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A comparison of methods to estimate canopy exchange at the Speulder forest

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SUMMARY

Differences observed between atmospheric deposition and throughfall fluxes in forests are often assumed to be the result of canopy exchange processes. To obtain more insight on these processes and to quantify them, several field experiments were performed at the Speulder forest research site. Relevant information was obtained by *i)* measuring open-field precipitation and throughfall fluxes with different time resolutions, using two canopy exchange models, *ii)* comparing deposition estimates from surface wash experiments using real and artificial twigs, respectively, and *iii)* comparing throughfall deposition estimates with estimates from micrometeorological techniques and inferential modelling. Specific information on canopy leaching of soil-derived sulphur was provided by a S^{35} nutrition experiment.

Sulphur was found to behave conservative within the canopy, with SO_2 uptake (35 $mol.ha^{-1}.a^{-1}$) more or less balancing leaching of soil-derived SO_4^{2-} (80 $mol.ha^{-1}.a^{-1}$). Stomatal uptake of NO_2 and HNO_2 amounted 130 $mol.ha^{-1}.a^{-1}$. Experiments did not indicate significant uptake of NO_3^- from water layers covering the tree surface, leaving an inexplicable gap of approximately 270 $mol.ha^{-1}.a^{-1}$ between the NO_3^- soil load and the NO_y deposition estimate. Stomatal uptake of NH_3 amounted 140 $mol.ha^{-1}.a^{-1}$, whereas uptake of NH_4^+ in solution equalled 115 $mol.ha^{-1}.a^{-1}$. The total above-ground uptake of inorganic nitrogen compounds amounted 385 $mol.ha^{-1}.a^{-1}$. About 180-200 mol H^+ $.ha^{-1}.a^{-1}$ was retained within the canopy. Canopy uptake of H^+ and NH_4^+ was encountered by leaching of K^+ (270 $mol.ha^{-1}.a^{-1}$), Ca^{2+} (50-75 $mol.ha^{-1}.a^{-1}$) and Mg^{2+} (0-40 $mol.ha^{-1}.a^{-1}$). Part of the leaching of K^+, Ca^{2+} and Mg^{2+} (15%) took place along with weak organic acids. No significant canopy exchange was found for Na^+ and Cl^-.

Differences observed between atmospheric deposition and throughfall fluxes could almost completely be explained by canopy exchange. For closing the gap between the throughfall flux of NO_3^- and the deposition flux of NO_y, additional research is necessary. More knowledge regarding canopy exchange of nitrogen compounds can be obtained by e.g. using tracers (^{15}N) in ecosystem studies. At the same time, NO_2, HNO_2, HNO_3 and NO_3^- dry deposition estimates from micrometeorological measurements and inferential modelling need to be improved.

Field experiments at the Speulder forest were mainly performed in the winter period (November until May) when the vegetation is physiologically less active. By scaling measurement results to one year, stomatal uptake as well as uptake and leaching in solution is probably underestimated. During the measurement period no episodes with winter smog, frost, drought or an insect plague occurred. Such stress factors may intensify canopy exchange processes considerably. Canopy exchange rates derived for the Speulder forest may not directly be considered representative for other forests in the Netherlands as canopy exchange is found to depend strongly on tree species and ecological setting. However, in general, Dutch forests will experience nil canopy exchange of SO_x, Na^+ and Cl^-.

A canopy exchange model developed by Ulrich (1983) and extended by Van der Maas & Pape (1991) has proven to be a useful tool for determining the impact of canopy exchange on throughfall fluxes. The combination of throughfall measurements and this model results in deposition estimates which are similar to deposition estimates derived from micrometeorological measurements and inferential modelling. Unfortunately, several basic assumptions in the canopy exchange model are not properly evaluated under different environmental conditions (ecological setting, pollution climate), which limits the models' utility up to now to forest stands growing on dry and sandy, nutrient poor podzolic soils under current air pollution levels. The model can be improved by taken into account the different mass median diameters of Mg^{2+}, Ca^{2+} and K^{+} containing particles compared to Na^{+} containing particles in the calculation of the dry deposition factors. Moreover, stomatal uptake of NO_2 and HNO_2 has to be included in the model.

SAMENVATTING

Verschillen in het verleden waargenomen tussen atmosferische depositie en doorvalfluxen in bossen worden voor een belangrijk deel toegeschreven aan kroonuitwisselingsprocessen. Ten einde inzicht te krijgen in kroonuitwisselingsprocessen en deze ook te kwantificeren zijn op de boslokatie Speuld verschillende veldonderzoeken uitgevoerd. Relevante informatie werd verkregen door *i)* meting van open-veld neerslag en doorvalfluxen met verschillende tijdresoluties, gebruikmakend van twee kroonuitwisselingsmodellen, *ii)* het vergelijken van resultaten van afspoelexperimenten met echte en kunstmatige twijgen, en *iii)* het vergelijken van doorval-depositieschattingen met schattingen van micrometeorologische metingen en inferentiemodellen. Specifieke informatie over kroonuitloging van uit de bodem afkomstig sulfaat is verkregen middels een S^{35} bemestingsproef.

Resultaten van de veldexperimenten lieten zien dat zwavel zich op langere termijn (maanden) in de boomkroon conservatief gedraagt. Afgezet tegen de totale atmosferische input van zwavel was de stomataire opname van SO_2 (35 mol.ha^{-1}.jaar^{-1}) min of meer gelijk aan de leaching van sulfaat afkomstig uit de bosbodem (80 mol.ha^{-1}.jaar^{-1}). De stomataire opname van NO_2 en HNO_2 bedroeg 130 mol.ha^{-1}.jaar^{-1}. Omdat geen indicaties werden gevonden voor een significante opname van NO_3^- uit waterlaagjes op het boomoppervlak, bleef er een onverklaarbaar verschil van ± 270 mol.ha^{-1}.jaar^{-1} bestaan tussen de NO_y depositieschatting en de NO_3^- doorvalflux. De stomataire opname van NH_3 bedroeg 140 mol.ha^{-1}.jaar^{-1} en de opname van NH_4^+ in oplossing 115 mol.ha^{-1}.jaar^{-1}. De totale bovengrondse opname van anorganisch stikstofkomponenten bedroeg 385 mol.ha^{-1}.jaar^{-1}. De bovengrondse opname van H^+ bedroeg 180-200 mol.ha^{-1}.jaar^{-1}. De kroonopname van NH_4^+ en H^+ werd gekompenseerd door uitloging van K^+ (270 mol.ha^{-1}.jaar^{-1}), Ca^{2+} (50-75 mol.ha^{-1}.jaar^{-1}) en Mg^{2+} (0-40 mol.ha^{-1}.jaar^{-1}). Een beperkt gedeelte van de uitloging van K^+, Ca^{2+} en Mg^{2+} (15%) vond plaats in samenhang met zwak organische zuren. Er vond geen significante opname of uitloging plaats van Na^+ en Cl^-.

De verschillen gevonden tussen atmosferische depositie en doorvalfluxen konden bijna geheel verklaard worden door uitwisselingsprocessen. Om het verschil tussen de atmosferische depositie van NO_y en de doorvalfluxen van NO_3^- te kunnen verklaren is echter aanvullend onderzoek noodzakelijk. Aanvullende informatie aangaande uitwisselingsprocessen voor stikstofkomponenten kan verkregen worden door bijvoorbeeld gebruik te maken van tracers (^{15}N) in ecosyteemonderzoek. Tegelijkertijd dienen de NO_2, HNO_2, HNO_3 en NO_3^- depositieschattingen van micrometeorologische metingen en inferentiemodellen verbeterd te worden.

