Indirect evidence of the importance of water-soluble continentally derived aerosols

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ABSTRACT

The Ca^{++}/Cl^{-} ratio is a logical index of the predominance of continental or marine water-soluble aerosols in precipitation. Use of this ratio and others indicates that, excluding immediate coastal areas, continental aerosols constitute a large majority of the soluble material brought down in precipitation over land. The correlation of the concentrations of various ions in precipitation with the regional distribution of these elements in the soil presents further support for this conclusion.

1. Introduction

The importance of the land surface as a source of water-soluble aerosols in precipitation is difficult to evaluate. It appears, however, that in the past this source of aerosols may have been seriously underrated. Although several investigators have touched briefly on the subject, it usually has been as a small part of a much larger program. The subject warrants more thorough consideration.

In this paper some of the existing data on the chemistry of precipitation in the United States are analyzed. The ratios Ca^{++}/Cl^{-}, Ca^{++}/K^{+}, and Ca^{++}/Na^{+} in continental precipitation are discussed and compared with their counterparts in sea water. Some general geologic features are brought out to illustrate the striking correlation between the concentrations of Cl^{-}, Ca^{++}, K^{+}, and Na^{+} in precipitation and the regional distribution of these elements in the soil. In addition, the significance of continentally derived areosols to the Cl^{-}/Na^{+} ratio is presented.

It has been postulated for some time that the ocean is the chief source of tropospheric aerosols. The composition of ocean water is relatively uniform and accurately known. This fact has offered a ready means for the study of the origin of water-soluble aerosols. Usually the ratios of various ionic constituents in precipitation are compared with their corresponding ratios in sea water. Past studies utilizing ratios have dealt almost exclusively with the Cl^{-}/Na^{+} ratio. As will be made evident, the Cl^{-}/Na^{+} ratio does not readily lend itself to the study of the source of aerosols.

2. Evidence from ionic ratios

The data used in this analysis are the annual average concentrations reported by JUNGE and WERBY (1958).

The Ca^{++}/Cl^{-} ratio in precipitation is a logical index of the origin of aqueous solutes. In sea water this ratio is 0.02. In contrast, calcium usually far exceeds chloride in that thin weathered film of the earth's crust that can be considered a source material for continental aerosols. There are some minor exceptions, of course, such as dessicated lake beds. Nevertheless, chloride so outweighs calcium in sea water and calcium so outweighs chloride on the land that these exceptions are unimportant for all practical purposes. Therefore, the Ca^{++}/Cl^{-} ratio is a reasonable index of the predominance of continental or marine water-soluble aerosols. A ratio of less than one suggests marine dominance and a ratio of more than one suggests continental dominance.

If we view the Ca^{++}/Cl^{-} map (Fig. 1) in this light, a very interesting feature becomes apparent. Those areas where marine aerosols are more abundant than continental aerosols (hatched area) comprise only a small fraction of the total land surface. In fact, in precipitation

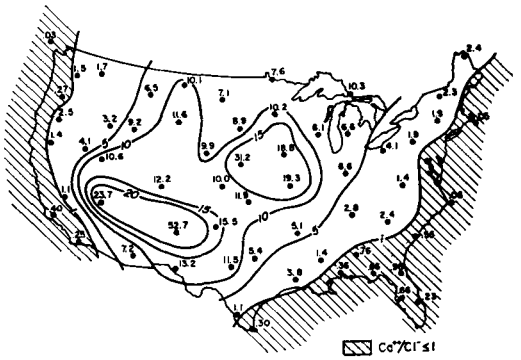


Fig. 1. Ca^{++}/Cl^{-} ratios, average July 1955 to June 1956. (Computed from data by JUNGE and WERBY, 1958.)

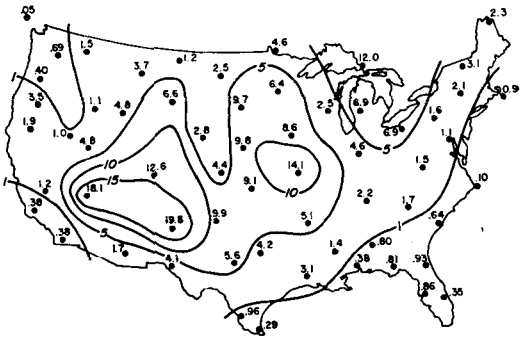


Fig. 3. Ca^{++}/Na^{+} ratios, average July 1955 to June 1956. (Computed from data by JUNGE and WERBY, 1958.)

over most of the country there is a large preponderance of continental aerosols—a somewhat different concept than that presented in most past studies. Further evidence is given in this paper to substantiate this concept.

