CHAPTER 3 DEPOSITION PROCESSES AND MEASUREMENT TECHNIQUES

Introduction

After transport and possible transformations, pollutants eventually deposit on a surface by wet, dry, or cloud/fog water deposition. Wet deposition is the process by which atmospheric pollutants are delivered to the earth's surface by rain, hail or snow. Dry deposition is the process where gases and particles are deposited directly from the atmosphere onto vegetation, soil or other surfaces without the hydrometer as medium. Cloud and fog water deposition is the process where cloud and fog water droplets are directly intercepted by the earth's surface. This deposition process is often referred to as 'occult' deposition. In this chapter, deposition processes will be explained and different measurement techniques described.

3.1 WET DEPOSITION

In this section the short process description will be followed by an overview of measuring methods for wet deposition and possible contamination of samplers. At the end of this section an overview of European chemical precipitation networks, with some details about sampling procedures, sampling equipment and time coverage, will be presented. The results of the network measurements have been used in Chapter 5 to compile a detailed wet deposition map of Europe.

3.1.1 PROCESS DESCRIPTION

Wet scavenging is defined as the natural process by which atmospheric pollutants are attached to and dissolved in cloud and precipitation droplets (or particles), and as a result are delivered to the earth's surface. The amount of compounds thus received per unit of surface area is defined as wet deposition. Figure 3.1 gives an impression of the processes involved.

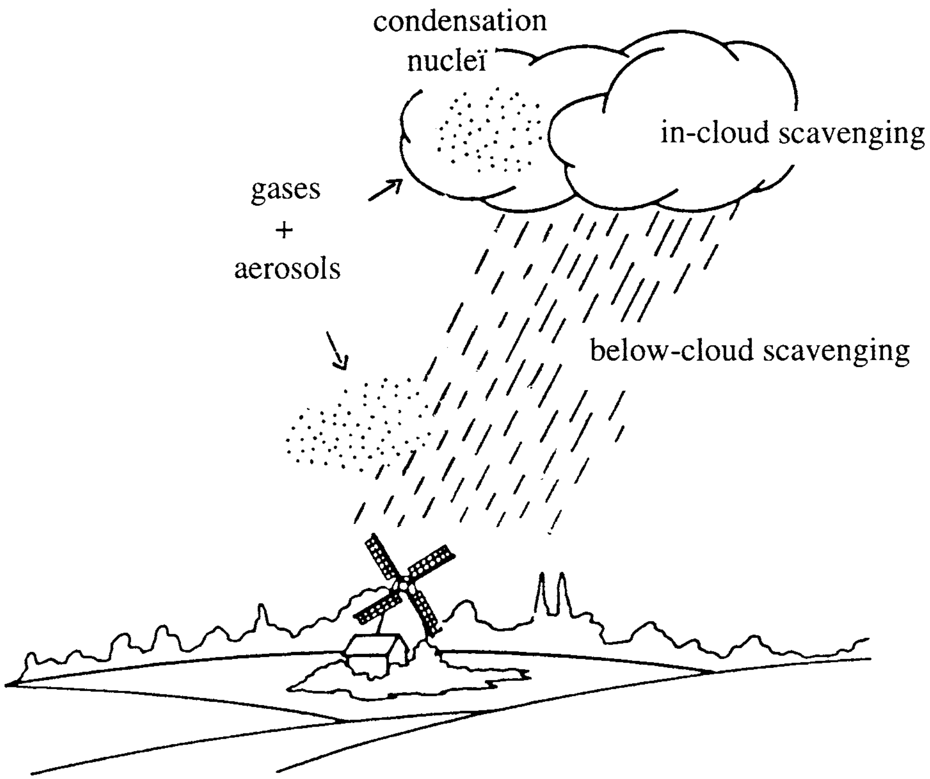

FIGURE 3.1 Wet deposition processes.

If air is cooled, its relative humidity will increase until the air becomes saturated, and droplets will be formed. Particles containing air will form droplets more rapidly, as the particles act as condensation nuclei. Hygroscopic particles form droplets when the humidity reaches a critical level below 100% rh. After these nuclei become droplets, the air continues to cool, water continues to be condensed onto the droplets that are now growing in size, and the concentration of pollutants in these droplets will tend to decrease with dilution. This process of nucleation scavenging of cloud condensation nuclei is the most important particle incorporation mechanism. Another important mechanism is the absorption, dissolution and subsequent chemical reaction of gases in droplets. Other processes contributing to ion enrichment in clouds are diffusional attachment of particles resulting from the diffusion of small particles through the air to the surface of cloud and raindrops, and inertial attachment of particles due to their collision with falling droplets. The in-cloud processes are referred to as *in cloud scavenging* or *rain-out* scavenging (Hov *et al.*, 1987)

During the downward transport of the droplet in the form of rain, snow, cloud ice, hail, etc. to the earth's surface, uptake of gases and/or particles can occur. This process is referred to as *below-cloud scavenging* or *wash-out*. Wash-out is an efficient removal mechanism for soluble gases and aerosols with a diameter larger than 1 μm (Hicks *et al.*, 1989). Wash-out will play an important role when air concentrations of these gases or aerosols below the cloud are much higher than concentrations in the cloud. This will be the case for plumes close to the source or sources at ground level. On the other hand, the reverse process may occur by evaporation of the droplet and re-volatilisation of the pollutant itself. This is the case only for gases in solution in the droplet not undergoing any reaction inhibiting their escape back to the gaseous phase (Hicks *et al.*, 1989).

It has been estimated that the cloud condensation nuclei removal route for aerosols containing SO_4^{2-}, and NO_3^- is responsible for most of the observed SO_4^{2-} and NO_3^- in precipitation (Garland, 1978; Fowler, 1984). The deliquescent nature of these aerosols makes them efficient as cloud condensation nuclei. The other sources are rain-out and wash-out of SO_2 and HNO_3. For NH_4^+ in precipitation, the wash-out of NH_3 will be of more importance, for instance, than for SO_2 in areas with high NH_3 emission found in such countries as the Netherlands, Denmark, Germany and France (Asman, 1992).

The amount of pollutant wet deposition is strongly dependent on the amount of rain and the location of the receptor with respect to sources. Wet deposition patterns depend on the topography (Fowler *et al.* 1991). At high altitudes an enhancement of wet deposition may occur because of increased aerosol scavenging due to so-called seeder-feeder effects (Fowler *et al.*, 1988). Seeder-feeder scavenging results from the incorporation of particles into orographic clouds above hills and the scavenging of the hill cloud droplets by rain droplets falling from a higher level cloud. Such effects are found to be pronounced in northwest Europe and western Scandinavia. Over the central and southern European uplands, where convective processes dominate, the above effect is less important (Fowler *et al.*, 1992; Lövblad and Erisman, 1992). The characteristics of the receptor area do not have much influence on the wet deposition. However, in areas with large roughness elements (like forests or urban areas), the catchment of small droplets could be expected to be possibly more efficient than it would over smooth homogeneous surfaces. This might be due either to increased turbulence or the kinds of scavenging effects associated with forest edges, for example.

3.1.2 MEASURING METHODS

Wet deposition is measured by placing samplers in the open field to collect precipitation. Precipitation is collected in bottles for two weeks or a month; after this the sample is analysed for its chemical composition. Wet deposition is the amount of precipitation multiplied by the concentration of the pollutant. The first measured wet deposition fluxes were reported in the late 19th and early 20th centuries (see section 1.2, for an overview). The first measurements in the Netherlands were made in Utrecht in 1825 (Mulder, 1825), and later in Groningen from 1910 - 1912 and in Hilversum from 1932-1937 (Leeflang, 1938).

Although the measurement of wet deposition seems relatively simple, there are some serious sources of errors (see e.g. Eriksson, 1952; Slanina *et al.*, 1982; Fowler and Cape, 1984; Buijsman and Erisman, 1988; Beier and Rasmussen, 1989). In former days, the most commonly used sampler was the bulk or open sampler, which has no provision to exclude dry deposition during dry periods. Dry deposition of gases and particulate matter may therefore influence the chemical composition of precipitation passing the contaminated funnel (Slanina *et al.*, 1982; Ridder *et al.*, 1984). The use of wet-only samplers, in which the funnel is open to the atmosphere only during precipitation events, is widely recommended. Short exposure periods are also recommended when sample deterioration due to bacterial or chemical action is expected.

Bulk samplers are used in the EMEP network. Wet-only samplers were introduced in the Dutch National Air Quality Monitoring Network after 1988. Before then, bulk samplers were used. Correction factors for the contribution of dry deposition to the funnels of the samplers have been derived from the literature and from parallel measurements with bulk samplers and wet-only samplers (Ridder *et al.*, 1984; Van Leeuwen *et al.*, 1995). Table 3.1 gives these correction factors as the ratio of wet-only and bulk fluxes, averages are given for the Netherlands obtained from Ridder *et al* (1984), whereas ranges are given for several comparison studies in Europe taken from Van Leeuwen *et al.* (1995). Values presented by Ridder *et al.* (1984) correspond well with those found in other experiments in the Netherlands comparing wet-only and bulk precipitation (Ruijgrok *et al.*, 1989; Slanina *et al.*, 1990). Slightly different values have been found by Grennfelt *et al.* (1985) in Sweden, Georgii *et al.* (1986) and Spranger (1992) in Germany, Clark and Lambert (1987) in the United Kingdom and Mosello *et al.* (1988) in Italy. Observed differences in wet-only/bulk ratios may be attributed to the distance to local sources and to the collecting efficiency of the samplers. Differences between bulk and wet-only samplers are different for different components. Ratios are lowest for measurements made near the coast, for components which deposit in the funnels as large particles (Na^+, Ca^{2+} and Mg^{2+}). Further land inward concentrations of these large particles quickly diminish and ratios become higher. For components which originate from both aerosols and gases (SO_4^{2-}, NO_3^- and NH_4^+) no clear relationships are found between air concentration and wet-only/bulk ratios. This is because several factors play a role, i.e. distance to sources, particle size, solubility of gases, the time the funnel stays wet, co-deposition, turbulence characteristics at the site, etc.

