In a syndrome as complex as Waldsterben, predisposing, inciting and contributing factors all play important roles in the death of an individual tree. Some of these factors will be assessed in the second part of this review series which will include articles by *B. Ulrich* and *E. Matzner* ('Implications of the chemical soil conditions for forest decline'), *A. Hütterman* ('The effects of acid deposition on the physiology of forest ecosystems'), *E.F. Elstner, W. Osswald* and *R.J. Youngman* ('Basic mechanisms of pigment bleaching and loss of structural resistance in spruce needles: advances in phytomedical diagnostics'), and *F. Nienhaus* ('Infectious diseases in forest trees caused by viruses, mycoplasm-like organisms and primitive bacteria'). Further parts of the series are in preparation.

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Formation of secondary air pollutants and their occurrence in Europe

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1. Introduction

Primary air pollutants are removed from the atmosphere by sink processes such as wet and dry deposition or chemical and photochemical conversion. The latter processes lead to the formation of secondary air pollutants. Among them, photochemical oxidants, primarily ozone and peroxyacetyl nitrate (PAN), and strong acids are of major concern because of their occurrence in long-range transported air masses and their biological and ecological impact.

Photochemical oxidants have attracted research and public interest since the 1940s, when substantial damage to crop plants and forest trees started to occur in southern California. Apparently, the problem has now spread over the entire United States, and ambient ozone concentrations at present reduce the yield of crop plants in all areas recently investigated[78]. Symptoms of severe ozone damage to forest trees can be observed at the present time at lower elevations on the western slopes of the Sierra Nevada Mountains[162], and, most strikingly, oxidant gas impact on successional plants has appeared in remote areas in the Blue Ridge Mountains[41]. Such an oxidant threat to plant life is also expected in other parts of the world, particularly in many countries of Europe. An involvement of oxidant gas (especially of ozone) in the process leading to the present forest dieback has been suggested for areas in Bavaria (higher elevations)[122], southern Germany and Nordrhein-Westfalen[121], and also in Switzerland[19, 47]. This presentation attempts to describe the processes possibly involved in the formation of oxidant gases in the atmosphere and to summarize some of the data available on ozone and PAN occurrence in Europe (mainly northwestern Europe). Although nitrogen dioxide (NO_2) is also considered to be one of the photochemical oxidant gases, it is only included here as it takes part in atmospheric transformations leading to ozone and PAN or nitric acid.

In recent years, another form of secondary air pollution has become an important scientific and political issue, namely that of 'acid rain'. This term refers to wet deposition in the form of rain, mist, snow, hail or intercepted fog and cloud water containing amounts of strong acids (sulfuric and nitric acid) in excess of what can be expected from the natural biogeochemical cycles of sulfur and nitrogen. Hence the phenomenon of acid rain reflects the disturbance of hydrochemical cycles[145]. Since acid or acid-forming substances can also be introduced into ecosystems by dry deposition, it is more appropriate to apply the term 'acid deposition'. This includes all deposition processes to be considered, i.e. 1) wet deposition by rain- or snowfall, etc., and dry deposition by sedimentation of particles *(= precipitation deposition)*, and 2) impactation of aerosols and mist, fog or cloud droplets together with the absorption of gases on wet surfaces or inside the stomata of leaves and needles *(= interception deposition)*[150]. The deposited acids can interfere with processes in aquatic[40] and forest ecosystems[52] and can affect agricultural crop productivity[44]. Acid deposition is believed to be the dominant factor leading to destabilization and forest dieback in Central Europe[149]. Continent-wide precipitation sampling networks in Europe and North America have provided us with a general picture of the widespread occurrence and the increasing frequency of highly acidic precipitation events[86, 87, 107, 113–115]. The formation of atmospheric acidity is largely driven by photochemistry and is therefore closely related to the formation of oxidant gases. In this review, mechanisms involved in the formation of atmospheric acidity are therefore considered together with those leading to secondary oxidant gases. Furthermore, the factors which may influence the free acidity of wet precipitation and fog are summarized, and a rough picture of the occurrence of strong acids in precipitation over Europe is given.

2. *Photochemistry of polluted atmosphere*

The photochemical reactions occurring in polluted air irradiated with UV light have been studied extensively in smog chambers and in the field where the behavior of single components was observed during episodes of high photochemical activity. A recent review by Altshuller[2] attempts to relate photochemical reaction products observed in laboratory experiments with concentrations of these compounds measured in ambient air. From the past research in this field, it can be concluded that photochemically produced secondary air pollutants (e.g. ozone, PAN, sulfate aerosols and nitrate), which are of biological and ecological concern, arise from reactions which depend on the presence of nitrogen oxides (NO, NO_2) and hydrocarbons (HC), both groups being emitted primarily from motor vehicles. But it must be remembered that HC emission from vegetation could also be important and might lead to photochemical reactions near the surface of leaves.

The photolysis of NO_2 by light in the wavelength range 300–400 nm forms oxygen atoms (table 1, eq. 1) and these react with oxygen molecules to form ozone (O_3) (table 1, eq. 2). The latter reaction requires as 3rd body (M) to remove excess energy (e.g. N_2, O_2, CO_2, H_2O or others). The subsequent oxidation of NO by O_3 yields NO_2 and O_2 (table 1, eq. 3) thus maintaining the overall balance between oxidizing and reducing components in the atmosphere. This balance is disturbed, and consequently ozone accumulates, when other reactions inhibit the destruction of O_3 by the reaction with NO. These competing reactions involve free radicals generated in the photo-oxidation of hydrocarbons, aldehydes (especially formaldehyde) or nitrous acid (HONO). Such species are the hydroperoxyl ($HO_2^{\cdot}$), the alkylperoxy ($RO_2^{\cdot}$), and the acylperoxy ($RO_2^{\cdot}$) radicals (table 1, eq. 4). Net ozone accumulation results according to equation 5. Ozone build-up in polluted air thus depends on hydrocarbon degradation. It has been shown[36] that peroxy radicals are formed by the attack of $OH^{\cdot}$ on methane, n-butane, ethylene or propylene. An example is given as equation 6 (table 1). Sources for $OH^{\cdot}$ radicals which initiate the photolytic cycle are for instance the reaction of electronically excited oxygen atoms formed during the photolysis of nitrous acid (HONO), O_3 or hydrogen peroxide (H_2O_2) (table 1, eq. 7–10)[36,37,74]. Photolysis of HONO, which accumulates during the night as a result of the heterogeneous reaction betweeen NO, NO_2 and H_2O or NO_2 and H_2O, yields an increased level of $OH^{\cdot}$ radicals in the early morning hours[74,89] thus contributing to smog formation during the following day.

Table 1. Some chemical and photochemical reactions occurring in polluted atmosphere

	Equation
$NO_2 \xrightarrow{h\nu} NO + O^{\cdot}$	1
$O^{\cdot} + O_2 \xrightarrow{M} O_3$	2
$NO + O_3 \longrightarrow NO_2 + O_2$	3
$RO_2^{\cdot} + NO \longrightarrow RO^{\cdot} + NO_2$	4
$RO_2^{\cdot} + O_2 \longrightarrow RO^{\cdot} + O_3$ (Esq. 1,2 and 4 combined)	5
$CH_3CHO + OH^{\cdot} \longrightarrow CH_3CO^{\cdot} + H_2O$	6
$O_3 \xrightarrow{h\nu} O(^1D) + O_2$	7
$O(^1D) + H_2O \longrightarrow 2\,OH^{\cdot}$	8
$HONO \xrightarrow{h\nu} OH^{\cdot} + NO$	9
$H_2O_2 \xrightarrow{h\nu} 2\,OH^{\cdot}$	10
$O_2 \xrightarrow{h\nu} 2\,O$	11
$CH_3CHO + OH^{\cdot} \longrightarrow CH_3CO^{\cdot} + H_2O$	12
$CH_3CO^{\cdot} + O_2 + NO_2 \rightleftarrows CH_3COO_2NO_2$ (PAN)	13

Although ozone is probably the major constituent of oxidant air pollution (smog)[2], its occurrence cannot give a complete picture of the extent of photochemical reactions involving man-made pollutants. According to equation 11 and in combination with equation 2 (table 1), it is formed naturally in an unpolluted atmosphere. Also, high O_3 concentrations in the lower troposphere may be due to the introduction of stratospheric ozone by turbulence. Therefore, another oxidant gas, peroxyacetyl nitrate (PAN), which is produced through oxidation of aldehydes (eq. 12 and 13, table 1), is an additional, reliable indicator for anthropogenic photochemical air pollution.

The presence of free radicals in the air not only determines the formation and build-up of O_3 and PAN, but also the oxidation of sulfur dioxide (SO_2) and NO_2. This process leads to the formation of strong acids. An excellent review of processes leading to the formation of atmospheric acidity was provided by Cox and Penkett[31]. They involve transformations in the gas phase, in droplets (liquid phase) or eventually on the surface of some aerosol particles. The rates of oxidation of acid precursors are thought to be the most important factor in determining rain acidity[65]. However, oxidation rate constants are highly variable in time and space.

Early evidence for a relationship between ozone and sulfuric acid aerosol and sulfate formation in the air came from observations made in southern England[4]. Good correlation was found between O_3 and H_2SO_4, but not for O_3 and sulfate. A correlation similar to that with sulfuric acid was found between O_3 and nitric acid[88]. The homogeneous (gas phase) oxidation of SO_2 in polluted air is predominantly due to the $OH^{\cdot}$ radical, but other reactions, e.g. photooxidation or ozone-olefin-induced oxidation, may be of some importance too[31]. Maximum rates of homogeneous oxidation of SO_2 are of the order of 3 to 4% per h[109] and the typical lifetime for SO_2 with respect to $OH^{\cdot}$-initiated oxidation in the summer is presumed to be about 10 days with an average oxidation rate of 2% per h[31]. Based on computer simulations, an average rate of SO_2 oxidation to H_2SO_4 of 0.5 to 1% per h was derived[22]. Rates of oxidation are up to 10 times slower during the winter, and very much slower during the night than during the day[27]. Reduced rates of SO_2 oxidation are also to be expected if conditions for slow dilution of plumes occur, i.e. when oxidant availability is limited[28]. An alternative to the oxidation of SO_2 in the gas phase is liquid phase oxidation, which is of great importance. It was first believed that sulfuric acid production in fog was catalyzed by transition metals like iron and manganese[31]. More recent findings suggest that the uncatalyzed oxidation of SO_2 by H_2O_2 or eventually by O_3 is the dominant process[31], especially outside urban areas. This view is supported by the negative correlation between H_2O_2 and SO_4^{2-} in cloud water (in the absence of formaldehyde)[131].

In droplets, H_2O_2-induced sulfate formation dominates under acidic conditions with a rate of about 1 $\mu g\ ml^{-1}\ min^{-1}$ at pH 4[31]. Hydrogen peroxide, which is an indicator of free radical levels in the air, occurs at rural, unpolluted sites in the range 0.3 to 3 ppb[88], but higher concentrations are expected in more polluted areas[81]. Because H_2O_2 formation depends on the photochemical activity, liquid phase oxidation of SO_2 must show temporal and spatial variations. Under conditions permitting high photochemical activity, it may be the dominant oxidation mechanism for SO_2. In urban areas, evidence for the catalytic oxidation of SO_2 in droplets was found[158], and it may be this mechanism which is responsible for the occurrence of urban smog.

Nitrogen oxide is predominantly oxidized in the gas phase by the hydroxyl radical during the daytime, which leads to the formation of nitric acid vapor[125]. NO_2 oxidation in droplets is not likely because of the low solubility of NO_2. At night, however, NO_2 can react with remaining O_3. This produces nitrate radicals which rapidly react with NO_2 to form N_2O_5[125]. The N_2O_5 yields HNO_3 upon reaction with water in droplets (e.g. in nightly fog) or on surfaces[125]. In the following early morning hours, when the fog evaporates, this nitric acid will remain as particulate nitrate (particle size > 0.5–1 µm) if sufficient basic material is present, or will volatilize. Since these mechanisms occur aloft, ground concentrations of nitrates will depend on vertical air exchange. Because of this nighttime oxidation process and the fact that NO_2 reacts with $OH^{\cdot}$ radicals much faster than does SO_2[42], daily average oxidation rates for NO_2 are much greater than for SO_2 (up to 10 times)[83]. The transformation of NO_2 to N_2O_5 and subsequently to nitrate, representing a multiphase oxidation system, contributes to the formation of oxidant smog during the next day. This underlines the importance of nitrogen oxide emission for the formation of secondary air pollutants[74,80]. Recently, Winer and co-workers[165] showed that the nighttime NO_3 radical reacts with biogenic organic compounds (dimethyl sulfide emitted from oceans; isoprene and monoterpenes emitted from vegetation) which may be an important sink mechanism of these compounds.

The oxidation products H_2SO_4, which can form aerosols, and HNO_3 are very readily incorporated into the precipitation elements. Because they are strong acids, their presence lowers the pH of clouds and rainwater. According to Harrison and Pio[76], who studied the ionic composition of aerosols and rainwater at a rural site in northwestern England, most of the acidity in rainwater can be due to the incorporation of sulphuric acid at cloud level.

To summarize the information given in this section, some possible reactions occurring in a polluted atmosphere are presented in figure 1. Special emphasis is placed on the link between processes leading to the formation of oxidant gases (O_3, PAN) and acidifying components (H_2SO_4, HNO_3) which are deposited as acid deposition.

