Chemical Events in the Atmosphere and their Impact on Environment
Pontifical Academy of Sciences, *Scripta Varia* 56, Vatican City 1985
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ATMOSPHERIC ACIDITY

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Atmospheric acidity is one of the atmospheric events to which great attention has been paid namely in the last decade when it has been realized that anthropic activity was able to affect substantial parts of the global atmosphere. The increase of the concentration of carbon dioxide from approximately 300 ppm by the turn of the century to a level of about 340 ppm at present, the haze formed over industrialized areas, easily recognized from aircraft and satellite observations, and the long range transport of air pollutants as well as the effects of the acidification of the precipitation are now well documented. It is theferore of great importance to evaluate the causes which determine atmospheric acidity, how it can be estimated and its impact upon the environment.

It has been suggested [1] that the atmosphere-hydrosphere-biosphere system with a present day atmosphere, which is 20% oxygen and 79% nitrogen, and a world ocean with a pH of 8 and an alkalinity of 2,3 µeq/l is determined by a set of gigantic coupled acid-base and redox titrations.

The volatile acids from the earth's interior (H_2O, HCl, SO_2, CO_2 and otbers) are neutralized by bases from the rocks and the reduced species formed are oxidized by oxygen. The system is however in a dynamic equilibrium upon which man's activity can have a relevant influence on a global as well as a local scale. The large amounts of atmospheric contaminants released by fuel combustion, industrial production and the extensive use of chemicals determine high fluxes of acidic precursors which contribute to alter atmospheric status.

Air pollutants are generally emitted near the surface or from stacks up to 100-200 m high. The initial concentration is rapidly reduced by atmospheric turbulence and thermal instability. Most pollutants stay within the lower part of the troposphere and will therefore be more or less evenly distributed within the mixing layer. These emissions, through photochemical and chemical reactions lead to an increase in the total acidity of the atmosphere and consequently an increase in fluxes of acidity to the earth's surface occurs through rainfall of increased acid content at a lower pH (wet deposition) and through absorption and fallout of gases and aerosols (dry deposition).

The mean residence time of pollutants depends upon various factors such as the presence of specific components of the atmosphere, atmospheric stability and precipitation frequency.

In order to handle the problem of atmospheric acidity it is envisaged to consider the emission sources of air pollutants, the reactions occurring in the atmosphere, the modification of the cycles of the atmospheric elements and the impact on the environment.

Emission of air pollutants

Most of the air pollutants are connected with the use of fossil fuels for heat and energy production, including motorized traffic and the emissions from industrial processes and large scale use of many industrial products e.g. fertilizers, solvents, pesticides, freons.

The main emission products from industrialized and densely populated areas are carbon dioxide, sulphur dioxide and nitrogen oxides, the last two species being the main precursors to acid precipitation after conversion to sulphuric and nitric acids.

Important in this connection is the formation of photochemical oxidants, which occur by photolysis of nitrogen dioxide in the presence of reactive hydrocarbons. The main "natural" ionic constituent in aerosols and precipitation is ammonium, which is emitted as ammonia from soil and animal manure.

The haze which can be seen in fair weather is mainly due to submicron ammonium sulphate particles. This aerosol also contains soot, agglomerates of very small carbon particles with adsorbed high molecular weight organic compounds and appreciable amounts of certain trace elements, e.g. lead, zinc, iron, nickel, cadmium etc.

The understanding of the chemical oxidation of the primary pollutants SO_2, NO_x and HCl is the most interesting aspect of atmospheric acidity and efforts have been made to describe the fate of these species from their sources to sink [2].

Sulphur dioxide

It is well known that SO_2 is a water soluble gas and its oxidation occurs in an oxygen saturated solution namely in the presence of ion metals, which may act as catalysts. A first order rate constant for its conversion to "sulphate" has been assigned; the conversion process in the atmosphere leads however to several oxidation products SO_3, H_2SO_4, NH_4HSO_4 $(NH_4)_2SO_4$ etc. so that the evaluation of the mechanism and rates of the heterogeneous paths of SO_2 oxidation within the troposphere have a great interest for atmospheric scientists.

The overall process of oxidation of SO_2 is a complex function of gas phase photochemical oxidation reactions leading to condensable vapours and the catalytic and non-catalytic oxidation on wetted aerosol surfaces. Though to a different extent according to local and metereological conditions all reactions might occur simultaneously in the troposphere and it is practically impossible to discriminate various processes which might influence each other, it is customary to examine separately homogeneous and heterogeneous reactions.

A thorough investigation of possible atmospheric homogeneous oxidation reaction has been carried out by Calvert *et al.* [3] and possible atmospheric processes in the gas phase are listed in table I.

These reactions might be grouped according to three main and distinct mechanisms:

a) Direct photo-oxidation involving the reactions of excited SO_2 molecules produced, following the adsorption of solar U.V. radiation in the first and second adsorption bands of SO_2.

b) Oxidation of SO_2 by reactive intermediates, e.g. atoms or free radicals, which are generated photochemically.

c) Oxidation of SO_2 by reactive intermediates generated in thermal reactions, e.g. ozone-olefin reactions.

The direct photo-oxidation of SO_2 by way of the electronically excited states of SO_2 is relatively unimportant for most conditions which occur within the troposphere. SO_2 molecules adsorb UV radiation quite strongly in the near UV region but the energy involved is insufficient to break the O-S-O bond. Though a number of reactions of electronically excited molecules have been reported, in ambient air the net oxidation of SO_2 does not occur at an appreciable rate as the excited states are quenched to the ground state by N_2, O_2 and H_2O [4].

TABLE I - *Possible atmospheric gas phase* SO_2 *oxidation processes.*

Initial Steps

(1) $SO_2 + h\nu\ (2400\text{-}3400\ \text{Å}) \rightarrow SO_2^*$

(2) $SO_2^* + O_2 \rightarrow (SO_4)$

(3) $SO_2 + O + M \rightarrow SO_3 + M$

(4) $SO_2 + O_3 \rightarrow SO_3 + O$

(5) $SO_2 + NO_3 \rightarrow SO_3 + NO_2$

(6) $SO_2 + N_2O_5 \rightarrow SO_3 + N_2O_4$

(7) $SO_2 + CH_3O_2^{\cdot} \rightarrow SO_3 + CH_3O^{\cdot}$

(8) $SO_2 + HO_2^{\cdot} \rightarrow SO_3 + OH^{\cdot}$

(9) $SO_2 + OH^{\cdot} + M \rightarrow HSO_3 + M$

Possible Subsequent Reactions

(10) $SO_3 + H_2O \rightarrow SO_3H_2O \rightarrow H_2SO_4$

(11) $SO_3 + H_2O \rightarrow \text{nucleus}$

(12) $HSO_3^{\cdot} + OH^{\cdot} \rightarrow H_2SO_4$

(13) $HSO_3^{\cdot} + OH^{\cdot} \rightarrow H_2O + SO_3$

(14) $HSO_3^{\cdot} + HSO_3^{\cdot} \rightarrow H_2S_2O_6$

(15) $HSO_3^{\cdot} + H_2O \rightarrow HSO_3\,(H_2O)$

(16) $HSO_3^{\cdot} + O_2 \rightarrow HSO_5^{\cdot}$

(17) $HSO_5^{\cdot} + H_2O \rightarrow HSO_5\,(H_2O)$

Several authors have been able to show experimentally that natural air containing trace amounts of SO_2, exposed to sunlight, is photochemically oxidized and that the rate of SO_2 oxidation was a complex function of the trace gas composition of the air mixture (NO, NO_2 - hydrocarbons level and composition).

