

Rainwater as a Chemical Agent of Geologic Processes—A Review

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1535-G



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GEOCHEMISTRY OF WATER

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Chemical composition of rainwater and its probable relation to soil water and exchangeable cations in weathering processes



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GEOCHEMISTRY OF WATER

RAINWATER AS A CHEMICAL AGENT OF GEOLOGIC PROCESSES—A REVIEW

By DOROTHY CARROLL

ABSTRACT

Chemical analyses of the rainwater collected at several localities are given to show the variations of the principal constituents. In rock weathering and soil-forming processes, the chemical composition of rainwater has an important effect which has been evaluated for only a few arid areas. In humid regions the important amounts of calcium, magnesium, sodium, and potassium added yearly by rain may be expected to influence the composition of the soil water and thereby the cations in the exchange positions of soil clay minerals. The acquisition of cations by clay minerals may slow down chemical weathering. The stability of soil clay minerals is influenced by the constant accession of cations from rainwater. Conversely, the clay minerals modify the amounts and kinds of cations that are leached out by drainage waters. The stability of micaceous minerals in soils may be partly due to accessions of K^{+1} ions from rainwater.

The pH of rainwater in any area varies considerably and seems to form a seasonal and regional pattern. The recorded pH values range from 3.0 to 9.8.

INTRODUCTION

There are now enough chemical analyses of rainwater from various parts of the world to permit an evaluation of its role in the chemical weathering of rocks and in soil development. An almost unexplored field in geochemistry is the interpretation of the effect of different types of rainwater on the composition of soil water, on the exchangeable cations of the soil clay minerals, and on the relation between exchangeable cations in soils, their addition by rain and from weathering rocks, and their redistribution by plants and animals. It is probable that the pH of rainwater, as well as the amount of rain and its contained cations and anions, has an important influence on the weathering of minerals and rocks in any locality.

The objectives of this short review are to inform geologists, geochemists, and hydrologists of the chemical data on rainwater, to indi-

cate the importance of the chemical composition of rainwater as an agent in rock weathering, and to express the hope that additional analyses of rainwater, particularly from tropical regions, will be made for use in studies of geologic processes.

Rainwater has a complex chemical composition that varies from place to place, as well as from shower to shower and season to season in the same place. Rainwater contains some constituents of local origin, and some that have been transported by winds from elsewhere. Even during rainless periods there is precipitation of mineral and organic dusts. Chemical constituents in both rain and dry precipitation are added continually to any area of the earth's crust to become part of the chemical weathering environment. Eriksson (1958, p. 177) calls this the chemical climate.

In 1955 a systematic study of rainwater in northern Europe was begun by the International Meteorological Institute, Stockholm (Engér and Eriksson, 1955). A network of more than 70 stations in Scandinavia, Great Britain, and elsewhere in northern Europe was organized to collect and analyze monthly samples of rainwater. The raw data are published regularly in *Tellus* (Svenska Geofysiska Föreningen). Rainwater has also been analyzed in the United States by Junge and Werby (1958), in England by Gorham (1955, 1957, 1958), and in Australia by Hutton (1958a), Hutton and Leslie (1958) and others. There have also been less comprehensive studies in other areas. Rainfall data have been evaluated by Eriksson (1958, 1959, 1960) and Gorham (1958, 1961).

The data in this paper were compiled for use in the chapter "Rock weathering and soils" for the revised edition of the "Data of Geochemistry."

CHEMICAL COMPOSITION OF RAINWATER

Rainwater is a mixed electrolyte that contains varying amounts of major and minor ions. Sodium, potassium, magnesium, calcium, chloride, bicarbonate, and sulfate ions are major constituents, together with ammonia, nitrate, nitrite, nitrogen, and other nitrogenous compounds (Hutchinson, 1957). Minor constituents are iodine, bromine, boron, iron, alumina, and silica. Dust particles are added locally. The sources of these constituents are the oceans, fresh water and saline lakes, landmasses, vegetation, manmade industries, and volcanic emanations.

In most studies of weathering processes it has been assumed that rainwater has an average composition. Miller (1952, p. 195) suggests that "* * * rain falling on a limestone area comes as close to approximating the system $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ as any occurring in nature."

However, even if an average rainwater is calculated, as in table 1, the figures show that there is a considerable range in the amounts of the ions present. So many analyses of rainwater now are available that the use of an average rainwater in geochemical studies could introduce errors and unwarranted assumptions.

The chemical composition of average rainwaters for northern Europe and southeastern Australia are given in table 1. These averages were computed from the monthly data of 62 stations in northern Europe over a period of 30 months, and from 28 stations in southeastern Australia over a period of 36 months. The figures are not unlike those of Gorham (1955) for average rain in the Lakes District of England.

Both northern Europe and southeastern Australia receive similar amounts of rain, and both are near oceans. There are few differences in the amounts of the major cations, but, except for calcium, the range in these constituents for the two areas differs. The range for both sodium and chloride in rainfall in Australia is greater than it is for rainfall in northern Europe. This difference may be due only to the distribution of the sampling stations in the two areas.

