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Rain acidification in India caused by nitrates

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RESUMEN

La contribución a la acidificación de la lluvia, causada por los óxidos de nitrógeno que son a su vez oxidados para formar nitratos y que subsecuentemente liberan iones de hidrógeno a la atmósfera al reaccionar con las gotas de lluvia, ha sido estudiada para el periodo 1976 a 1978, utilizando datos de 10 estaciones BAPMON en la India. Se observó que existe una fuerte correlación inversa ($r = -0.845 \pm 0.083$) entre el pH de la lluvia y la correspondiente concentración de nitratos al 1% L. S. aproximadamente, lo que indica que el rápido decremento en el pH de la lluvia se debe al abrupto incremento de los nitratos radicales que se forman por la oxidación de los óxidos de nitrógeno que son en última instancia un resultado de la contaminación producida por los automóviles, debida al aumento de la población vehicular en la India.

ABSTRACT

The contribution in rain acidification caused by the oxides of nitrogen which are further oxidised to nitrates and subsequently release of hydrogen ions in the atmosphere while reacting with rain droplets has been studied from the period 1976 to 1987 using the data of ten BAPMON stations of India. It was observed that there exists a significantly strong inverse correlation ($r = -0.845 \pm 0.083$) between the rainfall pH and the corresponding concentration of nitrates at about 1% L. S. which indicates that rapid decrease in rain pH in India is mainly caused by the sudden increase in nitrate radicals which are formed by the oxidation of nitrogen oxides which are the ultimate outcome of automobile pollution caused by the rise in vehicular population in India.

1. Introduction

Acid rain has become now-a-day a burning issue of all environmental studies because of its implications. It acidifies lakes, killing a large number of fishes thus affecting the government's economy, affects soils thus changing our vegetation system, threatening our food and fresh water supplies, damaging our forests, endangering the wild life and sensitive creatures, affecting structures and monuments and delustering metals. Acid rain is a worldwide problem. Advanced industrialized countries of Europe and America are already facing this problem while the developing countries, like India, are in a state of alertness. Acid rains are produced as a result of the increase in the acidic components (gases and particulates) of the pollutants in the atmosphere due to heavy industrialization, urbanization and vehicular traffic. These gases mostly oxides of sulphur, nitrogen and carbon are generated by burning of fossil fuel, petroleum products, and automobile exhausts. They are converted into the corresponding sulphates, nitrates and carbonates respectively in the atmosphere by oxidation (homogeneous or heterogeneous) due to the oxidants H_2O_2, O_3, HO or O_2 with or without catalytic agents (NO_2 or heavy metals). Thus in this process H^+ion is liberated in the atmosphere which is very important in rain acidification process. It is, however, neutralized by NH_3 and alkaline particulates present in the atmosphere.

2. Trends of pH in India

The trends of pH, which is the measure of H^+ion concentration in rain water, have been studied from the period 1976 to 1987 using the data of ten background air pollution monitoring (BAPMON) stations of India. There are about 140 BAPMON stations located at local pollution free sites all over the world. Their main aim is to observe the background level of various air pollutants, so that their atmospheric trends as well as their source region can be precisely

Table 1. Locations and particulars of Indian BAPMON stations.

Station	WMO index No.	Latitude °N	Longitude °E	Elevation (m)	Remarks
Allahabad	42475	25°27'	81°44'	98	Land Station
Jodhpur	42339	26°18'	73°01'	217	Desert Station
Kodaikanal	43339	10°14'	77°28'	2343	Hill Station
Minicoy	43369	08°18'	73°00'	2	Island Station
Mohanbari	42314	27°29'	95°01'	111	Land Station
Nagpur	42867	21°06'	79°03'	310	Land Station
Port Blair	43333	11°40'	92°43'	79	Island Station
Pune	43063	18°32'	73°51'	559	Coastal Station
Srinagar	42027	34°05'	74°50'	1587	Hill Station
Visakhapatnam (Waltair)	43150	17°41'	83°18'	72	Coastal Station