The oxidation of SO_2 within the natural troposphere is therefore expected to occur largely through reactions 7,8 and 9 of table I.

The main mechanism is through radicals which might be formed in various ways such as from ozone photodissociation and from the reaction of oxygen atoms, $O(^1D_2)$ with H_2O. These reactions can be followed by a series of fast elementary steps in which $OH^{\cdot}$ and $HO^{\cdot}_2$ radicals are interconverted

$$\begin{aligned} OH^{\cdot} + CO &\rightarrow CO_2 + H \\ H + O_2 (+ M) &\rightarrow HO^{\cdot}_2 \\ HO^{\cdot}_2 + NO &\rightarrow NO_2 + OH^{\cdot} \end{aligned}$$

Radicals are removed by reaction with each other, which may lead to oxidising products such as $HO^{\cdot}_2 + HO^{\cdot}_2 \rightarrow H_2O_2$, or to acid gases $OH^{\cdot} + NO_2 (+ M) \rightarrow HNO_3 (+ M)$.

Other pollutant species, namely organic vapours and NO_x, play an important role, the former being oxidized through peroxy radicals, $RO^{\cdot}_2$, to aldehydes including formaldehyde, which is photochemically active, the latter in converting the unreactive $RO^{\cdot}_2$ and $HO^{\cdot}_2$ to reactive $RO^{\cdot}$ and $OH^{\cdot}$ radicals and in removing $OH^{\cdot}$ radicals as HNO_3.

The fundamental reaction is thus

$$OH^{\cdot} + SO_2 (+ M) \rightarrow HSO_3 (+ \ )$$

$HSO^{\cdot}_3$ radical is rapidly converted to H_2SO_4 aerosol. It has to be stressed that, though in polluted air OH-initiated oxidation is the dominant process, other thermal reactions, such as the one between O_3 and olefinic hydrocarbons leading to reactive intermediates may occur. Also thermal ozone-olefin reactions can promote SO_2 oxidation at a rate which may be significant in the atmosphere; as high olefin concentrations are required, this process seems to be only of importance near large sources of these hydrocarbons. Homogeneous gas-phase oxidation of H_2S and organic sulphides by free radical species appears to be the dominant process and SO_2 is the most important oxidation product.

In conclusion the homogeneous photochemically initiated free radical reactions are the most significant mechanism for conversion of SO_2 to sulphate in the lower atmosphere. According to Eggleton and Cox [5] in the western European summer, SO_2 oxidation rates in sunlight are expected to be between 0.5% and 5% hr^{-1}, depending on the degree of pollution of the atmosphere, with the lower figure relating to clean air. In wintertime, rates in sunlight are expected to be a factor of 2 slower and, due to the reduced hours of sunlight, the overall removal rate of SO_2 by photochemical reactions is slower by an even greater amount.

Liquid phase oxidation reactions

Oxidation of SO_2 in liquid phase can occur in clouds, fogs and in rain droplets in the absence and in the presence of catalysts and of ammonia with formation of sulphate; ammonium sulphate in rainwater has been however always detected. SO_2 conversion to sulphate in clean water is a slow process but is known to be accelerated in the presence of ammonia. Oxidation of SO_2 can also occur through an uncatalyzed mechanism which involves ozone as the oxidizing agent as well as by means of dissolved hydrogen peroxide, originating from gas phase photochemical reactions. The former mechanism is very sensitive to pH, becoming dominant in an alkaline regime whereas the latter, which is rather insensitive to pH, prevails under acid conditions; it depends on hydrogen peroxide in the atmosphere and therefore on photochemical activity which has a noticeable seasonal variation.

Oxidation of SO_2 in droplets, which contain various products, detectable in the atmosphere, is the measurement accepted as being real as it approaches atmospheric conditions. Studies upon the oxidation of SO_2 in droplets, which contain soot particles, definitely show the effect of carbonaceous material in performing the conversion to $SO^{=}_4$. This process seems to be of relevant importance in polluted areas. As far as liquid phase oxidation of SO_2 is concerned, it seems that the uncatalyzed oxidation of SO_2 by ozone or hydrogen peroxide is probably the dominant mechanism in the droplet phase.

Reaction on the surface of particles

Atmospheric particles as well as any solid material interact with atmospheric SO_2, the interaction being characterized by two processes.

Adsorption and conversion to sulphate

The extent of both processes depends upon the nature and composition of the materials considered and is affected by a variety of factors, the more relevant being humidity and surface reaction. The adsorption process occurs in two steps; in the first one, which is very fast, a second step intervenes which might be due to the slow diffusion of SO_2 in the solid phase [6]. The conversion to sulphate takes place rapidly on an alkaline dust whereas no oxidation has been observed on neutral or acid material unless the material exhibits a catalytic effect as there has been observed in soot the presence of manganese salts and other metal salt aerosols; humidity has in both cases an important role, a higher sulphate conversion being observed at higher humidities.

These results show the same trend of those obtained for SO_2 in the liquid phase.

Nitrogen oxides

The tropospheric nitrogen cycle has been strongly affected by emission of nitrogen oxides mainly due to the oxidation of nitrogen in the air during combustion processes. About 50% comes from motorized traffic and most of the remainder from power stations and space heating. Oxidation of NO to nitrogen dioxide is reported in chemical smog but a variety of reactions can occur in gas phase involving in addition to NO and NO_2, higher oxides NO_3 and N_2O_5 as well as nitrous HONO, nitric and peroxynitric acid.

Chemical oxidation of NO to NO_2 occurs rapidly through reaction with ozone as well as in daylight with photochemically generated peroxy radicals (HO, CH_3O_2 ecc.) according to this reaction

$$O_3 + NO \rightarrow NO_2 + O_2$$

The net conversion of NO to NO_2 is limited to the photodissociation of NO_2 ($NO_2 + h\nu \rightarrow NO + O$). As atomic oxygen rapidly recombines with oxygen to yield ozone, a photostationary state is reached, which governs the concentration of NO, NO_2 and O_3, the ratio between the two nitrogen oxides being determined by the light intensity.

Oxidation of NO_2 leads to the formation of nitric acid, which can be formed through two different mechanisms. In daylight photochemically generated OH react with NO_2 according to the following reaction

$$OH^{\cdot} + NO_2 + M \rightarrow HONO_2 + M$$

Oxidation can occur through the reaction with ozone

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

Nitrogen pentoxide, is formed in the reversible reaction with NO_2,

$$NO^{\cdot}_3 + NO_2 + M \rightarrow N_2O_5 + M$$

which reacts with water to form HNO_3. In day-time the removal of NO_3 either through the reaction with NO to form NO_2 or through photolysis reduce the efficiency of this reaction. At nighttime the rate of oxidation of NO_2 by O_3 is of the same magnitude as the daytime rate for the reaction with OH radicals.