The relations and distributions of the cations and anions in rainwater will not be discussed in detail here. This has been ably done by Hutchinson (1957), Eriksson (1958, 1959, 1960), Junge and Werby (1958), and Gorham (1958, 1961). However, the following notes about some of the major constituents of rainwater are of interest in studies of chemical weathering.

The major cations and anions of rainwater come from several sources. Salts are picked up by winds blowing across large stretches of open ocean. Rain deposited near a coast by onshore winds has a composition similar to that of diluted sea water. During winter rains (April to August 1952) at Perth, southwestern Australia, the following amounts of constituents were deposited by the rain, according to Turton (1953).

	<i>Chemical constituents, in pounds per acre</i>				
	<i>Chloride</i>	<i>Sodium</i>	<i>Magnesium</i>	<i>Calcium</i>	<i>Potassium</i>
Rainwater.....	38	19.6	3.8	7.0	2.3
Sea water diluted to the same chloride content.....	38	21	2.5	.8	.8

In rain deposited farther inland, the ratios $Cl^{-1}:Na^{+1}$, $K^{+1}:Na^{+1}$, and $SO_4^{-2}:Cl^{-1}$, expressed as parts per million, differ from those in sea water. A decrease in chloride content of rainwater with distance from the coast has been observed in many countries. It was described by Simpson (1926), Wilsmore (1929), and Teakle (1937) for Western Australia; by Jackson (1905) and Junge and Werby (1958) for the

United States; by Leefang (1938) for the Netherlands; and by Blake-
more (1953) for New Zealand. The variation in composition of rain-
water with distance from the coast in southeastern Australia (Hutton,
1958b) is shown in table 2.

TABLE 2.—*Variation in composition of rainwater, in equivalents per million,
with distance from coast in southeastern Australia*

[Data after Hutton, 1958b]

Locality	Distance from coast (miles)	Average annual rainfall (milli- meters)	Sodium:chloride		Sodium:calcium		Sodium	
			Average	Range	Average	Range	Average	Range
Cape Bridgewater....	1	800	0.9	0.8-0.9	6.8	4.4-9.0	13.8	10.1-21.1
Heywood.....	20	828	1.0	.9-1.0	7.8	5.7-9.3	5.5	3.9-6.4
Cavendish.....	65	617	1.0	1.0-1.1	3.9	2.7-7.0	2.5	1.8-3.2
Horsham.....	120	447	1.5	1.0-2.8	1.4	1.0-2.5	.9	.9-1.1
Hopetoun.....	160	335	1.5	1.0-2.5	.9	.5-2.5	1.1	.7-1.4
Mildura.....	200	264	1.5	.9-2.5	.6	.2-1.7	2.3	.4-16.6

The composition of rainwater at several places in the conterminous
United States is given in table 3.

The places listed in table 3 were selected from the data of Junge and
Werby (1958) to show that considerable differences in the composi-
tion of rainwater are found. Several different environments are
represented, such as, near the oceans or near the Great Lakes, and
inland away from coastal influences.

Differences in composition are caused by several factors, principally
by the amount of rainfall, nearness to the ocean, and dust from the
atmosphere. However, even near the ocean—for example, Browns-
ville, Tex., Cape Hatteras, N.C., and San Diego, Calif.—rainwater
does not have the same chemical composition. Table 3 is presented
to bring out such differences and to show the importance of considering
the actual amounts of cations and anions deposited by rain in any
area as a geochemical factor. The cations and anions are known by
soil scientists to be either useful or harmful (depending on the climate)
additions to soils.

The chloride content of rainwater shows a marked seasonal trend;
and, as mentioned above, inland rain generally contains less chloride
than coastal rain. In arid countries, however, the influence of cyclic
salt is important. Hutton and Leslie (1958, p. 504) emphasize the
fact that the surface of dry soil in southern Australia usually con-
tains a quantity of sodium chloride amounting to about half the total
soluble salts. They consider that it is not possible to use rainwater
analyses to evaluate the amount of salt accumulating year by year
from the amount received in rain. In saline inland areas—for
example, Lake Eyre, central Australia (Bonython, 1958)—there is

TABLE 3.—*Chemical composition of rainwater from several localities in the conterminous United States*

[Data after Jung and Werby, 1968]

