CHAPTER 4 MEASUREMENT RESULTS AND DRY DEPOSITION PARAMETRISATIONS

Introduction

This chapter will describe experimental results on dry deposition. From these measurements the physical, chemical and biological processes that control deposition fluxes over surfaces are determined and translated in descriptions or parameterisations for modelling dry deposition fluxes. This is done separately for each gas and for particles. Most of the parametrisations have been derived from the literature and from experiments carried out in the Netherlands. These experiments comprise the Elspeetsche Veld three-year experiment to quantify atmospheric fluxes and derive deposition parameters for heathland vegetation; the Speulder forest long-term experiment to determine the input and impact of pollutants to a Douglas fir forest, and the Utrechtse Heuvelrug one-year experiment to determine the influence of complex terrain on deposition. These field experiments are described in some detail in Chapter 7.

4.1 MEASUREMENT RESULTS

4.1.1 SO_2

SO_2 dry deposition measurements have been made for several surfaces: coniferous forests (Galbally, 1979; Garland, 1977; Hicks *et al.*, 1982; Fowler and Cape, 1983; Lorenz and Murphy, 1985; McMillen *et al.*, 1987; Vermetten *et al.*, 1992; Erisman *et al.*, 1993d), deciduous forests (Petit et al., 1976; Matt *et al.*, 1987; Meyers and Baldocchi, 1988), heathland (Erisman *et al.*, 1993c), crops (Fowler, 1978), grasslands (Garland, 1977; Platt, 1978; Van Dop *et al.*, 1983; Hicks *et al.*, 1983, 1986; Neumann and den Hartog, 1985; Duyzer and Bosveld, 1988; Davies and Mitchell, 1983; Davies and Wright, 1985; Erisman *et al.*, 1992), water bodies (Welphdale and Shaw, 1974; Garland, 1977), bare soil (Payrissat and Beilke, 1974; Garland, 1977), and snow (Barrie and Warmsley, 1978; Welphdale and Shaw, 1974; Cadle *et al.*, 1985; Granat and Johanssson, 1983; Valdez *et al.*, 1987; Davidson and Wu, 1990; Garland, 1977). In the literature average values for the deposition velocity range from 0.1 to over 2 cm s^{-1} with daytime values usually between 0.8 and 1.2 cm s^{-1} Large values (> 2 cm s^{-1}) are observed above water surfaces and forests and relatively small values (< 0.13 cm s^{-1}) are measured above snow and bare soil.

Numerous field studies show that the surface resistance R_c controls the SO_2 dry deposition velocity. R_c is a function of the canopy stomatal resistance R_{stom}, the canopy cuticle resistance $R_{cuticle}$ and the soil resistance R_{soil}. In turn, these resistances are affected by leaf area, stomatal physiology, soil pH, and the presence and chemistry of liquid drops and water films on the surface. The stomatal, leaf surface (cuticle) and soil resistances act in parallel.

Physiological Control

Most SO_2 enter plants through the stomata. As gas molecules enter the leaf, deposition occurs as molecules react with the moist cells in the substomatal chamber and the mesophyll. Stomatal resistance decreases hyperbolically with increasing light and increases linearly with increasing vapour pressure deficits (Jarvis, 1976). Soil water deficits cause stomata to close after some threshold deficit level is exceeded. Low and high temperatures cause stomatal closure and moderate temperatures promotes stomatal opening. Leaf age, nutrition and adaptation are other factors affecting stomatal resistance. Elevated exposure to SO_2 causes stomata to close (Black, 1982). Stomatal resistance is different for different types of vegetation. Values of R_{stom} during daytime, range between 30 and 300 s m^{-1} for a variety of herbaceous annuals and woody perennials (Fowler, 1985; Baldocchi *et al.*, 1987; Matt *et al.*, 1987).

The canopy cuticle resistance exceeds by far the canopy stomatal resistance; $R_{cuticle}$ ranges between 3000 and 40000 s m^{-1} (van Hove, 1989). However, it is observed that the surface resistance decreases as relative humidity increases (van Hove *et al.*, 1989; Garsed, 1985; Erisman *et al.*, 1993a; Erisman and Wyers, 1993; Draaijers and Erisman, 1993). Under these circumstances, the surface will become moist e.g. through deliquesence of salts at the external leaf surface. SO_2 dry deposition will be enhanced (Garland and Branson, 1977; Fowler and Unsworth, 1979; Fowler, 1985; Vermetten *et al.*, 1992; Erisman *et al.*,1993a; Erisman and Wyers, 1993) and will occur via absorption and chemical oxidation reactions in the water layer.

Physico-chemical control

The absorption of SO_2 in water layers is associated with a series of reactions (Seinfeld, 1986):

$$\begin{array}{lll} SO_2\,(g) + H_2O \Leftrightarrow SO_2 \cdot H_2O & (R0) & \\ SO_2 \cdot H_2O \Leftrightarrow H^+ + HSO_3^- & (R1) & [4.1] \\ HSO_3^- \Leftrightarrow H^+ + SO_3^{2-} & (R2) & \end{array}$$

The total dissolved S(IV) in chemically clean solutions is related to the partial pressure of SO_2 over the solution (p_{SO2}) and the pH of the solution:

$$[S(IV)] = K_H \cdot p_{SO2}(1 + \frac{K_1}{[H^+]} + \frac{K_1 \cdot K_2}{[H^+]^2}) \qquad [4.2]$$

where K_H is the Henry coefficient for SO_2 (5.4 mol l^{-1} atm^{-1} at 15 ^{o}C) and K_1 and K_2 are the equilibrium coefficients for reactions 1 and 2, respectively. From Equation [4.2] it can be concluded that an increase in acidity will reduce the amount of dissolved SO_2. The oxidation of S(IV) to S(VI) by O_2, O_3 and H_2O_2 provides another source of protons. The oxidation of aqueous SO_2 by O_3 and H_2O_2 is fast; oxidation by O_2 is slow unless there is a metal catalyst (generally iron or manganese). An increase in acidity due to solution and oxidation of SO_2 in water films will reduce SO_2 dry deposition to wetted surfaces. The presence of acid-neutralising species, either from the atmosphere (base cations, NH_3) or from the inner parts of the leaves, will reduce the acidity of the water film, abolishing the SO_2 dry deposition reduction. At present, too little information is available to quantify these processes in terms of the influence on the magnitude of the surface resistance.

As the pH of the wetted surface is the deposition rate limiting factor, the origin of surface wetness through fog, cloud, rain, dew or guttation is important (Fowler and Unsworth, 1979). The pH of rain, cloud and fog is less than that of pure water. The chemistry of wetted surfaces is affected by the uptake of acidic precursors and oxidants, particles on the leaf surface, chemical lifetime, droplet size, leaching of nutrients from leaf and evaporation rate of wetness (Brimblecombe, 1978; Chameides, 1987; Wesely *et al.*, 1990)

Deposition of NH_3 will neutralise an acid solution. Thus simultaneous deposition of SO_2 and NH_3 should show higher SO_2 (and NH_3) dry deposition rates to water surfaces than would be found by SO_2 (or NH_3) alone (Wesely *et al.,* 1990; Erisman and Wyers,1993; Erisman *et al.,* 1993c). It has been suggested that the deposition of NH_3 can enhance the deposition of SO_2. This process, generally referred to as co-deposition, was first suggested by Brimblecombe (1978). Van Breemen *et al.* (1982) measured a 2:1 flux ratio of NH_4^+ to SO_4^{2-} in throughfall under a forest canopy. Houdijk (1990) observed that fluxes of both NH_4^+ and SO_4^{2-} were much higher in areas with intensive livestock breeding compared to background areas. Both effects were ascribed to co-deposition of NH_3 and SO_2. The high deposition of NH_3 in areas with intensive livestock production was assumed to decrease the acidity of the absorbing surfaces, thereby increasing the buffering of protons generated in SO_2 dissolution. Thus the SO_2 deposition increased. Recent measurements of throughfall under forest, heathland and grassland canopies have shown the same phenomena (Van Breemen *et al.*, 1988; Heil *et al.*, 1989; Bobbink *et al.* 1992; Draaijers *et al.*, 1989; Ivens 1990).

The wide range of deposition velocities for SO_2 measured during recent years in different locations of the world are ascribed partly to the difference in alkalinity and wetness of vegetation canopies (Fowler *et al.*, 1991). A higher V_d SO_2 in areas with high NH_3 emissions relative to remote areas was also suggested by Onderdelinden *et al.* (1984) and Lövblad and Erisman (1992).