In conclusion, secondary air pollutants are formed in the atmosphere as a result of complex chemical and photochemical reactions, involving gas and liquid phase transformations, as well as multiphase systems. Ozone accumulation depends on the balance between ozone formation due to the photolysis of NO_2 and ozone destruction due to the reaction with, for instance, NO. In the case of sulfate and nitrate, the incorporation of which into precipitation elements determines the acidity of rain, there seems to be some agreement that sulfate in precipitation derives from in-cloud and below-cloud scavenging of sulfate particles (which result from gas phase oxidation of SO_2) and gaseous SO_2 which is oxidized after its incorporation into falling raindrops (see also Charlson et al.[26]). Nitrates in precipitation are believed to result mainly from in-cloud and below-cloud scavenging of HNO_3 vapor and large nitrate particles. Scavenging of NO_2 by clouds and rainwater seems to be inefficient, but NO_2 may be absorbed to some extent by snow[24].

3. Free acidity and inorganic chemical composition of rain, fog and cloud water

The free acidity of a droplet system depends on the ionic balance of cations and anions. Chemical analysis of precipitation samples from collection networks in the USA[115] and Europe[166,167] have shown that the predominant cations in rain are H^+ and NH_4^+, while others, such as Ca^{2+}, Na^+, K^+ and Mg^{2+} (sometimes also heavy metals) occur to a lesser extent, and that the major anions are SO_4^{2-},

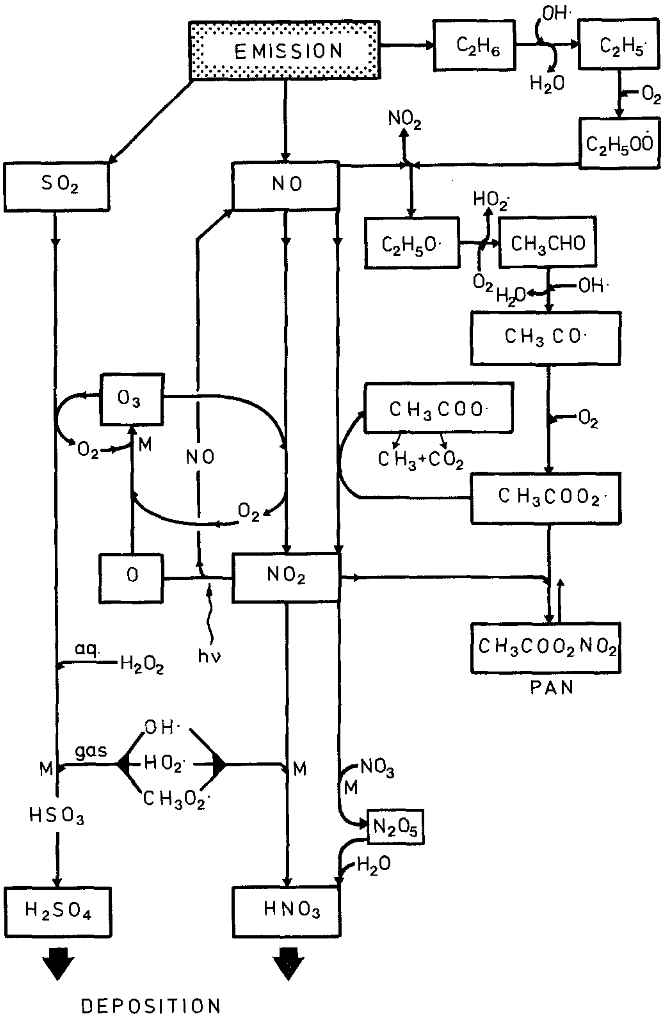

Figure 1. Possible chemical transformation reactions of atmospheric SO_2, NO, NO_2, O_3 and hydrocarbons.

NO_3^-, Cl^- and possibly F^- or PO_4^{2-}. The relative contribution of each compound to the total composition of a rainwater sample varies with time and location. According to the continent-wide survey carried out in North America, the composition of rain is determined mainly by the type of land use[107]. However, small-scale influences from local emission sources, or from the shape of the earth's surface, may affect the composition of rainwater in a specific location[99]. Also, photochemical activity in the atmosphere and mixing of air in the atmospheric boundary layer affect the composition of rain. Finally, the concentration of most ions is negatively correlated with the amount of rainfall[60,92].

In rain falling over Central Europe (West Germany, Switzerland), southern Norway, northern Britain or the northeastern USA, the sum of SO_4^{2-} plus NO_3^- (in equivalents) is very close to the sum of H^+ and NH_4^+. This is not the case in areas under the influence of maritime air like eastern England or the Netherlands. Often, it has been stated that the annual average contribution of sulfuric acid and nitric acid to the total acidity of rain is about 60 to 70% and 30%, respectively, based on data obtained in the late 1970s. This may still be correct at the present time, but it seems important to draw attention to the fact that the NO_3 to SO_4^{2-} ratio depends on the specific location[50], the time of the year[50], and on the type of deposition collector used. Values obtained with 'bulk' collectors (no separation between wet and dry precipitation deposition) are different from those obtained with 'wet-only' or 'dry-only' samplers. The data presented in table 2 for Switzerland illustrate that in wet-only samples the contribution of nitrate relative to sulfate can be much higher than in dry-only samples. The mean value, corresponding to a combined wet plus dry sample (bulk sample) for the NO_3^-/SO_4^{2-} ratio was slightly higher than what was found in bulk collectors used within the OECD network between 1974 and 1977. The slight increase is not surprising. According to the data from long-term studies it seems evident that the temporal trend of the nitrate concentration in rain and aerosol shows an increase[15,31,53].

According to Wallen[159] sulfate concentrations in rain increased in Europe between the 1950s and the 1970s on the average by about 50%, with a maximum increase in Central Europe (from 2.3 to 4.5 mg/l) and southern Scandinavia (from 1.0 to 1.5 mg/l)[57], and a minimum increase in northern Scandinavia. This trend analysis, however, has to be considered with care. Sampling and analytical procedures changed between the 1950s and the late 1970s. This might be one reason why Kallend[86] could not confirm the data presented by Wallen[159]. On the other hand, NO_3^--N deposition in the eastern USA increased dramatically from approximately 0.2 g $m^{-2}yr^{-1}$ around 1945 to 2.0 g $m^{-2}yr^{-1}$ in 1970, and in parts of Europe (England, Belgium, Netherlands) from 0.15 (1970) to about 0.5 g $m^{-2}yr^{-1}$ in 1980[15]. There was no increase in NH_4^+-N deposition over the same period of time and also no change in the average yearly precipitation amount. The increase in N deposition is therefore due to the higher NO_3^--N concentrations in rainwater. This could possibly have resulted from the increased number of motor vehicles, which are the most important source of NO_X. Increased amounts of NO_3^- in precipitation and increased rates of NO_3^--N deposition were reported for Scandinavia[144], Greenland[79], Hungary[82] and Switzerland[50]. However, in those cases where data have been collected continuously over the past 20 years, it appears that the increase in NO_3^- in rain occurred principally in the late sixties, and not in the last 10 years[124]. Hence, a clear relationship between NO_X emission and NO_3^- in rain has not yet been observed.

Table 2. Nitrate to sulfate ratio (concentration expressed in μeq/l) in weekly samples collected in 1983 at a rural site in Switzerland with a wet/dry precipitation collector and in monthly samples collected from 1974 to 1977 at five sites with a bulk collector[169]. Samples in the bucket collecting «dry deposition» were dissolved in distilled water and then analyzed in the same way as the «wet» samples. Further methodological details are given by Fuhrer[50].

	NO_3^-/SO_4^{2-} (± SD)
Wet sample	0.56 ± 0.28
Dry sample	0.37 ± 0.25
(Mean ratio)	0.46
Bulk sample	0.42

Similarly, the increase in SO_4^{2-} in rain is probably linked to the increased S emission from fossil fuel use, but the dependence of SO_4^{2-} concentrations on the rate of S emission is apparently not linear. Model calculations have suggested that the H_2SO_4 concentration in rain at short travel distances increased less over the past 20 years than the rates of S emission because of some (partially unknown) interactions between different chemical species involved[129]. About 10–20% of S dry deposition occurs within 50 km from the source (depending on the meteorological situation and the surface structure)[143]. Dry deposition is therefore high around the source and declines with increasing distance, while wet deposition is relatively evenly distributed over large areas[60]. It has been estimated for western Europe that approximately 19–28% of the emitted SO_2 is subsequently wet deposited[56,128]. This is similar to what was estimated for the eastern USA (18%[55]; 19%[64]). Similarly about 18% of the emitted NO_2 is wet deposited as nitrate[64]. These numbers agree with measurements made in Switzerland (1983). Wet NO_3^- deposition was 18% of the total deposition of NO_3^- plus NO_2, and wet SO_4^{2-} deposition was 28% of the sum of SO_4^{2-} and SO_2 deposition[50].

Interestingly, there seems to be no clear trend in the acidity of precipitation in Europe, in spite of the increasing amounts of sulfate and nitrate present[86,87,163]. The free acidity of an aqueous solution, i.e. the concentration of H^+, equals the excess of anionic over cationic charge at $pH \leqslant 5$ and is commonly determined with a pH electrode. This measurement, as well as the calculation of H^+ concentration from the difference in the concentrations of major anions and cations, determines the strong acids present in the sample at the time of analysis[73,148]. Distilled water in equilibrium with atmospheric CO_2 has a pH of about 5.6. The natural circulation of sulfur and nitrogen compounds in the atmosphere increases the potential acidity of precipitation, leading to expected pH values in the range 4.5 to 5.0[25]. The large variability of the pH of 'unpolluted' rainwater is due to spatial variations in emission and scavenging efficiency for acid precursors.

Measurements of rain acidity in remote areas of the world have indicated that the pH of rain not under the direct influence of anthropogenic emission of pollutants is ≥ 5.0[54]. Rainwater falling in Central Europe and in many other industrialized areas of the northern hemisphere, however, is consistently enriched with acidifying substances from anthropogenic sources. On a regional scale, yearly volume-weighted average pH varies between 4.1 and 4.5[9]. The acidity of individual rainstorms depends upon the history of the air mass (transport pathway, meteorological conditions), the presence of basic material in the air (NH_3, dust particles, etc.), which are often of local origin, and the amount of precipitation[147]. Careful analysis of the data from the European Atmospheric Precipitation Network (E.A.C.N.) has not revealed a clear temporal trend in average rain pH[86]. Only 29 out of 120 collection sites showed an increasing H^+ concentration during the period from 1956 to 1976. The increase at the respective sites arose from an increased frequency of intermittent high monthly values which started to occur around 1965. Other stations (e.g. in the Netherlands), however, showed a sudden drop in acidity around the same time[127]. In most cases, a significant trend towards more acidic precipitation is absent. It has been suggested that acid formation in precipitation could be limited due to limitations in scavenging processes or rates of specific reactions[163].

Apparently, the scavenging of acidifying substances seems to stop when an average pH of about 4.2 is reached. This threshold was reached in central Europe before 1935. The surplus of acidifying gases may thus be transported to remote areas leading to a spread of the acidic rainfall over larger parts of nothwestern Europe (maps for the distribution of pH in rain for 1972 and 1979 were presented by Georgii[58]).

The chemistry of a raindrop is determined by two processes, i.e. the incorporation of small particles and gases into the cloud droplets known as rainout ('in-cloud scavenging'), and the absorption of gases and aerosols below the cloud known as washout ('below-cloud scavenging'). Concentrations of SO_4^{2-} and NH_4^+ in rain over remote areas such as southwestern Norway, where air concentrations of SO_2 and NH_3 are commonly very small, are too high to depend only on washout processes[97]. During the average lifetime of a raindrop most sulfur scavenged below the cloud would remain in the S(IV) state[11]. On the other hand, it was found that S(IV) sulfur in rain ($SO_2 \cdot H_2O$, HSO_3^-, SO_3^{2-}) contributes less than 10–15% of the total S content[11]. Thus SO_4^{2-} concentrations in rain in remote areas are mainly determined by rainout. This agrees with more recent observations made at Whiteface Mountain (New York State) showing that 67 to 100% of ion concentrations depended on rainout and that the washout process was considerably less important[23]. In less remote areas with higher gas phase concentrations of SO_2, the composition of precipitation, e.g. the S content, depends on both washout and rainout[10, 33]. The contribution of S(IV) to the yearly wet deposition of S increased for instance up to 22% as observed in Norwich, UK[33]. This S(IV) is oxidized to SO_4^{2-} within 15–60 min and is therefore not seen as S(IV) in rainwater samples stored for longer periods of time[103]. The higher S(IV) content in urban rainfall may be associated with higher acidity[33]. A comparison between sites in England showed the highest acidity levels in samples from the outskirts of towns, while within towns values were lower than at open-country sites[101]. In this context it is interesting that under certain conditions washout may not even have a pronounced effect on rainfall acidity. Experimental data suggested that a raindrop with a pH of 4 does not undergo a change in free acidity during the passage through an air layer containing 100 µg m^{-3} SO_2[63]. This also relates to the problem of sample storage. Weakly acid rainwater samples, especially those in open collectors, are likely to undergo chemical changes due to the absorption of gases during storage[98]. This must not necessarily cause a change in pH.

