The Yearly Circulation of Chloride and Sulfur in Nature; Meteorological, Geochemical and Pedological Implications. Part II[1]

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IV. The yearly circulation of sea salts between continents and the oceans

1. *Introduction*

The yearly global circulation of sea salts between continents and oceans can be estimated in several ways. One is by actually measuring the yearly amounts brought down on land by available techniques. It is clear from the preceding chapter that this is technically difficult. It is easy to collect precipitation and analyse it for various sea salt constituents but it is more difficult to estimate how much is brought down by "dry deposition", i.e. by fallout and by gas absorption. It requires a good knowledge about the turbulent character of the air and the efficiency of the ground for impingement of particles. It also requires a knowledge about the properties of gaseous constituents in the ground. This can sometimes be anticipated, in other cases not.

The advantage of this method if it could be applied properly is relatively low cost as only precipitation and air sampling near the ground are required and a network for such sampling station need not be dense. It could be built up on a synoptic scale and still provide information also on large-scale geographic variations.

Another method, which at present is hardly feasible is to carry out regular vertical "soundings" of sea salt constituents on a synoptic network over continents. Together with simultaneous wind data the transport of sea salts could be followed and, by applying the first principle, the amounts brought to the ground calculated, irrespective if they are brought down by precipitation or by dry deposition. This method has been applied on a hemispherical scale for water vapor and has given very interesting results (cf. STARR et al. 1957).

There are at present no "sounding" devices of the types used in meteorology available for the study of sea salt constituents though they may be developed in future. If they are developed they will certainly be costly.

The third method is indirect but will be treated at some length in the present chapter though available data are by no means complete. It is possible with present available geochemical information to work out a tentative balance in the sea salt circulation between oceans and continents though no geographical details can be revealed except in parts where the composition of river water has been extensively studied. The result is a global balance and is certainly valuable as a foundation on which regional studies can be built. As will be shown later it can also furnish information on dry deposition, of great value for the application of the first method, when applied to regions where river water analyses have been done.

2. *Weathering and the composition of the oceans*

Not all salts found in river water are atmospheric, derived from the sea. Chemical

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weathering of rocks also provide river waters with sea salt constituent. Human beings active as they are also help in loading river waters with various salts that may be of oceanic origin. Mining of old sea salt deposits for various salts is done extensively as well as the more direct method whereby sea water is led into large basins and evaporated in order to produce salts that are distributed widely over the continents and finally, to a large degree, find the way to the sea in rivers.

Another possible source for salts in river water are volcanic exhalations which have been investigated chemically on many occasions.

Before starting the discussion on the quantitative aspects of various sources for salts in river water it should be pointed out that partly similar discussions and arguments are found in the geochemical literature. So has the rate of weathering been thoroughly treated by Clarke (1924 p. 31—35, 151—155) Goldschmidt (1954 p. 56—68), Conway (1924 a) and Rubey (1951) and is found in most textbooks on geochemistry. The present treatment is therefore far from unique though it may differ in some respects from the earlier ones.

a. *Amount of weathering and volcanic production in the past.* The constituents present in the sea may have been there when the sea was formed or may have been supplied entirely continuously by weathering and volcanic activity or may partly have been present when the sea was formed. The first possibility rules out weathering of igneous rocks as a contributor to the salt content of the sea as well as volcanic production of salt constituents. It is therefore not compatible with actual observations in nature and may be ruled out. The second possibility will obviously lead to maximum amount of weathering possible in the past as well as maximum amount of salts supplied by volcanic activities. From our point of view this gives the upper limit for the rate of weathering and volcanic production without dismissing the third possibility. The second possibility will therefore be used as a hypothesis for deriving the maximum rate of weathering and volcanic production.

One element in the oceans which is fairly abundant is sodium and as it is hardly likely that is has been supplied by volcanic activity it must have come from the weathering of igneous rocks. The chemical composition of igneous rocks is reasonably well known. The arithmetic mean from 5,159 analyses (cf. Clarke 1924 p. 29) is 2.83 per cent sodium. Goldschmidt (1954 p. 54—57) has discussed the representativeness and found that despite the fact that the procedure of averaging gave too much weight to rarer types of rocks other analyses confirmed their reliability as an average value. Sedimentary rocks which are formed in the sea from products of weathering are much lower in sodium, the shales being highest, near one per cent, while sandstones and especially carbonate rocks are much lower. Goldschmidt (l.c. p. 59) used a figure of one per cent for the sodium in sedimentary rocks. The difference is thus about 1.8 per cent which is to be found in the sea. There is 278 kg $\times$ cm_e^2 of sea water and the sodium content is 1.06 per cent, thus 2.94 kg $\times$ cm_e^2. Consequently $\frac{2.94 \times 100}{1.8} = 163$ kg $\times$ cm_e^{-2} of igneous rocks have been weathered in the past, at most.

This analysis can be refined to some extent. The sedimentary rocks have been classified by Clarke (1924) into three main groups: shales, sandstones and limestones. Naturally shales comprise all fine-textured sediments which are poor in carbonates while sandstones comprise similar course-textured sediments. In limestones carbonates of calcium and magnesium are predominant. The composition of these three types of rocks as well as of igneous rocks as given by Clarke are shown in table 4.1 on a carbonate (i.e. CO_3) free basis and only of the elements of interest, sulfur, chloride, calcium, magnesium, sodium and potassium. Again applying the second hypothesis it is apparently possible to set up a system of equations containing as the four unknowns the amounts of weathered igneous rocks, and formed shales, sandstones and limestones. The amounts of an element that has been supplied entirely from igneous rocks must be found in the sediments and the sea. These calculations may be done assuming the mass of sedimentary rocks formed to be the same as the mass of igneous weathered because the net loss is small, about 3 per cent (cf. Goldschmidt l.c. p. 59). Three different elements are needed.

TABLE 4.1

Element	Composition in per cent of				To sea from igneous rocks $g \times cm_e^{-2}$	To sediments from sea $g \times cm_e^{-2}$	Diff. $g \times cm_e^{-2}$	Present in the sea $g \times cm_e^{-2}$	Volcanic in the sea $g \times cm_e^{-2}$
	Igneous rocks	Slates corrected for CO_3	Sandstones corrected for CO_3	Limestones corrected for CO_3					
S.	0.05	.20[1]	.03	.25	76	261	—185	246	431
Cl.	0.02[2]	.02[2]	.02[2]	.02[2]	31	31	± 0	5,280	5,280
Ca.	3.63	2.30	3.68	70.50	5,540	5,429	+ 111	111	—
Mg.	2.11	1.52	.75	10.98	3,220	—	—	354	—
Na.	2.85	1.00	.35	.09	4,350	1,410	+ 2,940	2,940	—
K.	2.60	2.79	1.17	.62	3,970	3,862	+ 108	108	—
Per cent CO_3 in uncorrected rocks.	0.15	3.60	6.85	56.75					

[1] Mean value suggested by GOLDSCHMIDT & STROCK (1941) from determinations of MINAMI (1941). CLARKE (1924) gives the figure 0.16 per cent. MINAMI (1941) also got 0.45 for a composite sample of Japanese shales.

[2] From BEHNE (1953) cf. also KURODA & SANDEL (1953).

It is, however, found that magnesium cannot be used as it gives anomalous results. The reason is probably a too low magnesium-figure for the shales. GOLDSCHMIDT (l.c. p. 58) shows in a table the composition of various "shales" and it is seen from his table that the Mg/Ca ratio can vary quite widely. The best way seems to be to use Ca, Na and K for the calculations. The amounts of the various rocks involved in past weathering then becomes, all in kg × cm_e^2.

	CO_3-free	With CO_3 included
Igneous rocks weathered ..	152.5	152.5
Shales deposited.	128.2	133
Sandstones deposited.	21.9	23.5
Limestones deposited.	2.4	5.5

As to the total amount of weathering this does not differ much from the previous estimate. The figures for the sedimentary rocks have, of course, only a tentative value but do not look unreasonable. As to the total amount of carbonates the table gives the CO_3 amount that must have originated in the atmosphere, as 9.5 kg × cm_e^{-2} which corresponds to 7.0 kg × cm_e^{-2} of CO_2. As the CO_3 radicle is bound to Mg and Ca one may use GOLDSCHMIDT'S estimate (l.c. p. 62) of the $CaCO_3 : MgCO_3$ ratio in carbonates in nature namely 6.3 to 1.

With this ratio one finds 13.3 kg $CaCO_3$ and 2.1 kg $MgCO_3$ per cm_e^2. In a somewhat different way GOLDSCHMIDT (l.c. p. 60) arrived at 12.6 and 2.0 kg × cm_e^{-2} of these two carbonates. The agreement is thus good.

In order to get the magnesium to comply to the amounts in the general balance the concentration in shales has to be increased from 1.52 per cent as in table 4.1 to 1.90 per cent in the CO_3-free part of the shales.

The calculations made so far may seem to be outside the scope of the present work. However, in order to get an idea about the present rate of weathering of sulfur from sedimentary rocks it is necessary to have some idea about the amounts of different rocks present, especially on the proportion of carbonate to non-carbonate sedimentary rocks. This point will be discussed in some detail later.

Table 4.1 also shows that Cl and S in nature cannot be accounted for by weathering. They must have been added to the sea in some suitable form presumably through the atmosphere in volcanic exhalations unless they were present at some early stage which may be less probable. This was realized at an early stage by several geochemists. RUBEY (1951) who made similar computations introduced the term "excess volatiles" for the elements in nature which cannot be accounted for by weathering. Beside Cl and S also B, C, Br and I belong to this group as well as water.

3. *Average rate of weathering of igneous rocks and volcanic production*

Table 4.1 enables us to compute both the maximum average rate of weathering from *igneous rocks* of the sea salt components Ca, Mg, Na and K as well as the maximum average rate of *volcanic* addition of Cl and S. As to weathering is has certainly been enhanced by two factors which probably have acted through about 10^9 years, namely oxygen and plants. Before that time the atmosphere may have lacked oxygen (cf. UREY 1952 p. 124) and one of the processes important in the weathering of igneous rocks, namely the oxidation of ferrous to ferric iron, must presumably have started rather late, around the time when assimilating plants occurred. The only weathering prior to this time must have been through hydrolysis. Further, the introduction of land plants must have enhanced weathering due to the strong dissolving action of organic matter produced by plants. So a maximum figure for the rate of weathering could be arrived at by using 10^9 years as the weathering period.

As to volcanic production this may be taken to have lasted 3×10^9 years which, considering other possibilities again will give a maximum average rate of production.

Weathering products are removed by rivers only from land surfaces but part of the volcanic may go directly to the sea. Using the ratio 1 : 2 for the area of continents to oceans, only a third of the total volcanic production can be expected to appear in river waters.

We can now compute maximum amounts of Na, K, Ca, Mg, Cl and S due to weathering of igneous rocks and volcanic production, expected to be found in river waters. The amounts expressed in million tons × year^{-1} are shown in table 4.2 using the data in table 4.1.

The rate of weathering in table 4.2 refers to igneous rocks but the contribution from sedimentary may also be important, especially with regard to sulfur. If possible we should like to know the present rate of weathering of all rocks.

An attempt will be made in the following to compute this from river water run-off corrected for "cyclic" salts and from the composition of the rocks as listed in table 4.1.

TABLE 4.2
Maximum average rate of weathering of igneous rocks

Element	Amount from igneous rocks $g \times cm_e^2$	Amounts volcanic $g \times cm_e^2$	Rate of weathering million tons year^{-1}	Rate of volcanic addition million tons × year^{-1}
S	76	431	0.39	0.7
Cl	31	5,280	0.16	9.0
Ca	5,540		28.3	
Mg	3,220		16.4	
Na	4,350		22.2	
K	3,970		20.2	

4. *Actual rate of weathering*

The present rate of weathering can only be inferred from river water analyses and rates of discharge of river water, correcting for "cyclic salts" of marine origin. It is clear from table 4.1 that the amounts of chloride found in river water only to a very small degree can come from weathering of rocks. If larger amounts are present they must have come from the oceans in some ways. Some may be derived from old marine sea salt deposits, others from active human collection of sea salts by evaporation. Thirdly they may have been carried into the continents through the atmosphere. With the chloride other elements in the oceans are also deposited in continents in these processes and one may expect that they are derived from the oceans either in the same proportions as they occur in the sea or in other proportions. The latter is especially true for sulfur which, apparently passes from the sea into the atmosphere in some other way. This will not concern us at the moment, however.

CLARKE (l.c.) has presented available data on the composition of river waters from different parts of the world as well as the yearly discharge of dissolved inorganic substances in various parts of the world. The available river water analyses are quite large in number but unevenly distributed. Europe and the U.S. are by far best represented while large parts of Asia and Africa are hardly represented at all. Despite all these difficulties Clarke made an attempt to compute the total amount of discharge of dissolved inorganic solids for the whole continental area that is drained. He also worked out an average composition of river water. The average rate of discharge of inorganic solids in river water that he arrived at was 27 tons × km^{-2} × $year^{-1}$. This figure is probably too high for several reasons. Firstly he took the chemical denudation in Canada to be the same as in the U.S. which is certainly an overestimate. Available data were quite high but were computed mainly from the yearly run-off and a few analyses at low water which no doubt will give too high figures. More recent figures for the chemical denudation in Finland published by VIRO (1953) give a yearlyr un-off dissolved inorganic solids of around 10 tons × km^{-2} (when recalculated into the same form as CLARKE did, i.e. with CO_3 included). Finland is situated in about the same latitude as large parts of Canada, hence a more moderate figure should be used.

Also the run-off from Asia was certainly overestimated by CLARKE. The whole vast northern Asia can be expected to have a denudation of equal magnitude to that of Finland and recent figure from Mandchuria published by YAMAMOTO (1952) give as the highest value 11 tons × km^{-2} × $year^{-1}$ for one river while another, more southerly has only 6 tons × km^{-2} × $year^{-1}$.

Secondly, practically in all instance, the yearly denudation has been arrived at by computation from average composition of river water and from the yearly rate of discharge of water which will no doubt give too high figures. Some evidence can also be presented showing the likely overestimate. ERIKSSON (1925) discussed the quite detailed survey of river water analyses of Swedish rivers. In many of the rivers the rate of flow was recorded so he could compute the average rate of discharge of dissolved solids for the period covered by the sampling and add these to obtain the yearly discharge. Comparing these values with those obtained by using average concentration and yearly discharge of water, the first figure is mostly lower and the average for the whole material where comparison can be made gives as a result that the latter methods give around 10 per cent too high values. Other investigations in Norway by BRAADLIE (1930) give differences amounting to as much as 35 per cent in one river and when averaged 13 per cent.

It is likely that the discharge of dissolved solids in river water are estimated too high probably between 10 and 20 per cent.

However, no correction for this is planned presently but a new estimate of the world's discharge of dissolved inorganic substance in river water will be attempted. The drained parts of the continents have been divided into nine regions with the following characteristics.

1. U.S.A. 8 million km^2. Rate of discharge of inorganic dissolved solids 30 tons × km^{-2} × $year^{-1}$ as suggested by CLARKE. Average composition as given by CLARKE (p. 119).

2. Canada and Alaska. 11 million km^2. Probable yearly discharge of inorganic dissolved matter the same as for wooded areas of Sweden and of Finland, i.e. 10 tons × km^{-2} × $year^{-1}$. Composition of water as the average of Yukon river and Nelson river (cf. CLARKE p. 91 C in the table and p. 92 E in the table).

3. South America. 17 million km^2. Yearly rate of discharge of dissolved inorganic matter 19 tons × km^{-2}, and the same composition as CLARKE's (p. 119).

4. \Africa. 24 million km^2. Rate of discharge and composition same as CLARKE's (p. 119 E), i.e. 17 tons × km^{-2} × $year^{-1}$.

5. North Asia and Russia. 17 million km^2 and a rate of discharge of inorganic dissolved matter same as for Finland, i.e. 10 tons × km^{-2}. Composition same as for Finnish rivers (VIRO 1953).

6. China. 5 million km^2. Has similar soils and climatic position as the Mississippi Valley. Rate of chemical denudation can be taken as 30 tons × km^{-2} and the composition the same as Mississippi (see CLARKE p. 80) at New Orleans.

7. S. Asia 7 million km^2. Rate of chemical denudation similar to that of S. America, say 20 tons × km^2 × $year^{-1}$. Composition same as for S. American rivers (see 3).

8. Europe, 6 million km^2 (excluding Russia). Possibly 35 tons × km^2 as discharged inorganic dissolved solids. Composition same as given by CLARKE (p. 119 C).

9. Australia. 5 million km^2 and 15 tons × km^{-2} × $year^{-1}$. Composition same as S. America (see 3).

TABLE 4.3

Composition of standard rivers to be used for computation of average composition and global run-off

	1	2	3	4	5	6	7	Weighted average	Million tons × year^{-1}
CO_3	33.9	30.4	32.7	32.9	35.5	40.3	24.7	33.1	605
SO_4	15.5	27.9	8.1	8.7	15.6	12.1	13.6	12.0	219
Cl	7.5	2.4	5.8	5.7	6.3	3.5	5.4	5.5	101
Ca	19.6	20.2	19.0	19.1	20.8	23.3	11.5	19.1	349
Mg	4.9	5.4	2.6	2.7	5.5	2.4	4.2	3.5	63
Na	7.5	4.9	5.1	4.9	6.9	4.4	5.3	5.4	99
K	1.8	1.0	1.9	2.4	1.6	2.8	4.4	2.3	41
SiO_2	8.7	7.4	19.0	18.0	7.2	8.8	25.4	15.2	277
R_2O_3	.6	.4	5.8	5.5	.6	2.4	5.5	3.9	70

1. U.S.A.	U.S.A. Standard
2. Yukon & Sasketchawan	Canada & Alaska Standard
3. S. America, rivers	S. America Standard
4. Africa »	Africa Standard
5. Mississippi »	China Standard
6. Europe »	Europe Standard
7. Finland »	N. Asia & Russia Standard

R_2O_3 = Sum of Fe_2O_3 and Al_2O_3

The areas given refer to estimated peripheral run-off areas and amounts to 100 million km^2 in total. This leaves about 60 million km^2 with no peripheral drainage being either basins or deserts.

As to the composition of river waters it is seen that seven different types have been chosen as standards. These are shown in table 4.3. From the area and rates of denudation given the total discharge of the different constituents has been computed and is also shown in the table. From this the average composition of river water is computed as a weighted average. In table 4.4 CLARKE's weighted average for the whole world is also given together with the average computed here for comparison. It is seen that these averages do not differ too much. The greatest difference is in the SiO_2 which, no doubt influenced by the Finnish data, is greater in the new average than in CLARKE's.

The average discharge of dissolved inorganic matter becomes about 18 tons × km^{-2} × year^{-1} and is 2/3 of Clarke's estimate.

With the data on the world run-off of dissolved solids we may proceed to estimate the part of the dissolved solids which CONWAY (1942a) named "cyclic salts". These are the constituents that are derived from the oceans in old marine salt deposits, from active human collection of sea salts from ocean water and from airborne sea salts. Whether they are included in sedimentary rocks is of no concern here, we can subtract them from the river run-off and try later to divide these cyclic salts into different categories.

