

Microscopic processes governing the deposition of trace gases and particles to vegetation surfaces

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Abstract

The deposition of fine particles, consisting largely of ammonium and sulphate, as well as the deposition of SO₂ and NH₃, is often dependent on processes happening in the last mm of the atmosphere above the plant surface. Surface wetness plays an important role for trace gas deposition, and at the same time creates a link between particle and trace gas deposition, because water vapour condensation on leaf surfaces is initiated by hygroscopic aerosols. The interdependencies between these processes are described, and the plants role in regulation of deposition by their microroughness and transpiration are mentioned. The importance of acidity and hygroscopicity of deposited particles and salt-forming gases and their possible impact on plants, especially by a kind of 'wick effect', is outlined.

1. Introduction

Wind velocity and aerodynamic roughness of canopies are important for the biggest and first step in the transfer of atmospheric substances towards the plant surface. It may be the limiting factor in the deposition process as long as there is high atmospheric stability. In the presence of high atmospheric turbulence, however, the last mm above the plant surface may govern the deposition velocity. The laminar boundary layer, which is a zone of air without turbulence and in direct contact with the plant (Figure 1), represents the major resistance for deposition of fine particles between 0.1 and 1 µm diameter (Chamberlain and Little, 1981). The water soluble fraction of continental particles of this size consists mostly of ammonium and sulphate. The deposition of trace gases, especially SO₂ and NH₃ is dependent on stomatal opening, and also on the surface wetness (Fowler and Unsworth, 1979, Sutton et al., 1993). The present paper describes important processes during deposition of fine particles and gases, happening directly at the plant surface.

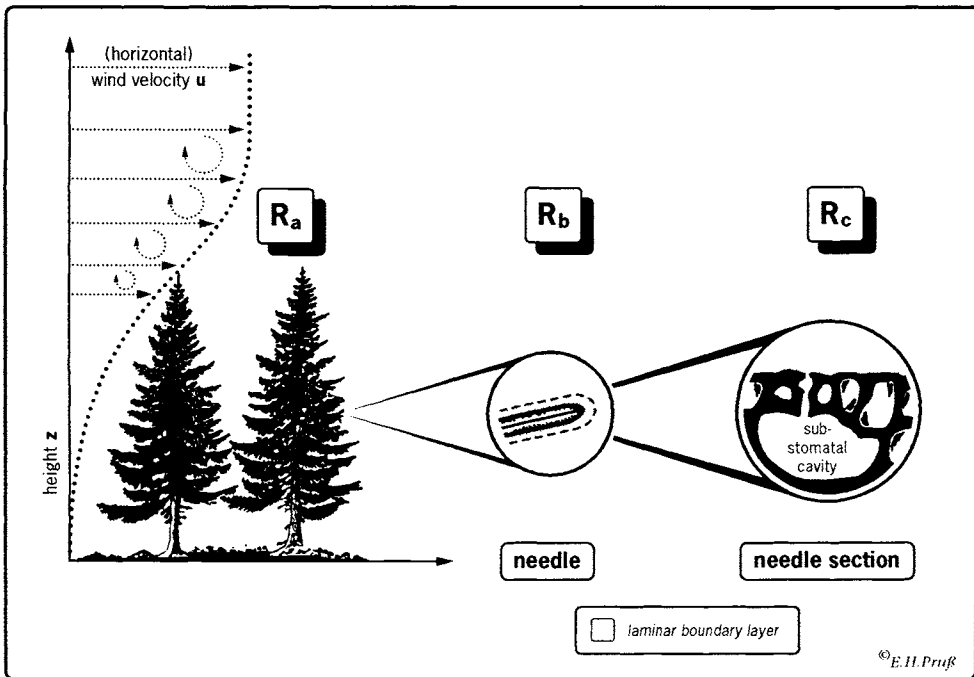


Figure 1. Resistance model for the transport from the free atmosphere to the plant surface

