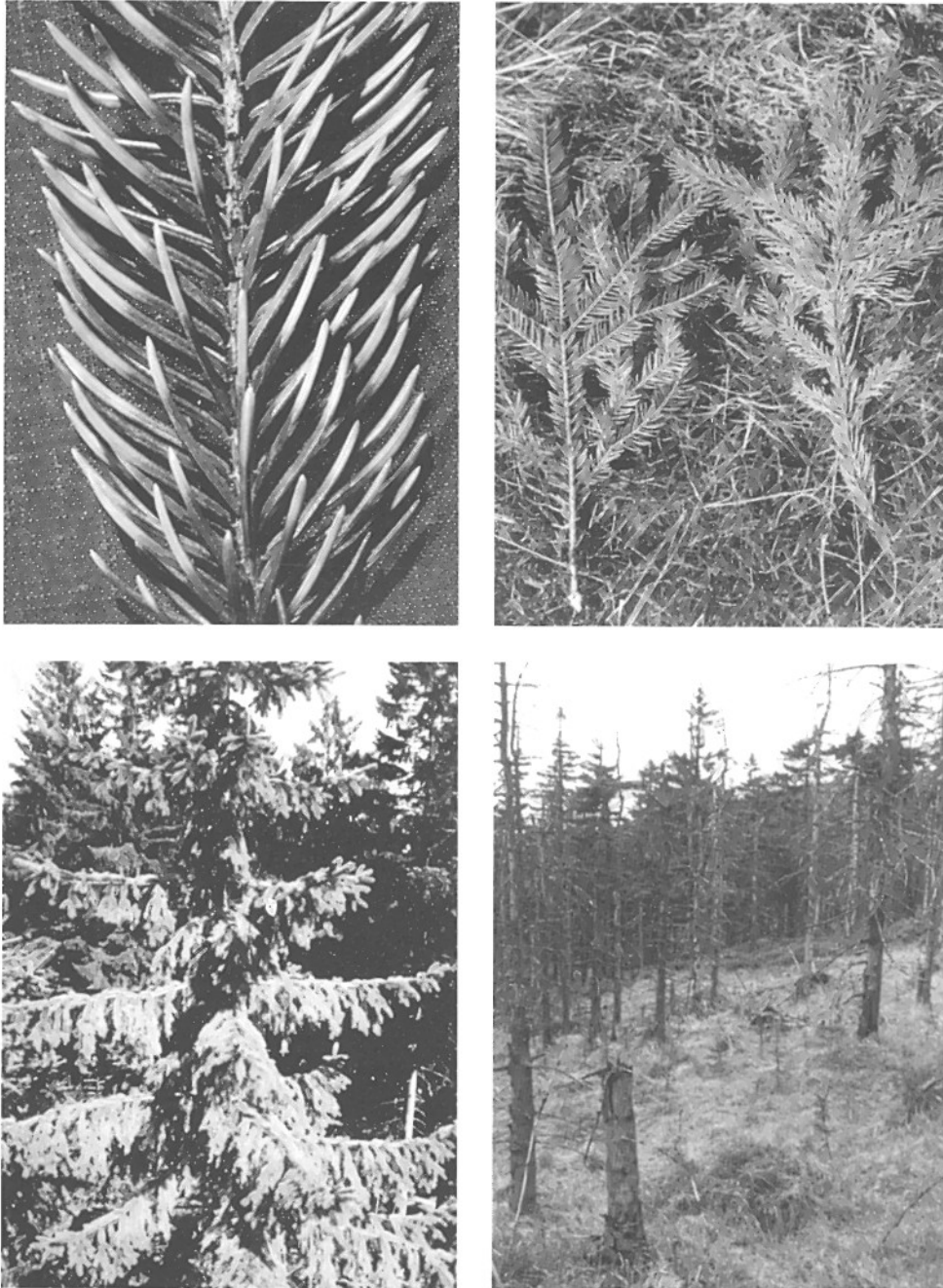


## Air Pollution and Forest Decline

Damage to Norway spruce (*Picea abies*) increased dramatically in central Europe, particularly in the CSSR and the German Democratic Republic. In the early 1980's forest decline spread to several mountainous areas of the Federal Republic of Germany (Uhlmann *et al.*, 1989). The symptoms of damage differ depending on the concentration of pollutants in the soil and the atmosphere. A typical symptom observed in the Fichtelgebirge (at the border between the CSSR and the Federal Republic) is the yellowing of needles, especially of the older age classes. Chlorosis, which is observed on the sun-exposed side of the needles, may cover a large part of the surface of the trees. It can result in needle and branch loss and finally in the death of the trees. Similar symptoms appeared at several locations in the United States. For example, there is considerable forest decline on Whiteface Mountain and Mt. Mitchell.