From the ecological point of view it is important that the pH of rain reflects only one portion of the acid deposited in a natural ecosystem. Emission-deposition-relationship studies have shown that even a drastic reduction in NO_X or SO_2 emission would reduce rain acidity only slightly[64]. Therefore, it may be more important to consider the total amount of acid deposition. This includes not only bulk H^+ deposition from rain, snow or aerosol deposition, but also the direct deposition of weak and strong acids or the H^+ transfer via dry deposition of gases in the presence of water (interception deposition)[9]. In an area of the Netherlands with intensive animal husbandry, it was found that large amounts of NH_3 are volatilized from liquid animal manure. This NH_3 can either be washed out or dry deposited as ammonium sulfate on leaf surfaces from which it can be leached by rainwater[154]. In the soil, the deposited ammonium sulfate is oxidized to nitric and sulfuric acids, which leads to strong acidification of the soil solution. Ammonium was the dominant cation in wet-only samples collected in an agricultural area of Switzerland during spring, summer and fall[50].

A very important kind of acid deposition results from dew, frost or, most substantially, from the interception of fog and cloud water[164]. These events may deposit acid components directly onto the ground or they may dissolve previously dry deposited substances on the surface of plants and soils. Interception deposition is particularly

Table 3. Comparison between concentrations of some inorganic ions and pH in cloud water (or fog) and in rainwater collected at five different locations. Concentrations are given in µeq/l

		pH	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	
Case 1:	Frankenwald, West Germany, 640 m a.s.l., Nov. 82–March 83[138]						
	Rain	3.86	106	372	560		(N = 5)
	Cloud	3.40	550	1198	1300		(N = 5)
Case 2:	White Mountains, New Hampshire (USA), 1500 m a.s.l., Summer 81/82[13]						
	Rain	4.11	19	23	77	28	(N = 30)
	Cloud	3.68	14	114	240	93	(N = 36)
Case 3:	Muskegon, Michigan (USA), 670 m and 1525 m a.s.l., March 1977[139]						
	Rain	4.1	23	181	250	294	(N = 1)
	Cloud						
	670 m	4.0	54	477	685	811	(N = 1)
	1525 m	3.7	11	165	250	150	(N = 1)
Case 4:	Whiteface Mountain, New York (USA), 1484 m a.s.l., August 1976[23] (1 event, precipitating cloud)						
	Rain	4.6	3	71	100	2	(N = 1)
	Cloud	4.0	8	130	170	70	(N = 3)
Case 5:	Bern-Belpmoos, Switzerland, 540 m a.s.l., Nov. 83–Jan. 84 (unpublished) (ground fog)						
	Rain	5.00	8	13	17	30	(N = 5)
	Fog	4.92	586	248	1170	1643	(N = 8)

important in conifer stands[67]. Generally, cloud water and fog, captured by means of various artificial impactation systems, contain much larger amounts of ions than rainwater and can be far more acidic. At Whiteface Mountain in the Adirondack Mountains of New York State nearly 90% of all (nonprecipitating) cloud water pH values were in the range 2.66 to 4.66 with a mean value of 3.55 in 1977 and 3.50 in 1979[45]. In table 3, concentrations of some inorganic ions in rain, clouds and fog are compared. The enrichment factor for the various ions depends on the distance to emission sources, the type of land use at the site of collection (forested versus agricultural land, case 1 and 2 versus case 5), altitude (case 3) and the type of cloud (case 4).

Studies of cloud water chemistry have increased in number in recent years because ecologists have observed that at specific sites interception of cloud water can increase the total deposition rate of water and various elements substantially. For instance in a subalpine balsam fir stand in New Hampshire (1220 m a.s.l.) 62% of H^+, 80% of NH_4^+, 68% of SO_4^{2-}, and 81% of NO_3 annual deposition derives from cloud droplet capture[95]. The total cloud water deposition at this site was 840 mm yr^{-1}. In table 4, the composition of cloud water and fog, as observed at various locations in Europe and the USA, is listed. It has to be noted, however, that the collection procedure for fog and cloud droplets needs further improvement. Many of the systems presently in use do not exclude contamination from dry particle deposition or do not allow separation between raindrops and cloud or fog droplets. Nevertheless, the analysis of fog and clouds in urban as well as in rural regions should be carried out intensively. This would also lead to a better understanding of spatial and temporal variations in liquid phase oxidation reactions. There is uncertainty about many aspects of cloud water chemistry, for example about the role of formaldehyde which can react with sulfite to form the strong acid hydroxy-methanesulfonic acid[126], or about the influence of the type of cloud (e.g. precipitating versus nonprecipitating clouds) on the ongoing conversion and scavenging processes. Also, the question of the source of acid in clouds needs further investigation.

In summary, the free acidity of rainwater is determined by the balance of cations (NH_4^+, Ca^{2+}, Mg^{2+}, K^+, Na^+) and anions (SO_4^{2-}, NO_3^-, Cl^-). A trend to more acidic rain is not evident, although SO_4^{2-} and especially NO_3^- concentrations have increased. The composition of rainfall is influenced by the type of land use, the proximity of emission sources, and the meteorological conditions. In single rainfall events, the concentration of most ions decreases with increasing precipitation amount. Substantial acidic deposition may occur from fog and cloud droplet interception. In cloud water, ionic concentrations are much higher than in rainwater. For further studies of the composition of rain and cloud water, however, improved procedures for the collection and analysis are needed urgently.

4. Area distribution of sulfate, nitrate and free acidity in precipitation, and of the respective deposition rates in Europe

In 1972, a worldwide precipitation chemistry network was established under the auspices of WMO and UNEP (UN Environmental Program). Today, approximately 110 sampling stations are included in the so-called 'WMO Background Air Pollution Monitoring Network' (BAPMoN). Based on the data obtained by these stations during the years 1972–1978, a picture of the global distribution of rain consitutents, e.g. rain acidity, has been presented[57,58]. Areas receiving rain with the highest average content of free acidity (expressed as lowest pH values) are central Europe and the northeastern part of North America. On the other hand, very recent data showed that the pH of rain in rural areas of Asia is relatively high[57,77]. Those low levels of free acidity are most likely due to the dispersion of alkaline aerosols from the ground, which are washed out by precipitation. A thorough examination of the precipitation chemistry data obtained by networks in North America (CANSAP, NADP, MAP3S/RAINE) has clearly revealed that the composition of falling rain is determined by local and regional land-use patterns and the proximity to anthropogenic emission[107,147]. Highest acidity levels are thus found where – at the same time – the abundance of precursor gases from anthropogenic emission is high, and the concentration of neutralizing soil components (e.g. NH_4^+, Ca^{2+}) is lowest[147].

Similar conclusions can be drawn from the 1980 data for wet precipitation given in table 5 for selected European

Table 4. Concentrations of major inorganic ions and pH in cloud water and fog (in µeq/l) collected at selected sites in Europe and the USA with the aid of ground-based collectors or collectors installed in aircrafts

Location	pH	H^{+a}	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}	Reference
Münstertal, Black Forest	4.1	79	377	147	390	399	121
Bad Steben, Frankenwald	3.4	398		550	1198	1300	138
Brocken, Harz	5.1	8	672	206	217	775	106
Pennine Hills, Northern England	3.5	342	215	186	118	252	61
Bern, Central Switzerland	4.9	12	1643	586	248	1170	unpublished
Kap Arkona, Baltic Sea	3.8	158	2335	1763	453	1860	106
Aircraft over Netherlands	5.5–3.2	3–630	12–1055	16–475	8–860	18–400	131
Aircraft over the North Sea	2.7	1995	2053	1859	803	2017	96
Aircraft over the USSR	5.3	5	28	23	3	56	120
Whiteface Mt., New York State	4.2–3.2	63–631	4–310	1–15	7–190	40–800	158
Mt. Moosilauke, New Hampshire	3.54	288	108		195	342	93
White Mountains, New Hampshire	3.7	209	93	14	114	240	13
Pasadena, California	2.25	5625	7870	676	12000	5060	158
Muskegon, Michigan	4.0	100	811	54	477	685	139

[a] Calculated from pH value.

Table 5. Annual average concentrations of major ions in wet precipitation and precipitation amounts for selected W.M.O. BAPMoN stations in 1980[166]. Concentrations are arithmetic means of monthly mean values expressed in mg/l. Precipitation amount is given in mm/month (numerically equal to l/m^2)

No.	Station	Precipitation amount		pH	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+-N	Cl^-	NO_3^--N	SO_4^{2-}-S
		NG[a]	SG[a]									
1	Austria, Retz	38.3	35.6	4.66	0.34	0.37	0.41	3.26	1.20	0.98	1.10	3.49
2	Czechoslovakia, Chopok		102.6	4.19	0.27	0.19	0.06	0.43	0.73	0.55	0.45	1.86
3	FRG[b], Deuselbach	66.7	80.1	4.22	0.37	0.10	0.13	0.30	0.39	0.84	0.47	1.26
4	FRG, Langenbrügge	47.9		4.02	0.68	0.14	0.13	0.68	1.22	1.57	1.07	2.79
5	Finland, Jokioinen	40.8	53.5	4.48	0.33	0.18	0.10	0.87	0.76	1.26	(0.49)[c]	2.40
6	France, Abbeville	56.6	75.9	5.11	3.07	0.64	0.40	1.35	1.74	5.07	0.91	2.54
7	GDR[b], Neuglobsow	56.4		4.06	0.57	0.24	0.16	0.82	(0.76)	(1.09)	(0.60)	(1.64)
8	Greenland, Godhaven	(215.7)		5.23	5.56	0.30	(0.54)	0.51	0.76	(0.98)	(0.07)	1.15
9	Hungary, Kecskemet		58.5	5.38	0.58	0.29	(0.78)	(1.63)	(1.28)	1.59	(0.72)	(2.56)
10	Ireland, Valencia Observ.	123.6	147.9	5.46	7.63	0.40	(0.96)	0.62	0.12	12.53	0.12	1.16
11	Italy, Trapani	(43.3)		6.36	7.69	1.11	(2.75)	(3.22)	(0.47)	(19.24)	(0.16)	(0.98)
12	Italy, Verona	73.1		4.92	0.40	0.22	0.57	1.73	1.37	0.72	0.56	0.82
13	Norway, Birkenes	93.0		4.18	0.74		0.11	0.28	0.72	1.38	0.66	1.47
14	Norway, Kise	38.0		5.12	0.16	0.69	0.16	0.77	1.59	0.37	0.44	1.63
15	Poland, Suwalki	47.5	54.7	4.67	0.35	0.21	0.10	0.82	1.31	1.10	0.74	2.10
16	Portugal, Barreiro		41.2	6.18						(1.39)	(0.22)	(1.61)
17	Romania, Turia	52.2	66.6	5.48		(1.33)	(1.43)	(7.59)			(0.28)	
18	Scotland, Dumfries	88.0	125.6	4.37	0.95	0.20	(0.16)		(0.79)	(1.98)	(0.43)	(1.43)
19	Sweden, Velen	51.9		4.53	0.35	0.17	0.07	0.28	1.13	0.58	0.66	1.61
20	Switzerland, Payerne		81.9	4.72	0.24	0.26	0.11	(0.53)	(0.65)	(0.74)	(0.62)	1.29
21	Yugoslavia, Lazaropole	88.5		6.14	1.08	0.28	0.24	2.37	0.43	2.08	(0.25)	2.11
	Mean value			4.93	1.65	0.38	0.52	1.48	0.92	2.80	0.53	1.80
	Minimum			4.02	0.16	0.10	0.06	0.28	0.12	0.37	0.07	0.82
	Maximum			6.36	7.69	1.33	2.75	7.59	1.74	19.24	1.10	3.49

[a] NG, National gauge; SG, sample gauge. [b] FRG, Federal Republic of Germany; GDR, German Democratic Republic. [c] Values in parenthesis are based on incomplete data sets.

BAPMoN stations. At remote locations (e.g. Godhaven, Greenland, or Valencia Observatory, Ireland) NO_3^--N concentrations are very low and most of the SO_4^{2-}-S is derived from sea salt. Consequently, pH values are between 5 and 5.5. The lowest pH values were reported for northeastern West Germany (Langenbrügge, pH 4.02) and southern Norway (Birkenes, pH 4.18). Highest SO_4^{2-}-S and NO_3-N contents were observed in Austria (Retz), but high Ca^{2+} and NH_4^+ concentrations partially neutralized the samples at this site.

The distribution of free acidity in rain over Europe can be derived from the measurements within the OECD program 'Long-range Transport of Air Pollutants' (LRTAP)[113] which was carried out in the mid-seventies with nearly 80 stations in northern and western Europe. Highest concentrations were observed in the central part of Europe (West Germany) averaging 60 to 80 μeq/l H^+, and in parts of southern England. However, the isopleth maps presented have to be considered with care, because of their inadequacy in showing the pattern of time variation over the years, the uncertainty associated with individual contours, and the nonexistence of geographical homogeneity which becomes evident by the comparison of results from adjacent sites[87]. Furthermore, erroneous values were often not excluded from the calculations (see Kallend et al.[87] for references), and different methods for sampling and analysis were applied at different sites. Interlaboratory comparison of analytical results showed significant differences when different methods were used[148]. The use of pH values to indicate rain contamination is dangerous, because the level of free acidity depends on the balance between a series of cations and anions. The concentrations of SO_4^{2-} and NO_3^- (after correcting for sea salt) may be more useful. Based on the monthly mean values obtained from 1972 to 1976 at 25 BAPMoN stations in Europe, isopleths on the annual mean concentrations of these two ions were drawn[159]. Such maps are reproduced in figure 2.