2. The importance of R_b and R_c for the composition of dew drops

Dew drops were collected from small conifers in the Fichtelgebirge, a mountainous region in NE-Bavaria, over a period of three years (1987, 1990, 1991). The droplets were collected directly from the needles, and were then analysed for inorganic components (Burkhardt and Eiden, 1990). Pairs of samples were taken; one of Scots pine (*Pinus sylvestris* L.) and one of Norway spruce (*Picea abies* (L.) Karst.), standing close together. Dew droplets from 30 pairs of trees were examined during the course of the experiment, some of them were sampled repeatedly. Separate samples were taken from different aged needles (recent year, 1-year-old, etc.).

Ratios were formed for each sample and each ion, dividing the ion concentration in dew sampled from Scots pine by that from Norway spruce. The geometric means of these ratios are shown in Figure 2, with the error bars indicating the 95% confidence range. Only results from needles of the recent year are shown. Concentrations of all ions in dew from Scots pine are significantly enhanced. A

difference in the amount of dew between the different tree species could be widely excluded by a comparison with lysimeter balances (Burkhardt, 1994).

The exchange of ions over the leaf surface is one possible explanation for the presence of ions in the dew droplets, and another one is atmospheric deposition. While leaching is probably an important source for some of the ions (e.g. Mn, K), this is not likely to be the case for a group of other ions, including Na, Cl, H, SO_4 , NH_4 . The differences observed for this group therefore is concluded to be due to atmospheric deposition. As the sampled pairs of trees stood close together and were of the same height, the air concentration of the trace substances as well as the aerodynamic resistance were the same for both individuals of each pair; as well as their climatological history. The differences in the concentrations are therefore due to different values of R_b and/or R_c .

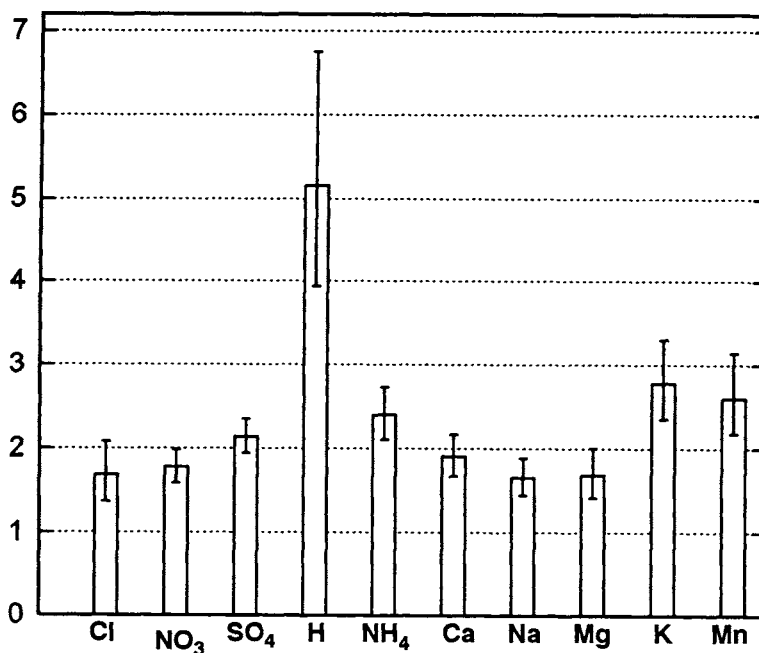


Figure 2: Ratios of the ion content of dew samples taken from pairs of immediately neighboured trees, each pair formed by one Scots pine and one Norway spruce. The geometric mean (i.e. the arithmetic mean of the logarithmic values) of the ratios was formed. The error bars indicate the 95% confidence level. The error bars are of different length on both sides due to the retransformation. For absolute concentration values see Burkhardt and Eiden (1990); Burkhardt (1994).

