Chemical Events in the Atmosphere and their Impact on Environment
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CHEMICAL REACTIONS IN THE ATMOSPHERE AND THEIR IMPACT ON HUMAN HEALTH AND ANIMAL LIFE

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INTRODUCTION

A report on the impact on human health and animal life of chemical reactions in the atmosphere, i.e., mainly of the secondary pollution, is not easy because direct cause-effect correlations are very difficult to establish even for primary pollution.

Therefore I wish to report here a number of data I was able so far to collect, and submit them to you for your comments and discussions which will surely bring new views and contributions. I may recall first of all that it is quite difficult to correlate in general air pollution with effects on human health. Only in very special events (London, Donora, Meuse Valley) there was evidence of a direct correlation of concentration of chemicals in the air and rise of human casualties or diseases. In effect as a general rule the figures of the variation of the number of deaths and of persons suffering from specific respiratory illness (bronchitis, emphysema, etc.) in relation to air contamination (composition and concentration) are statistically significant only in very few cases, because of other sources of contaminants, e.g., habit of smoking, which largely contribute to health effects (Lave and Seskin, 1970; Marini-Bettòlo, 1971 and 1981).

Moreover the above observations apply to global air pollution due to the direct effect of emissions, individual or public traffic, etc., and to the fall-out of the chemical reactions in the atmosphere.

These are the reasons of the difficulty to distinguish the effects on biological systems attributed to normal pollution (primary) and those due to chemical reactions in the atmosphere (secondary pollution).

THE FUNDAMENTAL CHEMICAL PROCESSES

At this point it is necessary to establish which are the chemical processes of the atmosphere which may have an impact on life on the earth.

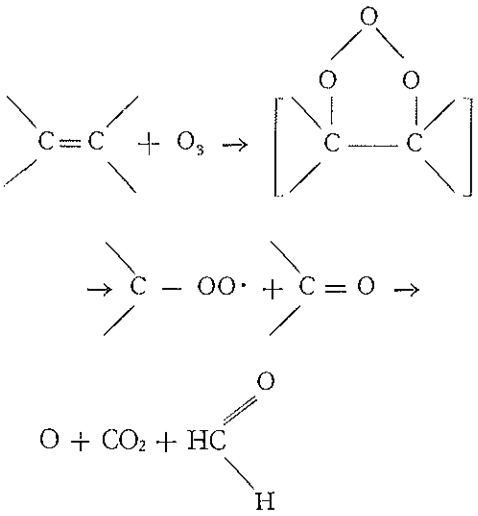
In the present approach we will deal only with the fallout of products which are detected and determined easily, not considering trace elements or other substances which may occasionally be present.

We may enumerate the most important chemical reactions occurring in the atmosphere, which have a direct effect, being then products deposited on the earth and in the lower atmosphere:

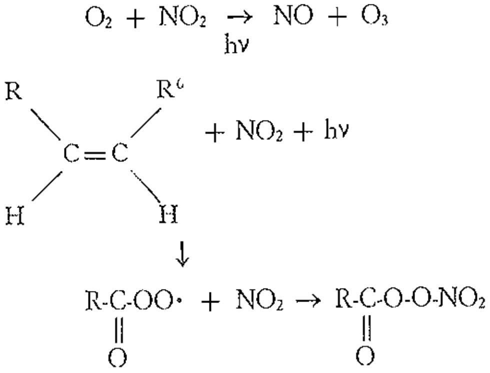
1) *Acid deposition*, e.g., acid fog, acid rain, acid snow.

The chemical composition of these products and their formation in the atmosphere are reported elsewhere in this volume (Brosset, Liberti) and thus I will only recall that the principal components are H_2SO_4 and HNO_3.