TABLE 3.1 Ratios of wet deposition fluxes obtained by wet-only and bulk samplers according to Ridder *et al.* (1984) and Van Leeuwen *et al.* (1995)

Component	Wet-only/bulk ratio (Ridder *et al.*, 1984)	Range of wet-only/bulk ratio (Van Leeuwen *et al.*, 1995)
NH_4^+	0.75	0.70 - 1.25
SO_4^{2-}	0.75	0.66 - 0.96
NO_3^-	0.85	0.80 - 0.79
Ca^{2+}	0.45	0.36 - 0.81
Na^+	0.75	0.37 - 0.93

Aspects which might influence the composition of the precipitation sample (Buijsman and Erisman, 1988) include:

- transformation of components under the influence of light or enhanced temperature,
- storage conditions or time elapsed before analysis of the samples,
- bird droppings, insects, etc.

Other errors may be introduced by analytical methods and handling of the samples. Usually, these error sources were minimised by using light protected bottles, by minimising the sampling (bi-weekly) and storage periods, and by quality assurance through standardisation in sampling handling and analysis (Schaug *et al.*, 1989; Buijsman, 1989).

Amounts of precipitation show large spatial variation on short time scales. The density of stations used to monitor precipitation for hydrological purposes (e.g. about 300 in the Netherlands, KNMI, 1979) is a clear reflection of this fact. Large variations during the year can be observed. When averaged over the year, precipitation amounts show much smaller spatial variations. When estimating the spatial variation in wet deposition it is recommended to use the precipitation measurements for hydrological purposes for the amount of precipitation, combined with the chemical composition measurements from the air quality monitoring networks (see also discussion in Chapter 6).

At the moment there are several national and international precipitation monitoring networks (EMEP, CaPMoN, NADP). Table 3.2 gives an overview of the networks in Europe with some information about sampling procedures. Most of the data measured in these networks are used in Chapter 5 to describe the wet deposition in Europe in 1989.

TABLE 3.2 Precipitation monitoring networks in Europe

Country/ region	Equipement	Sampling period	Number of sites	Period	References
Europe	bulk/wet-only	varies	90	1978 →	e.g. EMEP (1994)
eastern Alps	bulk/wet-only	varies	107	varies	Kovar and Puxbaum (1992)
Austria	wet-only	unknown	17	1983 →	questionnaire[a]
Belgium	wet-only	1 month	12	1984 →	IHE (1991)
Bulgaria	bulk	1 month	1	1989 →	questionnaire[a]
Czech Republic	bulk	varies	7	unknown	questionnaire[a]
Estonia	bulk	1 month	6	unknown	Kallaste et al (1992)
Finland	bulk	1 month	61	1971-1991	Leinonen and Junte (1991), Jarvinen and Vanni (1990)
France	wet-only	1 month	21	unknown	Codeville *et al* (1993), Dambrine (1992), Ulrich and Williot (1993)
Georgia	bulk	unknown	1	unknown	questionnaire[a]
Germany	bulk/wet-only	varies	202	varies	Klockow and Wintermeyer (1990), Bruggeman (1993)
Greece	wet-only	unknown	2	1987 →	questionnaire[a]
Hungary	wet-only	1 month	9	1978 →	questionnaire[a]
Ireland	bulk	unknown	17	unknown	Bowman (1991)
Italy	wet-only	unknown	122	unknown	Mosello and Morselli (1992)
Latvia	bulk	unknown	7	1985 →	questionnaire[a]
Moldava	bulk	unknown	7	1989 →	questionnaire[a]
the Netherlands	wet-only	1 month	14	1978-1993	RIVM (1993)
Norway	bulk	1 month	38	1971 →	SFT (1992)
Poland	bulk	unknown	5	1978 →	questionnaire[a]
Portugal	wet-only	unknown	6	1979 →	INMG (1989)
Russian Federation	bulk	1 month	10	1958 →	questionnaire[a]
Slovak Republic	bulk	unknown	7	1978 →	questionnaire[a]
Slovene	bulk	1 month	26	unknown	Hrcek (1992)
Sweden	bulk/wet-only	1 month	34	1975 →	Granat (1989), Persson *et al* (1993)
Switzerland	wet-only	unknown	4	unknown	NABEL (1992)
United Kingdom	bulk	1 month	58	1986 →	Campbell *et al* (1992), UKRAR (1990)
Ukraine	bulk	unknown	5	unknown	questionnaire[a]
Yugoslavia	bulk	unknown	5	unknown	questionnaire[a]

[a] A questionnaire was send to all authorities responsible for environmental monitoring programmes to obtain wet deposition data (see Van Leeuwen *et al.*, 1995 for more details)

3.2 DRY DEPOSITION

This section describes in short the general process, followed by the most important processes and then an overview of measuring methods for dry deposition. At the end of this section an overview of European dry deposition measurements is given, with a few details on sampling procedures, sampling equipment and time coverage. The results of these measurements will be used in the next chapters.

3.2.1 PROCESS DESCRIPTION

The dry deposition of gases and particles from the atmosphere to a receptor surface is governed by the concentration in air and by turbulent transport processes in the boundary layer, as well as by the chemical and physical nature of the depositing species and the capability of the surface to capture or absorb gases and particles. The process is illustrated in Figure 3.2.

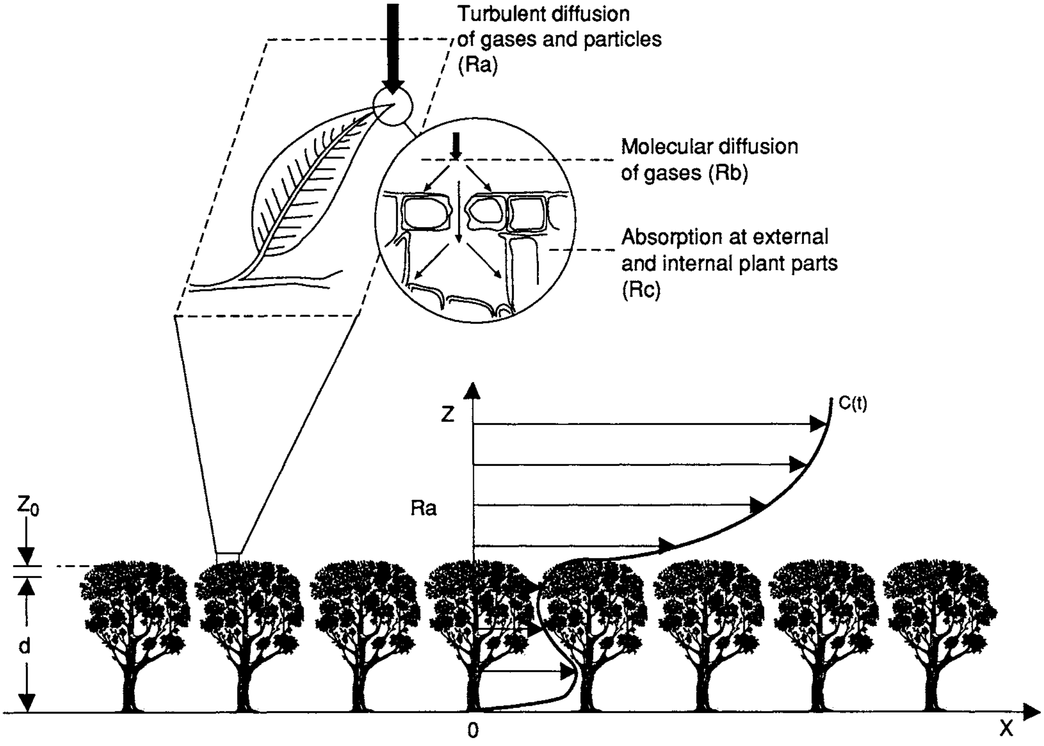

FIGURE 3.2 The dry deposition process.

The transport of gases and particles from the atmosphere to close to the receptor surface is governed by the level of atmospheric turbulence, generated by both wind shear and buoyancy. The higher the level of atmospheric turbulence, the more efficiently gases and particles are transported to a given receptor surface. Given a constant sink strength for a particular pollutant of interest, the concentration gradients above the receptor will vary according to the intensity of atmospheric turbulence. A well-mixed unstable boundary layer leads to relatively small concentration gradients and to low resistance to vertical transport. For a boundary layer with near neutral stability, buoyancy has essentially no influence on the level of turbulence. Stable stratified boundary layers are associated with much larger gradients, because vertical motions are suppressed.

In the vicinity of sources, the dry deposition is determined primarily by the configuration of the sources, the type of sources and the pollutant's mixing in the atmosphere. For high level sources, the deposition near to the source is small and increases with downwind distance from the source until it reaches a maximum and decreases again. For ground-level sources, dry deposition takes place directly next to the source, where concentrations are highest, decreasing downwind. At some distance, the influence of the sources on the concentration gradient is diminished. At this point, the pollutant is mixed throughout the boundary layer and the concentration gradient is determined primarily by the dry deposition process. If the receptor can act both as a source and sink, the shape of the gradient will be determined by the extent of the source or sink flux. The gradient will then show the shape of the net emission or net deposition flux.

Generally, two layers can be distinguished in the boundary layer for transport of pollutants to the receptor: the fully turbulent layer and the quasi-laminar layer. The quasi-laminar layer is introduced to quantify the way in which pollutant transfer differs from momentum transfer in the immediate vicinity of the surface (Hicks *et al.*, 1987). In this layer, the transport to the receptor surface is dominated by molecular diffusion. Once at the surface, the chemical, biological and physical nature of the surface determines the capture or absorbency of the gases and particles. For gases, surface uptake is frequently controlled by the ability of the surface to absorb the specific chemical species. For reactive trace gases, such as HNO_3, molecules are collected immediately upon contact with all surfaces (Huebert and Robert, 1985; Dollard *et al.*, 1986). Less reactive, but soluble, gases, such as SO_2 and NH_3, tend to be taken up through stomata or through the leaf cuticle (Garland, 1977; Schwela, 1977; Fowler, 1984; Duyzer *et al.*, 1987; Grennfelt, 1987). These gases can also be absorbed in water layers at the leaf surface, or at the soil (Fowler *et al.*, 1991; Hicks *et al.*, 1989). The chemical composition of the surface is important for snow, ice and water (Hicks *et al.*, 1989; see also Chapter 4).

