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A physical reason for higher pH of tropical rainwater

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ABSTRACT. pH measurements of monsoon rainwater in India indicate that pH values are near about 7.0 which is the neutral value of pure distilled water. However, similar measurements in Europe and USA yield much lower values which are close to the theoretically computed value of 5.65 at 20 deg. C. The above theoretical value is based on the assumption that dissolved carbon dioxide in rainwater is in equilibrium with the atmospheric carbon dioxide. An attempt has been made in this paper to explain the higher pH of tropical rain in terms of the temperature dependence of solubility and dissolution rate of carbon dioxide in rainwater.

1. Introduction

Due to increasing urbanization and industrialisation, atmospheric pollution is on increase and for the quantification of pollution status of a city or region, measurement of various parameters have been suggested from time to time. pH of the precipitation which is defined as the negative logarithm of the hydrogen ion concentration has been most widely used to study the pollution status of different regions in the world. Recently, Likens *et al.* (1979) had shown that in parts of the Eastern USA and of Western Europe, precipitation has changed from a nearly neutral solution 200 years ago to a dilute solution of sulphuric acid and nitric acid to-day. They attributed this trend to the increase in emission of sulphuric and nitrogen oxides to the atmosphere accompanying the rise in the burning of fossil fuels.

Carbon dioxide plays a very important role since it dissolves in the water and forms carbonic acid (H_2CO_3) which is a weak acid. This dissociates only slightly in distilled water and yields hydrogen (H^+) and bicarbonate ions (HCO_3^-). At normal concentrations and pressures of carbon dioxide in the atmosphere the equilibrium value of pH of rainwater would be 5.65 at 20 deg. C. Measurement of pH of rainwater in Europe and America (Barrett and Brodin 1955; Likens *et al.* 1979) do show such low values of pH but measurements in India indicate a much higher value (close to neutral value of 7.0). An attempt has been made in this paper to explain the higher pH of tropical rain in terms of the temperature dependence of solubility and dissolution rate of carbon dioxide in water.

2. pH measurements in India

Mukherjee (1957) made the first systematic pH observation in India at Calcutta and he observed pH values of rainwater close to 7.0. For continuous precipitation, initial values were close to about 5.7 but as the rain progressed pH values increased and approached to about 7.0. He concluded that monsoon rainwater is neutral under Calcutta conditions.

Mukherjee (1964) further made measurements of pH of rainwater from continuous rain at Calcutta and Bombay. He again observed pH values between 6 and 7. Recently, he (1978) reported pH values at 6.75 (at 25 deg. C) for rainwater samples collected on board Soviet Research Ship *Academic Shirshov*, far away from the land in the Bay of Bengal excluding the possibility of any contamination due to pollution.

The data collected from different Background Air Pollution Monitoring Network (BAPMoN) stations in India, which have been established to identify the current levels of pollution and for identifying the long term trends in the concentration of significant atmospheric constituents which may affect the environment and thus may induce climatic changes also suggest high pH values. These stations are located sufficiently away from built-up areas and thus the samples collected from these stations can be taken as representative of unpolluted area. Based on the study of pH data collected from above network, Krishna Nand *et al.* (1979) had concluded that at majority of the BAPMoN stations pH values were in the basic range near about 7.0, though in the beginning of the rainy season, at some of the stations they were slightly acidic (with respect to neutral value of 7.0). The above observations thus confirm that pH of monsoon rainwater over India is close to 7.0.

3. Discussions

Having established that pH of tropical rainfall is higher in comparison to the values reported in Europe and USA (Barrett and Brodin 1955) we may try to find out the reason for higher pH values over India.