Typical symptoms of forest damage in the Fichtelgebirge are shown in Fig. 1. The extent of damage in Bavaria and in the Fichtelgebirge (Federal Republic) is quantified in Fig. 2. There is considerable evidence that forest damage is a consequence of the air pollution caused by industry, domestic fuel consumption and traffic. Long-term deposition of pollutants has altered soils and changed nutrient availability. Gaseous pollutants enter the leaves and needles directly from the air and may damage cells and tissues.

Time trends of deposition of the major pollutants from the beginning of this century are shown in Fig. 3. It is important to note that sulphur dioxide and nitrogen dioxide, the major gaseous air pollutants which are toxic at high concentrations, can act as nutrients at low concentrations (Heber *et al.*, 1987). Obviously, metabolic detoxification of the pollutants is possible, in principle, and their toxicity becomes apparent only when the detoxifying and repair processes in the plant cannot cope with the influx of pollutants. Actually, the average annual rate of deposition of sulphur in forested areas is greater than the trees can utilize during a growing season. As can be seen from Fig. 3, both nitrogen and sulphur deposition are about  $0.2 \text{ mol m}^{-2}\text{a}^{-1}$ . Assuming that the average annual biomass production (in dry weight) of a



*Fig. 1. Typical symptoms of spruce damage in the Fichtelgebirge ; above left : bleaching of the tips of needles ; above right : branches of a damaged tree from below (left) and from above (right) ; below left : damaged tree with needle and branch loss and with chlorotic needles at the upper side of the branches ; below right : collapsed stand with dead and heavily damaged trees (Phot. by Köstner, Lange, Reif, Schulze, from Uhlmann et al., 1989).*

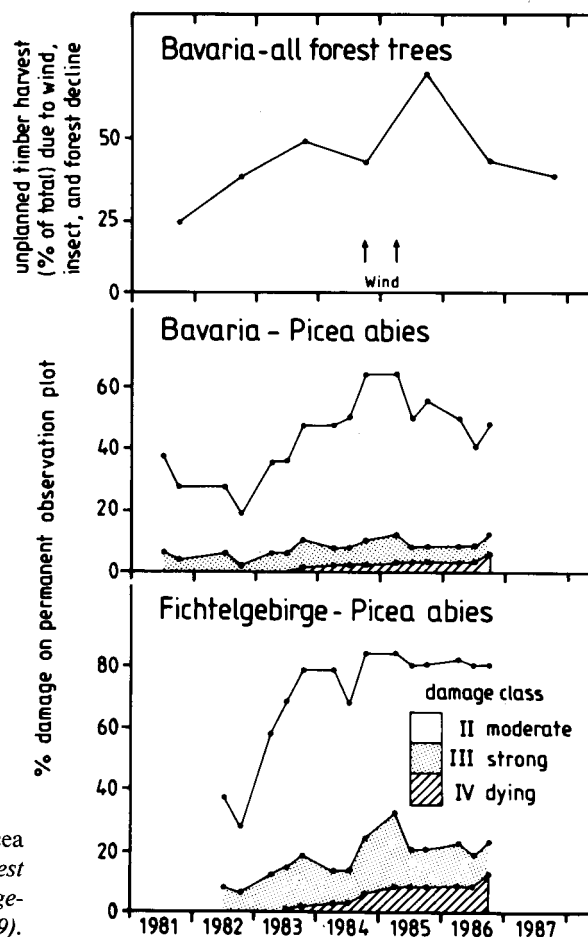


Fig. 2. Damage of spruce (*Picea abies*) and unplanned timber harvest for Bavaria and for the Fichtelgebirge (from Uhlmann et al., 1989).

forest is  $400 \text{ g m}^{-2}$  ground area ( $4000 \text{ kg ha}^{-1}$ ), the protein content of the dry biomass is 5 % (usually it is even lower) and the sulphur content in the protein about 1 %, we can calculate the annual sulphur need of the vegetation to be about  $200 \text{ mg m}^{-2}$  or about  $6 \text{ mmol m}^{-2}$ . The average deposition is more than 30 times greater. The deposition of nitrogen may be close to what the forest can consume. Sulphur and nitrogen are usually emitted into the atmosphere as  $\text{SO}_2$  and  $\text{NO}$ . The latter is rapidly autoxidized in the atmosphere to  $\text{NO}_2$ . In the last decades ammonia emission has also increased.