The process of co-deposition has been demonstrated in laboratory experiments. Adema *et al.* (1986) and Heeres and Adema (1989) showed a clear pH-dependence of SO_2 deposition on water layers in a small wind tunnel. Addition of NH_3 to the air in the wind tunnel increased the SO_4^{2-} concentration in the water layer. Van Hove (1989) showed stoichiometric adsorption of the two gases in leaf chamber experiments, with the adsorption of NH_3 being twice that of SO_2 (on a molar basis). At higher relative humidities, adsorption increased and this ratio was maintained. The thickness of water layers on the vegetation was strongly dependent on relative humidity, ranging from 40-200 μm for relative humidities between 60 and 90%.

So far there have only been a limited number of combined micrometeorological measurements of NH_3 and SO_2, needed to test the importance of this process in the field (Sutton, 1990; Erisman *et al.*, 1991; Erisman 1992; Fowler *et al.*, 1991). Van Hove *et al.* (1989), Fowler *et al.* (1991) and Erisman and Wyers (1993) present evidence showing that the surface SO_2 uptake at wet surfaces is enhanced in the presence of NH_3. One site of reaction is in the water-filled pores of the cuticle at relative humidities above about 70% and the other site is on the wetted leaf surface.

Deposition to soil and litter

Deposition to canopies involves deposition to both vegetation and soil. Early studies assumed that deposition to soils under vegetation was relatively small (5 - 10% of the total flux; Fowler, 1978). Recent work shows that a substantial amount of material can be deposited to the soil below vegetation. Meyers and Baldocchi (1992) report that 20 to 30% of SO_2 depositing on a deciduous forest is received at the forest floor. This substantial transfer occurs because large-scale intermittent eddies are able to penetrate through the vegetation and transport material to the soil. Differentiation of deposition to the canopy and to the soil is difficult to measure. Furthermore, it may be variable, both in time and for different canopies. Relatively large deposition amounts to the forest soil are to be expected in forest edges and in deciduous forests in wintertime when gusts can penetrate deeply through the forest canopy.

Deposition to soil decreases at a soil pH below 4 and increases with relative humidity (Garland, 1977; Payrissat and Beilke, 1974). When surface temperatures fall below zero or the surface is covered with snow, R_c values increase up to 200 - 500 s m^{-1} (Voldner *et al.*, 1986; Erisman and Wyers, 1993). The deposition of SO_2 to snow-covered surfaces depends on pH, snow temperature and probably the amount of SO_2 already scavenged by the snowpack (Cadle *et al.*,1985; Hicks *et al.*, 1989).

4.1.2 NOx

NO_2 is absorbed by water, soils and vegetation. However, uptake by water is slow. The conclusion to an analysis by Lee and Schwartz (1981) is that the solubility of NO_2 in water and the rate of subsequent reactions in the water are too low to produce deposition velocities of NO_2 to water higher than 0.1 cm s^{-1}. Gravenhorst and Böttger (1982) and Böttger *et al.* (1980) found values of 0.01 - 0.02 cm s^{-1} for water and sea water using the enclosure technique. For snow, Gravenhorst and Böttger (1982) and Granat and Johansson (1983) report V_d values below 0.03 cm s^{-1}.

Hanson *et al.* (1989) conclude that the uptake of NO_2 by plants is under stomatal control. Hanson and Lindberg (1991) conclude that the cuticular uptake is 1 or 2 orders of magnitude smaller than the stomatal uptake. Because of the slow uptake of NO_2 in water, the uptake on wet leaf surfaces of NO_2 is expected to be small. Vegetated surfaces can act either as a source or sink for NO_2 and NO. At high concentrations, the deposition of NO_2 to vegetation has been shown to be proportional to stomatal conductance, with minimal uptake on the external surfaces of leaves (Johansson, 1987; Fowler *et al.*, 1991; Duyzer *et al.*, 1991). At low concentrations there was hardly any uptake of NO_2. Leaf chamber measurements suggest the existence of a 'compensation point' in the order of 2-6 µg m^{-3}, below which forests may act as a (minor) source of NO_2 (Johansson, 1987). Glass cuvette measurements suggest that deposition of NO_2 to the forest floor, based on a soil surface area basis, may be 6- to 7-fold greater than deposition to foliar surfaces (Hanson *et al.*, 1989). However, measurements taken by Williams *et al.* (1987) showed that forest soils may emit NO_2 as well. According to Hanson and Lindberg (1991), the deposition velocity of NO_2 to broad-leaved forests is greater than to coniferous forests. Whole-canopy measurements of NO_2 deposition yield daytime overall deposition velocities between 0.1 and 2.8 cm.s^{-1} (Hanson and Lindberg, 1991).

Since NO_2 fluxes are usually small, and because the constant flux layer assumption might be violated by the surface sources and photochemical equilibrium between O_3, NO and NO_2, micrometeorological measurements have proven to be difficult. Duyzer *et al.* (1983) measured deposition velocities of 1.5 cm s^{-1}, with several periods of upward fluxes. Hargreaves *et al.* (1992) measured NO_2 deposition to grass and found minimum surface resistances of 60 - 100 s m^{-1}, increasing to around 1000 s m^{-1} in the early afternoon, indicating stomatal control. Measurements aboveheathland showed similar results (cf. Erisman *et al*, 1994).

The uptake of NO by vegetation is much more limited than for NO_2 due to the low solubility of NO in water. NO uptake is unaffected by the large change in stomatal resistance between day and night conditions (Hanson and Lindberg, 1991). Up to now, no significant downward fluxes of nitric oxide (NO) have been reported. Yet, upward fluxes of NO from soils have been measured and are found to depend on soil temperature, water content and ambient air concentration of NO and NO_2 (Hicks *et al.*, 1989). Deposition velocities for NO will be considerably less than for NO_2 (Hanson and Lindberg, 1991).

4.1.3 HNOx

Among the gases under consideration, HNO_3 is the most reactive and readily absorbed by surfaces. All field and laboratory measurements at temperatures above 0 °C show that the surface resistance for HNO_3 is zero, and that rates of deposition are determined entirely by atmospheric transfer (Huebert, 1983; Müller *et al*, 1993; Heubert and Robert, 1985; Harrison *et al.*, 1989; Erisman *et al.*, 1989; Hanson and Lindberg, 1991). On the basis of its chemical properties, one would expect deposition of HNO_3 to the cuticle to be very efficient and dominant over stomatal uptake. Deposition velocities of HNO_3 to forests may therefore become very large. Fowler *et al.* (1989) mentions V_d's of 4.0 cm.s^{-1} for wind speeds near 1 m.s^{-1} and V_d's of 10 cm.s^{-1} when wind speeds are near 4 m.s^{-1}. Only at snow surfaces or at temperatures below -5 °C could a surface resistance be detected: 500 s m^{-1} at -18 °C and 100 s m^{-1} at -3 °C (Johansson and Granat, 1987).

If the surface resistance for HNO_3 deposition is effectively zero, then calculating rates of deposition onto a wide range of surfaces requires only estimation of the atmospheric resistances (R_a and R_b). A major problem then arises in providing an appropriate formulation for R_b, the majority of which are based on wind tunnel studies for surfaces not necessarily representative for canopies of vegetation in the field (Brutsaert, 1982). Especially in very turbulent conditions, such as found above a forest, the rate of HNO_3 deposition is very sensitive to R_b (Duyzer and Fowler, 1994). In complex terrain near forest edges where turbulence is even more increased, the resistance to transport to these edges will be very small, leading to very high deposition fluxes of HNO_3 (Draaijers *et al.*, 1994; Duyzer and Fowler, 1994).

There is almost no knowledge on deposition mechanisms and deposition velocities of HNO_2 (Lövblad and Erisman, 1992). The canopy resistance for various seasons under different conditions, estimated by Wesely (1989) from chemical and physical properties of the gas, was assumed to correspond to the canopy resistance for SO_2, i.e. mainly stomatal-controlled uptake under dry conditions and efficient uptake to wet surfaces. Wesely (1989) estimated the maximum deposition velocity to a decidious forest at 1 cm s^{-1}. The deposition to a canopy wetted by dew or rain was also found te be around this value. Upward fluxes might be expected due to the formation of HNO_2 from NO_2 in the water layer on surfaces and the release of nitrous acid from the water phase (Northolt *et al.*, 1992).