According to these maps, the highest concentrations of both sulfate (> 4 mg/l) and nitrate (> 3 mg/l) occurred in rain over central West Germany; however, the continent-wide distribution of the two major anions in rain is not exactly identical. The concentration values given for West Germany were confirmed in the course of a more recent study (1979–1981) where 'wet-only' samples were analyzed[59, 60]. Measurements currently carried out in Switzerland tend to confirm the concentration of sulfate, but not that of nitrate[50]. The detailed study performed in West Germany (1979–1981) with 10 different wet-only sampling stations revealed highest SO_4^{2-} concentrations in the Ruhr area (approximately 120 μeq/l in the winter and 143 μeq/l in the summer), in the Rhein-Main area and around the city of Hamburg[60]. At a less polluted site (Deuselbach) 50 and 85–100 μeq/l SO_4^{2-} were found in the winter and summer, respectively. The time pattern of SO_4^{2-} and NO_3^- concentrations at several sites showed a sharp increase during springtime, while this peak was absent at other sites like Deuselbach or Hohenpreissenberg. Springtime peak concentrations were also reported for sites in England[103], Switzerland[50], and several other locations[66]. They seem to depend on photochemical activity and mixing in the atmospheric boundary layer. The strength of this peak depends to some extent on altitude (unpublished observation). Such topographic influences can lead to variations in rainwater composition on a small scale and, hence, are not seen in the isopleth maps presented[99]. A significant decrease in the concentration of several ions in wet samples (e.g. SO_4^{2-}, NO_3^-) can be found at sites well above the mixing layer (for instance at Jungfraujoch, Switzerland, at 3500 m a.s.l.)[50]. While the

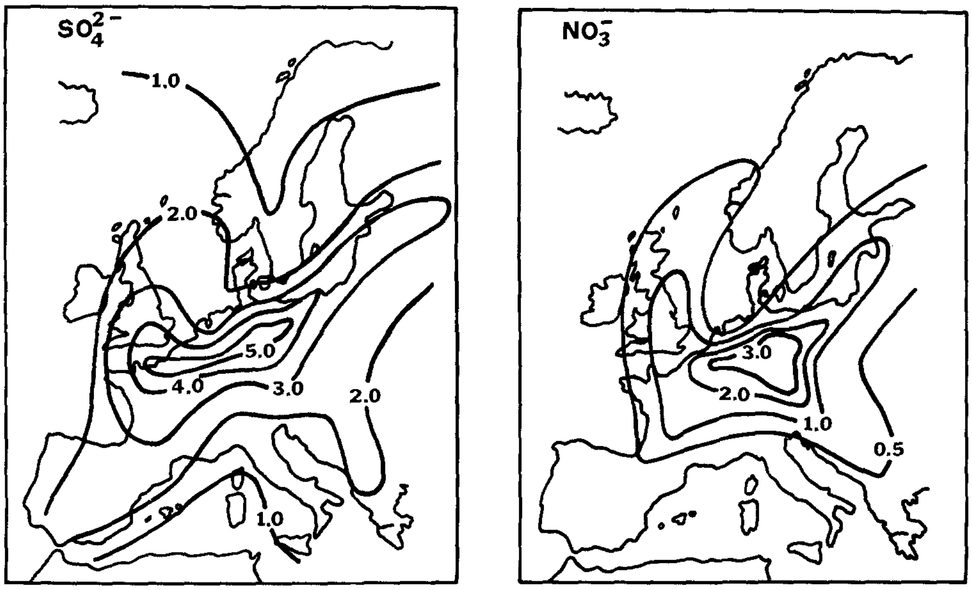

Figure 2. Average concentrations of sulfate and nitrate in West European precipitation (mg/l) for the years 1972–1976. Isopleths are derived from monthly mean values of 25 BAPMoN stations (after Wallen[159]).

concentration of some ions may be lower at elevated sites, however, the respective deposition rates can be higher due to higher precipitation amounts[59,60]. Another strong influence on the composition of rain is exerted by the sea. In the vicinity of the sea (e.g. in the Netherlands), sulfate concentrations can be as high as 120 to 150 μeq/l during wintertime[90]. In general, these observations underline the importance of specific criteria for the selection of sampling sites which should be representative for larger areas.

It has been stated in the literature that the relative contribution of sulfate and nitrate to the acidity of rainwater is about 70% and 30%, respectively, in the northeastern USA[53], and also in Scandinavia[114], and in the UK[48]. Areas with intense motor vehicle traffic show a higher relative contribution of NO_3^-[50,104]. Due to the high oxidation rate of NO_X to NO_3^- and the low height of emission from automobiles, emission of NO_X may affect the composition of rainwater within a relatively short distance from the source. Also, the NO_3^-/SO_4^{2-} ratio changes during the year, with the highest values in springtime[50]. Therefore, this ratio, which is often taken as an important parameter when discussing the causes for rain acidification, may vary considerably on a small scale and with time, and average values representing the situation in large areas are of limited accuracy.

The distribution of SO_4^{2-} and NO_3^- in rainwater shown in figure 2 demonstrates a relatively even distribution. There is a difference by only a factor of about 2–3 between less polluted and industrialized areas. This is unlike the distribution of gaseous S and N compounds (e.g. SO_2) where 10–15 times higher concentrations can be measured in industrialized areas than at remote locations[60]. This is important in the context of rates of wet versus dry deposition. Wet deposition rates depend upon both the concentration of a particular ion in rain, snow, etc., and the amount of rainfall. Topography is one major factor in determining the area distribution of wet (and to some extent also of dry) deposition rates. For instance, as moisture-laden air moves up a mountain slope, more rain tends to fall at higher elevations on the windward side, while the lee side receives less (see Bormann[14] for references).

Such orographic precipitation is of special importance in Scandinavia, Iceland, and in the vicinity of the Alps[112]. A clear example was given by Schrimpff[137] for northern Bavaria (Steigerwald and Fichtelgebirge). It should be noted that wet deposition rates may be inaccurate, especially at extreme locations such as hilltops, because of difficulties in accurately measuring rainfall amounts. In table 6, rates of wet deposition for sulfate, nitrate and free acidity (H^+) are listed for selected European sites.

Average wet deposition rates for SO_4^{2-}-S are in the range 2.7–5.5 mg m^{-2} day^{-1} in West Germany (except for the heavily industrialized Ruhr area), the Netherlands and Poland, 2.5–3.3 mg m^{-2} day^{-1} at lower altitudes in England and Ireland, and 1.4–2.5 mg m^{-2} day^{-1} in southern Scandinavia and Switzerland. The average deposition rates for NO_3^--N at the various locations seem to be distributed in a similar way, and they are commonly in the range 0.7–1.9 mg m^{-2} day^{-1}. Table 5 also contains wet deposition rates for free acidity, expressed as mg H^+ m^{-2} day^{-1}. These values show great variation within single countries. They tend to confirm high deposition rates in central West Germany and England. The high deposition rates of SO_4^{2-}, NO_3^- and H^+ in central West Germany are thought to be the reason for the changes in the chemical properties of forest soils[149,151].

Another important process of pollutant transfer to the ground in the liquid phase is the interception of fog and cloud water. There is, however, only limited information available at the time about the rate of this kind of deposition. An example was given already in section 3. Other data were obtained at Great Dune Fell in Cumbria (UK), where an average input of 0.7 and 0.38 mg m^{-2} day^{-1} was estimated for sulfur and nitrogen, respectively. This equalled up to 20% of deposition rates recorded with rainfall gauges[39]. According to Lovett[93], most of the cloud water deposition takes place in the top 3 m of a balsam fir canopy, and the deposition velocity increases linearly with wind speed (ranging from 10 to 80 cm sec^{-1}). Much lower deposition velocities in the range 24 to 70 mm sec^{-1} were observed in field measurements of turbulent fluxes of wind-driven fog droplets (diameter of approximately 20 μm) to a grass surface[38]. Therefore, deposition rates for elements contained in fog are likely to be insignificant over agricultural land at lower elevations (unpublished observation), but in areas where orographic cloud formation occurs (wind-exposed mountain slopes at higher elevations) high inputs are likely to occur, especially in forests[8,94]. In such areas, total wet deposition rates can be very high and effects of acid deposition on forests might be expected. A link between the dieback of forests and interception deposition of acidic fog and clouds was proposed in the literature recently[136,157]. Statistics on the occurrence of fog are therefore needed for extended areas. A good example was presented for the Swiss prealpine basins[160].

In summary, continental-scale distribution of secondary pollutants in rain (SO_4^{2-}, NO_3^-), as observed within the European sampling network (BAPMoN), can be seen in figure 2. Concentrations are high inCentral Europe and southern England. They are relatively low in France, Italy, Switzerland, and in Scandinavia. However, these maps fail to show important short distance and temporal variations. Also, concentrations in rain may not reflect accurately the actual deposition rates. These rates depend additionally on rainfall amounts and, importantly, on rates of fog and cloud water interception. Hence, extremely high rates of acid deposition are to be expected on wind-exposed, forested slopes at higher altitudes (exposed to frequent fog or upward moving clouds, and to orographic precipitation) in areas where sulfate and nitrate, together with free acidity and ammonium contents of fog, clouds and rainwater are high. Such locations may not only occur in Central Europe, but also in England, Scandinavia, Switzerland or southwestern Germany and Austria. It is this high spatial variability of acid deposition which confounds the evaluation of general cause-effect relationships[13] and which cannot be predicted by large-scale models.

Table 6. Rates of wet deposition for SO_4^{2-}-S, NO_3^--N and H^+ in different areas of Europe. Units are mg m^{-2} day^{-1}

Country	Area	SO_4^{2-}-S	NO_3^--N	H^+	Reference
Germany	Ruhr	7.95–11.78			119
		5.55	1.92		60
	Rhein-Main	3.84			119
		3.70		0.118	60
	Deuselbach	2.74			119
		3.00	1.21	0.104	60
	Schauinsland	5.48			119
		3.66			60
England	Central part	2.19–3.30			100
		2.50			84
		2.80			103
			0.82–1.60		15
				0.14–0.27	48
				0.06–0.21	7/101
Ireland	Open country	2.70			46/100
Sweden	Southern part	2.60			69
Norway	Southern part	1.70	0.91		1
				0.137	132
	Southwest	1.00			133
Poland	Urban area	8.50^a			85
	Rural area	4.10^a			85
	Mountain area	2.50^a			85
Netherlands	De Bilt	3.95	1.64	0.098	127
Switzerland	Dübendorf	3.2^1)	1.44^a	0.146^a	169
	Payerne	3.47	1.67	0.051	166
		3.28	2.18	0.010	167
	Jungfraujoch	1.26	0.34	0.003	166
		1.54	0.61	0.006	167
	Bern-Belpmoos	1.47	0.67	0.049	50

[a]) Values are from bulk samples and contain contribution from dry deposition.

5. *Occurrence of ozone in the lower troposphere*

Naturally-produced ozone is present at high concentrations in the stratosphere, centered about 25 km above the earth's surface, where it is the product of UV-light mediated dissociation of molecular oxygen. This stratospheric ozone can be introduced into the troposphere by turbulence[32,35]. The distribution of naturally-produced ozone in the troposphere therefore depends on stratospheric air circulation and on the transport across the tropopause (see Fricke[49] for references). Natural background ozone concentrations near the ground may reach 45 ppb at a latitude of 60°N or only 25 ppb in the tropics (1 ppb O_3 is equivalent to 2.1 μg/m^3). During short periods of time, however, extremely intensive vertical exchange may lead to concentrations of up to 100 ppb, as observed in England[35]. Ozone formation near the ground from photochemical conversion of precursor gases emitted from natural sources may contribute to a variable extent to the natural background ozone level. According to Rhode and co-workers[130], 1000 Tg of ozone are injected annually into the troposphere from the stratosphere and 2000 Tg are produced in the tropospheric gas phase. The main sinks for ozone are destruction at the surface (1100 Tg yr^{-1}) and gas phase destruction (2000 Tg yr^{-1}). In industrialized areas, as in most parts of Europe, the occurrence of ozone in the lower troposphere is predominantly determined by the emission of nitrogen oxides and C_2–C_8 hydrocarbons from anthropogenic sources, in combination with the synoptic weather conditions.

The widespread occurrence of elevated ozone concentrations in northwestern Europe was studied during 1971 to 1975[72]. It appeared that extremely high ozone levels over distances of several thousand kilometers could occur during periods when there was a slow-moving or quasi-stationary anticyclone over western Europe, associated with favorable conditions for photochemical conversion mechanisms (warm, dry, high solar radiation intensity). Under these conditions, the resulting large-scale distribution of ozone is very homogeneous with maximum concentrations around 100 ppb near the ground and 50 ppb in the free troposphere. Data collected in eight different countries from 1976 to 1979 confirmed these observations[135]. The correlation between high ozone levels and synoptic weather patterns showed that in the case of a high pressure system centered over Central Europe, Scandinavia or Finland, ozone concentrations are high in most parts of northwestern Europe. With a high pressure system located over the North Sea, ozone concentrations can still be high over the continent and England, but not in Scandinavia. On the other hand, Scandinavia may be the only area exposed to high ozone levels when a low pressure system is located over Central Europe. On a smaller scale, the synoptic ozone concentration can be enhanced when precursors from a local source are introduced into already-polluted air[84]. Possibly, the polluted air mass can originate from a distant source region[30]. The contribution of middle- and long-range transport of tropospheric ozone to pollution levels at a rural site in northwestern England was examined in 1978[75]. It was shown that long-range transported air masses introduced 50 to 80 ppb ozone, and that middle distance sources within England contributed an additional 20–50 ppb. Episodes with extremely high ozone concentrations in most parts of northwestern Europe occurred in June/July 1976. Maximum hourly concentrations reached 129 ppb in Austria (Vienna), 186 and 148 in West Germany (Frankfurt and Feldberg, respectively), 191 ppb in the Netherlands (Delft), 125 ppb in Sweden (Rörvik), 104 ppb in Norway (Björnstad) and even 258 ppb in England (Harwell)[135]. The high concentrations observed in southern England were clearly related to 1) the transport of air masses from the European continent, and 2) to local and meso-scale formation[3]. During other, less dramatic episodes, only one of the two formation scales was dominant.