If there were no cleaning processes, the accumulation of pollutants in the lower 2 km layer of the troposphere would cause a rapid increase in their concentrations. A level of  $50 \text{ mg m}^{-3}$  (which is the permissible upper limit of the average annual concentration of  $\text{SO}_2$  and  $\text{NO}_2$  (Jäger, 1989)) would be reached within 3 to 4 days. Within 10 days the atmospheric

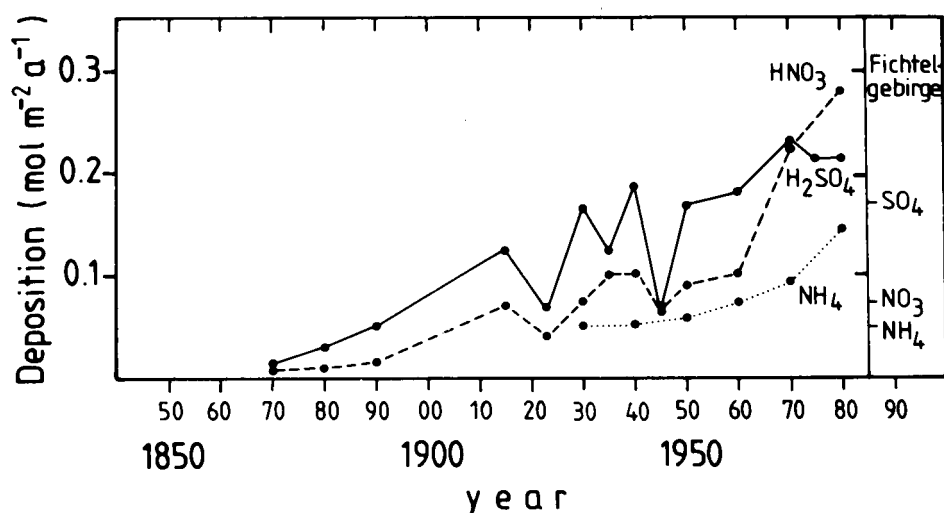
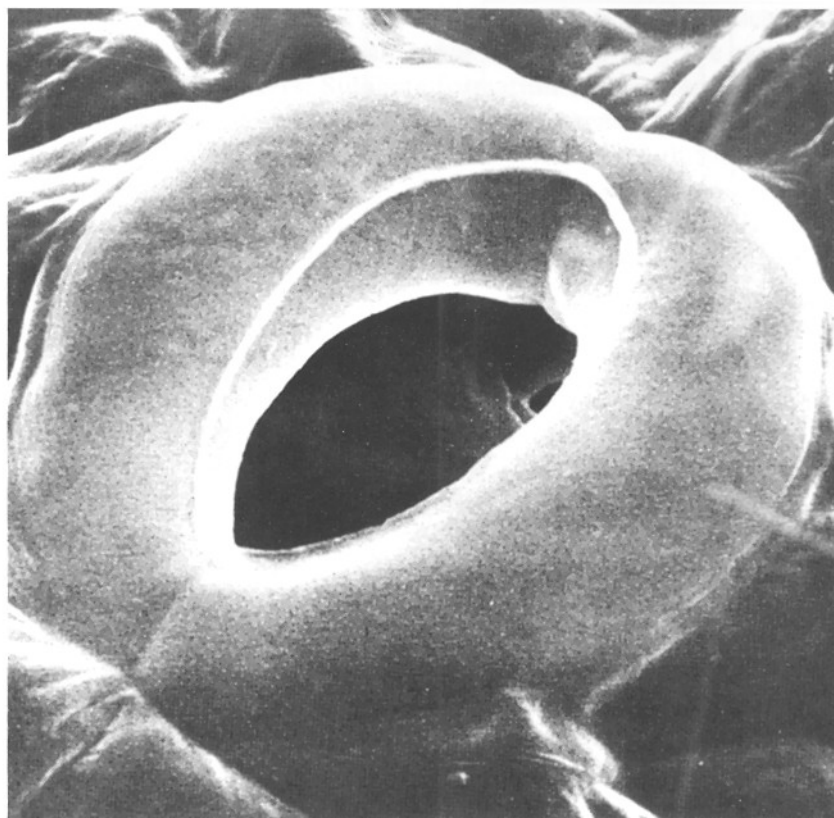


Fig. 3. The deposition of sulphate, nitrate and ammonium since 1870. The deposition rates of sulphate and nitrate were calculated from emission data on an area basis of Germany. The ammonium deposition data are from the Netherlands. Actual deposition rates in the Fichtelgebirge are lower than the calculated rates (from Schulze et al., 1989b).

concentrations of pollutants would become dangerous. Fortunately, the atmosphere is periodically washed by rains, and dry deposition also occurs. However, unfortunately, the cleaning of the atmosphere burdens the soil and water of terrestrial and aquatic ecosystems.