4.1.4 PAN

Few data are available for PAN deposition. Hill (1971) reports a deposition velocity for PAN to alfalfa of 0.6 cm s^{-1} from his measurements in a recirculating exposure chamber. In a wind tunnel study by Garland and Penkett (1976), values of $V_d = 0.21$ to 0.3 cm s^{-1} ($R_c = 290 - 340$ s m^{-1}) were found for soil, and $V_d = 0.14$ to 0.26 ($R_c = 380 - 700$ s m^{-1}) for grass. Deposition to water was very slow ($V_d < 0.02$ cm s^{-1}). Bos *et al.* (1978) reports values for the deposition velocity of PAN to sea water of 0.009 cm s^{-1}, to fresh water of 0.011 cm s^{-1}, to dune sand of 0.032 cm s^{-1}, to agricultural soil of 0.06 cm s^{-1} and to grass of 0.13 cm s^{-1}.

4.1.5 NH_3

Exchange of atmospheric ammonia with various surfaces may be bi-directional, depending on surface type and environmental conditions. Grazed pastures and arable cropland show a net ammonia emission over yearly periods (e.g. Jarvis *et al.*, 1989; Sutton *et al.*, 1989), whereas semi-natural ecosystems show net ammonia deposition (e.g. Duyzer *et al.*, 1987; Schjörring and Byskov, 1991; Erisman, 1992). Ammonia can be taken up efficiently, translocated and metabolised by living plants (Porter *et al.*, 1972; Lockyer and Whitehead, 1986) and by soil (Malo and Purvis, 1964; Hanawalt, 1969; Horvath, 1982).

Deposition of NH_3 to semi-natural vegetated surfaces can take place either by stomatal uptake or on external plant parts (Van Hove, 1989). In general, the presence of water layers on vegetation decreases the canopy resistance considerably. However, Van Hove (1989) found large deposition velocities even under dry conditions. With no free water present on the leaf, he found the surface adsorption of NH_3 to increase with relative humidity, suggesting that microscale water (which mediates the deposition process) may be present on leaf surfaces, even when the leaves appear dry. Moreover, the presence of SO_2 may decrease the canopy resistance of NH_3, as its solubility in water is pH-dependent (Adema *et al.*, 1986, see section 4.1.1). Leaf surface interactions with other acid gases such as HNO_3 and HCl may also be important. However, because the ammonium salts with these gases (NH_4NO_3 and NH_4Cl) have significant vapour pressure (Seinfeld, 1986), they may possibly re-dissociate back to the precursor gases, limiting accumulation of salts on leaf surfaces. This is in contrast to ammonium sulphates, which have negligible vapour pressure and may therefore accumulate (Sutton *et al.*, 1993).

Measurements of NH_3 deposition to forests have been reported by Duyzer *et al.* (1987), Sutton *et al.* (1989), Slanina *et al.* (1990), Duyzer *et al.* (1992), Wyers *et al.* (1992) and Erisman *et al.* (1994) (see Chapter 7). The low surface resistances (near zero) and accordingly high deposition velocities (1.5-3.6 cm s^{-1}) found in these studies suggest that NH_3 deposition rates are controlled to a large extent by atmospheric transfer which, in turn, is determined by wind speed and aerodynamic roughness of the canopy. In areas with exceptionally large NH_3 air concentrations, the canopy resistance may be substantially enhanced due to saturation of the water layer with NH_4^+ (Duyzer and Diederen, 1989). If saturation occurs, net deposition becomes lower and even emission can take place at rising temperatures or decreasing ambient air concentrations (Erisman, 1992) This may be recognised as a compensation point.

Measurements of Langford and Fehsenfeld (1992) in a forest in Colorado show that the forest emits NH_3 at low ambient NH_3 concentrations, whereas net dry deposition occurs at high NH_3 concentrations. Sutton *et al.* (1992) also determined a compensation point using gradient measurements over different types of vegetation. On a daily scale, emission was favoured during warm dry conditions, whereas deposition generally occurred when the surface was wet or frozen. Erisman and Wyers (1993) measured upward fluxes of NH_3 during dry conditions in daytime and in conditions where water-layer films on leaves evaporated and the ambient NH_3 concentration became small. When interpretating these measurements, however, one has to bear in mind that NH_3 is in equilibrium with HNO_3 and NH_4NO_3 in the atmosphere. Where deposition of both gases occurs it is possible that dissociation of the aerosol can occur. By contrast, a large emission flux of NH_3 enhances the concentration product of NH_3 and HNO_3 and may cause aerosol formation. The major consequence of rapid chemical conversion affecting ammonia exchange is complicating the interpretation of micrometeorological field measurements. Taking such reactions into account represents a substantial increase in complexity of the analysis. While the sum of both phases may be treated as a conserved species, such conversion processes may substantially alter the magnitude of both the component fluxes and their total flux (Sutton *et al.*, 1993).

The compensation point for NH_3 is a function of the NH_4^+ concentration in the water film at the leaf surface and of the NH_4^+ concentration in the substomatal cativity. The processes controlling the concentration of NH_4^+ within the cells of growing plants is extremely complicated and the dependence of the compensation point on species and growing conditions is poorly understood. Typical values appear to be in the order of 0.7 μg m^{-3} for trees (Langford and Fehsenfeld, 1992), 2 - 3.5 μg m^{-3} for herbaceous crop plants (Dabney and Bouldin, 1990; Farquhar *et al.*, 1980; Lemon and Van Houtte, 1980) and > 7 μg m^{-3} for wheat and perhaps other cereal-type grasses (Harper *et al.*, 1987; Lemon and Van Houtte, 1980; Morgan and Parton, 1989). The compensation point has an exponential temperature dependence consistent with the presence of a steady-state concentration of dissolved ammonia in the water film present on the mesophyllic surfaces of the substomatal cavities (Farquhar *et al.*, 1980). The compensation point is hypothesised to vary as a function of the balance between NH_4^+ releasing reactions (deamination, nitrate reduction and senescence-induced proteolysis) and NH_4^+-consuming reactions (N transport, assimilation via glutamine synthetase). The balance will shift to the former with increasing plant maturity, leading to higher intracellular NH_3 concentrations (Morgan and Parton, 1989; Parton *et al.*, 1988). Especially during ripening and senescence of crops high compensation points were found, promoting ammonia emission.

Duyzer *et al.* (1994) show that deposition of ammonia to sea water is only limited by atmospheric transport. Uptake may become limited, however, if significant amounts of NH_3 are already present in the sea water. In some cases even emission of NH_3 from sea water was observed (Quinn *et al.*, 1987; Asman *et al.*, 1994). The magnitude as well as the direction of the flux may be explained very well with a simple Henry's law equilibrium. The deposition velocity over sea water was as high as 1 cm s^{-1} when wind speed was high. Ammonia concentrations in the air were high and in the water low (Duyzer *et al.*, 1993).

4.1.6 HCl

Deposition rates of HCl onto vegetation were determined by Harrison *et al.* (1989). As for HNO_3, there was no evidence for surface resistance and the deposition mechanism of HCl is assumed to be identical to that of HNO_3.

4.1.7 PARTICLES

The dry deposition velocity of particles depends heavily on their diameter. Research on particle size distributions, along with chemical composition of particles, is therefore relevant to determining V_d. Milford and Davidson (1985) have summarised size distributions of 38 trace elements reported in the literature. From their review it becomes clear that elements with an MMD smaller than 2 µm (fine particles) generally have bimodal distributions. The dominant peak occurs in the range of 0.5-1 µm. Elements with larger MMDs (coarse particles) usually have a single peak. Most sulphate, nitrate and ammonium containing particles (e.g. $(NH_4)_2SO_4$, NH_4NO_3) are found to fall within the 0.1-1.0 µm size range. Coarse particles falling in the range 2-20 µm are mostly derived from alkaline soil dust (e.g. $CaCO_3$, $MgCO_3$) and sea-spray (e.g. NaCl, $MgCl_2$). Fine particles are, due to their low weight, more susceptible to long-range transport than coarse particles. Most soil-derived particles are likely to deposit near the area of origin (Milford and Davidson, 1985), although long-range transport of, for example, desert dust has also been reported (Ganor *et al.*, 1991; Swap *et al.*, 1992). Deposition will alter the mass distribution function of particles remaining airborne. The shift in the distribution is towards particles with small diameters (Ruijgrok and Davidson, 1992). The size distribution is also affected by hygroscopic growth of particles taking place at relative humidities above 80% (Fitzgerald, 1975).