De veldexperimenten op de boslokatie Speuld zijn verricht gedurende de winterperiode (november tot mei) wanneer, fysiologisch gezien, de vegetatie relatief inaktief is. Door opschaling van de meetresultaten naar één jaar is de stomataire opname en de opname en

uitloging in oplossing waarschijnlijk onderschat. Gedurende de meetperiode kwamen geen episodes met smog, vorst, droogte of een insecten plaag voor. Dergelijke factoren hebben grote invloed op kroonuitwisselingprocessen. De resultaten voor Speuld kunnen niet automatisch beschouwd worden als zijnde representatief voor andere bossen in Nederland. De mate van kroonuitwisseling hangt namelijk sterk af van de boomsoort en de groeiplaatsfactoren. Over het algemeen zal echter de kroonuitwisseling van SO_x, Na^+ en Cl^- in Nederlandse bossen verwaarloosbaar klein zijn.

Een kroonuitwisselingsmodel ontwikkeld door Ulrich (1983) en uitgebreid door Van der Maas & Pape (1991) is een bruikbaar hulpmiddel gebleken voor het kwantificeren van de kroonuitwisseling. De kombinatie van doorvalmetingen en dit model leidt tot depositieschattingen welke vergelijkbaar zijn met de schattingen van micrometeorologische metingen en inferentiemodellen. Verschillende aannamen in het model zijn echter nog niet geëvalueerd onder verschillende milieuomstandigheden (groeiplaats, verontreinigingsklimaat). Hierdoor blijft de bruikbaarheid van het model vooralsnog beperkt tot bosopstanden op droge, zandige, nutrienten arme podzolgronden, bij huidige niveau 's van luchtverontreiniging. Het model kan verbeterd worden door bij de berekening van de 'droge depositiefactor' rekening te houden met de verschillende massa-mediane diameters van Mg^{2+}, Ca^{2+} en K^+ aerosolen ten opzichte van die van Na^+ aerosolen. Daarnaast dient de stomataire opname van NO_2 en HNO_2 in het model ingebracht te worden.

1 INTRODUCTION

For the evaluation of emission abatement measures it is essential that a relation can be established between emission of air pollutants and adverse effects as a result of exposure and deposition. Most adverse effects of air pollutants in forest ecosystems occur due to changes in the soil system (Van Breemen & Van Dijk, 1989; Hey & Schneider, 1991). Critical loads are therefore directly referring to forest soil loads (Nilsson, 1986; Nilsson & Grennfelt, 1988). The soil load (usually determined by measuring throughfall and stemflow) may differ from the deposition flux (determined by a combination of air concentration and meteorological measurements and inferential modelling) as a result of canopy exchange processes. The mechanisms of these exchange processes are still not well known and debate continues on their contribution to the gap between soil loads and deposition fluxes (Ivens, 1990; Lovett et al., 1992; Cape et al., 1992; Erisman, 1992; Draaijers, 1993).

To obtain more insight in canopy exchange processes throughfall and precipitation fluxes were measured at the Speulder forest research site in the Netherlands with different time resolutions. Two canopy exchange models were applied to test assumptions on canopy exchange processes (Van Leeuwen & Bleuten, 1994). Sequential sampling during throughfall events allowed a detailed study of the highly dynamic mechanisms of canopy exchange (Hansen et al., 1994). Information on canopy exchange was also provided by comparing throughfall deposition estimates with estimates from micrometeorological measurements and inferential modelling (Erisman et al., 1994), and by comparing deposition estimates from surface wash experiments using real and artificial twigs, respectively (Römer & Te Winkel, 1994). Specific information on canopy exchange of root-derived sulphur at the Speulder forest was provided by a S^{35} nutrition experiment (Wyers et al., 1994). The main goal of this report is to evaluate all the present data available to quantify canopy exchange for the different components and to find the main exchange mechanisms at the Speulder forest. Findings are placed in a broader perspective for generalization purposes. Furthermore, present gaps in knowledge are elucidated.

2 CANOPY EXCHANGE: A REVIEW

Concentrations in the water layer covering leaves and needles are found to be influenced by passive diffusion and ion exchange between the surface water and the underlying apoplast of canopy tissues (i.e. aqueous layer outside of cell membranes). Passive 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 & Reiners, 1990). Diffusion is controlled by the (ion-specific) resistance of the cuticle and epicuticular wax and by the concentration gradient between leaf surface water and apoplast (Reiners & Olson, 1984). Ion exchange can take place for both anions and cations but cuticular anion exchange sites are far fewer in number than cation exchange sites. Cations (especially those abundant in the foliar apoplast) are released from cuticular ionic binding sites in exchange for hydrogen or ammonium ions retained by the foliage (Roelofs et al., 1985; Parker, 1990). Cations can also be released from foliage along with weak organic acid anions or along with inorganic anions (Cronan & Reiners, 1983).

Leaf wetness is important as the liquid at the outside of the foliage comprises the medium for canopy exchange. The wettability of foliage is found to differ considerably among tree species (Boyce et al., 1991). Moreover, an increasing rate of foliar wax degradation caused by e.g. air pollutants is thought to lead to a decrease in water repellency, which in turn will lead to longer retention of (polluted) moisture (Cape, 1983). In this context also the amount and duration of the precipitation is relevant. Relatively long residence times during drizzle account for relatively high leaching rates compared to short rain periods with large rainfall intensities. Large rain amounts may deplete leachable pools within the canopy, thereby inhibiting ion leaching (Lovett & 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).

The rate of canopy exchange depends on tree physiology and ecological setting. During the growing season deciduous tree species are found to lose more nutrients from the crown foliage through leaching than coniferous tree species. Conifers stay green all year around and continue to lose nutrients throughout the dormant season. Overall, however, deciduous trees tend to lose more nutrients than coniferous trees (Smith, 1981). The age distribution of leaves/needles affects the magnitude of leaching to a large extent. Young immature leaves/needles with intact cuticle tend to lose less nutrients compared to older ones (Parker, 1990). Canopy exchange also depends on the the soil nutrient status as shown by Matzner et al. (1983). They found enhanced canopy leaching after soil fertilization. Biotic stresses like insect plagues may initiate huge canopy leaching. Bobbink et al. (1990) monitored throughfall in a heather vegetation and observed a marked increase of canopy losses occurring simultaneously with an outbreak of a heather-beetle plague. Van Ek & Draaijers (1994) found enhanced leaching in Oak forests as a result of a mildew infection caused by

the fungus *Microshaera aliphilitoides*. Furthermore, abiotic stresses like drought and temperature extremes are found to enhance canopy leaching (Tukey & Morgan, 1963; Draaijers, 1993).

Part of the gap observed between throughfall fluxes and atmospheric deposition may be the result of canopy uptake of gases through stomata. Stomatal uptake of gases is governed by the ambient gas concentration, the solubility of the gas in the apoplast liquid, the equilibrium concentrations in the apoplast, and by stomatal opening. The latter is controlled to a large extent by global radiation, temperature, vapour pressure deficit and soil moisture availability.

2.1. Sulphur compounds

SO_2 may be taken up by the stomata to build up sulphur containing amino-acids. If a significant part of the SO_2 is retained in the foliage and translocated from the canopy to the roots, this would result in an underestimate of sulphur deposition by measuring throughfall. Gay & Murphy (1985) found that approximately half (30-70%) of the SO_2 absorbed by foliage during short-term experimental exposures could not subsequently be removed by washing. However, Schaefer & Reiners (1990) and Granat & Hällgren (1992) conclude that essentially all of the dry deposited sulphur dioxide is eventually extracted out of the apoplast pools by rain and appears in throughfall.