Pollutants can influence plants either by entering the leaves directly from the air or by changing the mineral balance in the soil. The path of entry not only of CO<sub>2</sub>, the substrate of photosynthesis, but also of SO<sub>2</sub>, NO<sub>2</sub> and ozone is through the stomata (Fig. 4) (Laisk *et al.*, 1988). The epidermis of the leaves is covered by a layer of waxy and polymerized substances called cuticula which is relatively impermeable to gases compared with the open stomata. In the leaf the gases distribute in the intercellular spaces and finally enter aqueous cellular phases where they continue diffusion as neutral solutes or, after reaction with water, in the form of ions. CO<sub>2</sub> is rapidly assimilated in the light as a result of photosynthesis but SO<sub>2</sub> and NO<sub>2</sub> cannot be metabolized rapidly. The diffusion rates of gases through the stomata depend on the difference between their concentrations in the atmosphere and in the intercellular air space of the leaves. At rather common pollution levels (Fig. 5), atmospheric concentrations relate as CO<sub>2</sub>/SO<sub>2</sub>/NO<sub>2</sub>/ozone = 340000/20/20/30 if expressed in nl l<sup>-1</sup>. Concentrations of SO<sub>2</sub>, NO<sub>2</sub> and ozone inside the leaves are almost zero owing to the high solubility or reactivity of these gases in the dilute solution which fills the micropores of the cell walls (Laisk *et al.*, 1989; Lange *et al.*, 1989). Taking into account that the CO<sub>2</sub> concentration in the intercellulars of a



*Fig. 4. Scanning electron micrograph of a stomatal apparatus showing the two guard cells which regulate the stomatal aperture. Mesophyll cells of the leaf interior are seen through the stomatal opening (from Plant Physiology, Second Edition, by F.B. Salisbury and C.W. Ross, 1978, Wadsworth Publishing Company, Inc. Reprinted by permission of the publisher).*

photosynthesizing leaf is about 2/3 of its concentration in the outer air and that one half of the once assimilated carbon is evolved as respiration during the growing season, we get, for the pollution levels common in the Fichtelgebirge (Fig. 3), an approximate estimate of the flux ratios of  $\text{CO}_2/\text{SO}_2/\text{NO}_2/\text{O}_3$  as 5700/2/2/3. Such flux ratios can be permanently maintained without damage to the plant if carbon, sulphur and nitrogen can be used in metabolism at similar or lower ratios, and if ozone is reduced before it can oxidize essential cellular constituents. Reduction also results in the detoxification of  $\text{SO}_2$ . Knowing the plant carbohydrate and protein content, it is possible to calculate that the ratio of the reduced sulphur to carbon is, on a molar basis, less than 1/10000 in the total biomass of conifer trees. Therefore, our calculation, which was based on a relatively low concentration of  $\text{SO}_2$  ( $20 \text{ nl l}^{-1}$ ) in the atmosphere, already shows a

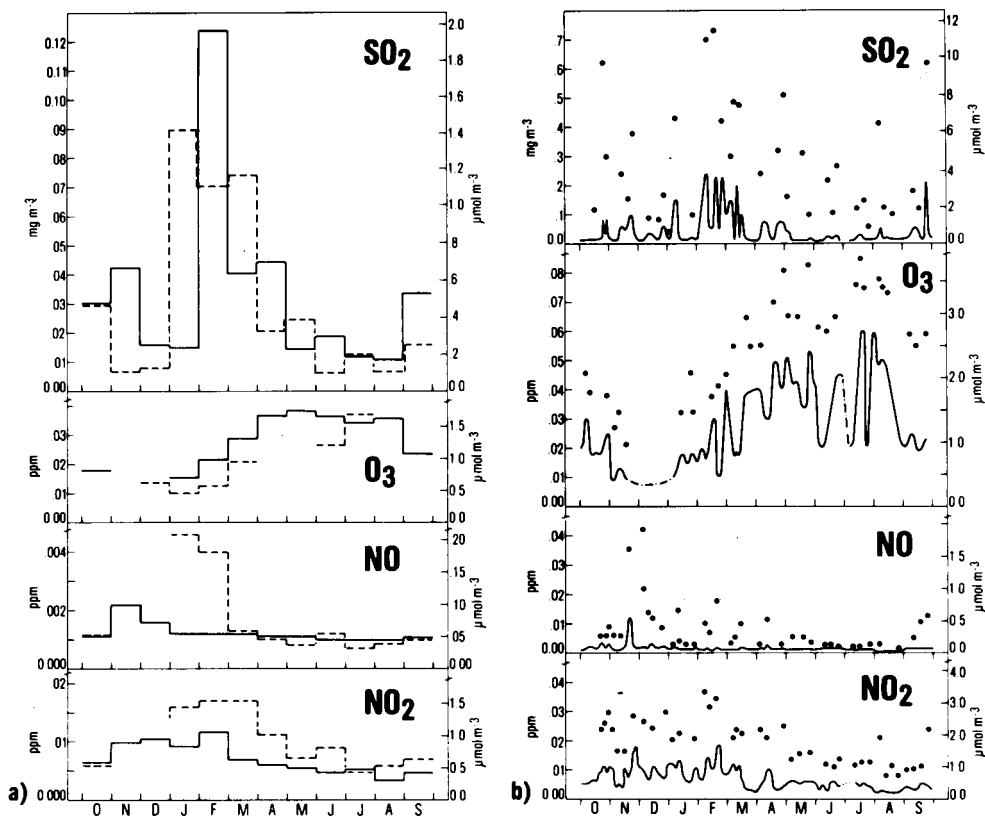
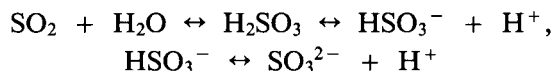