Experiments under controlled conditions in wind tunnels and theoretical models suggest relatively small rates of particle deposition onto vegetation, deposition velocities ranging from 0.1-1 mm.s^{-1} (Chamberlain, 1966; Sehmel, 1980; Nicholson, 1988; Ruijgrok *et al.*, 1992). However, recent field measurements on deposition velocities of particles indicate much higher deposition velocities, especially for forests (e.g. Hicks *et al.*, 1989; Waranghai and Gravenhorst, 1989; Fowler *et al.*, 1992; Sievering *et al.*, 1994; Erisman *et al.*, 1994; Wyers *et al.*, 1994; Duyzer *et al.*, 1994; see also section 7.3). Davidson and Wu (1990) have listed deposition velocities for particulate sulphate to low vegetation and forests derived from the following measurements: micrometeorological, surrogate surface exposure, foliar extraction and throughfall.

It appears that mean dry deposition velocity estimates depend to some extent on the methodology used to derive them. The mean deposition velocity obtained from throughfall measurements is larger than that obtained using other techniques. From the same literature review, Davidson and Wu (1990) conclude that deposition velocities for NO_3^- particles are somewhat higher than corresponding values for SO_4^{2-} particles, which should be attributed to a larger particle size usually associated with NO_3^- particles that are, besides through the reaction of HNO_3 and NH_3, also formed by the reaction of HNO_3 with soil-derived or sea-salt particles). Deposition velocities for particulate NH_4^+ are found to be similar to those of particulate SO_4^{2-}. The deposition velocity of particulate Cl^- is substantially higher (ranging from 1.0 to 5.1 cm.s^{-1}) than encountered for SO_4^{2-} and NO_3^-particles, probably reflecting the larger particle size distribution of Cl^-. Deposition velocities of Mg^{2+}, Ca^{2+} and K^+ particles are most likely to fall in the range of 1.0 to 3.0 cm s^{-1} but reliable data on this subject are practically non-existent (Davidson and Wu, 1990).

4.1.8 METEORITES

There is not much information about the deposition of meteorites to the surface. It can be speculated that deposition velocities of meteorites are high, but it is questionable if the input of components as the result of meteorite deposition significantly contributes to the total input of these components. In this section meteorite deposition will be described.

Hughes (1992) predicted the actual flux of meteorites to the earth from the flux of meteorite parent bodies to the top of the atmosphere and by using information on atmospheric ablation and fragmentation processes (Table 4.1). Ablation and fragmentation were found to depend on the composition, mass, density, velocity and angle of entry of the incident body.

For incident objects that have an out-of-the atmosphere mass between 10^{-9} and 10^{3} g, Hughes (1992) assumes the ablation process to be complete and the incoming particles to be broken up into its constituent atoms and molecules. Moreover, incident objects larger than 10^{9} g are believed to hit the earth's surface with a nearly out-of-the atmosphere velocity and produce between 10^3 and 10^9 g. The annual flux to the top of the atmosphere for incident bodies in this range is 12.4 million kg; this is made up of 871,000 individual bodies. In total 24,000-86,000 meteorites with masses larger than 1 kg are being retrieved by the earth's surface. Their total mass amounts 8-9.4 million kg, corresponding to 1.57-1.84 10^{-4} kg ha^{-1} a^{-1}.

TABLE 4.1 The number of meteorites above a certain mass retrieved by the earth's surface[b] as predicted by Hughes (1992)

Mass[a]	5 cm surface layer loss	10 cm surface layer loss
$10^{8.5}$	2	2
10^{8}	8	7
$10^{7.5}$	24	22
10^{7}	74	64
$10^{6.5}$	219	177
10^{6}	626	465
$10^{5.5}$	1716	1141
10^{5}	4454	2576
$10^{4.5}$	10767	5271
10^{4}	23867	9690
$10^{3.5}$	47864	15964
10^{3}	86131	23695

[a] Only incident objects with masses between 10^3 and 10^9 g are considered. It is assumed that from these incident objects a surface layer of 5-10 cm is lost during passage through the atmosphere.

[b] The earth has a surface area of $5.11*10^8$ km^2.

The assumption of Hughes (1992) that the ablation of incoming objects with masses smaller than 1 kg (i.e. smaller than approximately 9 cm diameter) is complete, most probably does not hold true. Lindner and Welten (1994), for example, found that more than 90 % of the meteorites collected on Antartica have masses smaller than 100g. As a general rule, ReVelle (1979) mentions ten times as many fall meteorites with masses between 10^n and 10^{n+1} g as there are with masses between 10^{n+1} and 10^{n+2} g.

Whipple (1950, 1951) found especially for micrometeoroid particles with masses smaller than 10^{-9} g (i.e. smaller than approximately 0.001 cm diameter), the surface area to mass ratio such that the heat produced on entry (by friction with the atmosphere) is radiated away more efficiently than it is generated. In this way these particles are retarded and then floated to the earth's surface essentially unablated. An estimate of the total mass of such particles annually retrieved by the earth's surface was made from stratospheric measurements with cosmic dust collectors. Their total mass was estimated at 20 million kg, corresponding to 3.91 10^{-4} kg ha^{-1} a^{-1} (Priem, personal communication). Micrometeoroid particles are also regularly observed in collectors. Their total mass was estimated at 20 million kg, corresponding to 3.91 10^{-4} kg ha^{-1} a^{-1} (Priem, personal communication). Micrometeoroid particles are also regularly observed in sediments in the central parts of the oceans (Pannekoek, 1976). The diameter of these particles is generally found to be smaller than 0.01 cm.

The chemical composition of meteorites depends on their origin. The vast majority of the meteorites that have been collected from the surface of the earth have asteroidal parents. Fewer than about 1% have been produced by cratering events on the surfaces of, for example, the moon or Mars. Usually three different kind of meteorites are distinguished on the basis of their iron content: *iron meteorites* with an iron content of more than 90%, *stone-iron meteorites* (approximately 50% iron) and *stone meteorites* with an iron content of less than 10%. The stone fraction of meteorites usually consists of iron and magnesium silicates. Stone meteorites may be seperated in *chondrites* which can be recognised by very small non-Earth like spherical shaped coagulations of silicates, and *achondrites* which do not contain such coagulations and hold only a very small portion of iron (Lindner and Welten, 1994).

Micrometeoroid particles found in sediments in the central parts of the ocean consist mainly of nickel-iron combinations with a crust of magnetite (Fe_3O_4), silicates like olivines ($(Mg,Fe)_2SiO_4$) and pyroxenes ($(Na,Ca,Fe,Mg,Al)_2(Si,Al)_2O6$) and micro-tectites (mainly consisting of SiO_2 and Al_2O_3) (Pannekoek, 1976). Tectites most probably represent molten parts from the moon's surface, which were thrown into space after the impact of large meteorites (Von Koenigswald, 1964).

Deposition of compounds due to meteorites may thus be significant for iron, nickel, silicium and aluminium. Deposition of micrometeoroid particles will thereby be of importance for the whole earth, while large meteorites will have a relatively large impact on only a few 'hot spots'. If we assume a mean iron content of 50%, the deposition of iron through micrometeoroid particles can be calculated to amount to 2 x 10^{-4} kg ha^{-1} a^{-1}. Van Breemen *et al.* (1988) measured 0.78-1.29 kg ha^{-1} a^{-1} of iron in throughfall in an oak-birch forest stand in the central part of the Netherlands, indicating the contribution of micrometeoroid particles (2 x 10^{-4}) to the total iron flux to the forest floor to be insignificant. Main sources of iron in throughfall include soil particles and aerosols emitted from the metallurgical industry. Probably the very black coarse particles sometimes seen in precipitation and throughfall samples/filters can be regarded as representing micrometeoroid particles.

Assuming a mean nickel content of 25%, the deposition of nickel through micrometeoroid particles can be calculated to amount to 10^{-4} kg ha^{-1} a^{-1}. The mean nickel deposition in the Netherlands was estimated 0.3-1.4 10^{-2} kg ha^{-1} yr^{-1} (Van Jaarsveld and Onderdelinden, 1986), suggesting a few per cent contribution of micrometeoroid particles to the total nickel deposition. The main sources of nickel in the Dutch atmosphere will be the combustion of fossil fuel and nickel-containing aerosols emitted from the metallurgical industry (Van

Jaarsveld, personal communication). The contribution of micrometeoroid particles to the total nickel deposition will be considerably larger in non-polluted areas.