Several radioactive $^{35}SO_4^{2-}$ studies have been conducted to estimate the contribution of soil-derived sulphur to the throughfall flux (Garten et al., 1988; Lindberg & Garten, 1989; Cape et al., 1992). Garten et al. (1988) added radiolabelled SO_4^{2-} through single-stem well injection into the internal nutrient store of two Red Maple and two Yellow Poplar trees and analyzed the amount of radiolabelled SO_4^{2-} and total sulphate present in throughfall. During a 104-day period in the growing season, less than 10% of the net throughfall flux of sulphate could be accounted for by foliar leaching of root-derived sulphur. Similar experiments with several individuals of Loblolly pine trees led to the same conclusion (Lindberg & Garten, 1989). Because the experiments conducted by Garten et al. (1988) and Lindberg & Garten (1989) were performed on isolated trees or trees situated at forest edges, the contribution of canopy leaching to net throughfall fluxes may be larger in forest interiors where deposition is much lower (Fowler et al., 1992; Draaijers et al., 1994).

Cape et al. (1992) applied radioactive sulphate to the soil below a closed Scots pine forest canopy during a four month period in summer. Results suggest (assuming rapid equilibrium of $^{35}SO_4^{2-}$ with sulphate in the soil) that root-derived sulphate contributed approximately 3% of sulphate in net throughfall and that dry deposition of SO_2 and sulphate particles contributed 97% to the total net throughfall flux of sulphate. However, there were some indications that equilibrium could not be safely assumed. For this reason, the possibility of a significant contribution of soil-derived sulphate to sulphate deposition in net throughfall

could not be ruled out on the basis of this experiment (Cape et al., 1992).

At catchments at Lake Gardsjön at the Swedish west coast forested with Norway spruce, the deposition and watershed output were studied during a period of 10 years by means of throughfall, precipitation and runoff measurements (Hultberg, 1985; Hultberg & Grennfelt, 1992). Runoff and throughfall sulphate fluxes were found to be very similar, suggesting uptake of sulphur by tree roots and transport to the tree canopy being of minor importance. Moreover, sulphate fertilization in several catchments did not enhance sulphate throughfall fluxes significantly, supporting the hypothesis that sulphate throughfall provides a reasonable good measure for sulphur (SO_2 + SO_4^{2-} aerosol) deposition (Hultberg & Grennfelt, 1992). Similar conclusions were drawn by Likens et al. (1990) for catchments covered with deciduous forest at Hubbard Brook, USA.

2.2. *Nitrogen compounds*

Present knowledge on canopy exchange of nitrogen compounds is limited due to the complexity of the exchange processes involved. Numerous reports indicate that inorganic nitrogen may be taken up by canopy foliage, stems, epiphytic lichens or other microflora (e.g. Lang et al., 1976; Parker, 1983; Reiners & olson, 1984; Johnson & Lindberg, 1992; Pérez-Soba & Van der Eerden, 1992; Lovett & Lindberg, 1993). The nitrogen taken up is incorporated into organic N via the glutamine synthetase-glutamate dehydrogenase pathway (Miflin & Lea, 1976). These organic N compounds are partly transported from the needles/leaves via the phloem to the roots where they can meet the N requirement (Pérez-Soba & Van der Eerden, 1992). Canopy foliage has been demonstrated experimentally to be capable of absorbing and incorporating gaseous NO_2, HNO_2, HNO_3 and NH_3, as well as NO_3^- and NH_4^+ in solution (Reiners & Olson, 1984; Bowden et al., 1989; Van Hove, 1989).

Recently, more insight has been gained on uptake of gaseous nitrogen compounds through stomata and canopy uptake of nitrogen in solution by performing experiments using ^{15}N as a tracer. Pérez-Soba & Van der Eerden (1992), for example, exposed young saplings of *Pinus sylvestris* to gaseous NH_3 in open top chambers and simultaneously added ^{15}N-labelled $(NH_4)_2SO_4$ via the soil. The N concentration in the needles was found to increase mainly as a result of direct foliar uptake of NH_3. Uptake of NH_4^+ at the root surface was found to be reduced when the needles got enough N from the gaseous NH_3. The N-status of the shoots was suggested to control the N-uptake from the roots. Experiments with ^{15}N made by Vose et al. (1989) show that foliar uptake of dry deposited HNO_3 by *Pinus strobus* is small. Bowden et al. (1989) simulated cloud water deposition by fumigating *Pinus rubens* seedlings with a fine water spray. Essentially, they conclude that the total uptake of NH_4^+ and NO_3^- ions from cloud water is small compared to the amount of nitrogen required to create new growth. Foliar retention of $^{15}NH_4^+$ appeared to be larger compared to uptake of $^{15}NO_3^-$. Garten & Hanson (1990) applied ^{15}N labelled NH_4^+ and NO_3^- to *Acer rubrum* and *Quercus*

alba through simulated rain. Approximately 80% of the $^{15}NO_3^-$ could be removed by washing with water, while about 75% of the $^{15}NH_4^+$ was retained and presumably assimilated into the leaf. Wilson & Skeffington (1994) applied NH_4^+ and NO_3^- in simulated rain to young *Picea abies* trees during a five month period. For both NH_4^+ and NO_3^- no significant foliar uptake was detected. Gebauer et al. (1991) observed for *Picea abies* trees larger uptake of NH_4^+ in solution in comparison to NO_3^-, indicating either a difference in uptake processes or a preferential uptake of NH_4^+. Similar observations were made by Garten & Hansen (1990), Eilers et al. (1992), Wilson (1992) and Lumme (1994). Gebauer et al. (1991) found the uptake of NH_4^+ in solution linearly related to the exposure time, while the uptake of NO_3^- followed a saturation curve. A slightly negative charge of the cuticle probably make the needle surface less permeable for anions (Martin & Juniper, 1970).

The uptake mechanism for NH_4^+ in solution remains uncertain. Throughfall measurements (e.g. Lovett et al., 1985; Ivens, 1990; Draaijers, 1993) and laboratory experiments with *Pinus nigra* needles (Roelofs et al., 1985) indicate that NH_4^+ uptake is mainly the result of exchange with base cations present in the leaf tissue. However, surface wash experiments conducted by Wilson (1992) suggest that NH_4^+ uptake may also occur through passive diffusion. In his experiments, NH_4^+ uptake by *Pinus sylvestris* and *Picea abies* shoots was found a function of the NH_4^+ concentration in the foliage and depended on the concentration gradient between the rain solution and either the symplast or apoplast. Hansen (1994) observed in a *Picea abies* stand in Denmark a linear relationship between the foliar uptake of NH_4^+ and the concentration of NH_4^+ in rain water.

Based on information available in the literature, Ivens (1990) suggested the above-ground uptake of inorganic nitrogen by forests to range between 150 and 350 $eq.ha^{-1}.a^{-1}$, depending on tree species and ecological setting of the forest. Within the Integrated Forest Study, Johnson & Lindberg (1992) measured throughfall and stemflow fluxes of NO_3^- and NH_4^+ in several forest stands in the United States. Simultaneously, dry deposition of NO_2, NO, HNO_3, HNO_2, NO_3^-, NH_3 and NH_4^+ was estimated. Moreover, wet and cloud water deposition fluxes of nitrate and ammonium were determined. Canopy retention of inorganic nitrogen was estimated by total deposition (dry + wet + cloud water) minus soil flux (throughfall + stemflow). It was concluded that, on the long term, 40% of all inorganic nitrogen input to forests was retained by the vegetation, whereas 60% was found back in the throughfall as NO_3^- and NH_4^+. (Johnson & Lindberg, 1992). 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 & Lindberg, 1992).