CONWAY (l.c.) who first used this procedure and who gives an excellent discussion on the whole present subject, concluded, as many before him that chloride in river waters must be entirely cyclic in the sense given above. He postulated that other oceanic elements occur in river water in the same proportions to Cl as in the sea. In this way he computed the cyclic portion of various elements and subtracted them from the river water amounts. This procedure will be followed also here as a first alternative and will be called Alternative 1. There are, however, indications found in the composition of precipitation which suggest that Cl and Na are not brought to the ground in the same proportions as in the oceans. The Cl/Na ratio in precipitation which was recently discussed by ROSSBY & EGNÉR (1955) is generally lower than in sea water. One possible explanation which will be discussed more in detail later, is that chloride is first released from sea salt particles over the sea and then partly transferred to the sea again by gaseous turbulent diffusion. If this should happen we should apparently base the computation on Na. We cannot, however, use the total amount but has to allow for some being derived by weathering of igneous rocks. Regarding 80 per cent of the Na as cyclic this leaves 19 million tons × year^{-1} as chemically weathered which is close to the computed maximum average rate of weathering of Na. When correction for sea salt is made in this way we will refer to is as Alternative 2.

The result of these computations are shown in table 4.4. It is seen that only a small amount of sulfur is accounted for by this procedure. The amount of Mg is reduced by more than 15 per cent while Ca and K are but little affected. Na is reduced to about half its value in Alternative 1 giving a rate of chemical weathering of Na from rocks about twice that computed as the maximum average rate. This seems to be too high especially as the main bulk of it has to come from igneous which at present occupy only a fraction of the land surface.

With the run-off it is possible to make some estimates of the present rate of weathering of different rocks. This cannot, however, be done in the same simple way as the amounts of rocks were computed. The river water analyses concern only the soluble inorganic part while there is practically no information on the composition of suspended inorganic matter in river water which seems to make up about 5/6 of the total load of inorganic matter in river water (cf. KALLE 1945, p. 118). The transport of suspended matter in river waters is referred to as mechanical denudation while the transport of dissolved matter is referred to as chemical denudation. In these processes some elements will be found mainly in solutions while other appear mostly in suspended particulate matter. Thus, we have to discuss which elements are more abundant in solution than in particulate matter. This may, however, differ in different rocks.

If we consider the least complicated type of rocks, the limestones, we can expect to find practically all of its constituents in solution because of the simple process by which limestones are denuded. Atmospheric carbon dioxide in solution reacts with the carbonates simply by

$$CaCO_3 + H_2CO_3\,(aq) \rightarrow Ca^{2+}\,(aq) + \\ + 2HCO_3^-\,(aq)$$

and when the carbonates are precipitated again in the sea the carbon dioxide used for making them soluble escapes into the atmosphere, thus acting as a transport band. As noted before we computed the amounts of $CaCO_3$ and $MgCO_3$ in sedimentary rocks by using the ratio 6.3/1 as suggested by Goldschmidt. Looking at the corrected river waters we find that the $CaCO_3$/$MgCO_3$ ratios are 7.2/1 for Alt. 1 and 7.8/1 for Alt. 2, thus higher than Goldschmidt's ratios. We may conclude that practically all

TABLE 4.4

Composition of river waters and computations of non-cyclic run-off on two alternatives

Constituent	Clarke's world average per cent	Present world average per cent	Uncorrected run-off in million tons	Alt. 1	Alt. 2
				Corrected for oceanic salts using Cl	Corrected for oceanic salts using 80 % of Na in river water
CO_3	35.5	33.1	605	605	605
SO_4	12.2	12.0	219	205	199
Cl	5.8	5.5	101	0	0
Ca	20.6	19.1	349	347	346
Mg	3.4	3.5	63	56	53
Na	5.8	5.4	99	43	20
K	2.3	2.3	41	39	38
SiO_2	11.8	15.2	277	277	277
R_2O_3	2.8	3.9	70	70	70

Ca and Mg in the corrected river water comes from carbonate rocks but that igneous rocks contribute also to the Ca in river waters.

As to igneous rocks only part of their constituents will appear in soluble form in river water. From studies on soil formations it is known that such processes lead to the formation of so called clay minerals which contain more water than the parent material from which they are derived. Most primary minerals which are the ingredients of igneous rocks are thermodynamically unstable at the prevailing temperature and moisture conditions and are thus broken down, more or less rapidly, into so called secondary minerals of which the clay minerals, including oxides of ferric iron and of aluminium, are most common. In this process some constituents go into solution and especially Ca and Na. Others like Mg can be built into the clay mineral-crystal structure and are thus removed by solution to a smaller extent. Potassium which competes strongly in ion exchange processes on clay mineral surfaces can also become "fixed", apparently by inclusion between layers in layer-structured clay minerals This means that in the case of igneous rocks we can maybe assume that quantitatively all Na and Ca goes into solution.

As to the remaining sediments their contribution of the cations discussed to river water is more doubtful. The quartz part in sandstones and shales will, of course, not enter the solution. As to the rest this is mainly made up of clay minerals which should be thermodynamically stable unless the rocks are strongly metamorphous which a small part may be. They should therefore be resistant to chemical weathering but naturally subject to mechanical disintegration. They may contain some soluble elements like sulfur which is in fact enriched in sediments compared to igneous rocks. Some of the Na may also go into solution as it is likely that an addition of this element has taken place in the sea by ion exchange. The proportion that goes into solution is probably small and may be neglected. If not neglected it will decrease the amount of igneous rocks weathered.

With this information we can estimate roughly the yearly chemical denudation of igneous rocks and limestones as follows. Assume that all Ca in igneous rocks and limestones on their weathering goes into solution and that all Na in igneous rocks is found as noncyclic in river water. In this way the rate of weathering of igneous rocks is somewhat overestimated, that of limestones slightly underestimated.

The rate of weathering of igneous rocks then becomes

Alt. 1. 1,500 million tons × year^{-1}
Alt. 2. 700 » » »

The release of Ca from igneous rocks becomes

Alt. 1. 54 million tons × year^{-1}
Alt. 2. 25 » » »

and consequently, Ca released from carbonates

Alt. 1. 293 million tons × year^{-1}
Alt. 2. 321 » » »

With a $CaCO_3 : MgCO_3$ of 6.3/1 in limestones (pure, including CO_3).

Alt. 1. 850 million tons × year^{-1}
Alt. 2. 930 » » »

thus practically the same.

The ratio of Ca and Mg carbonates in sedimentary rocks to the remaining sedimentary rocks is 1/9.5. As all sedimentary rocks are lifted from the sea in the proportions they are formed it is likely that on an average they are denuded at rates proportional to their masses. This means that the total denudation, chemical as well as mechanical, should be about ten times the figures for the carbonate rocks or, say, about 8,000 million tons × year^{-1} of shales and sandstones of which about 1/5 is sandstones. Together with igneous rocks the total rate of denudation should amount to 10,000 million tons × year^{-1} which is roughly six times the chemical denudation. It was mentioned earlier that from direct estimates about 1/6 of the total denudation was chemical in which case the total denudation works out to be about 8,000 million tons × year^{-1}. These estimates do not differ too much, in fact they agree well and the following rounded off figures for the yearly denudation can be used for estimating the weathering of sulfur.

Rock type	Alt. 1	Alt. 2
Igneous	1,500	700
Shales	6,500	6,500
Sandstones	1,500	1,500
Limestones (as listed)	300	300

The low figure for limestones is because 2/3 of the carbonates are found in shales and sandstones. It does not make much difference which alternative is chosen for weathered sulfur as igneous rocks are low in sulfur. Now it is assumed that by the mechanical denudation of shales and sandstones the sulfur and chloride in these rocks will appear in solution. The percentage of SO_4 in the different groups of rocks are given in table 4.1 on a CO_3-free basis. Without this correction for CO_3 the percentages for sulfur are: igneous 0.15, shales 0.60, sandstones 0.09 and limestones 0.33, all expressed as SO_4. The total amount of sulfate weathered then becomes 44 million tons according to Alt. 1 and 42 million tons according to Alt. 2, the difference being unimportant.

The amounts of more common oceanic constituents chemically weathered according to the different alternatives is seen below in million tons-year^{-1}.

	Alt. 1	Alt. 2
SO_4	44	42
Cl	2	2
Ca	347	346
Mg	56	53
Na	43	20
K	39	38

the main difference being in the Na. Comparing the figures for SO_4 with those in table 4.4 we see that less than a quarter of the sulfur is accounted for by weathering. The rest must come from other sources. It does not seem plausible that the sulfur content in shales is underestimated by a factor of four. Further, we have some other sources to consider. Of these human production may have some importance.

5. *Human production*

Oceanic constituents in river waters due to human activities are either disposed of directly into the ground or streams or passes through the atmosphere before they appear in river waters. Products of combustion which are fed into the atmosphere belong to the latter group and obviously only a part of the total output by chimneys will be precipitated over continents. The rest is precipitated over the sea. Naturally all elements of the first group will be fed into river waters.

One large item is chloride in salt production. CONWAY (1942b) estimated the total salt production by human activities to 9 million tons per year. However, available statistics give a figure of 35 million tons × year^{-1} as the present rate which corresponds to 23 million tons of chloride per year and may be taken as the rate around 1900. Assuming that corresponding quantities of other oceanic elements are produced at the same time and that they find their way to river water these amounts become

Chloride	23	million tons × year^{-1}
Sulfur	1.1	» » »
Sodium	13	» » »
Calcium	0.5	» » »
Magnesium	1.5	» » »
Potassium	0.5	» » »

These quantities do not appear in the atmosphere.

As to sulfur it is mined and used in various connections. The total industrial production for use (mainly in fertilizers) is about 10 million tons × year^{-1} which is taken from various sulfur deposits. Thus about 11 million tons of sulfur is annually brought to river waters without passing through the atmosphere.

The next large source of Cl and S is in the combustion of fossil fuels. The yearly production of coal is at present about nearly 2 × 10^9 tons. The chloride content is generally low and comparable to rocks while the sulfur content is appreciable, on an average 1.8 per cent (cf. JUNGE & WERBY 1958). The total amount of sulfur emitted to the atmosphere in various processes is estimated to 40 million tons by JUNGE. Of this 2/3 may be precipitated over the sea, while 1/3 is precipitated over land, i.e. 13 million tons. At the time the river water analyses were made (around 1900 and earlier) the corresponding figure was about 1/3 of this or 4 million tons. Now the total human production of various elements found in river waters can be tabulated.

	Million tons × year^{-1}
Cl	23
S	15
Na	13
Ca	0.5
Mg	1.5
K	0.5

TABLE 4.5

Balance of oceanic elements in million tons × year^{-1}

	In river water	Human activities	Weathering		Air borne	
			Alt. 1	Alt. 2	Alt. 1	Alt. 2
S	73	15	15	14	43	44
Cl	101	23	2	2	76	76
Na	99	13	43	20	43	66
Mg	63	1.5	56	53	5.5	8.5
Ca	349	0.5	347	346	1.5	2.5
K	41	0.5	39	38	1.5	2.5

6. *General balance*

We can now proceed to calculate a residue of oceanic components in river water after subtracting human production and weathering products from the total dissolved load, labelling this air borne. As to volcanic Cl we ignore it because it can hardly be as large as the maximum average computed in table 4.2. CORRENS (1956 p. 201) gives estimated output of Cl by known volcanos and this is only a few per cent of that computed in table 4.2. Further, 2/3 of it goes directly into the sea. We may therefore ignore it in the present balance. The air borne part which is shown in table 4.5 with the two alternatives in the weathering is quite substantial for some constituents while rather small for others. The sulfate is given as sulfur to facilitate comparisons later in this paper. More than half of the sulfur in river water is made up of this residue and 2/3 of the chloride. As to the cations only Na, is found in the air borne part to any larger extent while practically all Ca and K in river water can be accounted for by weathering. Mg is in an intermediate position.

The quantities in the air borne part should represent two sources, one is the atmosphere, the other old marine sea salt deposits which are being denuded. CONWAY (1942b) tried to account for the marine salts by including a quantity amounting to 2 per cent of the total amount of oceanic salts into the sediments and then compute from the estimated rate of weathering the amount of cyclic components derived from these deposits. He managed to account for 1.5 million tons of chloride in this way which obviously is insignificant. Two per cent of the total oceanic salts is about 0.1 kg × cm_e^2 of Cl which, if included into the sediments rises its Cl content by 0.06 per cent and in the present estimates of weathering of sedimentary rocks increases the release of Cl from sedimentary rocks by about 5 million tons which is small compared to the residue in table 4.5. Admittedly, the marine deposits may weather at a slightly greater rate than the rest of the sedimentary rocks because of their tendency to move upwards, penetrating other sedimentary strata. The effect cannot be large, however, else there should be no salt deposits left and there are apparently large deposits which are not influenced by weathering yet.

Further, two per cent of the oceanic salts is a large quantity. If spread uniformly over the continents it would cover them with a 3 metre thick crust which seems to be too much. And, besides, these main deposits could never account for the sulfur.

It seems likely that the air borne part in table 4.5 by and large represents oceanic constituents carried into continents by the atmosphere thus justifying the label used. Now, these quantities which are deposited on the land surface from the air will apparently appear in river waters sooner or later. Those precipitated in the drained parts of the continents will spend only a short time on land before brought back to sea. Those who are deposited in basins and deserts will apparently spend a much longer time before they are brought back to the sea. Basins and desert areas are not permanent features. Through changes in climate desert areas may gradually be washed out and new desert areas created. Also basins may be filled with enough water to cause a drainage to the sea; changes in elevation of the land surface may further cause

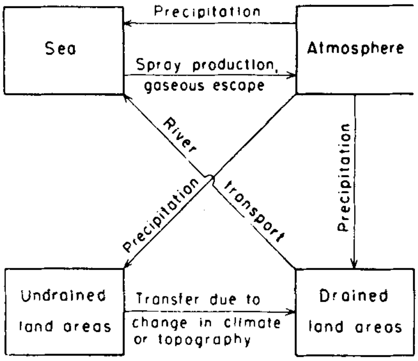

Fig. 4.1. Schematic representation of the circulation of sea salts in nature in a box model arrangement.

old basins to disappear and new ones to appear. If all such processes, climatic and epiorogenetic, work steadily, constantly changing the geographical location of drained and undrained areas, then the air borne part in table 4.5 would represent the rate of additions from the atmosphere of these oceanic constituents.

In this cycle of oceanic elements, in which the atmosphere takes part one could picture the land areas as reservoirs for these oceanic salts. The arrangement of these reservoirs can be made in two ways. One way is to arrange them as two main reservoirs, one representing the peripherally drained areas, the other the rest of the land areas. The first reservoir contains but little salts while the second contains much larger amounts. This can be expressed in other words in terms of residence times of oceanic salts. In the peripherally drained area-reservoir the residence time of oceanic salt may be of the order of 10 to 100 years while in the other reservoir the residence time may be of the order of 10,000 years or more. With this distinction of land reservoirs one can picture the circulation of oceanic salts as in fig. 4.1. They originate at the sea surface either as spray er by gaseous escape to the atmosphere from which they are precipitated over land and sea. The part precipitated over undrained land areas accumulate for some time until climate or topography changes when they are transferred to the drained area reservoir and from there back to the sea.

The idea of a steady accumulation of geologically recent sea salts in desert and basins is supported by the observation that recent salt deposits are much more widespread than old marine deposits (cf. **Spraker** 1909). A number of these recent salt deposits are no doubt airborne.

The other possible model of the land reservoir would have characteristics in principle similar to the ocean discussed recently by **Welander** (1959) and to the ground water reservoirs discussed by **Eriksson** (1958). In such a model the quantity of oceanic salts added to the ground is classified according to the length of time it will take before it enters the ocean again. Salt applied at a rate dF will spend say T years on the continents before it is brought back to the oceans again. The total amount of salt dM stored on the continents from this rate of addition and with this age will apparently be

$$dM = TdF \qquad (4.1)$$

and the total mass of oceanic airborne salt stored on the continents is therefore

$$M = \int_0^{F_0} TdF \qquad (4.2)$$

where F_0 is the total rate of addition. One can regard the rate of addition F as a function of T by arranging elements dF according to increasing T:s so that F for a certain T is the rate of addition over land surfaces where the time the added salt spends on the continents is equal to or less than T. Such a function may look like the one pictured in fig. 4.2. At very large values of T the function F approaches F_0 the total rate of addition to

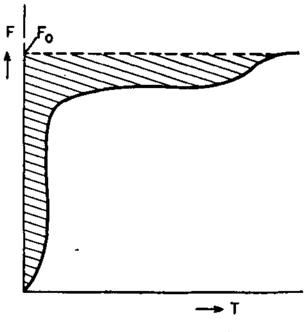

Fig. 4.2. Schematic representation of the flux of sea salts from continents to the oceans as a function of their residence time on the continents.

land surfaces. Then the area to the left of the curve (shaded in the figure) is the mass of salt on land. Such a model of a reservoir can be applied to many different kinds of circulations in nature.

The air borne part in table 4.5 will be discussed more in detail later when it will be compared to actual data on the additions of salts from the atmosphere to continents. If it was assumed that these amounts drained only from areas of peripheral run-off one obtains the yearly run-off in kg ha^{-1} by dividing the figures by 10.

7. *The "air borne" sulfur*

The geochemical circulation of sulfur has been an enigma, cautiously and vaguely discussed by authorities like GOLDSCHMIDT and CLARKE. The problem aroused after the detailed investigation on river waters in the United States when it was found that river waters discharged so large amounts of sulfur that it was hardly possible to account for by weathering. At that time the composition of different rocks were known well enough to make such a comparison. The problem seems to have been brought up by H. S. SHELTON in 1910 who by comparison of rock and river analyses concluded that the analytical method of sulfur determinations in river water used by the U.S. Geological Survey must have given far too high results. A reply by DOLE (1911) did not clarify the question and a new attack by SHELTON came in 1914 followed by a prompt reply by DOLE (1915). In 1915 SHELTON delivered two more papers on the subject of which the last is a noteable attempt to discuss the balance of different elements in river waters, ocean water and rocks. Again he found the sulfur concentrations in river water to be too high to be accounted for by known processes of transfer from sea to land and again he concluded that the discrepancy must lie in the analytical method for sulfur in river water. The discussion which was quite animated seems to have stopped by then and no alternative explanation was ever offered by DOLE.

In the 1924 edition of CLARKE's "Data on Geochemistry" CLARKE only touches the problem referring to the oceans by the statement: "On the whole, sulphates seem to accumulate in the ocean, but the figures are not wholly concordant or satisfactory. The extent of their precipitation is by no means clear, although they are found in all clays and oozes in trivial proportions." Now, Clarke believed in a comparatively young ocean of around 70 million years and yet he had difficulties to balance the sulfur in the oceans. The conditions apparently get worse if an age of the order of 10^9 years is used.

In 1942 CONWAY (1942 a, b) made a noteworthy and rather elaborate attempt to reconstruct the history of the oceans out from geochemical data. During this process he had to consider the balance of different elements in the oceans. At that time sea salt spray was known to be transported into continents in sizeable quantities and being aware of this he introduced the term cyclic salts for those salts in river water which had the composition of sea water. After subtracting these from river water salts he found a large fraction of sulfur—just as discussed earlier—which could not be accounted for by weathering or any other source. CONWAY was thus in the same position as SHELTON earlier but unlike him he did not think there was anything wrong with the analytical method of sulfur analyses in river water. Instead he postulated that this excess was of marine origin which escaped the sea in the form of H_2S, which is known to be volatile. As a suitable source for this H_2S he took the continental shelves which are covered to large extent by the so called blue mud, a strongly reducing media. Due to accumulation of organic matter on the bottom anaerobic conditions develops favouring reduction of sulfate to H_2S. That this process takes place in some areas is known, a well known example being the Black Sea the deeper parts of which is completely void of oxygen containing appreciable concentrations of H_2S. As to the continental shelves there is no evidence of such reducing conditions but CONWAY assumed the H_2S to diffuse to the surface of these shallow areas and escape into the atmosphere. This would not be completely impossible. It is true that hydrogen sulfide is never detected in waters where oxygen is present. On the other hand, the present analytical methods for H_2S in sea water are adjusted to quite large concentrations, far larger than needed for this process. Considering a turbulent diffusion coefficient of only 1 cm^2

× sec^{-1} a steady transport would not require a concentration difference of more than 10 $\mu g \times l^{-1}$ of H_2S through a depth of 100 meters to account for the whole quantity required. This is estimated for the area of the shelf, about 8 per cent of the total ocean area. Obviously, more refined technique than existing at present is required to detect such a small gradient. CONWAY's approach to solving the problem is interesting and quite reasonable and his ideas were apparently so advanced that no alternatives are found later in the literature.