No deposition estimates are available for silicium and aluminium but it may be expected that the contribution of micrometeoroid particles to the total deposition of silicium and aluminium is insignificant. The main sources of these components in the atmosphere will be blown-up soil dust and, for aluminium, also aerosol emissions from the metallurgical industry. Moreover, their respective levels in micrometeoroid particles is relatively low.

Despite the large meteorite deposition velocities, it can be concluded that meteorite input to the surface is insignificant for pollutants related to acidification. Although the input of metals can be significant, meteorite deposition is still much lower compared to other inputs.

4.2 SURFACE RESISTANCE PARAMETRISATIONS

Introduction

The surface exchange parametrisation of acidifying pollutants is based on the resistance analogy outlining the aerodynamic resistance R_a, the quasi-laminar layer resistance R_b and the surface resistance R_c (Chapter 3) These parameterisations are derived for use in regional- and local-scale deposition models (Chapter 5). The R_c parameterisation for different gases presented here are based on existing literature (see e.g. previous sections), conclusions from a Workshop on deposition held in Göteborg in November 1992 and a Workshop held in Aveiro in May 1993, and some results of recent dry deposition measurements (e.g. section 7.3).

4.2.1 SURFACE RESISTANCE PARAMETERISATION FOR GASES

Values for R_c can be obtained from theoretical considerations based on, for example, solubility and equilibrium calculations in combination with simulations of vegetation specific processes, such as accumulation; transfer processes through stomata, mesophyll and cuticles; absorption, etc. (Baldocchi *et al.,* 1987; Wesely, 1989). Many theoretical approaches are, however, hard to validate using measurements because of the complexity of the processes involved. R_c values presented in the literature are primarily based on measurements of V_d and on chamber studies. By determining R_a and R_b from the meteorological measurements, R_c can be calculated as the residual resistance using Eqn. 3.3. Values for R_c can then be related to surface conditions, time of day, etc., yielding parameterisations. Unfortunately, measurements using existing techniques are still neither accurate nor complete enough to obtain R_c values under most conditions. Furthermore, R_c is specific for a given combination of pollutant, type of vegetation and surface conditions; also, measurements are available for only a limited number of combinations. The R_c parameterisations must be based on routinely available data i.e., ambient temperature, relative humidity, global radiation, wind speed, land-use class, type of soil and vegetation (Van Pul *et al.*, 1992; Erisman *et al.*, 1994).

Equation (4.3) shows a resistance diagram for the transport of gases to various types of surfaces. R_c is a function of the canopy stomatal resistance, R_{stom}, and mesophyll resistance R_m; the canopy cuticle or external leaf resistance, R_{ext}; the soil resistance, R_{soil} and the in-canopy resistance, R_{inc}, as well as the resistance to surface waters or moorland pools, R_{wat}. In turn, these resistances are affected by leaf area, stomatal physiology, soil pH, and presence and chemistry of liquid drops and films. The stomatal resistance, leaf surface resistance and soil resistance act in parallel:

$$\begin{aligned} &\text{vegetative surface:} && R_c = [\frac{1}{R_{stom}+R_m} + \frac{1}{R_{inc}+R_{soil}} + \frac{1}{R_{ext}}]^{-1} \\ &\text{water surfaces:} && R_c = R_{wat} \\ &\text{bare soil:} && R_c = R_{soil} \end{aligned} \qquad [4.3]$$

Stomatal and mesophyll resistance
Most gases enter plants through the stomata. As gas molecules enter the leaf, deposition occurs as molecules react with the moist cells in the substomatal cavity and the mesophyll. Several conclusions can be drawn on environmental effects and inter-specific differences in pollutant deposition based on known stomatal physiology. Stomatal resistance decreases hyperbolically with increasing light and increases linearly with increasing vapour pressure deficits (Jarvis, 1976). Soil water deficits cause stomata to close after some threshold deficit level is exceeded. Low and high temperatures cause stomatal closure; stomatal opening is optimal at a vegetation-specific temperature. Leaf age, nutrition and adaptation are other factors affecting stomatal resistance (Jarvis, 1976). Elevated exposure to SO_2 causes stomata to close, whereas exposure to both O_3 and NH_3 may increase stomatal opening (Dueck, CABO, the Netherlands, personal communication). Stomatal resistance is different for different types of vegetation. Values of R_{stom} under ideal conditions during daytime are between 30 and 300 s m^{-1} for a range of herbaceous annuals and woody perennials (Fowler, 1985; Baldocchi *et al.*, 1987).

The stomatal resistance can be calculated using a scheme described by Baldocchi *et al.* (1987). This scheme is outlined in Erisman *et al.* (1994). Modelling the stomatal resistance in this manner is only possible if enough information is available. This might be a problem for the water potential and for the leaf area index (*LAI*). For the regions where such data are not available, the parameterisation for the stomatal resistance given by Wesely (1989) may be used. This parameterisation is derived from the method used by Baldocchi *et al.* (1987) and only needs data for global radiation Q and surface temperature T:

$$R_{stom} = R_i\{1+[\frac{200}{Q+0.1}]^2\}\{\frac{400}{T_s(40-T_s)}\} \qquad [4.4]$$

Values for R_i can be obtained from a look-up table for different land-use categories and seasons as listed in Table 4.2 (adopted from Wesely, 1989). This general framework for the bulk stomatal resistance can be used to describe stomatal uptake for each gas by correcting the R_{stom} using the ratio of the diffusion coefficient of the gas involved D_x to that of water D_{H2O} and adding the mesophyll resistance:

$$R_{stom,x} = R_{stom} \frac{D_{H_2O}}{D_x} + R_m \qquad [4.5]$$

The mesophyll resistances for different gases are in accordance with the literature (Voldner *et al.*, 1986 and Wesely, 1989) assumed to be zero.

TABLE 4.2 Internal resistance, R_i, to be used for estimating the stomatal resistance for different seasons and land-use types using Eqn. (4.4), with entities of 9999 indicating no air—surface exchange via that resistance pathway (Adopted from Wesely, 1989)

Land-use type: Seasonal category:	1	2	3	4	5	6	7	8	9	10	11
Mid-summer with lush vegetation	9999	60	120	70	130	100	9999	9999	80	100	150
Autumn with unharvested cropland	9999	9999	9999	9999	250	500	9999	9999	9999	9999	9999
Late autumn after frost, no snow	9999	9999	9999	9999	250	500	9999	9999	9999	9999	9999
Winter, snow on ground and subfreezing	9999	9999	9999	9999	400	800	9999	9999	9999	9999	9999
Transitional spring with partially green short annuals	9999	120	240	140	250	190	9999	9999	160	200	300

(1) Urban land, (2) Agricultural land, (3) Range land, (4) Deciduous forest, (5) Coniferous forest, (6) Mixed forest including wetland, (7) Water, both salt and fresh, (8) Barren land, mostly desert, (9) Non-forested wetland, (10) Mixed agricultural and range land, and (11) Rocky open areas with low-growing shrubs.

External leaf uptake

Many studies have shown that the external leaf surface can act as an effective sink, especially for soluble gases at wet surfaces (Hicks *et al.,* 1989; Fowler *et al.,* 1991; Erisman *et al.*, 1993a; b). Under some conditions the external leaf sink can be much larger than the stomatal uptake. When R_{ext} is negligible, R_c in Eqn.4.3 automatically becomes negligible, diminishing the effect of the other resistances in this equation. The external leaf resistance for individual gases will be discussed in the following sections.

SO_2

Deposition velocities measured using the enclosure technique in a pine stand in central Sweden showed that during dry conditions the external deposition of SO_2 could be as large as stomatal uptake (Richter and Granat, 1993). The canopy cuticle resistance is much larger than the canopy stomatal resistance; $R_{cuticle}$ ranges from 3000 to 40,000 s m^{-1} (Van Hove, 1989). However, the surface resistance is observed to decrease as relative humidity increases (Van Hove, 1989; Garsed, 1985; Erisman *et al.*, 1993a; Erisman and Wyers, 1993; Draaijers and Erisman, 1993). This might indicate that the cuticle resistance is lowered with increasing humidity (Van Hove, 1989) or that the surface becomes moist with increasing humidity, e.g. through deliquescence of salts at the external leaf surface. When the cuticle is wetted, or affected by pre-deposited particles or gases, SO_2 deposition to the surface also occurs via absorption and chemical oxidation reactions with the surface.

