Chemical Events in the Atmosphere and their Impact on Environment
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EFFECTS ON SOILS OF CHEMICAL EVENTS IN THE ATMOSPHERE

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1. Introduction

Once a basic understanding of plant nutrition was reached, there arose among the scientists an interest in the relationship between atmospherical chemistry and soil chemistry. At the very early stages attention was focused on nitrogen. This element had often proved to be a minimum factor — to use Liebig's term (Liebig, 1840).

It was soon shown that electrical discharge could result in binding atmospherical nitrogen to oxygen. This reaction principle was technically introduced in Norway at the beginning of this century in connection with the production of nitrate after Birkeland-Eyde's method (La Société Norvégienne . . . 1957). Before the problem of industrialized production of fixed nitrogen was solved, scientists were largely concerned with the amounts of this material added to the soil by precipitation. Comparatively comprehensive investigations were carried out at many places in the world (Eriksson, 1952). Even if the analysis methods were rather primitive, the results of the registrations were of great value. The results showed that the allowance of nitrogen from the atmosphere were small in comparison to the required amount in order to obtain large crops for most of the cultivated plants.

Likewise, contributions of other elements by precipitation were studied. Because the concentration of many elements was so sparse, it caused difficulties in analyses.

At an early stage it was proved that small particles derived from volcanic eruptions and from sand storms in deserts could be transported

a long way by global air currents. Such findings helped the understanding of important circulation processes in the atmosphere.

2. Nuclear explosions in the atmosphere

The nuclear bombs over Hiroshima and Nagasaki, and the later atmospherical detonations created a new type of soil problems. Radioactive elements in the air came with time into the soil, were later taken up by the plants and thus became dangerous in animal and human nutrition.

Throughout the world comprehensive investigations on quantities of radioactive fall-out took place. Because most of these registrations were carried out by military authorities only few of the results have been published. Investigations started to find out how to prevent or diminish the injurious effects. For example, other compounds were added to the soil to reduce the uptake of radioactive elements in plants. The results from this type of investigations were published to a greater extent.

After the decision that nuclear explosions in the atmosphere should come to an end, the interest for these problems ceased.

3. Investigations of chemical precipitation - the geophysical year 1957-1958

Great improvements in analytical techniques during the last fifty years have made it possible to start the investigation of problems previously thought to be practically impossible. The new methods resulted in quicker and more reliable analyses of chemical composition. Some trace elements, which earlier could only be determined semi-quantitatively, were now presented by exact data.

In the 1940's Swedish scientists took up the question of the chemical composition of the precipitation. A number of stations were established in order to collect samples. In Scandinavia we have a close cooperation for many agricultural scientific tasks. As the precipitation amount varies much more in Norway than in Sweden the question of establishing such stations in Norway was raised. In autumn 1954 sample collection was started at three places in Norway.

The establishment of the geophysical year 1957-1958 gave the

impetus for a great intensification of these precipitation investigations. The number of Norwegian stations was increased from 3 to 12.

4. Increasing interest in atmospherical pollution

As pollution with radioactive elements ceased, the allowances to the atmosphere from polluting material from industry and from common consumption in the urbane society increased. Many interesting discussions have taken place on whether the climate has been affected. The significance of changes of ozone, carbon dioxide, and dust has been researched.

Atmospherical pollution can have a direct influence on soil chemical conditions. Some gases formed by burning the fossil materials coal and oil, will go over to acids in the atmosphere. Acids from atmospherical pollution are added to the soil surface with precipitation. Recently extensive investigations related to damage caused by acid precipitation have taken place and in parts great injury has been observed. Other types of pollution as well as acids take place.

In many countries, both in Europe and America, data have been published from large projects. A number of textbooks have been written, and new journals have been established.

5. Some soil chemical investigations in Norway

a) *Geographical variations in the contents of elements in uncultivated soils*

The analyses of precipitation water from 12 different stations in Norway showed great geographical variations (Låg, 1963). For example, the quantities of Na and Cl added to the soil surface were respectively 111 and 191 times higher at Lista than at Vågåmo. We had expected great variations, but the differences were even higher. As the analytical material increased, so did the interest to reveal if the chemical differences could be traced back to the soil.