Together with wet deposition, particle dry deposition is responsible for the atmospheric load to ecosystems of such compounds as sulphate, nitrate, chloride and ammonium, and base cations such as calcium, magnesium, sodium and potassium. Deposition of particles containing SO_4, NO_3, Cl and NH_4 contributes to the potential acidification and eutrophication (nitrogen components) of ecosystems. Compared to gaseous deposition of acidifying compounds onto low vegetation, particle deposition velocities and fluxes are usually found to be small. However, it is believed that the dry deposition velocity of small particles, and with this the fluxes, is currently underestimated for very rough surfaces like forests (Wiman *et al.*, 1990; Erisman, 1993a). Erisman *et al.* (1994) found that deposition of aerosols to the Speulder forest contributed 20 - 40% to the total dry deposition of SOx and total nitrogen, respectively. Current knowledge is not sufficient to give an adequate assessment of the dry deposition of particulate sulphur and nitrogen in the Netherlands and Europe.

For submicron particles, the process of dry deposition is even more complex and the list of potentially determining factors is much longer. Mechanisms of deposition are diffusion, interception, impaction, gravitational settling and phoretic mechanisms (Slinn, 1982). Almost no particles are able to diffuse through stomatal openings (Slinn, 1982). Transfer through the quasi-laminar layer close to the surface presents a considerable restriction on the deposition of 0.1 - 1.0 μm particles. Uptake of particles by surfaces is thus largely controlled by microstructures and turbulence intensity.

3.2.2 FRAMEWORKS FOR THE DESCRIPTION OF ATMOSPHERE - SURFACE EXCHANGE

The dry deposition flux of gases and particles from the atmosphere to a receptor surface is governed by: 1) the concentration in air and turbulent transport processes in the boundary layer; 2) the chemical and physical nature of the depositing species and 3) by the efficiency of the surface to capture or absorb gases and particles.

Resistance analogy for trace gases

A common framework is provided to describe the exchange of a range of gases with very different chemical and physical properties. In this framework, three stages in dry deposition to the surface are distinguished. The most widely used is that of the resistance analogy (Thom, 1975, Chamberlain, 1966; Garland, 1977; Fowler, 1978). The analogy of trace gas fluxes to a current in an electrical circuit is described by Ohm's law (resistance = potential difference/current). Assuming one-dimensional transfer over a homogeneous surface, the total resistance R_t is defined by:

$$R_t(z) = \frac{c(z_1) - c(z_2)}{F} \qquad [3.1]$$

where z_1 and z_2 are two heights above the surface. The flux F is taken as negative when directed towards the surface. The absorbing surface is often assumed to have zero surface concentration; the flux is therefore viewed as being linearly dependent on atmospheric concentration. In this case, if z_2 is considered to be the notional height of the absorbing surface (z_0+d), the total resistance from a height z to the surface becomes:

$$R_t(z) = -\frac{c(z)}{F} = \frac{1}{V_d} \qquad [3.2]$$

In effect, (z-d) is the height above the aerodynamic ground level. In Figure 3.2, turbulent boundary layer flow over a receptor surface of uniform height h behaves as if the vertically distributed elements of the receptor were located at a certain distance d from the ground. The bulk effectiveness as a momentum absorber is specified by z_0, while the parameter d can be considered to indicate the mean level at which momentum is absorbed by the individual elements of the receptor surface. This concept is valid for the momentum flux, as the wind speed decreases to zero at the receptor surface. For mass transport, however, this does not hold, as surface concentrations might not be zero for gases (or particles). However, the concept of z_0 is used for mass transport (Thom, 1975). Values for roughness length, z_0, and displacement height, d, can be obtained from look-up tables, e.g. those proposed by Davenport (1960), revised by Wieringa (1981) or Voldner *et al.* (1986).

The inverse of the total resistance is the deposition velocity (V_d). The latter, providing a measure of conductivity of the atmosphere - surface combination for the gas, is widely used to parametrise gas uptake at the ground surface (Wesely and Hicks, 1977; Hicks *et al.*, 1989; Fowler, 1984; Fowler *et al.*, 1989; Wesely, 1989). V_d is the inverse of three resistances:

$$V_d(z) = \frac{1}{R_a(z) + R_b + R_c} \qquad [3.3]$$

The three resistances represent the three stages of transport: the aerodynamic resistance R_a for the turbulent layer, the laminar layer resistance R_b for the quasi-laminar layer, and the surface or canopy resistance R_c for the receptor itself. The atmospheric resistance to transport of gases across the constant flux layer is assumed to be similar to that of heat (see e.g. Hicks *et al.*, 1989 for an overview). R_a depends mainly on the local atmospheric turbulence intensities. Turbulence may be generated through mechanical forces of friction with the underlying surface (forced convection) or through surface heating (buoyancy or free convection). Unless wind speeds are very low, free convection is small compared to mechanical turbulence. In the case of rough (uneven) surfaces like forest canopies, the aerodynamic characteristics of the canopy and the wind speed control the generation of turbulence to a large extent and regulate vertical mixing of pollutant-laden air layers in the vicinity of the canopy. In this study R_a is approximated following the procedures used by Garland (1978):

$$R_a(z) = \frac{1}{\kappa u_*}[\ln(\frac{z-d}{z_0}) - \psi_h(\frac{z-d}{L}) + \psi_h(\frac{z_0}{L})] \qquad [3.4]$$

in which $u*$ is the friction velocity, L the Monin Obukhov length and $\psi[(z-d)/L]$ the integrated stability function for heat. These can be estimated using procedures described in Beljaars and Holtslag (1990) which will be described in section 3.2.3. The second atmospheric resistance component R_b is associated with transfer through the quasi-laminar layer in contact with the surface. R_b quantifies the way in which pollutant or heat transfer differs from momentum transfer in the immediate vicinity of the surface. R_b depends on both turbulence characteristics and the molecular diffusion of the gas considered (Thom, 1975; Garrat and Hicks, 1973; Erisman, 1992). Transport of a pollutant gas through the quasi-laminar layer by molecular diffusion depends on the thickness of the layer, the concentration gradient over the layer, and on a diffusion constant which, in turn, depends on the radius of the gas molecule considered and on temperature. Although a great deal is known about quasi-laminar layer transport to artificial surfaces, the complexity of vegetation limits the accuracy with which the magnitude of this transport mechanism can be estimated in the field. The thickness of the quasi-laminar boundary layer, for example, is found to depend on size, shape and orientation of the receptor surface, and on wind speed. Real-life events like 'fluttering' of leaves make it extremely difficult to model quasi-laminar boundary layer transport accurately (Chamberlain, 1975). The quasi-laminar layer resistance R_b can be approximated by the formulation presented by Hicks *et al.* (1987):

$$R_b = \frac{2}{\kappa u_*}(\frac{Sc}{\mathrm{Pr}})^{\frac{2}{3}} \qquad [3.5]$$

where Sc and Pr are the Schmidt and Prandtl numbers, respectively. Pr is 0.72 and Sc is defined as: $Sc = \upsilon/D_i$, with υ the kinematic viscosity of air (0.15 $cm^2\ s^{-1}$) and D_i the molecular diffusivity of pollutant i, and thus component specific. The Schmidt and Prandtl number correction in Eqn. 3.5 is listed in Table 3.3 for different gases. Usually R_b values are of less importance than values of R_a and R_c, so Eqn. 3.5 can be considered as appropriate. Over very rough surfaces such as forest canopies, however, R_a may approach small values and the accuracy of the R_b estimate becomes important. This is especially the case for trace gases with a small or zero surface resistance.

The surface or canopy resistance, R_c, is the most difficult of the three resistances to describe. R_c values can be obtained from theoretical considerations based, for instance, on 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 by measurements because of the complexity of the processes involved. R_c values presented in the literature are primarily based on measurements of V_d. 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 of R_c can then be related to surface conditions, time of day, etc., yielding parametrisations (see Chapter 4). Unfortunately, measurements by 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 component, type of vegetation and surface conditions; measurements are available for only a limited number of combinations. Bache (1986) demonstrated that in cases of low surface resistances, the R_c values obtained using the resistance analogy are likely to contain aerodynamic factors. In such conditions, the surface and aerodynamic components cannot be fully separated.

TABLE 3.3 Schmidt and Prandtl number correction in Eqn. 6 for several gases (Hicks *et al.*, 1987)

Component	$(Sc/Pr)^{2/3}$
SO_2	1.44
NO_2	1.30
HNO_3	1.44
H_2O	0.96
O_3	1.30

Particles

The resistance analogy is not used for particles. Transport from the free atmosphere to the receptor surface is more-or-less similar to gas transport. However, transport processes through the quasi-laminar layer differ considerably between gases and particles. Whereas gases are transported primarily through molecular diffusion, particle transport and deposition basically take place through sedimentation, interception, impaction and/or Brownian diffusion (Figure 3.3). *Sedimentation* under the influence of gravity is especially significant for receptor surfaces with horizontally oriented components. *Interception* occurs if particles moving in the mean air motion pass sufficiently close to an obstacle to collide with it. Like interception, *impaction* occurs when there are changes in the direction of airflow, but unlike interception a particle subject to impaction leaves the air streamline and crosses the laminar boundary layer with inertial energy imparted from the mean airflow. The driving force for *Brownian diffusion* transport is the random thermal energy of molecules. Transport is a function of atmospheric conditions, characteristics of the depositing contaminant and the magnitude of the concentration gradient over the quasi-laminar layer (Davidson and Wu, 1990).

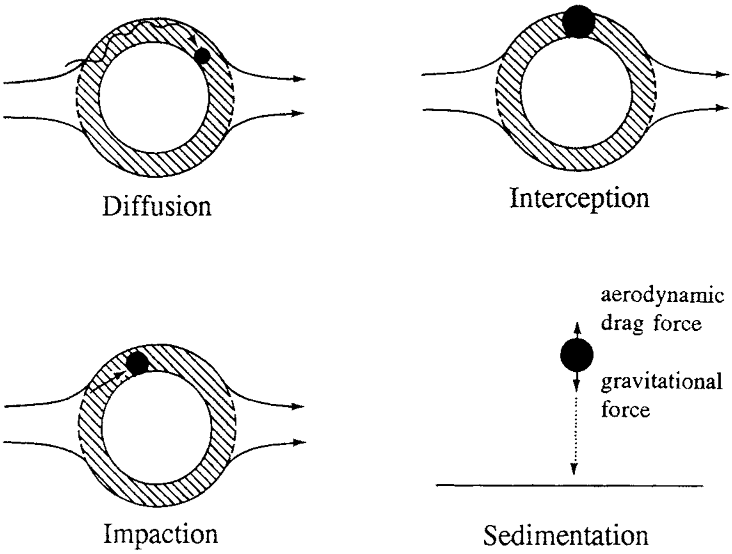

FIGURE 3.3 Schematic representation of four transport mechanisms for particles through the quasi-laminar boundary layer (adopted from Davidson and Wu, 1990). Shaded areas indicate the laminar boundary layer.