Ozone levels near the ground are often subject to distinct temporal variations. In the course of a year, the highest levels occur during the summer when photochemical activity is highest. The variation of solar radiation intensity during the year affects primarily the maximum ozone concentrations which result from anthropogenic emissions, while the large-scale background concentration is less affected[49]. During the day, the concentration is highest in the early afternoon and very low during the night[12]. Under the influence of episodes with pronounced long-range transport, the diurnal pattern can be displaced, with the peak concentration earlier or later than normal[102]. The decrease in the ozone concentration during the night (a similar observation can be made in the vicinity of a large NO_X-emission source) is due to the reaction of ozone with NO_X. This reaction is an important sink for ozone in the lower troposphere. Opposite time patterns for ozone and NO_X concentrations can thus be observed[12, 51, 102, 116]. This sink for ozone can be absent, for instance at higher altitudes in rural areas, especially above the mixing layer (see below). As a result, ozone accumulates in this 'aged' smog layer over two to three days, and the concentration remains high (80–100 ppb) for an extended period of time. This phenomenon is well documented by data obtained in 1976 at two German stations, Feldberg (800 m a.s.l.) and Michelsberg (490 m a.s.l)[134] and 1978[49]. A similar ozone behavior was observed in Austria at Wank Peak (1780 m a.s.l.) and Zugspitze (2964 m a.s.l.)[123], as well as at Patscherkofel (1954 m a.s.l.) and Hall/Tirol (560 m a.s.l.)[141]. At the higher sites, a diurnal pattern of the ozone concentration is virtually absent. Daily average values from these rural stations are thus often higher than at stations near the center of emission where the highest peak concentrations can be measured[121]. This is illustrated by the data given in table 6.

The consequence of a lack of ozone destruction by NO can also be observed at coastal sites. The sea breeze commonly contains only low NO concentrations and the level of ozone is relatively constant, also at night. This was observed at the west coast of England[29] and in Italy[62]. The difference between the diurnal behavior of ozone in the mixing layer and above the mixing layer is very important. For this reason it was studied in detail for instance in the heavily polluted Rhein-Ruhr area in West Germany[49] and in the Netherlands[155]. A possible change in the vertical profile of the ozone concentration in the course of a day is shown in figure 3.

During the night, ozone concentrations are higher above the mixing layer and they do not change much during the daytime. Within the mixing layer, changes in ozone levels

Table 7. Ozone concentrations (daily average and maximum hourly concentration in ppb) measured at different altitudes near Garmisch (Austria). Values were obtained between June 1 and September 30 from 1977 to 1980. A separation was made between sunny (relative sunshine duration > 80%) and cloudy (relative sunshine duration < 1 h/day) days.

		Mean (ppb)	Maximum (ppb)
Garmisch, Valley (740 m a.s.l.)	Sunny days	30.8	53.4
	Cloudy days	23.0	33.3
Wank Peak (1780 m a.s.l.)	Sunny days	43.8	49.0
	Cloudy days	36.4	39.4
Zugspitze (2964 m a.s.l.)	Sunny days	43.1	44.6
	Cloudy days	43.9	45.5

[a] Values were estimated from figure 2 in Reiter and Kanter[123].

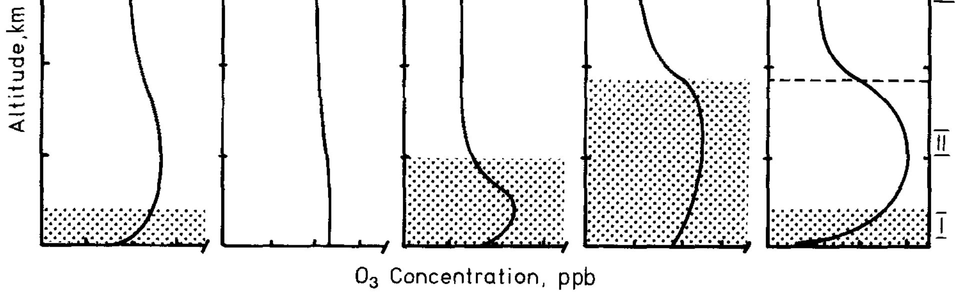

Figure 3. Possible behavior of the vertical ozone profile in polluted areas during a day: *a* at night; *b* after sunrise when vertical exchange starts; *c* before, and *d* after mixing is complete; *e* during photochemical episodes at night and in the early morning hours with an aged smog layer between the subsidence inversion and the radiation inversion. I, radiation in version layer; II, aged smog layer; III, free troposphere (after Van Duuren et al.[155]).

are much more pronounced. The fact that ozone levels are higher inside the mixing layer than above in the daytime indicates that ozone is produced near the ground and is not introduced from the stratosphere. The same observation has been reported previously by workers in the USA[156] and West Germany[49]. The destruction of ozone during the night can be restricted to the relatively low mixing layer. This leaves an 'aged' smog layer on top (see fig. 3e). This persistent ozone can then be transported over long distances. As a consequence, remote areas are exposed. For instance the coast of southern Scandinavia is well known to be subject to episodic high ozone concentrations (around 100 ppb) due to long-range transport of air masses from the European continent and England[68, 135]. In general, it can be said that the vertical ozone distribution depends upon atmospheric stability, mixing and dilution processes associated with ozone-sink and -generating mechanisms[108]. In table 8, values for average and peak concentrations of ozone are listed for different sites in Europe. In the absence of long-range transported air, ozone concentrations at remote rural sites are commonly in the range 30–50 ppb (average concentration during summer months). Elevated locations are exposed to higher average concentrations (50–90 ppb).

Table 8. Average and maximum ozone concentrations during summertime at selected sites in Europe

Location	Time	Mean (ppb)	Maximum (ppb)	Hours with more than 80 or 95 ppb[a]	Reference
Federal Republic of Germany:					
Schauinsland					
(1205 m a.s.l.)	May-August 82	56	95	13 (80)	152
	May-August 83	58			153
Brotjacklriegel					
(1016 m a.s.l.)	May-August 82	54	82	4 (80)	152
	May-August 83	57			153
Deuselbach	May-August 83	37			153
Waldhof	May-August 83	52			153
Frankfurt	May-August 83	23			153
German Democratic Republic:					
Arkona	June-August 77	32			161
Fichtelberg	June-August 77	29			161
Scandinavia:					
Rörvik	May-August 79	54	150	14 (80)	70
Lerum	May-August 79	39	92	5 (80)	70
Nääs	May-August 79	40	94	4 (80)	70
Alingsas	May-August 79	35	116	4 (80)	70
Göteborg	July-Sept. 80	32			111
Austria:					
Hall, Tirol					
(560 m a.s.l.)	May-August 81	16	81		141
Patscherkofel					
(1954 m a.s.l.)	May-August 81	92	140		141
England:					
Bottesford	May-August 78	25		37 (80)	102
	May-August 79	33	144	65 (80)	102
Switzerland:					
Sion	May-August 81	33			21
	May-August 82	31			20
Dübendorf	May-August 81	12			21
	May-August 82	25			20
Birmensdorf	May-August 82	29	130	126 (80)	18
				35 (95)	18

[a] The respective concentration in indicated in parenthesis.

When a site is located downwind of an emission source (industry, city), ozone levels can rise. This was shown in the Rhein–Ruhr area (Cologne/Bonn) where peak concentrations of 150–200 ppb were measured[49, 108], in southern England[6, 84], and in several areas in the USA[43]. A study carried out at a rural site in Switzerland demonstrated the rapid decrease in ozone concentration when the wind changed from north (downwind from emission sources) to south (mountain air)[51]. At Schauinsland (1205 m a.s.l.) near Freiburg (Black Forest, West Germany), 43 hourly mean ozone concentration values were higher than 100 ppb in 1982, and at the more remote Brotjacklriegel (1016 m a.s.l.) the corresponding number was 8[121]. These concentrations occurring in remote areas, where forested or agricultural land is dominant, should be compared with the threshold concentration for ozone damage to plants. This threshold is highly variable among plant species and under different environmental conditions[43]. Nevertheless, it can be accepted that in the case of many conifers exposure to concentrations above 80 ppb for several hours can cause symptomatic injury[142]. This concentration was exceeded at Brotjacklriegel during 188 h in 1981 and 419 h in 1982[121]! In industrialized areas like the Rhein–Ruhr valley, where more than 200 ppb ozone can be observed, the level of 90 ppb was exceeded in 1976 in the course of every second day[49]. Furthermore, chronic effects (e.g. suppression of photosynthesis) must be expected at even lower concentrations, especially when other trace gases are present which act synergistically[43, 91]. Unfortunately, there is only limited information available which shows the trend in the tropospheric ozone concentration over the past decades. Based on data for background ozone levels collected at various sites in the world, it has been suggested that the concentration near the ground increased sharply between the early 1960s and the early 1970s due to anthropogenic pollution (see Worth and Ripperton[168] for references). Values obtained over the past 20 years at the rural station Hohenpreissenberg (West Germany) also demonstrate the trend to increasing background concentrations[5]. The best evidence for this trend in Europe comes perhaps from observations made since the 1950s in the German Democratic Republic[161]. A statistically significant increase in annual average ozone concentrations near the ground was found at all of seven stations. Ozone increased until 1971 by about 2% yr^{-1}, and from 1972 to 1977 by about 5% annually.

To summarize, areas likely to be exposed to ozone concentrations which can be threatening to plant life during summertime could be described as follows:

- on a large scale in most parts of Europe under the appropriate synoptic weather conditions (concentrations can reach 100 ppb);
- on a regional scale, 50 to 100 km downwind of urban centers (peak concentrations may be between 100 and 150 ppb);
- on a local scale, in the lee of industrial areas (petrochemical plants) (concentrations may exceed 150 ppb);
- in areas subject to long-range transported air masses, especially at higher altitudes where elevated concentrations can occur over long periods of time.

Considering all these possibilities, it must be realized that ozone concentrations above 80 ppb can frequently occur at numerous locations in Europe during sunny, dry days in the summer, particularly at sites where ozone destruction is limited, e.g. remote, rural or elevated locations.

6. Occurrence of peroxyacetyl nitrate in tropospheric air

Peroxyacetyl nitrate (PAN) has been found during sunny days in substantial amounts in polluted atmospheres in many parts of the world[146]. Therefore, PAN is not only an indicator for photochemical activity, but also an important air pollutant. In clean maritime air (measured over the Pacific Ocean), PAN concentration ranged between 0.01 and 0.4 ppb at altitudes up to 8 km[140]. The first measurement in ambient air in Europe was made at Harwell (southern England) in 1974 and showed that concentrations over land can be higher[118]. The maximum level reported for 7 September (1974) was 2.3 ppb. During the same year, 3.8 ppb were measured in the Netherlands (Delft)[71]. In 1975, the highest PAN concentration at Harwell was 8.9 ppb (8 August) and in London 16.1 ppb (14 August)[117]. Usually, in southern England 0.1 ppb PAN is expected to occur in conjunction with 5 ppb ozone (50:1)[116, 117], and in the Netherlands (Delft) ratios of 50:1, 14:1, and 33:1 were observed, depending on the direction of the wind[110]. In California, ratios between 5:1 and 25:1 were recorded (see Altshuller[2] for references). PAN concentrations in southern California appear to be 5–10 times higher than elsewhere. In Riverside, average concentrations during the daytime were 8.1 ppb in July, 9.4 ppb in September, and 8.8 ppb in October of 1980[146]. It is worth noting that episodes of more than 15 ppb for 4 h in the morning and more than 4 h during the afternoon are considered to have phytotoxic effects[146].

PAN was also found to be present in long-range transported air reaching Risø (Denmark) and Göteborg (Sweden)[111]. Concentrations reached 4.2 ppb at Risø and 3.5 ppb at Göteborg between 2 and 4 September 1980. Interestingly, peak concentrations at Göteborg were observed at midnight which clearly excluded local formation. The latter would lead to highest levels during the day. The 850-mbar trajectories for the air mass showed transport from England and/or the northwestern part of the continent. In the absence of long-range transport, PAN concentrations were lower, 0.7–1 ppb during the day and 0.1 ppb at night. PAN measurements were also carried out in West Germany. Maximum concentrations in the summer in the Rhein-Ruhr area (1978–1980) were 6.1 ppb at Köln-Rodenkirchen and 3.6 ppb at Essen[16, 17]. Recently (September/October 1983), the vertical distribution of PAN over southern Germany was investigated. Concentrations were in the range 0.6–3.7 ppb at 300 m a.s.l. and decreased to values between 0.09 ppb and 0.55 ppb at approximately 5 km a.s.l.[105]. Measurements since 1974 at Delft (Netherlands) show a general increase in the maximum PAN concentration from 3.8 ppb (1974) to 10.7 ppb (1979)[71]. This agrees with the increasing ground-level ozone concentration discussed above[161]. As there are other products of photochemical reactions, such as formaldehyde, which tend to show the same directional trends, their occurrence in tropospheric air might have increased too. Little is known about the ecological implications this may have. In the western part of the South Coast Air Basin in California, on the other hand, PAN and formaldehyde concentrations show a moderate decrease from the late 60s to the late 70s.

