Estimation of the background contamination of the atmosphere from the chemical composition of precipitation[1]

By E. S. SELEZNEVA, *Voeikov Main Geophysical Observatory, Leningrad, USSR*

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ABSTRACT

The relationship of marine and continental constituents in precipitation is considered and the values of the background concentrations for different geographical regions are defined. On the basis of these relations, conclusions are drawn concerning the geographical variations of the background contamination of the atmosphere and of the local source contribution, which depends on natural conditions and man's activity. Over the continental areas of the USSR the background level averages 30–40 % of the total contamination, the local sources contribute 60–70 %, of which 20–30 % can be attributed to natural sources (soil dust, etc.), and the rest to contamination of anthropogenic origin, the latter even for the most remote clean regions being about 20–30 %.

Introduction

The investigation of the chemical composition of atmospheric precipitation on territories as vast as the continents prompts consideration of the question of the origin of pollutants and the relative estimation of background air pollution. Studies carried out in the USSR offer such a possibility. During the last 10–12 years a considerable number of stations, situated chiefly in the rural regions, have gathered monthly precipitation samples with necessary precautions to avoid additional pollution. Average characteristics drawn from the results of the analysis of these samples are summarized in the form of maps and give a geographical picture of the change of the chemical composition of precipitation.

By the spatial distribution of some components and the overall mineralization of precipitation their connection with geographical landscape zones is revealed (Petrenchuk & Selezneva, 1970; Selezneva & Drozdova, 1966). This can be considered as an index of the influence of natural factors. Marine and oceanic effects are clearly expressed, too, as is well known from many works of other authors (Junge, 1963; Leeflang, 1938; Zverev, 1962). We note that high concentrations of chlorides in the precipitation over coastal zones quickly decrease with distance from the shore, which shows the limited role of the sea (Svistov & Selezneva, 1966). Precipitation on land is influenced by other sources, among them human activity.

Depending on physical-geographical conditions, the relationship of the contributions of natural and anthropogenic factors to the mineralization of precipitation changes considerably. It is very difficult to determine the contribution of separate sources, though it is possible to try to estimate approximately the most important ones.

First of all, one can separate the constituents of marine and continental origin, the latter implying both terrestrial and anthropogenic substances caught by precipitation.

Various approaches can be used for estimation of the marine component of precipitation. One is based on the supposition that the composition of cloud water is determined by hygroscopic nuclei primarily of a marine nature and in the sub-cloud layer precipitation captures the contamination of continental, sometimes of limited local origin. This proposition is accepted unconditionally by some investigators (Alekin, 1970; Voronkov, 1968), but it needs specification. In the works of O. P. Petrenchuk et al. (Petrenchuk, 1968; Petrenchuk & Drozdova, 1969) it is stated that pollutant concentration in the water samples from low internal air-mass (especially subinversion) clouds depends on the

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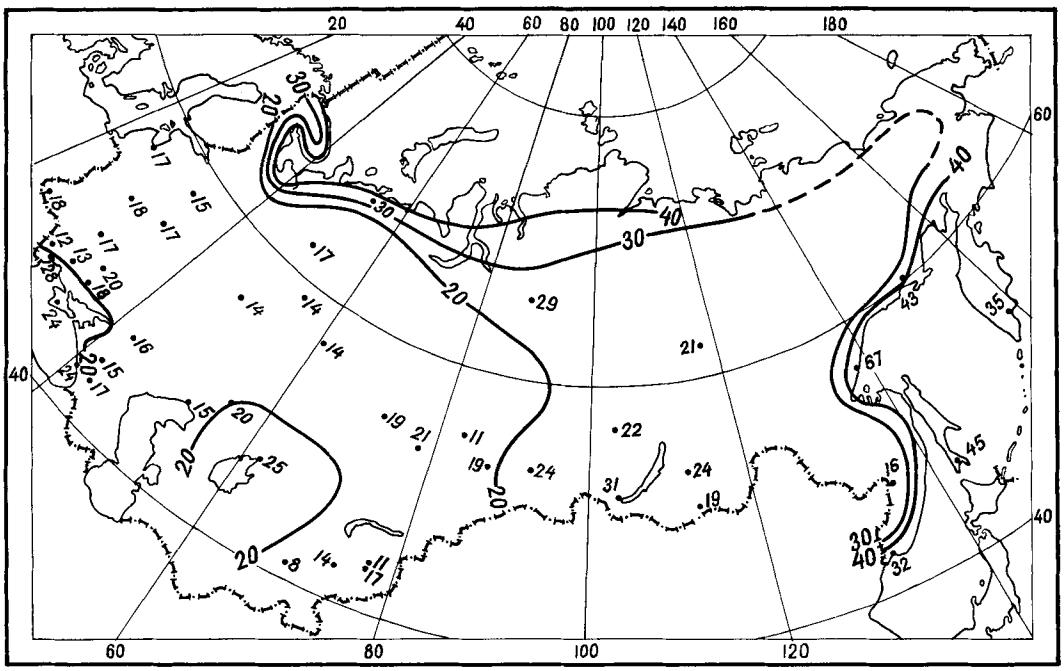