Hydrogen Chloride

Noticeable amounts of hydrogen chloride can be found in the emission namely due to incineration and combustion process of chlorine containing materials. HCl is quite stable towards oxidising agents and on account of its solubility can be incorporated into the rain or can be adsorbed by dry deposition. It can undergo an oxidation process similar to that of SO_2 with OH radicals to yield chlorine atoms

$$OH^{\cdot} + HCl \rightarrow H_2O + Cl$$

Atomic chlorine by reaction with hydrogen containing gases reforms HCl again whereas by reacting with ozone yields ClO radical which is further converted to chlorine nitrate, $ClONO_2$, which is a stable species. This compound can photodissociate to release chlorine atoms and can also react with water and hydrolize

$$ClONO_2 + H_2O \rightarrow HNO_3 + HOCl$$

According to this reaction in addition to the same strong acid input an oxiding species is produced.

Acidity formation in the atmosphere

A review of the main reactions occurring in the atmosphere emphasize the various processes which lead to the formation of species, which can alter the relative ionic equilibrium.

Sulphate aerosol production, which is by far the most important process, changes however noticeably under different atmospheric conditions and the various mechanisms may occur to a different extent. Factors affecting these changes are the concentration of photochemically produced gaseous species, temperature and aerosol acidity and size distribution. It is found that, in general, H_2SO_4 condensation and H_2O_2 oxidation on the wetted aerosol can be dominant pathways to sulfate aerosol formation under daytime conditions. Under summer daytime conditions sulfate formation is higher and H_2SO_4 condensation can be the more important mechanism. Under winter daytime conditions sulfate formation is lower and H_2O_2 oxidation can be the prevailing mechanism. Under nighttime conditions, the rate of sulfate aerosol formation is lower and catalytic and noncatalytic oxidation mechanisms on the wetted aerosol surface become the major sulfate formation mechanisms. In particular, catalytic oxidation by soot, iron and manganese appear to be the most important pathways under nighttime conditions.

The changes in the relative importance of sulfate aerosol formation mechanisms under different atmospheric conditions is shown in Fig. 1.

The soot mechanism appears to be the major sulfate aerosol formation mechanism which is not directly or indirectly related to photo-

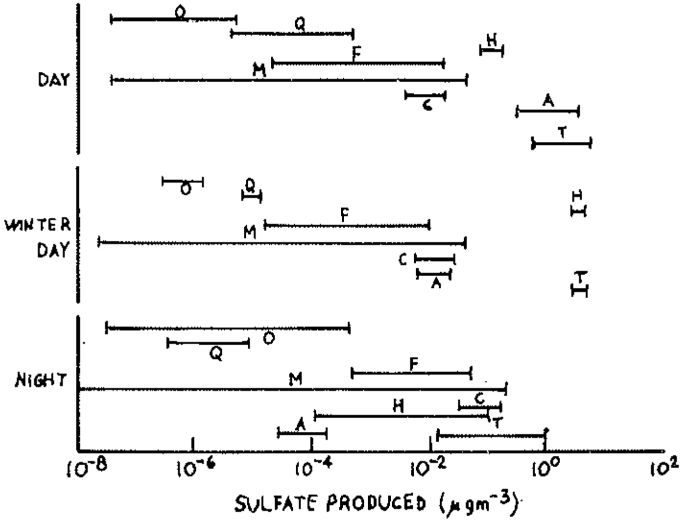

FIG. 1. Relative importance of various urban sulphate aerosol production mechanisms: T = total sulfate; A = H_2SO_4 condensation; H = H_2O_2 oxidation; O = uncatalyzed oxygen oxidation; Q = O_3 oxidation; F = iron catalyzed oxidation; M = manganese catalyzed oxidation; C = soot catalyzed oxidation.

chemical activity. The increase in soot has a negligible effect under summer daytime conditions with photochemical reactions. But under conditions of higher particle acidity (low NH_3) and reduced photochemical activity (low H_2SO_4 and H_2O_2) soot catalysis could be a competitive pathway to sulfate formation under daytime conditions.

The variety of reactions which have been described indicate tbe large number of chemical species which enter in the troposphere and which may have an impact upon the environment. It is necessary to emphasize that all species are in a dynamic equilibrium for the meteorological turbulence so that in some cases redox and acid-base reactions occur with the formation of stable compounds with high formation constants but nevertheless the reagent species are detectable in the atmosphere. A typical example is the evaluation of the atmospheric aerosol where besides the presence of ammonium sulphates, free ammonia and sulphuric acid may coexist.

In an ambient aerosol strong acids may exist in the gaseous state (HNO_3, HCl), in the form of aqueous droplets (H_2SO_4), or as species adsorbed at particle surfaces. Their fate can be foreseen by considering the reactions these acids may undergo, which are outlined in table II.

The main reaction is the neutralization with ammonia, which is the major reactant. In case of thermodynamic equilibrium temperature and partial pressure of H_2O, NH_3 and volatile acids (HNO_3, HCl) it would be possible to describe the NH_3-acid-ammonium salt system according to Gibbs phase rule, but in ambient air for the various meteorological factors affecting equilibrium this aim is not feasible.

Also a heterogeneous strong acid salt reaction leading to volatile acids is possible; as an example a loss of hydrochloric acid from marine aerosol particles can be observed in combination with NO_2 and SO_2 conversion. The third route of the conversion products of SO_2 and NO_x is their transport to the earth's surface. It is important to notice that H_2SO_4 and ammonium salts of strong acids are products of a gas to particle (droplets) conversion and as such are present in the fine particle mode ($0.05 - 2$ μm) of ambient aerosols. Particulate matter of this mode behaves physically different from coarse particles (> 2 μm) on one hand and gaseous atmospheric trace constituents (SO_2, NO_x, HNO_3, HCl) on the other. Fine particles exhibit low gravitational settling and brownian mobility and have therefore the highest overall residence time in ambient air compared to the other components.

