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Importance of natural dust in controlling the acidity of rain over India

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सार — भारत को मृदा तथा वर्षा जल नमूनों के पी एच आंकड़ों का बर्षा की अम्लता के नियंतण में प्राकृतिक धूल के महत्व को आंकने के लिए अध्ययन किया गया है। ऐसा पाया गया है कि आस पास के क्षेत्र की मृदा का पी एच वर्षा जल के पी एच को पर्याप्त सीमा तक प्रभावित करता है। साधारणतया भारतीय मृदा क्षारीय होती है (भी एच क्षारीय परास में) तथा हवा में धूल की मात्रा भी बहुत अधिक पाई जाती है। परिणामस्वरूप वर्षा के पी एच मान, आम तौर पर क्षारीय परास में होते हैं। इस प्रकार भारत के ऊपर (झीलों व मुदा पर) अस्ल वर्षा के प्रभाव को अधिक बढ़ा-चढ़ाकर प्रचार इसलिए न किया जाए क्योंकि मृदा की धनायन विनिमय क्षमता और सतही जल की पी एच क मान ऊंचे है।

ABSTRACT. pH data of rainwater samples and of soils from India have been studied to assess the importance of natural dust in controlling the acidity of rain. It has been found that pH of rainwater is influenced to a large extent on the pH of soil and the dust load in the surrounding region. Indian soils are normally basic in character (pH in basic range) and the dust load is quite high, as such, pH values of rain are in general in basic range. Further, the effect of acid rain over India (on lakes and soil), in general, may not be pronounced due to high values of cation exchange capacity of soils and pH of surface water.

1. Introduction

The phenomenon of acid rain which was earlier restricted to a few selected areas in the world is now covering wider areas, especially in Europe and USA. In addition to above, areas which were already getting acid rain have started getting rain with higher acidity content (Likens and Butler 1981). Likens et al. (1979) have shown that in parts of eastern USA and western Europe, rain has changed from nearly neutral solution 200 years ago to a dilute solution of sulphuric and nitric acids. Of late, in India also, people have started apprehending about the acid rain, in general, and in particular over Taj Mahal (Agra) area due to release of pollutants from Mathura refinery. However, recently Krishna Nand (1984) had shown that over India, lowering of pH to acidic values might be restricted close to highly industrialized cities only such as in Bombay (pH=4.5) and the phenomenon of acid rain may not be of regional scale. He had attributed it to the acidbase neutralization reactions in presence of basic particulate matter which are present in large (varying) quantities throughout the country. Krishna Nand (1984) had also concluded that due to the high level of suspended particulate matter over Agra of which a good fraction is expected to be of course mode, pH of rainwater over Taj Mahal, Agra, is not expected to be in acidic range. Above inferences were based on the study of pH data collected from 10 BAPMoN (Background Air Pollution Monitoring Network) stations

situated at Allahabad, Jodhpur, Kodaikanal, Minicoy, Mohanbari, Nagpur, Port Blair, Pune, Srinagar and Visakhapatnam alongwith the other published data regarding the precipitation chemistry and air pollution from different parts of India. Monsoon period rainfall weighted mean pH (1973-1980) at the above stations are given in Table 1. It can be seen that mean pH values of pH at Allahabad, Jodhpur and Srinagar are quite high (7.3) whereas at Pune it is close to 7.0. Even at Visakhapatnam which is comparatively more polluted, mean pH is about 6.6. Lowest value occur at Kodaikanal. pH data from other parts of India as obtained by various workers was also studied by Krishna Nand (1984) and are given in Table 2.

With a view to assess the influence of particulate matter on pH, rainwater samples had been analysed for base cations, *viz.*, calcium, sodium and potassium, and the total concentration of all these cations (milli equiv/litre) had been computed. Since, base cations, specially calcium and potassium are mainly soil derived, their concentrations can be taken as representative of the particulate matter load over the station. Very good correlation between pH and cation concentrations was observed by Krishna Nand (1984). Role of base cations in increasing the pH was very clearly brought out by comparing the pH values from Srinagar (7.35) and Kodaikanal (6.13) alongwith the cation concentrations (0.17 and 0.03 milli equi/litre, respectively).