Fig. 1. Relation of sea chlorides to the total sum of the admixtures in precipitation (% %)

pollution level in the lower layer of the atmosphere. The water pollutants from such clouds are of marine origin only in coastal conditions or directly above the seas, whereas inland they should be attributed to continental sources. The effects of local air pollution are considerably less evident in frontal cloud systems and are probably dispersed only within the lower part of the cloud layer. The mineralization of water gathered in Nimbostratus is comparatively stable and on the average the total concentration of soluble substances constitutes 6–7 mg/l (Petrenchuk, 1968, 1969) and in the distant northern regions 2–3 mg/l.

Yet, not all the constituents of cloud water can be attributed to marine sources, as is seen from their composition; besides chlorides, the ions of SO_4 are always found in the samples. Compounds of sulphur dispersed in the atmosphere contribute to the general background air pollution. We shall refer to this question later.

On the whole, according to the data of O. P. Petrenchuk, the contribution of clouds to the mineralization of precipitation constitutes 40–50 % in the northern regions of the USSR and in zones of tundra and taiga, 25–30 % in central Europe, 20–15 % in the inner continental regions and in Central Asia.

A second method of estimating the marine constituents of precipitation is based on the proposition that ion relations characteristic of sea water are retained in cloud- and rain-water. These relations are expressed in parts of chlorine, for example. Supposing that all chlorine in the precipitation is of marine origin, one can calculate the sum of sea ions on these relations. In this way Dr Junge calculated excess SO_4 over the USA (Junge, 1965).

The sum of sea ions is calculated in the above-mentioned way and their proportion (in per cent) of the total mineralization of precipitation is determined for all sampling stations. The results are presented in Fig. 1. Here it can be seen that the contribution of sea salts to the precipitation admixtures constitutes 70–80 % at the coastal stations, decreases to 40–30 % at a distance of some kilometres from the shore, and is equal to 15–20 % over the rest of the territory. From this, one can note that the proportion of sea admixtures is somewhat higher (20–25 %) in the cleanest regions than in the regions with a high level of air pollution where