The mechanism postulated by CONWAY is, however, not the only one possible. There are, at least, two more possibilities which should be mentioned. One is H_2S production in intertidal flats which cover an appreciable area. This possibility was suggested in 1955 by J. Bouquiaux (cf. ERIKSSON 1955b p. 394) and recently by Dr. Redfield, Woods Hole Oceanographic Institution (personal communication). The conditions for H_2S production in these flats are ideal. They are very rich in organic material and are strongly reducing, the sulfate being used as an oxygen source to a large extent. They are periodically fed with sea water sulfate and periodically laid bare which will facilitate the escape of H_2S. It is, however, impossible at the present state of knowledge to assess the total production of H_2S in these flats.

Another source is H_2S released during the metabolic turnover of organic material in the sea. During the breakdown of proteins sulfur will be released as H_2S. The larger part of the turnover of organic matter takes place in the surface water where escape of H_2S is quite easy. The total turnover of H_2S can be estimated from the yearly rate of assimilation and the S/C ratio in phytoplankton. As to the rate of assimilation in the sea estimates vary within an order of magnitude. HUTCHINSON (1959) gives a probable figure for the gross production of 260 × 10^9 tons CO_2 or 70 × 10^9 tons C per year and the net production about half as large. From data in SVERDRUP et al. (1949) the S/C ratio in this material is 0.0075 so the corresponding assimilation of sulfur becomes 260 million tons × $year^{-1}$. It is obvious that only a fraction of this is needed to account for the "residual" sulfur in river water. One would expect strong regional differences in H_2S production if this overturning of organic matter in the sea is important, the shelf areas being most important because of their productivity.

To see whether such a mechanism is likely one should look at the volatility of H_2S in sea water. At the pH of sea water about 90 per cent of dissolved hydrogen sulfide should be present as HS^-. The reaction of interest is thus

$$H_2S\,(g) \rightarrow H^+\,(aq) + HS^-\,(aq)$$

for which the standard free energy change is 10.9 kcal and the corresponding equilibrium constant $K = 10^{-8.0}$. The partial pressure of H_2S over sea water with pH 8 is then

$$P_{H_2S} = a_{HS^-}$$

when P_{H_2S} is measured in atmospheres and a_{HS^-} in moles × l^{-1}. Converting the partial pressure into $\mu g \cdot m^{-3}$ it can be shown that if the air contains 10 μg H_2S – S per m^3 then at equilibrium the sea water concentration of HS^- – S is 0.78 × 10^{-8} moles × l^{-1} or 0.25 $\mu g \times l^{-1}$ thus extremely small. An escape of released H_2S is therefore quite conceivable even if H_2S would be oxidized fairly easily in sea water. Such a low H_2S concentration in sea water cannot be detected by standard procedures.

Once in the atmosphere H_2S is probably easily oxidized to SO_2 which is a quite common constituent of the atmosphere.

All data on the rainwater composition in places remote from industrialization favours this mechanism of release of sulfur from the sea. The data by GRAY (1888) from Lincoln, Canterbury in New Zealand close to the coast, gave Cl/S ratios in rain water from 9 to 11 whereas the same ratio in sea water is 21.5. ERIKSSON (1957) has given data on the composition of rainwater in Hawaii collected close to the windward coast and for these samples the Cl/S ratios vary between 11.9 and 22.8. Further inland in Hawaii the ratio decreases and is always less than 10. Even in the most remote places this excess of sulfur over chloride in precipitation is noted.

V. Chemical reactions in the atmosphere involving oceanic components

It was observed early that the composition of precipitation in coastal regions differs from sea water composition with respect to the Cl-Na ratio. In fairly recent studies **Sugawara** et al. (1949) and **Miyake** (1948) made systematic studies of the chemical composition of precipitation of various origin and sampled at various distances from the sea. They found that the proportion of sulfur and calcium increased inland. To account for the changes in composition they postulated a mechanism that, though interesting, is very unlikely. They pointed out that when sea salt particles evaporate calcium sulfate first forms solid precipitation. They assumed that these crystals separate from the main sea salt droplet and are carried much further inland before precipitation as they are less hygroscopic.

Any mechanical separation of crystals forming in a sea salt particle seems, to the present writer, physically improbable. Small $CaSO_4$ crystals can hardly leave a drop penetrating through the air-liquid interface just by gravity. Firstly they are physically absorbed on a liquid surface which can be easily verified experimentally and secondly, if they fell out of a larger drop they would have a much lower fall velocity than the drop and then be caught by the drop.

Below 75 per cent relative humidity NaCl crystallizes and one may consider a physical separation at that stage. But a sea salt particle never get absolutely dry under ordinary conditions in the atmosphere because already the presence of magnesium and chloride will leave a wet film around the particles even at comparatively low relative humidities which can be observed under a microscope. Where such a wet film is present it is extremely doubtful if small crystals of $CaSO_4$ can be shaken off the much larger sodium chloride crystals.

Earlier **Cauer** (1938) suggested a chemical process by which chloride could be separated from both sea water and sea salt, a process which is qualitatively possible. This process involves ozone which is known to oxidize chloride to chlorine, Cl_2, which is volatile and thus can escape into the atmosphere. It reacts, however, with water forming equal proportions of hydrochloric acid, HCl and hypochlorous acid HClO. **Cauer** had observed that atmospheric vapor in coastal regions, condensed on a cold surface gave an acid reaction while sea water is slightly alkaline. He postulated a release of chlorine from sea water by ozone and then formation of HCl, giving the low pH observed. His theory, though probably not quantitatively important, is nevertheless a considerable progress in atmospheric chemistry. **Eriksson** (1955b) suggested another theory for the separation of chlorine namely through the addition to the sea salt particles of H_2SO_4 formed in the atmosphere by the slow oxidation of SO_2 in the atmosphere. Such an addition causes chloride to escape as HCl and gives the frequently observed low pH-values of precipitation. An account of the two chemical processes suggested will be given but, in order to see the background clearer, some data by **Junge** (1956) on the chemical composition of the gaseous phase and sea salt particles of different sizes will be given.

In his study of the chemistry of air **Junge** managed to separate gases and particulate matter in the sampling procedure. He further separated the particulate matter into two size groups, namely *giant particles* (radius 0.8—8 μ) and *large particles* (radius 0.08—0.8 μ). He analysed the samples for ammonia, chloride, sulfate, sulfur dioxide, nitrite, nitrate and sodium. Of his measurements those in Florida and on Hawaii are the most interesting and perhaps most significant for maritime air remote from industrial contamination. The average data from these places are shown in

TABLE 5.1

Average concentrations of Na, Cl and S in particulate and gaseous form in Hawaii and Florida. Values in $\mu g \times m^{-3}$. From Junge (1956)

	Large particles			Giant particles			Gas phase	
	Na	Cl	S	Na	Cl	S	Cl	S
Hawaii.........	—	.09	.10	—	4.96	.26	1.92	.37
Florida.........	.06	.05	.10	.85	1.49	.10	1.57	1.00

table 5.1. As to particulate matter chloride is found almost exclusively in the giant particles which in fact are those discussed earlier with examples from WOODCOCK's data. In so-called large particles, which are smaller than 0.8 μ in radius, sulfur seems to be enriched relative to chloride but even in the giant particle fraction sulfur is enriched compared to the composition of sea water. In Hawaii the Cl/S ratio is 19.1 as compared to the sea water value 21.5 while for Florida it is 14.9. There is thus an excess of sulfur in the salt particles which, in the case of Hawaii is also reflected in the composition of precipitation (cf. ERIKSSON 1957).

As to the gas phase there are appreciable concentrations of both chloride and sulfur. Chloride may occur in two forms, as ammonium chloride and as hydrochloric acid. Thermodynamic data on ammonium chloride are, however, lacking so it cannot be determined with certainty whether ammonium chloride, at those low pressures can exist in gaseous form or whether it is completely dissociated into ammonia and hydrochloric acid. As to sulfur it was determined as SO_2 which, from a chemical point of view, is the only compound of sulfur beside hydrogen sulfide, H_2S, which can exist in the gaseous state in the atmosphere. The excess sulfur is thus considerable at both places. And in Florida the concentration of S in the gas phase is about 5 times higher than the concentration of S in the particulate phase which is present as sulfate.

As it is most likely that the gaseous chloride originates in sea salt particles we may now consider the two chemical processes mentioned earlier to see if possible which is more important.

1. *Oxidation of chloride by ozone*

This reaction, suggested by Cauer to be responsible for the low pH-values of precipitation has been studied in detail by YEATTS & TAUBE (1949). The first step in the reaction is

$$O_3\,(g) + Cl^-\,(aq) \rightarrow O_2\,(g) + ClO^-\,(aq) \tag{5.1}$$

followed by

$$ClO^-\,(aq) + 2H^+\,(aq) + Cl^-\,(aq) \rightarrow Cl_2\,(g) + H_2O\,(liq) \tag{5.2}$$

The first reaction is rate determining and experimentally they found

$$\frac{d(Cl_2)}{dt} = k_1\,[O_3]\,[Cl^-] + k_2\,[O_3]\,[Cl^-]\,[H^+] \tag{5.3}$$

where the brackets denote concentrations in moles × 1^{-1}. The values of k_1 and k_2 found were

0° C	$k_1 = 0.0128$	$k_2 = 0.124$
9.5° C	$k_1 = 0.0379$	$k_2 = 0.366$

Dimensions $l \times mole^{-1} \times min^{-1}$ for k_1
$l^2 \times mole^{-2} \times min^{-1}$ for k_2

At the pH of sea water k_2 can apparently be neglected and, at a partial pressure of ozone of 6×10^{-8} atm and $[Cl] \sim 1$ the first product ClO^- is formed at a rate of 2.2×10^{-11} moles × 1^{-1} × min^{-1} at 0° C and about three times faster at 10° C. Considering a sea salt droplet the time constant of the reaction is about 10^4 years for converting the chloride to ClO^-. It does not seem likely that such a slow rate can account for the loss of Cl from sea salt particles actually observed. In coastal regions of Europe the Cl/Na ratio in precipitation is frequently around 1.6 and lower indicating at least 10 per cent loss of chloride. With the reaction above it would take 10^3 years to achieve this. At low pH value, say around unity, the reaction would go about twice as fast but even then the rate would be too slow. If sea salt existed in particulate form it is hardly likely that this would increase the rate by five orders of magnitude.

2. *Release of HCl by absorption of SO_3 or H_2SO_4*

As there is SO_2 in the atmosphere this is steadily oxidized to SO_3 which, being extremely hygroscopic, would soon be absorbed by any particulate matter as H_2SO_4. Then pH will be lowered and another reaction

$$HCl\,(aq) \rightarrow HCl\,(g) \tag{5.4}$$

has to be considered. This reaction must be fast as it is only a phase change involving no other molecules. The free energy change of this reaction is $\Delta F^\circ = 8.68$ kcal at 25° C and thus the equilibrium constant $10^{-6.36}$. Thus at equilibrium

$$P_{HCl} = 10^{-6.36} \cdot a_{HCl} = 10^{-6.36} \cdot a_H \cdot a_{Cl^-} \quad (5.5)$$

where a denotes the molar activity. Suppose the pH of rainwater is 4.5, a very common figure for the west coast of Europe, and the salt content is 30 mg × 1^{-1}, this represents sea water diluted 1,000 times except for the pH. The corresponding salt particle, while in the air must have been at least 10 times more concentrated than sea water and must consequently have had a pH of around unity. Further, the concentration of chloride in the drop must have been around 1 molar. At that state the partial pressure of HCl must have been $10^{-7.4}$ atm. As the pressure to be accounted for is around 10^{-8} atm it is seen that this is a very effective mechanism.

One can, considering this reaction, expect that for every SO_3 absorbed on sea salt particles approximately 2 HCl are released from the particle into the gaseous phase.

This mechanism thus explains two things, namely the often observed low pH of precipitation and the presence of gaseous chloride in the atmosphere. Then we may ask ourselves if the rate of oxidation of SO_3 is large enough to make the picture semiquantitative.

3. *Rate of oxidation of* SO_2

Gerhard (1953) investigated the reaction

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g) \quad (5.6)$$

and found it proceed with measurable speed in daylight. Further it was found to obey a first order reaction with a rate constant of around 0.1 to 0.2 per cent per hour. He also found that ozone was unable to oxidize SO_2 to SO_3. **Junge & Ryan** (1958) later studied the oxidation of SO_2 in a cloud under which condition the oxidation takes place in solution and found that when ammonia was present, the reaction was rapid. The simple interpretation of this observation is the fact that the rate of oxidation of SO_2 in water is pH sensitive which is known from polarography where sulfite in alkaline solution effectively and rapidly removes dissolved oxygen. From **Junge**'s experiments it appears as if the rate of reaction at low pH is extremely slow. This means that SO_2 is oxidized to sulfate to a degree corresponding to the excess base being present initially.

Johansson (1959) correlated the annual sulfur amounts in precipitation to the concentration of sulfur in air from the Swedish data which for all practical purposes can be taken as sulfur dioxide sulfur and obtained as a result an increase in the yearly precipitated sulfur of 0.9 kg × ha^{-1} for an increase in the sulfur concentration in air of 1 $\mu g \times m^{-3}$. Assuming that only sulfate sulfur is removed by precipitation the rate of removal must be proportional to the rate of oxidation of SO_2-S in the atmosphere. 1 $\mu g \times m^{-3}$ of SO_2-S mixed uniformly throughout the atmosphere amounts to 1 $\mu g \times cm^{-2}$ in a column of air. With a rate of oxidation of 0.1 per cent per hour, the lower figure given by Gerhard, we arrive at a yearly rate of oxidation of $\frac{0.1 \cdot 24 \cdot 365}{100} = 8.8 \mu g \times cm^{-2}$ or 0.88 kg × ha^{-1} for each $\mu g \times m^{-3}$ of SO_2-S present. This agrees very well with the figure found by **Johansson**. Considering, however, dry deposition of sulfate sulfur in particulate matter it is possible that the average rate of oxidation is 0.2 per cent per hour. It is difficult to decide how much of this oxidation takes place in the gas phase and how much takes place through oxidation in the liquid phase of clouds in the way studied by **Junge**. If we set a probable value of 0.1 per cent per hour for the gaseous process, the two processes become of equal importance.

4. *Transfer of oxidized* SO_2 *to sea salt particles*

The SO_3 formed by oxidation of SO_2 in the gas phase has a great affinity for water and will either as SO_3 or as H_2SO_4 molecules be absorbed on particles in the atmosphere. The transfer is of course simply by diffusion. If the gas density of SO_3 or H_2SO_4 is $\Delta\varrho$ the rate of mass increase of sulfate sulfur in any particle will be

$$\frac{dm}{dt} = 4\pi r D \Delta\varrho \quad (5.6)$$

where D is the diffusion coefficient and r the radius of the particle. The rate of concentration increase of sulfate sulfur will, however, be

$$\frac{dc}{dt} = \frac{3\pi D \Delta\varrho}{r^2} \quad (5.7)$$

thus inversely proportional to the square of the radius. Smaller particles will therefore increase their concentration of sulfate sulfur much more rapidly than larger particles. This accounts well for the greater proportion of sulfate found by JUNGE in the large particle fraction compared to the giant particle fraction. Considering the replacement of Cl taking place, smaller salt particles will lose proportionally much more of their chloride than larger sea salt particles. Quantitatively, however, the greatest loss will occur in the larger particles though the percentage loss will be small.

The loss of chloride from sea salt particles will, of course, change their Cl/Na ratio and the degree to which this occurs will depend upon the size of the particles and their residence time. A complication is, however, coalescence processes that so to speak transfer low Cl/Na ratios from small particles to larger particles. It is therefore not possible to predict quantitatively the Cl/Na ratios as a function of particle size.

Also soil particles will absorb the SO_3 formed by oxidation of SO_2 in the gas phase and one can expect that the solvent action of the concentrated acid formed will attack them severely. Calcium carbonate particles will be converted into calcium sulfate and feldspars will probably partly dissolve. How much they are attacked will, however, also depend on their residence time in the atmosphere. It is apparent that the elements released will modify the chemical composition of the soluble part of particulate matter in the atmosphere. Of special interest is, of course, addition of sodium from soil particles which will affect the Cl/Na ratio. There are, however, indications that this addition of sodium is relatively unimportant whereas the addition of calcium is much greater. This is, perhaps, understandable considering the chemical composition of soils in arid regions, important source regions for soil particles in the atmosphere.

If the process suggested for the release of HCl is likely then on an equivalent basis, the excess of sulfur in precipitation should be at least as large as the deficiency of chloride using sodium as a reference. This may be tested as some coastal stations in West Europe where addition of sodium from soil particles is least likely. In table 5.2 a few coastal stations have been selected and the excess of S and deficiency of Cl calculated and expressed in gramequivalents per ha and year. It is interesting to note that in three places, Bo, Li and Bs, the excess of sulfur is far greater than the deficiency of chloride. In one place, Rjupnahed in Iceland, there is practically no deficiency of chloride nor any excess of sulfur. In the remaining two, den Heldern in the Netherlands and Lerwick on Shetland, the deficiency of chloride is somewhat greater than the excess of sulfur. One should, however, include also nitrate nitrogen in this calculation as this can be added as an acid and will behave like sulfuric acid in the replacement of chloride. This will increase the excess of replacing anion by 298 g.equiv. in den Heldern and by 77 in Lerwick.

TABLE 5.2

Yearly excess sulfur and deficiency of chloride at a few coastal stations for 1958

Station	g. equivalents per ha	
	S	Cl
Bornö (Bo), Sweden	186	43
Lista (L), Norway	586	175
Rjupnahed (Rj), Iceland	3	0
Den Heldern (DN), Netherlands	476	627
Borris (Br), Denmark	645	167
Lerwick (Lw), Shetland	509	862

5. *Other possible reactions*

There are some reactions involving nitric oxide and chlorine which should be mentioned as they have been suggested recently as a process for the release of chloride from sea salt particles. Nitrosyl chloride, NOCl, can form from chlorine and nitric oxide by the reaction

$$Cl_2\,(g) + 2NO\,(g) \rightarrow 2NOCl\,(g) \qquad (5.8)$$

From thermodynamic data (see LATIMER 1953 p. 91) one can compute the free energy of reaction to -9.72 kcal × mole^{-1}. Thus, the equilibrium constant becomes $10^{7.22}$ so

$$P_{NOCl} = 10^{3.61} \cdot P_{NO} \sqrt{P_{Cl_2}} \qquad (5.9)$$

In the atmosphere P_{NO} is of the order 10^{-9} atm. Chlorine on the other hand must be extremely low in the presence of free hydrogen and light and could hardly exceed 10^{-10} atm. This means that P_{NOCl} should be less than 10^{-10} atmospheres, thus more than two orders of magnitude less than the gaseous chloride present in the atmosphere. In presence of water it hydrolysis rapidly forming HNO_2 and HCl. The reaction rate has been studied by ASHMORE & CHANMUGAN (1953 a and b).