The value of pH at 5.65 (at 20 deg. C) had been arrived on an assumption that only carbon dioxide is present in the atmosphere and the dissolved CO_2 in rainwater is in equilibrium with atmospheric CO_2. However, if ammonia in even trace quanity ($3 \mu g/m^3$) is present in the atmosphere, the pH of the rainwater would be 7.0 (Junge 1963). According to Junge (1963), since pH values of 5 to 6 are common in rain (in Europe) they must, in the presence of NH_3 be determined by constituents other than CO_2 and should result in good removal efficiency of NH_3. However, observations do not seem to indicate exceptionally high removal for NH_3 compared to other gases like SO_2 and NO_2. Absorption of NH_3 is not the only way in which the pH value can be raised. Soil particles which are usually slightly basic when swept into the atmosphere by wind get dissolved in the rainwater and release into solution base cations (positive ion) such as calcium, magnesium, potassium and sodium (Ca^{++}, Mg^{++}, K^{+} and Na^{+}) with bicarbonate usually the corresponding anion or negative ion.

In addition to above, another important physical reason for higher pH value of tropical rain is the high temperature dependence of solubility of carbon dioxide in water. pH of rain depends directly on the amount of carbon dioxide which actually gets dissolved in the water. This is now being discussed in the following paragraphs :

3.1. *Role of carbon dioxide*

Let us consider the mechanism of growth of droplet and absorption of carbon dioxide by the droplet together. Asume that a droplet is growing in favourable conditions and during the process it is capturing also the molecule of CO_2. Let r be the radius of the droplet and m be its mass. The rate of growth of cloud droplet by condensation of water vapour on it is given by

$$\frac{d\, m_r}{d\, t} = 4 \pi D_r \, (\rho - \rho_r) \tag{1}$$

where, D is the molecular diffusion coefficient of water vapour, ρ_r the water vapour density at the surface of the droplet and ρ that of the ambient air. Since rate of dissolution of a soluble gas on a droplet of radius r is proportional to the area, $4\pi r^2$, and the mass of gas molecules striking unit area per unit time of the droplet denoted by μ, rate of dissolution of the gas will then be given by

$$\frac{d\, S_r}{d\, t} = A \, \mu \, 4 \pi r^2 \tag{2}$$

where, S_r is the mass of the gas dissolved and A is the fraction of gas captured by the droplet. Value of A is quite low for slowly soluble gas and may be assumed to be near unity for very highly soluble gas like ammonia. Further

$$m_r = \frac{4}{3} \pi r^3 \tag{3}$$

assuming the density of water as unity, the concentration of the dissolved gas in the droplet is given by

$$C_r = S_r - m_r \tag{4}$$

The rate of change of concentration with time

$$\frac{d\, C_r}{d t} = \frac{d}{d t} \left(\frac{S_r}{m_r} \right) = \frac{1}{m_r} \frac{d\, S_r}{d\, t} - \frac{S_r}{m_r^2} \frac{d\, m_r}{d\, t}$$

$$= \frac{3 A \mu}{r} - \frac{3 C_r \, D (\rho - \rho_r)}{r^2} \tag{5}$$

Now let us consider the significance of the term A. This is the fraction of gas captured by the drop. We can assume that,

$$A = a \, (C_s - C_r) \tag{6}$$

where a can be assumed to be constant at constant temperature provided there is no chemical reaction in the liquid phase other than the reversible reaction of the dissolved gas and water. C_s is the solubility of CO_2 in water and is constant at constant temperature and partial pressure. Eqn. (5) can thus be written as

$$\frac{d C_r}{dt} = \frac{3 \, a \, C_s \, \mu}{r} - \frac{3 C_r}{r} \left\{ a \mu + \frac{D \, (\rho - \rho_r)}{r} \right\} \tag{7}$$

From the Eqn. (7) it can be seen that rate of dissolution of gas is directly dependent on the solubility of the CO_2. Since the solubility of CO_2 decreases rapidly with increase in temperature, lower the ambient temperature, greater is the rate of dissolution and lower the pH value.