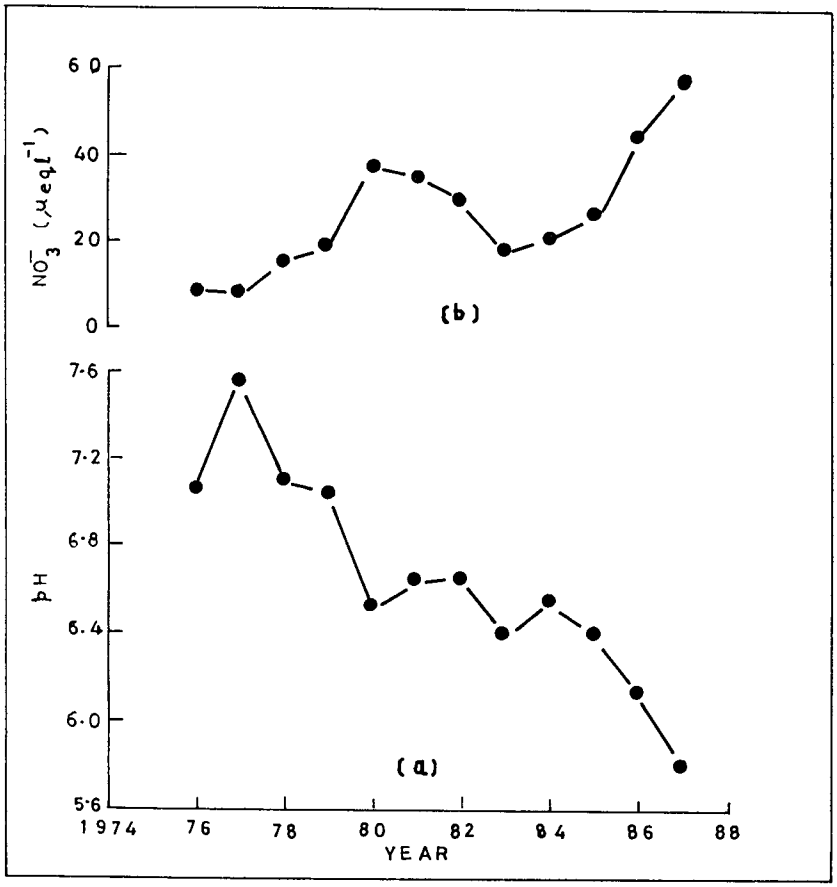

Fig. 1. Temporal Trends of (a) pH of precipitation and (b) NO_3^- – (μ eq. 1^{-1}) in India (1976-1987).

located and studied. In India there is a rich network of ten BAPMON stations well spreaded out geologically and geographically (desert stations, hill stations, coastal stations, island and inland stations) throughout the country as detailed in Table 1. pH of rain water is measured by the standard pH meter and then each pH value is converted to its equivalent H^+ion concentration, multiplied by the precipitation and the sum of these values is divided by the sum of the corresponding monthly precipitations in millimeter in a year. The resulting H^+ion concentration is reconverted to pH value to get the annual precipitation weighted mean pH value. The data of the ten stations then have been pooled together and the rainfall weighted averages have been worked out. These rainfall weighted averages, which have been used in this study throughout, give the representative value of pH for the country as a whole. The trend as studied is coming down (Fig. 1a) successively indicating the growing influence of acidic radicals in the atmosphere. Varma (1989a) observed decreasing pH trends at 8 out of 10 BAPMON stations in India, for which this study was done. In a more recent study Varma (1990a) found that the pH values in India are coming down as low as 4.00 at Indian BAPMON stations and consequently the pH regionalization of the country have been made (Varma, 1989b).

3. Trends of nitrate radicals

Similarly, the trends of nitrate concentration in the precipitation have been determined (Fig. 1b) which on the contrary exhibit increasing trends. The concentrations of the samples have been determined as per instructions received from WMO (World Meteorological Organization). Nitrate in analysis, is reported as nitrogen and is estimated by the modified method as described by Jekins and Medkar (1964) which uses controlled heating and chloride masking. Absorbance is measured at 410 nm. Nitrates are caused mostly by (i) vehicular traffic (ii) nitrogenous fertilizers and to some extent by (iii) lightening discharges in the atmosphere. Automobile emission is the single largest source of nitrates in the lower troposphere. The increase in the nitrate pollution in the country is therefore the outcome of rapid increase in the vehicular population in India. The statistics (1987) reveal that more than 12 million of vehicles were on the road up to 1986 in India and this figure is likely to be increased in the coming years (Table 2).

Table 2. Number of motor vehicles registered in India.