Locality	Distance from sea (miles)	Average annual rainfall (milli-meters)	Constituents													
			Sodium (Na)		Potassium (K)		Calcium (Ca)		Chloride (Cl)		Sulfate (SO ₄)		Nitrate (NO ₃)		Ammonia (NH ₄)	
			(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Cape Hatteras, N. C.	0	1, 370	4.49	0.195	0.24	0.006	0.44	0.022	6.50	0.183	0.88	0.019	1.03	0.016	0.11	0.006
San Diego, Calif.	0	277	2.17	.084	.21	.005	.67	.053	3.31	.092	1.66	.084	3.13	.060	1.13	.063
Brownsville, Tex.	1	885	22.30	.965	1.00	.025	6.30	.323	21.94	.618	5.84	.111	1.76	.029	.28	.015
Akron, Ohio	197	899	.53	.084	.13	.008	.69	.084	5.6	.04	1.62	.033	4.78	.075	.38	.021
Tallahassee, Fla.	27	1, 397	1.18	.067	.13	.008	.83	.071	13	.003	.48	.010	2.72	.011	.07	.009
Greenville, N. C.	50	1, 624	14.50	.600	.69	.015	.73	.086	22.58	.036	1.56	.031	2.77	.048	.04	.007
Yacouza, Wash.	75	2, 032	14.50	.600	.69	.015	.73	.086	22.58	.036	1.56	.031	2.77	.048	.04	.007
Urbana, Ill.	182	1, 059	.23	.010	.18	.004	.33	.011	36	.009	1.39	.022	1.27	.030	.09	.002
Washington, D. C.	85	1, 240	.26	.013	.15	.004	.37	.019	35	.009	1.33	.023	1.24	.034	.09	.002
Lasno, Calif.	112	946	.30	.011	.11	.029	.37	.034	36	.009	1.33	.023	1.24	.034	.09	.002
Indianapolis, Ind.	1128	995	.26	.011	.11	.003	.69	.034	18	.005	4.00	.083	2.06	.033	.21	.015
Albany, N. Y.	150	914	.21	.009	.09	.002	.43	.021	23	.006	4.00	.083	2.06	.033	.21	.015
Rome, N. C.	200	1, 270	.22	.009	.13	.003	.32	.016	23	.006	1.33	.027	3.12	.050	.24	.013
Ely, Nev.	410	1, 381	.69	.080	.14	.003	3.79	.190	30	.008	1.05	.022	1.61	.013	.35	.019
El Paso, Tex.	540	534	.22	.009	.23	.006	2.17	.108	14	.003	1.03	.000	1.84	.026	.28	.015
Grand Junction, Colo.	625	380	.40	.017	.26	.006	1.72	.086	17	.005	1.30	.027	1.82	.030	.75	.041
Grand Junction, Colo.	650	226	.69	.080	.17	.004	3.41	.170	28	.007	2.37	.049	2.63	.042	.33	.018
Columbia, Mo.	650	1, 016	.33	.014	.31	.007	2.18	.106	15	.004	1.20	.025	3.81	.061	.44	.024

1 Distance from fresh-water lake system.

a recycling of salt from one land surface to another. The various salts in the basin are picked up as mineral particles by winds and deposited elsewhere.

Calcium, magnesium, and potassium ions in rainwater come both from oceanic salts and from land surfaces. Both calcium and magnesium increase with respect to sodium and chloride over land areas, and calcium increases more than magnesium. Calcareous dunes, as reported by Hingston (1958), are a greater source of calcium than sea water. Hutchinson (1957) points out that when sea spray evaporates, two kinds of solid particles form in the atmosphere. Calcium sulfate (gypsum) first crystallizes, and then later both sodium and magnesium chlorides crystallize. Thus sulfate and chloride become separated in the atmosphere. Fine-grained gypsum can also be readily picked up from playas. Salt rains containing sodium chloride crystals are not uncommon in the Salt Lake City-Ogden area, Utah (J. H. Feth, U.S. Geological Survey, written communication, 1960).

Sulfate ions in rainwater come from several sources. In industrial areas the principal source is the combustion of fuels containing sulfur. In other areas sulfate comes from shallow-water marine environments, particularly tidal estuaries and lagoons, from fresh-water lakes, from salt flats, and from ocean waters. Some sediments contain pyrite that oxidizes slowly to SO_2 . Sea salts supply some sulfate as gypsum. The amount of sulfate in rainwater varies greatly. In the United States sulfate ranges from <1 to 8 ppm (parts per million) (Junge and Werby, 1958, p. 422). The amounts of sulfate in the rainwater collected at northern European stations average 2.19 ppm with a range from 0.18 to 6.52 ppm (data from table 1). The amounts of sulfate in Australian rainwater are rather low, two stations average 1.20 and 0.48 ppm (Hutton and Leslie, 1958, p. 505). At other localities sulfate ranges from 2.40 ppm in coastal rain to 0.72 ppm in rain about 120 miles inland (Hingston, 1958; Drover, 1960). In Uganda, Visser (1961) reports a range of sulfate from 0 to 68 ppm in samples of rainwater analyzed during 1 year. The source of this sulfate is Lake Victoria which is only a few miles from where the samples were collected. Rainwater on the Island of Hawaii analyzed by Eriksson (1957, p. 520) contained from 6.4 ppm sulfate near sea level to 0.8 ppm at 5,550 feet above sea level. The interrelation of factors of height, prevailing winds, and volcanic emanations are probably responsible for these variations. Bermuda, the only other oceanic island for which figures are available, has rain with an average of 2.12 ppm sulfate (Junge and Werby, 1958, p. 422). The Australian rainwater samples are therefore somewhat low in sulfate in comparison with amounts found elsewhere.