3. A new concept of surface wetting

The influence of humidity without visible dew formation on trace gas deposition first gained scientific attention with the experiments of van Hove et al. (1989, 1990), although it had been recognised several times before (Spedding, 1969; Garland and Branson, 1977; Fowler and Unsworth, 1979). In the years that followed, it became clear that the gap which had been observed between modelled values and measurements of trace gas fluxes to canopies could be explained by gaseous deposition on the plant cuticle at high relative humidity (Draaijers and Erisman, 1993; Padro et al., 1993).

Use of newly developed wetness sensors (Burkhardt and Gerchau, 1994) enabled an invisible surface wetness to be detected even on the hydrophobic surfaces of spruce needles (Burkhardt and Eiden, 1994). This was recognised by the very strong correlation between relative humidity and electrical conductance along the needle surface (Figure3), which can only be explained by a liquid bridge between the two electrodes, i.e. extending over a distance of 5 mm.

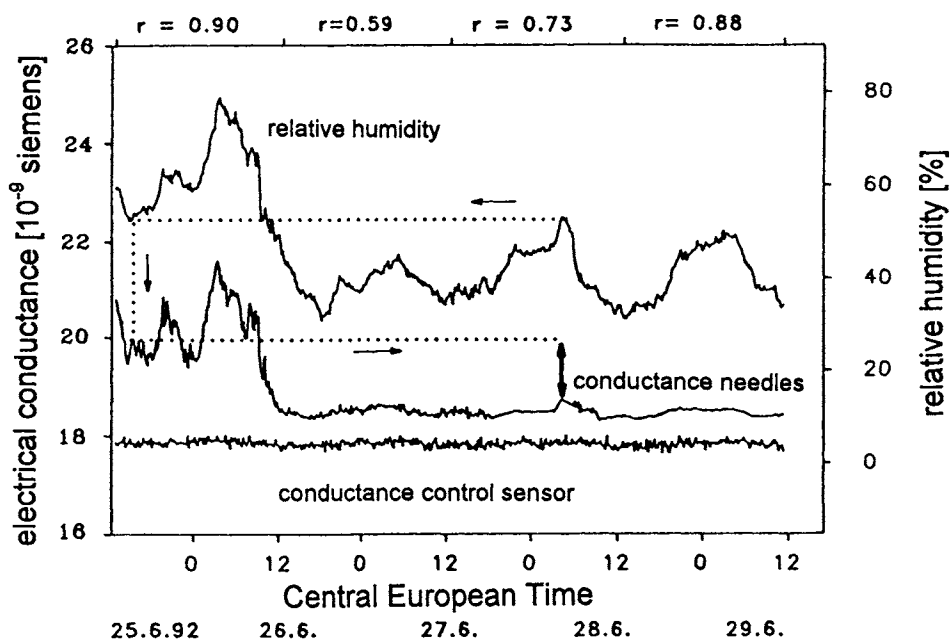


Figure3: Electrical conductance of a sensor on spruce needles (14 m height), of a control sensor without contact to a surface (hanging free), and relative humidity. The correlation coefficients between conductance on the needles and relative humidity are indicated on top of the plot. A significant overall decrease of the signal occurred when the relative humidity fell due to a change of air masses. Nevertheless, the correlation was still high. The pointed line and the double arrow indicate the difference of conductance at the same relative humidity, once during the regimen of high humidity, once during a generally lower humidity.

Continuous measurements were carried out on needles in the crown of a 40-year-old spruce over a period of 5 months, using a meteorological tower. Apart from the conductance measurements, which took place in 6 heights, relative humidity and temperature were measured in 3 heights. Rainfall was detected by the use of a rain gauge on top of the tower.

The results are shown in Table 1. The fraction of time is shown, during which correlation coefficients of $0.7 < r < 1$ were found between relative humidity and conductance along the needle (Table 1). This is interpreted as wetting by thin water films. The time of visible wetting by rain or fog which amounted to about 30% of total time, is not included. The remaining 70% without visible wetness are the basis (i.e. 100%) for the numbers indicated.

