Letters To The Editor

551·579·1 : 551·464

SALINITY IN RAIN WATER

1. Introduction

Saline matters in the atmosphere, as coming into the rain water may have its origin in two processes—(1) The salt itself may act as condensation nucleus, and (2) the salt may come by being washed out by the rain water from air in between the cloud and the ground. The washing out may again take place in two ways—(*a*) the salt in the air may get dissolved in the falling drop, or (*b*) it may be mechanically carried down although not dissolving wholly in it. The mechanical carriage is possible specially when the salt particles are bigger, the smaller particles having the higher chance of getting dissolved since solubility is known to increase as the size diminishes.

In this note an equation has been derived connecting the concentration of the salt washed out by rain water and the amount of precipitation and cases of different salts as observed by different workers have been considered in the light of the equation.

2. Derivation

Let us assume that rain is falling on a unit area from a cloud at a constant height, H. Let r be the average radius of cross-section of the rain drops and n the number of drops falling through unit area in unit time. Since rain drops are falling through the same viscous medium under the influence of gravity and since we have considered the size of the rain drop to be the same by assuming an average size, we may assume that the average velocity of drops to be the same for all drops. Let the decrease of concentration of the salt in air be $-dc$ during the time interval dt. Then

$-dc \propto C$ (concentration of the salt in air)
$\propto n$
$\propto \pi r^2$ (since velocity is constant =average velocity)
$\propto dt$

$$\therefore dC = -\sigma C n \pi r^2 dt$$

where σ is a constant and may be termed the rate of capture of salt particles by a rain drop of unit cross-section when the concentration of the salt is unity. Hence for a time interval t from the beginning of the precipitation, it is given by

$$\int_{C_0}^{C_t} \frac{dc}{C} = -\int_0^t \sigma \pi r^2 n dt$$

$$\text{or} \quad C_t = C_0 \cdot e^{-\sigma n \pi r^2 t}$$

where C_t = concentration of the salt in air after time t and C_0 = concentration of the salt in air at the beginning of the precipitation.

The fall in concentration is, therefore,

$$C_0 - C_t = C_0 \left(1 - e^{-\sigma n \pi r^2 t}\right)$$

Hence the amount of salt falling on a unit area of the ground being washed out by rain water is (from volume $H \times 1$)

$$H\left(C_0 - C_t\right) = H C_0 \left(1 - e^{-\sigma n \pi r^2 t}\right)$$

If P be the volume of precipitation, then

$$P = \tfrac{4}{3} \pi r^3 n t \text{ or } \pi r^2 n t = \frac{3P}{4r}$$

Therefore, the concentration of the salt in rain water

$$S = \frac{H\left(C_0 - C_t\right)}{P}$$
$$= \frac{HC_0}{P}\left(1 - e^{-3\sigma P/4r}\right) \qquad (1)$$

3. Some special cases and verification

From this equation, we can consider two cases:

(*i*) If $\sigma >> r$, we get as an approximation

$$S \times P = \text{a constant} \qquad (2)$$

(on the assumption $P > r$, since the amount of rain is measurable)

Sugawara, Oana and Koyama (1949) empirically arrived at the same relationship in the case of chlorinity in rain water. The equation (2) is expected to be obeyed by the salt for which σ is of high value. It is possible only when the solubility of the salt is high or when salt particles are quite big. In the case of ammonia, ammonium salts and nitrates, it is well known that their solubilities are very high. So that the curve obtained by plotting concentration of ammonia against the amount of precipitation from the same cloud will give as a rectangular hyperbola. The data of analysis of rain water at Tokyo in 1936 to 1938 by Miyake show that such a relationship is actually obtained. The fact that chlorides also conform to it has an important bearing that the most abundant chloride found in the air is sodium chloride whose solubility is low. The agreement with equation suggests that the lower solubility is probably compensated by its higher size which makes σ assume considerable magnitude. Probably NaCl particles of bigger dimensions remain as aerosol. Miyake (1948) also arrived at the same conclusion from the analysis of relative amounts of chlorides and sulphates in rain, rime and sea water.

It has, however, been observed by Miyake and Sugiura (1950) that equation (1) fits better with Sugawara, Oana and Koyama's (1949) data than equation (2). These authors derived equation (1) from different considerations and tested the equation with the data on chlorinity only.

(*ii*) If $\sigma << r$, so as to make $\sigma P < r$

$$S \times P = HC_0(1-1+\frac{3\sigma P}{4r}),$$ neglecting higher powers of (σ/r)

$$\text{or} \qquad S = \text{constant} - \frac{3HC_0\sigma}{4r} \qquad (3)$$

If we take upto the second power σ/r we get

$$S = \frac{3HC_0\sigma}{4r} - \frac{9HC_0\sigma^2P}{16r^2} \qquad (4)$$

Miyake found from the experimental data on nitrite content in rain water in Tokyo and Kobe in 1936 that such a relation *i.e.*, linear variation of S against P, is actually obtained. The behaviour of nitrates may probably be attributed to this. Although the solubility of nitrates is high, the concentration of nitrites in air is very low, so that the actual capture and the rate both are low. Miyake and Sugiura reached this same conclusion from their data of analysis of nitrogen compounds in the atmosphere.

4. Assumptions

In our derivation we made certain assumptions. They are,

(1) Height of the base of cloud remains constant,

(2) No fresh supply is maintained in the area where rain is falling,

(3) σ remains constant, and

(4) The intensity of the rain is not very low so that we, as an approximation, may use differential quantities and integrate them. At low intensity of rain the process of dissolution of the salt cannot be assumed to be a continuous process.