In the same study, part of the inorganic nitrogen retained by the canopy was supposed to be converted into organic substances and subsequently leached. Total nitrogen (organic + inorganic) in throughfall and stemflow was about 84% of the total inorganic nitrogen deposition (Johnson & Lindberg, 1992). Microbes were assumed to play an important role in the

conversion of inorganic to organic N, if it occurs. However, it was recognized that organic N in throughfall also arises from internal pools and surfaces of plants and lichens, and from microparticulate detritus and pollen (Johnson & Lindberg, 1992). Averaged over the whole earth, atmospheric deposition of organic nitrogen compounds is estimated to be small, i.e. < 100 $eq.ha^{-1}.a^{-1}$ (Gregory, 1973). Organic N-deposition is mainly in the form of spores (Beringen et al., 1992). Amines emitted from manure probably contribute to organic N deposition in agricultural areas (Leemans, 1989). Carlisle et al. (1966) reported for a *Quercus petraea* stand an organic nitrogen throughfall flux of ± 350 $eq.ha^{-1}.a^{-1}$. Similar or somewhat larger throughfall fluxes of organic nitrogen were measured by Alenäs & Skärby (1988) in *Picea abies* forest stands. Thus, leaching of organic nitrogen seems to more or less counterbalance the above-ground uptake of inorganic nitrogen.

2.3. *Sodium and chloride*

Sodium and chloride are normally considered to be more or less conservative elements showing only minor canopy exchange (Parker, 1983). Even so, Fassbender (1977) reported some sodium uptake by young spruce trees during his laboratory experiments and Bobbink et al (1990) found relatively large leaching in heather vegetation during the outbreak of a heather-beetle plaque. Leeflang (1938) and Bredemeier (1988) found clear downwards gradients in sodium and chloride in bulk precipitation as well as in throughfall with increasing distance from the North Sea, indicating a major contribution of sea-salt particles to these fluxes. Ivens (1990) found a strong correlation between sodium and chloride in both bulk precipitation and throughfall samples, compiled from all over Europe. Sodium and chloride were found to occur in the same molar ratio as in sea water (i.e. 0.86), suggesting sea water being the only source of these components (formation of e.g. NH_4Cl aerosol through reaction of HCl with NH_3 seems insignificant). Moreover, sodium in throughfall was linearly related to sodium in bulk precipitation with an intercept of the regression line not significantly different from zero, suggesting nil canopy exchange (Ivens, 1990). Based on a comparison of throughfall data with deposition measurements on a large number of sites in the United States, Johnson & Lindberg (1992) also conclude that Na^+ in throughfall may be considered as solely derived from atmospheric sea salt deposition.

2.4. *Magnesium, calcium and potassium*

A substantial part of magnesium, calcium and potassium in throughfall is normally assumed to be the result of canopy leaching (Parker, 1983). These ions are leached in association with foliar excretion of weak organic acid anions (Tukey, 1980; Hoffman et al., 1980) or through exchange with H^+ and NH_4^+ in leaf tissues (Roelofs et al., 1985). K^+ is

found to be relatively more susceptible to canopy leaching compared to Mg^{2+} and Ca^{2+} because it is not so tightly bound in structural tissues or enzyme complexes (Wood & Bormann, 1975). A literature compilation made by Parker (1990) indicates that it is not clear to which degree these base cations 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, where at coastal forest sites, magnesium in throughfall was predominantly caused by atmospheric deposition of sea-salts (Parker, 1983). Johnson & Lindberg (1992) suggest that calcium in throughfall may be enhanced at sites located in areas with calcareous soils or near calcium fertilized arable land. Observations done by White & Turner (1970), Abrahamson et al. (1976) and Alcock & Morton (1981) suggest that magnesium and calcium may also be irreversibly retained within the canopy. Ivens (1990) hypothesizes that canopy uptake may occur if tree canopies suffer from base cation deficiencies due to limited cation supplies from the soil.

2.5. *Hydrogen, bicarbonate and phosphate*

Deciduous stands in regions remote from acid precipitation are usually found to have a higher throughfall pH in comparison to incident precipitation indicating canopy retention of protons (Parker, 1983). There are, however, a number of exceptions (e.g. Künstle et al., 1981; Skeffington, 1983). For coniferous stands, reports of higher throughfall pH (e.g. Abrahamsen et al., 1976; Miller, 1984) are as common as reports of lower pH (Parker, 1983). In polluted areas remote from ammonia emission sources, throughfall is generally more acid than bulk precipitation (Georgii et al., 1986; Bredemeier, 1988). In the Netherlands, the proton flux under the forest canopy is found to be smaller than in the open field (Van Breemen et al., 1982; Houdijk, 1990; Ivens, 1990). This is attributed to canopy uptake of protons through exchange with cations like magnesium, calcium and potassium, and to the neutralizing effect of dry deposition of ammonia onto the water layers present on the tree surface (Ivens, 1990).

Bicarbonate in throughfall is usually found in regions away from acidified precipitation where it originates from atmospheric CO_2 (Cronan, 1978). In such regions, bicarbonate may even be the dominant anion because leachate cations commonly transfer as bicarbonate salts (Tukey, 1970). Partly, bicarbonate in throughfall may originate from bird droppings and canopy leaching of carbon (Parker, 1983).

Negligible amounts of phosphorus in ambient air and precipitation suggest that canopy leachate contribute more than 90% to throughfall phosphate (Parker, 1983). Minor amounts of phosphate in throughfall may originate from pollen and soil dust, the latter especially in forests situated near fertilized arable land (which will often be the case in the Netherlands). Furthermore, bird droppings may contribute to phosphate in throughfall (Van der Maas et al., 1990; Ivens, 1990).

3 METHODOLOGY

3.1. Site description

The Speulder forest research site is located at the national park 'de Hoge Veluwe' in the central part of the Netherlands (52°15'N, 5°41'E). De Hoge Veluwe is an approximately 100 m high ice-pushed morainic ridge with dry and sandy, nutrient poor podzolic soils. The measuring site consists of a homogeneous 2.5 ha monoculture of Douglas-fir, 35 years old with a stem density varying between 785 and 1250 tree.ha^{-1}. Mean tree height equalled 21.6m (Steingröver & Jans, 1994). The canopy is well closed with a one-sided leaf area index varying from 9 in early spring to 12 at the end of the summer (Steingröver & Jans, 1994). The site is surrounded by a larger forest area of approximately 50 km^2. Directly adjacent to the site are stands of Pine, mixed Beech/Oak, Douglas-fir and Larch with mean tree heights varying from 12-25m. Large sources of SO_2 and NO_x are located 200 km to the south east (industrial Ruhr area) and 100 km to the south west (Rotterdam port) of de Hoge Veluwe. The forested area of de Hoge Veluwe is surrounded by large agricultural areas emitting NH_3 due to ammonia volatilization from animal manure.

3.2. Precipitation and throughfall measurements

Precipitation and throughfall fluxes were measured continuously on a weekly basis between 26 October 1992 and 21 July 1993 (Van Leeuwen & Bleuten, 1994). Bulk precipitation was sampled in a clearing approximately 300 m from the Speulder forest site by means of four continuously open funnels. Two of these funnels were connected to a mechanical sequential sampler after March 1993. During several months wet-only precipitation was measured to estimate the contribution of dry deposition onto the funnels and to derive bulk to wet-only correction factors. Throughfall was sampled weekly by 25, 4m long gutters. Throughfall was additionally sampled on an event basis by two gutters connected to a tipping bucket rain gauge and a sample changer. Division between events was made when the time lap between two tips of the recording tipping bucket was larger than two hours. Several throughfall events were also sampled sequentially (Van Leeuwen & Bleuten, 1994).

Wet deposition was estimated by correcting bulk precipitation fluxes for dry deposition to the funnels. Stemflow was estimated from literature to be 6% of the throughfall flux (Van Leeuwen & Bleuten, 1994). By subtracting the wet deposition flux from the throughfall+stemflow flux (= net throughfall) and assuming nil canopy exchange an estimate for dry and fog deposition was obtained. All fluxes presented in this report are expressed as annual averages, unless stated otherwise.

