On the origin and composition of atmospheric calcium compounds

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ABSTRACT

Measurements were carried out using an impactor and a photometric method, to determine the mass-concentration of both soluble and insoluble calcium particles. The calcium content of precipitation waters was also investigated. On the basis of the obtained data some estimations were made on the possible origin and composition of atmospheric calcium compounds.

1. Introduction

In a previous paper the numerical concentration and size distribution of both soluble and insoluble calcium particles were presented (MÉSZÁROS, 1965*a*). The identification was carried out in this case by the so-called single particle method using an impactor of circular jet (MÉSZÁROS, 1965*b*). However, it seems that, in some cases, the bulk analysis is more suitable for the determination of the total mass-concentration (MÉSZÁROS, 1964). For these reasons analyses were made employing a bulk method, to identify atmospheric calcium particles aiming at the estimation of their origin and composition. It should be mentioned that the operative measurements of the mass-concentration of atmospheric calcium in the European network (EGNÉR & ERIKSSON, 1955) are carried out for monthly periods. In this work, however, the identification of calcium was made on aerosol samples collected for relatively short time intervals by an impactor (MÉSZÁROS, 1965*b*).

2. Experimental procedure

Atmospheric particles were captured on clean glass slides by an impactor having about 50 per cent collision efficiency in case of particles with a radius of 0.3 μ. Several cubic meters (5–20 m^3) of air were sucked and in the case of soluble calcium particles the sample was washed out by 2 ml of distilled water. But if the total concentration of atmospheric calcium (both soluble and insoluble) was measured, the sample was placed, before the washing-out, in the vapour of hydrochloric acid for ten minutes.

After filtration the obtained solutions were analysed using a photometric method (BARCZA, 1964) similar to that proposed by WILLIAMS & MOSER (1953). In this method the calcium is tested by murexide (ammonium purpurate). The colour of the murexide in an alkaline medium (pH > 11) is bluish violet, but it gives with calcium ions a complex of reddish colour. The colour difference, which is characteristic of the quantity of calcium ions, was determined by a Pulfrich photometer (Carl Zeiss, Jena, East Germany). The method follows Beer's law in concentrations of calcium up to 1.2 mg/l, while the minimum measurable concentration is about 0.2 mg/l. The calcium content of precipitations presented in this paper were also determined by the aid of this procedure.

In some cases the identification of chlorides and sulfates were carried out simultaneously. The analyses of these ions were made by nephelometric methods (MÉSZÁROS, 1964).

3. Atmospheric calcium particles

Samplings were carried out in the period July 1964 to August 1965 in the Aerological Observatory of Budapest. During this time 73 samples were taken for soluble and 37 samples for all calcium particles. The results are summarized in the Table 1 for the summer (April-September) and winter (October-March) half-years. The values of calcium concentrations are expressed in μg/m^3 STP, while the number

of observations are in parentheses. First of all it can be seen that the greatest difference occurs between summer and winter half-years in the case of water-insoluble calcium (greater concentration in summer). This fact seems to help the hypothesis according to which these particles are of mineral origin (composed most probably of $CaCO_3$).

Concerning the water-soluble calcium particles the situation is more complicated: The mass-concentration of these particles is greater in the winter half-year, but the difference is not characteristic. The corresponding values gained by the single particle method are in the summer 0.013 $\mu g/m^3$ and in the winter 0.006 $\mu g/m^3$ (MÉSZÁROS, 1965*a*). That is, the discrepancy between these two types of analyses in the summer is not significant. This means (MÉSZÁROS, 1964) that the soluble calcium particles in the summer are relatively pure. On the other side the difference in the winter is more appreciable, the particles in this half-year are partly mixed. However, it is indubitable that in the summer the soluble particles take their origin directly from insoluble calcium particles. This is confirmed by the data of Fig. 1. in which the connection of soluble and insoluble calcium is plotted according to ten simultaneous samplings taken in the summer. In spite of the fact that the number of observations were small, the direct correlation is evident, as contrasted with the winter half-year when no such a correlation was found. Thus it follows from these data that soluble calcium particles are partly of mineral origin and partly man-made. It is interesting to note that as long as in the summer the majority of calcium (two thirds) is insoluble, in the winter half-year the quantities of insoluble and soluble calcium are roughly the same.