SO_2 dry deposition is enhanced over wet surfaces (Garland and Branson, 1977; Fowler and Unsworth, 1979; Fowler, 1985; Vermetten *et al.*, 1992; Erisman *et al.*, 1993a, 1993c; Erisman and Wyers, 1993). The involved reactions and the possibility of co-deposition with NH_3 are described in section 4.1.1. Erisman *et al* (1993b) derived a R_{ext} parameterisation for wet surfaces (due to precipitation and an increase in relative humidity) of heather plants (see section 7.1):

$$\begin{array}{lll} \text{during or just after precipitation:} & R_{ext} = 0\ s\ m^{-1} & \\ \text{in all other cases:} & R_{ext} = 25000\ EXP[-0.0693\ rh]\ s\ m^{-1}\ \text{ at } rh < 81.3\% & [4.6] \\ & R_{ext} = 0.58\ 10^{12}\ EXP[-0.278\ rh]\ s\ m^{-1}\ \text{ at } rh > 81.3\% & \end{array}$$

where *rh* is the relative humidity. Equation (4.6) is applied to air temperatures above -1 °C. Below this temperature it is assumed that surface uptake decreases and R_{ext} is set at 200 ($-1 < T < -5$ °C) or 500 ($T < -5$ °C) s m^{-1}. R_{ext} will be zero for some hours after precipitation has stopped. The number of hours will vary with the season and depend on environmental conditions. Drying of vegetation is approximated to take two hours during daytime in summer and four hours in winter. During night-time vegetation is expected to be dry after four hours in summer and after eight hours in winter (Erisman *et al.*, 1993a).

Where rain chemistry will not allow for SO_2 uptake, R_{ext} will be significantly different from zero, depending on the extent that rain is saturated with S(IV), on the pH of rain water and on the plant neutralisation capacity. This parameterisation is derived and tested for Dutch environmental conditions in areas with an annual average NH_3 concentration approximately equal to that of SO_2. For conditions where the neutralisation ability of plants or of NH_3 is not sufficient, this parameterisation will probably yield underestimates of R_c. Erisman and Wyers (1993) have presented a table with average R_c values observed under different conditions (Table 4.3). Values were obtained for heathland, but are expected to be representative for other extensively managed low vegetation. This table also shows the influence of R_c under conditions where one gas was in excess of the other in the atmosphere.

TABLE 4.3 Average R_c values for SO_2 and NH_3 observed under different conditions; negative values denote emissions (Erisman and Wyers, 1993)

Condition	R_c SO_2 (s m^{-1})	Remark	R_c NH_3 (s m^{-1})	Remark
Dry (rh<60)				
Low[a] NH_3/SO_2	500 (day) 1000 (night)	function of stomatal behaviour	-500 (day) 1000 (night)	emission/ deposition
High[a] NH_3/SO_2	500 (day) 1000 (night)	function of stomatal behaviour	1000(day) 1000 (night)	
Humid, no rain or fog				
Low[a] NH_3/SO_2	50	function of rh and T	0	
High[a] NH_3/SO_2	0	*rh* > 80%	< 100	increasing to 200 with large excess
Wet, rain				
Low[a] NH_3/SO_2	5 0	function of water layer pH, with much rain: 0	0	
High[a] NH_3/SO_2	0		< 100	function of water layer pH, with much rain: 0
Wet, fog				
Low[a] NH_3/SO_2	100 - 500	low pH	0	
High[a] NH_3/SO_2	0		200 - 800	high pH
$T < 0$ C	200		200	

[a] Low NH_3/SO_2 molar ratio means below 1, high ratio means above 3.

NH_3

While most other pollutant gases are consistently deposited, NH_3 is both emitted from and deposited to land and water surfaces. For semi-natural vegetation, fluxes are usually directed to the surface, whereas fluxes are directed away from the surface above agricultural grassland treated with manure. For arable cropland, fluxes may be bi-directional, depending on atmospheric conditions and the stage in the cropping cycle (Sutton, 1990). Nitrogen metabolism has been shown to produce NH_3 and as a result there is a compensation point (Farquhar *et al.*, 1980) at which deposition might change into emission when ambient concentrations fall below the compensation concentration and vice versa. In this case $c(z_2)$ in Eqn. 3.1 is different from zero.

To describe NH_3 exchange it is necessary to consider natural and managed vegetation separately. For managed vegetation the compensation point approach seems to be the most promising for use in models. However, the current state of knowledge is insufficient to define canopy resistance terms or compensation points reliable over different surface types and under different environmental conditions relevant to model parameterisation (Lövblad *et al.*, 1993). Furthermore, the compensation point is expected to be a function of many (undefined) factors and not a constant value. There are also some difficulties in using the compensation point approach, since it defines emission independent of gridded emission inventories. It was therefore recommended to base the deposition of NH_3 on resistance formulation to reflect the systematic variations with meteorological conditions and vegetation or receptor characteristics (Lövblad *et al.*, 1993). There are only a few measurements available on surface exchange of NH_3 above different types of vegetation. On the basis of the limited number of data it is not possible to separate the surface resistance into several subresistances. The external leaf resistance is therefore described as matching observed R_c values, taking into account stomatal uptake or emission (see 'External leaf uptake') and in-canopy transport (see 'In-canopy transport').

Ammonia generally deposits rapidly to semi-natural (unfertilised) ecosystems and forests. Results show R_c values mostly in the range of 0-50 s m^{-1} (Duyzer *et al.*, 1987; 1992; Sutton *et al.*, 1992; Erisman *et al.*, 1993b). There is a clear effect of canopy wetness and relative humidity on R_c values (Erisman and Wyers, 1993). Under very dry, warm conditions (*rh* < 60%, T > 15 °C) deposition to the leaf surface may saturate, so that exchange is limited to uptake through stomata, even allowing for the possibility of emission at low ambient concentrations. In this context, a larger R_c may be appropriate (~ 50 s m^{-1}). The influence of co-deposition with acidic species is addressed in the section on SO_2 (Table 4.3). R_c values for managed vegetation are given in Table 4.4.

TABLE 4.4 R_{ext} for NH_3 (s m^{-1}) over different vegetation categories in Europe, negative values for R_{ext} denote emission for estimating a net upward flux

Land-use category	Day		Night	
	Dry	Wet	Dry	Wet
Pasture during grazing: summer:	-1000	-1000	1000	1000
winter:	50	20	100	20
Crops and ungrazed pasture: summer:	$-R_{stom}$	50	200	50
winter:	$-R_{stom}$	100	300	100
Semi-natural ecosystems and forests (see also Table 4.3 for excess NH_3 over SO_2)	-500	0	1000	0

Winter conditions: T> -1 °C, otherwise R_{ext} =200 s m^{-1} (-1 < T < -5 °C) or R_{ext} =500 s m^{-1} (T < -5 °C)

NOx

A very small stomatal uptake might be observed for NO at ambient concentrations. Fluxes are, however, very low and uptake is therefore neglected (Wesely *et al.,* 1989; Lövblad and Erisman, 1992). R_{ext} is set at 9999 s m^{-1}.

Uptake of NO_2 seems to be under stomatal control with no internal resistance. At a few sites, a mesophyllic resistance has been observed at concentrations of about 1 ppbv. It is uncertain whether this effect is relevant to other sites (receptors). External uptake of NO_2 is negligible (e.g. Fowler *et al.*, 1991). R_{ext} is set at 9999 s m^{-1}.

HNOx, HCl, PAN

Data on HNO_2 deposition are lacking. On the basis of chemical properties one would expect the same behaviour as for SO_2, i.e. mainly stomatal-controlled uptake under dry conditions and efficient uptake to wet surfaces. R_{ext} is assumed to equal that of SO_2.

The difficulty of measuring nitric acid and hydrochloric acid concentrations at ambient levels has limited the number of flux measurements for these gases. Recent investigations, however, consistently show that for vegetative surfaces these gases deposit rapidly, with negligible surface resistances (Huebert and Robert, 1985; Erisman *et al.*, 1988; Meixner *et al.*, 1988; 1990; Meyers *et al.,* 1991; Harrison *et al.,* 1989; Dollard *et al.,* 1986, 1990). Deposition of HNO_3 and HCl seems to be limited by the aerodynamic resistance only. For these gases the surface resistance is found to be negligible. R_{ext} is set at 0 s m^{-1}.

Very little is known about the dry deposition of peroxyacetylnitrate, PAN. The limited number of PAN deposition measurements above various low vegetation types indicate a low uptake rate, with surface resistances in the order of 500-1000 s m^{-1} (Dollard *et al.*, 1990). The deposition velocity showed dependence on the pH of the surface, with lower pH values leading to lower deposition velocities than for surfaces with higher pH values. R_{ext} is set at 9999 s m^{-1}.