The removal of these species from the atmosphere can take place

TABLE II - *Fate of atmospheric strong acids.*

1) Reaction with ammonia

$$H_2SO_4\ aq \rightleftarrows H^+ + HSO_4^-\ aq$$

$$NH_3\ (g) + H_2O\ (l) \rightleftarrows NH_3\ aq$$

$$NH_3\ aq + (H^+ + HSO_4^-)\ aq \rightleftarrows (NH_4^+ + HSO_4^-)\ aq \rightleftarrows \begin{array}{l} NH_4HSO_4 \\ (NH_4)_3H(SO_4)_2 \\ (NH_4)_2SO_4 \end{array} + H_2O\ (g)$$

$$HNO_3\ (g) + H_2O\ (l) \rightleftarrows HNO_3\ aq \rightleftarrows (H^+ + NO_3^-)\ aq$$

$$NH_3\ aq + (H^+ + NO_3^-)\ aq \rightleftarrows (NH_4^+ + NO_3^-)\ aq \rightleftarrows \begin{array}{c} NH_4NO_3 + H_2O\ (g) \\ \downarrow\uparrow \\ NH_3\ (g) + HNO_3\ (g) \end{array}$$

2) Conversion of nitrates and chlorides during heterogeneous H_2SO_4 formation:

$$2\ H_2SO_4\ aq + (NO_3^- + Cl^-)\ aq \rightleftarrows 2\ HSO_4^-\ aq + \begin{array}{c} HNO_3\ aq \\ \downarrow\uparrow \\ HNO_3\ (g) \end{array} + \begin{array}{c} HCl\ aq \\ \downarrow\uparrow \\ HCl\ (g) \end{array}$$

3) Transport of strong acids and their salts to the earth's surface by dry and wet deposition.

through their deposition in rain and for direct deposition of gases and particles into natural surfaces. For the two groups of processes the collective terms wet and dry deposition have been applied. Wet deposition is transfer of a certain species from the atmosphere to the earth's surface within or on the surface of rain, snow or hail; it is therefore an indirect process where precipitations act as a vector. Dry deposition is the direct transfer with the absorption of gases and particles by natural surfaces (vegetation, soil material, water). Wet and dry deposition are largely independent of each other although rain-wetted surfaces affect rates of dry deposition.

Wet deposition

The general picture for acid and basic components which are known to take part in rain acid base chemistry is summarized in fig. 2.

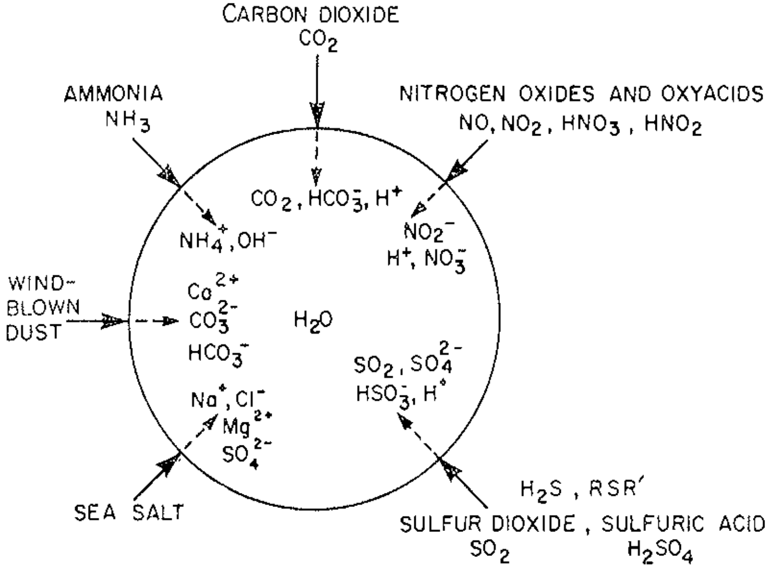

FIG. 2. Acid and basic components of the rain.

For a consideration of wet deposition mechanism it is useful to make a distinction between processes transferring material to cloud droplets before they begin their descent as a raindrop, known collectively as rainout and processes transferring material to falling raindrops known as washout. There are five mechanisms [8] by which particulate and gaseous compounds may be captured by cloud or rain drop: diffusiophoresis, brownian diffusion, impact and interception, solution and oxidation of gaseous species (notably SO_2 and NO_2) and the cloud condensation nuclei (CCN) pathway.

These processes are outlined in Fig. 3.

Quantification in the contribution to sulphur and nitrogen in rain by the above processes has been summarized in table III.

Equilibrium concentrations of gas phase SO_2 and dissolved sulphur species in the same oxidation state (SO_2, HSO_3^-) are reached in a few seconds for droplets smaller than 100 μm diameter. However, for the time scales involved in rainout, oxidation of S(IV) to S(VI) dominates this mechanism for the accumulation of S by cloud droplets. The oxidation may proceed through the variety of mechanisms previously described ranging from catalytic reactions in solution often assisted by the presence of NH_3,

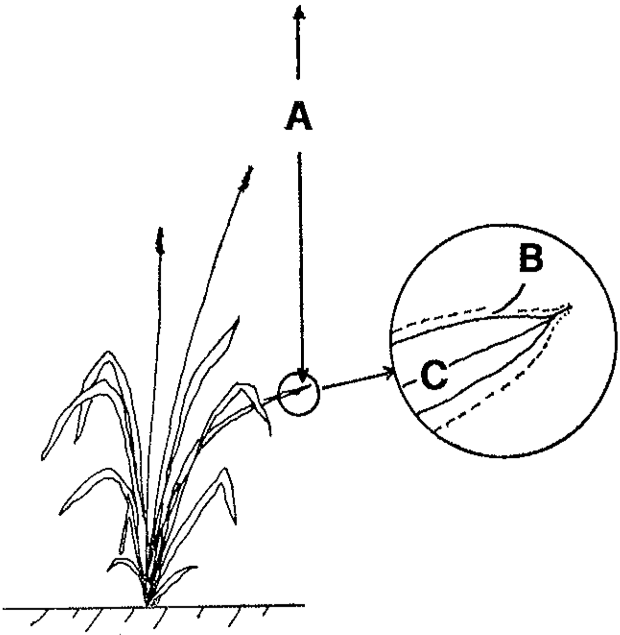

FIG. 3. The main wet deposition processes.

to more effective reactions involving H_2O_2, $HO^{\cdot}_2$ and O_3. NO_2 is converted to HNO_3, both in solution and in gas phase, which then reacts with atmospheric ammonia forming NH_4NO_3 aerosol contributing to the CCN pathway.

Sulphur and nitrogen containing aerosols play a major role in the production of cloud water droplets as they form a dominant fraction of the particles, suitable for condensation of water vapour. The aerosol contains sulphur and nitrogen compounds in the concentration range from 0.04 $\mu g\ m^{-1}$ to 80 $\mu g\ m^{-1}$. Sulphur and nitrogen are present in a variety of compounds, though sulphur is almost invariably present in its most oxidised S^{VI} state. The major compounds are $(NH_4)_2SO_4$, $(NH_4)_3H(SO_4)_2$, H_2SO_4, NH_4HSO_4 and NH_4NO_3. The hygroscopic nature of sulphur- and nitrogen-containing aerosols enhances their efficiency as CCN, and this, with their ubiquitous presence in both polluted and clean air, makes this pathway for removal an important one, although it is difficult to quantify directly.