In the course of further investigations it was

TABLE 1. *Mean mass-concentrations ($\mu g/m^3$ STP) of different calcium particles in the summer and winter half-years. Number of observations in parentheses.*

Half-year	Soluble	Insoluble	All
Summer	0.020 (28)	0.056	0.076 (27)
Winter	0.026 (45)	0.030	0.056 (10)

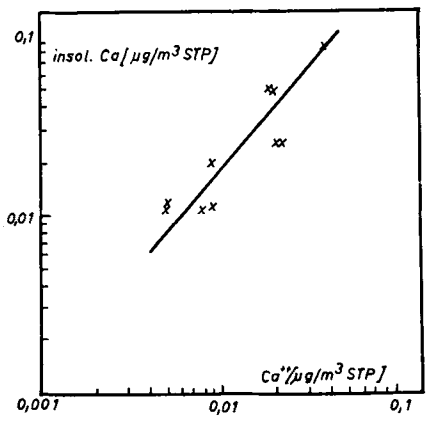

FIG. 1. Connection between mass-concentrations of soluble and insoluble calcium particles in the summer half-year.

considered to be desirable to determine whether these soluble calcium particles contain calcium bicarbonate or not. For this purpose a very simple test was used (BARCZA, 1964). In some cases air-samples of 40 m^3 were sucked through the impactor. The samples were washed out by 4 ml of distilled water. 2 ml of the obtained solution were analysed immediately, while 2 ml were boiled during fifteen minutes to transform calcium bicarbonate to calcium carbonate (the loss caused by evaporation was retrieved by distilled water). After filtration this solution was also analysed and the results were compared. No differences were found.

Efforts were also made to determine the connection between the soluble calcium and sulfates. But the connection was found to be fairly poor (there is rather some tendency to an inverse relation mainly in the summer). The same was the result with chloride particles, but in some cases relatively high calcium and chloride concentrations were simultaneously measured. Thus it is not impossible that a part of soluble calcium particles contains chloride. But these results are not very characteristic, because the quantities of sulfates and chlorides are much higher than those of calcium (the proportions are far greater than stoichiometric proportions), that is, other effects may efface occasional relations.

It should be mentioned that the calcium concentrations presented in this paper are rather low, but this fact can be explained if one takes into consideration that samplings were

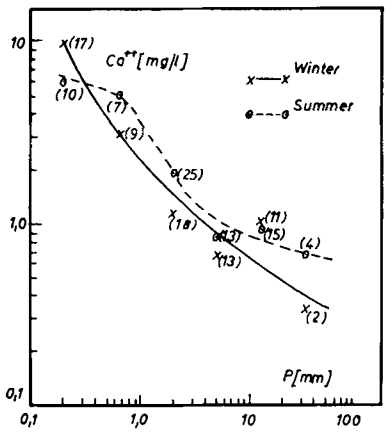

FIG. 2. Correlations between the quantity and calcium content of precipitations in the winter and summer half-years. The number of cases are in parentheses.

made regularly at noontime (great thermal exchange) with clean glass slides (loss of insoluble dry particles).

4. Atmospheric precipitations

It is rather difficult to determine seasonal variations of the mass of certain ions in precipitation waters, because this also depends upon the quantity of precipitations (JUNGE, 1963). For these reasons the mass of calcium and the quantity of precipitations were compared for both the summer and winter half-years in order to expose seasonal variations. The connections, plotted in Fig. 2, were calculated from data obtained by daily precipitation samplings carried out in the Aerological Observatory of Budapest during the period mentioned above. It can be seen that the summer values are generally higher, which also confirms the mineral dust hypothesis. It is interesting to note here that in winter months (December–February) the quantity of calcium ions in rainfall is smaller (0.94 mg/l on an average) than in snowfall (2.4 mg/l on an average). This means that an average snow crystal has a better collection efficiency for calcium particles than an average rain-drop.