Ozone and Olefins



Peroxyacylnitrates formation



$$O_2 + NO_2 \underset{h\nu}{\rightarrow} NO + O_3$$

$$\underset{\underset{O}{\|}}{R\text{-}C}\text{-}OO\cdot + NO_2 \rightarrow \underset{\underset{O}{\|}}{R\text{-}C}\text{-}O\text{-}O\text{-}NO_2$$

2) *Oxidants*

Oxidants formed in the atmosphere mainly by photochemical activity are O_3, NO_2 and peroxyacylnitrates.

a) *Ozone* - O_3 is the main oxidant representing 90% of the oxidants present in the air, and is formed by photochemical reaction from O_2 in the presence of ultraviolet radiation (see pag. 341-375).

b) *Nitrogen dioxide* - NO_2 is formed, mainly from $NO+O_3$ NO_2+O_2. Moreover ozone can react with hydrocarbons to give other oxidants. Recent studies have cleared the mechanism of these reactions (Niki *et al.*, 1983).

c) *Peroxyacylnitrates* - Peroxyacylnitrates are compounds characterized by a peroxy group and by an adjacent NO_2 which makes the substances a strong oxidant but also very reactive and unstable.

These properties may account for their biological behaviour. Peroxyacylnitrates — mainly represented by peroxyacetylnitrate, indicated as PAN — originate in the atmosphere over towns and industrial areas, through a mechanism not fully clarified, from olefins, and other hydrocarbons (car exhausts, fuel from car tank evaporation, gas formed in the refineries of crude oil) under photochemical conditions by NO_x in the presence of O_2 (Stephen, 1969).

Peroxyacylnitrates constitute a part (about 10%) of the total oxidants and are formed in the city atmosphere in conditions of bright light.

The fallout, i.e., O_3+PAN, in particular atmospheric conditions, constitutes the so called *oxidant smog* or photochemical smog.

3) *Radioactive fallout*

It has been of great importance in the 1950's as a consequence of nuclear explosions in the atmosphere, and mainly for the contamination of food chain by the radioisotopes Sr^{90} and Cs^{137}. At present, since the nuclear explosions in the atmosphere have been abandonned by practically all countries, radioactive fallout does not have any more importance (except in the case of a nuclear war) and thus we shall not discuss this topic.

These phenomena were studied mainly in the northern hemisphere: it is very important that similar studies may be undertaken in the southern hemisphere where in some areas particular atmospheric conditions may occur (Marini-Bettòlo, 1972).

BIOLOGICAL EFFECTS

As mentioned, it is very difficult to establish clearly a direct correlation between global air pollution and the health of man. This because a great number of other causes may influence health, and only on a strictly statistical basis is it possible to establish some correlations.

Thus it is easily understandable that it is even more difficult, if not impossible, to establish a correlation of human health with a single aspect of the air pollution, i.e., of the secondary pollution, and with the pollutants formed by physico-chemical reactions in the atmosphere.

The same considerations apply to many animal species and even in this case it is very difficult to discriminate between the various causes.

It is statistically demonstrated that fog or smog with low pH are very dangerous for people suffering from respiratory and cardiocirculatory diseases, and that generally in areas where air pollution is present, the incidence of bronchitis and other respiratory diseases is also higher. Even in these cases it is not possible to determine a direct correlation of incidence of disease with a specific contaminant, although the greatest part of the responsibility of health troubles and even casualties has been attributed to SO_2 and H_2SO_4.

Many chemicals which have become ubiquitous contaminants of the earth: PCB, chlorinated hydrocarbons, have been recognized to be responsible for damage to wildlife, whereas it was not possible to correlate with specific effect the products formed in the atmosphere by secondary pollution.

This is not the case of fishes and other animals which live in lakes and streams. Although in this case also there is a great amount of other pollutants in the environment there is clear evidence of the effect due to the so-called acid deposition, for its complex impact on the surface waters.

Health effects on man

To establish the effects on human health of the fallout of the chemical species formed in the atmosphere, we have to distinguish between acid depositions and substances like ozone, PAN or other peroxides. In this case we have to follow a different approach, that is, we must establish, as proposed by WHO, the limits for some characteristic contaminants.