TABLE III - *Processes contributing to the sulphur and nitrogen in rain.*

PROCESS	SULPHUR		NITROGEN	
		Note (1)		Note (2)
	Range of concentrations in rain at ground level $\mu g\ g^{-1}\ SO_4^{-2}$	Average contribution to wet-deposited sulphur %	Range of concentrations in rain at ground level $\mu g\ g^{-1}\ NO^{-}_3$	Average contribution to wet-deposited nitrogen %
Diffusiophoresis	10^{-2} - 10^{-1}	2.5	10^{-3} - 10^{-2}	2.5
Brownian Diffusion	10^{-2} - 10^{-1}	2.5	10^{-3} - 10^{-2}	2.5
Impaction and Interception	10^{-1} - 1.0	10	10^{-2} - 10^{-1}	
Solution and Oxidation of Gaseous 'Species'	0.5 - 3.0	20	10^{-2} - 0.4	15 - 25 (3)
Cloud Condensation Nucleus Pathway	2.0 - 20.0	65	10^{-1} - 5.0	60 - 70
(5)	(4)		(4)	

NOTES

(1) Considering rain with geometric mean SO_4^{2-} concentration of 3.5 $\mu g\ g^{-1}$ (weighted for rain quantity).

(2) Considering rain with geometric mean NO^{-}_3 concentration of 0.5 $\mu g\ g^{-1}$ (weighted for rain quantity).

(3) Uncertainty in this component necessarily leads to uncertainty in other components.

(4) Lower limits of range deduced from average contribution and range of concentrations measured.

(5) This table considers the whole wet deposition pathway, no distinction between RAINOUT and WASHOUT.

Dry deposition

The mechanisms by which gaseous and particulate pollutants are transported to and dry deposited on natural surfaces are examined in order to enable prediction of deposition rate for a variety of surfaces in a range of atmospheric conditions.

The process of dry deposition for gases and particles has three stages which are outlined in Fig. 4. The first one is the transport from the free atmosphere to the laminar boundary layer of air close to the surfaces of objects. The second one is the transport through this layer and in the third the gas or particles must be absorbed and captured or otherwise entrained by the surface. As various species are transported to successive stages in this process the number of individual mechanisms influencing rates of transport increases and rates of transport for different materials diverge.

For gases and particles small enough for gravitational settling to be unimportant (this is the case for particles with diameters < 5 μm, which have terminal velocities less than 0,5 mm s^{-1}), transport in the free atmosphere is effected by turbulent diffusion. Rates of turbulent diffusion exceed molecular diffusion rates by several orders of magnitude so that for the free atmosphere, molecular diffusion may be ignored. The turbulence is generated by frictional forces at the earth's surface, close to which rates of turbulent diffusion may be estimated from mean vertical gradients in wind velocity and air temperature.

The very shallow ($\sim$ 1 μm) layer of air in contact with the surfaces, where stream lines for air-flow are approximately parallel to the surface and turbulence is suppressed by the viscosity of the air, is known as the laminar boundary layer. The thickness of this layer is determined by physical characteristics of the object (size, shape and surface structure) and by the velocity of air outside the laminar boundary layer. Although gases and small particles are transported by the same mechanism and at about the same rates in the free atmosphere, their transport through the laminar boundary layer differs considerably. Gases must diffuse through this layer by molecular diffusion, the concentration gradient and diffusion coefficient for the gas in question controlling the rate of transfer.

Particles smaller than 0.1 μm diameter are able to diffuse through the laminar boundary layer by Brownian diffusion, the efficiency of the mechanism increasing as particle size decreases below 0.1 μm. In general, rates of Brownian diffusion, which are small even by comparison with molecular diffusion, and do not therefore, represent an efficient process for the transport of sulphur and nitrogen containing particles across the laminar boundary layer. Another mechanism for transport of particles through this layer is inertial impaction. For this process the particle must

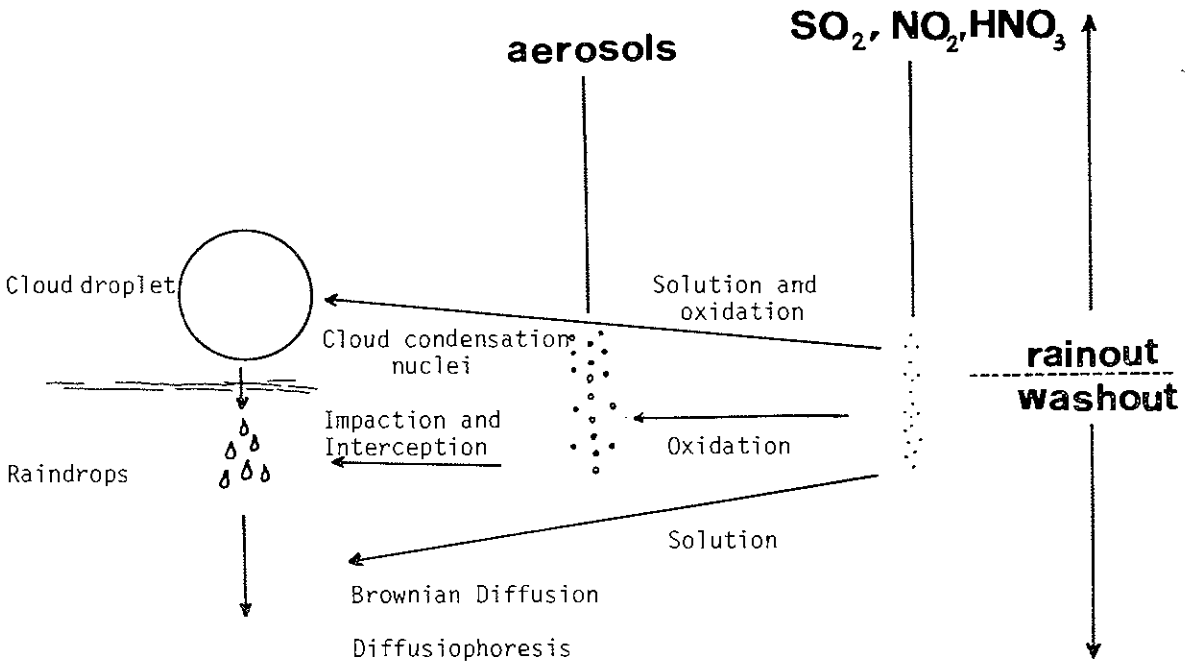

FIG. 4. The dry deposition process: A free atmosphere; B laminar boundary layer; C plant surface.

have sufficient momentum when reaching the laminar boundary layer to penetrate the layer of relatively still air and be captured by the surface.

Having reached the surface, the mechanism for dry deposition now enters its most complex phase as here gases behave in a manner entirely dependent on the chemical and physical affinity of the gas for the surface in question. For active gases like SO_2, NO_2 and HNO_3 (gas) and a uniform surface like water the relative simplicity of the system lends itself to theoretical treatment. For more complex surface like a canopy of vegetation a wide range of materials are simultaneously presented to the gas molecules: the epicuticular wax covering on leaf surfaces, a matrix of cell wall material and intercellular fluids lining the sub-stomatal cavity, surfaces of dead tissues and in many cases a second canopy of vegetation and the soil surface.

Surface properties also strongly influence the capture of particles, though the small fraction of sulphur and nitrogen containing particles that are captured by the surface are in a size range for which bounce-off and re-suspension are very unlikely.