By the help of this simple test described above, the concentration of calcium ions, probably associated with bicarbonate ions in precipitation water, was also determined in fifteen

TABLE 2. *Ratio between the quantity of calcium ions associated with bicarbonate ions and all calcium ions in precipitations.*

The mean ratio was calculated from mean concentrations. The concentration values are expressed in mg/l.

All Ca^{++}	Ca^{++} with HCO_3^-	Ratio %
1.4	0.80	57
2.7	1.1	41
2.9	0.5	17
16.4	6.8	41
1.5	0.9	60
2.8	2.8	100
1.2	1.2	100
0.90	0.90	100
1.1	0.90	82
0.54	0.16	30
0.91	0.52	57
1.9	1.1	58
1.2	0.77	64
1.3	0.71	55
0.34	0.34	100
Mean: 2.47	1.30	53

cases. Table 2 gives the results obtained. It can be seen that the proportion of calcium associated with bicarbonate to all calcium is in the range of 17–100 %. On an average about one-half of calcium is calcium bicarbonate. That is, in precipitation waters the lime and dolomite particles become partly soluble calcium bicarbonate through the action of atmospheric carbone dioxide (but it seems to be interesting to note that this reaction does not take place in aerosol particles).

Thus the following question arises. How do

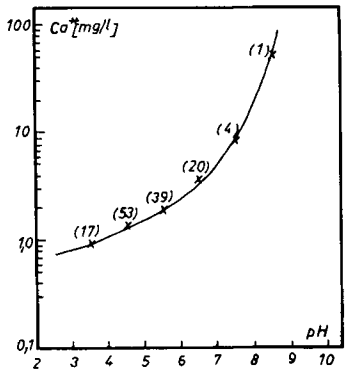

FIG. 3. Connection between pH values and calcium concentrations of precipitations. The number of cases are in parentheses.

the other calcium ions come into being in the precipitations? It is not impossible that a part of these ions is formed by the interaction of some acids and calcium carbonate particles (of course in winter the effect of soluble particles, the composition of which is not known, may also be important). To prove this hypothesis the connection between the quantities of calcium ions and pH values was determined. The curve obtained is plotted in Fig. 3. One may see that the correlation is very good, but the increase of pH continues after the value of 7, which cannot be explained by the decrease of the quantity of acids. It is not improbable that this phenomenon is caused by the hydrolysis of bicarbonate ions also formed from lime particles, but for the correct elucidation of this problem more researches are needed.

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REFERENCES

Barcza, L., 1964, Private communication.

Egnér, H., and Eriksson, E., 1955, Current data on the chemical composition of air and precipitation. *Tellus*, **8**, pp. 134–139, and subsequent issues.

Junge, C. E., 1963, *Air Chemistry and Radioactivity*. Academic Press, New York and London.

Mészáros, E., 1964, Remarks about chemical methods used in aerosol researches. *Tellus*, **16**, pp. 469–471.

Mészáros, E., 1965*a*, Identification of calcium particles in the atmosphere. *Studia Geoph. et Geod.*, **9**, pp. 68–73.

Mészáros, E., 1965*b*, Mesure de la concentration des particules de chlorures atmosphériques. In *Aerosols, the Physical Chem. and Appl.*, Prague, Publ. House of the Czechos. Ac. of *Sci.*, pp. 529–534.

Williams, M. B., and Moser, J. H., 1953, Colorimetric determination of calcium with ammonium purpurate. *Anal. Chem.*, **25**, pp. 1414–1417.

ПРОИСХОЖДЕНИЕ И СОСТАВ АТМОСФЕРНЫХ СОЕДИНЕНИЙ КАЛЬЦИЯ

Была измерена с помощью импульсного и фотометрического методов массовая концентрация частиц растворимого и нерастворимого кальция. Также был исследован кальций, содержащийся в воде атмосферных осадков. На основе полученных данных сделаны некоторые заключения о возможном источнике и составе соединений кальция в атмосфере.