It has been found, however, that solid NaCl can react with nitric-acid to form sodium nitrate, nitrosyl chloride, chlorine and water (NIKONOVA & EPSHTEIN 1952). This reaction has been studied also by ROBBINS et al. (1959) who found it to be of negligible importance in the atmosphere. They, however, suggested that nitric acid released HCl just as H_2SO_4 does.

6. *Conclusions*

Of all the possibilities discussed here the simplest process, namely release of HCl from sea salt particles by absorption of SO_3 or H_2SO_4 from the air, seems to account for the deviation in the composition of sea salt particles from the composition of sea water. But unless the HCl released is separated from the particles in space no effect will be seen on rainwater composition. These aspects will be discussed in another section.

VI. Deposition by gravitational fallout, impingement and gaseous absorption

The total deposition over land is the amount in precipitation plus the deposition of particulate matter by fallout and impingement and absorption of gaseous compounds by soil and vegetation. As to the rate of fallout over the sea this was computed from available data to average about 0.7 cm · sec^{-1}. Considering the great role played by the large, shortlived sea salt particles in the fallout the rate of fallout over land must be considerably slower. It is possible, however, that impingement on vegetation becomes much more important, and naturally this can also be expressed as a velocity times the concentration.

For gaseous components the vertical transport velocity over the sea was estimated from the rate of evaporation to be around 1 cm · sec^{-1}. Considering conditions in a few meters of air above the ground level we may expect this vertical transport velocity to be much larger over land due to the roughness of the ground which certainly increases the turbulent character of air motion.

In the following these two processes, dry deposition of particulate matter and gaseous absorption will be considered in some detail.

1. *Dry deposition of particulate matter*

It is possible from available data on the composition of Swedish and Finnish air and precipitation published quarterly in Tellus and on the run-off of chloride in river waters as presented by ERIKSSON (1955 a) to compute the deposition velocity for chloride in Sweden. For this purpose the years 1955 to 1957 were chosen. Average yearly amounts of chloride in precipitation were computed and the result corrected to normal precipitation as estimated by a precipitation map worked out by BERGSTEN (1954). The reason for this correction is that the measured precipitation in the equipments used for precipitation sampling in the chemical network is always less than those measured by standard rain gauges. The chemical sampling funnel is unfavourably exposed to winds so that the efficiency at light rainfall and especially during snowfall is rather low. Yearly figures may be as much as half the officially reported values for the north of Sweden while differences are smaller further south where snowfall is less abundant. It also varies from station to station depending upon the local exposure of the chemical sampling equipments to winds.

Similar considerations have also been applied to Norwegian, Finnish and Danish data. For Norwegian and Finnish stations all values have been increased by 25 per cent while Danish values are increased by only 15 per cent. The resulting distribution of yearly chloride amounts in precipitation over Scandinavia is shown in the map in fig. 6.1.

As to Scandinavian air data the monthly average of chloride in air at the different stations were used with the following exceptions (Station symbols refer to the symbols used when publishing data. Their name and location is recently described by FONSELIUS, 1958).

a. *Ki.* 1957 data discarded because chloride concentrations are nearly two orders of magnitude higher than normal apparently due to contamination by $CaCl_2$.

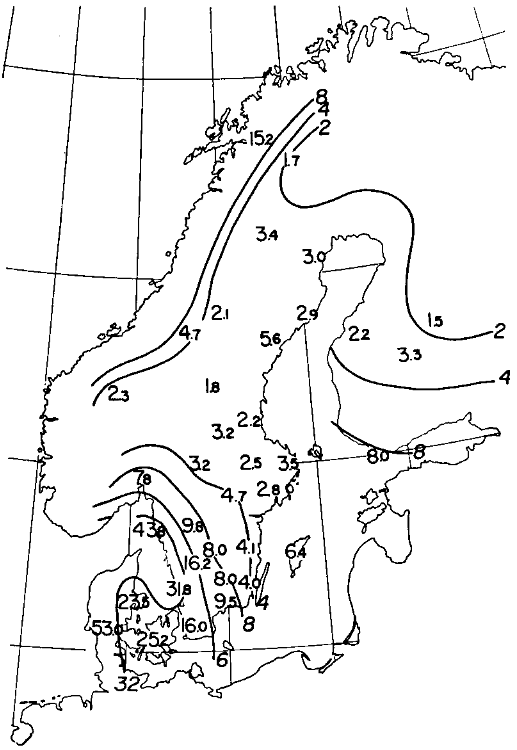

Fig. 6.1. Chloride in precipitation over Scandinavia in kg · ha^{-1} · $year^{-1}$. Average for 1955 to 1957 (3 years).

b. *Of.* Jan. 1956 excluded, far above normal with Cl/Na = 29.1.

c. *Fa.* July 1957 excluded. Conc. of Cl = 86 μg · m^{-3} and Cl/Na = 143.

d. *Fl.* July 1957 excluded for similar reasons.

e. *Vå.* Sept. 1957 excluded as excessive Cl and Ca suggests contamination by $CaCl_2$.

f. *Ka*, *Ku*, *Jy*, and *Tv*. Only 1955 values used. In 1956 and 1957 some extremely high Cl-values.

Normally some months may be missing during a year for various reasons. The averages are therefore simply computed from the remaining monthly averages.

The computed averages are found on the map in fig. 6.2 which shows about the same geographical pattern as chloride in precipitation.

From the map on the distribution of yearly run-off of chloride shown by Eriksson (1955 a) the run-off at the Swedish and Finnish stations that carry out air sampling was estimated. By subtraction of chloride in precipitation from the run-off chloride the amounts of dry deposited chloride were computed and from these and the average concentrations in air the deposition velocities expressed in cm · sec^{-1}. These are entered on the map in fig. 6.3.

The computations are thus made on the tacit assumption that no dry deposition occurs into the sampling funnels. This may not be entirely true as large salt particles, especially during night-time when there is no wind have a fair chance of being collected by the funnels. These large particles may be to a large extent, especially in places remote from the sea, a result of coalescence of cloud droplets and evaporation as discussed in section III. The dry deposition looked for here is therefore mainly due to the impingement of smaller salt particles upon vegetation. The effectiveness of this impingement depends on the size distribution as the efficiency of the process decreases strongly for smaller particles.

The deposition velocities on the map are naturally to be compared to the average

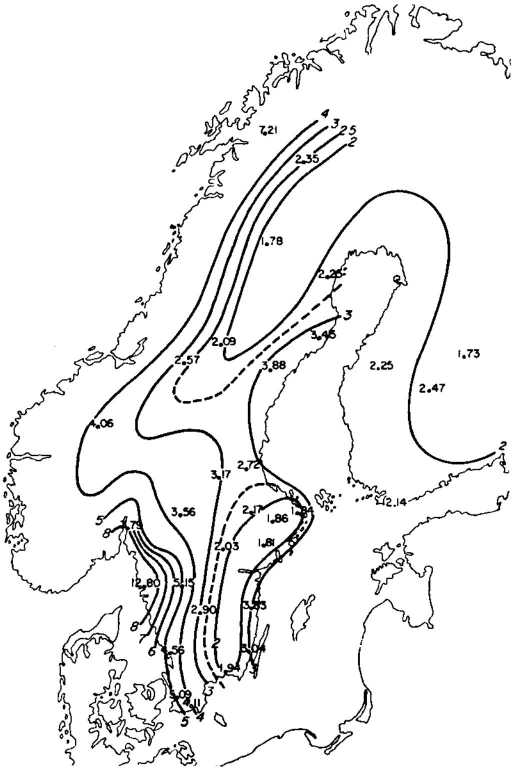

Fig. 6.2. Chloride concentration in surface air in Scandinavia except Denmark. In μg · m^{-3}. Average for 1955 to 1957 (3 years).

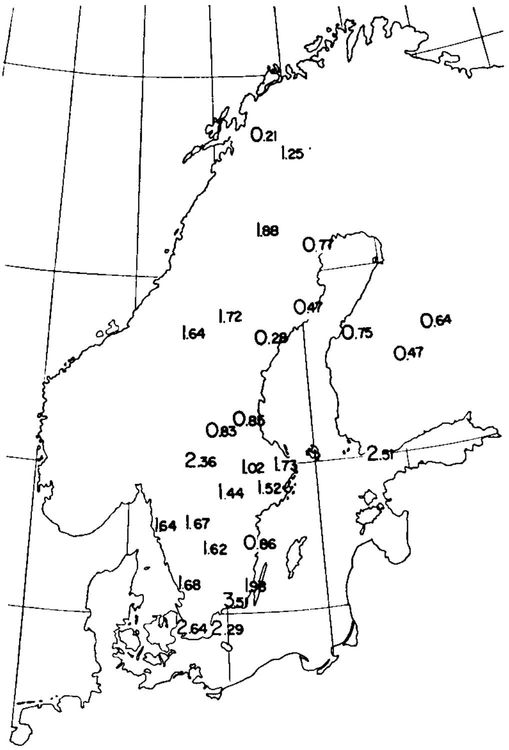

Fig. 6.3. Deposition velocities in cm · sec^{-1} for chloride. Computed from chloride in precipitation, in river water and in air.

deposition velocity for sea salt particles over the sea, computed to be on an average 0.7 cm · sec^{-1}. If the large end of the particle spectrum is removed at an earlier state one can expect to find values lower than 0.7 cm · sec^{-1} over land. On the other hand over forested region not too far from the sea one can expect to find higher values due to the effectiveness of vegetation for the impingement process.

The data in fig. 6.3 seem to confirm by and large the conclusions drawn above. The very low value at Riksgränsen in the far north of Sweden may be due partly to a too low estimate of river run-off chloride but partly on the absence of forest vegetation and the long lasting snow cover which smoothes the ground considerably. The other low values for the north of Sweden are close to the coast of the Bothnian Sea, and are, furthermore, situated in coastal plains, largely deforested. On the other hand, the other places in the north which have high deposition velocities are all situated in densely forested regions where the conditions for impingement to take place are favourable and where the distance to the source of the air, the Norwegian Sea, is not too great.

In the middle part of Sweden the influence from the North Sea is well known and shows up in the deposition velocities which, even on deforested areas are appreciable.

As to Finland the values are on the whole somewhat lower and comparable to the deposition velocity over sea. As Finland can be regarded as a continental area with respect to the sea this salt transportation is of considerable interest. Similar values can be expected also further inland.

In order to be able to use deposition velocities for estimation of dry fallout of salt one has to know the concentration of salt in the air near the ground. This is known so far only in the West-European chemical network. As it is of interest to get an idea about the dry fallout or total fallout, in areas where precipitated amounts are known, like the USA, some other way may be explored empirically. As it happens there seems to be a strong correlation between river-run-off chloride and chloride brought down by precipitation. The ratios of chloride in precipitation to chloride in river-run-off have been computed for Sweden and Finland and are entered on the map in fig. 6.4. It is seen that, on the whole, they are remarkably constant varying closely around 0.30 (average 0.316). Larger deviations occur in places where the river-run-off has been difficult to estimate as on water divides or at the coasts. There are no systematic deviations depending upon geographical location. It looks from these data as if precipitation chloride as a rule constitutes one third of the total amount delivered to the ground. Multiplying rain-water chloride amounts by three can therefore be expected to give a fair estimate of the total amount brought to the ground.

The question now is open whether this "rule of the thumb" can be applied to other elements in particulate form. It can be applied to other non-volatile oceanic elements provided they are of oceanic origin and no doubt this is largely true for sodium. But in the case of potassium and calcium some caution is necessary because the size distribution of particles of land origin containing these may be quite

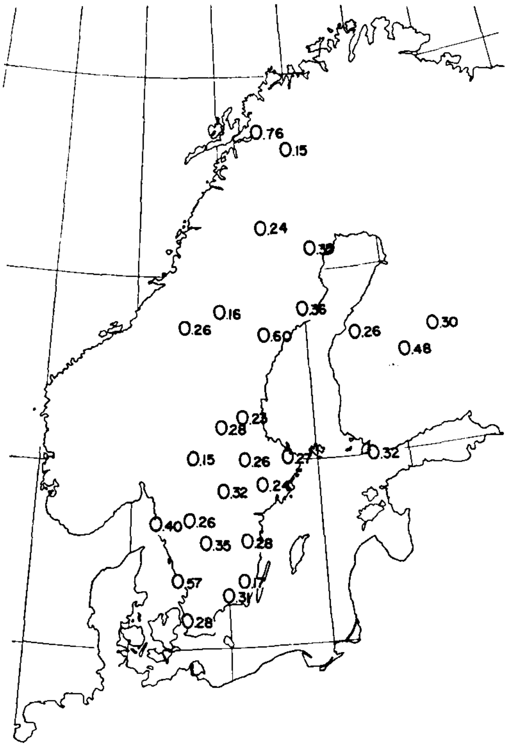

Fig. 6.4. Ratios chloride in precipitation to chloride in river run-off over Scandinavia.

different from sea salt particles, thus showing differences in efficiency of the impingement process which to a great extent is responsible for the dry deposition. However, the percentage removed from air by precipitation of the total amount removed cannot differ too much from that of chloride particles if these soil particles have travelled long distances. It may be somewhat greater because the hygroscopic sea salt particles are steadily growing by coalescence which favours dry deposition. As a conservative estimate one may assume, for the sake of computational purposes, that the total fallout of these particles is twice that found in precipitation. This is low also for another reason. Mineral particles containing potassium, calcium and magnesium are certainly attacked by sulphur compounds in the atmosphere and made partly soluble. But in rainwater a residue of insoluble particles will escape detection, at least in the procedures used in the West-European network. In the early Swedish network described by **Egnér** et al. (1947) precipitation was filtered through ion exchangers which through their strong dissolving action probably dissolved all mineral particles except quartz. The yearly calcium values reported by **Emanuelson** et al. (1954) from this network are as a rule higher than present day figures by a factor of about two.

As to sulphur in precipitation conditions are somewhat different. In the atmosphere it can exist both as SO_2 in gaseous form and as sulphate in particulate form. Liquid water in a cloud contains practically all the sulphate sulphur and some of dissolved SO_2. As to chloride all particulate chloride is included and probably all gaseous chloride (as HCl or H_4NCl) existing earlier in gaseous form. On the other hand there is proportionally much more sulphur in the gaseous phase than chloride, most of the chloride being found in particulate matter. Therefore one can expect chloride and sulphur to be removed by precipitation in their proportions in particulate matter. But precipitation also contains freshly dissolved SO_2 so the "rule of the thumb" cannot be applied immediately to the deposition of sulphur. The total deposition of sulphate sulphur is therefore probably not much greater than sulphur in precipitation. This sulphate sulphur does, however, not necessarily appear in river run-off. It is also likely that this deposition is not the total deposition of sulphur. Gaseous absorption by soil and vegetation has to be considered.

2. *Absorption of gaseous compounds*

In the case of gases that are absorbed by soil and vegetation the concept of a vertical transport velocity discussed in section II can be rigorously applied and data computed on this velocity are therefore a physical interpretation of the effect of turbulent diffusion. It was derived earlier that over the sea a probable value of this transport velocity is around 1 cm · sec^{-1}, while over land, especially vegetation covered areas, it must be much larger. In experiments with radioactive iodine **Chamberlain & Chadwick** (1953) computed a deposition velocity, which is equivalent to the vertical transport velocity defined here, of about 2 cm · sec^{-1} over pasture vegetation. These experiments and other pertinent data have recently been discussed by **Bolin** (1959).

As to sulphur dioxide, the main sulphur constituent in the atmosphere, it has been

TABLE 6.1

Sulphur content of air in $\mu g \cdot m^{-3}$	Sulphur added by precip. $kg \cdot ha^{-1}$	Added from the air $kg \cdot ha^{-1}$	Vertical transport velocity $cm \cdot sec^{-1}$
78	38	260	1.05
45	20	100	.70
43	12	74	.54
23	12	24	.33
12	7	10	.26
10	4	7	.22

shown experimentally that it is readily absorbed by plants which utilize the absorbed sulphur in their green parts (for a short review see JOHANSSON 1959). In a very interesting and penetrating work by JOHANSSON (l.c.) the absorption of sulphur from the air by soils and vegetation has been studied quantitatively. From his data it is possible to compute vertical transport velocities with the a priori assumption that the absorption is so rapid that the laminar boundary layer is the real bottleneck for transfer into the soil and into plant leaves.

JOHANSSON worked with pot experiments at different distances in the downwind direction from an industrial plant that produced sizeable amounts of sulphur emitted into the atmosphere. In one series of experiments pots filled with a soil low in sulphur and with no vegetation were exposed in the open at various distances. Simultaneously the average sulphur concentration in air was measured as well as sulphur brought down by precipitation. Water drained from the pots was collected and analysed, and after 6 years the soils in the pots were analysed for sulphur. From these data he was able to make a balance computation for sulphur and thus compute the direct contribution from the atmosphere. The following data, all referring to yearly amounts in $kg \cdot ha^{-1}$, were obtained (see table 6.1).

As the soil was bare dry deposition of particulate sulphur can hardly have occurred by impingement and if it has occurred due to purely gravitational fallout it is certainly accounted for in the precipitation. We may therefore compute the vertical transport velocities from the amounts delivered from the air and regard this as absorption by the soil of SO_2 from the air. These velocities are also entered in the table. We note that these velocities are not constant, they are highest for the highest air concentrations decreasing regularly with the air concentrations. This does not seem to confirm the assumptions made and it is quite possible that the rate of absorption by the soil is not so fast that the concentration at the soil particles surfaces can be regarded as zero which is actually the assumption made for this computation. However, the relation between concentration and amount absorbed is not linear either, which it should be under such circumstances. This indicates that there are processes in the soil that release sulphur in volatile form, which is not impossible. If the amounts released by presumably metabolical processes involving micro-organisms were added, a much higher transport velocity should be arrived at for lower air concentrations. It can be expected that such a release is a fairly constant quantity except under conditions where hardly anything is added. The first three set of data would give a practically constant velocity if air concentrations minus 25 were used in the computations. This means that under this assumption the transport velocity should be about 1.5 $cm \cdot sec^{-1}$ and that the rate of release should amount to about 110 $kg \cdot ha^{-1} \cdot year^{-1}$. This is more than delivered by precipitation. For those pots which obtained much less proportionally less should be released.

This reasoning may seem highly hypothetical but more evidence favouring the hypothesis of a continuous process of sulphur turnover and release, presumably as H_2S, in soil will be presented.

