Separation of the Components of Atmospheric Salt and their Distribution.

By Ken SUGAWARA, Shinya OANA and Tadashirô KOYAMA.

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Introduction. It is a wellknown fact that the splash of sea water is carried up into the air and plays an important role as the primary source of the salt in rain and snow.

Now, it is worth attention that the salt in rain and snow differs so much in composition from sea salt that the ratios Mg: Cl and SO_4: Cl of such salt are larger than those of sea water as shown by H. Lipp⁽¹⁾ of the fog from Mt. Sonnblick and by Y. Miyake⁽²⁾ of Japanese rain.

As the cause of this difference, we can assume that, by evaporation, there occurs a partial crystallization on the suspending particles of sea water in the air with the production of at least two kinds of daughter particles; the one, hygroscopic in nature and consisting mainly of sodium and chloride, is unstable and falls down earlier from the air, while the other, crystalline in nature and consisting mainly of magnesium and especially of calcium and sulphate, is stable and keeps to remain longer in the air. It is quite natural that these circumstances lead to the relative concentration of the latter kinds of components in the air, which explains well the observations by Lipp and Miyake.

Now, be such a view right, it can be expected that there may occur a distribution of the atmospheric salt with such a variation in composition that the ratios of magnesium, calcium or sulphate to sodium or chloride increase horizontally as we get along from sea coast towards inland, and also we may find a similar distribution vertically as we get higher from sea level upwards.

In the next, be such a variation in salt distribution actually shown, a second question will arise; how does the selective falling down of the unstable components occur?

The present paper deals with these two kinds of problems and answers them by the chemical study of the precipitation, the atmospheric salt itself and also of the salt caught by pine needles on their surfaces from the air.

Horizontal Distribution of the Components of Sea Salt in the Air from Sea Coast towards Inland. Observation was carried out at three stations; the one next sea beach, Sugashima-Island in Ise Bay, the second Nagoya (Higashiyama), 4 km. receding from the head of Ise Bay, and the third the most receding place, Matsumoto, Nagano Pref., 180 km. from

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(1) H. Lipp, *Jahresber. des Sonnblickvereins*, **1931**, 27, Wien.

(2) Y. Miyake, *J. Meteorol. Soc. Japan*, **II**, **17** (1939), 20.

the Pacific coast and some 90 km. from Japan Sea.

On more than one hundred samples of rain and snow, taken during 1946–1947, chemical analyses were carried out and their ratios Na : Cl, Mg : Cl, Ca : Cl, and SO_4 : Cl determined, the result of which (columns A of Table 1) tells that, as was expected above, the ratios Ca : Cl, SO_4 : Cl and also Mg : Cl increase markedly as it recedes into inland.

Table 1.

Ratio in equivalent	Sea water	Rain (A)			Washings of pine needles (B)		
		Sugashima	Nagoya	Matsumoto	Sugashima	Nagoya	Matsumoto
Na/Cl	0.850	0.85	0.90	0.63	0.83	0.85	2.1
Mg/Cl	0.196	0.23	0.31	0.99	0.22	0.27	1.4
Ca/Cl	0.038	0.25	0.31	6.84	0.09	0.55	3.8
SO_4/Cl	0.103	0.35	0.33	2.25	0.17	0.72	2.7

A similar relation is also shown in the salts which were caught by pine needles.

Studies along this line were made as follows: a certain twig was chosen among pine woods and their needles were washed thoroughly with distilled water. After a few days, during which there fell no precipitation, the needles were washed again and the salt, caught by them on their surfaces during the period, was gathered in the washings, of which chemical analyses were carired out.

The Columns B of Table 1 give the result. The increase of Ca : Cl, SO_4 : Cl and Mg : Cl is found also here and more evidently.

Vertical Distribution of the Components of Sea Salt in the Air from Sea Level upwards. This kind of distribution is shown by the comparison of the three different kinds of meteorological water-substances; the ordinary rain from 500–1000 m., the fog-ice from the summit of Mt. Fuji (3376 m. high) and the waters of thunderstorm, gathered in Nagoya and in Utsunomiya, Tochigi Pref., the latter kind of water being said to be given rise to at a height of 4–15 km.

The result (Table 2) shows that the ratios Ca : Cl, SO_4 : Cl and Mg : Cl grow larger with height, proving a denser distribution of calcium, sulphate and also magnesium relatively to other components in the height.