Table 1: Times of correlation coefficients $0.7 < |r| < 1$, between electrical conductance on the spruce needles and the relative humidity. The basis is the time of visually dry needles, i.e. about 70% of total time (for details of data analysis see Burkhardt and Eiden, 1994).

height above ground	time (%) with $0.7 < r < 1$ (invisible wetness)
18 m	62.4
16 m	55.5
14 m	59.5
12 m	65.6
10 m	54.0
8 m	20.7

In order to investigate the importance of these water films on gas deposition, a dew chamber experiment was carried out. By holding the relative humidity stable in the dew chamber, a constant electrical conductance evolved (for detailed description of operating conditions see Burkhardt and Eiden, 1994). After several hours, ammonia was introduced in the dew chamber, which led to an instantaneous increase of conductance, indicating the dissolution of ammonia in the water film and the formation of ammonium ions (Figure 4). The experiment was repeated at different humidities and applying different ammonia concentrations. The lower values where a significant conductance increase could be detected were 65% relative humidity and $600 \mu\text{g m}^{-3}$.

The correlation between relative humidity and conductance disappeared, when needles were washed with deionised water and subsequently allowed to dry before the measurements were taken (Burkhardt and Eiden, 1994).

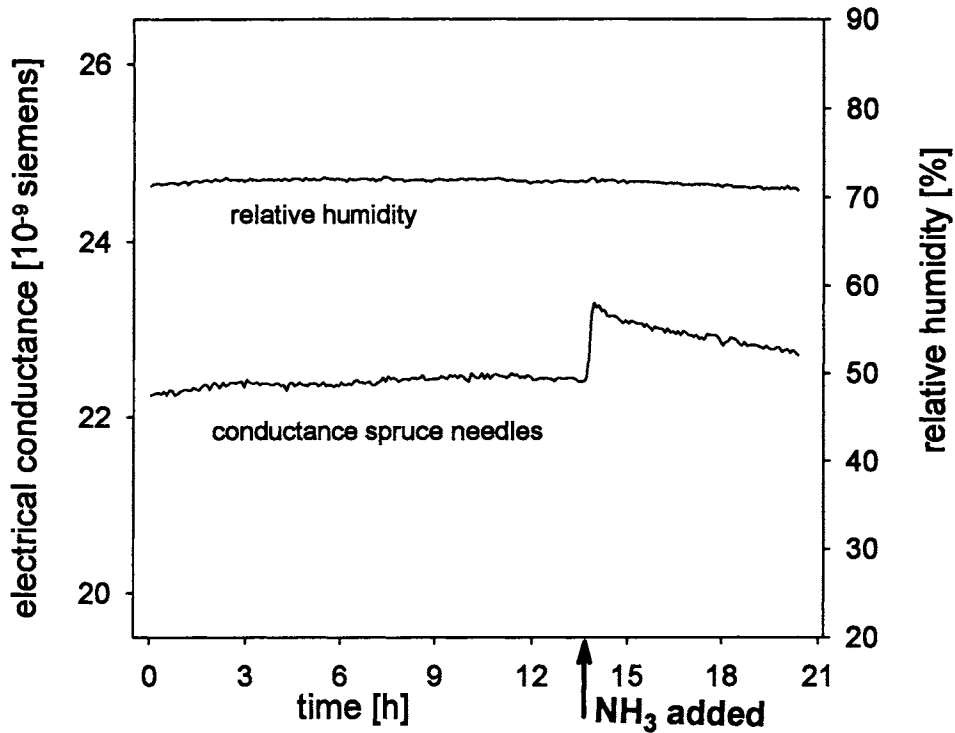


Figure 4: Measurement on needles of a spruce seedling, made in a dew chamber. The relative humidity was held constant, which lead to a constant conductance signal on the needle. The sudden conductance increase when ammonia was added to the dew chamber, is due to the dissolution of ammonia and formation of ammonium ions. It proofs the possibility of gas dissolution in invisible water films.