JOHANSSON also made experiments with pots where the soil was planted with different kinds of vegetation trying in the same way to assess the amount of sulphur absorbed by the plants directly. This experiment was done at a place remote from the source of sulphur with a normal sulphur content of air. The experiments were further made with varying applications of phosphate and sulphur to the pots in order to study the effect of phosphorus on the uptake of sulphur. The experiment run for five years during which the pots were exposed to the atmosphere only in growing seasons (average 155 days per year). The results are of such general interest that they are reproduced nearly to full extent in table 6.2. As seen in the table a positive balance is obtained with small additions of sulphur to the

TABLE 6.2

p [in part from JOHANSSON (1959)]

Sulphur balance in a five year pot experiment. Amounts in g per pot for the whole period. Surface area of pot 31.4 cm^2. Air concentration of sulphur 6 $\mu g \cdot m^{-3}$

Phosphorus supply	Original sulphur supply	Sulphur added with precip.	Sulphur added as fertilizer	Balance from air or loss	Computed vertical transport velocity $cm \cdot sec^{-1}$
without phosphorus	.29	.03	.00	+ .34	2.64
	.29	.03	.20	+ .21	1.63
	.29	.03	1.00	— .59	—
	.29	.03	5.00	— 2.54	—
	.29	.03	25.00	— 2.07	
normal phosphorus supply	.29	.03	.00	+ .38	2.95
	.29	.03	.20	+ .44	3.42
	.29	.03	1.00	+ .31	2.41
	.29	.03	5.00	— 1.45	—
	.29	.03	25.00	— 1.39	—
very high phosphorus supply. ..	.29	.03	.00	+ 0.50	3.88
	.29	.03	.20	+ 0.49	3.80
	.29	.03	1.00	+ 0.26	2.02
	.29	.03	5.00	— 1.36	—
	.29	.03	25.00	— 0.85	—

soil as fertilizer. This indicates absorption from the air of sulphur. The presence of negative values was attributed by Johansson by uncontrolled leaching, i.e. loss of drainage water by overflow so that an amount of sulphur, not accountable for by leaching, caused the negative values. It is indeed hard to see how this uncontrolled leaching can be influenced by the phosphorus application especially as the final sulphur in the soil is practically the same for the same application of sulphur, independent upon phosphorus supply. It seems more likely to assume losses of sulphur as H_2S from the pots, due to microbiological turnover of organic matter. The more plants can take up, due to a better phosphorus supply, the smaller can this loss from the soil be assumed to be because plants and micro-organisms are competing for the sulphur. This view point seems to be more in line with the results obtained. The vertical transport velocities are, as seen, high for those pots that have not received any extra sulphur in the soil and especially in the case a good phosphorus supply is present. It must be remarked, however, that the values obtained are not directly *comparable to those* applicable to field conditions because of a greater exposure of these plants to moving air when grown in pots. The difference may not be great, however, and a quite likely figure is 2 $cm \cdot sec^{-1}$.

The results thus show that a substantial absorption of sulphur in the air by plants can take place, expressable by use of a vertical transport velocity times the concentration in the air. But the results also indicate that a release of sulphur can take place from the soil, presumably through microbiological activity in which H_2S, which is very volatile, is formed and escapes. Finally, the results indicate that there is a state in which an equal amount of sulphur is absorbed by plants and released from soil. This state of affairs is strongly indicated in Sweden when comparing the amounts of sulphur brought down by precipitation to the amounts in river run-off. Using ERIKSSON'S (1929) data on the composition of Swedish river water and VIRO'S (1953) on the composition of Finnish river water a map showing the distribution of run-off of sulphur can be constructed in the same way as done for chloride by ERIKSSON (1955a). Isolines can also be drawn, though with a substantial amount of smoothing, and from the map run-off of sulphur at the sampling stations for air and precipitation can be read off. Using

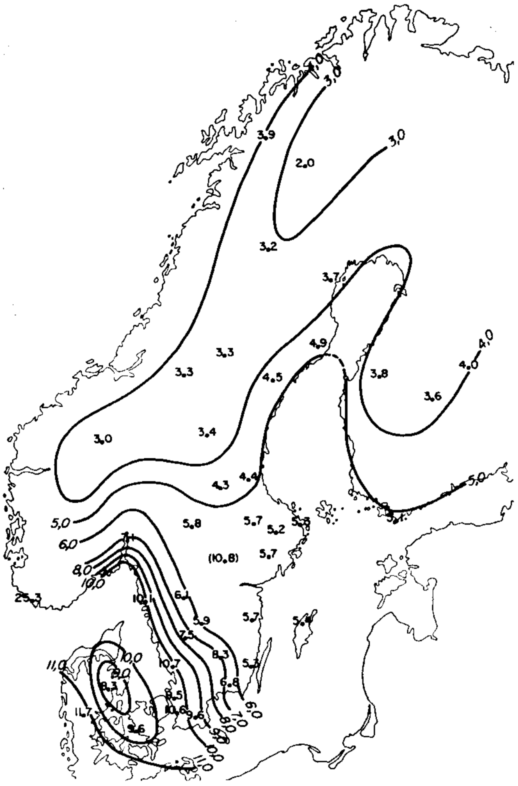

Fig. 6.5. Sulphur in precipitation over Scandinavia in kg · ha^{-1} · year^{-1}. Average for 1955 to 1957 (3 years).

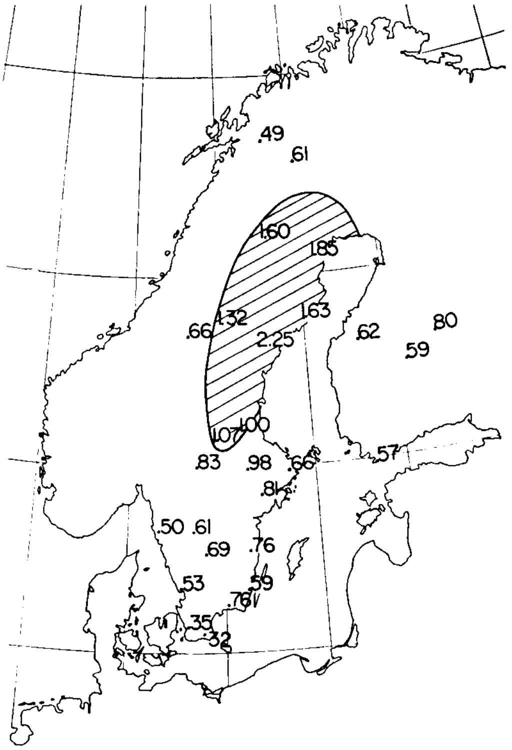

Fig. 6.6. Ratios sulphur in precipitation to sulphur in river run-off over Scandinavia.

the average yearly sulphur in normal precipitation for the period 1955—1957 (three years) shown in fig. 6.5 the ratio sulphur in precipitation to sulphur in river water can be computed and is shown in fig. 6.6.

A remarkable feature in this figure is the area in the north of Sweden where run-off of sulphur is apparently lower than sulphur in precipitation and in the remaining area run-off sulphur rarely exceeds precipitation sulphur by a factor of two. The sulphur concentrations in the air in this area varies between 1.5 and 8 $\mu g \cdot m^{-3}$, and with a vertical transport velocity of 2 cm · sec^{-1} already the lowest concentration would give much more than in rainfall. It seems likely that all these features are due to the biological turnover of sulphur in soil in which H_2S is involved, escaping largely into the atmosphere. It looks as if this turnover is such as to balance the absorbed SO_2 from the air by a release of H_2S into the air. Leaching and run-off are mainly those parts which are balanced by precipitation.

The question about the absorption rate of plants for atmospheric SO_2 is yet not solved satisfactorily. Probably use of radioactive sulphur can solve it properly. As to the vertical transport rates it looks as if 2 cm · sec^{-1} is not an unreasonable figure for gaseous components over land.

VII. Deposition of chloride and sulphur over the continents

Though our knowledge on the chloride and sulphur in precipitation is rather incomplete, it is still possible to get some idea on the geographical distribution on the total deposition. One can use the distribution of precipitated chloride in areas where it has been extensively studied and correlate the results with prevailing winds and topography to infer transports into regions where no data exist. The total deposition is, however, certainly greater than that carried down by precipitation and to estimate this one can use the "rule of the thumb" discussed in section VI, i.e.

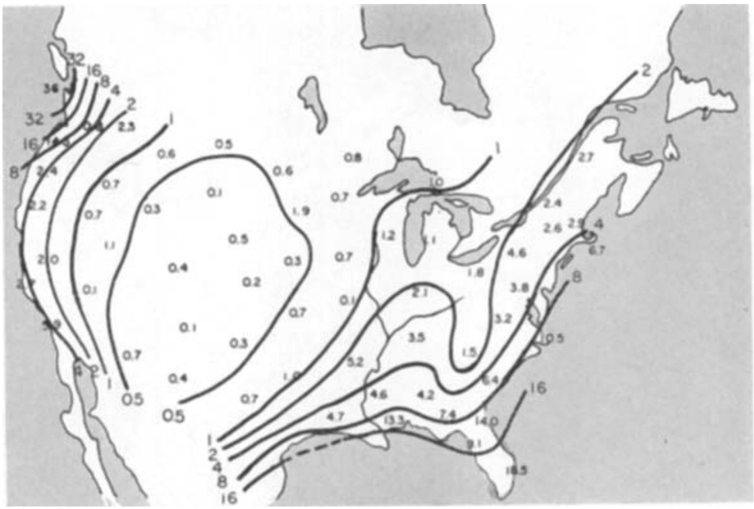

Fig. 7.1. Chloride in precipitation over the USA inkg · · ha^{-1} · year^{-1}. Computed from rainfall data and data on the average concentration of chloride in precipitation by Junge & Werby (1958).

multiplying the chloride in precipitation by a factor of three. This will apparently give a fair idea about the total deposition of this element. As to sulphur it seems likely from previous discussions that the net sulphur deposition is roughly that carried down by precipitation.

1. *Chloride*

Two areas are up to the present fairly well investigated with respect to chloride in precipitation, namely the USA where Junge (cf. Junge & Werby 1958) made an admirable work in organizing a network of collecting stations and analysing the samples during a whole year, from July 1955 to June 1956, and in Western Europe where a similar network gradually developed through collaboration of a number of countries. The original network is described by Egnér & Eriksson (1955) but additions of stations have taken place continuously. At the beginning of the International Geophysical Year a rather complete list of stations was published by Fonselius (1958).

As to Junge's network the sampling technique differed slightly from that of the West-European network insofar that the collecting funnels were kept closed during intervals with no precipitation. This may prevent bigger salt particles, formed in clouds by coalescence processes to fall into the funnels as they may in the West-European net. For that reason the concentrations of chloride, published by Junge may be somewhat too low compared to concentration data in the European network. Nevertheless they can be used to estimate the minimum precipitated chloride. Rainfall data at Junge's sampling stations were obtained from the monthly precipitation charts published by the U.S. Weather Bureau in the Monthly Weather Review. These rainfall data were then used to compute the yearly amounts of precipitated chloride in kg · ha^{-1} using Junge's concentration data. The result is shown in fig. 7.1.

As to the general pattern it is interesting to note the transport of salt along the Mississippi Valley, a transport predicted earlier by Eriksson (1955 a) in his study on the run-off of chloride from the eastern half of the USA. Multiplying the data by three should give the minimum amounts of chloride deposited per year. If these data are compared with the run-off map in Eriksson's paper it is found that the agreement is not too bad. In fact one should perhaps increase the precipitation chloride somewhat more to account for the "dry" precipitation of chloride taking place during dry intervals.

Thus, in the northern central part of the USA, the Great Lakes region, a yearly deposition of 5 kg · ha^{-1} seems reasonable, increasing to about 10 in the central continental part. In the arid areas to the west a yearly deposition of 1—2 kg · ha^{-1} seems reasonable. The high mountains in the west effectively impede the

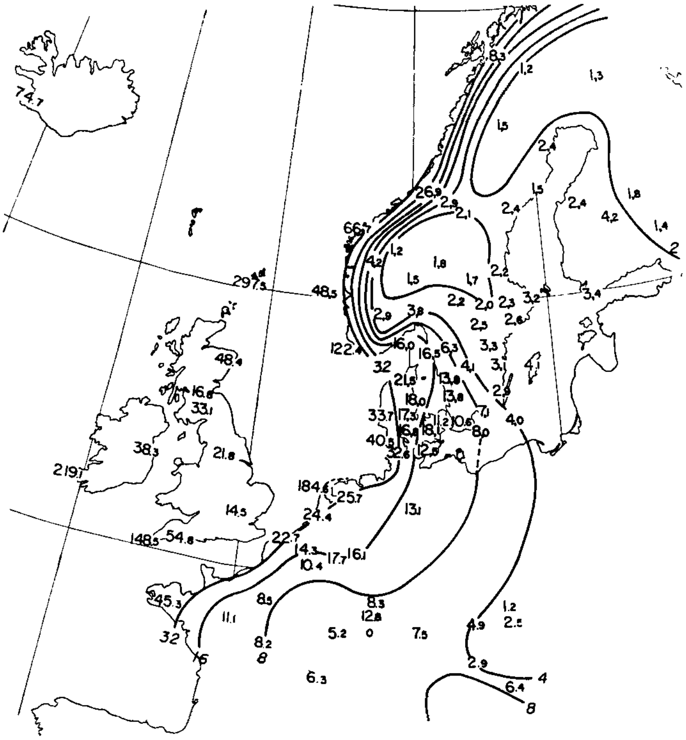

Fig. 7.2. Chloride in precipitation over Europe for 1958 in kg · ha^{-1} · year^{-1}.

transport of both moisture and salt into these areas.

It should be noted that the isochlors are logarithmically spaced so that the decrease inland is exponential. The decrease in the west is fairly rapid due to the topography despite the prevailing westerlies in the north west part. On the east coast the decrease inland is also fairly rapid, perhaps not so much because of the Appalachians as of the prevailing winds. Continental heating in summer naturally causes onshore winds but they do not penetrate deeply in this part where prevailing winds are from west. As to the inflow along the Mississippi this is, of course, a rather typical monsoon effect.

Actually, the distribution of deposited chloride discussed can most probably be expected also in parts of Asia. Thus knowing prevailing winds, quite good forecasts of the distribution of deposited chloride can be made.

For Western Europe the present network makes it possible to construct a similar map for the year 1958. This map is shown in fig. 7.2, and has many interesting features. Again the isochlors are logarithmically spaced and we notice the steep gradient along the Norwegian coast in strong contrast to the gentle gradient further south. South of the Baltic Sea data are regrettably missing. It can be inferred from older data cited by ERIKSSON (1952) that in the interior of Russia south of Moscow about 8 kg · ha^{-1} · year is found in precipitation. From this it seems likely that also the central eastern Europe is fairly uniform with respect to deposited chloride. Recently DUROV & FEDEROVA (1955) averaged 190 analyses from 41 samples collected over the whole of Russia (the European part) and found about 25 kg · ha^{-1} · year. However, half of the sampling stations were situated along shores and mountains at the Black Sea, the Azov Sea, the Arctic Ocean and the Sea of Okhotsk. This may have contributed proportionally too much to the average as the decrease from source regions is exponential. In the southern part in Kharkov, DENISOV & BUGAEV (1955) found about 28 kg · ha^{-1} · year^{-1} in precipitation which, considering the presence of the Black Sea and the low lying area to the north is not excessively high.

Recent studies in Czecho-Slovakia by

Macku, Podzimek & Šramik (1959) show rather high chloride concentrations concordant with appreciable yearly amounts precipitated. It is apparent that the low region south of Norway (Denmark, South of Sweden, the Netherlands and North Germany) allows a considerable salt transport into the continent enhanced by the strong westerly winds frequently sweeping through this opening in the continent.

As to Asia data are extremely scanty. Considering India only one place, Bombay, seems to be represented. India is, however, strongly influenced by a monsoonal flow of moisture and salt laden maritime air under a considerable period of the year.

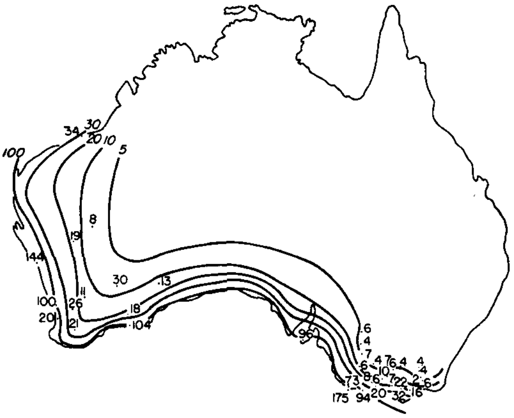

Fig. 7.3. Chloride in precipitation over parts of Australia in kg · ha^{-1} · year^{-1}.

Considering the monsoonal transport into the USA it is likely that India receives ample amounts of chloride, more in the south where the monsoon current is more persistent and with a maximum on the west coast which faces the monsoon current. Some salt is, of course, also transported from the east on occasions.

From the rest of Asia there is one investigation from Frunze in Tien-Shan, south of the Lake Balkash in the north of Kirgizia by Denisov (1956). The amount of chloride precipitated is rather high, 16 kg · ha^{-1} · year^{-1}, mostly from snow. The place is not situated very high and it is possible that salts are carried from the Caspian Sea and the more saline Aral Sea across the low lying region to this place. In the south east a summer monsoonal air flow from the Pacific may have the same influence as the monsoon flow into the USA. River water analyses from Manchuria resemble Finnish river waters much hence 5—10 kg · ha^{-1} · year in total deposition is a likely figure for this part.

In Australia some information on precipitated chloride is available. From older data cited by Eriksson (1952) a rainfall map over Australia and recent data by Hutton and Leslie (1958) for Victoria and by Hingston (1958) for West Australia a map can be constructed showing yearly amounts of chloride in precipitation. This is shown in fig. 7.3. Again the coastal gradient is much less pronounced in the western, low lying region, than in Victoria where a coastal water divide causes a steep gradient. Behind this water shed about 5 kg · ha^{-1} · year^{-1} is precipitated, so the total deposition is probably three times as high.

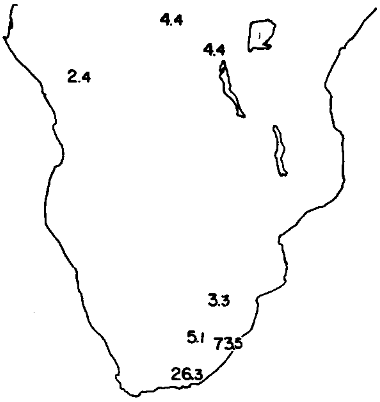

Fig. 7.4. Chloride in precipitation over South Africa in kg · ha^{-1} · year^{-1}.

From Africa only a few data are available. Some of these have been reviewed earlier (Eriksson 1952) but at four places sampling and analyses started recently. Three of these are situated in Belgian Congo[1] and the fourth in Pretoria[2]. Older data are available from Bloemfontein, Durban and Grahamstown. The data in kg · ha^{-1} · year^{-1} are plotted on the map in fig. 7.4. As to Belgian Congo influx

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[1] Samples analysed by Dr. J. Bouquiaux, Institut de Chimie et de Physique, Brussels and reported to WMO Data Centre for the I.G.Y.

[2] I am indebted to Dr. J. F. Nagel of the Weather Bureau, Pretoria for these data.

of moist air takes place mainly in the Gulf of Guinea but inland it is deflected south at least during the southern hemisphere summer. This is reflected in the data where the places in the center of the continent receive more than the western place, which is close to Leopoldville.

The two inland stations in the south receive their moisture and salt from the Indian Ocean.

The uniformity of the inland values is remarkable and suggests that over large parts of the humid parts of Africa about 10—15 $kg \cdot ha^{-1} \cdot year^{-1}$ of chloride is deposited. In the south west where arid regions dominate, from the Orange River up to the Congo River the yearly deposition is certainly much smaller, except on the coast where fog, due to upwelling sea water, carries appreciable amounts of salt across the shore. From investigations by BOSS (1941) the yearly deposition at the coast may be as high as 80 $kg \cdot ha^{-1}$ and about half as much 50 km inland.