Which type of transport process dominates is largely controlled by the size distribution of the particles (Chamberlain, 1966; Sehmel, 1980; Slinn, 1982). In Figure 3.4, a calculated deposition velocity of particles is plotted against their mass median diameter (*MMD*) for an Eucalyptus forest canopy. This figure clearly demonstrates that deposition of particles with *MMD*s near 0.1-1.0 μm is the least efficient. Deposition of particles falling in this *MMD* range is very much affected by turbulent transfer from the free atmosphere to the receptor surface and, therefore, depends heavily on wind speed and the aerodynamic roughness of the receptor surface (Slinn, 1982). Deposition velocity for particles to low vegetation with a diameter in this range can be obtained from parametrisations on u_* (Eqn. 4.9, Wesely *et al.*, 1989; Erisman *et al.*, 1994). Particles with *MMD*s smaller than 0.1 μm deposit through Brownian diffusion, which efficiency is inversely related to particle size (Fowler, 1980). For particles with *MMD*s between 1 and 10 μm, the deposition velocity increases sharply with the *MMD*. These particles deposit mainly through impaction and/or interception. Here we see relatively efficient removal processes, which depend to a large extent on wind speed and aerodynamic characteristics of the receptor surface. This determines transport from the free atmosphere to the receptor surface. The processes also depend on in-canopy wind speeds controlling inertial impaction through quasi-laminar boundary layers (Thorne *et al.*, 1982). For particles with *MMD*s larger than 10 μm, turbulent transfer is less important and sedimentation is the main deposition process. Bounce-off or blow-off effects may be important for such large particles (Slinn, 1982; Wu *et al.*, 1992). Sticky or hairy surfaces limit these effects considerably.

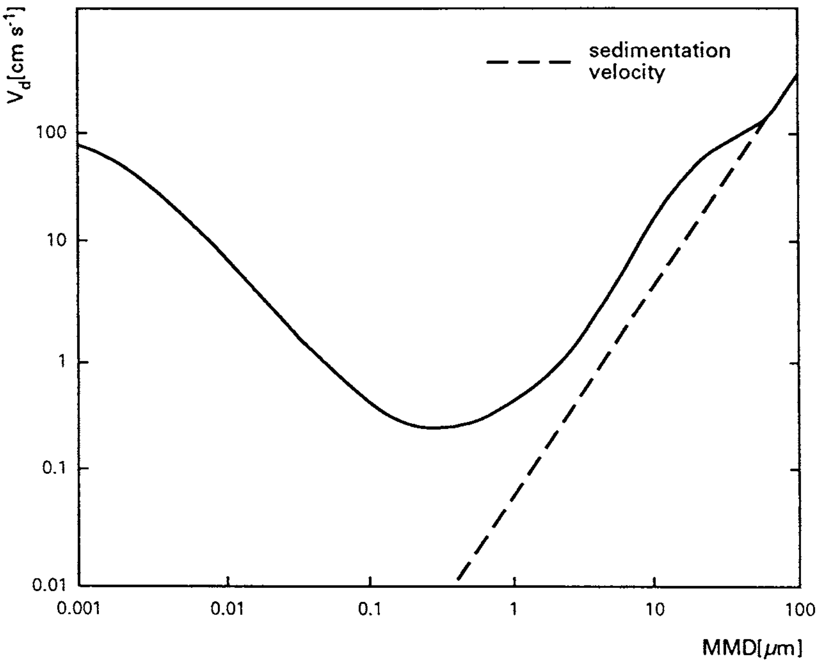

FIGURE 3.4 Relationship between the deposition velocity of particles and their mass median diameter for an Eucalyptus forest canopy (adopted from Slinn, 1982). The dashed line indicates the sedimentation velocity (i.e. where the deposition rate is a linear function of the fall velocity of the particles). Canopy height = 27.4 m; friction velocity = 75 cm s^{-1}; roughness length = 1.86 m; zero plain displacement height = 21.6 m; particle density = 1 g cm^{-3}.

3.2.3 MEASURING METHODS FOR DRY DEPOSITION

This section contains a summary of measurement methods, mainly based on existing excellent reviews by Hicks *et al.* (1986, 1989) and Davidson and Wu (1989). The applicability of the different methods will be addressed. An overview and assessment of possibilities for measuring deposition of specific substances is presented in Chapter 4.

Micrometeorological methods for estimating dry deposition

Among the methods for measuring dry deposition, micrometeorological methods are the most suitable for determining the dry deposition of many gases (Fowler and Duyzer, 1989). The flux to the total system may be determined with these methods, and the relationship between air concentrations, meteorology and the flux is directly established. In a flat homogeneous terrain, the flux measured at a sampling point above the surface within the constant flux layer represents the average vertical flux over the upwind fetch. A constant flux layer is required to make sure that the flux measured above the surface is that at the surface. Several micrometeorological measuring methods exist for measuring dry deposition. The flux is derived from measurements of the vertical component of the wind velocity and the gas concentration with the most direct of these methods, the eddy correlation method. With another method, the gradient technique, the flux is derived from measurements of air concentrations at several heights above the receptor surface and from meteorological variables. The principles of the eddy correlation method and gradient technique will be described in this section. Other techniques consist of Bowen ratio approaches, variance and a variety of so-called conditional sampling methods. The latter are not described in this book; information on these techniques can be found in such references as Businger (1986), Hicks *et al.* (1986), Baldocchi *et al.* (1988) or Fowler and Duyzer (1990)

Eddy correlation

The vertical flux density F of an entity is given as

$$F = \overline{\omega\rho} \qquad [3.6]$$

where ω is the vertical wind velocity and ρ the density of the entity. This may be considered as the sum of two components, the product of mean vertical wind speed ω and density ρ, and fluctuations about the means of the same quantities ω' and ρ':

$$F = \overline{\omega}\,\overline{\rho} + \overline{\omega'\rho'} \qquad [3.7]$$

where w' and ρ' are the instantaneous vertical wind velocity and the departure from the mean concentration, respectively (Baldocchi *et al.*, 1988). When ρ represents a pollutant concentration, F is simply the flux. When ρ is the momentum, F represents the momentum flux, more commonly denoted as the stress τ. The sensible heat flux H is represented as

$$H = \rho_a c_p \overline{\omega\,\theta} \qquad [3.8]$$

where ρ_a is the air density, c_p the specific heat of air and θ the potential air temperature. In the constant flux layer, the eddy correlation method provides direct fluxes from measurements of the co-variance of ω and ρ. In order to measure the contribution of all eddies to the flux, fast sensors are necessary. For meteorological quantities such as momentum or sensible heat fluxes this method has proven to give reliable results (Montheith, 1975; Businger, 1986; Baldocchi *et al.*, 1988; Duyzer and Bosveld, 1988; Fowler and Duyzer, 1990).

When conducting an experiment with the eddy correlation technique, the length of the sampling period must be carefully chosen to ensure that the sampling period accounts for the spectrum of eddies that contribute to the transfer processes. Sampling rates in the order of 5 - 10 Hz are normally required for this method over most surfaces when measurements are made from tower-based systems.

The eddy correlation technique provides a direct measurement of the vertical flux for gases and small particles. The requirement for fast responding chemical instruments limits the application of this technique to just a few chemical species. Relatively fast response analysers are available for O_3 and NO_2.

Aerodynamic gradient method

Before the measurements required for the aerodynamic gradient method are described, the basic theory will be summarised. In the turbulent layer, transport of heat, momentum and mass are similar (Thom, 1975). The diffusivity K of a property at any point in a particular fluid medium can be defined as the ratio of the property flux through the medium to its concentration gradient (in the same direction) at that point. The flux towards or away from the surface is found as the product of this gradient and the diffusivity.
For the momentum flux (τ):

$$\tau = K_m(z)\frac{\partial(\rho u)}{\partial z} \qquad [3.9]$$

For sensible heat flux (H):

$$H = K_h(z)\frac{\partial(\rho_a c_p \theta)}{\partial z} \qquad [3.10]$$

For mass flux (F):

$$F = K_c(z)\frac{\partial c}{\partial z} \qquad [3.11]$$

where u is the wind speed, z the vertical distance, c_p the specific heat of air, θ the potential temperature and c the pollutant concentration.
The approximate similarity of:

$$K_m \approx K_h \approx K_c \qquad [3.12]$$

appears to be valid in neutral and stable conditions (Thom, 1975; Droppo, 1985; Zeller, 1990). In unstable conditions, experiments showed that the equality of K_h and K_c with K_m does not hold (Droppo, 1985). K_h and K_c were observed to be similar in these conditions too (Hicks *et al.* 1989; Droppo, 1985; Zeller *et al.*, 1989).

The shearing stress, or momentum flux τ, is defined as the drag force per unit area of a horizontal plane caused by horizontal air motion (Thom, 1975). τ is related to the air density and the effectiveness of vertical turbulent exchange in the air flow over the surface:

$$\tau = \rho_a u_*^2 \qquad [3.13]$$

The 'eddy velocity' or friction velocity associated with the momentum flux is u_*. The term u_* may be defined in terms of gradient theory, such that:

$$u_* = l\frac{\partial u}{\partial z} \qquad [3.14]$$

where l is the mixing length for momentum, or rather the effective eddy size, at level z. The value for l may be given by:

$$l = \frac{\kappa(z-d)}{\phi_m} \qquad [3.15]$$

where κ is the Von Karman constant, established experimentally to be about 0.41 (see discussion in Pasquill and Smith, 1983); ϕ_m is the empirically estimated dimensionless correction for stability effects upon this ratio, while d is the zero displacement height.