Table 2.

Ratio in equivalent	Ordinary rain	Fog-ice from the summit of Mt. Fuji	Thunderstorm
Na/Cl	0.90	1.09	2.43
Mg/Cl	0.31	0.40	0.63
Ca/Cl	0.31	1.90	2.19
SO_4/Cl	0.33	1.00	3.24

Ways in which Unstable Components fall down earlier. As to the question, by what processes the unstable components fall down earlier, we can give an answer that there are at least two different kinds of way;

the one the selective washing down by rain and the other selective capturing by various occupants extruding themselves from the earth surface (for examples, shrubs, woods or artificial edifices, etc.) on which some explanations must be given below.

(a) Selective Washing by Rain. This action of rain can be shown from two different sides.

(1) First we can show it by the direct comparison of the composition of atmospheric salt at a certain place to that of the rain which falls there. We can mention one example of Nagoya (Table 3, A, B) in which we find that the values Ca : Na and SO_4 : Na are smaller in rain than in the air itself, while the value Mg : Na remains practically constant. The relation is quite comprehensible when we assume that rain prefers sodium, magnesium and chloride to calcium and sulphate in the course of its washing action.

Table 3.

Ratio in equivalent	Atmospheric salt (A)	Salt of rain (B)	Salt caught by pine needles (C)
Ca/Na	1.36	0.34	0.65
Mg/Na	0.30	0.33	0.31
SO_4/Na	0.68	0.38	0.60

(2) The second way which proves the selective washing by rain is indirect and needs a somewhat precise explanation.

First we must make clear the relation between the chloride concentration of rain and the amount of its precipitation. The relation is shown by Fig. 1, drawn from the data of 60 kinds of rain in Nagoya, where

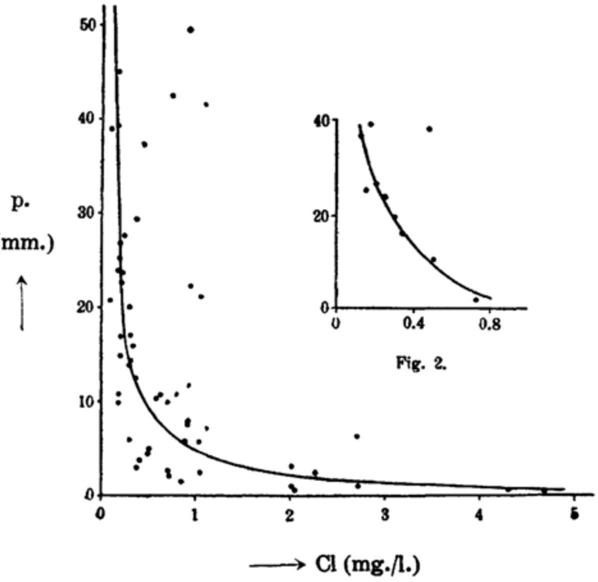

Fig. 2.

Fig. 1.

abscissae denote chloride concentration and ordinates the amount of precipitation.

As it is evident, all the values, except ones with particular nature such as ones of thunderstorm, lie practically on a line of hyperbolic form, expressed by Cl mg./l.$=4.2/p$ mm. The relation is far more evident in the case of rains in rainy season, when practically even meteorological conditions keep to prevail. (Fig. 2)

How can we understand the relation here found?

May we liken it to the case in laboratory where a certain amount of solute is treated with a sufficient or an insufficient amount of solvent?

A dilute solution will be obtained in the former case. The rain of a large precipitation poor in chloride might be likened to this, while another case, where only an insufficient amount of solvent is available, corresponds naturally to a rain of a smaller precipitation rich in chloride.

Now let us go further to imagine a case, where a mixture of a number of solutes, differing in solubility, be treated by solvent. Be the amount of solvent enough in this case, all the mixture will go into solution, while be it insufficient, dissolution will be incomplete and partial, components with larger solubilities going into solution first, and ones less soluble being left unattacked. Can we find the same relation also in the case of rain? Speaking more concretely, can we distinguish two kinds of rain, the one a dilute rain with larger ratios of Ca:Cl and SO_4:Cl, i.e., one the salt composition of which is nearer to that of atmospheric salt, and the other a rather concentrated one with smaller values of Ca:Cl and SO_4 :Cl, which seems to have dissolved the salt in the air partially?