Effects of atmospheric acidity

In the case of atmospheric acidity, the biological components are H_3O^+, H_2SO_4 and HNO_3. The concentration of H_3O^+ is toxic, especially by inhalation. Therefore acid fogs, where pH is found also under 5, may be rather dangerous especially for persons suffering from respiratory diseases (Hilleman, 1983a). It is quite interesting that in acid fog SO^{-2}_4 and NO^-_3 content is different in ratio from the content in rain water, because of the concentration process due to the formation of fog. Nevertheless, the assessment of the effects on health, according to a recent report on acid fog, would be extremely difficult to evaluate, except in the case of dramatic events like the London smog of 1952 and 1957. There the SO^{-2}_4 concentration was measured at 680 g/m^3 and the pH could be calculated about 1.5-1.8.

But even in this case, the direct correlation was not possible because the other chemical species and particulates which are contemporarily present may be responsible in part for the effects on health. According to WHO panel of experts an annual average of 125-200 g/m^3 (WHO, 1969, 1971) SO_2 causes higher incidence of respiratory diseases in comparison with those communities where levels do not exceed 40-60 μg/m^3. Even in this case the global effects on health of atmospheric pollution may be misinterpreted by the pollution due to cigarette smoke. The exposure limits for protection of human health are 100-150 μg/m^3 per 24 hours.

In acid rains and fogs there is also present NO_2. In this case a security limit was established at 190-320 μg/m³/ml (0.10-0.17 for one hour). The average range is 20-90 g/m³ per year and the highest daily means of 130-400 g/m³.

The lowest level of NO_2 at which adverse reaction can occur is 940 g/m³ (0.5 ppm).

For nitrogen oxide, NO, the annual average concentration is between 4-5 μg/m³.

Effects of oxidants

Ozone is the main component of oxidative smog. 200 g/m³ (0.1 ppm) concentration for 2 hours causes disturbances in human health; thus a limit of 100-200 μg/m³ for 1 hour is considered the limit to protect public health. And 120 g/m³ (0.06 ppm) represents the average acceptable for 1 hour exposure (Muller, 1983).

Effects of peroxyacylnitrates

The most evident effects on human health of PAN, studied particularly in the Los Angeles area, are strong eye irritation and photophobia which causes a considerable nuisance for the population affected.

Their activity on plants is specific, so that plants can be assumed to be biological indicators for their presence in the air (Jaffe, 1969). The effect is shown by the silvering, bronzing and glazing of the lower part of tobacco leaves as well as of *Petunia* leaves, which are used for this purpose, as biological indicators.

Anyhow we must call attention to the fact that experiments have shown that the *toxic effect of air pollution on man is the result of the combined and synergic activity of all the pollutants present.*

In effect the global toxicity is higher than the sum of the toxicities in the single components.

Effects of acid deposition on life aquatic systems

The fallout of acid rains of surface waters has been studied for the last 15 years because of the impact on life in the lakes and rivers of Scandinavia, Scotland, and Canada as well as in the northeastern regions of the United States (Kramer and Tessier, 1982; Hilleman, 1983b).

The acidity of rains — due both to SO_4^{-2} and NO_3^- — formed in the atmosphere — which may bring the pH of lakes to figures of 5-6 and even 4.5 is not the sole factor responsible for the toxicity of water for fishes, phytoplankton and zooplankton. In effect there are several chemical processes due to the interaction of acid rains and the soil, as well as the water of lakes. First of all it may occur that in the water, owing to the presence of carbonic acid system $HCO_3^-/(Na)^+(CO_3^-)$ may act as buffer in many lakes. This is not the case of the lakes in Scandinavia because the soil is mainly constituted by granites.