The eddy diffusivity K_m may be found from Eqns. 3.9, 3.13, 3.14 and 3.15:

$$K_m = \frac{\kappa(z-d)u_*}{\phi_m} \qquad [3.16]$$

This equation may be used to estimate K_c, given the similarity between K_m, K_h and K_c. For K_c, ϕ_h is used rather than ϕ_m. Thus given the equality of ϕ_h and ϕ_c:

$$K_c = \frac{\kappa(z-d)u_*}{\phi_h} \qquad [3.17]$$

which may be substituted into the mass flux (Eqn. 3.11), yielding:

$$F = \frac{\kappa(z-d)u_*}{\phi_m}\frac{\partial c}{\partial z} \qquad [3.18]$$

u_* is derived from 3.14 and 3.15:

$$u_* = \frac{\kappa(z-d)}{\phi_m}\frac{\partial u}{\partial z} \qquad [3.19]$$

Similarly, the eddy concentration can be defined as:

$$c_* = \frac{\kappa(z-d)}{\phi_h}\frac{\partial c}{\partial z} \qquad [3.20]$$

and thus the mass flux becomes:

$$F = u_* c_* \qquad [3.21]$$

As a result, the flux of a pollutant may be derived from information on the wind profile, the concentration gradient and the effect of stability. The empirical estimation of ϕ_h for different conditions has been the subject of much investigation (Dyer and Hicks, 1970; Pasquill and Smith, 1983). The stability function is a correction for the departure of the neutral profile. Therefore under neutral conditions ϕ_m=ϕ_h=ϕ_c=1. The stability correction is a function of height. Therefore ϕ should be included in the integration of Eqns. (3.19) and (3.20). In the literature, results obtained by Dyer and Hicks (1970) are widely used (e.g. Thom, 1975; Denmead, 1983). Under stable conditions:

$$\phi_m = \phi_h = \phi_c = 1 + 5.2\frac{(z-d)}{L} \qquad [3.22]$$

and unstable conditions, ϕ_h and ϕ_c are represented by the square of ϕ_m:

$$\phi_m^2 = \phi_h = \phi_c = [1 - 16\frac{(z-d)}{L}]^{-0.5} \qquad [3.23]$$

where L is the Monin Obukhov stability length used as stability parameter (L>0: stable; L<0: unstable; $|L|$ -> ∞: neutral), given as:

$$L = \frac{-T\rho_a c_p u_*^3}{\kappa g H} \qquad [3.24]$$

where T is the absolute temperature and g, the acceleration of gravity. The sensible heat flux H can be calculated from the net radiation using the Priestly-Taylor model parameterised (modified by Holtslag and De Bruin, 1988). This modified model was tested using experiments at a meteorological mast at Cabauw in the centre of the Netherlands. The model was used in subroutines for the calculation of H, L and u_* by Beljaars *et al.* (1987).

Integration of (3.19) and (3.20) between the roughness length z_0 and z, yields:

$$u_* = \frac{\kappa u(z)}{\ln(\frac{z-d}{z_0}) - \psi_m(\frac{z-d}{L}) + \psi_m(\frac{z_0}{L})} \qquad [3.25]$$

and:

$$c_* = \frac{\kappa c(z)}{\ln(\frac{z-d}{z_0}) - \psi_h(\frac{z-d}{L}) + \psi_h(\frac{z_0}{L})} \qquad [3.26]$$

where

$$\psi_m(\frac{z-d}{L}) = \psi_h(\frac{z-d}{L}) = -\ 5.2\frac{(z-d)}{L} \qquad [3.27]$$

for stable conditions and,

$$\psi_m(\frac{z-d}{L}) = 2\ln(\frac{1+x}{2}) + \ln(\frac{1+x^2}{2}) - 2\arctan(x) + \frac{\pi}{2}$$

$$\psi_h(\frac{z-d}{L}) = 2\ln(\frac{1+x^2}{2}) \qquad [3.28]$$

$$x = [1 - 16\frac{(z-d)}{L}]^{0.25}$$

for unstable conditions. $\psi_m((z-d)/L)$ is the integrated stability correction for momentum and $\psi_h((z-d)/L)$ is the integrated stability correction for heat.

In this calculation scheme a problem arises in the calculation of L, u_* and H because of the interdependence of these variables. Beljaars *et al.* (1987) derived an iterative calculation scheme for the Dutch situation for day and night-time heat fluxes based on publications by Holtslag and Van Ulden (1983), Van Ulden and Holtslag (1985) and Holtslag and De Bruin (1988). The calculation scheme of Beljaars *et al.* (1987) is used here to estimate these values.

An alternative way of estimating u_* values is by using measurements of the standard deviation for wind direction, instead of the wind profile or eddy correlation. According to Hicks *et al.*, (1987), u_* can be estimated from wind speed measurements and the standard deviation of wind direction σ_θ. Information both on atmospheric stability and surface roughness is contained in σ_θ. Measurements of σ_θ can be used directly as a measure for turbulence. In this method, the value of u_* is estimated directly from u and σ_θ by Hicks *et al.* (1987):

$$u_* = \frac{\sigma_\theta u}{c_v} \qquad [3.29]$$

Here, c_v is a scaling parameter of the standard deviation of the lateral wind fluctuations on u_*. This method for calculating u_* relies heavily on estimates of c_v, of which the values depend on atmospheric stability and the boundary layer height (z_i). The boundary-layer height dependence is the result of a whole variety of large-scale, thermal-like structures in the convective boundary layer. The scaling parameter c_v is independent of height in the surface layer and not heavily affected by terrain irregularities (Beljaars *et al.*, 1983). Various parametrisations of c_v can be found in the literature; a short overview is presented in Erisman *et al.*, (1989A). A c_v value of 2 has been adopted for neutral cases according to Hicks *et al.*, (1987). From the same reference, values of 2 and 3 have been taken for stable and unstable conditions, respectively. These values have been confirmed by experiments performed by Erisman and Duyzer (1991).

An alternative approach for u_* is to first estimate the roughness length of the surroundings from the σ_θ measurements. After that, wind speed measurements at one height are used together with Eqn. 3.25 to estimate u_* values. Values for z_0 are commonly derived from measurements of the wind profile (see e.g. Thom, 1975). Under neutral conditions, where the stability correction is negligible, a linear fit of $ln(z)$ against $u(z)$ can provide information on d and z_0. Empirically, z_0 may be approximated as $0.1h$ (Stull, 1988).

Another way of estimating z_0 values is by using measurements of the standard deviation of wind direction, with σ_θ used by other research groups to estimate atmospheric stability and surface fluxes (Erbrink, 1986,1989; Hicks *et al.*, 1987; Erisman *et al.*, 1990) and roughness lengths (Hanna, 1981; Beljaars, 1988; Erisman and Duyzer, 1991). A value for σ_θ is calculated from wind direction measurements and averaged over several minutes to one hour. In order to minimise the effect of systematic change in wind direction, the total measuring period must be as short as possible. However, to minimise statistical errors, a large averaging time is desirable. Erisman and Duyzer (1991) showed that even at 7-min averages, σ_θ can be seriously influenced by change in wind direction at low wind speeds. Beljaars (1988) suggests using 10-min averages in near neutral conditions at high wind speed (> 4 m s^{-1} at 10 m height) to estimate z_0 values, thus minimising the effect of a change in wind direction at short averaging times.

Following Hanna (1981), z_0 is derived for each wind sector according to:

$$z_0 = zEXP\left[\frac{-\kappa c_v}{\sigma_\theta}\right] \qquad [3.30]$$

Under near neutral stability at $u > 4$ m s^{-1}, c_V values can be assumed to be independent of stability and Eqn. 3.30 can be applied directly (Beljaars, 1988).

Although the aerodynamic gradient method permits longer sampling times (generally at least one hour) and thus a more accurate measurement of a pollutant concentration, the application of the aerodynamic gradient method is limited by the accuracy of chemical instruments. Concentration differences between two levels in the order of 1 - 5% have to be detected. To avoid systematic differences, gradients are often determined with the same sensor.

Concentrations at two or more heights within about 10 m above a horizontally homogeneous surface (low vegetation) are used to evaluate a local gradient that is assumed to be representative of the area of interest. Next to the concentration gradient, measurements are made to estimate K_c (Eqn. 2.18) and the stability corrections to estimate the pollutant flux. These measurements usually comprise wind profile measurements, sonic anemometer measurements, or measurements on wind speed and standard deviation of wind direction at one level. Typical instrumentation for flux gradient measurements is illustrated in Figure 3.5.

Limitations to the micrometeorological methods

Time-average measurements at a point provide an area-integrated average of the exchange rates between the surface and the atmosphere. The measuring height must be well within the constant flux layer and near to the earth's surface (5 - 10 m). This means that usually only local fluxes can be measured (low measuring heights to meet these demands). Extrapolating these fluxes or derived deposition parameters to larger areas is still a great problem because of varying surface properties and roughness characteristics, and accordingly non-homogeneous turbulent behaviour. Fluxes cannot be measured with these methods in a complex terrain or near to sources where there is no constant flux layer. Measurements must be made over a terrain with an upwind fetch over a homogeneous surface large enough to establish a fully developed constant flux layer. In addition to fetch requirements, the development of the constant flux layer requires that no sources or sinks exist in the atmosphere above the surface, and that the concentration of the constituent does not vary significantly with time (Baldocchi *et al.*, 1988; Hicks *et al.*, 1987; Businger, 1986; Erisman *et al.*, 1990). Sources or sinks might be the result of rapid reactions among reactive species between the point of flux measurement and the surface. The influence of reactions has been suggested for NH_3 and acidic gases, such as HNO_3 and HCl (Huebert and Robert, 1985; Erisman *et al.*, 1988; Brost *et al.*, 1988; Allen *et al.*, 1989) and has been demonstrated for the photostationary equilibrium between NO, NO_2 and O_3 (Lenschow, 1982; Duyzer, 1991; Wesely *et al.*, 1989; Kramm, 1989).