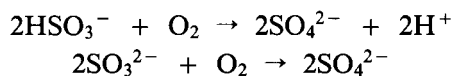
Fig. 5. Near surface atmospheric trace gases SO<sub>2</sub>, O<sub>3</sub>, NO and NO<sub>2</sub>; observation site Oberwarmensteinach (Fichtelgebirge). a. Mean monthly concentrations: — Oct. 1985 to Sept. 1986; ---- Oct. 1986 to Sept. 1987. b. Mean daily concentrations: — smoothed; dots designate the three maximum half hourly peak concentrations of the month, Oct. 1985 to Sept. 1986 (from Eiden et al., 1989).

discrepancy between the metabolic need and the supply of sulphur from the polluted air to conifer needles. Plants that are growing more rapidly than conifers, and which contain relatively more protein in their biomass, can detoxify SO<sub>2</sub> fluxes at correspondingly higher atmospheric SO<sub>2</sub> concentrations (Laisk et al., 1988).

Sulphur dioxide that cannot be reduced and assimilated into proteins causes acidification of the cell medium by its reaction to sulphurous acid:



The bisulphite and sulphite anions which are formed are toxic. They are oxidized to sulphate anions:



Oxidation that takes place in the chloroplasts is light-dependent. It involves reactive radicals which can cause damage if they are not destroyed by cellular radical scavengers. Sulphate formation contributes to the acidification of the cytosol of the cells. A cytosolic pH decrease must be prevented by exporting  $H^+$  or by neutralizing it with a base. Coping with the accumulation of excess protons in the cytoplasm is one of the major problems which plants have to solve in order to tolerate the influx of potentially acidic air pollutants. Concentrations of sulphate in spruce needles are often higher than 30 mM. They may even reach 80 mM in forests which are exposed to air containing high  $SO_2$  levels. As two  $H^+$  are produced during the formation of a sulphate anion from  $SO_2$ , 160 mM  $H^+$  need to be removed at a sulphate concentration of 80 mM in order to maintain cellular metabolism which is highly sensitive to changes in the proton concentration. It is still not entirely clear how plants achieve this feat. Cellular buffering is strong but still insufficient to cope with such amounts of  $H^+$ . Mesophyll cells of spruce contain a large vacuole with acidic cell sap. When the proton concentration in the cytosol of mesophyll cells increases as a result of  $SO_2$  influx, excess protons are pumped into the vacuoles. However, it appears that they cannot be stored there permanently, because the proton concentration of both the cytosol and the vacuoles returns to normal levels after experimental gassing with  $SO_2$  is discontinued (Dittrich *et al.*, 1989). Apparently, the plants are capable of degrading endogenous acids to compensate the influx of external acid, and of mobilizing bases to neutralize excess external acid. They control the intracellular proton concentration by metabolic reactions. However, there are limits to the degradation of endogenous acids. Organic acids take part in, and are needed for, the maintenance of metabolism. The capacity of cells to mobilize bases is also restricted. Some of the sulphur of the sulphate or sulphite formed from  $SO_2$  and most of the nitrogen of the nitrate and nitrite formed from  $NO_2$  are reduced in cells and incorporated into proteins. Nitrate is reduced in the cytosol first to nitrite and then further to ammonium in the chloroplasts at the expense of light energy :



Sulphite reduction may be formulated as



The reduction of sulphate is similar. The amino acid in the left part of the equation describing sulphite reduction is serine, the product is the sulphur-containing amino acid cysteine which does not accumulate but is used in protein synthesis. The reductions of nitrate, nitrite, sulphate and sulphite are accompanied by the production of hydroxyl ions which contribute to neutralize acids in the cells. Therefore, rapid growth which requires rapid protein synthesis helps to decrease sulphate and nitrate accumulation and also the acidification accompanying accumulation of these ions. From the above it is

easy to see that rapidly growing plants like grasses or young twigs of trees are less susceptible to the direct attack of the acidic gases than the slowly growing old and mature parts of plants in which protein synthesis is slow or absent.