7. Summary and conclusions

In this review an attempt is made to describe qualitatively some processes involved in the formation of secondary air pollutants, namely of strong acids in wet and dry deposition and of photochemical oxidants (ozone and PAN), and to summarize information on the occurrence of these pollutants in Europe. It is shown how the cycles of carbon-, nitrogen- and sulfur-containing compounds interact in the atmosphere and how the formation of atmospheric acidity is related in a complex way to the processes leading to the accumulation of ozone and PAN. Gas and liquid phase oxidation driven by photochemistry produces strong acids from sulfur and nitrogen oxides emitted from combustion of fossil fuels. On the other hand, ozone accumulation strongly depends upon hydrocarbon degradation. In both cases, free radicals (e.g. $OH^{\cdot}$) and strong oxidants play an essential role. More information will be needed, however, on the factors (chemical, climatic, topographic, etc.) influencing the rates of atmospheric transformation (especially of nitrogen compounds) in order to understand small-distance and short-term variations in the occurrence of secondary products.

The composition of wet precipitation deposition (e.g. of rain) is determined by photochemical and scavenging processes, and by the mixing of air in the atmospheric boundary layer. Many of these processes are not well understood at the present time. It is therefore difficult to establish acid deposition-precursor relationships. The area distribution of sulfate and nitrate, the major anions in rain, shows the highest concentrations over the central part of Europe (West Germany, Netherlands) and England. The rates of deposition of these ions, which determine their ecological importance, are further influenced by topography and meteorology. Importantly, the interception of fog, containing high concentrations of many ions, adds to the total amount of acid deposition, especially on wind-exposed, forested slopes in the uplands. Therefore, it is important to establish the relative contribution to the total deposition from all different deposition processes at each location of interest. The small-scale variability of the acid deposition phenomenon does not allow large-scale extrapolation.

In contrast to the emission of SO_2, NO_X-emission is increasing at the present time. This is of special interest because of the close interactions between NO_X and the formation of nitrous acid vapor and ozone or PAN. Strategies to reduce NO_X emission must take the complex interactions into account. For instance, a reduction in NO_X and to a lesser degree in hydrocarbon emission would lead to increased ozone concentrations.

Ozone concentrations in the lower troposphere above the ecotoxicological threshold of approximately 80 ppb are widespread in western Europe under the appropriate weather conditions (high pressure system, high solar radiation intensity, warm and slowly moving dry air). Under the influence of industrial emission of NO_X and hydrocarbons, maximum ozone concentrations on a regional or local scale may reach 100 to 150 ppb. Unlike that inside the mixing layer, ozone in the air above is often not destroyed at night. As a consequence, ozone concentrations can stay elevated at higher altitudes for extended periods of time, or ozone is subject to long-range transport. The latter process exposes remote areas episodically to relatively high ozone levels (also PAN). With respect to the widespread appearance of the current forest dieback in many parts of Europe, it must be pointed out that areas receiving high rates of acid deposition are often identical with those exposed to high oxidant levels. This is certainly true in the case of the central part of the continent, especially within some hundred kilometers downwind from industrialized areas, but it may also be the case at remote locations of Bavaria, Austria or Switzerland. Certainly, exposure to high acid inputs and oxidant gases is not restricted to lower altitudes. Therefore, the combined occurrence of secondary air pollutants must be considered an important factor in causing alterations in vulnerable ecosystems on a continent-wide scale. However, the evaluation of stress from single pollutants on complex systems such as forests will be difficult because of overlaping effects and high variability of deposition processes. Consequently, research efforts will be time-consuming. During the time needed to establish clear cause-effect relationships, the deposition of acid compounds and the concentration of ozone in the air are likely to follow an upward trend.

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1 Abrahamsen, G., Impact of atmospheric sulphur deposition on forest ecosystems, in: Atmospheric Sulfur Deposition, pp. 399–341. Eds D.S. Shriner, C.R. Richmond and S.E. Linberg. Ann Arbor Science 1980.
2 Altshuller, A.P., Measurements of the products of atmospheric photochemical reactions in laboratory studies and in ambient air – Relationship between ozone and other products. Atmosph. Envir. *17* (1983) 2383–2427.
3 Apling, A.J., Sullivan, E.J., Williams, M.L., Ball, D.J., Bernard, R.E., Derwent, R.G., Eggleton, A.E.J., Hampton, L., and Waller, R.E., Ozone concentrations in southeast England during the summer of 1976. Nature *269* (1977) 569–573.
4 Atkins, D.H.F., Cox, R.A., and Eggleton, A.E.J., Photochemical ozone and sulfuric acid aerosol formation in the atmosphere over southern England. Nature *235* (1972) 372–376.
5 Attmansbacher, W., The behaviour of atmospheric ozone during the last 15 years, based on results of ozone soundings at Hohenpreissenberg, FRG, in: Biological Effects of UV-B Radiation. BPT-Bericht 5/82 (1982) ISSN 0721-1694.
6 Ball, D.J., and Bernard, R.E., An analysis of photochemical incidents in the greater London area with particular reference to the summer of 1976. Atmosph. Envir. *12* (1978) 1391–1401.
7 Barrett, C.F., Fowler, D., Kallend, A.S., Martin, A., Scriven, R.A., Tuck, A.F., and Irwin, J.G., Acidity of rainfall in the United Kingdom – A preliminary report. Warren Spring Laboratory Report (1982).
8 Baumgartner, A., Nebel und Nebelniederschlag als Standortfaktoren am Grossen Falkenstein (Bayrischer Wald). Forstwiss. Zentbl. *77* (1958) 257–272.
9 Beilke, S., Acid deposition – The present situation in Europe, in: Acid Deposition, Proc. CEC Workshop Berlin 9 September 1982, pp. 3–30. Eds S. Beilke and A.J. Elshout. D. Reidel Publ. Comp., Dordrecht 1983.
10 Beilke, S., Untersuchung über das Auswaschen atmosphärischer Spurenstoffe durch Niederschläge. Ber. Inst. Met. Univ. Frankfurt a.M. *19* (1970).
11 Betz, M., Untersuchungen über die Absorption und Oxidation von Schwefeldioxid in natürlichem Regenwasser. Diplomarbeit Institut für Meteorologie und Geophysik der Universität Frankfurt a.M. (1976).
12 Birkle, M., Immissionsmessungen von O_3 zur Erfassung photochemischer Umsetzungen in bodennahen Luftschichten. Staub Reinhalt. Luft *35* (1975) 41–76.
13 Bormann, F.H., Factors confounding evaluation of air pollution stress on forests: pollution input and ecosystem complexity, in: Acid Deposition – A Challenge for Europe, pp. 147–166. Eds H. Ott and H. Stangl. Preprint Proc. CEC Symposium Karlsruhe, 19–21 September 1983.
14 Bormann, F.H., The effect of air pollution on the New England landscape. Ambio *11* (1982) 338–346.
15 Brimblecomb, P., and Stedman, D.H., Historical evidence for a dramatic increase in the nitrate component of acid rain. Nature *298* (1982) 460–462.
16 Bruckmann, P., and Eyck, P., Messung von Photooxidantien (Ozon and PAN) im Rhein-Ruhrgebiet, in: Photochemische Luftverunreinigung in der Bundesrepublik Deutschland, pp. 92–107. VDI-Tagungsbericht, Düsseldorf 1979.
17 Bruckmann, P., and Mülder, W., Die Messung von PAN in Aussenluft – Verfahren und erste Ergebnisse. SchrReihe Landesanst. Immissionsschutz Nordrh.-Westf. *47* (1979) 30–41. Verlag W. Girardet, Essen.
18 Bucher, J.B., Bemerkungen zum Waldsterben und Umweltschutz in der Schweiz. Forstwiss. Zentbl. *103* (1984) 16–27.
19 Bucher, J.B., Physiologische Veränderungen und ökotoxikologische Wirkmechanismen. Probleme der Differentialdiagnose, in: Waldschäden durch Immissionen, pp. 91–109. Tagungsbericht Gottlieb-Duttweiler-Institut, Rüschlikon/Zürich 1982.
20 Bundesamt für Umweltschutz, Bern/Schweiz, Luftbelastung 1982 – Messresultate des Nationalen Beobachtungsnetzes für Luftfremdstoffe (NABEL) (1983).
21 Bundesamt für Umweltschutz, Bern/Schweiz, Luftbelastung 1981 – Messresultate des Nationalen Beobachtungsnetzes für Luftfremdstoffe (NABEL) (1982).
22 Calvert, J.G., and Stockwell, W.R., Acid generation in the troposphere by gas-phase chemistry. Envir. Sci. Technol. *17* (1983) 428A–443A.
23 Castillo, R.A., Jiusto, J.E., and McLaren, E., The pH and ionic composition of stratiform cloud water. Atmosph. Envir. *17* (1983) 1497–1505.
24 Chang, T.Y., Rain and snow scavenging of HNO_3 vapor in the atmosphere. Atmosph. Envir. *18* (1984) 191–197.
25 Charlson, R.J., and Rodhe, H., Factors controlling the acidity of natural rainwater. Nature *295* (1982) 683–685.
26 Charlson, R.J., Vong, R., and Hegg, D.A., The sources of sulfate in precipitation: sensitivities to chemical variables. J. geophys. Res. *88* (1983) 1375–1377.
27 Cocks, A.T., Fletcher, I.S., and Kallend, A.S., Chemical modelling studies of long-range dispersion of power plant plumes. Proc. 12th NATO/CCMS Int. Tech. Meeting on Air Pollution Modelling and its Application. Palo Alto, California 1981.
28 Cocks, A.T., Kallend, A.S., and Marsh, A.R.W., Dispersion limitations of oxidation in power plant plumes during long-range transport. Nature *305* (1983) 122–123.
29 Cox, R.A., Some measurements of ground level NO, NO_2, and O_3 concentrations at an unpolluted maritime site. Tellus *29* (1977) 356–362.
30 Cox, R.A., Eggleton, A.E.J., Derwent, R.G., Lovelock, J.E., and Pack, D.H., Long-range transport of photochemical ozone in north-western Europe. Nature *255* (1975) 118–121.
31 Cox, R.A., and Penkett, S.A., Formation of atmospheric acidity, in: Acid Deposition, Proc. CEC Workshop, Berlin, 9 September 1982, pp. 56–81. Eds S. Beilke and A.J. Elshout. D. Reidel Publ. Comp., Dordrecht 1983.
32 Danielsen, E.F., and Mohnen, V.A., Project duststorm report: ozone transport, in situ measurements, and meteorological analyses of tropopause folding. J. geophys. Res. *82* (1977) 5867–5877.
33 Davies, T.D., Dissolved sulphur dioxide and sulphate in urban and rural precipitation (Norfolk, U.K.). Atmosph. Envir. *13* (1979) 1275–1285.
34 Davies, T.D., and Nicholson, K.W., Dry deposition velocities of aerosol sulphate in rural eastern England, in: Deposition of Atmospheric Pollutants, pp. 31–42. Eds H.W. Georgii and J. Pankrath. D. Reidel Publ. Comp., Dordrecht 1982.

35 Derwent, R. G., Eggleton, A. E. J., Williams, M. L., and Bell, C. A., Elevated ozone levels from natural sources. Atmosph. Envir. *12* (1978) 2173–2177.

36 Derwent, R. G., and Hov, Ø., Computer modelling studies of photochemical air pollution formation in northwest Europe. AERE Rep. R-4934 (1979).

37 Demerjian, K. L., Kerr, J. A., and Calvert, J. G., The mechanism of photochemical smog formation. Adv. Envir. Sci. Technol. *4* (1974) 1–262.

38 Dollard, G. J., and Unsworth, M. H., Field measurements of turbulent fluxes of wind-driven fog drops to a grass surface. Atmosph. Envir. *17* (1983) 775–780.

39 Dollard, G. J., Unsworth, M. H., and Harve, M. J., Pollutant transport in upland regions by occult precipitation. Nature *302* (1983) 241–243.

40 Drablos, D., and Tollan, A., (Eds), Ecological impact of acid precipitation. SNSF Project, Oslo, Norway 1980.

41 Duchelle, S. F., and Skelly, J. M., Response of common milkweed to oxidant air pollution in the Shenandoah Park in Virginia. Pl. Dis. Reptr *65* (1981) 661–663.

42 Environmental Protection Agency, USA, The acidic deposition phenomenon and its effects, vol. 1: Atmospheric Sciences. Publ. No. EPA 600/8-83-016A (1983).

43 Environmental Protection Agency, USA, Air quality criteria for ozone and other photochemical oxidants. Publ. No. EPA 600/8-78-004 (1978).

44 Evans, L. S., Biological effects of acidity in precipitation on vegetation: a review. Envir. exp. Bot. *22* (1982) 155–169.

45 Falconer, R. E., and Falconer, P. D., Determination of cloud water acidity at a mountain observatory in the Adirondack Mountains of New York State. J. geophys. Res. *85* (1980) 4765–4770.