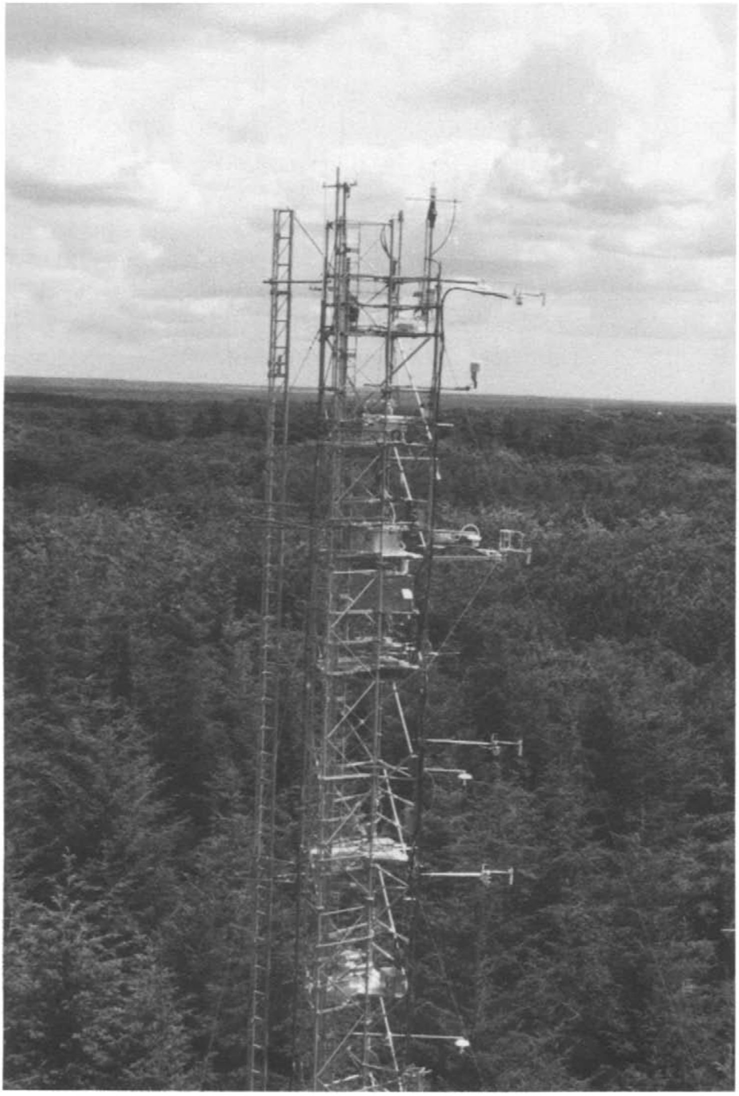

FIGURE 3.5 Illustration of instrumentation used for flux gradient measurements at the Speulder forest.

FIGURE 3.5 (*continued*) Illustration of instrumentation used for flux gradient measurements at the Elspeetsche Veld and throughfall measurements at the Speulder forest.

Surface wash methods to estimate dry deposition

Measurements of dry deposition can also be made by measuring the deposition at the surface itself directly or indirectly (surface accumulation methods). Direct methods comprise the measurement of deposition to natural surfaces using the throughfall method (see below), or to surrogate surfaces such as dustfall buckets, flat plates, petri dishes or other devices intended to approximate natural surfaces. All these methods may be useful for measuring deposition of large particles. Other direct methods include measurements of accumulated material by electron-microscope counting, laboratory studies (e.g. stomatal conductance), and wind-tunnel and chamber studies. Here the discussion is limited to field experiments. While inert surfaces have provided useful data in process level studies (e.g. Davidson *et al.*, 1985), they do not directly simulate vegetation. The direct method with the most potential in this regard is the throughfall method.

Throughfall method

Throughfall has typically been used for quantification of soil loads with nutrients and not for atmospheric deposition estimates. Throughfall refers to anything from the water dripping from canopies and stemflow to water running down tree trunks. By measuring the amount and quality of the rain water passing through a forest canopy, an estimate of the total (i.e. wet + dry + occult) deposition onto this canopy can be made. Water dripping from leaves/needles and branches, and falling through gaps in the canopy is referred to as throughfall, whereas water running down tree trunks is called stemflow. The contribution of stemflow depends on stem density, bark structure and inclination of branches; it is usually only measured if considered significant for the total flux to the forest floor. The difference between throughfall (+ stemflow) flux and open field wet deposition is often called 'net throughfall'. The net throughfall flux of an ion or insoluble element below the canopy to the extent that deposited material is washed from the canopy by rain provides information on the dry deposition.

Using the throughfall method for the estimation of dry deposition has some important advantages over the micrometeorological methods. First of all, it is not restricted to adequate fetch as micrometeorological methods are, and thus is well suited to monitoring deposition in a complex terrain. Secondly, throughfall contains all gases and particles deposited, including coarse particles. Thirdly, the throughfall method allows fairly easy continuous monitoring, and thus provides the opportunity to study deposition processes. Lastly, the throughfall method is less expensive than micrometeorological measurements and relatively easy to implement. For this reason, the throughfall method is well suited for monitoring at a large number of sites.

However, the throughfall method also has several weak points. Most important are the problems associated with canopy exchange processes. If pollutants are irreversibly taken up or leached by the canopy, throughfall deposition estimates will be obscured. Another problem in using the throughfall method is related to the large spatial variability of throughfall fluxes usually observed within forest stands (e.g. Duijsings *et al.*, 1986; Ivens, 1990; Beier *et al.*, 1992b). Experimental devices used for throughfall measurements should reveal this large spatial variability so as to obtain representative deposition estimates. Moreover, litterfall, insects, pollen, bird excrements and dry deposition in the throughfall devices, as well as changes in throughfall chemistry during storage due to biological activity may obscure the deposition estimates. To address these problems, throughfall devices and reservoirs must be cleaned regularly. Slanina *et al.* (1990) tested the chemical stability of throughfall samples and concluded that NO_3^-, NH_4^+, SO_4^{2-} present in throughfall samples stored in opaque bottles stay chemically stable in the field for one full week.

Canopy exchange processes

Throughfall fluxes are found to be influenced by diffusion and ion exchange between the surface water and the underlying apoplast of canopy tissues. Diffusion is found to be the major cause of elevated anionic concentrations in throughfall, while both diffusion and ion exchange contribute to cationic concentrations in throughfall (Schaefer and Reiners, 1990). The rate of canopy exchange depends on tree species and ecological setting. For example, during the growing season deciduous tree species tend to lose more nutrients from the crown foliage through leaching than coniferous tree species. Conifers, however, stay green all year round and continue to lose nutrients throughout the dormant season (Smith, 1981). The age distribution of leaves and soil nutrient status also affect the magnitude of leaching to a large extent. Young immature leaves/needles tend to lose less nutrients compared to older ones (Parker, 1990), and fertilisation is found to enhance canopy leaching considerably (Matzner *et al.*, 1983). Biotic stresses like insect plagues may initiate large canopy leaching. Bobbink *et al.* (1990; 1992) monitored throughfall in a heathland vegetation and observed a marked increase of canopy losses occurring simultaneously with an outbreak of a heather-beetle plague. Furthermore, abiotic stresses like drought and temperature extremes are found to enhance canopy leaching (Tukey and Morgan, 1963). The presence of certain pollutants may also be of importance. Large concentrations of ozone, for example, were found to enhance the permeability of cell membranes in canopy foliage, thereby increasing ion leakage (Evans and Ting, 1973). Moreover, the amount and timing of precipitation is found to be relevant with respect to canopy leaching. Relatively long residence times during drizzle account for relatively high leaching rates compared to short rain periods with large rainfall intensities. Large amounts of rain may deplete leachable pools within the canopy, thereby inhibiting ion leaching (Lovett and Lindberg, 1984). Losses from leachable pools within the canopy are believed to be replenished within 3-4 days after a large storm by increased root uptake or translocation from other parts of the tree (Parker, 1983).

In general the throughfall method provides reasonably good estimates for sulphur, sodium and chloride deposition. Furthermore, the atmospheric deposition of base cations can be estimated using throughfall measurements, provided corrections are made for canopy exchange (see also the results reported in Chapter 6). Nitrogen compounds are found to be retained in the canopy and the throughfall method seems less suitable for estimating atmospheric input. Potentially, part of the deposited inorganic nitrogen retained in the canopy may be converted into organic substances and subsequently leached.

Watershed mass balance method

The outflow from catchments is equal to the sum of wet and dry deposition, weathering release and net change in storage in biomass and soil. By measuring the outflow flux, an estimate for the deposition to the catchment is obtained when the latter two are negligible or can be quantified. Up to now, this approach has been applied successfully to the Lake Gårdsjön area in Sweden (Hultberg and Grennfelt, 1992) and the Hubbard Brook forest ecosystem in the USA (Likens *et al.*, 1990); it has given reliable deposition estimates for S, Na and Cl to whole catchments. The possibility of using this method is limited to those areas where the necessary assumptions are valid. Where the facilities (gauged watersheds with routine stream chemistry monitoring) already exist, it is a simple and cheap method for estimating deposition.

Inferential technique

As an alternative to the direct measuring methods, knowledge on dry deposition processes can be used to infer dry deposition fluxes from basic information on routinely measured air concentrations and meteorological parameters. The flux is inferred as the product of ambient concentration of the chemical of interest and its dry deposition velocity. The dry deposition velocity is derived using a multiple-resistance transfer model (Hicks *et al.,* 1987). The resistance model provides a framework for coupling individual processes, some being surface-dependent or pollutant-dependent. This resistance analogy is described in section 3.2. The quality of results obtained by this method depends on the availability and quality of data, and on the description of the resistances.

Flux estimations on a routine basis using the inferential technique are made in two networks in the USA (Hicks *et al.*, 1991; Clarke *et al.*, 1992). Weekly mean measurements of HNO_3, SO_2, NO_3, SO_4 and NH_4 concentrations in these networks are combined with meteorological parameters to obtain weekly average fluxes (Hicks *et al.*, 1985). This technique has also been applied in studies done in the UK (UK Review Group on Acid Rain, 1990), in Sweden (Lövblad and Erisman, 1992) and in the Netherlands (Erisman *et al.,* 1989; Erisman, 1992; 1993a; Chapter 5) and, recently, also for Europe as a whole (Van Pul *et al.*, 1994; 1995; Chapter 5).

Eder and Dennis (1990) developed an inference technique allowing the estimation of the annual and monthly air concentrations of Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}. The technique is based on the strong correlation between concentrations in precipitation and the surface-level air at 23 stations in Ontario, Canada. The technique is used in Chapter 5 to determine concentrations and subsequently the dry deposition of base cations in the Netherlands and Europe.

Chamber methods

Chamber methods, in which gas uptake by the depositing surface is measured, are used in the laboratory or in the field. In open-top or closed chambers, deposition is studied in relation to the characteristics of the vegetation. Factors thought to affect deposition are carefully controlled and measured. The response of different plant species or plant components can be studied in semi-isolation. The deposition to the surfaces (soil or vegetation) in the chambers can estimated by comparing the in and out flux of the chamber over a certain time interval (e.g. Milne *et al.,* 1979; Taylor *et al.,* 1983; Granat and Johansson, 1983). In addition, cuvette and mini-cuvette studies with branches or single leaves provide insight in fundamental physical, chemical and biological processes related to trace gas exchange (see Murphy and Sigmon, 1989).