O_3

Ozone is a very strong oxidiser and as such it is destroyed rapidly at various surfaces. The uptake of ozone by vegetation is mainly via the stomata (Rich *et al.*, 1970; Turner *et al.*, 1974). So the uptake can be modelled by parameterising the transpiration of the vegetation. The resistance of the remaining plant parts (the cuticle) to ozone is found in experiments to be larger than 1000 s m^{-1} (Baldocchi *et al.,* 1987; Meyers and Baldocchi, 1988). Ozone is destroyed slowly at a wetted surface due to low water solubility. R_{ext} is set at 1000 s m^{-1}.

In-canopy transport

Deposition to canopies involves deposition to both vegetation and soil. Early studies assumed that deposition to soils under vegetation was relatively small (5 - 10% of the total flux; Fowler, 1978). Recent work shows that a substantial amount of material can be deposited to the soil below vegetation. For maize crops about 20-50% of the total O_3 flux was found to be deposited to the soil below the canopy (Leuning *et al.*, 1979; Wesely, 1978). Meyers and Baldocchi (1992) report that 20 to 30% of SO_2 depositing on a deciduous forest in wintertime is received at the forest floor. This substantial transfer occurs because large-scale intermittent eddies are able to penetrate through the vegetation and transport material to the soil. Differentiation of deposition to the canopy and to the soil is difficult to measure. Furthermore, it may be variable both in time and for different canopies. The in-canopy aerodynamic resistance R_{inc} is modelled tentatively according to data from Van Pul and Jacobs (1993):

$$R_{inc} = \frac{b\,LAI\,h}{u_*} \qquad [4.7]$$

where LAI is the one-sided leaf area index, h the vegetation height and b an empirical constant taken as 14 m^{-1}. In winter, when deciduous trees are leafless, LAI is set at one. In this way the exchange caused by penetration of gusts is accounted for in a very straightforward way. The results obtained with Eqn. (4.7) are in reasonable agreement with those estimated by Wesely (1989). The resistance to uptake at the soil under the canopy R_{soil} is modelled similarly to the soil resistance to bare soils (section 4.2.1). This will probably underestimate uptake to surfaces under forests (partly) covered with vegetation.

Deposition to soil and water surfaces

SO_2

Deposition of SO_2 to soil decreases at a soil pH below 4 and increases with relative humidity (Garland, 1977; Payrissat and Beilke, 1975). When surface temperatures fall below zero or the surface is covered with snow, R_c values increase up to 200-500 s m^{-1} (Voldner *et al.*, 1986; Erisman and Wyers, 1993). The deposition of SO_2 to snow-covered surfaces depends on pH, snow temperature and probably the amount of SO_2 already scavenged by the snow pack (Caddle *et al.*, 1985; Valdez *et al.*, 1987; Hicks *et al.*, 1989). Onderdelinden *et al.* (1984) and Erisman *et al.* (1993b) found the following relationships for snow-covered surfaces:

$$\begin{aligned} R_{snow} &= 500\ s\,m^{-1} \text{ at } T < -1\ ^oC \\ R_{snow} &= 70\,(2 - T)\ s\,m^{-1} \text{ at } 1 < T \leq -1\ ^oC \end{aligned} \qquad [4.8]$$

NO_x

For NO at ambient concentrations, emission from soils is observed more frequently than deposition. This emission, the result of microbial activity in the soil, is dependent on soil temperature, water content and ambient concentrations of NO (Hicks *et al.*, 1989). This has been observed from grassland, agricultural land and forest soils. Wesely *et al.* (1989) concluded that at their measuring site (moist, unsaturated soil overgrown with grass at soil temperatures of 15 ^{o}C), emission fluxes are probably most important during daytime. Similar conclusions were obtained from the Halvergate experiment by Fowler *et al.* (1991) and Duyzer *et al.* (1990). Emissions are to be expected at locations with low ambient NO and NO_2 concentrations (< 5 ppb). Average NO_2 concentrations are higher in most of Europe. The surface resistance for NO_2 to soil surfaces was found to be about 1000-2000 s m^{-1}. If the soil is covered by snow, the resistance will be even higher (Table 4.5). Resistances of NO_2 to water surfaces are also expected to be high due to the low solubility of this gas.

NH_3

Deposition of NH_3 to soil, snow and water surfaces is similar to that of SO_2; only the pH dependence is different (Table 4.5). Resistance's to unfertilised moist soils will be very small provided that the soil pH is below 7. Fertilised soils, or soils with a high ammonium content will show emission fluxes, depending on the ambient concentration of NH_3. Resistances to water surfaces will be negligible if the water pH is below 7. Resistances to snow will be similar to that of SO_2 at pH<7. Resistance's will increase rapidly above a pH of 7.

HNOx, HCl, PAN

No measurements exist for PAN and HNO_2. Resistances for PAN are expected to be high (see section 4.2.1.2), whereas resistance's for HNO_2 are assumed to follow those of SO_2. Resistances to water surfaces (pH>2) and soils for HNO_3 and HCl are assumed to be negligible. A surface resistance for HNO_3 and HCl to snow surfaces at temperatures below -5 ^{o}C is expected (Johansson and Granat, 1986).

O_3

Ozone is destroyed slowly at a wetted surface or free water due to its low water solubility. The surface resistance to ozone deduced from measurements above water and snow is about 1000-2000 s m^{-1} (Galbally and Roy, 1980; Wesely *et al.*, 1981). The soil resistance to ozone is largely dependent on the type of soil and the soil water content. This water content dependency is due to the low water solubility of ozone and the reduced effective surface at which ozone can be destructed due to the presence of water films around the soil particles. The soil resistance is typically 100 s m^{-1} under dry soil conditions (Turner *et al.*, 1973; Galbally and Roy, 1980). This value increases typically up to 500 s m^{-1} at a waterlogged stage of the soil (20-30% water content) (Turner *et al.*, 1973; Galbally and Roy, 1980; Van Pul, 1992).

R_{snow} and R_{wat} values for different gases are summarised in Table 4.5.

TABLE 4.5 R_c values for soil surfaces, snow-covered surfaces and water surfaces (negative values denote emission)

Gas	Soil surfaces		Water surfaces	pH	Snow-covered surfaces	Temperature (°C)
	Wet	Dry				
SO_2/HNO_2	0	1000	0	>4	$70(2-T)$	$1<T<-1$
	500	R_{ext} (Eq. 9)	500	<4	500	$T<-1$
NH_3	250	-500	500	>8	$70(2-T)$	$1<T<-1$
	0	50	0	<8	500	$T<-1$
NO	-1000	-1000	2000	-	2000	-
NO_2/PAN	2000	1000	2000	-	2000	-
HNO_3/HCl	0	0	0	>2	0	$T>-5$
					100	$T<-5$
O_3	500	100	2000	-	2000	-

4.2.2 PARTICLES

The resistance analogy is not used for particles. Most knowledge on deposition processes and deposition rates of particles has been obtained from studies in wind tunnels (Chamberlain, 1966; Sehmel, 1980). The deposition velocity depends strongly on the particle diameter and surface characteristics (Davidson and Wu, 1989; Ruigrok and Davidson, 1993).

For submicron particles, the transport through the boundary layer is more or less the same as for gases. However, transport of particles through the quasi-laminar layer can differ. For particles with a diameter < 0.1 μm, deposition is controlled by diffusion, whereas deposition of particles with a diameter > 10 μm is more controlled by sedimentation. Deposition of particles with a diameter between 0.1 and 1 μm is determined by the rates of impaction and interception and depends heavily on the turbulence intensity. Deposition velocity for particles with a diameter in this range can be obtained from parameterisations on $u*$, for low vegetation according to Wesely *et al.* (1985):

$$\begin{aligned} V_d &= \frac{u_*}{500} & L>0 \\ V_d &= \frac{u_*}{500}\left[1+\left(\frac{300}{-L}\right)^{\frac{2}{3}}\right] & L<0 \end{aligned} \qquad [4.9]$$

Slinn (1982) proposes using a simplification of his model for forests by splitting V_d in a turbulent contribution and a surface deposition velocity, the latter being dependent on the collection efficiency of the surface and thus surface properties:

$$V_d = [V_{dt}^{-1} + V_{ds}^{-1}]^{-1}, \qquad [4.10]$$

where the surface deposition velocity is given as $V_{ds} = E\, u_*^2/u_h$, with u_h the wind speed at canopy height; E is the collection efficiency and V_{dt} is the turbulent contribution, represented by the inverse of the aerodynamic resistance: $R_a(z=50)^{-1}$. The collection efficiency, E, is different for different size classes as different processes become important. E is determined by parametrisation of modelled E values for Speulder forest based on data such as u_*, z_0, d, u_{50}, rh, surface wetness, etc. (Ruigrok *et al.*, 1994). A description of the experiments and model results are extensively described in section 7.3. The following relationships were found.