Wattenberg had prepared tables showing the dependence of the solubility of carbon dioxide in sodium chloride solutions on the temperature and the salinity. Table 1 is an extract of the same (Defant 1961). Solubility of carbon dioxide decreases considerably with increasing temperature and salinity. One litre of sea water at 0 deg. C and zero per thousand salinity when in equilibrium

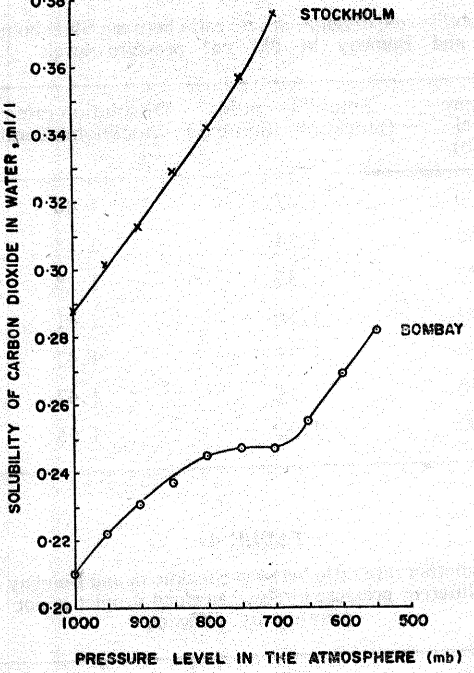

Fig. 1. Vertical profile of Solubility of carbon dioxide in water at Bombay and Stockholm during July

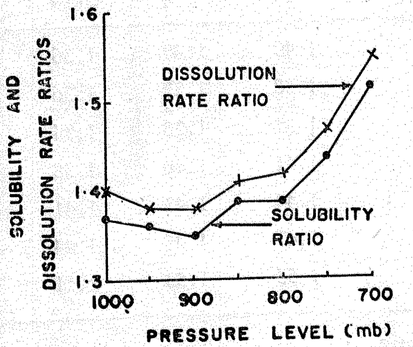

Fig. 2. Solubility and dissolution ratio between Stockholm and Bombay (for the case when $C_r=0$)

TABLE 1

Solubility of carbon dioxide in water

Temperature (°C)	Solubility (ml/lit)
—2	1890
0	1713
5	1424
10	1194
15	1019
20	878
25	759
30	666

TABLE 2

Mean vertical temperature profile over Bombay and Stockholm (July) and partial pressure of carbon dioxide

Pressure level (mb)	Partial pressure of CO_2 (atm)	Temperature (°C)	
		Bombay (India)	Stockholm (Sweden)
1000	0.000300	28.1	16.8
950	0.000285	23.9	13.8
900	0.000270	20.7	20.9
850	0.00255	17.8	8.0
800	0.000240	15.1	5.1
750	0.000225	12.6	2.1
700	0.000210	10.6	—0.8
650	0.000195	7.4	—
600	0.00180	3.7	—
550	0.000165	0.2	—

Note : Original temperature data for Sweden is available only for two pressure levels, *viz.*, 850 and 700 mb. Data for intermediate levels have been interpolated and from 850 to 1000 mb have been extrapolated assuming the same lapse rate as is given between 850 and 700 mb.

with the atmosphere (partial pressure of carbon dioxide 0.0003 atmosphere) contains 0.52 ml of carbon dioxide.

It would be interesting to compare the solubilities and rate of dissolution in rain at different levels in the atmosphere for two typical cities of Europe and tropical area. The mean vertical temperature profile for Bombay and Stockholm (Sweden) representing tropical area and Europe respectively for the month of July have been taken for comparison purposes. Mean vertical temperatures for Bombay and Stockholm are given in Table 2 along with partial pressure of carbon dioxide at different levels. Vertical solubility profile as calculated from Tables 1 and 2 for Bombay and Stockholm is shown in Fig. 1. It can be seen from Fig. 1 that solubility of CO_2 at Stockholm is about 1.5 times higher than at Bombay (for the same pressure level).

It is rather difficult to calculate the rate of dissolution of carbon dioxide from complete Eqn. (7) since the value of '*a*' for different levels in the atmosphere is not exactly known. However, the ratio of dissolution rate can be calculated between two typical cities of Europe and India under special conditions, *viz*, initial cloud formation stage ($C_r=0$) and when drops are not growing by diffusion ($\rho=\rho_r$) with assumption that '*a*' is same in two cities at the same pressure level. The above assumption may not be fully justified but in absence of any experimental data giving the value of '*a*' it is felt that the above approach