3.3 CLOUD AND FOG DEPOSITION AND DEW

3.3.1 PROCESS DESCRIPTION

Vegetation may intercept cloud and fog droplets or directly collect water vapour that forms dew. Hill cloud and lowland fog droplets generally have diameters between 3 and 50 µm, and can be efficiently captured by vegetation (Fowler, 1984; Fowler *et al.*, 1989; Hicks *et al.*, 1989; Fowler *et al.*, 1992). Deposition of such droplets occurs similar to that of coarse particles and thus is only limited by the resistance to aerodynamic transfer (Dollard *et al.*, 1983; Gallagher *et al.*, 1988). As the droplets are rather small, their sedimentation rate is slow, but impaction and interception by foliage, and other obstacles in their path can be effective. Cloud droplets usually contain higher concentrations of pollutants than are found in rain, and cloud water deposition may exceed annual precipitation, especially at high elevation sites (Lovett, 1988). In Europe at altitudes of 400 m above sea level and above, low clouds are present between 500 and 2000 h per year (Fowler *et al.*, 1991). Cloud water deposition might be a significant input mechanism for such regions in Europe. The major limitation for estimating inputs by cloud and fog droplet deposition is the lack of information on cloud and fog water composition, and on liquid water content. In general, concentrations of SO_4^{2-}, NO_3^- and NH_4^+ in cloud and fog droplets are found to be 10-50 times those in precipitation.

3.3.2 MEASURING METHODS

Recently, much research has been conducted on cloud and fog deposition (Fowler *et al.*, 1991; Weathers *et al.*, 1986; Schemenauer, 1986; Mohnen., 1988; Johnson and Lindberg, 1990; Lovett and Kinsman, 1990; Mitchell *et al.*, 1990; Wyers *et al.*, 1995; Vermeulen *et al.*, 1995; Erisman *et al.*, 1994). Several techniques have been applied by which droplet deposition can be separated from wet and dry deposition. Cloud water can be collected by impaction of the droplets on a collection surface (Weathers *et al.*, 1986; Waldman *et al.*, 1982; Mallant and Kos, 1990). Furthermore, estimates of cloud water deposition have been made using throughfall measurements, together with sensors for cloud occurrence and measurements of cloud water amount (Joslin and Wolfe, 1992). Dollard *et al.* (1983) and Gallagher *et al.* (1988) report micrometeorological measurements of cloud water deposition to short vegetation, while Wyers *et al.* (1995) and Vermeulen *et al.* (1994) report similar measurements over the Speulder forest (see also section 7.3). From these studies, it was found that cloud water deposition rates averaged over the droplet size spectrum in these measurements are close to the reciprocal of the aerodynamic resistance for momentum.

The annual input of cloud water in the UK has been determined using annual precipitation chemistry, cloud base and wind statistics, and an average relationship between ionic composition of precipitation and orographic cloud water obtained at one site (Fowler *et al.*, 1991; Weston and Fowler, 1991).

In the Netherlands about 200 nights per year with one or more hours of dew were observed (Römer *et al.*, 1990). Dew is aqueous vapour condensed on cool bodies (vegetation) and therefore clean, containing very low concentrations of pollutants (Van Aalst and Erisman, 1991; Römer *et al.*, 1991). Dew may play an important role in the process of dry deposition by enhancing surface wetness; in this way, surface resistance to soluble gases will be lowered and dry deposition increased. This process is included in dry deposition estimates.

3.4 EVALUATION AND COMPARISON OF DIFFERENT METHODS FOR ESTIMATING DEPOSITION

3.4.1 WET DEPOSITION

Comparisons between wet-only and bulk precipitation fluxes have been made by Grennfelt *et al.* (1985), Georgii *et al.* (1986), Clark and Lambert (1987), Mosello *et al.* (1988), Ridder *et al.* (1984), Ruijgrok *et al.*(1989), Slanina *et al.* (1990); Stedman *et al.* (1990) and Richter and Lindberg (1988). In these studies, bulk precipitation of SO_4^{2-}, NO_3^- and NH_4^+ is found to be between 4 and 34% higher than corresponding wet-only precipitation fluxes (see also Table 3.1). Even larger differences are reported for base cations like Na^+, Ca^{2+}, Mg^{2+} and K^+ (7-75%). Especially coarse particles seem to deposit onto bulk precipitation funnels during dry periods (through sedimentation). The amount of dry deposition onto bulk precipitation funnels is influenced by the distance to local sources, ambient concentrations, wind-shading effects around the funnel, design of sampler, sampling frequency and cleaning protocols.

Intercomparison of wet-only samplers have shown that the results obtained are very sensitive to the type of sensor used for the registration of onset/offset of the precipitation events (Graham *et al.*, 1988).

It used to be thought that bulk samplers could be used to determine the total deposition (wet plus dry and fog deposition). The fog and dry deposition measured with bulk samplers, however, is the fog and dry deposition to the funnels of the samplers and does not have any relation with the fog and dry deposition to ecosystems. The 'extra' deposition is therefore considered as 'contamination' of the wet deposition measured with bulk samplers. Bulk samplers might be useful in specific conditions (high elevation, remote areas). However, wet-only samplers are generally recommended. Sampling procedures need to be designed with great care and sampling locations should be selected to be representative for the area under study (not near sources or obstacles such as fences, trees and buildings). In addition, measures should be taken to preserve the samples if biologically or chemically active species are to be studied; i.e. using light-protected bottles, addition of preservatives, reducing storage temperature or by minimising the storage period in the field.

3.4.2 DRY DEPOSITION

Measurement of dry deposition of different pollutants exhibits different difficulties and no single method can probably be regarded as the 'best' for monitoring. In this section we will summarise the results of comparison studies between different measuring methods applied for sulphur, nitrogen and base cations.

Sulphur

Detailed long-term comparisons between dry deposition estimates from inferential plus deposition plate methods on the one hand, and dry deposition estimates from the throughfall method on the other, were made by Lindberg and Lovett (1992) during the integrated forest study (IFS). Sulphur was found to behave more-or-less conservatively in the canopy. For a large number of sites scattered over the USA, Canada and Europe, minor SO_2 uptake balanced, to some extent, foliar leaching of soil derived sulphate. The estimated total annual deposition of sulphur compounds was found to be within 15% of the measured sulphate fluxes in throughfall plus stemflow in each case (R^2=0.97).

Experimental evidence for canopy uptake of SO_2 was found by Gay and Murphy (1985), but Schaefer and Reiners (1990) and Granat and Hällgren (1992) concluded that essentially all the dry deposited sulphur dioxide retained by the canopy (taken up via the stomata) is eventually extracted out of the apoplast pools (i.e. aqueous layer on the outside of cell membranes) by rain, and appears in throughfall. Furthermore, several radioactive $^{35}SO_4^{2-}$ studies have shown that, in general, less than 4% of the total throughfall flux of sulphate is caused by foliar leaching of soil-derived sulphate. (Garten *et al.*, 1988; Lindberg and Garten, 1989; Cape *et al.*, 1992).

Comparisons between inferential dry deposition estimates on the one hand, and dry deposition estimates from micrometeorological measurements and/or throughfall data on the other, were made by Ivens (1990), Draaijers and Erisman (1993), Lovett *et al.* (1992) and Erisman (1993B). Ivens (1990) compared SO_4^{2-} throughfall fluxes from all over Europe with deposition estimates of SOx from the long-range transport model RAINS (Eliassen and Saltbones, 1983; Alcamo *et al.*, 1987). For coniferous tree species, sulphate throughfall fluxes were found to be significantly higher (on average, 80%) when compared to sulphur deposition estimates from the RAINS model. For deciduous tree species, neither estimate was significantly different.

Erisman (1993B) compared SOx dry deposition estimates using the inferential technique with throughfall measurements of SO_4^{2-} in 24 forest locations in the Netherlands. The two estimates showed large differences, throughfall fluxes being 45% higher than inference estimates. However, variations in time and space were similar. Draaijers and Erisman (1993) made a detailed comparison of net throughfall measurements of sulphate in 30 different forest stands in a small area in the Netherlands (Van Ek and Draaijers, 1991) and sulphur dry deposition estimates from the same receptor-oriented inferential model (Erisman, 1992; 1993A). Similar results were obtained as those by Erisman (1993B). However, by extending the surface resistance parametrisation for SO_2 in the inferential model with results obtained by a field study on co-deposition of NH_3 and SO_2 (Erisman and Wyers, 1993), the difference between both estimates disappeared. Erisman *et al.* (1993B) and Erisman (1992) compared SO_4 throughfall measurements under heathland (Bobbink *et al.*, 1992) with results of the annual average flux of SO_2 measured on heathland using the dry deposition monitoring system for SO_2 (sulphate particle deposition was estimated by inference). They found good agreement between the two estimates. For the Hubbard Brook forest ecosystem, Lovett *et al.* (1992) reported higher (65%) sulphur dry deposition estimates from the throughfall method compared to estimates from an inferential model (Hicks *et al.*, 1987). The inferential model is known to underestimate dry deposition in complex terrain (Hicks and Meyers, 1988).

Inference estimates of sulphur dry deposition in the Netherlands compared well with estimates using the LTRAP model TREND (Van Jaarsveld and Onderdelinden, 1992) on a 5 x 5 km scale. Furthermore, inference results compared well with dry deposition measurements using micrometeorological methods (Erisman, 1992; 1993A). Wesely and Lesht (1989) compared RADM SO_2 dry deposition results with site-specific estimates using inference. Their results showed some systematic differences between the two techniques due to differences in the algorithms for computing resistances. Weekly averages of the deposition velocities were within approximately 30% of each other.

Comparisons between dry deposition estimates obtained from the throughfall method and dry deposition estimates from the watershed mass balance method are reported by Hultberg and Grennfelt (1992) for the Lake Gårdsjön area in Sweden and by Likens *et al.* (1990) for the Hubbard Brook Forest Ecosystem in the USA. Runoff and throughfall fluxes of sulphate were found to be very similar, suggesting the change in storage in biomass and soil, and weathering release were of minor importance. Sulphate fertilisation in several catchments did not enhance sulphate throughfall fluxes significantly, supporting the hypothesis that foliar leaching is insignificant, and that throughfall provides a reasonably good measure for sulphur (SO_2 + SO_4^{2-} aerosol) deposition.