The Ca^{++}/K^{+} ratio map (Fig. 2) presents a further anomaly if one adheres to the concept that continental aerosols are unimportant. In sea water the Ca^{++}/K^{+} ratio is approximately 1. Except for two stations in southern California the observed values are considerably above those in sea water. The increase of this ratio in an inland direction is indicative of continental influences. Water-soluble salts of calcium are more abundant than those of potassium in the surficial mantle of the earth.

The Ca^{++}/Na^{+} ratio map (Fig. 3) displays features somewhat similar to those on the Ca^{++}/K^{+} map. This map as a whole, however, is in many ways more striking than the Ca^{++}/K^{+} map. The Ca^{++}/Na^{+} ratio in sea water is approximately .04. Sodium, unlike potassium, is very abundant in the sea. Yet the Ca^{++}/Na^{+} ratios do not differ significantly from the Ca^{++}/K^{+} ratios. This fact certainly indicates that very little sodium from the sea is being precipitated very far inland.

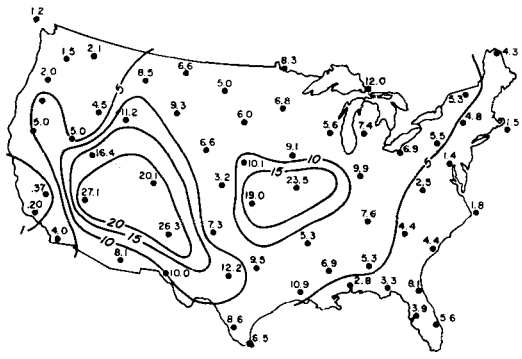


Fig. 2. Ca^{++}/K^{+} ratios, average July 1955 to June 1956. (Computed from data by JUNGE and WERBY, 1958.)

The areal distributions of the preceding ratios are in themselves evidence of continental influence. Equally significant is the correlation of geochemical features of soil with the distributions of the individual ionic concentrations.

Junge and Werby's maps of calcium and sodium concentrations show three very pronounced features. The first two area-calcium concentration maxima in the Southwest and in the central loessial part of the country. The third is a sodium maximum in the Great Basin. It was noted by Junge and Werby that the two calcium maxima occurred where they would be logically expected. The first occupies much of the arid Southwest but is specifically centered over the Colorado Plateau. The rocks of this region are almost all sedimentary with a high proportion of limestones and calcareous shales. Thus we have an abundant source of calcium. The aridity of this region allows little vegetation. That this is conducive to ground-to-air transport of material is evidenced by the dust storms characteristic of the Southwest.

The second calcium maximum is located over the eastern portions of Kansas and Nebraska, and the western portions of Iowa and Missouri. This area receives more rain than the Southwestern United States, but extensive cultivation of the land furnishes the wind ready access

to loose soil. The prevalence of calcareous loess deposits and soils developed from limestones provides an abundant source of calcium.

The high sodium concentrations in precipitation in the West correlate well geographically with the Great Basin. In contrast to the other two areas just discussed, the Great Basin consists chiefly of igneous rocks, which are relatively richer in sodium than most sedimentary rocks. The detrital material from these igneous rocks and saline residues on ancient dessicated lake beds comprise the so called "alkali plains and flats" common in this region. Here again we are dealing with an extremely dry climate, which allows much wind erosion and consequent production of aerosols.

One other interesting feature is noted in an examination of these three areas. In all cases the various ionic maxima are found in close proximity to their respective likely source areas. Apparently the bulk of these continentally derived constituents is brought down within a few hundred miles of its point of origin.

3. Chloride-sodium ratios

To date, the Cl^-/Na^+ ratio has been studied in connection with two extensive precipitation sampling networks, one in Scandinavia, currently in operation, and a second in the United States, operated in 1955 and 1956 (JUNGE and WERBY, 1958). Data from both networks show a large disparity between the Cl^-/Na^+ ratios in sea water and those in precipitation. The Cl^-/Na^+ ratio in sea water is approximately 1.8. Although precipitation samples from stations under predominantly marine influence do occasionally approach this figure, they are generally much lower. Inland a short distance the ratios are very low without exception in the United States and with few exceptions in Scandinavia.

Chloride is present in significant quantities only in the sea. Sodium, on the other hand, is relatively abundant both in the sea and on the land. This leads us to two hypotheses that could explain the low Cl^-/Na^+ ratios:

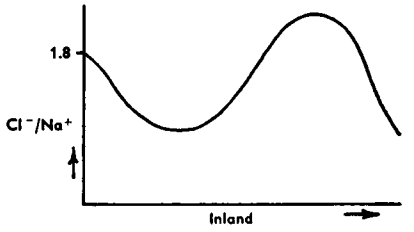
1. An addition of sodium from the land surface, and/or
2. A chemical separation or "fractionization" of the chloride in sea salt, part of which is then carried farther inland to be brought down at some later time.