In winter growth is restricted. Evergreen trees are then particularly susceptible to damage which, however, can be retarded and reduced or prevented by the closure of the stomata, the entry ports of the pollutants, whose aperture is subject to metabolic regulation. It is evident from the above that the isolation properties of the cuticle are important for the survival of evergreen trees under pollution stress, particularly in boreal and temperate regions.

If cellular degradation of endogenous organic acids and mobilization of bases are insufficient to accommodate the entering acid without a change in the cellular proton concentration, there is still the possibility of pumping protons out from the endangered cells in exchange for other cations. An ATP-powered enzyme in the plasmalemma, which encloses the cells, is capable of catalyzing  $H^+$ /cation exchange across this biomembrane. As proton concentrations outside the cells are as controlled as intracellular proton concentrations, further export of protons, e.g. by phloem transport from leaves to roots would be necessary. Root hairs are known to take up cations in exchange for protons which are excreted into the soil. So far, attempts to demonstrate proton extrusion from the roots in response to the gassing of plants with  $SO_2$  have failed (Lanzl and Kaiser, personal communication). Still, it should be noted that needles of declining spruce trees contained similar concentrations of sulphate but much less  $Ca^{2+}$  and  $Mg^{2+}$  than trees from the same site which appear to be healthy (Lange *et al.*, 1989b). Therefore, the possibility of pollution-related proton extrusion from the roots cannot yet be discounted.

The direct penetration of acidic gases into leaves is only one possible cause of pollution-related plant damage. As has already been mentioned, a large proportion of the acidic pollutants is washed out by rainwater. The resulting acid acts on the soil. Also, air pollutants primarily absorbed by the green biomass of the forest vegetation will finally enter the soil after the death of the trees and the decomposition of organic matter by microorganisms. Protons imported into the soil may cause considerable changes in the amount and composition of nutrients available to the trees (Oren and Schulze, 1989). This may affect root and mycorrhiza growth directly, or it may result in mineral deficiencies and in a disharmony of the nutrition regime of the trees. Cations important for plant nutrition, such as  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ,  $NH_4^+$ , are bound to soil particles which act as cation exchangers (Kaupenjohann *et al.*, 1989). The relative strength of binding is indicated by the sequence of the Hofmeister lyotropic power series

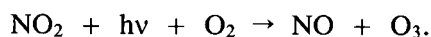




Thus, availability of excess  $H^+$  in the soil will result in its binding and in the release of less strongly bound cations such as  $Ca^{2+}$  or  $Mg^{2+}$ . Under normal conditions of growth, plant roots can liberate cations and absorb them in exchange for the hydrogen ions which they pump out through the root cell membranes at the expense of respiratory energy. When acid rains bring the strong acids (sulphuric acid and nitric acid) into the soil, more cations than are necessary for plant growth are liberated. They may be leached into the ground water (Horn *et al.*, 1989). For this leaching, accompanying anions are necessary in order to maintain the charge balance. It could be sulphate or nitrate. Model calculations (Kaupenjohann *et al.*, 1989) show that sulphate is efficiently trapped on aluminium hydroxy-compounds forming aluminium hydroxysulphate as long as the pH of the soil solution is not too low. For nitrate there is no trap in the soil. Therefore, nitric acid in rainwater will be most efficient in facilitating the leaching process. The effect of nitric acid is enhanced by the simultaneous deposition of ammonium salts. If  $NH_4^+$  reaches a level at which it is preferably taken up by roots, nitrate is left in the soil and adds to the leaching. Critical loads for N have been calculated and found to be about 3 to 15 kg N ha<sup>-1</sup> a<sup>-1</sup> (Nilsson and Grennfelt, 1988). With about 15 - 25 kg N ha<sup>-1</sup> a<sup>-1</sup>, declining forest sites in the Fichtelgebirge and other monitored areas in West Germany receive more than this load (Kaupenjohann *et al.*, 1989). In addition to increased leaching, uptake of ammonium competes with the uptake of magnesium and other cations by the roots (both require proton extrusion). At low soil pH, even aluminium can be liberated into the soil solution. It is an efficient antagonist of  $Mg^{2+}$  and  $Ca^{2+}$  uptake. Podzol soils in the Fichtelgebirge are low in  $Mg^{2+}$ . As a matter of fact, declining trees in this area were shown to be  $Mg^{2+}$  deficient (Lange *et al.*, 1989b). They contained much less  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Mn^{2+}$  and  $Zn^{2+}$  in their needles but more aluminium than needles of healthy trees.  $Mg^{2+}$  deficiency causes photosensitivity. Pigment destruction in the light accounted for the chlorosis of the upper side of the needles (see Fig. 1). Under such conditions, in turn, the sensitivity of mesophyll to acidification by gaseous pollutants is also increased (Dittrich *et al.*, 1989). Thus, no single cause can be made responsible for the observed forest decline. Rather, several factors contribute to weaken tree resistance not only to air pollutants but also to natural stress factors such as frost, drought or diseases resulting finally in tree death.