Acidification Processess in Water

$$CO_{2\,g} + H_2O = H_2CO_3$$

$$H_2CO_3 \leftrightharpoons HCO_3^- + H^+$$

$$HCO_3^- \leftrightharpoons CO_3^{-2} + H^+$$

$$[H^+] \sim 1.10^{-5,7} \text{ a } 25°C$$

Thus the changes of the geochemical composition of lakes represents a rather composite system which gives origin to:

1) Lowering of pH value of surface waters.
2) Increase of HCO_3^- in waters.
3) Indirect action of the acidity on the soils.

In effect higher H_3O^+ concentration in surface waters may remove from soils metal ions, mainly Al^{+++}, Mn^{++}, which are solubilized in water. The toxicity of these ions is rather high for aquatic life and can be a cause of the destruction of the fish species and even of the disappearance of fish population! A concentration of Al^{+3} μg/1,270 is considered toxic for most fish species. Attention was drawn to this fact in 1979 by Cronan and Schoefield in the U.S.A. Successively the study of the influence of these chemical changes on fish population has been thoroughly studied by Oden and Hultberg in Sweden, by Chester (1983) in the U.K., by Likens in the U.S.A. and by Hutchison and Whitby in Canada.

An impact on wildlife of acid precipitation in forests may cause the accumulation of heavy metals like lead and cadmium in mushrooms and mosses, which constitute a part of the food chain and thus may be dangerous for both wildlife and man.

Acid precipitations may also lower the Ca^{++} content of water in lakes, thus reducing the buffering capacity of the system. In addition to

Al^{+3} and Mn^{+2} also other metal ions like copper, metal, cobalt, iron are formed. Also the presence of mercury in a lake's water has been studied. There is no evidence of the mobilization of mercury by acid rain. However, for one group of lakes in Sweden there is a correlation between the concentration of Hg in fish and pH. Airborne mercury may be responsible for that (communicated by Prof. Brosset). Moreover in northern countries the snow accumulated on the soil after scavenging from the atmosphere high quantities of acids, which when melting cause a decrease pf pH of the lakes.

A further damage in the acidified lakes is the development of a moss, *Sphagnum* sp which leads to eutrophication of the water body as reported by Grahn and coworkers.

According to a recent report by Hultberg (1983), toxicity in aquatic systems is due not only to direct action of the low pH of the water and to the increase of metal ion content but also to the change of the carbon source from HCO_3^- to CO_2. This may influence the retention of phosphorous in soils by alluminium precipitation. This indicates substantial modification in the ecological equilibria in the aquatic system.

According to Hultberg (1983), in Sweden after 1978 a great number of observations have shown that in the lakes fish population has disappeared or decreased year by year, mainly perch, trout, and evach. After heavy rainfalls (1972) when the pH of Lake Bredvatten went down to 4, all the perch population died although perch is the most resistant fish species. Other populations affected by low pH are arctic char, sea trout, atlantic salmon, brown trout, and crayfish.

The same has happened in Norwegian lakes with black trout; also in West Germany some fish populations have disappeared from the lakes. The same observations were made in Canada and in U.S.A. The main toxic agent considered together with low pH is the increase of Al^{+3} concentration and the simultaneous decrease of Ca^{+2}. These events make acceptable the explanation of the toxic effect versus fishes based on the physiological stress of the fish to regulate, through the gill membrane, ion concentration which causes also difficulties in establishing the osmotic regulation. The same factors affect phytoplankton as the ecological equilibria of the lake is modified, and even the algae-invertebrate equilibria.

The increase of *Sphagnum*, as that of weeds, on the other hand is attributed to the presence of CO_2 instead of HCO_3^- as the main source of carbon.