This supports the hypothesis that particles on the plant surface are responsible for the formation of water films (Eiden et al., 1994). A new concept is thereby confirmed; explaining invisible surface wetness as a consequence of the presence of hygroscopic salts at the needle surface. Water vapour escaping from the stomata creates a humid environment, leading to dissolution of the salts on the leaf surface. As almost all water soluble substances of atmospheric aerosol will be dissolved at a relative humidity of 80% (Winkler, 1988; Pilinis et al., 1989), this is likely to happen to deposited aerosols over extended times. This concept therefore explains the considerable length of observed needle wetness in the field. In addition, the different behaviour on the lowest needles (Table 1) can be explained. This is most probably due to closed stomata since stomata close earlier in the lower part of the tree crown, where photosynthesis is not so effective, to prevent water loss (Larcher, 1984). Partial closure of stomata could as well be the reason for the 'step' in conductance in Figure 3.

4. The importance of salts on the leaf surface for gas deposition

This wetting concept has several implications for gas deposition since invisible wetness is likely to control gas deposition on the cuticle. Therefore, the conditions in this wetness are important. As particles form an important prerequisite for the formation of the films, the particle characteristics are of primary importance. Of particular importance are the amount, hygroscopicity, chemical composition, and also the deposition pattern of the particles on the needles. The history of the leaf is therefore important, i.e. for how long did it not rain, which particles were deposited etc.

The chemical composition of thin water films is likely to be dominated by deposited particles. The chemical composition of these particles is especially important since SO_2 and NH_3 deposition are pH-dependent. Most continental aerosols contain large amounts of NH_4 and SO_4 which contribute almost 80% of the water soluble part (Ludwig and Klemm, 1990). Particles of about 0.1-1 μm diameter presumably have pH values between 1 and 3 in the atmosphere (Winkler, 1986). On such deposited particles, therefore, NH_3 would dissolve very easily, whereas in the presence of NaCl salts, with a much higher pH, the deposition of SO_2 will increase and NH_3 deposition will be low. If both gases are in the atmosphere and the pH of the wetting solution is more or less neutral, codeposition of both gases in similar quantities is likely to happen. This will be especially important if SO_2 is oxidised on the leaf surface. In this case, NH_4HSO_4 or $(\text{NH}_4)_2\text{SO}_4$ salt will be formed, which will not be volatilized again and will therefore stay on the leaf surface. As new water vapour condenses on the newly formed salt, there is the potential for dilution of more trace gas, producing a positive feedback mechanism.

The extent of hygroscopicity of the salt is important because the more water that is absorbed, the more trace gases can be dissolved. Hygroscopicity is characterised by the deliquescence point, i.e. the relative humidity value at which water vapour saturation is reached at the salt surface, or the relative humidity at which the particle will dissolve. The deliquescence points of important atmospheric salts are NaCl 75%, $(\text{NH}_4)_2\text{SO}_4$ 80%, and NH_4HSO_4 40% (Pilinis et al., 1989).

The closer the particles are deposited to transpiring stomata, the longer they will be dissolved. Jagels (1991) found preferential deposition of polydisperse particles at stomatal regions and the same observation was made for monodisperse fine aerosols of about 0.5 μm and attributed to the presence of structured waxes (Burkhardt, 1994). Particles within this size range are very ineffectively deposited in general, and are therefore transported over long distances (Heintzenberg, 1989).

5. The possible impact of salts on the leaf surface to plants

Particles deposited in the stomatal regions of the leaf surface will be nearly permanently dissolved. Some work has been done in the past regarding the acidity on the leaves by evaporation of rain drops or by acidic fog. Most of the continental fine particles are much more acidic (pH 1-3) than these visible drops and so can be NH_4HSO_4 , which is newly formed on the leaf surface.

The pH of a solution is defined operationally, for measurement with the glass electrode. Ludwig and Klemm (1990) proposed a water activity of $a_w=0.9$ as the lower limit of pH definition. Due to $a_w = rh$ (e.g. Stumm and Morgan, 1981), this means a relative humidity of 90%. Other concepts of pH for appliance in highly saline environments have also been proposed (Knauss et al., 1990), and could be sensible in the case of particles on the surfaces of leaves.