One of the important conclusions from the complex study of the ecosystem nutritional balance in the Fichtelgebirge (Schulze *et al.*, 1989a) is that the processes in the soil are progressing towards imbalance and that these processes must be expected to result in forest decline in the near future even at sites where no symptoms of damage are apparent at present. Though ammonium and nitrate are fertilizers, their deposition together with protons will lead to serious disharmonies in the nutritional status of large areas of forest stands.

A potentially dangerous atmospheric pollutant which has only briefly been mentioned above is ozone (Guderian, 1985). It is formed from NO<sub>2</sub> under the influence of ultraviolet radiation :



During the summer months, ozone concentrations in the air are higher than in the winter. The monthly average may be higher than 30 nl l<sup>-1</sup>, and peak concentrations are much higher than this. In areas heavily polluted by nitrogen compounds, and in the presence of strong solar radiation, levels may temporarily rise to 100 nl l<sup>-1</sup> or more (Fig. 3). Ozone is highly reactive. It is therefore already decomposed in cell walls and the outer layers of the cytoplasm. When it reaches the plasmalemma, it oxidizes the double bonds of the unsaturated fatty acids which are components of this cell membrane (Lange *et al.*, 1989a). During exposure to ozone the activity of cellular antioxidants increases. This appears to reflect the response of cells to this aggressive agent. Not much is known about the possibilities available to leaf cells to repair damage caused by the oxidation of membrane constituents. However, as the mineral deficiency caused or increased by acid deposition is known to make plants sensitive to photooxidation and to increase their sensitivity to acidification by air pollutants such as SO<sub>2</sub>, it is not unlikely that it will also affect cellular defences against oxidizing agents such as ozone.

In summary, we wish to point out that forest decline, as observed during recent years over extended areas in Europe, is caused by the combined effects of different stress factors, man-made and natural. It appears that the former are indirectly or directly related to potentially acidic atmospheric pollutants. The indirect effects of the gases are nutrient depletion of the soils and the production of photochemical oxidants in the air. Deficit and disharmony in the nutrient supply increases the sensitivity of trees to other factors. The direct effects of air pollutants are oxidation and acidification reactions in leaf and needle tissues.

#### ACKNOWLEDGMENTS

This work was supported by the Sonderforschungsbereich 251 of the Deutsche Forschungsgemeinschaft « Ökologie, Physiologie und Biochemie pflanzlicher Leistung unter Streß » of the University of Würzburg.

A. LAISK

Eesti TA Astrofüüsika ja Atmosfäärifüüsika Instituut  
EE - 2444 Tõravere, TARTU, Estonia

O.L. LANGE, U. HEBER

Institut für Botanik und Pharmazeutische Biologie der Universität Würzburg  
Mittlerer Dallenbergweg 64  
D - 8700 WÜRZBURG