TABLE 1 Rainfall weighted mean pH at RAPMoN stations

TABLE 2 Mean pH at different stations (other than RAPMoN stations)

RAPMoN stations	pH	S. No.	Station	pH	
Allahabad	7.28	(1)	Amritsar	7.0	
Jodhpur	7.34	(2)	Bay of Bengal	6,75	
Kodaikanal	6.13	. (3)	Bhopal	6-7.2	
Minicoy	6.74	(4)	Bikaner	7.8	
Nagpur	6.36	(5)	Bombay	6-7, 4.5	
Port Blair	6.49	(6)	Calcutta	6-7	
Pune	7.06	(7)	Delhi	7-8.4	
ringger	7.35	(8)	Jaisalmer	7.2	
ninagai	1.35	(9)	Lucknow	7.45	
Visakhapatnam	6.62	(10)	Palsana	7.8	

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1.17		L L	2	

Composition of natural dust (Winkler 1976)

Terrestrial dust, the most essential component of windblown silt	Mineral composition	Approx. reactivity	
 (a) Dust from carbonate rocks (limestone, dolomite): Agricultural soils Flood plains Construction sites 	Clay, quartz Calcite, some clay Calcite, clay	Little reactive Calcite most reactive Calcite most reactive	~
 (b) Dust from crystalline rocks (granite, gneiss, slate, etc) : Agricultural soil Flood plains Construction sites 	Quartz, clay Quartz, clay, silicates Quartz, clay, silicates	Little reactive Do. Do.	
 (c) Dust from glacial till (moraines) : Agricultural soils Flood plains Construction sites (d) Dust from glacial outwork 	Quartz, clay (silicates) Quartz, clay calcite Quartz, clay, calcite	Little reactive Reactive (calcite) Do.	
(sand and gravel) : Agricultural soils Flood plains Construction sites	Quartz, silicates (calcite) Quartz, silicates, calcite Quatrz, silicates, calcite	Reactive Do. Do.	

It may be mentioned here that both are hill stations and no polluting chemical industry is situated around the above monitoring stations. It was also found that pH is affected more by the concentration of calcium in comparison with Na and K. The above studies indicate that if soil characteristics and dustload at different places can be studied in advance, a forecast regarding the likely pH of rainwater over the region can be made. Keeping in view the importance of natural dust in controlling the acidity of



Fig. 1. pH of soil (1:2.5 H2O) at different locations in India

rainwater, pH data alongwith local soil characteristics have been studied. These studies can give a clue regarding the probable areas where potential of acid rain is high.

2. Sources of natural dust

Wind blown dust, from dry river beds, flood plains and beaches, ploughed fields, construction sites and desert regions are important sources of natural dust. Quartz, carbonates, feldspars and clay minerals are the most important constituents of the above natural dust.

Dust from volcanic eruptions, mainly consisting of silica, glass also settle back on the earth's surface but they are the least reactive as such they are not important from precipitation chemistry point of view.

Mineral content of natural dust and relative reactivity with air pollutants (Winkler 1976) are given in Table 3.

It can be seen from Table 3 that quartz, the carbonate minerals calcite and dolomite, the feldspars, ferro-magnesium silicates and clay minerals are the minerals components of importance. Calcite in dust reacts readily with the acids in the rainwater. It is important to mention here that sulfate ion is not eliminated from rain but it gets converted from sulfurous or sulphuric acid to relatively harmless gypsum, CaSO₄. The presence of water-soluble gypsum appears to explain the frequent high calcium content of rainwaters. Quartz is inert and non-reactive but clay crystals, can absorb ingradients and hold them tightly on their crystal surfaces which may help to neutralize some acid components in the air temporarily until they can be released again to the soil. Feldspars and the ferro-magnesium silicates react with the tiny H^+ cation in acid rain producing less acid conditions of the rain when tied up during the weathering process.

Minerals are involved in dissolution and exchange reactions with rainwater that consume H^+ ions. The congruent dissolution of calcareous minerals:

$$M (CO)_3 + H^+ = M^{+2} + HCO_3^-$$
 (1)

with M (CO₃) generally being CaCO₃ or Ca Mg (CO₃)₂ is known to be highly efficient at neutralizing H⁺. Aluminosilicate minerals neutralize H⁺ by incongruent dissolution of silicate minerals;

$$M = A1 \text{ silicate (S)} + ZH^{+} + H_2O$$

= H_SiO_4 + MZ^{+} + A1 = silicates (S) (2)

Absorption of protons on various substrates (organic matter, oxides, silicate minerals) :

$$M - Substrate + ZH^{+} = (H)_Z \text{ substrate} + MZ^{+}$$
(3)

with M being typically Na, K, Ca or Mg also helps in consuming the H⁺ ions.