However, pH might not be the most important factor with respect to the damage these particles cause the plants. Moreover, the wick function of aerosols/salts may be more important, a deductive concept which becomes possible as soon as continuous water films between substomatal cavities and the leaf surface are 'allowed'.

Thin water films have been investigated in laboratory measurements by several authors and the water film thickness has been calculated to be far below 100 nm (van Hove, 1989; Benner et al., 1992; Burkhardt and Eiden, 1994; Burkhardt, 1994). It is impossible for water droplets to enter the stomata due to the surface tension and stomatal architecture (Schönherr and Bukovac, 1972), but water films of a finite thickness notably below the dimensions of the stoma or the openings in the wax mesh could form a liquid connection along the wall with the liquid water film inside the substomatal cavity. Hygroscopic salts on the surface would therefore attract water from inside of the plant (Figure 5). Due to the hydraulic

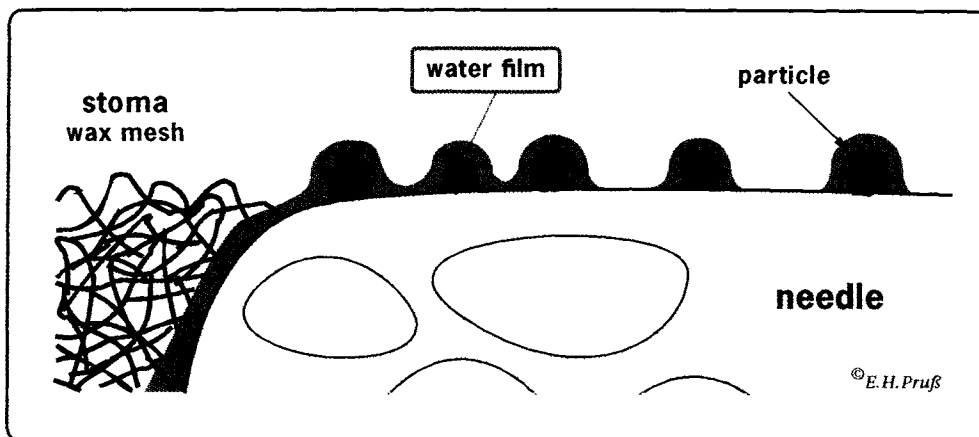


Figure 5: Model of the wick effect caused by hygroscopic aerosols.

junction rapid equilibrium formation will evolve. When the equilibrium is disturbed by the influence of Sun and wind, the evaporating water is replaced by liquid water out of the stomata. Thus, the transpiring area of the tree is increased. Stomatal movements would not affect this mechanism as long as the stomata would not close completely.

This mechanism might be more important than the acidity. Needle loss as observed in forest decline is a drought phenomenon (Ulrich, 1990), and winter dessication would also be aggravated by this kind of additional transpiration.

6. Conclusions

Although particles contribute only in part to the overall picture of dry deposition, they may have an important influence on trace gas deposition by the formation of surface wetness. They could also be of importance by forming an impact to the plants, both by providing very deep pH on the leaf surface for extended times as well as by their hygroscopic action, which leads to an increased transpiration area. This might be of importance during times of drought and times of frozen soil in the winter.

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References

- BURKHARDT J. (1994): Dünne Wasserfilme auf Fichtennadeln und ihr Einfluß auf den Stoffaustausch zwischen Atmosphäre und Pflanze. *Bayreuther Forum Ökologie*, **9**, 1-137. ISSN 0944-4122.
- BURKHARDT J., EIDEN R. (1990): The ion concentration of dew condensed on Norway spruce (*Picea abies* (L.) Karst.) and Scots pine (*Pinus sylvestris* L.) needles. *Trees*, **4**, 22-26.
- BURKHARDT J., EIDEN R. (1994): Thin water films on coniferous needles. *Atmospheric Environment*, **28A**, 2001-2017.
- BURKHARDT J., GERCHAU J. (1994): A new device for the study of water vapour condensation and gaseous deposition to plant surfaces and particle samples. *Atmospheric Environment*, **28A**, 2012-2017.