EVALUATION OF ATMOSPHERIC ACIDITY

On account of the various reactions which may occur in the atmosphere it is a challenging activity for te analytical chemistry to succeed in evaluating the chemical composition of the atmosphere in order to obtain a real representative picture. As all components are in a dynamic equilibrium and in most cases at levels not directly measurable, it is required to obtain the real concentration of a certain species and prevent artifacts which might take place along the sampling. The speciation of atmospheric acids is a major difficulty because these compounds must be detected simultaneously with their precursors (SO_2, NO_x) neutralizing agents (NH_3) and ammonium salt particles (ammonium sulphates and nitrate). It is therefore necessary to combine a selected detection system with an appropriate sampling and sample pretreatment procedure in order to ohtain a detailed insight into the complex acid-base-salt system.

Most of the interaction responsible for artifacts can be prevented by replacing the traditional sampling system, consisting in the filtration and in the selective collection of reactive trace gases with the combination of diffusion separation and filtration; this aim is reached by making use of denuders. The air under investigation is drawn through a denuder, which is a tube the inner walls of which are coated with a suitable trapping agent for trace gases.

During the laminar flow of air through the tube the gas molecules diffuse to the tube walls, which are actually acting as irreversible sink, while the particles larger than 0.01 μm in diameter proceed unaffected because their diffusion coefficients are several orders of magnitude lower than those of gaseous species. In addition to an effective gas particle separation this procedure offers the possibility to determine selectively reactive gases by analyzing directly the sorbed species.

Flow limitations which require a long sampling time have been overcome by the use of recently developed annular denuders, consisting of two coaxial glass cylinders. This system can operate at higb flowrate and by combining denuders with selective adsorbers, as is shown in fig. 5, it is possible to sample simultaneously SO_2 (tetrachloromercurate coating), HCl and HNO_3 (sodium carbonate coating) and NH_3 (oxalic acid coating) [9].

Impact of atmospheric acidity upon the environment

The mechanisms relative to acid deposition make it possible to draw some conclusion regarding the uptake of gases and particles and the impact atmospheric acidity may have upon the environment. The following items will be considered:

— Water acidification.

— Chemical modifications of precipitation in contact with soil and vegetation.

— Effect on architectural structures and monuments.

WATER ACIDIFICATION

Though water acidification is one of the most important aspects, one would certainly not expect significant changes in water acidity in all exposed areas. The effect is highly dependent on bedrock geology and the nature of the overburden. No acidification of fresh water is to be expected in areas with appreciable amounts of calcareous rocks. The most well known susceptihle areas are those with shallow overburden and quartz-bearing bedrock. Acidification can occur in catchments with highly weathered sandy soils with low neutralization capacities.

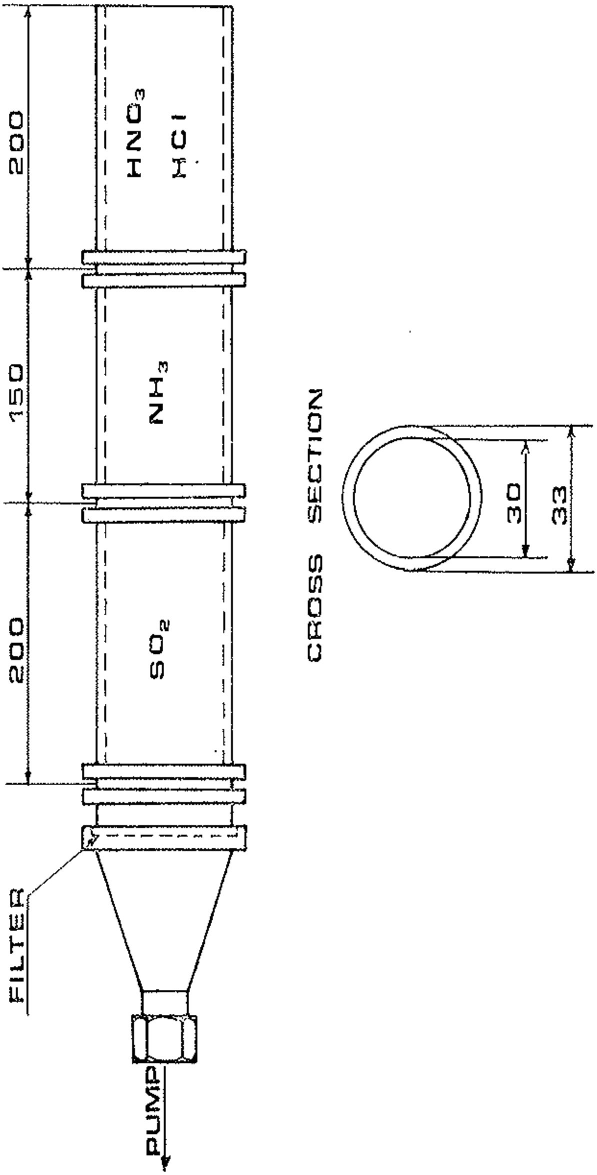

FIG. 5. Scheme of a multistage annular denuder for the simultaneous sampling of SO_2, HCl-HNO_3 and NH_3.

The alkalinity or better the acid neutralization capacity is the key in estimating the sensitivity of fresh water to acidification.

There is a convincing evidence of a decrease in pH in fresh waters during recent decades. Though it is difficult to quantify the change, acidification of fresh water observed in several areas corresponds well with the changes in the composition of precipitations.

High acidity affects aquatic life in two ways by altering the tolerance of individual species and through changes in the dynamic of seasonal succession and interactions between species.

A conspicuous phenomenon in many acid lakes and rivers is the heavy growth of filamentous algae and mosses. The ratio of chlorophyl to carbon is low in an acid system demonstrating that much of the algae is photosynthetically inactive. A reduced efficiency of carbon assimilation per unit of chlorophyl is observed with a reduction in productivity. Algae accumulation at low pH is probably due to reduced grazing activity by invertebrates and less decomposition. It has been shown that decomposition of organic matter is reduced in acid lakes and that organic detritus is accumulating on lake bottoms often covered by dense felts of fungal hyphae.

The mineralization of water organisms, which are specialized to decompose into slowly degradable compounds, is retarded in acid water and heterogeneous matter may accumulate on lake bottoms increasing the rate of moss formation. The dense gelatinous fungal mats reduce the oxygen available for aerobic degradation. Respiration i.e. oxygen consumption is decreased and also a reduced recycling of phosphorus, which is of a great importance for lake productivity, is observed.

Consequently a change in the invertebrate species which are importat links between primary producers and fish in the aquatic food chain occurs with a serious impact on the energy flow.

There is also a change in the benthic invertebrates which constitute an important group of fish food animals and are a quite sensitive pH indicator. Below pH 4.5 no crustaceous, snails and mussels are found and no important fresh water fish can live.

There are several factors however which are related to water acidity (low Ca^{++}, high content of heavy metals and aluminium) and other abiotic factors (temperature, transparency) which mask or enhance the pH effect. It now seems proven that aluminium is a real toxic agent in lakewater in acidified catchments, this metal being leached in high amounts from soils under acidification. Aluminium buffer system replaces the normal bicarbonate buffer system when lakes are acidified and Al concentrations have led to heavy fish mortality with an Al toxicity having a maximum around pH 5.