3.3. *Canopy exchange model of Ulrich (1983) and Van der Maas & Pape (1991)*

Continuous monitoring of throughfall and precipitation fluxes at the Speulder forest (Van Leeuwen & Bleuten, 1994) allowed the application of the canopy exchange model developed by Ulrich (1983) which was extended by Van der Maas & Pape (1991). The first part of the calculation method used in this model is often referred to as the 'sodium-filtering approach' (Ivens, 1990; Draaijers, 1993; De Vries et al., 1993; Bleeker et al., 1994). Model assumptions and a short overview of the calculation scheme are presented here. The following abbreviations are used: TF = throughfall flux, DD = dry deposition flux, BP = bulk precipitation flux, CL = canopy leaching, CU = canopy uptake, wa = weak acids, cat = total cations and an = total anions.

In the model, Na^+ in throughfall is assumed not to be influenced by canopy exchange and particles containing Ca^{2+}, Mg^{2+}, K^+, Cl^- and PO_4^{3-} are assumed to have the same mass median diameter as Na^+ containing particles. Dry deposition amounts of Ca^{2+}, Mg^{2+}, K^+, Cl^- and PO_4^{3-} can subsequently be calculated according to $(TF_{Na}\text{-}BP_{Na})/BP_{Na}$ (= dry deposition factor) multiplied by the BP of the ion of interest (Ulrich, 1983; Ivens, 1990; Beier, 1991). Canopy leaching of these ions is calculated according to TF-BP-DD. Because Cl^- leaching is assumed zero, the canopy leaching computed for Cl^- is regarded as deposition of HCl(g).

A second model assumption is that the total canopy uptake of H^+ and NH_4^+ equals the total canopy leaching of Ca^{2+}, Mg^{2+} and K^+ minus canopy leaching of Ca^2, Mg^{2+} and K^+ associated with foliar excretion of weak acids (canopy uptake should always balance canopy leaching). To calculate the latter, Van der Maas et al. (1991) define an excretion factor equal to $CL_{wa}/(CL_{Mg}+CL_{Ca}+CL_K)_{total}$, where CL_{wa} is computed according to $TF_{wa}\text{-}BP_{wa}\text{-}DD_{wa}$. TF_{wa} is assumed equal to $TF_{cat}\text{-}TF_{an}$ and BP_{wa} to $BP_{cat}\text{-}BP_{an}$ (Hoffman et al., 1980; Keene et al., 1983; Guiang et al., 1984; Ivens, 1990). Dry deposition of weak acids is assumed equal to bulk precipitation of weak acids.

Canopy uptake of H^+ and NH_4^+ is subsequently calculated from the sum of exchanged ions of Ca^{2+}, Mg^{2+} and K^+ where, based on laboratory experiments with Douglas-fir twigs from the Speulder forest (Van der Maas et al., 1991), H^+ has an exchange capacity six times larger than NH_4^+ (thus $CU_H/CU_{NH4}=6$). Knowing their canopy uptake, the dry deposition flux of H^+ (from H_2SO_4, HNO_3 and HCl) and NH_4^+ (NH_3 and NH_4^+ aerosol) can be computed from TF+CU-BP. Finally, it is assumed that canopy leaching of SO_4^{2-} and NO_3^- is zero allowing the calculation of dry deposition of SO_4^{2-} and NO_3^- according to TF-BP.

3.4. *Multiple regression model of Lovett & Lindberg (1984)*

Throughfall and bulk precipitation were sampled on an event basis during 9 months (Van Leeuwen & Bleuten, 1994) which allowed the application of the canopy exchange model of Lovett & Lindberg (1984). This empirical model is based on the calculation of a multiple

regression using event net throughfall (= throughfall minus precipitation, NTF) as the dependent variable and the duration of the antecedent dry period (DDP) and precipitation amount (P) as independent variables: $NTF = b_1*DDP + b_2*P$. The regression coefficients (b_1 and b_2) represent the mean dry deposition and canopy exchange rate, respectively. These coefficients can be used to calculate yearly mean dry deposition and canopy exchange amounts if information on the total duration of dry periods and the annual rainfall amount is available. The model assumes dry deposition to be only related to the duration of the antecedent dry period (Lovett & Lindberg, 1984; Puckett, 1990; Ivens, 1990). Meteorological circumstances during the antecedent dry period are not included in the model. Canopy exchange is assumed to occur exclusively and continuously during rain events when the canopy is wet and is for this reason taken proportional to the water flow across the canopy.

3.5. Sequential sampling during throughfall events

Individual events were sampled sequentially (Van Leeuwen & Bleuten, 1994) which allowed a detailed study of the mechanisms of the highly dynamic canopy processes. This is not possible when throughfall is sampled over longer time periods such as weeks or events. The following framework can be used to explain throughfall concentration curves during single events. During dry interstorm conditions, canopy surfaces accumulate dry deposition, based on air concentrations and specific deposition velocities. Canopy apoplastic and exchangeable cation pools (depleted during the previous rain) are recharched, based on mass flow on the transpiration stream. The combination of these factors sets the height of the decay function for each ion. This function consists of a dry deposition curve and a canopy source (diffusion and ion exchange) curve, in different proportions for each ion. During the storm, ion-specific flux rates depend on wash-off, cation exchange, and diffusion rates based on rain intensity and concentration gradients between diffusible pools and external water (Schaefer & Reiners, 1990). The intensity, duration, acidity and ionic composition of the incident precipitation may all affect net throughfall fluxes. During long-lasting storms, dry deposition will be washed off. Diffusion out of the apoplastic pool will occur as a result of the concentration gradient with the waterlayer covering the surface. After the storm ends, the water left in the canopy evaporates and the ions left behind contribute to the surface deposit. When all dry deposition is washed off net throughfall will approach a constant value. This value will equal zero when canopy interaction is absent. Net throughfall remains positive in case of canopy leaching and will drop below zero in case op canopy uptake (Schaefer & Reiners, 1990).

3.6. *Deposition estimates from micrometeorological measurements and inferential modelling*

Information on canopy exchange can also be obtained by comparing throughfall deposition estimates (Van Leeuwen & Bleuten, 1994) with estimates from micrometeorological measurements and inferential modelling. Between 23 November 1992 and 10 May 1993 the dry deposition flux of SO_2, NH_3 and NO_2 was estimated using the gradient technique (Mennen et al., 1994; Erisman et al., 1994). The performance of the instruments used and the monitoring system as a whole are extensively described by Zwart et al. (1994). In the same period dry deposition of HNO_3 HNO_2 and HCl was inferred from measured air concentrations and parametrisized dry deposition velocities (Erisman et al., 1994). A model describing stomatal conductance as a product of response functions for water vapour deficit, global radiation, temperature, soil moisture status and leaf area index (Bouten & Bosveld, 1992) was used to estimate gaseous uptake through stomata. Dry deposition of acidifying aerosols (SO_4^{2-}, NO_3^-, NH_4^+ and Cl^-) and base cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) was inferred using results of air concentration measurements performed by Römer & Te Winkel (1994), and a parametrization of the deposition velocity according to Slinn (1982) modified by Ruijgrok et al. (1994). During two campaigns in December 1992 and February 1993, respectively, fog deposition was estimated by measuring the turbulent water flux of fog droplets using the eddy correlation technique (Wyers et al., 1994). The fog water flux through sedimentation depends on the fog droplet radius and was estimated using Stoke 's law. The fog droplet size distribution was measured using a FSSP measuring device (Wyers et al., 1994). Fog deposition fluxes of SO_4^{2-}, NO_3^- and NH_4^+ were obtained by multiplying total fog water fluxes with the average chemical composition of the fog droplets which was measured by Römer & Te Winkel, (1994) using a CWP string collector (Daube et al., 1987). Fog deposition estimates were extrapolated to the whole measurement period on the basis of fog duration measurements from a nearby meteorological station (Vermeulen et al., 1994).