Nitrogenous compounds are always present in the atmosphere and are carried down in rainwater. Recent analyses record the nitrogen in three forms— NH_4 , NO_3 , and total nitrogen—depending on the method of analysis. Ammonia and nitrate are of terrestrial origin and are in particles of organic matter in dust and in soils. The amounts in rainwater are variable. The influence of vegetation on the nitrogen content of rainwater is shown by analyses of water from the open and from beneath trees

	<i>Total nitrogen, ppm</i>	
	<i>Rainwater in open</i>	<i>Rainwater under trees</i>
Natal (Ingham, 1950)-----	0.96	2.6
Connecticut (Voigt, 1960)-----	.05	0.03-12

Bromine, iodine, and boron also are constituents of sea water, and salts containing these elements can be expected to accompany other salts in rainwater derived from the oceans. Data on bromine and iodine are scanty. Hutchinson (1957) suggests that these constituents will show a seasonal variation similar to that of chloride ions. There is a cyclic circulation of iodine between soils and air. The only published figures for boron are those of Odum and Parrish (1954), who found 0.009-0.015 ppm boron in rain at Gainesville, Fla. Additional data on bromine, iodine, and boron in rainwater would be useful.

pH OF RAINWATER

Water in clouds is assumed to be in equilibrium with the carbon dioxide of the atmosphere. The pH of rainwater in equilibrium with atmospheric carbon dioxide at 25° C. is 5.7. Barrett and Brodin (1955) consider a pH of 5.7 as the neutral point for atmospheric water, not in a chemical sense, however, but as a reference point from which to discuss changes that may take place by the addition of cations and anions. Water of pH 5.7 is acid, and therefore rainwater in clouds is acid.

The average pH of rainwater in northern Europe is 5.47 (table 1). This figure was obtained by averaging 1,552 readings from the monthly data published in the journal "Tellus" for the period 1954-56. The range in pH values is from 3.9 to 7.7 (table 1). The pH of rainwater from the same locality at different times varies, as does the pH of rain from different localities. The monthly values of pH for 18 localities in northern Europe are given in table 4.

Rainwater having a pH below 5.7 contains gases or acid such as SO_2 , H_2SO_4 , or HCl. The bicarbonate-ion content is extremely low. Table 5 gives the pH of rainwater from various localities, but it should be noted that figures for tropical rainwater are very scarce.

TABLE 4.—pH of rainwater samples collected each month in selected places in northern Europe

[Data from Svenska Geofysiska Föreningen, 1955-1956]

Place	Lat	Long	Distance from sea (miles)	Rainfall ¹ (milli-meters)	Year	Jan-uary	Feb-ruary	March	April	May	June	July	Aug-ust	Sep-tem-ber	Oc-tober	No-vem-ber	De-cem-ber
Aberdeen, Scotland	57.1° N.	2.1° W.	1	819	1956	4.5	4.4	4.6	5.7	---	6.5	5.5	5.2	5.3	6.3	6.7	5.8
Leeds, England	53.8° N.	1.3° W.	60	621	1956	4.1	4.4	4.8	4.5	5.5	4.8	5.3	4.6	5.2	5.7	5.3	4.2
Rothamsted, England	51.8° N.	0.3° W.	50	685	1956	4.3	---	5.1	4.3	5.5	4.5	5.0	5.1	5.2	4.9	5.2	4.5
Odum, Denmark	52.6° N.	10.1° E.	10	457	1965	6.7	4.5	4.8	6.6	5.3	4.8	4.8	5.2	5.0	5.1	4.5	4.9
De Bilt, Holland	51.° N.	5.1° E.	10	650	1935-59	3.6	3.4	4.0	3.9	4.3	4.3	4.3	4.5	4.6	4.0	4.0	4.3
Bonn, Germany	50.7° N.	7.8° E.	180	554	1935-59	3.6	4.2	3.0	4.2	3.8	3.6	3.9	6.5	6.1	6.0	6.0	6.3
Felber, Germany	47.9° N.	8.3° E.	240	552	1955	3.7	4.1	3.0	4.5	3.7	4.9	3.9	6.2	6.1	5.3	5.2	4.8
Ås, Norway	57.° N.	10.5° E.	350	350	1955	6.0	4.2	3.6	3.7	4.7	5.7	5.2	5.4	6.2	4.8	4.7	4.8
Oslo, Norway	59.° N.	16.° E.	125	319	1956	6.1	4.6	3.6	3.7	5.3	5.2	5.2	5.4	6.2	5.9	5.9	6.3
Bjergsnes, Norway	62.° N.	18.° E.	145	319	1956	6.1	6.2	5.6	6.1	5.9	5.9	5.1	6.2	5.7	5.2	5.9	6.2
Kitmu, Sweden	67.8° N.	20.° E.	145	358	1956	5.1	5.5	7.0	5.7	5.9	6.3	6.3	6.2	5.9	5.7	5.2	5.7
Lilla, Sweden	58.4° N.	13.1° E.	70	383	1955	6.5	6.8	7.0	5.7	5.9	4.6	6.0	6.5	6.9	4.6	6.2	4.5
Scarb, Sweden	57.0° N.	13.1° E.	45	463	1955	4.6	6.8	7.3	5.0	6.6	4.6	6.0	5.1	5.9	6.1	6.1	5.0
Kvarnort, Sweden †	59.1° N.	15.3° E.	110	423	1955	3.9	4.5	6.5	6.0	4.8	6.0	4.6	6.4	6.0	4.5	4.4	4.1
Kvarnort, Sweden †	59.2° N.	15.3° E.	105	475	1955	4.4	4.6	5.2	4.8	4.4	4.8	4.5	4.4	4.4	4.5	4.4	4.6
Tvarnima, Finland	59.9° N.	23.0° E.	1	385	1955	4.4	4.6	6.1	5.4	5.9	5.6	6.6	5.9	5.3	5.0	5.1	4.9
Kauhava, Finland	63.1° N.	23.0° E.	30	411	1955	5.0	6.2	6.4	6.7	4.9	5.9	5.8	5.9	5.0	5.0	5.1	5.5
Kuopio, Finland	62.9° N.	27.7° E.	65	345	1955	5.4	6.2	6.1	6.0	5.1	6.5	6.3	7.5	5.3	5.3	5.2	46.4

¹ Amount of rainfall is that collected and analyzed; it may not be the total

rainfall during the year.