This is actually the case. In order to show it, we had better to begin with examples (Table 4). We may choose the rain of Sept. 13th, 1946 as an example of a smaller precipitation rich in chloride and that of Feb. 20th, 1947 as one of a larger fall poor in chloride.

Table 4.

	Sept. 13th, 1946	Feb. 20th, 1947
Amount of precipition	4.2 mm.	10.3 mm.
Cl	0.121 milliequiv./l.	0.0273 milliequiv./l.
Na	0.105 ,,	0.0195 ,,
Ca	0.0068 ,,	0.0163 ,,
Mg	0.0283 ,,	0.0073 ,,
SO_4	0.0273 ,,	0.0142 ,,
Na/Cl	0.872	0.696
Ca/Cl	0.056	0.597
Mg/Cl	0.233	0.267
SO_4/Cl	0.226	0.521

In comparing the ratios of the salt components of these two kinds of rain, we find, as expected, that, while Na:Cl and Mg:Cl remain not differing much, difference is so marked of Ca:Cl and SO_4:Cl that the values of the dilute Sept. 13 rain attain 2–10 times as high as those of the concentrated Feb. 20th one.

Now the relation is no accidental one, particular to the examples cited, but a more general one. This can be shown by Fig. 3 in which, referring to the chloride values (abscissae), the corresponding ones of sodium, magnesium, calcium and sulphate (all expressed in milliequivalent/l.) are taken as ordinates and four kinds of lines, Na-Cl, Mg-Cl, SO_4-Cl and Ca-Cl are drawn.

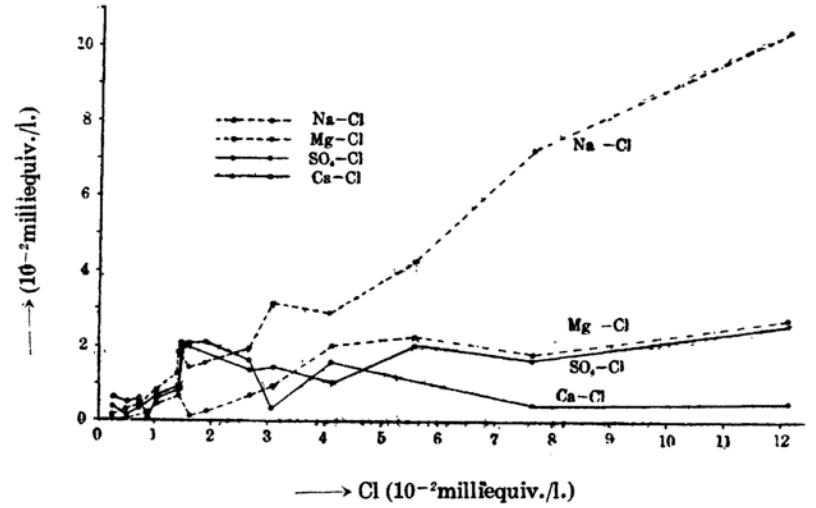

Fig. 3.

The perusal of the lines tells us much of the different behaviours of the individual components in their course of dissolution into rain, but here we must confine ourselves to focus our attention solely upon the point now in question. Then the primary point to be considered is that in contrary to the Na-Cl line, which runs with a gradient practically constant throughout the entire range, the lines SO_4-Cl and Ca-Cl start with rather acute gradients and then immediately tend to run along rather horizontally.

These circumstances can be taken to indicate that, when the amount of rain is small, among the salt components in the air, it chooses more soluble ones, such as sodium, chloride or magnesium and washes down them first, with the production of a rather concentrated water whose content of calcium and sulphate is relatively small, and on the other hand, when the amount of water is sufficient, or when the washing action keeps to continue longer, the action comes over to less soluble calcium and sulphate, thus yielding a water dilute but relatively rich in the latter components.

Further it must be added that the figure tells that such is the case of wide and general occurrence.

(b) Selective Capturing by various Occupants extruding themselves on the Earth Surface. This is shown by the comparison of the composition of the atmospheric salt and that of the captured by pine needles. The columns A and C of Table 3 show it. As it was shown in the comparison of rain and the atmospheric salt itself, we find also here that Ca : Na and SO_4 : Na show smaller values in the pine salt than the atmospheric one, while Mg : Na remains to be practically constant.

Geochemical Laboratory, Chemical Institute,
Faculty of Science, Nagoya University.