CHEMICAL MODIFICATIONS OF PRECIPITATION IN CONTACT WITH SOIL AND VEGETATION

Only a small fraction of the precipitation falls normally directly into rivers and lakes (often 5-10%). The main part is affected by a number of processes in the catchment resulting in a runoff composition which may be very different from that of the precipitation. The first change in the composition occurs as the precipitation passes the canopy of the vegetation.

Plant stomata represent the major sink for SO_2 as well for other acid components, other sinks being cuticular surfaces and soil surface. Particles and adsorbed gases accumulated in the tree crowns may be washed off by the precipitation.

The effectivity of forests in scavenging and retaining atmospheric components has ecological significance and this may imply that forests are particularly at risk from atmospheric pollutants.

In addition the runoff should be considered with respect to effects of vegetation and ion exchange. The roots take up various cations and release H^+, resulting in a soil acidification.

Cation exchange is one of the most important processes we have to consider. Soil particles have normally a negatively charged surface and therefore a layer of cations close to the surface. These cations may be interchanged with those in the solution. Thus when a dilute solution of neutral salts percolates through acid soils, the leachate hecomes acid because of exchange of other cations with hydrogen ions.

Under the influence of a continuous acid load, soils pass through three phases: In the first phase they retain the whole acidity and load the seepage water with basicity (calcium and magnesium ions released from the cation exchangers). They pass then over in the second phase where part of the acidity deposited is changed into cation acids (manganese and aluminium ions) which leave the soil with the seepage water by determining the weathering of the soil; the other part of the acidity is accumulated in the solid soil phase, partly as aluminium sulfate. In the third phase this accumulated acidity is lost and leaves the system with the seepage water. In this phase the acid load to the hydrosphere increases strongly. The risk existing for the hydrosphere can hardly be overestimated.

EFFECTS ON ARCHITECTURAL STRUCTURES AND MONUMENTS

The common masonry materials as limestones, marble, sandstones basalt and granite as well as artificial materials as brick, concrete and mortar are composed primarily of carbonate and silicate mineral. The natural weathering of these materials, due mainly to atmospheric CO_2, increases at an alarming rate due to atmospheric acidity and acid precipitation.

It has been postulated [10] that silicate minerals as feldspar exposed to atmospheric agents undergo hydration and decay through the polarization and the ensuing dissociation of the water dipole into H^+ and OH^- due to the attractive forces of the free valencies. In this interaction the oxygens are converted to hydroxyl groups and part of the potassium is removed in solution. A partial or total cationic (K^+, Na^+, Ca^{++}) depletion decomposes the feldspar. Since the neutral water now reaches an increased pH, introduction of acids neutralizes these alkali and facilitates a further decay of these minerals.

Calcite and dolomite are the common carbonate materials of sedimentary (limestone, sandstone) and metamorphic (marble) rocks used as building stones. These materials are highly susceptible to attack by acid deposition and by the presence of atmospheric SO_2 according to the following reactions:

$$\mathrm{CaCO_3} \xrightarrow{\mathrm{H^+,\ H_2O}} \mathrm{Ca^{2+} + 2HCO_3^-}$$

$$\mathrm{CaCO_3} \xrightarrow{\mathrm{H_2O,\ SO_2}} \begin{array}{c} \mathrm{CaSO_3\ 1/2\ H_2O + CO_2} \\ \\ \mathrm{CaSO_3\ 2H_2O + CO_2} \end{array} \xrightarrow[\mathrm{H_2O}]{\mathrm{O_2}} \mathrm{CaSO_4\ 2H_2O}$$

Atmospheric acidity is responsible for the attack in the presence of humidity whereas the SO_2 reaction continues to occur in the presence of liquid water as well as water vapours. The calcium sulfate that forms is less preserved when the structures are exposed to direct rainfall. In protected regions SO_2 continues its attack almost continuously and the gypsum obtained from this reaction forms crusts on protected surfaces. As a consequence most ancient buildings in the industrialized countries have a black appearance in some areas and a clean aspect in others. The black appearance is due to gypsum crusts, which have incorporated soot in the process of crystallization whereas the areas directly showered with the acid precipitation are largely clean. The condensed water vapours in a shaded area keep the building from drying and once the crust has formed it continues to grow inwardly for not having been washed away by driving rain. These crusts of weathering are much less permeable to water than is the marble itself but do not behave as a protective coating as the transport of SO_2 along the water films corrodes the marble behind the crust rendering these regions highly friable. The rate of decay in these areas is accelerated with regard to marble in unprotected areas.

The main reaction responsible for marble decay and damage to monuments is therefore the sulphation which occurs on the surface of these materials. Oxidation of SO_2 to SO_3 occurs by catalytic action due to surface impurities such as Fe_2O_3, soot, colloidal deposits, $CaSO_4\ 2H_2O$ already formed, humidity and also to sulphur oxidising bacteria.

The mechanism of sulphation has been explained [11] by means of an electrochemical process described by a galvanic cell formed between $CaCO_3$ acting as a negative pole and the corrosive environment (SO_2 + air + water vapour) activy as the electrolyte.

$$(-)\,CaCO_3\,(S)\,/\,CaSO_4\ 2H_2O\,/\,SO_{2\,(g)}\ O_{2\,(g)}\ H_2O\,(g)^{+}$$

According to this mechanism the rate determining step for the second stage of the sulphation of $CaCO_3$ is a solid state diffusion in which the diffusion species could be Ca^{2+}, CO_3^{2-} or SO_4^{2-}.

Decay of stone can take place through efflorences which are encrustations formed at the surface; they produce discoloration at the facades of buildings and upon repeated crystallization and hydration, they mechanically disintegrate the stone.

They may be formed as a result of attack of chemically active gases on masonry material and atmospheric acidity is thus responsible for this effect.

Damage to stone occurs also for the corrosion of metallic bars used for anchoring blocks of stone with each other and with the structural framework. Oxidation of iron produces the mineral limonite (FeO-OH) which has greater volume than the parent iron. This volume increment generates stresses sufficient to disintegrate the stone. The presence of SO_2 and other acid components decidedly accelerates the decay phenomenon.

The net effect of the entire deterioration process is to alter physical and chemical properties so that the weathering stone becomes even more susceptible to atmospheric attack.

CONCLUSIONS

The origin of atmospheric acidity has been analyzed through various reactions which occur in the atmosphere. Though natural phenomena such as volcanic eruptions, forest fires and the breakdown of organic substances by bacteria can produce the acid compounds of sulphur and nitrogen which mainly cause acid rain to form, it is believed that to the main sources of pollution such as thermal power stations, district heating, motor vehicles (particularly foundries and smelteries, industries and households emitting sulphur dioxide and oxides of nitrogen, should be attributed the origin of atmospheric acidity. This event is however related also to a variety of reactions involving a large number of human activities.