In North Africa deposition of chloride must be much less because of the aridity of large areas. Along the coast line of the Mediterranean and the Atlantic normal coastal values can be expected. In Tel-Aviv MENCHIKOWSKY (1924) found 131 $kg \cdot ha^{-1} \cdot year^{-1}$ and $^1/_3$ of this amount further inland.

In South America no investigations have ever been done. Large parts in the north are, however, influenced by easterly winds that carry water vapour over the Amazon area. Part of this air is deflected southwards carrying moisture into Argentine. This air flow can be pictured as a broad monsoon flow which, of course, can penetrate deep into the low lying continent and can be expected to carry and deposit appreciable amounts of chloride in the area.

In the south the coastal mountains to the west effectively block the moisture transport with the westerlies. Some moisture is, however, transported in from the east but on the whole this part of the country is arid with frequent recent salt accumulations which most probably are air borne in origin.

In section IV the cyclic chloride estimated from the run-off of chloride in river waters was about 100 million tons. This does not include coastal deposited chlorides as sampling was seldom done so close to seas. The main part of human pollution chloride is disposed into rivers close to the sea so a value of 90 million tons per year of cyclic chloride seems more likely than the 76 million tons arrived at earlier. With an estimated deposition over humid and arctic areas, 12 and 5 $kg \cdot ha^{-1} \cdot year^{-1}$ respectively the total deposition over drained land areas should be close to 100 million tons, thus close to the estimated run-off. With the present knowledge of the composition of precipitation and river water one cannot expect better agreement.

Within the continental land masses it is possible that smaller circulations of salts between inland lakes and seas and the surroundings take place. BROECKER & WALTON (1958) have recently pointed out that a complete salt balance for such a water mass must take into account loss of salt by spray which may become a very important item in saline lakes. Similar ideas, though without this specific mechanism have been advanced by HUTTON (1958) and BONOYTON (1956) in Australia from considerations on the balance of salts in lakes without apparent run-off. Such conditions cause, of course, a greater deposition of salt than anticipated if the salt originated from the open seas. The high yearly precipitation of chloride in Tien-Shan south of the Lake Balkash, mentioned earlier, may be due to such a intracontinental circulation of salts, the Caspian and Aral Sea being generating areas. The salinity in these waters is lower than in the sea, about 10 per mille but conditions for the evaporation of large droplets are extremely good in this dry climate. It is quite conceivable that these salts in winter are transported eastward and precipitated on the higher parts. This has probably led to a considerable accumulation of salts in the region east of these lakes. It may be interesting to discuss the chloride balance of the Caspian Sea. It receives water by river Volga from an area approximately three times the size of the sea. Assuming an average depth of 500 m and a chloride concentration of 0.5 $g \cdot l^{-1}$ (cf. CLARKE 1924 p. 169) it contains 250.000 $kg \cdot ha^{-1}$ of chloride. Thus, the whole catchment area must have received at least four times less, i.e. about 60,000 $kg \cdot ha^{-1}$ during the last 20,000 years, the approximate length of time since the Caspian Sea was a fresh water lake draining to the sea. The average deposition thus becomes 3 $kg \cdot ha^{-1} \cdot year^{-1}$, a minimum figure.

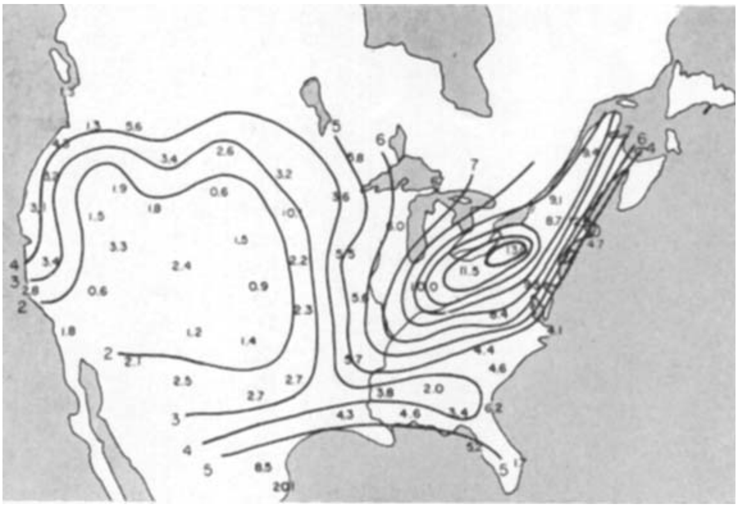

Fig. 7.5. Excess sulphur in precipitation over the USA in kg · ha^{-1} · year^{-1}. As to origin of data cf. fig. 7.1.

Considering the conditions in this part of Russia a yearly deposition of at least three times this figure is more likely, the main part of the salt being delivered by the Black Sea. This leaves quite a good space for losses of salt, presumably through spray to the atmosphere, precipitated to the east of this area.

This loss of salt to the atmosphere can be estimated in another way. Taking the rate of production of bubbles to be the same as over the open sea this is roughly ten times greater than the transport into continents, thus amounting to about 30 kg · ha^{-1} · year^{-1} of chloride. Due to lower salinity a third of this can be expected over the Caspian Sea of which quite a large part could be carried ashore in the air.

Looking at it from another angle the Black Sea produces the salts that are precipitated in the catchment area of the Caspian Sea which after receiving them releases them again so that they are carried by the air further east.

2. *Sulphur*

As to sulphur the Scandinavian data indicates that roughly the same amount is drained of the land as is received in precipitation. Further, the sulphur in precipitation originates only to a smaller extent from sea salt particles. In the discussion on the yearly circulation a "residual" sulphur was computed amounting to about 40 million tons per year. This was supposed to originate from the sea released in gaseous form. In order to compare this amount with the "excess" sulphur in precipitation—the excess being the part left after subtraction of sea salt particle sulphur—available data over the sulphur in precipitation will be reviewed. As to continents where very little information exists inferences about the sulphur deposition will be drawn in the same way as for chloride.

From JUNGE's data on the sulphur concentration in the precipitation over the USA a map of the yearly amounts of excess sulphur has been prepared in the same way as for chloride. This map is shown in fig. 7.5 where isolines have been drawn. The pattern is rather striking. Firstly one notices the maximum in the north-east situated in the most populous and industrialized area. This area also influences the surrounding states quite clearly, especially in the downwind direction. Another feature is a weak coastal gradient which is indicative for the origin of the excess sulphur. JUNGE & WERBY (l.c.) concluded from their map on the concentration of sulphate in the precipitation that the sulphur originated in the soil but this is hardly borne out by fig. 7.5. The concentration is not a good indicator because it is strongly dependent upon the amount of water vapour present in the air, subject to condensation.

From the map one can conclude that in more humid areas about 4 kg · ha^{-1} · year^{-1} of sulphur is precipitated while in arid and desert regions the yearly precipitation varies from 1 to 2 kg · ha^{-1} · year^{-1}.

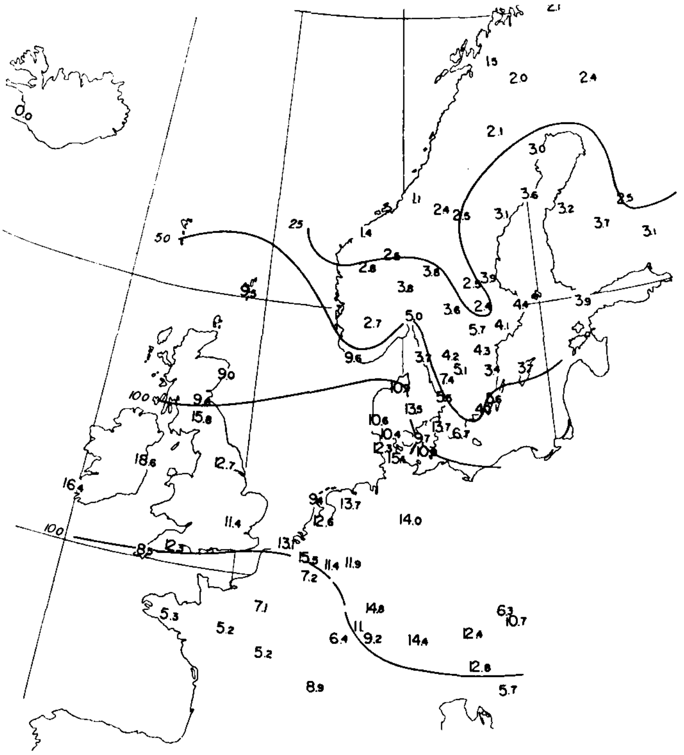

Fig. 7.6. Excess sulphur in precipitation over Europe in 1958 in kg · ha^{-1} · year^{-1}.

The figure for the humid but unpolluted places agrees well with those reviewed by Eriksson (1952). Investigations in Alabama gave yearly rates of addition varying from 3.2 to 6.8 kg · ha^{-1} except in the town Birmingham where the amount rose to 34.2 kg · ha^{-1} · · year^{-1}. Oklahoma showed values from 6.5 to 10.8 kg · ha^{-1} · year^{-1} while Texas ranged from 4.6 to 17.4, but were mostly around 11 kg · ha^{-1} · year^{-1}. These were results of several years of investigation of total sulphur. They seem to fit quite well into the pattern in fig. 7.5. These states are practically free from industrial pollution of sulphur as can be seen from a series of 16 years in Stillwater, Oklahoma, compared to a 8 year series from Ithaca, New York (cf. Eriksson l.c. p. 283).

The network in Western Europe gives quite a good picture of the excess sulphur in precipitation for 1958 shown in fig. 7.6. Most striking is the large excess in the south west of Ireland and England. An addition occurs, of course, over England from the industrial centers but they alone could hardly affect the North Sea stations on the Shetland Isles and Lista in Norway. It looks from the map as if the whole North Sea was a source region for this sulphur and that it is very hard to distinguish the industrial source from the marine source. A southern border to these high figures is found in the south where the French stations give much lower values. The high values persist in practically the whole north west continental part of Europe but decrease rapidly northward in Scandinavia.

Some data from Eriksson's review may be interesting to cite for comparison. In England the station Rothamsted (just north of London) gave 7.9 kg · ha^{-1} · year^{-1} as an average for 1881/82 to 1886/87 or about 7 kg · ha^{-1} · year^{-1} as excess sulphur while the figure for 1958 is 11.4 kg · ha^{-1} · year^{-1}. The increase may be attributed to industrial pollution but even so the pre-industrial figure is appreciable. Another interesting comparison can be made near Leeds. In 1907/08 the excess sulphur in Garforth just outside Leeds was 9.2 kg · ha^{-1} · year^{-1} while in 1958 it was 12.7 kg · ha^{-1} · year^{-1}. It is unfortunate that no more comparisons can be done in Europe.

Some old and new data from Russia are of interest. Older values (1909/10) in rural areas of

Russia range from 2.0 to 3.6 kg · ha^{-1} · year^{-1} excess sulphur while urban areas like Leningrad were high. DUROV & FEDOROVA (1955) found as an average of 190 analyses from 41 different places in Russia 2.8 mg · l^{-1} excess sulphur (computed by using Cl as reference for correction) which with an average rainfall of around 500 mm gives 14 kg · ha^{-1} · year^{-1}. Again, this may be due to the fact that a number of stations were situated along the Black Sea in the south. DENISOV & BUGAEV (1955) found in the northeastern part of the Ukraine about 26 kg · ha^{-1} · year of "excess" sulphur as an average for three years. This is fairly close to the Black Sea which no doubt is an important source for sulphur in the atmosphere, considering the peculiar hydrogen sulphide content of its deeper water. The older data are all from the central part of Russia.

The data from Europe may thus seem confusing but can be summarized as follows. There is a definite latitudinal variation showing up in the Scandinavian and the older Russian data. The yearly deposition of excess sulphur by precipitation in this northerly zone is around 3 kg · ha^{-1} · year^{-1}. Further south it is appreciably higher, about 10 kg · ha^{-1} · year^{-1} or more but seems to decrease again further south, judging from the French values and the Yugoslavian station in Zagreb. It is possible that the Mediterranean region receives about 6 kg · ha^{-1} · year^{-1} of excess sulphur of which none is industrial. In Russia high values around the Black Sea are conceivable.

Of other available data from other parts of the world one from New Zealand (cf. ERIKSSON 1952) shows 3.7 kg · ha^{-1} · year^{-1} as excess sulphur. Recent data from South Africa are of great significance also for the southern hemisphere. In the central part, i.e. eastern Belgian Congo the deposition in 1958 at two stations was 4.7 and 7.5 kg · ha^{-1} · year^{-1} with a lower figure, 2.6, for Leopoldville in the west and somewhat drier part. In Pretoria in the south the precipitation brought down 7.0 kg · ha^{-1} · · year^{-1}.

Some determinations of sulphur in precipitation were also made in Australia though the accuracy of the method used does not seem to be very high. The low data reported by HUTTON and LESLIE (1958) at three coastal stations do not give any excess sulphur from the sea, and they conclude that the total precipitated sulphur in Victoria is less than 2 lbs/acre (~ 2 kg · ha^{-1}). HINGSTON (1958), however, has some more data on the concentration of sulphate in precipitation in Western Australia. Using his data one computes excess sulphur varying between 1.3 and 6.9 kg · ha^{-1} · · year^{-1}, the highest values again found at the coast in Perth. Thus it looks as if also here there is a definite excess precipitated amounting to about 2 kg · ha^{-1} · year^{-1}. This is interesting in view of ANDERSON'S (1945) data on the composition of coastal river and lake waters where always a deficit of sulphur, relative to chloride in sea water, is found. This deficit is, however, always accompanied by a deficit in calcium and sometimes magnesium and an alkaline reaction indicating a far reaching reduction of the sulphate brought down by precipitation followed by an increase in pH and consequently a precipitation of calcium and magnesium carbonates.

Comparing all these data on the yearly precipitation of excess sulphur one gets the impression that the southern hemisphere is somewhat poorer in excess sulphur than the northern hemisphere. The higher values for the northern hemisphere are probably due to a much more active industrial pollution or, in other words, combustion of fossil fuels. However, accepting CONWAY'S (1942b) hypothesis about the origin of the excess sulphur the northern hemisphere has also by far the largest shelf areas. The excess sulphur has quite a long residence time in the atmosphere if it has to pass through the SO_2 stage which is strongly indicated as discussed earlier. It is quite obvious that more information on the concentration of SO_2 in the atmosphere on a global scale is needed and could possibly become of great meteorological importance.

Concluding this survey it seems as if continental humid areas receive at least 4 kg · ha^{-1} · · year^{-1} of sulphur which cannot be accounted for by either combustion of coal or sea salt production. Drier areas receive less, maybe around 2 kg · ha^{-1} · year^{-1}. These amounts are, however, large enough to account for the "residual" sulphur in river run-off, discussed in section IV.

Returning for a moment to the pattern in fig. 7.6 on the distribution of excess sulphur in Europe, conditions around the British Isles deserve further attention. In 1958 a few more

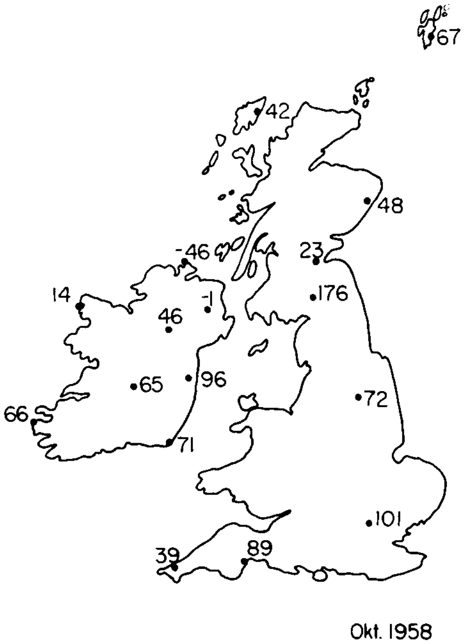

Fig. 7.7. Excess sulphur in precipitation over the British Isles for Oct. 1958 in mg · m^{-2}.

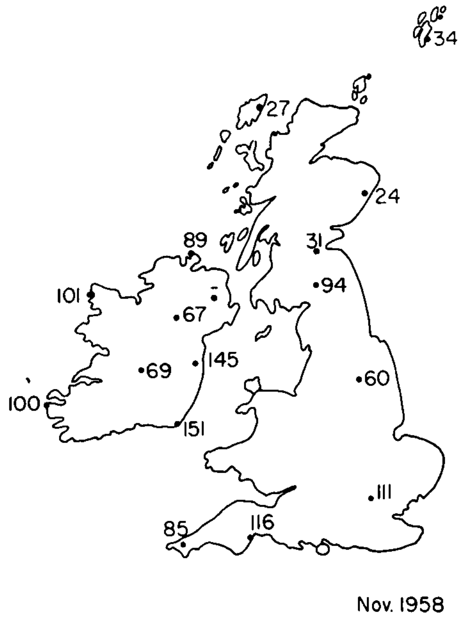

Fig. 7.8. Same as fig. 7.7 for Nov. 1958.

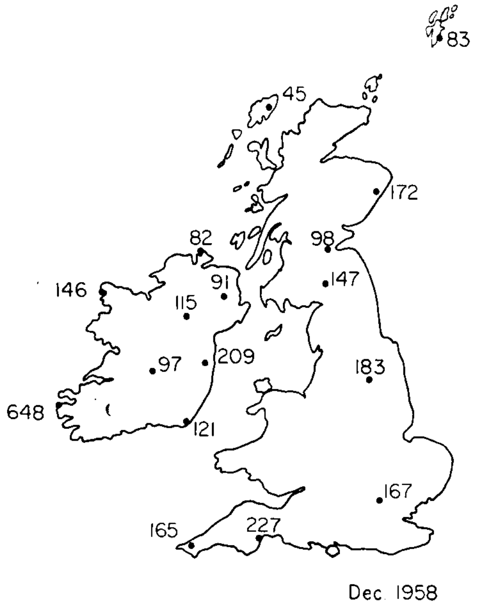

Fig. 7.9. Same as fig. 7.7 for Dec. 1958.

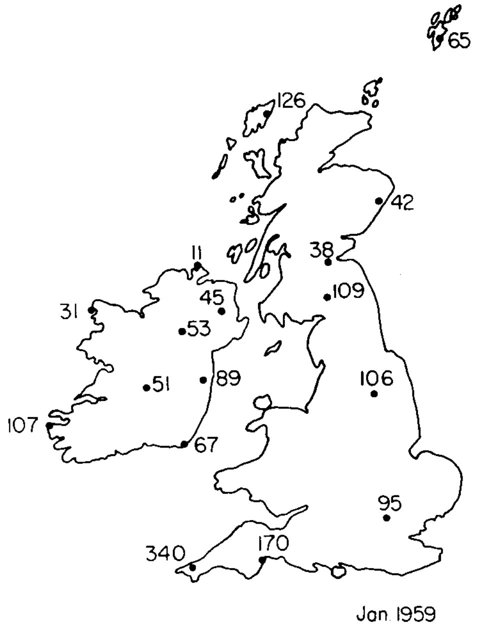

Fig. 7.10. Same as fig. 7.7 for Jan. 1959.

stations were added in Ireland providing very interesting information on the excess sulphur. Four months have been selected and data on excess sulphur over the British Isles plotted in figures 7.7, 7.8, 7.9 and 7.10. Studying these figures one gets the impression that a large part of the excess sulphur originates in the sea around Ireland, especially in the southeast.

