LETTERS TO THE EDITOR

"*The Yearly Circulation of Chloride and Sulfur in Naturel, Meteorological, Geochemical and Pedological Implications*", by Erik Eriksson, *Tellus*, **11**, pp. 375—403, and **12**, pp. 63—109 (1959—1960).

Dear Sir,

In his paper Eriksson makes a worthwhile attempt to combine a large number of observations about sea salt components into a comprehensive picture. Included in his discussion is some of our data from the U.S. rain water analyses project. In a number of cases, the conclusions drawn in this paper differ from those of the original authors. Most of this disagreement originates because Eriksson prefers to present these data in a different way. Since this seems to touch on a more fundamental question in the interpretation of rainfall data, a few remarks may be justified.

Our interpretation of rain analysis data (JUNGE and WERBY 1958) was based on maps of average *concentration* of various ions, (Cl^-, Na^+, K^+, SO_4^{--} etc.), in rain, expressed in milligrams per liter. The purpose was to obtain from such data, if possible, information about the origin and source areas of these atmospheric constituents. Eriksson uses for the same purpose maps of *total deposition* of these constituents, expressed in kilograms per hectar per year. These latter maps are calculated from the concentration maps by multiplication with the average yearly amount of rainfall. As the title of his paper indicates, he is concerned with land-ocean circulation of such constituents, and, for yearly budget considerations, maps of the total annual deposit are undoubtedly of great value. If they are used, however, for interpretation of the origin of these components, objections must be raised.

The main reason that we used rain water concentration maps for our interpretation, is that they reflect the average tropospheric air concentration much better than maps of total deposit. Although we gave specific reasons for this in the publications of our rain water results (JUNGE and WERBY 1958, JUNGE and GUSTAFSON 1957, JUNGE 1958), Eriksson restricts his discussion of this question to the sentence: "The concentration is not a good indicator because it is strongly dependent upon the amount of water vapor present in the air, subject to condensation" (page 56). We would like to discuss this point in more detail. The amount of water available for the removal of the chemical constituents from a certain volume of cloud air is largely controlled by the liquid water content of this cloud at the onset of rain. This value varies with the type of cloud, but in the rather narrow limit of about 1.5 to 3.0 grams per cubic meter. In warmer climates, where the water vapor content of the air is higher, this liquid water content is released by a smaller amount of cooling than in colder areas. There is a small, but systematic decrease in the average liquid water content of precipitating clouds, from the equator to the poles, because of a variation in the composition of the cloud population. In warmer climates, there is generally a higher percentage of convective clouds which tend to have a higher liquid water content. But this is a smooth and gradual decrease, with a gradient much smaller than those exhibited on most of the concentration maps of rain water constituents.

Basically, the material which is contained in rain water comes from two predominant sources: Collection of material within the cloud, during the formation process of the cloud and rain drops, and secondly, from the interception of aerosol particles by falling rain drops *below* the cloud. Unless the original air concentration of the aerosol is much larger *below* the cloud than *within* the cloud (i.e., sea salt particles over the ocean and along the coasts), the first source is the predominant one (JUNGE and GUSTAFSON 1957). This can be expressed quantitatively. If, within the cloud, l is the liquid water content (gr/m^3), C the concentration of the chemical constituent in air ($\mu g/m^3$), K the same in rain ($\mu g/cm^3$ = mg/liter) and ε the fraction of material removed from the air within the cloud, we obtain:

$$K = \frac{\varepsilon}{l} \cdot C \qquad (1)$$

During the periods of months or longer, the fluctuations of ε/l with cloud type, etc., will average out, and $\left(\frac{\varepsilon}{l}\right)$ will vary only slightly with location, season and surface (land, ocean). As a good approximation, therefore, $\overline{K}$ will be proportional to $\overline{C}$. If, for sea spray, $C = 10\ \mu g/m^3$, $\varepsilon \cong 1.0$ and $l = 2\ g/m^3$, we we obtain $K = 5$ mg/liter, a figure which is of the right order. The increase of this concentration by interception of particles below the cloud—if important—will, again, on the average, vary only slightly with latitude, season and surface (land, ocean).

The question now arises, to what extent the air concentration is modified by preceding rainfalls and washout or by the average amount of rainfall if we think in terms of geographical distribution rather than air mass history. There is no doubt that in an individual precipitating cloud or cloud system, constituents can be almost completely removed. This is demonstrated by the fact that during individual rains, the concentration decreases considerably with time. But if we deal with large air masses, as we do when we use monthly averages, *the distribution of rain in time and space is such that only a small fraction of the constituent is removed per day*. With $\varepsilon = 1$ we calculated residence times (JUNGE and GUSTAFSON, 1957) of 6 days for an average rainfall intensity of 0.1 inch per day, and a liquid water content of 2.0 g/m^3, conditions which prevail over most of the U.S. These calculations with a simplified model give the right magnitude. Observations indicate a range from 5 to 40 days, which can be explained by an ε smaller than 1, and by simplifying the assumption for other parameters. Residence times of this order show that, on the *average*, even when air masses cross large areas like the U.S., the constituent in the air is not decreased considerably.