Zooplankton and zoobenthon are also modified by the chemical pheno-

Ions Formation Processes from Soils

$$\text{M-Al-Silicate} + zH^+ + H_2O = \quad (*)$$

$$H_6SiO_3 + M^{z+1} + \text{Al-Silicate}$$

$$\text{M-Substrate} + zH^+ = \text{(H)z-Substrate} + M^{z+1}$$

$$\text{Kaolinite} + 2H^+ \rightarrow Al^{+3}$$

$$\text{Oxides } (**) + 2H^+ \rightarrow Al^{+3}, [Fe^{+3}], [Mn^{+3}]$$

$$M(CO_3)_n + H^+ \rightarrow M^+ + HCO_3^- \; (*)$$

mena occurring in acid lakes, e.g., the presence of *Keratella* sp., *Bosmina* sp. and *Diaptomus sp.* may be considered as biological indexes of the changes in the aquatic system. In zooplankton and in zoobenthon some species, like *Gammarus* sp. *Lepidurus* sp. *Astacus astacus*, are highly affected.

Moreover, lake acidity favours the development of aquatic insect like *Coleoptera*, *Hemoptera*, and *Megaloptera*, as well as some species of Diptera.

Amphibians, e.g. *Rana temporaria* and *Bufo bufo* suffer from lake acidification because of the ecological change and development of new species of algae.

Birds living near lakes are also affected because the content of metals, mainly Al, increases in fishes and plankton. Another important aspect of the effect of acid deposition is on soil microorganisms, especially in poorly buffered soils, as reported by R.J. Buck both affecting bacteria and fungi and their relative equilibria.

Even microorganisms affecting plants may find, as reported by W.H. Smith for foliar stem disease in trees, a stimulating agent in the increase of acidity and a modification in their behaviour toward plants.

CONCLUSIONS

The present data, which with the available literature on this subject, give us an overall idea of the present state of knowledge and indicate a

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(*) M = Na, K, Ca, Mg

(**) Fe^{+3}, Mn^{+3}, Al^{+3}

number of gaps in the effects on life of acid precipitations, which represent so far the most important aspect of the fallout of chemicals formed in the atmosphere.

This means that more research is required. Although important progress has been made (e.g., a special program is devoted to crop diseases and insects and to vulnerable life steps) in the acid precipitation assessment programs planned in U.S., not sufficient space has been given to research on the effects on animal life and human health (E.B. Cowlings, 1982).

We believe that these correlations should be better studied and cleared because only from an exact diagnosis can it be possible to better protect the life of man and animals and all the ecological equilibria in the biosphere.

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DISCUSSION

RANZI

The effects of acid rain on living beings, both animals and plants, are considerable. These effects are more evident in the north of Europe, where the soil is more acid than in the south, where it is more alkaline. Cases are known in which acid precipitation has caused great harm to persons, as well as to things. Deaths which have occurred in London, in the Mosa Valley, at Donora (U.S.A.) seem to be related to SO_2 perhaps in combination with other toxic substances. An example usually given is that of Ducktown (Tenn.), where the discharge of SO_2 from copper foundries completely destroyed the vegetation in the area and damaged the soil to such an extent that even today, a half century later, the vegetation has not managed to grow again.

Acid rain acts in a very complex way. Experiments, in which plants are sprayed with strongly diluted solutions of H_2SO_4, seem to show that the acidity of these solutions helps the hase of the stem to grow. However, after a short time, the growth of plants treated in this way slows down. It appears that the acid acts on the soil by mobilizing a part of the available nitrogen. Forests are certainly affected to a great extent by the action of acid rain, and very serious damage can be seen in the industrialized areas of Germany, France, Poland and North America. Besides forestry production, which is affected the most, damage is also done to agricultural production. Interest in acid rain first arose to consider its repercussions in the agronomical field. As regards plants in general, and woods in particular, air pollutants penetrate into the leaves through the stomata and damage the plants' foliar parenchyma. The leaves exposed to SO_2 become covered in spots and dry up, until only the venation remains.

Soil acidification causes the mobilization of cations, such as calcium, magnesium, potassium and aluminium, followed by lixiviation of metals: cadmium, copper, zinc and lead.

These alerations in soil composition lead to considerable changes in the related flora and fauna. Bacteria decrease and fungus flora increases. The chemical transformations occurring in the soil, due to the microorganisms contained in it, undergo change. The reduction in nitrifying bacteria brings about a slowing down in mineralization of nitrogen and in its fixation, while the decomposition of organic matter is altered.