The impact of atmospheric acidity upon the environment occurs through wet deposition by returning to the surface dissolved in rain, or through dry deposition by depositing directly on structures and crops.

Acid rain alters the pH of lakes and rivers when it falls directly into them, causing their biological death. When absorbed by soils it leaches out the natural base minerals such as potassium, calcium and magnesium, and drains them into the subsoil, thus removing a major source of mineral nutrients for plants and trees. The damage continues when the rainwater reaches the water table, and often carries a load of dissolved toxic metals, such as aluminium, which may arrest the growth of aquatic organisms or kill them outright by destroying in some areas any aquatic life. In soil the dissolving of toxic metals may cause the roots of trees to rot away. Besides the death of lakes and forests and rotting of stonework, the damage to architectural structures and monuments should also be considered.

The size of these problems and the impact which atmospheric acidity may have upon mankind are a challenge for all scientists in these areas.

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DISCUSSION

Brosset

We have discussed the term "total acid deposition" because the total impact of acidic material is, as you pointed out very beautifully, due to the gas phase, to the liquid phase and also to the solid phase. We have been working with these problems in Scandinavia for many years and we were really interested to get a rather detailed picture of the acidity, discriminating between strong acids in the precipitation and weak acids, and examining all the details we could get from the analysis of the material. Now we have started to consider the problem in more general terms. For example there are two components: hydrogen ion and ammonium ion. Ammonium does not represent the final neutralization of the hydrogen ion with ammonia, because the reaction is reversible and depends on the ammonium present in the air. And you know very well that plants can just use their ammonium ion and release their hydrogen ion. So the total acidification is the impact or the deposition of hydrogen and ammonium ion together. Now concerning the particles we have still the hydrogen ion, and of course you can identify the different species analyzing a filter. The gas phase is a little more complicated because the acid present in the gas phase is nitric acid, but there are also precursors of acids like sulphur dioxide.

I have just put forward these points because I think we should consider, as our Chairman has said, acid rain as a part of the total acid deposition.

Liberti

I believe that the term acid precipitation, which is widely used, is to a certain extent quite misleading in describing this atmospheric event. It gives rise to a feeling that the environment may get some damage from the rain, only when its pH is lower than 5 and no detectable effects are observed in the absence of rain. This is definitely incorrect as in most areas there is in the atmosphere a measurable concentration of acid components which determine an atmospheric acidity. The lack of suitable analytical methods has prevented so far the measuring of this important parameter. It is difficult to say if the damage to the environment is due mainly to the adsorption of gaseous components from the atmosphere, to acid deposition or to acid rain, but definitively all causes contribute to a certain extent.

It must be added that rain acidity might have different sources; it might be due to the solution of acid components of the atmosphere as well as to the formation of the rain itself in the clouds; in some cases the pH of the rain remains constant and sometimes changes towards higher values.

I think that deterioration of the environment due to atmospheric acidity is a general phenomenon which appears to a larger extent in those areas where there is either a high and direct input of anthropogenic activities or a consistent transport over a long range.

Canuto

Is there any sign of deterioration of monuments in Sicily? If it rains it is not very often, as you say. In Rome, where there are great monuments about 2000 years old — and others only 300 years old, which means they are made of different material — is there any example of deterioration of monuments that you have seen over the last 40 years — due to this dry deposition that you are talking about?

Liberti

When damages to forest and buildings in specific areas are observed, very likely a variety of factors occur simultaneously. As an example not all pine forests are decaying, but there are areas like in the coast of Tuscany in Italy and Southern France where damages are very considerable.

In my opinion atmospheric acidity always plays an important role, but additional factors should be mentioned. Tensioactive agents present in the sea are found in the aerosols and certainly their presence increases the wettability of the plants and their sensitivity to toxic agents.

Marini-Bettòlo

Thank you, Professor Liberti. I think that an important point has been cleared. We should not generally speak about *acid rains* but better of *acid deposition*.

Liberti

I believe it is more correct to talk about *atmospheric acidity* to describe this effect on the environment.

MARINI-BETTÒLO

I agree, and even the rain should be considered the scavenger of acidity as well as the snow. As the snow accumulates on the soil the effects of acid deposition appear when the snow melts.

BROSSET

What happens in snow, in fact, if the snow is falling, is that there will be in snow the different salts, mainly ammonium sulphate salts — and where there are temperature changes, of course there will be in the system a freezing point depression, so finally during the season everything of these particles will be collected just over the soil, down there, and now when the melting period comes, you have the shock, and the shock, especially when the snow is lying on a frozen lake, can kill all the fish population in a few days.

KNABE

I would like to comment on one item: the dying forest close to the seashore. According to what was here reported it may be due to a combination of sea aerosol and tensioactive agents now largely present in the environment.

They could remove the coat of waxes on the leaf surface, and so then the sea salt could penetrate into the cells and could kill the cells. I just wanted to know if this has been cleared in your country, or is it still in discussion? The other point: you mentioned quite rightly that NH^{+}_{4} is no really neutralizing agent. In the soil it will be transformed into NO^{-}_{3}, and nitric acid will contribute to acidity. The measurement of total acidity by just titrating the amount of acidity is a questionable thing. You have to determine the species of NO^{-}_{3} and NH^{+}_{4} in the precipitation and add it to the acidity, so you have to do more than titrating... Well, I have a question: what happens on the surface of leaves or other material in dry deposition of acids? Maybe if you have a coat of SO_2 which is then transformed into sulphuric acid, will this sulphuric acid be a permanent coat on the leaves and can nitric acid then be added to this?

I mean we have some examples which we really cannot interpret and it would be very interesting to know what happens on the surface of the leaves during long dry periods.

LIBERTI

Thank you for your suggestion. The problem of the decay of forests close to the seashore takes place in several areas, and according to some scientists this event has been attributed to tensioactive agents. I strongly support that surfactant agents are not poisonous for the plants but contribute to dissolve the protecting oil layer of the leaves and leave the stomata opened for a fast adsorption of any toxic substance. I do not believe in a toxic action of sodium chloride, as all pines along the seashore have always been exposed to such substance and damages have been observed only in some cases.

What has been definitely established in these areas is the presence of small concentrations of strong acids such as nitric and hydrochloric acids. It is difficult to state, however, in the present state of scientific knowledge, if these species are directly responsible for the decay of the pines.

BROSSET

You pointed out a very important thing; that is what happens really on the needles and the leaves when we have an acid deposition in the system. Probably when you have a fall through a needle tree, it will be much more acid than the rainfall itself. If you have a leaf tree, it is usually more alkaline. Does something happen? But exactly what happens I do not think we really understand.

MARINI-BETTÒLO

Do you have any evidence of the influence of acid deposition on the mobilization of some of these ions in the soil? That is, after acid deposition is there an increase of these soluble ions in the soil or not? For instance the effect on selenium in the soil, mainly, in Norway.

LAG

The first question: we do not know too much about that, but we have an increase of aluminium ion in fresh water which is harmful for a fish.

As for selenium it is very small quantities of this element that we get from the South Sea. I mentioned the differences from the coast to the inland, there we have comparatively more material.