2.1. Characteristics of Indian soils

Detailed data regarding the characteristics of Indian soils are, in general, lacking. Recently, National Bureau of Soil Survey and Land Use Planning (ICAR 1982) had published Bench Mark Soils of India. pH data of soils from different locations in the country as mentioned in the above report are plotted in Fig.1. pH values of soils give an idea about the chemical balance between cations and anions in the soil and it is expected that rainwater pH would be influenced to a large extent on the pH of local soil.

From Fig. 1 it can be seen that pH values of soils are quite high between 15°N and 35°N. However, the values are significantly low in the longitude belt of 85°E to 95°E covering the northeast region of the country. Quite interestingly, high pH values have been observed in Jammu & Kashmir, Punjab, Haryana, U.P., Rajasthan, Madhya Pradesh, Gujarat, Maharashtra, Karnataka, Andhra Pradesh and some parts of Tamil Nadu. Quite low values of pH are observed in coastal Kerala and also at hill station in Tamil Nadu (Kodaikanal). In Bihar and West Bengal, broadly, pH is low. East of the above two States, pH is quite low. From Fig. 1 it can be inferred that western parts of the country are having basic soils whereas soils in eastern part have (about 15°N) lower pH. It is important to mention here that natural dust load in the atmosphere over northwestern parts of India are expected to be high in comparison to eastern locations. It has been also observed that at the hill stations or locations where rainfall is high, pH of soils are low due to the leachnig effect. At such locations mainly laterite soils occur.

3. Effects of acid rain

There are various evidences suggesting that acid rain adversely affects public welfare. These include the loss of fish and other aquatic life in lakes, increased leaching of nutrient cations from the soil, reduction in crop and forest productivity, release of heavy metals or nutrients from rocks and soils, release of copper and lead from water pipes into drinking water supplies, corrosion of materials such as limestone buildings and automobile finishes.

Recent studies on the problem of acidification of lakes indicate that soils and bedrock play a very important role in controlling the acidity. Studies show that for rain of pH=4.0, pH of different lakes may vary between 4.8 and 7.0 due to the buffering action of different types of soils and bedrock. Limestone and sandstone, rich in calcium carbonate are potent neutralizers of acid whereas impervious granites are poor bufferer. In fact, the alkalinity of surface water which is an important parameter controlling the acidity of lakes (from acid rain) depends on the weathering of base cations from the watershed and can be used as an indicator regarding the susceptibility of lake or stream to acidification.

A study of quality of irrigation waters (rivers) in India by Chaddha (1965) indicate quite high pH values (7-9) for the water samples collected from different rivers (from different parts) in India. This suggests basic nature of Indian river water having good buffering capacity.

In order to study the sensitivity of different soils and lakes to the acid rain, a program was undertaken in USA (Glass et al. 1982) and generalized sensitivity maps, were prepared based on bedrock geology. In addition to above, data on the chemistry of surface waters was also collected. It was found that alkalinity and calcium were significantly related to rock type. From the study of surface water sensitivity it was inferred that lakes containing calcium less than 2.5 mg/litre were quite sensitive to acidification. Similarly, soil maps were also prepared in USA from sensitivity point of view. Main parameter for above mapping had been cation exchange capacity of the soils and the presence of free carbonates as well as management system imposed on the soil, e.g., whether cultivated and fertilized or limed or renewed by flooding or other additions.

The limited cation exchange capacity data of soils and pH of surface waters which are available from India indicate that the Indian soils and surface waters in most of the regions may not be very sensitive from acidification point of view. However, for detailed classification regarding sensitivity of soil and lakes from acidification point of view it would be essential to have additional information on the chemical characteristics of Indian soils such as exchangeable bases and percentage of carbonates as well as the chemistry of lake waters.

4. Conclusions

Study of pH of soil and rainwater over India indicates that the latter is influenced to a large extent by the former. In general, pH of soils is in basic range and the concentration of suspended particulate matter representing mainly the natural dust load over India is quite high. Due to the above, the pH values of rainwater, in general, are in basic range over India. Main reason for the above is acid base neutralization reactions in presence of basic particulate matter.

The limited available data on cation exchange capacity of soils and the pH of surface waters indicate that the Indian soils and surface water in most of regions may not be very sensitive from acidification point of view. This suggests that possible effect of acid rain over India on lakes and soil may not be pronounced.

It is important to stress here that in India detailed studies regarding the soil characteristics and chemistry of surface waters may be made specially in the areas where rainfall with low pH have been observed. This would help in the study of problem of acid rain in a scientific manner and also provide a tool to tackle the problem efficiently.

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