The general form for V_d at 50 m high is:

$$V_d = \frac{1}{\dfrac{1}{V_{ds}} + Ra(50)} + V_s \qquad [4.11]$$

where V_s is the deposition velocity due to sedimentation, Vds can be estimated from:

$$V_{ds} = \frac{u_*^{\;2}}{u_h} E \qquad [4.12]$$

where u_h is the wind speed at canopy height. Relations for E voor different components and conditions are given in Table 4.6. These were derived from model calculations and multiple regression analysis.

TABLE 4.6 Parametrisations of E values for different components and conditions

	Wet surface		Dry surface	
Compound	$rh \leq 80\%$	$rh > 80\%$	$rh \leq 80\%$	$rh > 80\%$
NH_4^+	$0.066u_*^{0.41}$	$0.066u_*^{0.41}[1+0.37EXP\left(\frac{rh-80}{20}\right)]$	$0.05u_*^{0.23}$	$0.05u_*^{0.23}[1+0.18EXP\left(\frac{rh-80}{20}\right)]$
SO_4^{2-}	$0.08u_*^{0.45}$	$0.08u_*^{0.45}[1+0.37EXP\left(\frac{rh-80}{20}\right)]$	$0.05u_*^{0.28}$	$0.05u_*^{0.28}[1+0.18EXP\left(\frac{rh-80}{20}\right)]$
NO_3^-	$0.10u_*^{0.43}$	$0.10u_*^{0.43}[1+0.37EXP\left(\frac{rh-80}{20}\right)]$	$0.063u_*^{0.25}$	$0.063u_*^{0.25}[1+0.18EXP\left(\frac{rh-80}{20}\right)]$
Na^+, Ca^{2+}, Mg^{2+}	$0.679u_*^{0.56}$	$0.679u_*^{0.56}[1+0.37EXP\left(\frac{rh-80}{20}\right)]$	$0.14u_*^{0.12}$	$0.14u_*^{0.12}[1-0.09EXP\left(\frac{rh-80}{20}\right)]$

For the large particles, represented by Na in Table 4.5 and for low vegetation in Eqn. 4.9, the sedimentation velocity has to be added:

$$V_s = 0.0067\ ms^{-1} \qquad \text{rh} \le 80\%$$

$$V_s = 0.0067 EXP\left(\frac{0.0066rh}{1.058 - rh}\right) \text{m s}^{-1}\ \text{rh} > 80\% \qquad [4.13]$$

The data for Na^+ in Table 4.6 are those also representative for K^+ if the outcome is halved, because of the smaller MMD.

4.2.3 SYNTHESIS

This section gives a short overview of the most important resistances for each component. In Table 4.7, at the end, examples of surface resistances obtained with the parameterisations presented here will be given for three different pollution climates. A short discussion on uncertainties will end this section.

SO_2

The deposition of SO_2 on vegetation has been shown to be regulated mainly by stomatal resistance and the presence of surface water on the foliage. The stomatal uptake can be modelled satisfactory. However, an understanding of the variations of surface resistance with surface wetness chemistry is limited. It is assumed that when the surface is wet, deposition of SO_2 is regulated by external leaf uptake. At low SO_2 concentrations, the buffering capacities of vegetation leaves are probably sufficient to maintain low R_c values. At high SO_2 concentrations other neutralising components, such as NH_3, might become important. The surface wetness may be provided by increased relative humidity, dew, guttation, rain or fog, and cloud deposition.

Deposition of SO_2 to soil decreases at a soil pH below 4, and increases with relative humidity. When surface temperatures fall below zero or the surface is covered with snow, R_c values increase up to values of 200 - 500 s m^{-1}.

NO_x

NO is not taken into account here as a depositing pollutant. Deposition of NO_2 is mainly regulated by stomata. The deposition to external leaf surfaces, water surfaces and soils is one order of magnitude smaller.

NH_3

NH_3 is emitted from fertilised soils and from pasture during grazing. In addition, emission takes place from crops, ungrazed pasture and semi-natural vegetation under dry, warm conditions during daytime at low ambient concentrations. In other cases NH_3 is mainly deposited. Deposition in these cases is regulated by stomatal uptake and by deposition to external leaf surfaces. R_c values for semi-natural vegetation and forests are low (in the range of 0-50 s m^{-1}) and dependent on surface wetness.

HNOx, HCl, PAN

PAN deposition is slow with an overall surface resistance of 500-1000 s m^{-1}. HNO_2 is treated like SO_2 until more information becomes available. Thus, uptake of HNO_2 is regulated by stomata and external leaf surfaces when the surface becomes moist. HNO_3 and HCl deposit efficiently to all surfaces with negligible R_c values. Only at low temperatures with a surface covered with snow does R_c increase up to 50-100 s m^{-1}.

O_3

The uptake of ozone by vegetation is mainly via the stomata. The resistance of the remaining plant parts (the cuticle) to ozone is found to be larger than 1000 s m^{-1}. Ozone is destroyed slowly at a wetted surface or free water due to its low water solubility. The surface resistance to ozone deduced from measurements above water and snow are about 1000-2000 s m^{-1}. The soil resistance to ozone is largely dependent on the type of soil and the soil water content. The soil resistance is typically 100 s m^{-1} under dry soil conditions. This value increases typically up to 500 s m^{-1} at a waterlogged stage of the soil (20-30% water content).

TABLE 4.7 Surface resistances for different gases during daytime under different pollution climates.

	Moist (rain or *rh*>90%), moderate temperature		Winter, snow covered surface		Dry, warm summer (*rh*<60%), well watered soil	
	Coniferous forest	Grassland	Coniferous forest	Grassland	Coniferous forest	Grassland
R_{stom}	200	60	400	-	150	50
SO_2	$0^{\#}$	0	500	500	300	100
NH_3	$0^{\#}$	0	500	500	-500^{*}	-500
NO_2	320	100	640	1000	240	80
HNO_2	$0^{\#}$ (?)	0 (?)	500	500	300	100
HNO_3	$0^{\#}$	0	10	50	$0^{\#}$	0
HCl	$0^{\#}$	0	10	50	$0^{\#}$	0
PAN	500	500	1000	1000	500	500
O_3	320	100	640	1000	240	80

* negative values denote emission.

\# R_c values are set to 1 s m^{-1} to avoid unrealistically high deposition velocities at low values of R_a and R_b values.

Uncertainties

There are several sources of uncertainty associated with the proposed parameterisations. The main uncertainty arises from the fact that a highly variable and complex process (dry deposition) is captured in a simple scheme. Secondly there are far too little data which can be used for validation. Indications of uncertainty ranges can be obtained from comparison with micrometeorological measurements (Padro *et al.*, 1991; 1992; Wesely and Lesht, 1989; Erisman, 1992; 1994), balance studies using long-range transport models (e.g. van Jaarsveld, 1989; 1990; Erisman, 1993a) or from comparison with throughfall measurements (Ivens *et al.*, 1988; Draaijers and Erisman, 1993; Erisman, 1993b). The uncertainty in the proposed parameterisations was usually found to be large (>40%).

A few important uncertainty sources will be mentioned briefly. In estimating yearly average fluxes for areas or specific sites using the proposed parameterisation, a constant flux layer is assumed through which the resistance analogy can be applied. However, in many situations this assumption is not valid because of advection, nearby sources, chemical reactions, very stable conditions, complex terrain and roughness transition zones. This can lead to large underestimates and overestimates of fluxes. For gases which can react very fast under ambient conditions (e.g. NO, NO_2 and O_3, Duyzer, 1992; Kramm *et al.*, 1993), the influence of reactions can be very large. Emissions might be of importance for gases with many scattered ground level sources (NH_3 and NO/NO_2). If area average fluxes are estimated, there is much uncertainty in the way area average R_c and z_0 values are derived (Van Pul *et al.,* 1993). For many land-use categories, i.e. for cities, seas, and many types of vegetation and soils, the parameterisation is incomplete. The parameterisation of particle deposition velocities for forests is only based on experiments performed at the Speulder forest. Whether the parameterisation is applicable to other forests remains, up to now, unsure.