Almost at the same time as we planned the chemical investigation of precipitation, we started a simple systematical registration of tbe forest soils. It began with investigations in the field, but from 1960 to 1964 also sampling of humus from the three counties: Nord-Trøndelag,

Oppland, and Buskerud, for laboratory analyses was included. A comparison of the investigations of precipitation and humus gave very interesting results.

The analytical figures for the humus samples in Nord-Trøndelag showed that the exchangeable sodium and magnesium decreased strongly from the coast towards inland (Låg, 1962). The concentration of calcium had a corresponding increase. The analysis of the samples taken in Oppland and Buskerud confirmed these tendencies. A similar distribution as in sodium and magnesium was found for the three halogenes: chloride, bromine, and iodine (Låg and Steinnes, 1976). We were somewhat surprised to find a rather similar geographical distribution pattern for selenium as for the mentioned typical sea-salt elements (Låg and Steinnes, 1974, 1978). As far as I know, this is the first time such relationship between the amount of soil selenium, precipitation, and distance from the sea has been pointed out.

In earlier times the precipitation water was supposed to be almost as pure as distilled water. We are now aware that from the sea-waves drops come into the atmosphere and, in that way, sea-salts are included in the precipitation. The influence of the sea-water on the precipitation is greatest near the coast. It is supposed that some elements, to a certain extent, may evaporate directly from the sea-water and be transported by the air currents into the inland areas.

Attempts to find out how fast the content of sea-water salts decreases from the coast towards inland have been made. A distance corresponding to a 50% reduction is called "sea-salt decrease index". Preliminary figures for West-Norway show 50-100 km for some elements.

b) *Pollution from industry and ordinary public activities*

Many various types of industrial activities result in pollution of the atmosphere. The furnaces at the earlier mines were sources of pollution. Modern electrochemical industry brought other types of problems. Fluorine exhausted from aluminum factories has caused great damage in the vicinity. Some of these factories emit organic components that may be dangerous to health. Smoke from ferrosilicium, ferromanganese, and ferrochrome factories is really noticeable. Many factories which refine heavy metals spread polluting material.

More restrictive orders from the government with regard to combustion techniques have given improvements.

Cities and other densely populated regions have problems in getting rid of municipal waste. With the increase in oil prices a special interest for building incineration plants in order to exploit the waste material as a source of energy arose. But with present combustion techniques, great amounts of polluting material escape through the chimneys.

Common oil and coal combustions add pollution to the atmosphere. Sulphuric acid is a main factor in acid precipitation. Both industrial production and ordinary consumption are responsible for this type of pollution. In addition to sulphuric acid we also find some nitric acid in the precipitation. Both sulphur and nitrogen are vital plant nutrition elements. As a rule the plants will find sulphur enough in the soil but lack sufficient nitrogen sources. Many other elements are included in the incinerating gases.

In Norway comprehensive investigations of acid precipitation effects have taken place (Overrein, Seip and Tollan, 1980). Fish death caused by such influences in some districts in southern Norway has been proved. The soil material in this region is often shallow, coarse grained and derived from bedrock rich in silisium. The buffer capacity is therefore low and the acid effect of the precipitation will quickly be noticed. On the other hand, there has so far not been proved any decrease in the growth of the forest. In this connection we must remember that the acid precipitation also contributes with the nutrient element nitrogen.

We suppose that most of the sulphuric acid in the precipitation is transported with the global air streams. Approximately 10% come from inland sources. External air currents deliver many other elements. Micropulluting organic material that may cause cancer has been determined in very small concentrations. Whether the amounts in which they appear in the precipitation in Norway have any influence is unknown.

Investigations of soil samples have showed that lead, cadmium, arsenic, and to a small degree selenium have been brought with external air streams (Låg and Steinnes, 1978; Steinnes, 1978).

From our own road traffic the soil is contaminated through the atmosphere. But the lead quantities are lesser here than in countries with a more comprehensive car traffic.

Locally some industrial factories are responsible for a strong soil pollution.