² Figure for 1957.

³ Figure for 1955.

⁴ Figure for 1956.

⁵ 0.6 mile from a large shale-oil plant.

⁶ 4.5 miles from a large shale-oil plant.

Only the figures for the pH of rainwater in northern Europe can be used for geochemical interpretation because the reporting stations form a network; in other places the pH readings are very scarce or lacking. The significance of the pattern of the pH values of rain in Scandinavia has been discussed by Barrett and Brodin (1955). They show the monthly variation in pH in a series of synoptic maps. The main features of the distribution of pH values are: (a) a region of acid rain along the west coast, pH 4.8–5.4; (b) nearly neutral areas at the southwestern tip of Sweden and along the southern coast, pH 5.2–6.0; (c) an acid tongue that separates the two neutral regions, pH 3.9–4.9; (d) an acid region along the northeastern shore, pH 4.8–5.0; (e) a large neutral or alkaline region covering the more elevated interior of northern Sweden, pH 6.3–6.9; and (f) an acid corridor that joins the west coast and northeastern shore regions, pH 4.7–5.2. This corridor shows a marked tendency to meander from month to month. The mean pH of the entire network shows a distinct annual cycle, the acidity being greatest in winter and the alkalinity greatest in late spring. These facts are of considerable geochemical significance because the pH values characterize the reaction of the water that is leaching rocks and soils in Scandinavia. It is probable that rainwater in every country has a pattern of pH values, but data are not at present available to disclose it.

TABLE 5.—pH of rainwater samples collected at several localities

Locality	pH		Description	Reference
	Average	Range		
Lakes District, England.	4.45	4.0–5.8	Partly polluted by industrial gases.	Gorham (1955, p. 236).
West coast, Ireland.....	6.5	5.9–7.6	Contains sea salts.....	Gorham (1957, p. 2).
Canberra, Australia.....	-----	3.0–7.17	769 samples collected mostly from unpolluted mountain area.	Baas Becking and others (1960, p. 248).
Hawaii Island, Hawaii...	5.2	4.8–6.3	Collected at different heights on saddle road between Mauna Loa and Mauna Kea.	Eriksson (1957, p. 520).
Kauai Island, Hawaii....	13.7	-----	Collected at Wailua by Sam H. Patterson, U.S. Geological Survey, January 1960, during eruption of Kilauea, Hawaii.	J. H. Feth (U.S. Geological Survey, written communication, 1960).
Menlo Park, Calif.....	6.0	-----	Average of 30 analyses.....	Do.
Los Angeles, Calif.....	4.9	4.15–5.80	Average of 6 analyses.....	I. R. Kaplan (written communication, 1960).
Perth, Western Australia.	16.0	-----	Collected during very stormy weather.	Simpson (1926).
Nigeria.....	-----	5.8–6.8	-----	Alexander (1959).
Uganda.....	7.8	5.7–9.8	78 analyses made during 1958–59.	S. Visser (1961).

¹ One sample.

GEOCHEMICAL IMPLICATIONS OF THE CHEMICAL COMPOSITION OF RAINWATER

In humid, well-drained regions, water selectively removes cations from weathering rocks and soils, but in areas of limited rainfall and stream activity the continued addition of water of definite chemical composition changes the composition of the soil water, which, under these circumstances, is only present during rainy periods. This effect is a result of the accumulation of sodium chloride deposited by rain.

The amounts of chloride in certain Western Australian soils from humid and arid areas illustrate this point (Teakle, 1929, 1937) :

<i>Locality</i>	<i>Distance from ocean (miles)</i>	<i>Annual rainfall (inches)</i>	<i>Sodium chloride deposited by rain (pounds per acre per year)</i>	<i>Chloride in soil solution (as ppm dry soil)</i>
Bakers Hill.....	50	45	25	40
Salmon Gums.....	100	12.5	27	570
Merredin.....	250	10.5	16	200

The cations of the soluble salts in saline soils occupy the exchange positions of the clay minerals and modify or prevent development of soil profiles, particularly with regard to the movement of clay. Sodium in exchange positions may cause a flocculated, jellylike mass of clay similar to a sodium bentonite when wet. Eluviation of sodium clay produces a columnar structure in a soil profile. This structure is due to the shrinking and swelling of the clay on change from a dry to a wet condition (Byers and others, 1938, p. 976-977). Such soils are characteristically developed in saline areas and are known as solonchaks.