46 Fisher, B. E. A., Deposition of sulphur and the acidity of precipitation over Ireland. Atmosph. Envir. *16* (1982) 2725–2734.

47 Flückiger, W., Flückiger-Keller, H., and Braun, S., Untersuchungen über Waldschäden in der Nordwestschweiz. Schweiz. Z. Forstw. *135* (1984) 389–444.

48 Fowler, D., Cape, J. N., Leith, I. D., Paterson, I. S., Kinnaird, J. W., and Nicholson, I. A., Rainfall acidity in northern Britain. Nature *297* (1982) 383–386.

49 Fricke, W., Die Bildung und Verteilung von anthropogenem Ozon in der unteren Troposphäre. Ber. Inst. Met. Geophys. Univ. Frankfurt a.M. *44* (1980).

50 Fuhrer, J., Study of the chemical characteristics of wet and dry deposition in Switzerland, in: 3rd Eur. Symp. on Physico-chemical Behaviour of Atmospheric Pollutants, Varese, 10–12 April 1984, pp. 423–432. Eds B. Versino and G. Augeletti, D. Reidel Publ. Comp., Dordrecht 1984.

51 Fuhrer, J., Der Ozongehalt der bodennahen Luftschicht in der Region Bern. Wasser, Energie, Luft – Eau, Energie, Air *27* (1980) 167–171.

52 Fuhrer, J., and Fuhrer-Fries, C., Interactions between acidic deposition and forest ecosystem processes. Eur. J. Forest Path. *12* (1982) 377–390.

53 Galloway, J. N., and Likens, G. E., Acid precipitation: the importance of nitric acid. Atmosph. Envir. *15* (1981) 1081–1085.

54 Galloway, J. N., Likens, G. E., Keen, W. C., and Miller, J. M., The composition of precipitation in remote areas of the world. J. geophys. Res. *87* (1982) 8771–8786.

55 Galloway, J. N., and Whelpdale, D. M., An atmospheric sulfur budget for eastern North America. Atmosph. Envir. *14* (1980) 409–417.

56 Garland, J. A., Dry and wet removal of sulphur from the atmosphere. Atmosph. Envir. *12* (1978) 349–362.

57 Georgii, H. W., Global distribution of the acidity in precipitation, in: Deposition of Atmospheric Pollutants, pp. 55–66. Eds H. W. Georgii and J. Pankrath. D. Reidel Publ. Comp., Dordrecht 1982.

58 Georgii, H. W., Review of the acidity of precipitation according to the WMO-network. Idöjaras *85* (1981) 1–10.

59 Georgii, H. W., Perseke, C., and Rohbock, E., Deposition of acidic components and heavy metals in the Federal Republic of Germany for the period 1979–1981. Atmosph. Envir. *18* (1984) 581–589.

60 Georgii, H. W., Perseke, C., and Rohbock, E., Feststellung der Deposition von sauren und langzeitwirksamen Luftverunreinigungen aus Belastungsgebieten. Ber. Inst. Met. Geophys. Univ. Frankfurt a.M. (1982).

61 Gervat, G. P., Kallend, A. S., and Marsh, A. R. W., Composition and origin of cloudwater solutes, in: Proc. 3rd Eur. Symp. on Physico-chemical Behaviour of Atmospheric Pollutants, Varese, 10–12 April, 1984, pp. 506–516. Eds B. Versino and G. Angeletti. D. Reidel Publ. Comp., Dordrecht 1984.

62 Giovanelli, G., Fortezza, F., Minguzzi, L., Strocchi, V., and Vandini, W., Photochemical ozone transport in an industrial coastal area, in: Proc. 2nd Eur. Symp. on Physico-chemical Behaviour of Atmospheric Pollutants, Varese, 29 September to 1 October 1981, pp. 492–501. Eds B. Versino and H. Ott. D. Reidel Publ. Comp., Dordrecht 1982.

63 Glover, G. M., Kallend, A. S., and Marsh, A. R. W., The role of sulphur in acid rain, in: Proc. 1st Europ. Symp. on Physico-chemical Behaviour of Atmospheric Pollutants, Ispra, 16–18 October 1979, pp. 419–430. Eds B. Versino and H. Ott. Commission of the European Communities, Brussels 1980.

64 Golomb, D., Acid deposition – precursor emission relationship in the northeastern USA: the effectiveness of regional emission reduction. Atmosph. Envir. *17* (1983) 1387–1390.

65 Golomb, D., Batterman, S., Gruhl, J., and Labys, W., Sensitivity analysis of the kinetics of acid rain models. Atmosph. Envir. *17* (1983) 615–653.

66 Granat, L., Sulfate in precipitation as observed by the European Atmospheric Chemistry Network. Atmosph. Envir. *12* (1978) 413–424.

67 Gravenhorst, G., Höfken, K. D., and Georgii, H. W., Acidic input to a beech and spruce forest, in: Acid Deposition, Proc. CEC Workshop Berlin, 9 September 1982, pp. 155–171. Eds S. Beilke and A. J. Elshout. D. Reidel Publ. Comp., Dordrecht 1983.

68 Greenfelt, P., Ozone episodes on the Swedish west coast. Proc. int. Conf. on Photochemical Oxidant Pollution and its Control, pp. 329–337. Publ. No. EPA-60013-77-001 Raleigh NC (1976).

69 Greenfelt, P., Bengtson, C., and Särby, L., An estimate of the atmospheric input of acidifying substances to a forest ecosystem. Swedish Water and Air Pollution Res. Inst. Publ. No. B 438, Gothenburg 1978.

70 Grennfelt, P., Berglind, B., and Lord, E., Studier av lokal bildning av fotokemiska oxidanter kring Göteborg sommaren 1979. Swedish Water and Air Pollution Res. Inst. Publ. No. B 591, Gothenburg 1981.

71 Guicherit, R., Data from the national network for air pollution measurement. Personal communication (1983).

72 Guicherit, R., and van Dop, H., Photochemical production of ozone in western Europe (1971–1975) and its relationship to meteorology. Atmosph. Envir. *11* (1977) 145–155.

73 Hansen, D. A., and Hidy, G. M., Review of questions regarding rain acidity data. Atmosph. Envir. *16* (1982) 2107–2126.

74 Harris, G. W., Carter, W. P. L., Winer, A. M., and Pitts, J. N. Jr, Observations of nitrous acid in the Los Angeles atmosphere and implications for predictions of ozone-precursor relationships. Envir. Sci. Technol. *16* (1982) 414–419.

75 Harrison, R. M., and Holman, C. D., The contribution of middle- and long-range transport of tropospheric photochemical ozone to pollution at a rural site in north-west England. Atmosph. Envir. *13* (1979) 1535–1545.

76 Harrison, R. M., and Pio, C. A., A comparative study of the ionic composition of rainwater and atmospheric arerosols: implications for the mechanisms of acidification of rainwater. Atmosph. Envir. *17* (1983) 2539–2543.

77 Harte, J., An investigation of acid precipitation in Quinghai province, China. Atmosph. Envir. *17* (1983) 403–408.

78 Heck, W. W., Taylor, O. C., Adams, R., Bingham, G., Miller, J., Preston, E., and Weinstein, L., Assessment of crop loss from ozone. J. Air Pollut. Control Ass. *32* (1982) 353–361.

79 Herron, M. M., Impurity sources of F^-, Cl^-, NO_3^- and SO_4^{2-} in Greenland and Antarctic precipitation. J. geophys. Res. *87* (1982) 3053–3060.

80 Hileman, B., Acid fog. Envir. Sci. Technol. *17* (1983) 117A–120A.

81 Hileman, B., Acid deposition. Envir. Sci. Technol. *16* (1982) 323–327A.

82 Horvath, L., Trend of the nitrate and ammonium content of precipitation water in Hungary for the last 80 years. Tellus *35B* (1983) 304–308.

83 Hov, Ø., The turnover of sulphur dioxide and nitrogen oxides in the atmospheric boundary layer, in: Proc. 2nd Europ. Symp. on Physicochemical Behaviour of Atmospheric Pollutants, Varese, 29 September to 1 October 1981, pp. 625–634. Eds B. Versino and H. Ott. D. Reidel Publ. Comp., Dordrecht 1982.

84 Hov, Ø, Hesstvedt, E., and Isaksen, I. S., Long-range transport of tropospheric ozone. Nature *237* (1978) 341–344.

85 Kasina, S., On precipitation acidity in southeastern Poland. Atmosph. Envir. *14* (1980) 1217–1221.

86 Kallend, A. S., Trends in the acidity of rain in Europe: a re-examination of European Atmospheric Chemistry Network data, in:

Acid Deposition, Proc. CEC Workshop Berlin, 9 September 1982, pp. 108–113. Eds S. Beilke and A.J. Elshout. D. Reidel Publ. Comp., Dordrecht 1983.

87 Kallend, A.S., Marsh, A.R.W., Pickles, J.H., and Proctor, M.V., Acidity of rain in Europe. Atmosph. Envir. *17* (1983) 127–137.

88 Kelly, T.J., Stedman, D.H., and Kok, G.L., Measurements of H_2O_2 and HNO_3 in rural air. Geophys. Res. Lett. *6* (1979) 375–378.

89 Kessler, C., Perner, D., and Platt, U., Spectroscopic measurements of nitrous acid and formaldehyd – implications of urban photochemistry, in: Proc. 2nd Eur. Symp. on Physico-chemical Behaviour of Atmospheric Pollutants, Varese, 29 September to 1 October 1981, pp. 393–400. Eds D. Versino and H. Ott. D. Reidel Publ. Comp., Dordrecht 1982.

90 KNMI-Bericht, Meetnet voor Bepaling von chemische Samenstelling van de Neerslag in Nederland. Ann. Rep. No. KNMI 156-3/RIV 217810003 (1980).

91 Lichtenthaler, H.K., and Buschmann, C., Das Waldsterben, Verlauf, Ursachen und Konsequenzen. Fridericana *33* (1983) 39–66.

92 Lindberg, S.E., Factors influencing trace metal, sulfate and hydrogen ion concentrations in rain. Atmosph. Envir. *16* (1982) 1701–1709.

93 Lovett, G., Rates and mechanisms of cloud water deposition to a subalpine balsam fir forest. Atmosph. Envir. *18* (1984) 361–371.

94 Lovett, G., and Reiners, W.A., Cloud water: an important vector of atmospheric deposition, in: Proc. 4th int. Conf. on Precipitation Scavenging. Dry Deposition and Resuspension, pp. 171–180. Eds H.R. Pruppacher, R.G. Semouin and W.G.N. Slinn. Elsevier/North Holland, Amsterdam 1983.

95 Lovett, G.M., Reiners, W.A., and Olson, R.K., Cloud droplet deposition in subalpine Balsam fir forests: hydrological and chemical inputs. Science *218* (1982) 1303–1304.

96 Marsh, A.R.W., Studies of the acidity and chemical composition of clouds, in: Acid Deposition, Proc. CEC Workshop Berlin, 9 September 1982, pp. 185–194. Eds S. Beilke and A.J. Elshout. D. Reidel Publ. Comp., Dordrecht 1983.

97 Marsh, A.R.W., Sulphur and nitrogen contribution to the acidity of rain. Atmosph. Envir. *12* (1978) 401–406.

98 Martin, A., Sulphate and nitrate related to acidity in rainwater. Water, Air Soil Pollut. *21* (1984) 271–277.

99 Martin, A., A short study of the influence of a valley on the composition of rainwater. Atmosph. Envir. *16* (1982) 785–793.

100 Martin, A., Sulphur in air and deposited from air and rain over Great Britain and Ireland. Environ. Pollut. (ser. B) *1* (1980) 177–193.

101 Martin, A., A survey of the acidity of rainwater over large areas of Great Britain. Sci. tot. Environ. *13* (1979) 119–130.

102 Martin, A., and Barber, F.R., Sulphur dioxide, oxides of nitrogen and ozone measured continuously for two years at a rural site. Atmosph. Envir. *15* (1981) 567–578.

103 Martin, A., and Barber, F.R., Some observations of acidity and sulphur in rainwater from rural sites in central England and Wales. Atmosph. Envir. *12* (1978) 1481–1487.

104 McColl, J.G., Monette, L.K., and Bush, D.S., Chemical characteristics of wet and dry fallout in northern California. J. envir. Qual. *11* (1982) 585–590.

105 Meyrahn, H., Hahn, J., Helas, G., Warneck, P., and Penkett, S.A., Cryogenic sampling and analysis of peroxyacetyl nitrate in the atmosphere, in: 3rd Eur. Symp. on Physico-chemical Behaviour of Atmospheric Pollutants, Varese, 10–12 April 1984, pp. 38–43. Eds B. Versino and G. Angeletti. D. Reidel Publ. Comp., Dordrecht 1984.

106 Mrose, H., Measurements of pH, and chemical analyses of rain-, snow, and fogwater. Tellus *18* (1966) 266–270.

107 Munger, J.W., and Eisenreich, S.J., Continental-scale variations in precipitation chemistry. Envir. Sci. Technol. *17* (1983) 32A–42A.

108 Neuber, E., and Georgii, H.W., Aircraft measurements of oxidants and precursors in the plumes of heavy-industrialized areas, in: Proc. 2nd Eur. Symp. on Physico-chemical Behaviour of Atmospheric Pollutants, Varese, 29 September to 1 October 1981, pp. 469–481. Eds B. Versino and H. Ott. D. Reidel Publ. Comp., Dordrecht 1982.