- CHAMBERLAIN A.C., LITTLE P. (1981): Transport and capture of particles by vegetation. In: GRACE J., FORD E.D., JARVIS P.G. (Hrg.): *Plants and their Atmospheric Environment*, 147-173.
- DRAAIJERS G.P.J., ERISMAN J.W. (1993): Atmospheric sulphur deposition to forest stands: throughfall estimates compared to estimates from inference. *Atmospheric Environment*, **27A**, 43-55.
- FOWLER D., UNSWORTH M.H. (1979): Turbulent transfer of sulphur dioxide to a wheat crop. *Quarterly Journal of the Royal Meteorological Society*, **105**, 767-783.
- GARLAND J.A., BRANSON J.R. (1977): The deposition of sulphur dioxide to pine forest assessed by a radioactive tracer method. *Tellus*, **29**, 445-454.
- HEINTZENBERG J. (1989): Fine particles in the global troposphere - A review. *Tellus*, **41 B**, 149-160.
- JAGELS R. (1991): Biophysical aspects of fog deposition on the needles of three conifers. *Journal of Experimental Botany*, **42**, 757-763.
- KNAUSS K.G., WOLERY T.J., JACKSON K.J. (1990): A new approach to measuring pH in brines and other concentrated electrolytes. *Geochimica et Cosmochimica Acta*, **54**, 1519-1523.
- LARCHER W. (1984): W. Larcher 1984. *Ökologie der Pflanzen auf physiologischer Grundlage*, 4th ed., Ulmer, Stuttgart.
- LUDWIG J., KLEMM O. (1990): Acidity of size-fractionated aerosol particles. *Water, Air and Soil Pollution*, **49**, 35-50.
- PADRO J., NEUMANN H.H., DEN HARTOG G. (1993): Dry deposition velocity estimates of SO₂ from models and measurements over a deciduous forest in winter. *Water, Air and Soil Pollution*, **68**, 325-339.
- PILINIS C., SEINFELD J.H., GROSJEAN D. (1989): Water content of atmospheric aerosols. *Atmospheric Environment*, **23**, 1601-1606.
- SCHÖNHERR J., BUKOVAC M.J. (1972): Penetration of stomata by liquids. *Plant Physiology*, **49**, 813-819.
- SPEDDING D.J. (1969): Uptake of sulphur dioxide by barley leaves at low sulphur dioxide concentrations. *Nature*, **224**, 1229-1231.
- SUTTON M.A., PITCAIRN C.E.R., FOWLER D. (1993): The exchange of ammonia between the atmosphere and plant communities. *Advances in Ecological Research*, **24**, 302-393.
- ULRICH B. (1990): Waldsterben: Forest decline in West Germany. *Environmental Science and Technology*, **24**, 436-441.
- VAN HOVE L.W.A., ADEMA E.H., VREDENBERG W.J., PIETERS G.A. (1989): A study of the adsorption of NH₃ and SO₂ on leaf surfaces. *Atmospheric Environment*, **23**, 1479-1486.
- VAN HOVE L.W.A., VREDENBERG W.J., ADEMA E.H. (1990): The effect of wind velocity, air temperature and humidity on NH₃ and SO₂ transfer into bean leaves (*Phaseolus vulgaris* L.). *Atmospheric Environment*, **24A**, 1263-1270.
- WINKLER P. (1986): Relations between aerosol acidity and ion balance. In: JAESCHKE W. (Hrg.): *Chemistry of multiphase atmospheric systems*, Springer, Berlin, 269-298.
- WINKLER P. (1988): The growth of atmospheric aerosol particles with relative humidity. *Physica Scripta*, **37**, 223-230.