Possible influence of ozone on vegetation has been discussed in later years.

c) *The uptake of elements in plants*

To a certain extent the plants may take up pollution elements directly from the air. The harmful fluorine components from the aluminum factories may to a great extent appear as a cover on the green plants. This type of consequence is only present as long as the pollution persists, contrary to effects from elements added to the soil.

Litter material from the vegetation returns to the soil and many compounds may again be taken up by the plants. In this way a circulation process continues between the soil and the vegetation. Whether the plants have been food for animals or humans before the remnants are integrated to the soil, making the circulation chain longer, has in principle no importance.

Many elements in the waste are essential in plant nutrition. Other elements are unnecessary for the plants but are needed for animals and humans. It is therefore favourable for these organisms tbat the elements are taken up by the vegetation when the plant material is meant for nutrition. Some elements are unnecessary both for plants and other organisms; but they are not harmful in adequate proportions. Other elements, again, are poisonous for plants and animals as well as for human beings. The plant species vary greatly with regard to the uptake of the various elements. If the soils are contaminated with poisonous elements which are easily taken up by the plants it may have a catastrophic result. With great concentrations the plants will die. If the quantities are not so high the plants may grow up, but may have such a concentration of toxic substances that it is dangerous to use the plant products in nutrition.

Until now the elements lead, cadmium, mercury, and arsenic have been mostly discussed as pollution elements. Of these the correlation between the content in soil and plant seems to be highest for cadmium.

With time we expect that other elements will be strongly involved when pollution is under consideration.

d) *Geomedical consequences*

With the expression geomedicine we understand the science dealing with the influence of ordinary environmental factors on the geograpbical distribution of problems of human and animal health (Låg, 1980).

During the last half of the nineteenth century relationships between iodine deficiency and goitre were described (Underwood, 1977). A

relationship between phosphorus deficiency in the soil and osteomalaci in cattle was mentioned in Norway (Vogt, 1888). These are typical, old examples of deficiencies of geomedical character.

The discovery of relationships between atmospherical and soil chemistry opened new possibilities for explanations of geomedical causes. Earlier, cases of goitre were often ascribed to the fact that people used too little salt-water fish in their diet. Recent investigations have shown, however, that in inland districts with low precipitation, the soil as well as the vegetation has a low iodine content (Låg, 1972). Whether the differences in the bromine content, which also was found, has any influence, is unknown.

Magnesium is essential for both plants and animal organisms. Grass tetany has caused difficulties in animal husbandry and the reason seems in many cases to be magnesium deficiency. In an agricultural experiment station in Smøla, western Norway, nearly every plant nutrient has been proved missing except magnesium and chlorine. We suppose that the soil is amply supplied by these elements through precipitation.

In human medicine magnesium has with time received greater attention, i.e. in relation to cardiovascular diseases. For example, it is mentioned that the relationship between magnesium and calcium may have an interference. Differences in climate chemistry giving variation in magnesium concentrations may have medical consequences.

Selenium is an element which for some time has captured great medical interest (see e.g. Spallholz *et al.*, 1981). About fifty years ago it was pointed out that a dangerous disease in animals, discovered in the USA in the last century, was caused by selenium toxicity (Underwood, 1977). Lately investigations have been particularly concentrated on selenium deficiency.

When the soil selenium decrease from the coast to the inland was proved, it was easy to understand that muscle degeneration in domestic animals due to selenium deficiency (Mikkelsen and Hansen, 1967, 1968) was concentrated in the valleys with low precipitation in the eastern part of Norway. Our neighbour country Finland, with a mostly typical continental climate, has from an early stage taken up the problem by adding selenium to the cattle fodder. In Finland, and in other Scandinavian countries as well, there is now a discussion on the possibilities of adding a selenium compound to commercial fertilizers to increase the selenium content in the plants.

A number of medical doctors are working intensively on the problems

of cancer, multiple sclerosis, and cardiovascular diseases which may perhaps be traced so selenium deficiency. In China the so-called Keshan disease has received a lot of attention in recent years. Selenium compounds are used for preventing this endemic disease (Chen *et al.* ,1981).