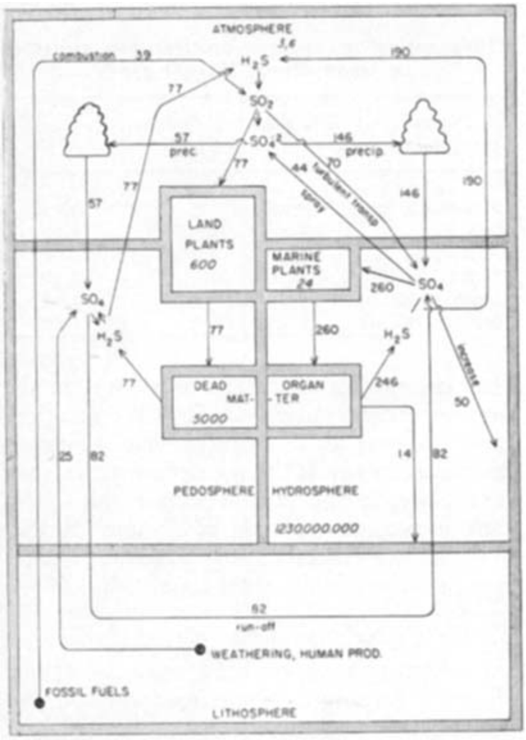

Fig. 7.11. The circulation of sulphur in nature with estimated fluxes. Leaning figures are amounts present in the reservoirs, erect figures are yearly fluxes, all in 10^6 tons units.

A closer study of the influence of monthly circulation on the pattern of deposition of sulphur over the British Isles should, however, no doubt give interesting information.

3. *Yearly circulation of sulphur in nature*

It may seem premature to present a picture of the yearly circulation of sulphur in nature on a quantitative basis but the subject is of such great concern that even a tentative quantitative effort seems justified. The result is seen in fig. 7.11 in a box-model arrangement of the type discussed in section II. The figures require some comments. All figures are in million tons units, erect types representing yearly amounts transported while leaning types are amounts stored in each box. The amounts stored in plants and circulating through plants have been estimated in the following way. The yearly assimilation of carbon dioxide by plants has recently been discussed by HUTCHINSON (1959) and his data have been used by and large. The land plants assimilate a yearly net amount of 77.10^9 tons per year of CO_2 while the corresponding figure for marine plants is $130 \cdot 10^9$ tons. With an average life time of between 15 and 16 years for land plants the amount stored is $1{,}200 \cdot 10^9$ tons CO_2. Marine plants have a rapid turnover, probably 10 times a year, hence their storage is around $12 \cdot 10^9$ tons CO_2. The sulphur content of land plants has been investigated to some extent. JOHANSSON (l.c.) found 1.4 mg S per g dry matter in grass. THOMAS et al. (1950) investigated leaves from various trees, bushes and shrubs. From all these investigations the sulphur content seems to be around 1 mg per g CO_2 in organic matter, at least for assimilating parts. Thus we can use a yearly sulphur turnover in land plants of 77 million tons. As to the storage, cellulose must contain less than leaves, so in computing this a sulphur content of 0.5 mg per g CO_2 in organic matter has been used.

As to marine plants a S/C ratio of 0.0075 has been used computed from data by SVERDRUP et al. (1942 p. 230) assuming about equal proportions of carbohydrates, lipides and proteins in the organic matter of marine plants. This corresponds to 2 mg sulphur per g CO_2 in organic matter, a figure which is not unreasonably high considering that marine plants in general lack structural tissues like the cellulose of land plants. This figure gives the yearly turnover of 260 million tons.

It was found above that sulphur in river water was practically accounted for by sulphur in rainwater. This means that the sulphur assimilated by plants must be given back to the atmosphere by the soil on decay. The precipitated sulphur is therefore the residual sulphur discussed in section IV increased by 13 allowing for a greater amount of combustion (⅓ of 39 million tons); of these 57 million tons 4 are generated from the sea together with chloride. As the total production of sea salts over the sea was estimated to about 10 times that of continental run-off a total production of 44 million tons in spray over the sea must result of which 40 is precipitated over ocean areas. Precipitated over sea will be 2 (57—4) + 40 = 146 million tons.

A turbulent transfer of SO_2 which has a relatively long half-life of 2—3 weeks must take place over the sea to the sea surface which readily absorbs SO_2 at a pH of 8. This transport has been estimated as follows.

JUNGE's averages of SO_2—S in the air at Florida and Hawaii are 1.0 and 0.37 $\mu g \cdot m^{-3}$ respectively (table 5.1) and their average 0.7 $\mu g \cdot m^{-3}$. Using a vertical transport velocity of 0.9 $cm \cdot sec^{-1}$ as computed in section II from the rate of evaporation in trade wind regions gives a total vertical transport of 70 million tons · $year^{-1}$. The same average SO_2—S applied over land to account for the 77 million tons · $year^{-1}$ absorbed by plants require a vertical transport velocity of 2.2 $cm \cdot sec^{-1}$ which is in no way unreasonable considering the greater turbulence over land.

In the circulation diagram the rate of weathering, 14 million tons, plus the human production of non-volatile sulphur of 11 million tons are also entered. If 14 million tons · $year^{-1}$ are weathered an equal amount must be deposited in the sea sediments. There must further be an increase of 50 million tons · $year^{-1}$ in the sea due to released sulphur in combustion 39 million tons · $year^{-1}$ and the human production, 11 million tons · $year^{-1}$. With this information the amounts going into and out of the sea can be balanced resulting in a balance of 190 million tons · $year^{-1}$ which has to go into the atmosphere presumably as hydrogen sulphide. Incidentally, this is not much less than the rate of biologic turnover in the sea though the correspondence may be fortuitous. It looks as if the biological cycle of sulphur in soil and in the sea should have the same pattern except for the uptake.

It has been found recently that the S^{32}/S^{34} ratio in precipitation is extremely constant (ÖSTLUND 1959) compared to the same ratio in other materials like sulphide minerals (cf. RANKAMA 1956) and is definitely higher than the ratio in sea water sulphate which is also very constant. If the sea is so dominating in the yearly circulation of sulphur as fig. 7.11 indicates this constancy is well understood. It must, however, be pointed out that the figures listed in the figure are highly tentative.

VIII. The proportions of sea salt components in precipitation

In the last section various likely processes for the separation of chloride in sea salt particles were discussed. Experimentally it is also found that chloride occurs in gaseous form in the atmosphere, presumably as HCl. No mention, however, was made about possible separation processes already at the sea surface which may take place. In the present section the Cl/Na ratio in precipitation will be discussed further as well as the general ionic balance in precipitation in oceanic and coastal areas.

TABLE 8.1

Cl/Na ratios in various precipitation collected in Japan (From MIYAKE 1949)

Type of precipitation	Altitude in metres	Na $mg \cdot l^{-1}$	Cl/Na
Mountain fog	1,930	5.9	3.25
Sea fog.....	1,200	3.8	1.18
Rime.......	3,780	0.48	1.08
Rime.......	1,200	2.2	1.36
Rain water..	—	0.70	2.06
Sea water....			1.80

1. *The Cl/Na ratio in precipitation*

In MIYAKE's paper from 1949 a detailed chemical investigation was made of fog and precipitation collected in Japan at different altitudes. The Cl/Na ratios found by them for different types of precipitation are quite interesting and are shown in table 8.1. It is interesting to note the large excess of chloride found in what he calls mountain fog and the depletion in sea fog. Already this suggests that the sea fog has been enriched by sodium due to previous escape of gaseous chloride. The excess chloride is then found at higher altitudes.

ROSSBY & EGNÉR (1955) discussed Cl/Na ratios in Swedish precipitation and showed that their distribution was a function of the prevailing circulation. With prevailing westerly winds the Cl/Na ratios were always lower than 1.80, the ratio in sea water, and around 1.2—1.5 at the Swedish westcoast, decreasing regularly inland and to the north. Extremely low Cl/Na ratios were found during months with winds from the north whereas very high ratios were obtained during months with southerly flow, at least in the southern part of Sweden. Based upon these results they made a schematical diagram showing the variation in Cl/Na ratios inland. At the coast separation of chloride has taken place, hence coastal ratios are always below the sea water value and they decrease further inland until the separated

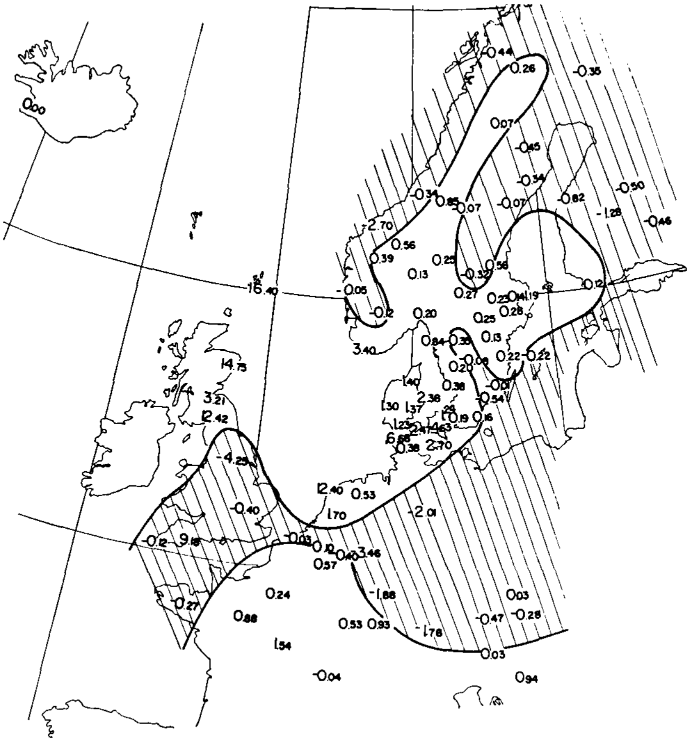

Fig. 8.1. Excess sodium in precipitation over Europe in 1958. Values in kg · ha^{-1} · $year^{-1}$.

chloride is being precipitated when the Cl/Na ratio rizes above the sea water value. Further inland additions of sodium from soils decrease the ratio far below the sea water value. In light of the previous discussion on the mechanism of separation this can be expected to occur in Europe where a considerable sulphur source exists at the western border. A fairly good picture of the conditions in Western Europe can be constructed from the 1958 data from the present chemical network which covers also inland areas fairly well. Instead of using Cl/Na ratios the effect of the separation of chloride is shown as excess sodium in precipitation by subtracting the "oceanic" part using chloride. One reason for chosing this procedure is the fact that chloride, at least, is of marine origin, though the meaning of a negative excess of sodium is obscure and should be taken as indicating an excess of chloride.

Fig. 8.1 shows the "excess" sodium at the West European stations. Generally it can be said that the prediction made by Rossby and Egnér about the variation in the Cl/Na ratio inland is substantiated in the figure. The geographical pattern is, however, puzzling and should be studied more in detail on monthly maps much in the same way ROSSBY & EGNÉR did.

Of special interest is the large excess of sodium found at the coast. This, of course, excludes the possibility that the sodium is of land origin. As a matter of fact the map does not give any support to JUNGE's (JUNGE & WERBY 1958) view that the excess Na is of land origin. ODDIE (1959) has recently discussed this excess of sodium at Lerwick on the Shetland Isles and concluded that it is impossible for these large excesses to originate in remote land areas which themselves show much less excess sodium in precipitation. A similar map over the USA constructed from data on concentrations of sodium and chloride in precipitation published by JUNGE & WERBY (1958) and on precipitation data for the same period from Monthly Weather Review is shown in fig. 8.2. Again it is seen that the largest excesses of sodium occur at the coasts. No negative values are, however, observed

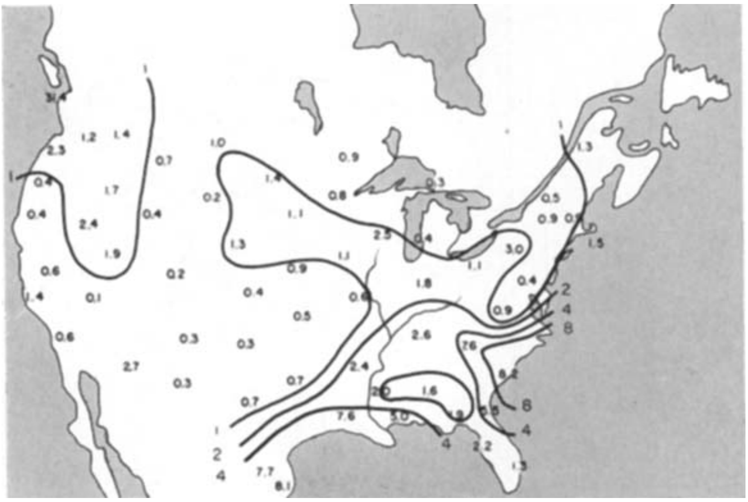

Fig. 8.2. Excess sodium in precipitation over the USA in kg · ha^{-1} · year^{-1}. As to origin of data, cf. fig. 7.1.

probably because there is no prominent coastal source of sulphur on the North American continent like in Europe.

Looking globally at this separation process we might inquire whether the separation of chloride from sea salt particles which takes place mainly over the sea has any effect on the average Cl/Na ratio over continents. When a separation occurs over the sea there are two processes that remove the chloride, namely fallout of sea salt particles and gaseous diffusion through the laminar boundary layer while only fallout removes sodium. This applies to dry fallout. For removal by precipitation the removal rate may be taken as proportional to the total concentration of sodium and chloride in the air so no differentiation in the transport of these two can be expected to take place in this case. But the dry removal favours the chloride, and on a steady state basis this will lead to a lower Cl/Na ratio of the sea salt components in the air than in sea water. The air that passes into continents is consequently enriched in sodium. In Western Europe there seems to be a large source of sulphur, partly industrial which causes a large separation of chloride from sea salt particles. A stationary state like that over the open sea can, however, never be established with the result that the proportions of chloride and sodium in the invading air are about the same as in sea water. When the main mass of sea salt particles is removed near the coasts an excess chloride is left which is precipitated further inland giving the negative excesses of sodium found in fig. 8.1.

2. *Possible separation processes at the sea surface*

This is a question which has been investigated to some extent earlier. Köhler & Båth (1953) made spray from sea water collected and analyzed it for sea salt components. The deviations from sea water composition were, however, very small and probably fall within the experimental error. The conditions under which the experiment was conducted was, however, remote from reality. Sea water always contains organic material and part of it have such composition as to form surface films which, when exceedingly thick can be noticed on the sea surface as so-called slicks. It can be expected that such surface films can modify the composition of the generated spray. Now Kientzler et al. (1954) noticed in their experiments on bursting bubbles that a most effective way of clearing a surface from an organic film was to flush the water by air i.e. by bubbling air through it. Consequently one can expect that a good deal of organic matter is removed from the sea by bursting bubbles. And as the biological processes are steadily going on new material will steadily be formed supplying surface films. In a small, confined volume as in the experiments of Köhler and Båth, this renewal of surface films can hardly have time to take place.

TABLE 8.2

Ionic balance in the yearly precipitation at some coastal stations in 1958

Station	Yearly amounts in gramequivalents · ha^{-1}								sum of anions	sum of cations	cations—anions
	Cl	S	NO_3	H_3N	Na	K	Mg	Ca			
Lista (Li) Norway..	3,465	959	247	257	3,118	112	980	515	4,671	4,982	311
Rjupnahed (Rj) Iceland............	2,107	219	27	32	1,805	58	476	225	2,353	2,596	243
Lerwick (Lw) Shetland............	8,395	1,459	77	121	7,920	187	2,080	451	9,931	10,759	828
Den Heldern (*DH*) Netherlands.....	5,700	1,174	298	172	5,422	128	1,717	525	7,172	7,864	692
Camborne (Ca) England............	4,190	576	98	267	3,590	137	952	309	4,864	4,255	609

A surface film like that on the sea surface has properties which will favour a separation of cations in sea water. They behave like ion exchangers because of acid groups that dissociate hydrogen ions which are replaced by cations, and they repell anions. As to cations those which have a double charge like magnesium and calcium have a greater affinity for such a "charged" surface than single charged cations like sodium and potassium. The composition of sea water close to the film must therefore differ appreciably from that of sea water. A general enrichment of cations can be expected and especially of divalent cations.

It was noted earlier (see MORDY 1957) that precipitation in coastal regions had a large excess of inorganic cations compared to inorganic anions on an equivalent basis. Also in Hawaiian rains the same seems to be true (ERIKSSON 1957). This can be exemplified by using 1958 year data from selected coastal stations. In table 8.2 the stations Lista (Li) in Norway, Den Heldern (DH) in the Netherlands, Lerwick (Lw) on the Shetland Isles, Camrose (Ca) in southwest England, and Rjupnahed (Rj) on the western shore of Iceland have been selected. The yearly amount has been calculated as gramequivalents (amount/equivalent weight) neglecting the pH which is on the acid side anyway. The sum of equivalents of cations and of anions is also shown as well as the differences between these sums. It is interesting to note that there is always an excess of cations amounting to about 10 per cent of the sodium. If hydrogen ions were included the difference would be greater. This excess must consequently be balanced by organic anions as there are no other inorganic anions which can be considered. It is known that precipitation contains appreciable amounts of organic matter the composition of which has been reported by NEUMANN et al. (1959). The organic matter seems to be wide-spread and uniform in composition so that it is quite possible that a substantial part of it comes from the sea carried into the air from surface films by bursting bubbles.

The results in table 8.2 indicate that the sea salt particles, already when generated, have a composition differing from sea water and that there is already an excess of cations e.g. of sodium. This makes the present computation of excess sodium based on chloride more understandable in a way but requires some caution in interpreting the excesses of the other cations.

Such computations are still interesting. Even if the chloride in sea salt particles is non-conservative one may use it for the purpose of calculating excesses of potassium, magnesium and calcium. If the sea were a source of this excess it would show up around the coast. In fig. 8.3 the 1958 excess of potassium in Western Europe is shown, and in fig. 8.4 the corresponding map over the USA, while the map over excess magnesium in Western Europe is shown in fig. 8.5. As to potassium the USA map shows indications of higher coastal values while in Europe they are more irregular. As to magnesium there are large excesses at the coastal stations in the North Sea area. If sodium had been used as a reference for computing the excess Mg, these stations would still give the largest excesses of magnesium. As to calcium shown in figs. 8.6 and 8.7 coastal

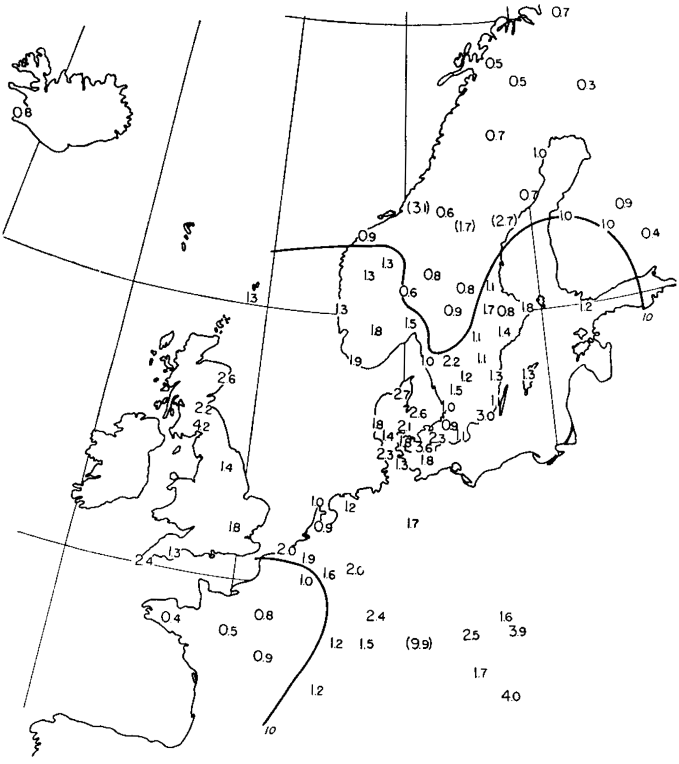

Fig. 8.3. Excess potassium in precipitation over Europe in 1958. Values in kg · ha^{-1} · · year^{-1}.