(5) Amount of rain is measurable.

For all practical purposes σ may be taken to be constant. But in the case of heavy downpour when the salts are almost washed out the actual capture and also the rate may become less.

5. Continuous supply of a highly soluble salt

Angström and Hogberg (1952) have reported that the rate of collection of nitrogen salts decreases as the rainfall endures, and this they have attributed to washing out of nitrogen salts from air. From extensive study of such compounds in rain water they have proved that nitrogen compounds are actually washed out by rain water. But Mordy (1953) obtained a different result from the analysis of rain water collected at the Hawaiian Sugar Planter Association's Observatory on the leeward side of Koolau mountains on 22 April 1953. In his case cloud was formed by the orographic ascent of the air coming from sea. Generally in such cases rainy area is small. The rainfall can be considered stationary with new air pouring into the rainy zone with the speed of the wind. His data are given in Table 1.

An inspection of the values of total nitrogen concentrations, will show that constantly fresh nitrogen salts were introduced. If it was not so we would have found the equation (2) to hold good. There is a continuous supply of nitrogen salts into the rainy zone and we can deduce the different relationships obtained by Mordy in the following way.

Equation (2) states that for highly soluble salts $S \times P$=constant. But $S \times P$ denotes the total amount of salt brought down by the rainfall of amount P. So if the total amount does not vary with amount of rain, it is due to the fact that practically whole of the salt is dissolved in the first portion of the rain. So we can conclude that in the case of a highly soluble salt, almost whole of the salt is immediately dissolved by the falling rain.

Let S_1 be the concentration of the salt in the precipitation P_1 (measured from the beginning of rain) and S_2 be the concentration of the salt in precipitation P_2. The corresponding time intervals are t_1 and t_2. Therefore the concentration of salt in the fraction of rain collected between t_1 and t_2 is given by

TABLE 1

Elapsed time from start of rain (min)	Rainfall intensity (mm/hr)	Vol. of sample (ml)	Total Nitrogen (mg/litre)	N_2 (gm/min)
25	1·8	740	0·51	$15\cdot1\times10^{-6}$
31	1·4	715	0·39	9·0 ,,
11	3·9	720	0·10	6·6 ,,
17	2·1	591	0·24	8·4 ,,
62	0·7	707	0·66	7·5 ,,

$$S_{12} = \frac{S_2P_2 - S_1P_1}{P_2 - P_1}$$

This quantity is zero in the case of highly soluble salts by equation (2). If there is a continuous supply of the salt from outside the rainy zone this will however have some measurable values. Let C_1 be the concentration of salt in the incoming fresh air which is continuously replacing the air in the rainy zone. The amount of salt brought by the air inside a column of unit cross-section between the cloud and the ground can be given by $HC_1(t_2-t_1)$. Since these salts are almost immediately dissolved by rain, this whole amount will be brought down by the rain which fell during the interval of t_2-t_1. Hence we get,

$$S_2P_2-S_1P_1 = HC_1\,(t_2-t_1) \tag{5}$$

$$\text{or } S_{12} = \frac{S_2P_2-S_1P_1}{P_2-P_1} = \frac{HC_1\,(t_2-t_1)}{(P_2-P_1)}$$

$$= HC_1/I_{12} \tag{6}$$

where I_{12}=intensity of rain during the interval between t_1 and t_2 and S_{12}= concentration of salt in the rain water collected during this interval. Thus we get an inverse relationship between nitrogen concentration and the rainfall intensity.

In equation (5), let $t_1=0$, when P is also$=0$

$$\text{Then } S_2P_2 = KC_1t_2$$

$$\text{or} \quad SP = KC_1t \tag{7}$$

Hence a plot of total nitrogen against time elapsed from the start of the rain will be a straight line. Mordy's data also appear to support this view.

It is a general belief that drizzle is the most beneficial for land. Reason put forward is that soil can absorb water more efficiently. Of course, this belief may be justified by some other considerations as well. It is easy to see that this type of precipitation can dissolve the salts more efficiently. From equations (3) and (4) it is obvious that small droplets can better dissolve the salts whose rate of capture is low. So salts of low solubility are better dissolved by drizzle than by rain. From equation (6) we find that precipitations of low intensities dissolve more salt in the case of a highly soluble salt which is continuously supplied in the rainy zone. Hence drizzle brings more salt than rain, since in general the former is of low intensity. From equation (7) we see that the more the duration of rain the more is the dissolution. Drizzles, in general, and thick drizzles in particular are known to continue for a long time. Hence, it is natural that they will bring down salts. Last two conclusions are specially applicable in case of nitrates and ammonium salts which are so useful in agriculture.

A. K. MUKHERJEE

Meteorological Office,
Jodhpur
March 14, 1955.

REFERENCES

Angström, A. and Hogberg, L.	1952	*Tellus*, **4**, p. 31.
Miyake, Y. and Sugiura, Y.	1950	*Papers in Meteorology and Geophysics*, **1**, 2-4, p. 22.
	—	*Geophys, Mag.*, **22**, 1, pp. 1-4.
Mordy, W.A.	1953	*Tellus*, **5**, p. 470.
Sugawara, K., Oana, S. and Koyama, C.	1949	*Bull. Chem. Soc. Japan*, **22**, p. 47.