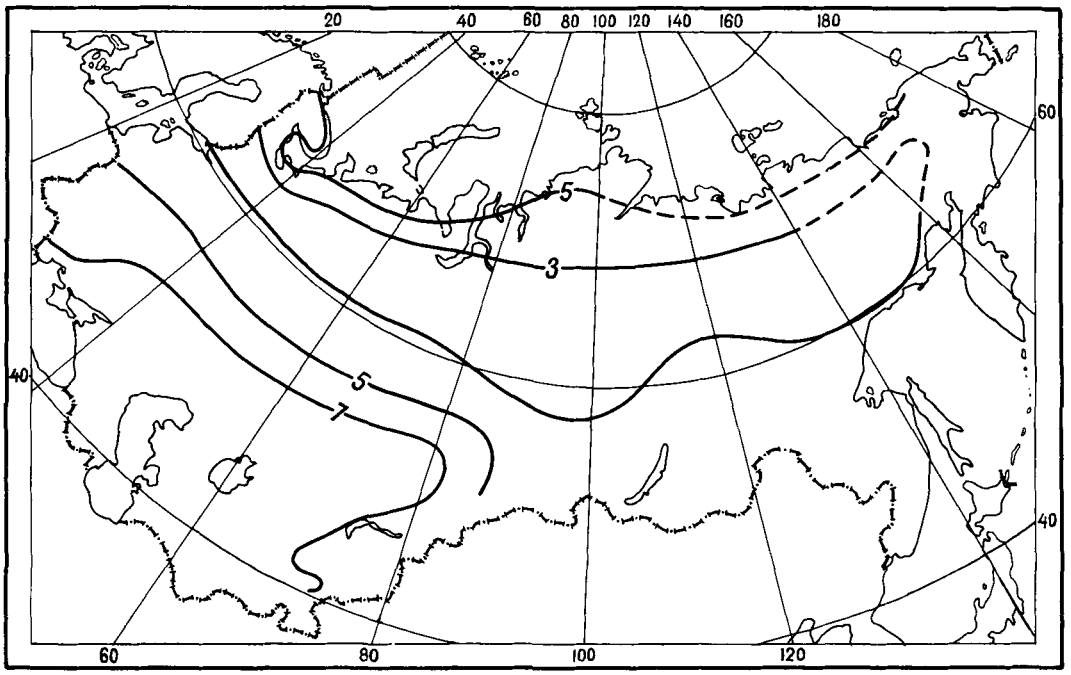

Fig. 2. Minimum monthly sum of ions in precipitation (mg/l).

the contribution of the sea constitutes only 10–15 %.

The given values for continental regions are probably overestimated as there may be additional sources of salt aerosols and chlorine, for instance saline soils, industrial discharges, etc. But even this overestimated proportion of marine admixtures in the precipitation is not large (15–20 %), and the greater part of precipitation constituents on the continent (80–85 %) is of another nature.

In each region the pollution of the air and consequently of the precipitation is a result of combined background and local sources. An estimation of the proportion of background pollutants in precipitation may be attempted by either of two methods.

1. First, we presume, as mentioned above, that aerosols dispersed everywhere in the atmosphere include sulphur compounds besides chlorides of marine origin. This proposition follows from a consideration of experimental data. In reality, the ions of SO_4 are always discovered both in the precipitation and in the cloud water. In the cleanest samples the concentration of these ions constitutes 2–3 mg/l, sometimes about 1 mg/l; the same values are found for cloud water, too. We shall take these values as background levels for the given ingredient of precipitation. According to these experimental data it is possible to state approximate geographical differentiations of this value.

The total amount of sulphates estimated in this way and of the sea chlorides calculated above will comprise a 'background' part of precipitation composition. This is equal approximately to 30–40 % of the total mineralization of the precipitation.

2. The second method of estimating the background is based as follows. In the periods of the most abundant precipitation (mainly in the warm half-year) the atmosphere is cleansed of local pollution and mineralization of precipitation becomes insignificant. One can suppose that precipitation constituents in these conditions are determined by the general background state of the atmosphere. As we have carried out long-term observations (about 10 years) and for this period the number of monthly samples at each station is about 100 (at some stations even more), the minimal sums of ions obtained from the results of the analysis can be considered

characteristic for each of them. We take these minimal values as background levels. Their distribution is shown in Fig. 2.

The background contribution to the mineralization of the precipitation is equal to 3–5 mg/l over most of the area; this value is increased to 7–9 mg/l in the most polluted regions to the south.

On the basis of these data one can note the non-uniformity of the background of air pollution and the zonal character of its change, approximating the average mineralization of precipitation.

We may note that the minimum concentrations of the pollutants in the precipitation (Fig. 2) are close to those obtained from the sum of marine chlorides and background sulphates; in most cases they differ by 10–20 %, which difference is considerably greater in only a few stations.

Thus, according to these two estimations, background components in the precipitation constitute 30–40 %; the other 60–70 % of the admixture is due to regional sources which can be both natural and anthropogenic. To separate these pollutants according to their origin is even more difficult, but calculations may be made and a rough approximation given.

Thus, natural soil dust (mineral and organic) is found in the precipitation mainly in summer; in the cold half-year in the presence of stable snow cover this pollution source in the precipitation is excluded. In winter, besides principal background constituents, there are admixtures which are due to man's activity, mainly to industrial furnaces and household heating. The following ingredients of summer precipitation can be conditionally considered as terrestrial: HCO_3^-, Mg^{2+}, K^+, Ca^{2+}, NH_4^+ and NO_3^-. The same ions in the cold half-year plus excessive SO_4^{2-} for the whole year can be considered as ingredients of anthropogenic origin.

To make these estimations more detailed it is necessary to take into account the composition of soil in different regions and also the periods of snow cover and abundant moistening of the soil which prevents the formation of dust. Of course, there are known cases of violent dust storms in the southern regions in winter. But these phenomena are rare and must be studied separately.

For previous estimation the year was divided in two half-years: cold (from November to April) and warm (from May to October). For the stations in Central Asia the warm period is increased to 8 months (from April to November).

The calculations fulfilled in these conditions show that the terrestrial components of precipitation amount to 20–30 %, in arid regions 35–40 %, increasing to 10–15 % in some northern coastal stations. The total contribution of terrestrial and background components of precipitation is 50–60 %. Consequently, 40–50 % derives from anthropogenic pollutants.