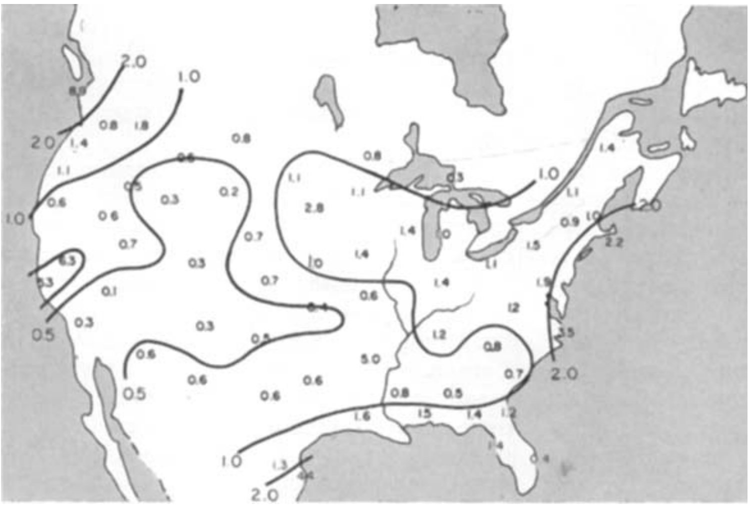

Fig. 8.4. Excess potassium in precipitation over the USA in kg · ha^{-1} · year^{-1}. As to origin of data cf. fig. 7.1.

values are as a rule smaller than continental values. In the USA a maximum is found over the most prominent agricultural areas, and the same is true also for Europe.

As a conclusion it can be said that there are strong indications that at least some of the excess potassium and magnesium in precipitation originates from the sea. The same may be true for calcium too but it is well masked by the influence of land.

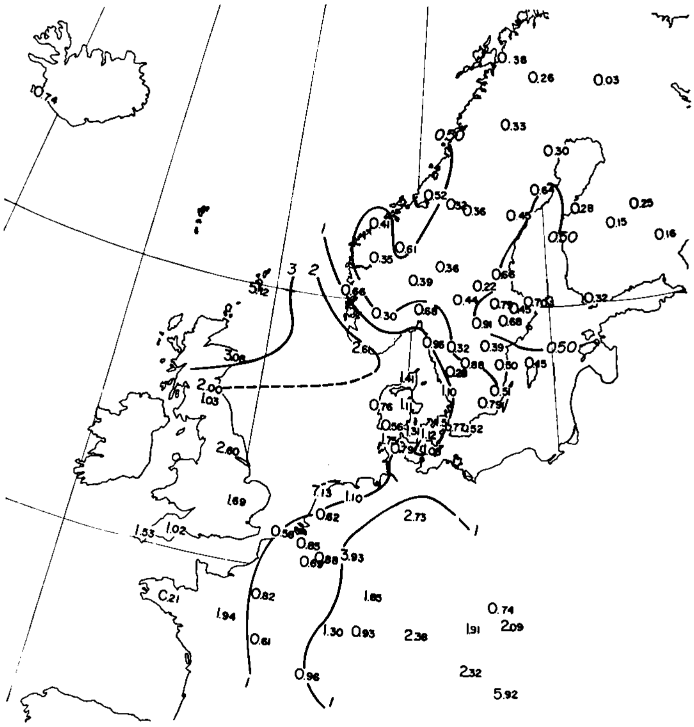

Fig. 8.5. Excess magnesium in precipitation over Europe in 1958. Values in kg · ha^{-1} · year^{-1}.

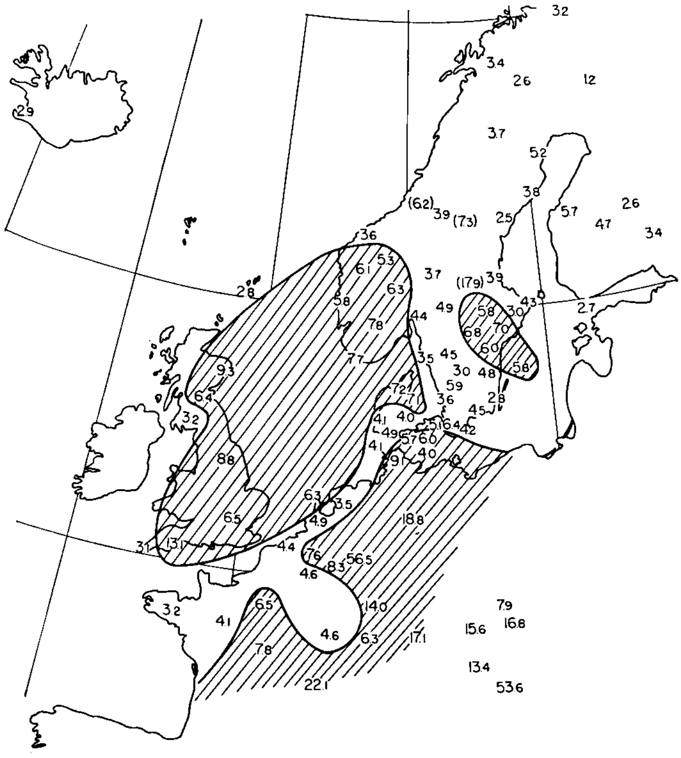

Fig. 8.6. Excess calcium in precipitation over Europe in 1958. Values in kg · ha^{-1} · year^{-1}.

Fig. 8.7. Excess calcium in precipitation over the USA in kg · ha^{-1} · year^{-1}. As to origin of data cf. fig. 7.1.

IX. On chemical hydrology

Air borne salts deposited in continental areas are found in the ground, in streams, rivers and lakes, where it mingles with weathering products. During the time between addition to soils and run-off to sea changes in the chemical composition can occur by various processes. Evaporation of plants increases the concentration of ions drained off, and reduction of sulphate and escape of hydrogen sulphide might cause important changes in groundwater and lake water pH, in extreme cases leading to the precipitation of calcium and magnesium carbonates. It may be of interest to discuss these processes in the light of experimental evidence on ground and lake water composition and on the composition of atmospheric precipitation and the chemical behaviour of certain elements.

1. *Evaporation and chloride concentration.*

ANDERSON (1945) made an interesting study in Victoria, Australia, of the relation between air borne salts and the composition of river and lake waters on both sides of the coastal water divide. Chosing chloride as an indicator he was able to predict the chloride concentrations of river water from the concentrations of chloride in precipitation and from the ratio of run-off to precipitation. The results he obtained are of great interest in the present discussion and are shown in table 9.1. The agreement between calculated and actual chloride concentration is remarkable. One might ask, however, why these results do not indicate removal of sea salt particles by impingement on vegetation as data no doubt indicate in Sweden.

Anderson also found that in areas of com-

TABLE 9.1

Actual and computed chloride concentrations in some Australian river waters. From Anderson (1945)

Catchment area	Area in sq.miles	Precipitation in inches	Ratio of discharge to precipitation	Mean concentrations of chloride		
				In precipitation	In river water	
					Calculated	Actual
Upper Murray . . .	10,234	33·19	·283	1·0	3·5	3·4
O'Shamassy R. . .	46·7	63·74	·520	2·7	5·2	4·75
Yarra R.	972	44·61	·311	4·4	14·2	15·3
Barwan R.	1,425	25·33	·075	8·4	112	134
Helena R. (W. Australia)	559	28.05	·034	6·7	197	203

paratively high ratios of run-off to precipitation lake and river waters were more influenced by chemical denudation than in areas with low run-off/precipitation ratios.

The role of evaporation for the chloride concentrations in lake and river waters has also been discussed by ERIKSSON (1955 a). If the yearly precipitation is N, the yearly evaporation E and the concentration of chloride as it enters the ground is C_N, then at a stationary state the concentration in the ground water, C_g, is

$$C_g = C_N \frac{N}{N-E} \tag{9.1}$$

derived from simple continuity considerations. It is, of course, not valid when $N-E$ is negative because then no stationary state can exist.

Before discussing the implications of the relation above, the term "stationary state" must be qualified. There are, obviously, no stationary states whatsoever in nature, periodicity and random fluctuation being basic features of all systems. It is, however, possible to realize quasi-stationary states, chosing the time and space scales so that important periodicities and small amplitude fluctuations have little influence. In the discussion below it should be understood that the time scale is in years and that the so-called stationary system is only quasi-stationary.

If the ratio $\frac{N}{N-E}$ as well as C_N is constant for a given drainage area, C_g will also be constant in the groundwater body in the drainage basin. If the average depth of this groundwater body is known, as well as the porosity P of the water bearing strata, it is also possible to calculate the amount of accumulated air borne chloride in the groundwater per unit area. As an example assume the depth of the groundwater is 10 m and the pore space is 30 per cent. Then the amount of chloride per m² is $M_g = 10 \times 0.3 \times C_g = 3\ C_N \times \times \frac{N}{N-E}$. If C_N is expressed in $\text{mg} \times \text{l}^{-1}$, M_g is given in $\text{g} \times \text{m}^{-2}$.

This can be exemplified by keeping the evaporation E constant $= 500\ \text{mm} \times \text{year}^{-1}$ and C_N constant $= 1\ \text{mg} \times \text{l}^{-1}$, varying the precipitation. The results are shown below:

N in mm.	1,000	750	600	550	525	510	505
C_g in $\text{mg} \times \text{l}^{-1}$.	2	3	6	11	21	51	101
M_g in $\text{g} \times \text{m}^{-2}$. .	6	9	18	33	63	153	303
M_g in $\text{kg} \times \text{ha}^{-1}$	60	90	180	330	630	1,530	3,030
Time constant in years. . . .	6	12	30	60	120	300	600

The time constant is simply the amount accumulated divided by the yearly amount in precipitation. It gives some idea of the length of time required to reach a stationary state.

The calculations above cannot, of course, be applied immediately to a drainage area where $\frac{N}{N-E}$ varies from place to place. If the drainage takes place along a slope, the groundwater depth will vary approximately as $\frac{N}{N-E}$ and in the extreme case the accumulation will be independent of variation in the $\frac{N}{N-E}$ ratio except for transient changes. The other extreme is represented by an area where groundwater accumulates in a basin and drains over a sill. In this case the example above can be strictly applied. It is especially interesting to note that as the aridity increases the time constant for such a basin also increases. The effect of a more permanent change in the precipitation—run-off ratio can be exemplified as follows. Suppose that a stream is fed from two areas of equal size, one where E is 400 and one where E due to fairly good vegetation cover is 500. The precipitation is the same for both and equal to 510 mm. The groundwater amount corresponds to 1,000 mm and the chloride concentration in precipitation is $1\ \text{mg} \times \text{l}^{-1}$. At a stationary state the run-off from the area of higher evaporation is $10\ \text{l} \times \text{m}^{-2} \times \text{year}^{-1}$, that from the other $110\ \text{l} \times \text{m}^{-2} \times \text{year}^{-1}$. The amount of chloride drained from both is the same, namely that contained in 510 mm precipitation. The chloride concentration in the stream will thus be $\frac{2 \times 510}{110+10} = 8.5\ \text{mg} \times \text{l}^{-1}$. If, however, the evaporation from the drier area is decreased by removing vegetation to the same value as the other area, i.e. 400 mm per year^{-1}, the run-off from the drier area will be $110\ \text{l} \times \text{m}^{-2} \times \text{year}^{-1}$ but the chloride concentration will not be changed very much initially so that 11 times more chloride will be drained off from this area per year than supplied by precipitation. The chloride concentration in the stream will thus rise to $\frac{510 + 11 \times 510}{110 + 110} = 27.8 \text{ mg} \times \text{l}^{-1}$, i.e. a threefold increase. This condition should last for an appreciable time until the whole groundwater amount has been replaced. This is interesting in view of the theory of WOOD (1924) concerning the salt increase in the streams of Western Australia following the destruction of native vegetation.

The example above is, of course, extremely simplified as groundwater exchange is by no means so simple. The slope of the water body will determine the streamline flow pattern and consequently the velocity of flow in various parts of the basin. Due to the strongly varying velocities of laminar flow in a porous body, mixing must occur along the streamlines, making the contact between two different water masses diffuse. In the example above, following the removal of vegetation, one would expect first a sudden rise of the chloride concentration of the stream, although perhaps less than that calculated, and then a continuous decrease from year to year until after a considerable length of time, much greater than the time constant for the resulting groundwater body, the new stationary state is reached.

Changes in the ratio $\frac{N}{N-E}$ can, of course, also occur due to yearly trends or long periodic changes in the rainfall intensity. This is perhaps of still greater importance in long term planning. Trends in the yearly rainfall have recently been shown to occur in Mexico (WALLÉN 1955) and must be of great significance for salinity variations in ground waters and streams in the arid areas of this country. Precipitation can very well be pictured as long period fluctuations. If the period should happen to coincide with the "time constant" for a groundwater mass, discussed earlier, the effect of the precipitation variations upon the salinity of streams and groundwaters would be greatest.

When aridity is so extreme that salts precipitate, salt layers will be found. If evaporation balances precipitation, salts accumulate. This may go on for geologic time periods. Very long periodic changes in the precipitation climate will cause alternating deposition and washout of salts. Ground, spring and stream waters will be highly saline during the wetter periods. It is therefore apparent that estimates of the yearly precipitation of sea salts in arid regions from river water analyses must be made with caution. One year's river water data collection may be very misleading.

2. *Reduction of sulphate and precipitation of calcium and magnesium carbonates*

Reduction of sulphate to hydrogen sulphide can modify the groundwater composition considerably. The sulphate ion is a considerable oxygen source and in absence of dissolved oxygen in water oxidation of organic matter continuous with concomitant sulphate reduction. When sulphate as an anion disappears hydrocarbonate and carbonate is formed instead. This is known to occur frequently in deep groundwaters as discussed by RIFFENBURG (1925) in which case groundwaters, seeping through butiminous bed, are turned into alkaline waters.

As the sulphate disappears and carbonate appears the water gets alkaline. If a substantial reevaporation occurs so that the water is made concentrated, calcium carbonate is precipitated and later magnesium carbonate. A completely alkaline water is now the result. Thus evaporation and sulphate reduction can have a strong influence on the quality of groundwater. Naturally, arid regions will show most of these peculiar types of waters. If such alkaline groundwater is later evaporated, alkaline soils will be formed. This is, in fact, a much more probable process of alkaline soil formation than the process generally suggested through washout of chloride from saline soils. The latter process requires an extensive change in the water economy and can certainly develop as a transient state as it did in the inundated areas of the Netherlands after the World War II.

Some examples on the change of the composition of waters can be found in northwest India in a large arid region, the Rajputana Desert. A lake in this region, Sambhar Lake, was investigated by HOLLAND & CHRISTIE (1909). They were aware of that the salts in this lake were atmospheric in origin but the composition of the lake differed much from sea water, being nearly devoid of sulphate calcium and magnesium. They explained the absence of calcium and magnesium as due to a selective transport of sodium chloride from the Runn of Cutch, a low laying coastal region frequently inundated, leaving the more hygroscopic calcium and magnesium chloride behind. In view of the sea salt transport in the air by the summer monsoon in this place, a reduction of sulphate in the ground with the formation of calcium and magnesium carbonate is much more likely.

CLARKE (1924) has given a number of analyses from the Great Salt Lake region where similar processes are clearly seen at work. ANDERSON (l.c.) in his investigation on various waters in Victoria, Australia, noticed also the deficiancy of calcium and magnesium in coastal lakes where reduction of sulphate was going on.

X. Soils and airborne salts

The role of atmospheric salts in soil formation has received some attention in the past. MATTSON et al. (1944) studied the Ca/Mg ratio in plants and in peat formations and found a considerable maritime influence on the composition of peat near the west coast of Sweden. This work was thoroughly discussed also in a later paper (MATTSON & KOUTLER-ANDERSSON, 1954). The influence of sea salts on coastal soils has also been studied in New Zealand (GIBBS, 1949) and fairly recently similar work was started in Australia by the C.S.I.R.O. Division of Soils (HUTTON & LESLIE 1958, HINGSTON 1958).

This type of work will no doubt be extended in future. In the general philosophy of soil science the part played by the atmosphere in supplying chemical compounds has never been properly considered. It may, therefore, be beneficial to future research if the chemical climate is introduced as another factor in soil formation, and to develop some general and simple principles delineating the role of atmospheric salts.

It is known that soils contain appreciable amounts of cations such as sodium, potassium, calcium and magnesium in exchangeable form. This implies that they are held in the soil by negative charges on the surfaces of clay minerals and of humified organic matter. As soils also contain moisture, there is an aqueous phase present, usually called the soil solution. This can be separated from the solid phase which includes the exchangeable ions. When equilibrium is attained the various cations will be distributed in some ordered manner between the soil solution and the solid phase. The solid phase dominates the soil solution quantitatively, so that the former acts as a big reservoir preventing drastic changes in the soil solution. The static conditions for cations in the soil are thus determined.

Soils are, however, dynamic systems. Plants take up cations as well as water from the soil. On decay these cations are released and added mainly to the top part of the soil, where they are later transported down into the soil and divided between the soil solution and the solid phase. In this way a circulation of cations is steadily going on, the necessary energy being supplied by the sun. Some cation losses will occur to the groundwater but this is compensated by the release in weathering of soil minerals.

This circulation is well known and scientifically accepted. The question remains, however, whether this picture is complete. Since precipitation contains salts, there will be a flow of these salts through the soil. This flow is superimposed on the biological circulation of ions. This additional flow makes the dynamic picture more complete.

The question arises to whether the flow of atmospheric salts through the soil influences the biological circulation.

The answer can be in the following general example. Suppose precipitation contained no salts at all. A certain plant species growing in soil produces a constant circulation of various cations, these cations being carried into the soil from decaying plants by percolating precipitation. At the top of the soil the concentration of cations in the soil solution will be greatest, decreasing downwards as cations are taken up by the plant roots. The proportions of various cations in this circulation depend on the characteristic properties of the plant. A stationary state thus exists. If now the same kind of cations are added by precipitation, but in proportions which differ from these in the biological circulation, the system is thrown out of balance, as it must be postulated that the uptake of cations by the plants is affected by the composition of the soil solution. A gradual change in the proportion of the different exchangeable ions will occur, and a new stationary equilibrium be attained. Thereby the presence of salts in the precipitation has affected the biological circulation.

As atmospheric salt influences the biologic circulation due to mutual interaction it also influences the soil properties. For quantitative purposes much more work should be devoted to a study of these relationships.

In a stationary state such as described, the atmospheric cations have no nutritional value. However, such a stationary state can only be found in virgin soils.

In cultivated soils where products are continuously removed from the soil, no stationary state can exist. Here the dynamic picture of a soil will be quite different. If a stationary state is to be achieved without fertilizer application a compensation for the cations removed by crops must occur by the cations supplied in precipitation. This means that the precipitation would supply fewer cations to the groundwater than to the soil. Cations in precipitation will thus become of nutritional value.

Only cations have been considered above but similar reasoning obviously also applies to the anions.

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