Nitrogen

There is considerable experimental evidence for significant uptake of inorganic nitrogen by canopy foliage, stems, epiphytic lichens or other micro-flora. Much insight has been gained from experiments with radio-labelled ^{15}N. Canopy foliage has been demonstrated to be capable of absorbing and incorporating gaseous NO_2 and HNO_3, as well as NO_3^- and NH_4^+ in solution (Reiners and Olson, 1984; Bowden *et al.*, 1989). In laboratory experiments, NH_4^+ in solution was found to be exchanged with base cations present in leaf tissues (Roelofs *et al.*, 1985). Epiphytic lichens have also been shown to be active absorbers of NO_3^- and NH_4^+ in solution (Lang *et al.*, 1976; Reiners and Olson, 1984).

The absorption or removal of nitrogen in the canopy will generally cause throughfall measurements to underestimate the total deposition. Based on information available in the literature, Ivens (1990) suggested the above-ground uptake of inorganic nitrogen to be between 150 and 350 eq ha^{-1} a^{-1}. Johnson and Lindberg (1992) conclude that, on average, 40% of all inorganic nitrogen input to the IFS forests was retained by the vegetation, whereas 60% is found back in the throughfall data as NO_3^- and NH_4^+. Total inorganic nitrogen uptake amounted up to 850 eq ha^{-1} a^{-1}, with a strong positive relationship between deposition and uptake for spruce and spruce-fir stands. Other tree species showed a rather constant inorganic nitrogen uptake (200-300 eq ha^{-1} a^{-1}), with only little response to deposition amount (Johnson and Lindberg, 1992). Part of the inorganic nitrogen retained by the canopy may be converted into organic substances and subsequently leached. Total nitrogen (organic + inorganic) in throughfall and stem flow is found to be about 84% of the total inorganic nitrogen deposition (Johnson and Lindberg, 1992). Microbes were assumed to play an important role in the conversion of inorganic to organic N, if it occurs. However, it was recognised that organic N in throughfall also arises from internal pools and surfaces of plant and lichens, and from micro-particulate detritus and pollen (Johnson and Lindberg, 1992).

In comparing throughfall with model estimates of nitrogen input to forests in Europe, Ivens (1990) found no significant difference between NO_3^- throughfall fluxes and NOy (= total oxidised nitrogen) deposition estimates, but NH_4 throughfall fluxes were significantly lower (on average, 70%) compared to NHx (= total reduced nitrogen) deposition estimates. The correlation between throughfall fluxes and deposition estimates from the RAINS model were very poor. This was attributed to the large deposition variability introduced by local sources and local differences in aerodynamic and/or surface resistance not accounted for in the RAINS model, and by canopy exchange processes obscuring deposition estimates from the throughfall method.

In a separate study, NO_3^- net throughfall fluxes were found significantly lower (on average, 30%) compared to NOy dry deposition estimates using the inferential model (Erisman, 1992; 1993A). NOx dry deposition estimates from micrometeorological measurements made above forest in the Netherlands were also somewhat lower compared to NOx deposition estimates from this model. NH_4^+ net throughfall fluxes were not significantly different from NHx dry deposition estimates, but their correlation was rather poor. NH_3 deposition estimates from micrometeorological measurements made over heather and forests in the Netherlands were found both lower and higher compared to inferential model estimates. This is attributed to the large spatial variability in NH_3 dry deposition amounts due to the impact of local sources and short atmospheric residence times of NH_3 (Erisman, 1992; 1993A). An extensive comparison between throughfall measurements and atmospheric deposition estimates at the Speulder forest and at several locations in the Netherlands can be found in section 6.2.

Nitrogen cycles within ecosystems are very complex. Up to now, no reliable estimates for inorganic nitrogen deposition can be made using the watershed mass balance method.

Base cations

Na is normally considered to be more-or-less conservative in the canopy, showing only minor canopy exchange (Parker, 1983; Ivens, 1990; Johnson and Lindberg, 1992). Consequently, Na in throughfall was suggested for use as a substance for modelling particle dry deposition (Ulrich, 1983). This model has been widely used (Freiesleben *et al.*, 1986; Bredemeier, 1988; Horn *et al.*, 1989; Ivens, 1990; Beier, 1991; Beier *et al.*, 1992A; 1992B; Draaijers, 1993; Van

Leeuwen *et al.*, 1994). However, canopy exchange of Na^+ may occur; Fassbender (1977) found uptake of Na^+ by young Spruce trees. Furthermore, Reiners and Olsson (1984) reported leaching of Na^+ from canopies of Balsam Fir in a low input area.

Lovett and Lindberg (1984) developed an approach to estimate dry deposition from net throughfall for a number of ions based on a multiple regression model. Lindberg *et al.* (1988) compared this method with deposition measurements of Ca^{2+} to inert surfaces to develop scaling factors for relating fluxes on scales from small plates to whole canopies. This scaling method has also been applied to the dry deposition of Na^+. On the basis of a comparison of throughfall data with deposition measurements of a large number of IFS sites in the United States, Johnson and Lindberg (1992) conclude that Na^+ in throughfall may be considered as solely derived from atmospheric deposition. Besides the throughfall method and the surface accumulation method, the mass balance approach in watersheds is also found to provide reliable estimates for atmospheric deposition of Na^+ (Hultberg and Grennfelt, 1992).

Unlike Na^+, a substantial part of Mg^{2+}, Ca^{2+} and K^+ in throughfall is normally assumed to be caused by canopy leaching (Parker, 1983). However, a literature compilation made by Parker (1990) indicates that it is not clear to what degree Mg^{2+}, Ca^{2+} and K^+ present in throughfall originate from atmospheric deposition and foliar leaching, respectively. Canopy leaching contributed between 10 and 80% to the total flux of these base cations reaching the forest floor. However, at coastal forest sites, Mg^{2+} in throughfall may be predominantly caused by atmospheric deposition of sea-salt particles (Parker, 1983; Beier *et al.*, 1992A). Calcium in throughfall may be enhanced at sites located in areas with calcareous soils or near calcium fertilised arable land (Johnson and Lindberg, 1992). For the IFS data, Johnson and Lindberg estimated that leaching represented an average of ~70% of the annual throughfall plus the stem flow flux of K^+ below 12 diverse forests, while Ca^{2+} leaching represented about 40% and Mg^{2+} leaching about 50%. Magnesium and calcium may also be irreversibly retained within the canopy in the case of limited supplies from the soil (White and Turner, 1970; Abrahamson *et al.*, 1976; Alcock and Morton, 1981). A new method for estimating the dry deposition of K^+, Ca^{2+} and Mg^{2+}, based on the Na^+ deposition in a forest edge, was recently suggested by Beier *et al.* (1992A). Section 6.2 will report on a comparison between deposition estimates of base cations using the inferential method at the Speulder forest and at other sites in the Netherlands. The canopy exchange of these components is quantified in the Speulder forest.

3.4.3 CLOUD AND FOG DEPOSITION

Joslin and Wolfe (1992) concluded that net throughfall may be used as a gross estimate of total cloud S deposition by subtracting precipitation and dry inputs from total throughfall sulphate in high cloud environments. Meuller (1992) compared two techniques for estimating cloud deposition to a high-elevation spruce forest; i.e. throughfall and precipitation chemistry, and a mechanistic cloud deposition model with a cloud event database. The comparison showed a discrepancy of about 30-35% for sulphate, throughfall being higher than model estimates.

3.4.3 SYNTHESIS

As can be concluded from section 3.4, the throughfall method, micrometeorological methods (supplemented/supported by inference) and watershed balance methods (S saturated systems) yield similar estimates of the annual mean total deposition of sulphur within generally acceptable uncertainly limits (~30%). A larger uncertainty exists to estimate reduced or oxidised nitrogen and base cation fluxes.

It is clear that for individual ecosystems deposition in general, and dry deposition in particular, can still not be quantified with sufficient accuracy. The various methods have different advantages and drawbacks and the choice of a certain method for estimation of the flux of a specific pollutant to a specific ecosystem may in many cases depend on the purpose of the study and on requirements on accuracy and costs. For the time being, it is impossible to obtain an accurate annual average deposition map of the Netherlands or of Europe based on actual deposition measurements. Dry, cloud and fog deposition show very strong horizontal gradients due to variations in ambient concentrations in land use, in surface conditions and in meteorology. Therefore deposition maps based on a combination of models and measurements are generated. This is explained in Chapter 5. Regarding spatial and temporal scales, measurements are supplementary to models in such a method. Furthermore, measurements are used for developing process descriptions and for evaluation of model results. Finally, measurements can act as an independent tool for assessing policy targets (trend detection). These issues, outlined below, require different measuring/monitoring strategies.

Process-oriented studies
The process-oriented studies are primarily used to provide insight into deposition processes for different components, and to obtain process descriptions and parameters to be used in models. Micrometeorological methods provide the best methods for these purposes. In cases where micrometeorological methods cannot be used, such as complex terrain and within forest stands, the throughfall method is the only one available up to now. Process-oriented studies can be used to test or verify simple/cheap measuring methods, which might be used for other purposes such as monitoring.

Evaluation of models
For evaluation or validation of model results, preferably simple and cheap monitoring methods are desired. In general, monthly to annual average fluxes are used for validation. The uncertainty in results obtained by these monitoring methods should be within acceptable limits. Furthermore, results should be representative for areas used as receptor areas in the model. Validation of LTRAP model results can be done using area representative

measurements of wet deposition and of ambient concentrations. Micrometeorological measurements suitable for monitoring might be used for evaluating model dry deposition fluxes (Hicks *et al.*, 1991; Erisman *et al.*, 1993A; Erisman and Wyers, 1993). Throughfall measurements might be used as a validation method for spatial variability in S, Na^+ and Cl^- dry (and total) deposition, provided that several criteria on the method and site are met (e.g. Beier and Rasmussen, 1989; Ivens, 1990; Draaijers, 1993). It is advisable to equip several monitoring locations in Europe with dry deposition monitoring systems, wet-only sensors, and cloud and fog deposition measuring methods. These locations should be selected on the basis of pollution climates and type of vegetation. Furthermore, the surroundings should be homogeneous and no sources should be near the site.

Detection of trends

If the purpose of measurements is trend detection, the annual averages should be measured as accurately as the magnitude of the trends. Ambient concentration and wet deposition measurements can be used (EMEP monitoring network) for trend detection. The trend in concentrations is representative for the dry deposition trend, which cannot be measured accurately enough at present. The disadvantage of using only concentration measurements is that a change in dry deposition due to ecosystem response (as a result of reduced loads or climatic change) or due to changes in surface conditions (interaction with other gases, etc.) cannot be detected. Extensive deposition monitoring (see previous section) might be useful for trend detection, especially at larger emission reductions.