situated (north-west India). But, the specific causes for these variations are not known and these have to be ascertained. Investigations carried out in different geographical regions elsewhere have pointed out that the chemical composition of rain varies in space and time under the influence of both macro-circulation conditions and local factors (Petrenchuk & Selezneva, 1960), which in turn determine the nature and extent of air-pollution in the region. Extension of measurements to selected stations in different geographical regions of the country, where the rain processes obtaining in clouds are not likely to be the same, may help to throw some light on these basic aspects.

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ХИМИЧЕСКИЙ СОСТАВ ДОЖДЕВОЙ ВОДЫ И ХАРАКТЕРИСТИКИ ДОЖДЯ В ДЕЛИ. II

Пробы дождевой воды, собранные в Дели в период 1964–67 гг. были проанализированы на нитраты, аммиак и сульфаты. Полученные данные были классифицированы и изучены в зависимости от природы дождей, их интенсивности и полного количества дождей за сезон. Меньшие пропорции нитратов к аммиаку и нитратов к сульфатам характерны для ситуаций с более интенсивными дождями. Высказаны некоторые замечания в попытке объяснить эти наблюдаемые особенности.