The effect of the cations in rainwater on the exchangeable cations of soil clay minerals and on chemical weathering is difficult to determine in the laboratory, but the overall effect is a regional pattern that has developed as a result of the chemical climate in which soil formation and weathering occurs. The work of the U.S. Salinity Laboratory Staff (1954) on saline soils, and recent investigations by Bower (1959) and Reeve and Bower (1960) on the effect of saline irrigation waters on soils, point the way in which similar studies using rainwater of known chemical composition to leach soils and clay minerals can be made.

The cations adsorbed by the exchange complex of soils, clay minerals, or minerals in weathering rocks are dependent on several factors—availability of different kinds of cations; their concentration and proportion in a soil solution or leaching water; the nature and number of exchange sites on the exchange complex; and the volume of water that is in contact with the exchange complex. Investigations in the U.S. Salinity Laboratory (1954) have shown that the proportion of bivalent to univalent cations in the exchange positions in soil

exchange material is a function of the ratio of bivalent to univalent cations and of their individual concentration in a soil solution or irrigation water. Under equilibrium conditions, where the principal cations are Na^{+1} , Ca^{+2} , and Mg^{+2} , the sodium adsorption ratio (SAR) is: $\text{SAR} = \text{Na}^{+1} / \sqrt{1/2(\text{Ca}^{+2} + \text{Mg}^{+2})}$, the ionic concentrations being expressed in milliequivalents per liter.

The amount of sodium ions available for reaction depends on the sodium ions in the water in contact with the exchange material, and on those adsorbed as exchangeable cations on this exchange material. The SAR is therefore directly related to the exchangeable sodium percentage (ESP). The exchangeable sodium percentage is defined as the degree of saturation of the exchange complex with sodium. It may be calculated by the formula,

$$\text{ESP} = \frac{\text{Exchangeable sodium (meq per 100 g soil or mineral)}}{\text{Cation exchange capacity (meq per 100 g soil or mineral)}} \times 100.$$

On the basis of data obtained by correlating the compositions of the dissolved and adsorbed cations in many soils from arid regions, the U.S. Salinity Laboratory Staff (1954) has adopted an equation for relating the ratio, adsorbed Na^{+1} : (exchange capacity of the complex minus adsorbed Na^{+1}) to the Na^{+1} , Ca^{+2} , and Mg^{+2} concentrations of an equilibrium water. This is,

$$\text{Na}_{(\text{ad.})} / (\text{exchange capacity} - \text{Na}_{(\text{ad.})}) = k \times \text{Na}^{+1} \sqrt{\frac{(\text{Ca}^{+2} + \text{Mg}^{+2})}{2}}.$$

This is related to the exchangeable sodium percentage. For an exchange of Na^{+1} for Ca^{+2} the relation is,

$$\text{Na}_{(\text{ad.})} / \text{Ca}_{(\text{ad.})} = k \times \text{Na}^{+1} \sqrt{\text{Ca}^{+2} / 2}.$$

If the solution in contact with an exchange complex is diluted, the SAR is decreased and less sodium can be adsorbed from a solution containing bivalent and univalent cations. The adsorption of Na^{+1} ions from highly saline ground waters is dependent on the valence dilution. As the solution becomes less concentrated, the bivalent ions become more effective in entering the exchange positions of the clay minerals of soils. Many experiments have confirmed this effect which was first noted by Jarusov (1937).

The equilibrium exchangeable sodium percentage varies with some function of SAR, and it follows that leaching a soil with successively more dilute volumes of sea water, or any saline water containing appreciable amounts of Ca^{+2} and Mg^{+2} ions will result in a corresponding decrease in the figure for SAR. Average sea water has a SAR of 42, and at this value Ca^{+2} and Mg^{+2} ions are adsorbed preferentially to Na^{+1} ions by clay minerals (Carroll and Starkey, 1960). A much

higher concentration of Na^{+1} to $\text{Ca}^{+2} + \text{Mg}^{+2}$ ions than that in sea water is required before Na^{+1} ions can be adsorbed preferentially. Reeves and Bower (1960, p. 140) report that Ca^{+2} and Mg^{+2} ions in the Salton Sea water (SAR 57) were adsorbed by soils. Most rainwater does not contain a sufficiently high concentration of sodium ions for them to be adsorbed preferentially to calcium and magnesium ions by clay minerals that are leached by rainwater. Many rainwaters have SAR values of about 1.

Calcium and magnesium are the dominant exchangeable cations in most soils with a neutral or alkaline reaction. Rainwater dilutes the soil solution, but at the same time it adds appreciable amounts of cations. Dilution of the soil solution by the addition of water containing much Ca^{+2} and Mg^{+2} favors the leaching of Na^{+1} and the retention of the calcium and magnesium in the exchange sites of clay minerals and organic matter in soils.

The relations between rainwater, the soil solution, and the removal or retention of cations in any soil or weathering rock are extremely complex. Plate 1 is an attempt to show some of the probable reactions between percolating solutions and clay minerals in soils in a simplified form.

On plate 1 the accumulation of salts in the soil solution under arid conditions with no removal of cations added by rainwater is shown on the left. The exchange sites of montmorillonite originally contain calcium, magnesium, and a little sodium. As the soil water becomes saturated with sodium, the calcium and magnesium are gradually replaced by sodium until all the exchange sites are filled. The concentration of sodium in the soil solution, which is only intermittently present after showers, is much greater than that of calcium and magnesium. The clay mineral does not break down or alter.