Currently sentiment in the literature seems to favor the second conclusion. A few of the better known theories offered to explain this fractionization are summarized here.

CAVER (1949), theorizes that chloride in sea spray droplets may be oxidized by ozone to free chlorine gas which is changed to HCl by sunlight in the presence of water vapor. The HCl may then form droplets or remain as gaseous HCl. The HCl droplets are presumably not hygroscopic because of their small size. In either form the chloride can be transported easily by the wind, thereby producing the needed fractionization.

ERIKSSON (1959) suggests the possible addition of H_2SO_4 to sea salt particles, the H_2SO_4 having been formed by oxidation of SO_2. This reaction would release chloride as HCl and consequently explain the frequently observed low pH values found in precipitation. (Cauer observed that in coastal regions atmospheric vapor when condensed on a cold surface gave an acid reaction, whereas sea water itself is alkaline.) Speculation on processes similar to this has undoubtedly been heightened by the identification of small amounts of gaseous chlorine in the atmosphere (JUNGE, 1956).

ROSSBY and EGNÉR (1955) speculate that the precipitation falling near the coast contains a mixture of sodium chloride and other sodium salts. The sodium chloride aerosols are then selectively used up as condensation nuclei, falling out in precipitation near the coast. The air mass moving inland is deficient in sodium chloride, but relatively rich in the other sodium salts. When these other sodium salts have been removed, the much smaller HCl droplets become dominant. When this happens the Cl^-/Na^+ ratio will exceed 1.8. Proceeding along this line of reasoning, the air continuing on a continental trajectory would have access to small amounts of sodium but not chloride, again lowering the ratio. This explanation was offered to fit the trend of the Cl^-/Na^+ ratio observed in Sweden, shown in the graph below.



It should be noted that this trend is not evidenced in the United States, and thus far no suitable theory has been offered to explain this difference in observations for the United States and Sweden.

MIYAKE (1948) and SUGAWARA (1949) proposed an explanation based on a mechanical separation of the salts in sea spray, the separation presumably effected by the order of formation and release of solid precipitates as the sea spray droplets evaporate. Because of their relatively low hygroscopicity, certain components would then be carried much further inland before being brought down in precipitation.

All of the preceding theories are conjecturable. The author does not attempt to appraise the validity of any of them. However, in view of the evidence presented here for ground-to-air movement of material, a complex hypothesis of chloride fractionization is not necessary to explain the Cl^-/Na^+ ratios in precipitation over the United States. The Cl^-/Na^+ ratios are no more anomalous to sea-water composition than the other ratios presented in this paper.

In addition, further support for the likely importance of continental aerosols is provided by TWOMEY (1960). He has shown that large numbers of cloud nuclei are released from the soil surface when it is heated by radiation in dry conditions. This process, together with wind erosion, could conceivably furnish the quantities of continental material to the atmosphere that are indicated in Fig. 1.

4. Conclusions

From the observations presented the following conclusions seem justifiable:

1. Excluding the immediate coastal areas, marine aerosols appear to constitute a small portion of the soluble material brought down in precipitation over the United States.

2. The major portion of the continentally derived aerosols do not appear to travel very far from their source areas before being brought down in precipitation. Some extended transport with the prevailing circulation is evident; however, 200 to 400 miles appears to be the approximate maximum displacement of most particles.

If we assume these conclusions to be true, then it is likely that other large land masses, not just the United States, produce large quantities of aerosols. Even though much of the material blown into the atmosphere is apparently brought down close to its source region, a considerable amount likely finds its way into the upper atmosphere. Once into the prevailing wind field aloft, the material would be carried great distances and be distributed widely, both vertically and horizontally. For this reason it is improbable that an air mass can be found that is truly "pure" oceanic or "pure" continental in respect to the aerosols contained therein. This effect, together with small quantities of meteoric and volcanic dust, might explain why even over exclusively oceanic areas the ratios in precipitation seldom duplicate those in sea waer. Particular locations in point are Tatoosh Island, the most northwestern point of Junge's network, and Bermuda, where it can be assumed that there is little probability of a local addition of continental aerosols.

If, on the other hand, we assume the preceding conclusions to be invalid, then the chemical processes affecting aerosols must be a great deal more complex than previously considered. Potassium and sodium would have to be undergoing some sort of fractionization processes similar to those already theorized for chloride. With the data presently available, this would seem to be the least plausible of the two explanations.

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