Let us now consider two extreme cases of washout in the atmosphere, and the effect on concentration maps as well as on total deposition maps. We assume a certain constant geographical distribution of continuous sources of chemical constituents at the ground. In the first case, the residence time of the pollutant may be extremely short, so that it will be removed before it can spread out to any degree. It is obvious that in this case the concentration, as well as the total deposition, will reflect very closely the distribution of the sources. Both maps could be used for source interpretation. In the second case, the residence time shall be long, so that considerable horizontal mixing and transport occurs before any appreciable amounts are removed. The air and rain concentrations will now show almost uniform values, and the total deposit will reflect the map of total rainfall. In reality, conditions are somewhere between these extremes. With residence times of 6 to 40 days, it should be expected that the air concentration gives only a blurred picture of the source distribution, with extension of the areas of main concentration downwind. But the maximum concentration will still be close to the source area, and the pattern will give information about the main source and sink areas. For total deposit, however, the pattern of the rainfall distribution is superimposed upon that of air concentration, and a reliable interpretation becomes more or less impossible.

The example of Sr^{90} may illustrate this. It is now commonly agreed that, over wide areas of uniform climatological structure, the deposition of Sr^{90} is proportional to the total amount of rainfall. The average release of Sr^{90} into the troposphere is primarily latitude dependent, and because of the speed of circulation and of residence times of 4 weeks, the air concentration is fairly uniform within latitude belts. The higher rainfalls along the west coast of the U.S. result, therefore, in higher Sr^{90} deposition than further inland, but nobody would draw the conclusion that Sr^{90} comes from the sea.

In a similar way the conclusions Eriksson draws from total rainfall deposition maps as to the origin of the constituents are doubtful in some cases, and incorrect in others.

His map 7.5 of the excess sulfur in precipitation over the U.S., exaggerates the influence of industrial sulfur and obscures the gradients along the coast. Because total rainfall changes considerably with the distance from the coast, we cannot expect that this map can bear out our conclusion that most of the sulfur is of continental origin. The concentrations of excess sulfur, however, are clearly lower over the oceans than over the continents.

Similarly, we cannot agree with the conclusion (pages 62 and 64) that excess Na^+ and K^+ come from the sea (pages 62 and 64), because we think that his maps 8.2 and 8.4 (to stay just with the U.S. data) should not be used for this argumentation. In addition, our data on which these maps are based, are not regarded reliable enough along the coasts to draw any conclusions from them. We indicated (JUNGE and WERBY 1958, page 420), that our data for the excess Na^+ and K^+ along the coasts are not too reliable because they appear as small differences

of two comparatively large figures, whereas they become very reliable further inland. A similar caution should be exercised with most of the other excess data over or near the ocean. For this reason, we did not use the pattern of the excess concentration maps of Na^+ and K^+ for our considerations. Our line of reasoning was based on the important fact that the average concentrations of Na^+ and K^+ over most of the U.S. are very much the same despite the fact that the ratio K^+/Na^+ is only 0.041 in sea water and thus 20 times smaller than in rain. There is no basis for the assumption that the ionic composition in sea spray particles deviates that much from sea water. On the contrary, coastal rains in unpolluted areas have ratios close to that of sea water. We concluded, therefore, that most of the K^+ must come from the soil. Because of the similarity in chemical behavior of Na^+ and K^+, we suggested that it is very likely that the excess Na^+ is also derived from the soil.

As we pointed out earlier, KALLE (1953—1954) in a very interesting study, provided considerable evidence of the mineral origin of the excess Na^+. K^+, Ca^{++} and other cations in rain over Europe, It would have been very useful if this paper had been included in Eriksson's discussion. Also, the reader would have appreciated a reference of METHAM's (1950) paper on the SO_2 concentration and SO_4^- deposition over England in connection with Figures 7.7 to 7.10. Metham's work indicates that industry is an important, if not the predominant source of sulfur over England, in contrast to the conclusions drawn from Figures 7.7. to 7.10. The heavy rainfalls on the west coast of Ireland certainly increase the deposit, but, as with our Sr^{90} example, this does not indicate that the ocean is the source of sulfur.

Sincerely yours,

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Reply

Dear Sir,

The main question raised by Dr. Junge is no doubt of fundamental importance for the correct interpretation of chemistry data on precipitation, though his analysis perhaps can be extended somewhat. Firstly, as most precipitation comes from disturbances which are moving comparatively slowly we can regard precipitation as a quasi-stationary state where horizontal convergence of moisture is steadily replacing the moisture precipitated. Neglecting contribution to the precipitation by sub-cloud air is probably permissible. Provided also that most of the precipitation is due to accretion of cloud droplets into larger aggregates, i.e. condensation on ice nuclei is quantitatively unimportant, the equation given by Dr. Junge is, of course, correct. But K in his formula is an instantaneous value so it has to be averaged and the way it is done by Dr. Junge may be too simple.

Denoting by m the amount of a substance precipitated, by R the rate of precipitation, and using instead of $1/l$ a specific volume v (volume per gram liquid water) we can write

$$m = \int_0^T \varepsilon R v c \, dt \qquad (2)$$

from which also the average weighted concentration can be derived. The integration is, of course, carried out only during precipitation.

Now we can assume ε to be constant, a reasonable assumption for most compounds of interest. In order to carry out the integration we use a common method writing $R = \bar{R} + R'$, $v = \bar{v} + v'$ and $c = \bar{c} + c'$.