In many parts of the world deficiency of selenium and deficiency of iodine are found in the same regions. Often the soils in such places are comparatively young. Quaternary glaciation is the reason for a short time for soil formation in large areas. In mountain areas with disected landscapes erosion processes may lead to young soil profiles. Where soil formation has gone on for only a short period, the accumulation of selenium and iodine may be scarce. However, we should be aware that special concentration of selenium compounds in the bedrock may result in a high content in the soils in districts generally poor in the element.

Pollution elements in the atmosphere may result in changes in the soil with geomedical consequences. It has been reported that acid precipitation may be responsible for changes in soil and fresh-water causing such health problems as fish death.

Many other polluting compounds in addition to acids are transported long distances with the air currents. Analyses of soil samples from southern Norway have shown an increase in many undesired elements. Of course a very great accumulation of such material has not yet taken place.

From local sources poisonous elements have been spread through the atmosphere to the soil. Close to a zinc factory in Odda, western Norway, great concentrations of heavy metals in the soil and plants have been proved. The content of cadmium for example, is so high that warnings have been issued against substantial dependence upon food plants grown in the vicinity of the factory (Låg, 1975).

At Modum Blåfargeverk cobalt was produced from an ore with arsenic content. The factory was abandoned at the end of the last century. Soil and plant analysis showed a greater arsenic content than normal (Låg, 1978). Most probably the concentrations in the plants were much higher as long as the factory was driven. Comparison with preliminary figures given by FAO and WHO (1974) for acceptable limits for man show that it should not be dangerous now to use the plant products for nutrition.

Near abandoned furnaces an accumulation of copper has been found in the soil in Røros, mercury in Kongsberg, and nickel in Evje. In the

neighbourhood of a ferrochrome factory in Hardanger a great enrichment in the soil has been proved.

Incineration plants for municipal waste may lead to considerable soil pollution (Låg, 1982). Little has been done to evaluate such injury possibilities, but with the combustion technique and the gas discharges used nowadays, the natural content of some dangerous elements in the soil in the neighbourhood may be doubled during a relatively short period of time.

Because the injurious consequences of soil pollution may remain for an extremely long time, due to the circulation processes, special care should be taken into consideration in order to avoid unnecessary problems.

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DISCUSSION

MARINI-BETTÒLO

Thank you, Professor Låg. I have another question. You have mentioned a very important factor, that influences very much also the effect of acid deposition. The poor buffering properties of your soil. Which are mainly, granitic.

LAG

That is quite right, we have granite, gneiss and so on, compared with limestone and dolomite and such things; you have plenty of carbonates. We are in a worse situation in my country.

BROSSET

Thank you, Professor Marini-Bettòlo. I would just follow up your question about the mobilization of ions.

Now the problem is not only that there is acidification of soil, it is the acidification of ground water, and in the ground water there is a clear mobilization of aluminum ions, which is chemically quite normal. But what is a pity is that there are leakages, which means that we have dissolving and precipitating aluminum, and I am not an expert in that region but my colleagues who are studying just the forest damages tell me that there may be some deposition of aluminum hydroxide on the fine roots of the trees. There is another thing that I can tell you, that on the Swedish west coast, most of the beaches, when the households are using their own water, in copper tubes, they get their hair green now, because the acidity of water dissolves copper from the tube and young children have got stomach diseases. So that is similar to a catastrophe.

SALATI

I just want to add a comment on this new word that the scientists are introducing: *a geomedicine*. It will probably lead to a better knowledge of these diseases and of great ecological problems. In Brazil we have developed a research program in a central part of the Amazon, trying to understand a

little more about the immunology deficiency of the human being. And after several years of research it was found that there is zinc deficiency in the water and in the food in general. And this lack of zinc may raise a problem in the immunology of the internal human body.

LAG

That is very interesting to hear. I think that we have pointed to this type of problems, very complicated problems, so complicated that we must have specialists from different branches brought together in order to try to solve them. We must have medical doctors, we must have veterinarians, we must have physiologists, biologists and chemists etc. it is necessary to bring together persons with quite different backgrounds in order to go farther in what I think is a very important question. The Kashan disease in China was studied quite anxiously on now for a few years, and now seems to have got a practical solution. I do not think it is only selenium deficiency; maybe there are other factors too, but to help the population many are using selenium. Now we have some information, and it is very positive to read here how they have been able to help the population since they have results, where it may be possible to come to a positive conclusion.