It is significant that the anthropogenic contribution to precipitation admixtures is 20–30 % even in the cleanest regions at a great distance from industrial centres.

One can judge, to some extent, the spread of industrial effects by the content of sulphur in the precipitation. For this purpose, excess sulphur, that is its estimation above the background concentration, was calculated. The following ratios of excess SO_4 to total SO_4 content in precipitation were determined: in most regions, 60–70 %; in more polluted regions, 70–80 %; in cleaner regions, 30–40 %.

It is interesting that in some regions the excessive concentration of SO_4 exceeds by more than twice the background concentration of this component stated above.

Let us compare this estimation of excess sulphur, in relation to background levels, with some global indices.

The emission of sulphur into the atmosphere from combustion of coal and other fuels by world industry and sulphur removal by precipitation have been evaluated more than once, by different authors.

The first to do so were Eriksson (1959) and Junge (1960), followed by other authors (Selezneva & Drozdova, 1966; Alekin, 1970). The estimations differ somewhat due to the variation in the accepted amount of world coal consumption and average values of SO_4 concentration in the precipitation. Thus, Junge accepts as an average for the land the value of 2 mg SO_4/l. Evidently this value is reduced in modern conditions.

The average concentrations of SO_4 in precipitation over the territory of the USSR vary between 2 and 12 mg/l; in the USA (Junge, 1965) between 1 and 10 mg/l. On the average, for the continents of the northern hemisphere, one can accept the value of SO_4 of 4–6 mg/l and the value evaluated for sulphur of 1.5–2 mg S/l.

Over the oceans, judging from our coastal stations, even the excess concentration from the point of view of Junge (that is, exceeding only the marine component) constitutes not less than 2–3 mg SO_4/l or about 1 mg S/l.

Taking into account these values we obtain that 2.4×10^8 tons of sulphur is removed from the atmosphere by precipitation (1.8×10^{17} l) in the northern hemisphere annually.

If it is assumed that at present 3×10^9 tons of coal and $(1–2) \times 10^9$ tons of oil are consumed in the world, 2×10^9 tons of ore and other materials are processed; as a result, 8×10^7 tons of SO_2 or 4×10^7 tons of sulphur are discharged into the atmosphere during the year.

These values grow from year to year. Thus, the world consumption of coal, the burning of which discharges the bulk of sulphur into the atmosphere, was recently estimated as 2×10^9 tons (Selezneva & Petrenchuk, 1968). It is necessary to take into account its present growth in value which will probably continue to increase in the future. It can be pointed out that some authors are already indicating higher values than the above-mentioned (for example, Robinson & Robbins, 1970).

If these discharges refer only to the northern hemisphere, they then constitute 17 % of the sulphur removed by precipitation. When calculating for the world as a whole, this percentage will decrease, but will still constitute a rather considerable value, probably about 10 %.

The above-mentioned relations received for various regions differ considerably from this global relation. In most of them the proportion of excess SO_4 exceeds 50 % of the total content of SO_4 in the precipitation; only in the cleanest regions is it 30–40 %. This result cannot be explained only by high air pollution by industrial sulphur. The fact is that the sulphur compounds in the atmosphere evidently have other sources which are not completely known and not yet evaluated.

One can hope that it will be achieved in the nearest future, particularly in connection with the investigation of background characteristics of the atmosphere. The cited approximate estimations of the relation of components of varying origin in the precipitation give an idea of the contribution of main sources in the air pollution. This is important because it is so very difficult to make an estimation of the origin of the natural atmospheric pollutants in any other way.

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ОЦЕНКА ФОНОВОГО ЗАГРЯЗНЕНИЯ АТМОСФЕРЫ ПО ДАННЫМ О ХИМИЧЕСКОМ СОСТАВЕ АТМОСФЕРНЫХ ОСАДКОВ

Рассмотрено соотношение примесей морского и континентального происхождения в атмосферных осадках, определены значения фоновых концентраций для разных географических районов. На основании этих соотношений сделано заключение также и о географической изменчивости фона загрязнения атмосферы и вклада местных источников, связанных с природными условиями и деятельностью человека. Над континентальными районами СССР вне городов фоновая часть в среднем составляет 30–40 % от общего загрязнения, локальные источники вносят 60–70 %, из них 20–30 % можно отнести за счет естественных источников (почвенной пыли и др.), остальное — загрязнения антропогенного происхождения, причем даже для наиболее удаленных чистых районов антропогенный вклад составляет около 20–30 %.