109 Newman, L., Atmospheric oxidation of sulphur dioxide: a review as viewed from power plant and smelter plume studies. Atmosph. Envir. *15* (1981) 2231–2239.

110 Nieboer, H., and van Ham, J., Peroxyacetyl nitrate (PAN) in relation to ozone and some meteorological parameters at Delft in the Netherlands. Atmosph. Envir. *10* (1976) 115–120.

111 Nielsen, T., Samuelsson, U., Grennfelt, P., and Thomsen, E.L., Peroxyacetyl nitrate in long-range transported polluted air. Nature *293* (1981) 553–555.

112 Ottar, B., The transfer of airborne pollutants to the arctic region. Atmosph. Envir. *15* (1981) 1439–1445.

113 Ottar, B., An assessment of the OECD study on long-range transport of air pollutants (LRTAP). Atmosph. Envir. *12* (1978) 445–454.

114 Overrein, L.N., Seip, H.M., and Tollan, A., Acid precipitation – effects on forest and fish. Final Report of the SNSF-Project 1972–1980. SNSF Project Oslo-As.

115 Pack, D.H., Precipitation chemistry patterns: a two-network data set. Science *208* (1980) 1143–1145.

116 Penkett, S.A., PAN in the natural atmosphere. Nature *302* (1983) 293–294.

117 Penkett, S.A., Photochemical air pollution in the U.K. Envir. Pollut. Management *January/February* (1978) 8–12.

118 Penkett, S.A., Sandalls, F.J., and Lovelock, J.E., Observations of peroxyacetyl nitrate (PAN) in air in southern England. Atmosph. Envir. *9* (1975) 139–140.

119 Perseke, C., Beilke, S., and Georgii, H.W., Die Gesamtschwefeldeposition in der Bundesrepublik Deutschland auf der Grundlage der Messdaten des Jahres 1974. Ber. Inst. Met. Geophys. Univ. Frankfurt a.M. *40* (1980).

120 Petrenchuk, O.P., On the budget of sea salts and sulfur in the atmosphere. J. geophys. Res. *85* (1980) 7439–7444.

121 Prinz, B., Krause, G.H.M., and Stratmann, H., Waldschäden in der Bundesrepublik Deutschland. Ber. Landesanst. Immissionsschutz Nordrh. Westf. *28* (1982). Essen.

122 Rehfuess, K.E., Walderkrankungen und Immissionen – eine Zwischenbilanz. Allg. Forstz. *24* (1983) 601–610.

123 Reiter, R., and Kanter, H.J., Reasons for seasonal and daily variations of CO_2 and O_3 at 0.7, 1.8 and 3.0 km altitude recorded since 1977, in: Proc. 2nd Eur. Symp. on Physico-chemical Behaviour of Atmospheric Pollutants, Varese, 29 September to 1 October 1981, pp. 551–560. Eds D. Versino and H. Ott. D. Reidel Publ. Comp., Dordrecht 1982.

124 Reiter, R., Pötzl, K., and Mungert, K., Results of many years' analyses of precipitation chemistry on samples obtained simultaneously at 3.0 km, 1.8 km and 0.7 km a.s.l., in: 3rd Eur. Symp. on Physico-chemical Behavior of Atmospheric Pollutants, Varese, 10–12 April 1984, pp. 480–491. Eds B. Versino and G. Angeletti. D. Reidel Publ. Comp., Dordrecht 1984.

125 Richards, L.W., Comments on the oxidation of NO_2 to nitrate – day and night. Atmosph. Envir. *17* (1983) 397–402.

126 Richards, L.W., Anderson, J.A., Blumenthal, D.L., McDonald, J.A., Kok, G.L., and Lazrus, A.L., Hydrogen peroxide and sulfur (IV) in Los Angeles cloud water. Atmosph. Envir. *17* (1983) 911–914.

127 Ridder. T.B., and Frantzen, A.J., Acid precipitation over The Netherlands, in: Acid Deposition, Proc. CEC Workshop, Berlin, 9 September 1982, pp. 123–128. Eds S. Beilke and A.J. Eleshout. D. Reidel Publ. Comp., Dordrecht 1983.

128 Rodhe, H., An atmospheric sulphur budget for N.W. Europe in nitrogen, phosphorus and sulphur-global cycles. Ecol. Bull. *22* (1976) 123–134.

129 Rodhe, H., Crutzen, P., and Vanderpol, A., Formation of sulfuric and nitric acid in the atmosphere during long-range transport. Tellus *33* (1981) 132–141.

130 Rodhe, H., Eliassen, A., Isaksen, I., Smitz, F.B., and Whelpdale, D.M., Tropospheric chemistry and air pollution. WMO Technical Note No., 176, Geneva.

131 Römer, F.G., Viljeer, J.W., Van Den Beld, L., Slangewal, H.J., and Reijnders, H.F.R., Preliminary measurements from an aircraft into the chemical composition of clouds, in: Acid Deposition, Proc. CEC Workshop, Berlin, 9 September 1982, pp. 195–203. Eds S. Beilke and A.J. Elshout. D. Reidel Publ. Comp., Dordrecht 1983.

132 Rosenquist, I.Th., Influence of forest vegetation and agriculture on the acidity of fresh water, in: Advances in Environmental Sciences and Engineering, vol. 3, pp. 56–79. Eds J.R. Pfafflin and E.N. Ziegler. Gordon and Breach Science Publishers, New York, London, Paris 1980.

133 Schaug, J., LRTAP ground sampling stations yearly precipitation and mean concentration values, frequency distributions of sulphur dioxide and sulphate air concentrations, July 1972 to December 1974. NILU Rep. LRTAP *13* (1975).

134 Scherer, B., and Stern, R., Analysis of a photochemical smog episode and preparation of the meteorological input data for a three dimensional air quality dispersion model, in: Proc. 2nd Eur. Symp. on Physico-chemical Behaviour of Atmospheric Pollutants, Varese, 29 September to 1 October 1981, pp. 561–571. Eds D. Versino and H. Ott. D. Reidel Publ. Comp., Dordrecht 1982.

135 Schjoldanger, J., Dovland, H., Grennfelt, P., and Saltbones, J., Photochemical oxidants in north-western Europe 1976–1979. A pilot project. NILU Rep. *19* (1981).
136 Schrimpff, E., Waldsterben infolge hoher Schadstoffkonzentrationen im Nebel? Staub Reinhalt. Luft *43* (1983) 240.
137 Schrimpff, E., The relationship between relief and deposition of some organic and inorganic contaminants in snow of northern Bavaria, FRG, in: Ecological Impact of Acid Precipitation, SNSF project, pp. 130–131. Eds D. Drablos and A. Tollan (1980).
138 Schrimpff, E., Klemm, O., Eiden, R., Frevert, T., and Herrmann, R., Anwendung eines Grunow-Nebelfängers zur Bestimmung von Schadstoffgehalten in Nebelniederschlägen. Staub Reinhalt. Luft *44* (1984) 72–75.
139 Scott, B.C., and Laulainen, N.S., On the concentration of sulfate in precipitation. J. appl. Met. *18* (1979) 138–147.
140 Singh, H.B., and Salas, L.J., Peroxyacetyl nitrate in the free troposphere. Nature *302* (1983) 326–328.
141 Smidt, S., Über das Auftreten von Ozon und Stickstoffoxiden in Waldgebieten Österreichs. Eur. J. Forest Path. *13* (1983) 133–141.
142 Smith, W.H., Air Pollution and Forests. Springer-Verlag, New York, Heidelberg, Berlin 1981.
143 Smith, F.B., and Hunt, R.D., The dispersion of sulphur pollutants over western Europe. Phil. Trans. R. Soc. (A) *290* (1979) 523–542.
144 Söderlund, R., NO_X pollutants and ammonia emissions – a mass balance for the atmosphere over N.W. Europe. Ambio *6* (1977) 118–122.
145 Stumm, W., Morgan, J.J., and Schnoor, J.L., Saurer Regen, eine Folge der Störung hydrochemischer Kreisläufe. Naturwissenschaften *70* (1983) 216–223.
146 Temple, P.J., and Taylor, O.C., World-wide ambient measurements of peroxyacetyl nitrate (PAN) and implications for plant injury. Atmosph. Envir. *17* (1983) 1583–1587.
147 Thornton, J.D., and Eisenreich, S.J., Impact of land-use on the acid and trace element composition of precipitation in the north-central U.S. Atmosph. Envir. *16* (1982) 1945–1955.
148 Tyree, S.Y. Jr, Rainwater acidity measurement problems. Atmosph. Envir. *15* (1981) 57–60.
149 Ulrich, B., Effects of air pollution on forest ecosystems and waters – The principles demonstrated at a case study in central Europe. Atmosph. Envir. *18* (1984) 621–628.
150 Ulrich, B., Interaction of forest canopies with atmospheric constituents: SO_2, alkali and earth alkali cations and chloride, in: Effects of Accumulation of Air Pollutants in Forest Ecosystems, pp. 33–45. Eds B. Ulrich and J. Pankrath. D. Reidel Publ. Comp., Dordrecht 1983.
151 Ulrich, B., Mayer, R., and Khanna, P.K., Chemical changes due to acid precipitation in a loess-derived soil in central Europe. Soil Sci. *130* (1980) 193–199.
152 Umweltbundesamt, FRG, Monatsberichte aus dem Messnetz *2* (1983) 54–56.
153 Umweltbundesamt, FRG, Monatsberichte aus dem Messnetz *1–12* (1983).
154 Van Breemen, N., Burrough, P.A., Velthorst, E.J., Van Dobben, H.F., De Wit, T., Ridder, T.B., and Reijnders, H.F.R., Soil acidification from atmospheric ammonium sulphate in forest canopy throughfall. Nature *299* (1982) 548–550.
155 Van Duuren, H., Römer, F.G., Diederen, H.S.M.A., Guicherit, R., and van den Hout, K.D., Measurements by aeroplane of the distribution of ozone and primary air pollutants, in: Proc. 2nd Eur. Symp. on Physico-chemical Behaviour of Atmospheric Pollutants, Varese, 29 September to 1 October 1981, pp. 460-468. Eds D. Versino and H. Ott. D. Reidel Publ. Comp., Dordrecht 1982.
156 Vukovich, F.M., Bach, W.D. Jr, Crissman, B.W., and King, W.J., On the relationship between high ozone in the rural surface layer and high pressure systems. Atmosph. Envir. *11* (1977) 967–983.
157 Waldmann, G., An analysis of factors presumably responsible for large scale dieback of trees. Allg. Forst Jagdztg. *155* (1984) 80–85.
158 Waldman, J.M., Munger, J.W., Jacob, D.J., Flagan, R.C., Morgan, J.J., and Hoffman, M.R., Chemical composition of acid fog. Science *218* (1982) 677–680.
159 Wallen, C.C., A preliminary evaluation of the WMO-UNEP precipitation chemistry data. Monitoring and Assessment Res. Ctr. (MARC) Rep. *22* (1980). Chelsea College, University of London.
160 Wanner, H., and Kunz, S., Klimatologie der Nebel- und Kaltluftkörper im schweizerischen Alpenvorland mit Hilfe von Wettersatellitenbildern. Arch. Met. geophys.-biocl. Ser. B *33* (1983) 677–680.
161 Warmbt, W., Ergebnisse langjähriger Messungen des bodennahen Ozons in der DDR. Z. Met. *29* (1979) 24–31.
162 Williams, W.T., Brady, M., and Willison, S.C., Air pollution damage to the forests of the Sierra Nevada Mountains of California. J. Air Pollut. Contr. Ass. *27* (1977) 230–234.
163 Winkler, P., Zur Trendentwicklung des pH-Wertes des Niederschlags in Mitteleuropa. Z. PflErnähr. Bodenk. *145* (1982) 576–585.
164 Wisniewski, J., The potential acidity associated with dews, frost and fogs. Water, Air Soil Pollut. *17* (1982) 361–377.
165 Winer, A.M., Atkinson, R., and Pitts, J.N. Jr, Gaseous nitrate radical: possible nighttime atmospheric sink for biogenic organic compounds. Science *224* (1984) 156–158.
166 WMO-EPA-NOAA, Global atmospheric background monitoring for selected environmental parameters. BAPMoN data for 1980. Natn. Satellite Data and Information Service, Ashville N.C. 1984.
167 WMO-EPA-NOAA, Global atmospheric background monitoring for selected environmental parameters. BAPMoN data for 1979. Natn. Satellite Data and Information Service, Ashville N.C. 1983.
168 Worth, J.J.B., and Ripperton, L.A., Rural ozone – sources and transport, in: Advances in Environmental Science and Engineering, vol. 3, pp. 150–170. Eds J.R. Pfafflin and E.N. Ziegler. Gordon and Breach Science Publishers, New York, London, Paris 1980.
169 Zobrist, J., and Stumm, W., Wie sauber ist das Schweizer Regenwasser? Neue Zürcher Zeitung, Beilage Forschung und Technik, No. 146, 27 June 1979.

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Uptake and effects of air pollutants on woody plants

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Key words. Forest decay; air pollution; woody plants; sulfur oxides; nitrogen oxides; ozone.

Introduction

Plant damage due to air pollution has aroused public concern for many years. It is therefore not surprising that numerous publications have sought to establish a better understanding of the injury development and its biochemical and physiological basis – and the literature flood is increasing daily.

Important reviews have been written by Ziegler[138] on the action of sulfur dioxide and by Heath[43] who compared