Therefore the effect of soil lixiviation is to cause a reduction in the amount of nutrient elements.

A certain amount of aluminium is mobilized through the effect of acid precipitation and ends up in streams which carry it to lakes, where all life, both plant and animal, is harmed, to the extent, in many cases, of all the fish dying out. The increase of aluminium in the water causes intense production of mucus on the surface of fish gills, the result of which is to reduce gas exchanges through the gills, leading to death by asphyxia.

Besides aluminium, the amount of lead, manganese, cadmium, copper and cobalt is also rising in fresh water. In some cases analyses show an increase in methylmercury.

The increased concentration of such elements provokes mortality among algae, above all chlorophyceae, leading to a decrease in biomass and productivity of lakes. However, in some cases, if the acidity of the water succeeds in mobilizing phosphates, perhaps by solubilizing apatite or other phosphorus compounds, eutrophization of the water is aided.

The effect is more evident when the catchment basin lies in rock rich in silica (granite, quartziferous porphyry, etc.) with a thin covering of humus.

An effect of acid rain in streams is to increase the amount of filamentous algae. It is doubtful, however, that it is a case of direct action resulting from the composition of the water, rather than being due to a decrease in herbivorous animals. As acidification increases, the number of animal species in the water decreases. There is a sharp reduction in herbivorous insects, while in the case of carnivorous insects no such dramatic result can be seen.

In some cases the effects of acid rain can be partly offset by the hardness of water. One can take as an example the harmful effect of acid rain on mollusks' tests, less evident in lakes containing harder water.

The crustacean *Gammarus lacustris* can be regarded as a valid indicator of changes in the pH of a lake environment. It can, in fact, survive in water with a pH below 6.0. The bottom limit for *Asellus acquaticus*, on the other hand, is 5.0.

Fresh-water fish have disappeared from many lakes and fish-ponds in Scandinavia and Canada, causing serious economic loss. The first to disappear, due to their greater susceptibility, are the salmonids. So, for example, in the south of Norway where there is high acid precipitation whereas the neutralizing action of the soil is poor, about half of the lakes have lost their trout population. In an area of 13,000 km^2 almost all the lakes have lost their fish. In another further area of 20,000 km^2 the number of fish has been drastically reduced and they will soon disappear altogether. Between Telemark and Lista there are 14 streams where several years ago 10,000 kg of salmon used to be caught per year. Today this fish is practically non-existent, with at most 100 kg being caught per year. This is a tragic situation and will not improve until a stop is put to acid rain (*).

MARINI-BETTÒLO

Professor Ranzi has mentioned some points that I had missed and I thank him very much for this. I think it is most important to have more information on these things because the impact is not only the theoretical aspect, there is also an economic aspect and I think it should be looked into with great care.

PHILLIPS

I have just a comment rather than a question. At the beginning of his talk Professor Marini-Bettòlo gave a list of emitted species which could cause direct harm to man, and missing from that list was lead. I think you could exclude it from the list on the grounds that there really is no interest in chemistry of the atmosphere; the chemistry really taking place in the internal combustion engine, or on the ground, is a local problem. In effect as it is emitted from internal combustion engines it does not travel very far, and this is a subject for action by individual governments rather than for a global approach, although there are studies around now which show that there may well be harmful effects of the direct ingestion of airborne lead.

MARINI-BETTÒLO

I thank you for this observation. It is quite important that the various governments take steps for the control of airborne substances. The phenomenon for the moment is limited or better known in the Northern Hemisphere, but we should be aware of the possibility of transport of substances which can cause damages to other countries.

(*) A large part of the data referred to is taken from O. Ravera: *Un inquinamento recente: Le deposizioni acide e i loro effetti ecologici*, Cultura e Scuola, in press, and from bibliography in the article quoted.

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