3.7. *Surface wash experiments using Douglas fir and artificial twigs*

Between November 1992 and May 1993 several surface wash experiments were performed at the Speulder forest using Douglas-fir twigs and artificial twigs (Römer & Te Winkel, 1994). The artificial twigs had similar geometrical characteristics as the Douglas-fir twigs and were chemically inert. Measurements with Douglas-fir twigs were performed at 11, 15, 17 and 19 m above the forest floor, while measurements with artificial twigs only took place at 15, 17 and 19 m height. After exposure to dry deposition for a few days, the twigs were rinsed with demineralised water (Römer & Te Winkel, 1994). The rinsing water was analyzed for all major components. Deposition on the twigs was extrapolated to the whole canopy using the ratio between twig leaf area and the corresponding canopy stratum leaf area

as measured by Steingröver & Jans (1994). Information on canopy exchange was obtained by comparing deposition to real and artificial twigs, respectively (Römer & Te Winkel, 1994).

3.8. S^{35} nutrition experiment

To estimate the amount of sulphate in throughfall originating from root-derived canopy leaching, a S^{35} nutrition experiment was performed from June 1993 to April 1994 (Wyers et al., 1994). Two plots (containing 5 and 7 trees, respectively) were fertilized each month with an artificial rain water solution containing radioactive $(NH_4)_2{}^{35}SO_4$. Fertilization took place by means of a drainage system installed at a depth of 10 cm in the mineral soil. One plot (plot 1) received an amount equal to the yearly mean deposition of ammonium and sulphate. The other one (plot 2) was fertilized with twice this amount. Specific activity was measured in the soil, needles and throughfall water on a monthly basis. Every month, freshly collected needles were soaked in water for 24h, and the portion of root-derived sulphur leached from the needles was obtained. The relative contribution of foliar leaching of root-derived sulphate to sulphate in throughfall was calculated by the ratio of the ^{35}S specific activity of sulphate and the water-leachable sulphur from the canopy (Wyers et al., 1994).

4 RESULTS AND DISCUSSION

4.1. Canopy exchange model of Ulrich (1983) and Van der Maas & Pape (1991)

Table I presents results of the canopy exchange model of Ulrich (1983) and Van der Maas & Pape (1991) applied for the Speulder forest. If foliar leaching is expressed as percentage of net throughfall, values for K^+, Ca^{2+} and Mg^{2+} equal 89, 46 and 29%, respectively. Minor canopy uptake of phosphate was calculated. About 88% of the total H^+ deposition and approximately 9% of the total NH_4^+ deposition was taken up by the canopy.

	Na	K	Ca	Mg	Cl	HCl(g)	PO4	H	NH4	NO3	SO4	SO4s	wa
	dry deposition factor = 1.27; excretion factor = 0.12												
TF	1153	322	396	392		1379		7	24	2452	697	2563	138	77
BP	507	23	110	137		614		2	167	739	340	716	61	8
WD	461	17	78	115		577		2	139	724	303	630	55	19
DD	646	29	140	174	765		15	3	38	1968	357	1847	78	8
TD	1153	52	250	311		1394		5	205	2707	697	2563	139	16
CL	0	270	146	81		0		2	-181	-255	0	0	0	61

Table I Results of the canopy exchange model of Ulrich (1983) and Van der Maas & Pape (1991) applied on throughfall measurements performed between 23-11-92 and 10-05-93 at the Speulder forest research site ($eq.ha^{-1}.a^{-1}$). TF = throughfall, BP = bulk precipitation, WD = wet deposition, DD = dry deposition, TD = total deposition, CL = canopy leaching, SO_4s = sea salt sulphate and wa = weak acids.

The canopy exchange model is built on assumptions which are sometimes questionable. When a particular assumption is not valid this propagates into successive calculations through which an accumulation of errors may arise. For instance, the assumption that Mg^{2+}, Ca^{2+}, Cl^- and K^+ containing particles are deposited with equal efficiency as Na^+ containing particles will certainly introduce an error as the particle size distribution of these constituents is not the same. At the Speulder forest mass median diameters (MMDs) of Ca^{2+} (7.7μm) and to a lesser extend Mg^{2+} (5.9μm) were found to be larger than those of Na^+ (5.1μm) while the MMD of K^+ (2.6μm) was considerably smaller (Ruijgrok et al., 1994). As a result dry deposition of Ca^{2+} and to a lesser extend Mg^{2+} containing particles will be underestimated by the model and dry deposition of K^+ containing particles will be overestimated. Based on these dry deposition values, canopy leaching of Mg^{2+}, Ca^{2+} and K^+ is computed which, in turn, is used to calculate canopy uptake of H^+ and NH_4^+. The ratio of canopy uptake efficiency between H^+ and NH_4^+ is obtained from foliar extraction experiments with small Douglas-fir twigs in the laboratory (Van der Maas et al., 1991). Whether these results may be

extrapolated to field situations remains uncertain. The model assumes nil canopy exchange of SO_4^{2-} and NO_3^-. As elucidated in chapter 2 this assumption is probably valid for SO_4^{2-} but invalid for NO_3^-. Uncertainties associated with the computation of the excretion factor include the incompleteness of the ion balance (e.g. manganese, iron and aluminium were not measured in this study, probably resulting in an underestimation of the excretion factor) and the assumption that the dry deposition of weak acids equals the bulk precipitation flux of weak acids. The computation of the excretion factor is very sensitive for possible analytical errors.

4.2. *Multiple regression model of Lovett & Lindberg (1984)*

Table II presents results of the multiple regression model of Lovett & Lindberg (1984) applied for the Speulder forest. The use of this model requires independent throughfall collections. For this reason rain events larger than 15mm were used to separate between deposition periods. In this way, all dry deposition washed-off was assumed to belong to the antecedent dry period (Van Leeuwen & Bleuten, 1994). Only for K^+ and H^+ significant relationships ($p<0.05$) were found between event net throughfall on the one hand and the duration of antecedent dry period and precipitation amount on the other hand. By multiplying mean canopy leaching rates (b_2) presented in Table II with annual rainfall amounts (842mm), canopy leaching for K^+ can be estimated to be 190 (±43) $eq.ha^{-1}.a^{-1}$ and canopy uptake of H^+ 200 (±40) $eq.ha^{-1}.a^{-1}$. Model results with respect to dry deposition are discussed in Van Leeuwen & Bleuten (1994).

	b1		*b2*		*n*	*r2*
	avg	std	avg	std		
K	0.0037	0.001	0.0225	0.0051	8	0.84
H	ns	ns	-0.0238	-0.0047	8	0.85

Table II Mean dry deposition rates (b_1) (in $mmol.m^{-2}.hr^{-1}$), mean canopy leaching rates (b_2) (in $meq.m^{-2}.mm\ rainfall^{-1}$), number of observations (n) and coefficients of determination (r^2) for the no-intercept regression equations between event net throughfall of K^+ or H^+ on the one hand and the duration of antecedent dry period and precipitation amount on the other hand. Regression equations for all other ions were not significant ($p>0.05$), and for this reason not presented in this table (after Van Leeuwen & Bleuten, 1994).

The model has proven to be valuable in areas with convective storms and extended dry weather periods (Lovett & Lindberg, 1984; Puckett, 1990). However, at the Speulder forest events are characterized by extended periods of low-intensity rainfall and short antecedent dry periods. This will have important implications for canopy exchange and dry deposition processes. Long-duration, low-intensity rainfall is conducive to accelerated foliar leaching of plant nutrients (Schaefer & Reiners, 1990), and wetness on vegetation may reduce the resistance to dry deposition, leading to higher fluxes of SO_2 and NH_3. Moreover a wet canopy during 'dry periods' may facilitate canopy leaching. The climatic conditions in the Netherlands thus do not favour the application of the model which may be the reason for the small amount of significant relationships observed (Table II). Another reason for this may be the small number of independent throughfall collections (8) which could be distinguished.