## REFERENCES

- DITTRICH, A., YIN, Z., WAGNER, U., KOLBOWSKI, J. and HEBER, U., 1989, *Wirkung von SO<sub>2</sub> auf Chloroplasten und Blätter*. 1. Statusseminar der PBWU zum Forschungsprojekt « Waldschäden », in *GSF-Bericht*, 6/89, p. 165-184.
- EIDEN, R., FÖRSTER, J., PETERS, K., TRAUTNER, F., HERTERICH, R. and GIETL, G., 1989, *Air Pollution and Deposition*, in *Forest Decline and Air Pollution. A Study of Spruce (Picea abies) on Acid Soils*, (SCHULZE, E.-D., LANGE, O.L., OREN, R., eds), (*Ecological Studies*, 77), Springer, Berlin, p. 57-103.
- GUDERIAN, R. (ed.), 1985, *Air Pollution by Photochemical Oxidants*, (*Ecological Studies*, 56), Springer, Berlin.
- HEBER, U., LAISK, A., PFANZ, H. and LANGE, O.L., 1987, *Wann ist SO<sub>2</sub> Nähr- und wann Schadstoff? Ein Beitrag zum Waldschadensproblem*, in *Allg. Forstzeitschr.*, 27/28/29, p. 700-705.
- HORN, R., SCHULZE, E.-D. and HANTSCHHEL, R., 1989, *Nutrient Balance and Element Cycling in Healthy and Declining Norway Spruce Stands*, in *Forest Decline and Air Pollution. A Study of Spruce (Picea abies) on Acid Soils*, (SCHULZE, E.-D., LANGE, O.L., OREN, R., eds), (*Ecological Studies*, 77), Springer, Berlin, p. 444-455.
- JÄGER, H.J., 1989, *Stand der Diskussion über Richtwerte für Schadstoffkonzentrationen in der Luft*, in *Proc. of the International Congress on Forest Decline Research. State of Knowledge and Perspectives*, Friedrichshafen, in press.
- KAUPENJOHANN, M., NÄTSCHER, L., SCHWERTMANN, U., SÄSSER, P., HORN, R., TAUBNER, H., HANTSCHHEL, R., ZECH, W. and SCHNEIDER, B.U., 1989, *Effects of Acid Rain on Soil Chemistry and Nutrient Availability in the Soil*, in *Forest Decline and Air Pollution. A Study of Spruce (Picea abies) on Acid Soils* (SCHULZE, E.-D., LANGE O.L., OREN, R., eds), (*Ecological Studies*, 77), Springer, Berlin, p. 297-340.
- LAISK, A., KULL, O. and MOLDAU, H., 1989, *Ozone Concentration in Leaf Intercellulars is Close to Zero*, in *Plant Physiol.*, 90, p. 1163-1167.
- LAISK, A., PFANZ, H. and HEBER, U., 1988, *SO<sub>2</sub> Fluxes into Different Cellular Compartments of Leaves Photosynthesizing in a Polluted Atmosphere*. II. *Consequences of SO<sub>2</sub> Uptake as Revealed by Computer Analysis*, in *Planta*, 173, p. 241-252.
- LANGE, O.L., HEBER, U., SCHULZE, E.-D. and ZIEGLER, H., 1989a, *Atmospheric Pollutants and Plant Metabolism*, in *Forest Decline and Air Pollution. A Study of Spruce (Picea abies) on Acid Soils* (SCHULZE, E.-D., LANGE, O.L., OREN, R., eds), (*Ecological Studies*, 77), Springer, Berlin, p. 238-273.
- LANGE, O.L., WEIKERT, R.M., WEDLER, M., GEBEL, J. and HEBER, U., 1989b, *Photosynthese und Nährstoffversorgung von Fichten aus einem Waldschadensgebiet auf basenarmem Untergrund*, in *AFZ*, 3, p. 55-64.
- NILSSON, J. and GRENNFELT, P., 1988, *Reprint of the Workshop Report on Critical Loads for Sulfur and Nitrogen*, in *Miljörapport*, Stockholm, 16, p. 1-31.
- OREN, R. and SCHULZE, E.-D., 1989, *Nutritional Disharmony and Forest Decline: A Conceptual Model*, in *Forest Decline and Air Pollution. A Study of Spruce (Picea abies) on Acid Soils* (SCHULZE, E.-D., LANGE, O.L., OREN, R., eds), (*Ecological Studies*, 77), Springer, Berlin, p. 425-443.
- SCHULZE, E.-D., LANGE, O.L., OREN, R. (eds), 1989a, *Forest Decline and Air Pollution. A Study of Spruce (Picea abies) on Acid Soils* (*Ecological Studies*, 77), Springer, Berlin.

- SCHULZE, E.-D., OREN, R. and LANGE, O.L., 1989b, *Processes Leading to Forest Decline : A Synthesis*, in *Forest Decline and Air Pollution. A Study of Spruce (Picea abies) on Acid Soils* (SCHULZE, E.-D., LANGE, O.L., OREN, R., eds), (*Ecological Studies*, 77), Springer, Berlin, p. 459-468.
- UHLMANN, W., ALTNER, H., SCHULZE, E.-D. and LANGE, O.L., 1989, *Introduction : The Problem of Forest Decline and the Bavarian Forest Toxicology Research Group*, in *Forest Decline and Air Pollution. A Study of Spruce (Picea abies) on Acid Soils*, (SCHULZE, E.-D., LANGE, O.L., OREN, R., eds), (*Ecological Studies*, 77), Springer, Berlin, p. 1-7.