	Public service vehicles								
Year/State	Two wheelers	Autorickshaws	Jeeps	Cars	Taxis	Buses	Goods vehicles	Miscella neous	Total no. of vehicles
1	2	3	4	5	6	7	8	9	10
1950-51	26,860	..	..	147,712	11,551	34,411	81,888	3,891	306,313
1955-56	40,961	..	..	187,866	15,318	46,461	119,097	15,857	425,560
1960-61	88,360	6,235	31,670	256,243	21,663	56,792	167,649	35,863	664,475
1965-66	225,631	16,070	60,901	359,195	35,725	73,175	258,977	69,369	1,099,043
1970-71	575,893	36,765	82,584	539,475	60,446	93,907	342,577	133,668	1,865,315
1975-76	1,045,428	59,445	94,132	601,823	80,429	114,193	364,671	309,178	2,679,299
1980-81	2,528,364	142,033	18,549	898,143	100,009	153,757	564,843	667,315	5,173,013
1984-85	5,120,562	276,006	205,525	1,186,661	153,608	213,410	847,090	1,346,511	9,006,265
1985-86	6,264,348	336,911	188,298	1,350,038	171,524	227,608	915,176	1,027,235	10,481,138
1986-87(P)	7,658,269	385,924	266,980	1,442,175	185,946	246,848	1,017,840	1,142,563	12,346,545

4. Correlation of pH with nitrates radicals

In order to see the nature of the correlation, the pH values have been plotted against the

corresponding values of nitrates using the least square method, it was observed that the plote can be satisfactorily represented by a linear regression equation as follows:

$$pH = (7.362 \pm 0.133) - (0.028 \pm 0.001)NO_3^- .$$

A strong inverse correlation ($r = -0.845 \pm 0.083$) has also been observed between the above two variables significant at 1% L. S. indicating greater influence of nitrate ions in decreasing the pH values of precipitation. Thus the increase generation of NO_x will cause a decrease of pH values of rain water.

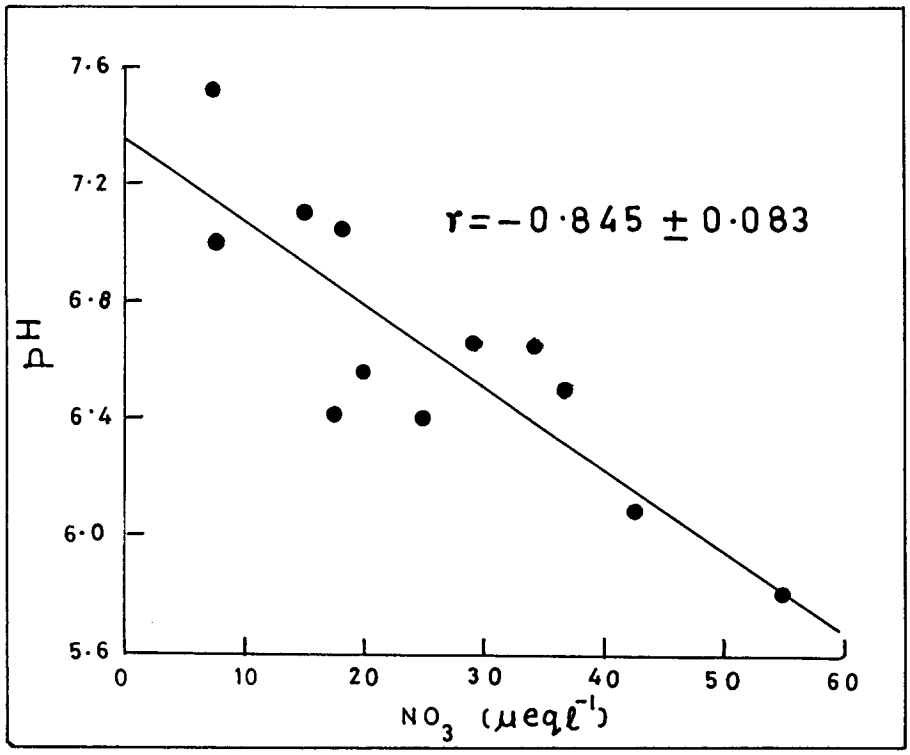

Fig. 2. Correlation of pH with NO_3^-.

5. Discussion

Many studies have been conducted in India by various workers such as Handa (1969); Das *et al.* (1981), Subramaniam and Saxena (1980), Maske and Krishnanand (1982), Mukherjee *et al.* (1985) and Khemani *et al.* (1985) on the chemical composition of precipitation aimed at indentifying the radicals which contribute greatly towards its acidification and it was observed that the presence of excess H^+ion in the atmosphere is actually balanced by the anions SO_4^{2-} and NO_3^- which are the potential contributers of the rain acidity. Varma (1190b) observed decreasing trends of sulphur in India which will definitely minimize the chances of sulphuric acid rains in the country. But the nitrate pollution level in India is rising fast due to increased automobile emissions, which is considered as an important anthropogenic source of inorganic nitrogen compounds in the atmosphere of India. Not only in India, but in many parts of the world the nitrate pollution has far exceeded the sulphur pollution and rising at an alarming rate thus causing enough downfall of rain pH.