BROSSET

Regarding this selenium I have heard different opinions. One is that it is acting as an antagonistic agent, immobilizing for instance mercury. It may immobilize also cadmium, because the selenites in question are quite insoluble. We know that in lakes where we have higher selenium content there is less mercury in the fish. This is of course not conclusive, but that may be an idea.

LAG

Yes, it is right that selenium has some antagonistic effects on other poisoning elements, and also I can mention interference with vitamin E, so that a combination of selenium and vitamin E can give quite a good result. The fact is that we know too little about it, but in other ways this is a question for further research.

MARINI-BETTÒLO

I think that selenium has a very complicated task in biogeochemical work. In small quantities it is necessary to build up some enzymes, which are necessary to animal metabolism. When it is in higher quantities, it can cause big drawbacks in the animal feed, and so on. So we must look at that as a quantitative phenomenon and not only as the presence of selenium itself.

HARE

I am sure Professor Låg knows this, but it is worth making the comment that of course the distribution of a very large number of diseases displays what is quite obviously non-random geographical distribution. There are concentrations of goiter obviously in iodine-deficient areas where the water supply is local. I can off-hand remember a dozen or more such diseases which display similar geographical inequalities, some of which are so far inexplicable, and in some jurisdictions there has been a similar geochemical mapping of those species that are known to be effective in a human physiological sense. British Columbia, for example, has been handled in this fashion in my own country.

There is a fascinating experimental possibility that has emerged there. There is one region of the province where there are two populations of human beings: those who derive their water from wells and those who derive their water from piped water supply which comes from a very long way off by pipeline. And one of my British Columbian friends is talking about taking these two populations and looking at the statistics of their health, of the incidence of deficiency disease in their health. I am sure that Norway and Sweden have done this kind of work. Is this the case? Have you parallel mapping of the geochemistry and the geomedicine?

LAG

Yes, that was very interesting to hear. I can mention then that we had in our Academy a symposium and we issued a book: *Geomedical Aspects in Present and Future Research.* That was arranged in 1978, and now in March next year we shall have a new symposium on the possibility of connecting geomedical work to geochemical mapping in the far North, north of the Polar circle; that is a mapping going on in Finland, Sweden and Norway and there is also some small activity in Denmark. So in 1984 we shall have a new

arrangement dealing very likely with your type of work and we should like very much to have good connections with scientists in Canada and USA.

Let me also add that selenium is comparatively a dangerous element in that way, that it is poison, toxic, and there is not a great difference between the necessary and the toxic dose. That makes it quite difficult to deal with these problems i.e. to add selenium in concentrats for animals. So has been done in Finland and Norway for quite a long time. But you see in the inland part of Norway with continental climate, we have much less of selenium than in the coastal area, so we must be somewhat more careful about this business because we could run the risk of giving too much. And exactly now there is being discussed in some countries the possibility of adding selenium to artificial fertilizers. I think in a few months the question will be settled. Certainly they have technical equipment all arranged, so perhaps next summer such fertilizers with selenium will be used.

CRUTZEN

I asked the word when I had not heard about Finland yet. You mentioned Finland in the last minutes of your talk, but there is a very interesting region in eastern Finland where the average life span is remarkably low and heart disease plays a role, and I know that some years ago the World Health Organization, instituted a major study there; and I wonder what came out of that, or it this study is still ongoing.

ROWLAND

A comment on the question of selenium distribution versus sulphur distribution. Although they are in the same column in the periodic table, the chemistry of sulphur and selenium is probably quite different. In rain water I think specifically that the action of peroxide on SO_2 is to oxidize it, but the action on selenium-4 is to reduce it. So that the probability of having sulphur and selenium behave the same in rain water, I think, is very low; but also when one thinks of the possible antagonism of selenium it's behaving as a reduced selenide rather than as being oxidized to selenate. I think the chemistry of selenium has to be considered quite separately from that of sulphur. Even selenium has been suggested as a possible tracer for sulphur in the eastern United States.