The simple formulation of the model is subject to a number of other caveats. First, the migration of a substance to the surface of the needle in the transpiration stream during dry periods (exudation) will appear in this model as dry deposition, even though it represents an internal source of the element. Second, dry deposition that is washed off the canopy slowly and continuously as the rain continues will affect both coefficients of the model. Ions associated with deposited particles are probably quickly dissolved when wetted, suggesting that they would be removed from the canopy in the initial stages of a rain event and therefore would not be confused with canopy exchange. The fate of gaseous deposits is more problematic, since they may be strongly but reversibly adsorbed to canopy surfaces. Third, to the extent that any dry-deposited material is taken up by the canopy, chemically transformed, or re-released to the atmosphere, the coefficient b_1 will represent the net dry deposition, i.e. that fraction which is removable by the rain. Similarly, b_2 represents the net aqueous exchange between canopy surfaces and the rainfall and could be the sum of a positive (efflux from the surface) and a negative (influx) component. Fourth, several factors would be expected to provide substantial variability about a mean dry-deposition rate. These include variations in air quality, meteorological conditions, and structural and physiological properties of the canopy. Similarly, the coefficient b_2 represents a mean canopy exchange rate and does not account for physiological variations in the tree nor any non-linearity of exchange with precipitation amount during an individual rain event or during seasons (Lovett & Lindberg, 1984).

4.3. Sequential sampling during throughfall events

Throughfall events collected sequentially all show more or less similar concentration variations (Figure 1). A slight increase in concentration is apparent in the beginning of the event followed by a steady decrease. The concentration gradient is steepest in the beginning of the event whereas later on the concentrations change only slowly and approach a more or less constant value. At the end of each event ion concentrations increase again. These patterns

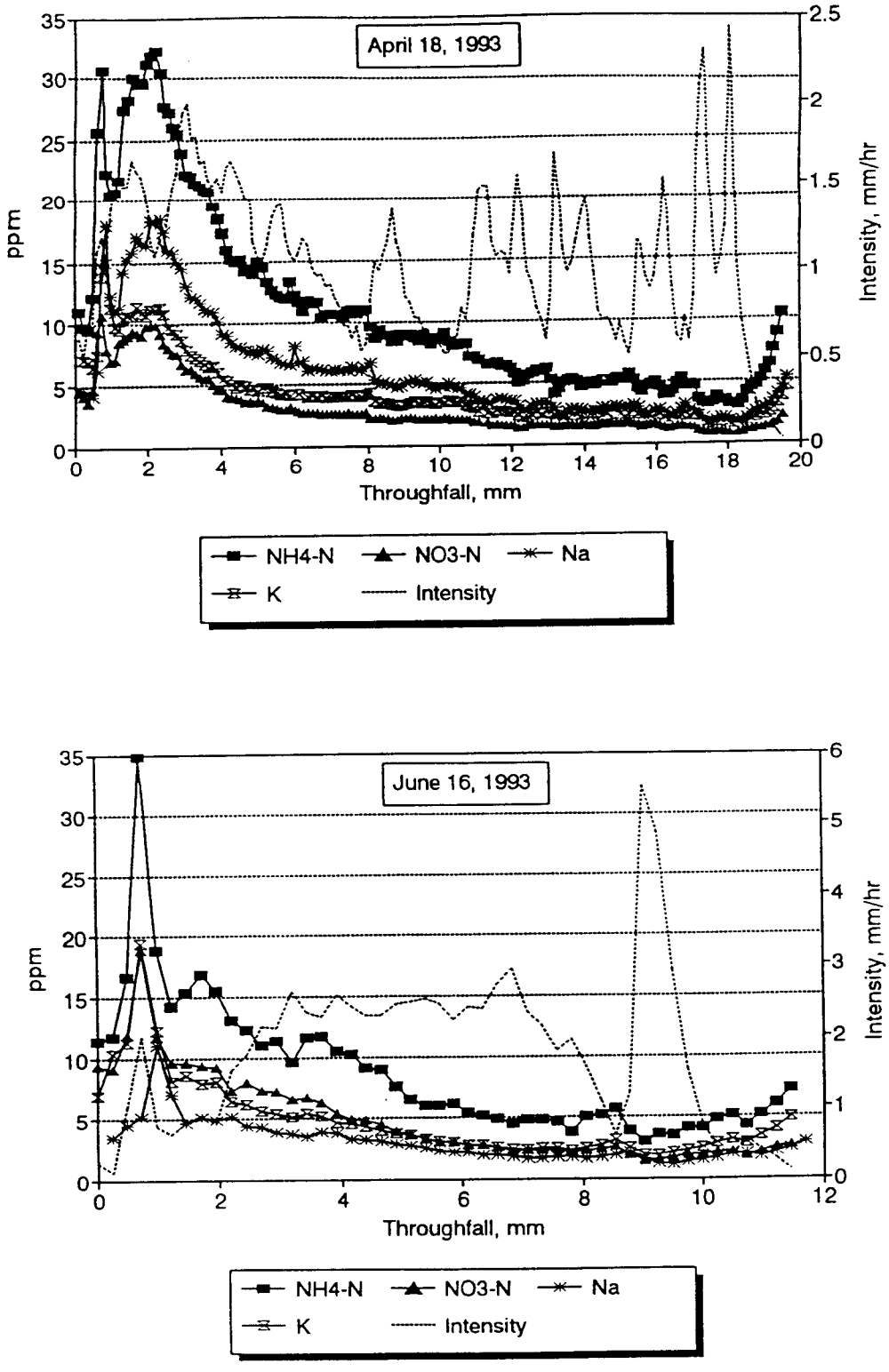
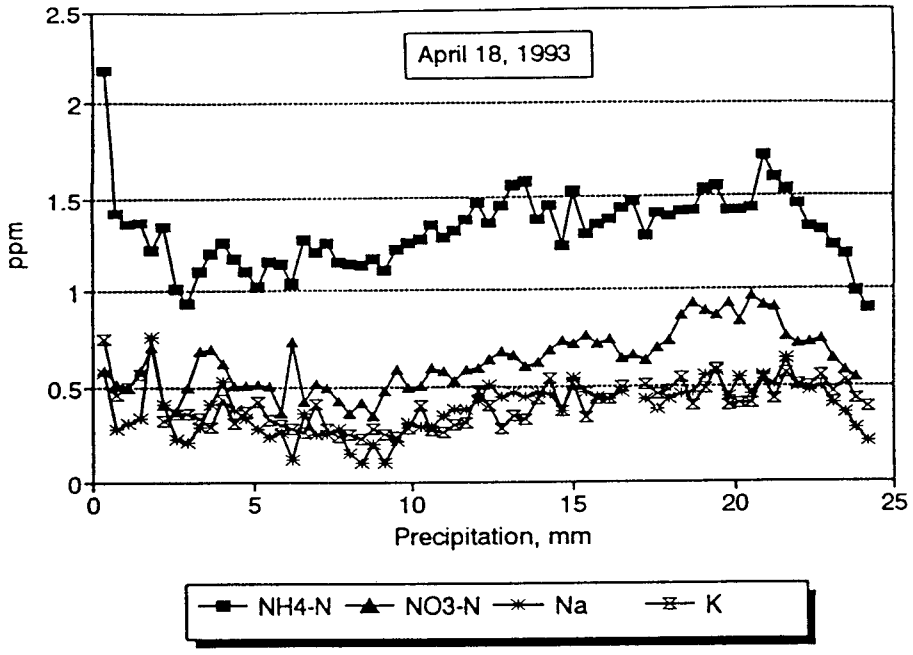


Figure 1 Concentration of SO_4^{2-}, NO_3^-, NH_4^+, Na^+ and K^+ in throughfall collected sequentially, and throughfall intensity, during two rain events (18 April and 16 June 1993, respectively) at the Speulder forest research site (after Hansen et al., 1994).