Brimble and Pitman (1980) observed a marked shift in the seasonal distribution of nitrate in the rain resulting in the change in the deposition values from < 0.1 g m^{-2} Y^{-1} in the middle of nineteenth century to 0.2 g m^{-2} Y^{-1} in 1980 in Southern England. Similar results were obtained by Salman *et al.* (1978) earlier in U.K. Likens *et al.* (1977) found that the contribution of H_2SO_4 declined from 83% to 66% of the total acidity between 1964 and 1974 at Hubbard Brook, NH, while the contribution of HNO_3 increased from 15% to 30% during the same period.

Nesbet (1975) observed that the fraction of H^+ deposition in Eastern United States attributable to HNO_3 rose from 19% in 1955-56 to 24% in 1972-73 while the deposition attributable to H_2SO_4 decreased from 80% to 73% during the same period. Liljestrand and Morgan (1978) reported that HNO_3 and H_2SO_4 accounted for 58% and 42% respectively of the acidity in the precipitation of Pasadena, California, where more than twice as much NO_x as SO_2 is emitted annually. According to Galloway and Likens (1981), the NO_x emissions have increased relative to SO_2 which is reflected by the increased NO_3^- in precipitation relative to SO_4^{2-} in United States.

Vermeulan (1979) observed in Neatherlands that from 40,000 tons of NO_x generated by traffic in 1960, the figure has risen to 130,000 tons in 1976. Thus accounting for more than 40% of the total NO_x emissions. Salina *et al.* (1979) found higher correlation of H^+ with NO_3^- than with SO_4^{2-} in Neatherlands, indicating more probability of HNO_3 rains there than H_2SO_4 rains, Asman (1983) also got similar results in Neatherlands. According to Environmental Agency report (1974), in Japan, the mean concentration of SO_2 was reduced from 0.056 ppm, in 1965 to 0.031 ppm, in 1972, while that of NO_x was increased from 0.0227 ppm in 1968 to 0.0283 ppm in 1972. The level of all pollutants are decreasing there except NO_x and HC_s which are rising due to increased vehicular traffic there.

Harvath and Meszaros (1984) observed 39% increase in NO_x in Hungary from 1970 to 1980, while a decrease of 7% in SO_2 concentration was observed by them.

In many parts of NH, man's NO_x production greatly exceeds that of natural sources (e.g. from soil microbes). In USA anthropogenic NOx sources are 5-10 times larger than natural ones. In Western Europe and USA 30-50% typically comes, from vehicles and the rest comes from other sources. USA and Europe are the largest NO_x sources in the world producing around 15-22 metric tons of NO_2 annually.

In Venezuela, the anthropogenic emissions of NO_x and SO_2 are increasing rapidly. Between 1970 and 1985, NO_x emissions (mainly from motor vehicles and burning of natural gas) nearly doubled and SO_2 emissions (mainly from power plants and other fuel consumption) more than trepled according to Rodhe and Herrera (1988).

According to WMO special report (1988), NO_x emissions have far exceeded the SO_2 emissions in Austria, France, Federal Republic of Germany, Neatherlands, Norway, Sweden, Luxemburg and Switzerland. Thus NO_x which is a key precursor to HNO_3 is rising globally due to man's disruption of the natural nitrogen cycle and India cannot be an exception to it considering the global air circulation. Thus the possibility of HNO_3 rains in the country cannot be altogether ruled out specially in near future as the vehicle production and the consumption of petrolium products are increasing fast. Cars and two wheelers which are the main culprits have become the symbol of man's status now-a-days. Thus in the light of all this, Charles and Brejonik (1980) have rightly said that the relative importance of H_2SO_4 and HNO_3 contributions to rain acidity has changed with time tilting towards the later.

Conclusions

Thus, comparing the results achieved in the present study with the work done by various other

authors in different industrialized advanced countries of the world, it is concluded from this paper, that automobile exhaust emissions are bound to increase in the future in India. As a result of which, NO_x will dominate in the atmosphere which is a precursor to HNO_3. Therefore, the chances of HNO_3 rains in India are quite high unless the vehicle pollution control strategies are rigorously enforced by the government.

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