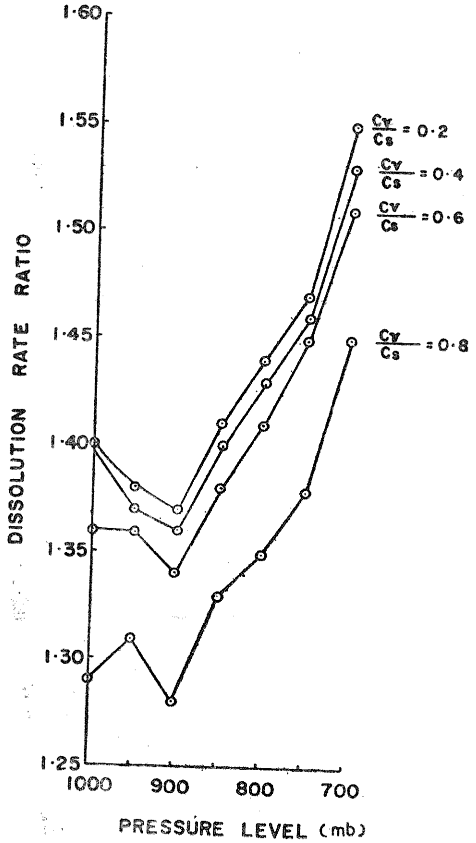

Fig. 3. Dissolution rate ratio between Stockholm and Bombay (for the case when $\rho=\rho_0$)

of the calculation of the ratio of dC_r/dt may not be unreasonable and many meaningful results can be still derived from the above computations.

3.2. *Calculation of dissolution rate for initial cloud formation stage* ($C_r=0$)

For the above condition Eqn. (7) reduces to

$$\frac{dC_r}{dt}=\frac{3\,a\,C_s\mu}{r} \tag{8}$$

where,

$$\mu=\frac{3}{13}\,\rho_g\sqrt{RT/\pi\,m}$$

where, m=molecular weight of carbon dioxide.

ρ_g =density of carbon dioxide

T =temperature in absolute degrees

R =gas constant

Let, p=atmospheric pressure

Then, $$\frac{dC_r}{dt}=\frac{9}{13}\,\frac{a\,C_s\,p}{R\,T\,r}\sqrt{RT/\pi\,m}=\frac{K\,a\,C_s\,p}{r\sqrt{T}} \tag{9}$$

where, $K=\frac{9}{13}\,1/\sqrt{R\,\pi\,m}$ and is constant.

TABLE 3

Solubility and dissolution rate ratio between Stockholm and Bombay at different pressure levels

Pressure level (mb)	Solubility ratio (Stockholm/Bombay)	Dissolution rate ratio (Stockholm/Bombay)
1000	1.37	1.40
950	1.36	1.38
900	1.35	1.38
850	1.39	1.41
800	1.39	1.42
750	1.44	1.47
700	1.52	1.55

TABLE 4

Dissolution rate ratio between Stockholm and Bombay at different pressure levels when cloud droplet is not growing by diffusion

Pressure level (mb)	Dissolution rate ratio when C_r/C_s (Stockholm/Bombay)			
	0.2	0.4	0.6	0.8
1000	1.40	1.40	1.36	1.29
950	1.38	1.37	1.36	1.31
900	1.37	1.36	1.34	1.28
850	1.41	1.40	1.38	1.33
800	1.44	1.43	1.41	1.35
750	1.47	1.46	1.44	1.38
700	1.55	1.53	1.51	1.45

To simplify the computations it has been assumed here that value of r is same in two different cities (under consideration here) for the same pressure level.

Substituting the values of temperature and solubility in the Eqn. 9, dissolution ratio between Stockholm and Bombay have been computed and are given in Table 3. Solubility and dissolution rate ratios have been plotted also for different levels and are shown in Fig. 2.