In the center of plate 1, the relation for saturated soils (gleyed soils) at a pH of 7 and over and at a pH of 4-5 is shown. In both instances the cations in the exchange positions are in chemical equilibrium with those in the soil and ground water present. This is a situation similar to that which one obtains in a laboratory experiment. Cations added by rainwater to the surrounding water of the clay mineral will establish equilibrium with those in the exchange positions, and little weathering or removal of cations can take place.

The leaching of cations from soil or weathering rock under medium to heavy rainfall in well-drained situations is shown on the right-hand side of plate 1. Here the cations added by rainwater have little influence. If the rainwater is alkaline, the leaching solution will not be as effective as if it were acid. The net effect is to remove cations from the exchange sites of the clay minerals, and to make original

montmorillonite unstable, whereby changing it first to halloysite and later to kaolinite. The reduction in size of the circles indicates that the exchange capacity of the minerals formed is less than that of the original montmorillonite, that is, the number of exchange sites is reduced. These exchange sites are, in kaolinite, not present in sufficient numbers to retain all the cations being removed by leaching rainwater, and H^+ ions occupy them. This is the situation in lateritic weathering in which the soil minerals have an acid reaction.

No allowance has been made on plate for the very considerable effects of the presence of organic matter either in the production of acids or in the complexing of Ca^{+2} , Mg^{+2} , and other cations by organic solutions.

The role of potassium, and to a lesser extent of ammonia, seems to be more complex than those of Na^{+1} , Ca^{+2} , or Mg^{+2} . Potassium ions may react somewhat like Na^{+1} , but K^{+1} ions may be largely withdrawn from circulation by fixation in micaceous clay minerals. The K^{+1} ion enters the interlayer positions of these minerals, thereby partially or wholly reconstituting them to true micas and preserving them in a relatively unweathered condition by maintaining their original uncharged state. The abundance of "illite" in soils and sedimentary rocks is due to its stability.

From the chemical composition of the rainwater in any locality, the normality of the solution with respect to the various cations and anions that it contains can be calculated. For example, the rainwater at Rothamsted, England, has the following composition (average figures computed from data in *Tellus*, v. 7 and 8, 1955 and 1956, respectively):

	ppm	epm	Normality in rainwater
Sodium.....	1.3	0.056	56×10^{-5}
Potassium.....	.3	.007	7×10^{-5}
Magnesium.....	.3	.025	85×10^{-5}
Calcium.....	1.7	.085	25×10^{-5}
Sulfur.....	1.8	.056	56×10^{-5}
Chloride.....	2.7	.078	77×10^{-5}

The SAR is 0.25 and the pH is 4.9.

Few studies have been made of the effect of rainwater passing through soils. Analyses of the water collected in lysimeters are available in agricultural literature, but the composition has not been compared with that of rainwater from the same locality.

Analyses of rainwater, spring, seepage, and river water in British Guiana were made in the period 1916-1918 by Harrison (1934) for use in studies of rock weathering. However, Harrison himself did not evaluate his results or relate them to the process of lateritization in the area.

A comparison of the composition of rainwater falling on oak woods and that of the soil water in the Lakes District, England, was reported by Gorham (1958, p. 175). He found that the bases neutralized a considerable part of the acidity of the rainwater. These bases were supplied by the weathering of soil minerals and ammonia released by organic matter.

Hutton and Leslie (1958, p. 504-505) in discussing the effect of rainwater on the exchangeable cations of soil calculated the SAR and percentage of sodium ion to be expected in rainwater in to localities in southeastern Australia. They compared the composition of these rainwaters with that of diluted sea water. Their figures are:

<i>Solution</i>	<i>Sodium adsorption ratio</i>	<i>Sodium ion (percent ¹)</i>
Rainwater, Warragul:		
Initial composition.....	0.6	<1.0
Concentrated 100 times.....	6.0	7
Rainwater, Horsham:		
Initial composition.....	.2	<1.0
Concentrated 100 times.....	2.3	2
Sea water:		
Diluted 10 times.....	20	22
Diluted 1000 times.....	2.0	1.5

¹ Percentage of total exchange capacity occupied by sodium.

Hutton and Leslie (1958) emphasize that even the most saline rainwater, by itself, cannot produce saline soils by acting directly on the exchangeable cations of the soils. A major factor is the recycling of cations and anions in arid areas to produce a sufficiently concentrated soil solution to affect the composition of the exchangeable cations of the clay minerals.

Experimental work by Nash and Marshall (1956) shows how the composition of a leaching solution, such as soil water, affects the alteration of feldspars. Much of the release of cations from feldspars occurs in weathering rocks and soils. Experimental acid treatment of feldspars produces proportionally more exchange sites of low bonding energy than does leaching with neutral salt solutions. Although the acid used in these experiments was stronger than that in acid rainwater, time is an important factor in natural weathering, and the same effect may be attained in time with a more dilute acid. Continued leaching at pH 4 may be expected to produce faster, and probably, different results from those of leaching at pH 7. In fact, the stability of soil clay minerals is adversely affected at pH 4, but not at pH 7. Plate 1 shows the change in clay minerals with leaching.