3.3. *Calculation of dissolution rate when raindrops are not growing by diffusion* ($\rho=\rho_r$)

Under the above condition, Eqn. (7) reduces to,

$$\frac{dC_r}{dt}=\frac{3\,a\,C_s\,\mu}{r}-\frac{3\,a\,C_r\,\mu}{r}$$
$$=\frac{3a\mu}{r}\Big(C_s-C_r\Big) \tag{10}$$

From Eqn. (10), it can be seen that dissolution rate is dependent on the difference in C_s and C_r. Dissolution rates would be different for different values of C_s and C_r. Ratio of dC_r/d_t cannot be evaluated from Eqn. (10) unless value of C_r is known. However, for different concentration ratios of C_s and C_r, relative dissolution rates can be calculated between two cities of Europe and India. To begin with if we assume that $C_r=O$ and *say* after a certain time, C_r becomes 0.2 C_s in Stockholm then in the same time C_r would be less by a factor of 1.40 at 1000 mb of pressure level in Bombay. Substituting the values of different parameters in Eqn. (10), ratio of dC_r/dt can be thus calculated and the same are given in Table 4. The calculated ratios for different values of C_r/C_s have been plotted also and are given in Fig. 3.

Above calculations suggest that due to higher dissolution rates, rainwater gets saturated early and equilibrium is reached quickly between the dissolved carbon dioxide and atmospheric carbon dioxide in colder European countries whereas in tropical rainwater equilibrium may not be reached. Since the dissolution rate decreases as the rainwater approaches ground level, probability of reaching an equilibrium between dissolved and atmospheric carbon dioxide further decreases. Thus, higher dissolution rate and solubilities would lower the pH values, measured at a fixed temperature (*say* 20 deg. C), as observed in colder European countries. However, it may be argued that the dissolved carbon dioxide may not be saturated. Let us assume that the rainwater is 80 per cent saturated. But then when the rainwater collected at 10 deg. C at 80 per cent saturation is brought to 20 deg. C it becomes saturated whereas the rainwater collected at 25 deg. C and at a saturation of 80 per cent will be more unsaturated when brought down to 20 deg. C. This would mean tropical rainwater should show higher pH than of extra-tropical one.

From Eqns. 2 and 4, concentration of dissolved carbon dioxide (C_r) in the droplet can be computed if the value of constant '*a*' is known. Also assuming that all dissolved carbon dioxide gets converted to H_2CO_3, C_r can be directly used (after converting to proper units) in place of H_2CO_3 for calculating the pH of rainwater alongwith the following equations as given by Junge (1963) :

$$H_2CO_3 \leftrightharpoons H^+ + HCO_3^- ; \quad K_1 = \frac{[H^+]\,[HCO_3^-]}{[H_2CO_3]}$$

$$HCO_3^- \leftrightharpoons H^+ + CO_3^{--} ; \quad K_2 = \frac{[H^+]\,[CO_3^{--}]}{[HCO_3^-]}$$

$$H_2O \leftrightharpoons H^+ + OH^- ; \quad K_3 = [H^+]\,[OH^-]$$

And for pH $<$ 6.5, we may write

$$[H^+] = \sqrt{K_1\,[CO_2]}$$

For higher values of pH all equations are to be used.

K_1, K_2 and K_3 are constants.

Above equations can be utilised for the computation of pH value provided the value of *a* is known. This would require an experimental determination. In absence of the same, only comparisons regarding the solubility and dissolution rate of carbon dioxide in rainwater between two typical countries of Europe and tropics have been made in this paper and physical reasons for higher pH in tropics have been offered based on these considerations.

4. Conclusion

Theoretically calculated value of pH at 5.65 (20 deg. C) is based on the assumption that the dissolved carbon dioxide is in equilibrium with atmospheric carbon dioxide. In European countries such as Sweden where temperatures are quite low in comparison to tropical countries like India, solubility of carbon dioxide in water is quite high (1.5 times of tropics) and the dissolution rate of carbon dioxide in rainwater is also higher by a factor of about 1.5. It suggests that for rainwater in colder countries (Europe, USA), the assumption that at the reference temperature the dissolved carbon dioxide is in equilibrium with atmospheric carbon dioxide is valid whereas for tropics this may not be correct. It can be thus concluded that pH values of monsoon rainwater over India should be close to 7.0 which is the neutral value of pure distilled water. The higher atmospheric temperatures in tropics, lower solubility and dissolution rate of carbon dioxide added with rapid process of cloud formation and precipitation result in higher pH. Greater depth of saturated air during southwest monsoon may be another contributing factor but this has not been discussed here.

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