CONCLUSIONS

This review of part of the extensive information about rainwater suggests the use that may be made of rainwater analyses in studying the chemical climate of rock weathering and soil formation. The discussion has been almost exclusively about cations, as they are probably more important than anions although relatively little is known about the behavior of anions in exchange reactions.

The rainwater data available are concerned mainly with temperate and cold temperate populated parts of the earth's surface. The chemical composition of rainwater varies regionally, seasonally, and with local conditions. Use of an average composition for rainwater over a large area would be misleading.

The effect of composition of rainwater on rock weathering has not been studied in much detail, although the effect of yearly increments of salts in arid countries is well known. An examination of the exchange reactions of water containing sodium, calcium, and magnesium in contact with clay minerals illustrates the behavior to be expected of rainwater added to soil water that is in contact with soil clay minerals. To enlarge the picture of these reactions, data on the composition of rain from tropical and relatively uninhabited countries are needed.

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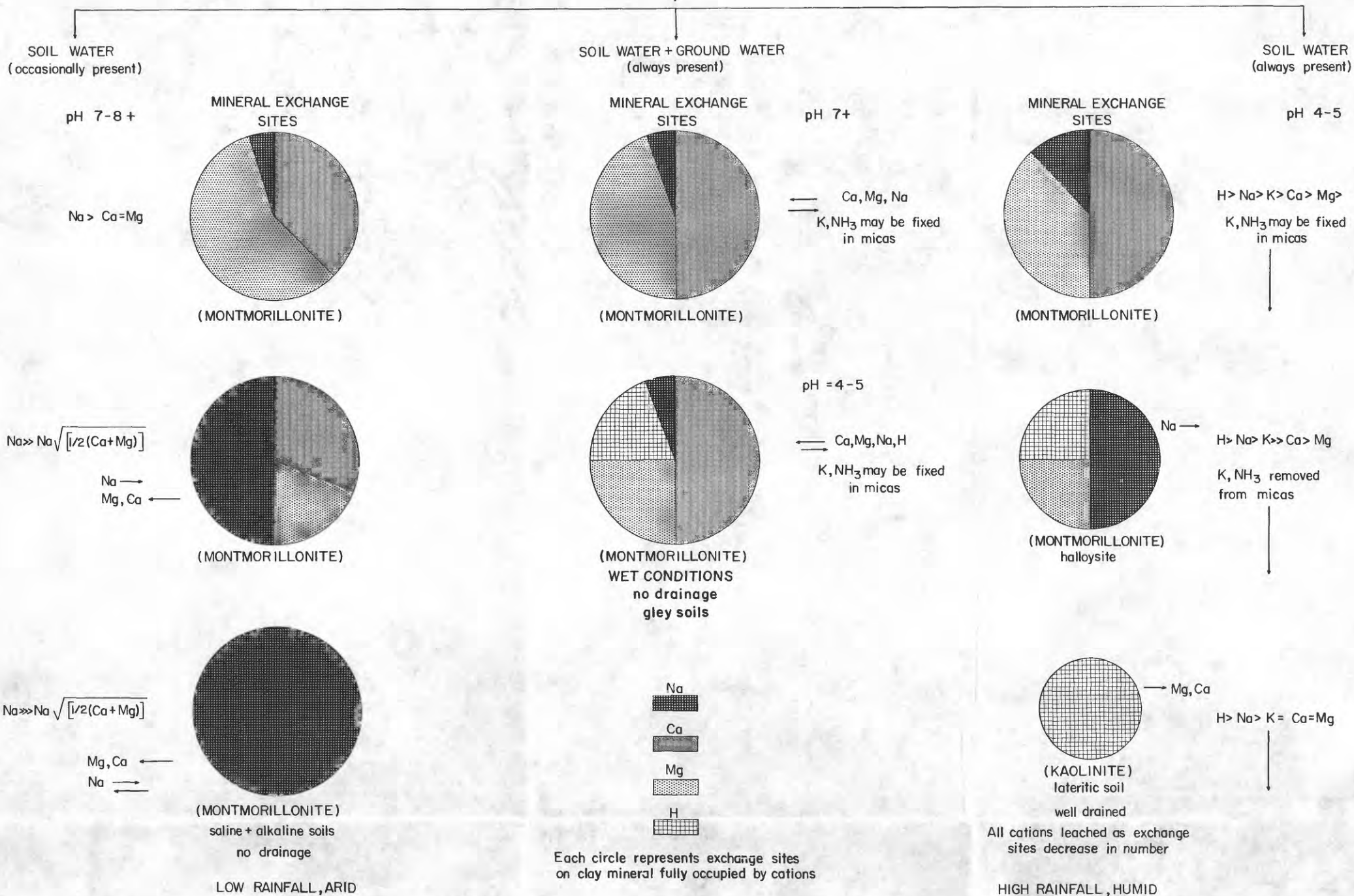
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RAINWATER
H, Na, K, NH₃, Ca, Mg, IONS
ADDED TO SOIL



SCHMATIC REPRESENTATION OF THE RELATION OF RAINWATER
TO SOIL FORMATION AND ROCK WEATHERING