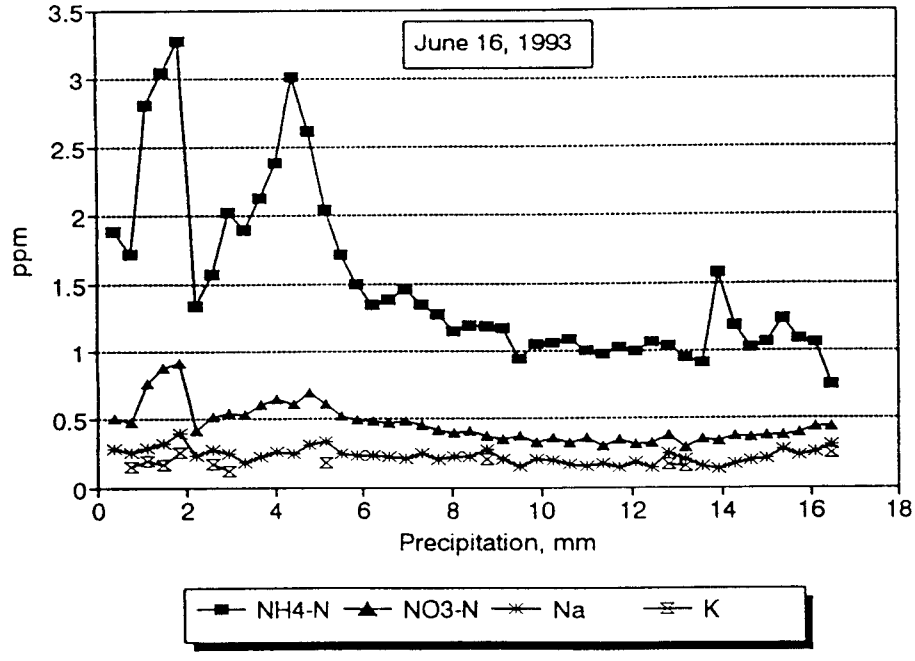


Figure 2 Concentration of SO_4^{2-}, NO_3^-, NH_4^+, Na^+ and K^+ in precipitation collected sequentially during two rain events (18 April and 16 June 1993, respectively) at a clearing near the Speulder forest research site (after Hansen et al., 1994).

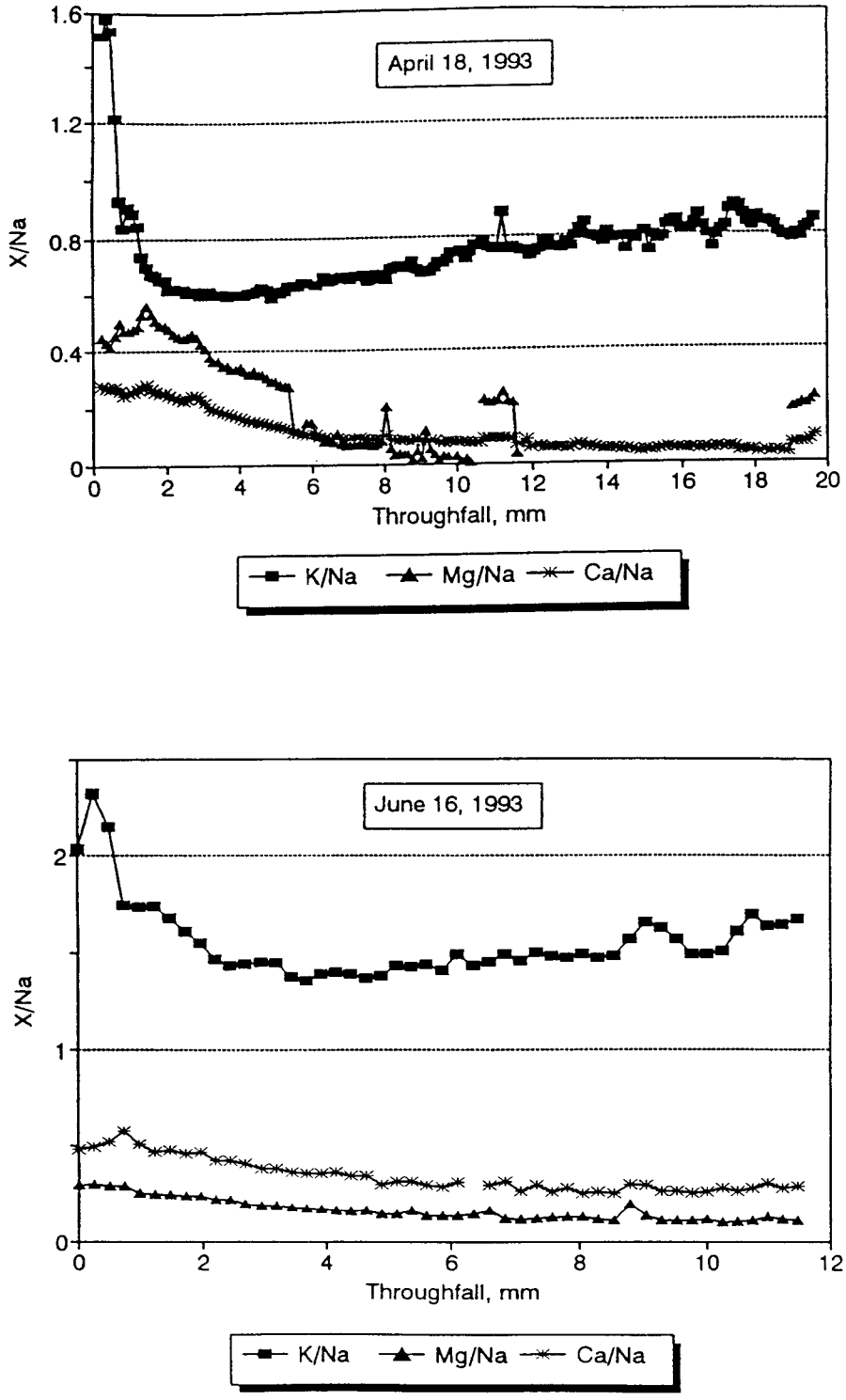


Figure 3 K^+/Na^+, Mg^{2+}/Na^+ and Ca^{2+}/Na^+ ratio ($mg.l^{-1}/mg.l^{-1}$) in throughfall as function of time during two rain events (18 April and 16 June 1993, respectively) at the Speulder forest (after Hansen et al., 1994).

resemble the ones found by Ivens (1990) in Kootwijk (the Netherlands). The decreasing concentrations observed during individual events can be attributed to both wash-off of dry deposited material and exchange between the internal parts of the vegetation and the throughfall water. The ion pools assessable to throughfall, whether internal or external, are depleted during the event. The relatively large concentrations in the initial and the final throughfall water are furthermore related to the moisture content in the canopy, the rain intensity and the evaporation rate during the event (Hansen et al., 1994). Rain water usually show the highest concentrations in the initial stages of the event (Figure 2). In subsequent fractions, the ion concentrations usually decrease and finally approach a more or less constant value. These observations are in accordance with sequential rain sampling performed by Raynor & Hayes (1982).

Comparing sequential throughfall and precipitation concentrations it is apparent that the ion concentrations in the initial throughfall are up to 15 times higher than concentrations in precipitation. Moreover, throughfall concentrations in the final part of the event were always larger than the concentrations observed in the corresponding rain, even in intensive, long lasting rain storms. For Na^+, which in a region relatively close to the sea is supposed to originate solely from dry deposition (no canopy leaching), and for NH_4^+ for which one could expect some foliar uptake, the concentrations never decreased to those in the rain either.

The remaining difference between throughfall and precipitation concentrations was found for all ions which points to an evaporation effect. During light rain or just after rain has stopped, the water stays relatively long on the foliage allowing evaporation to become more important through which concentrations in canopy drip increase. Another reason may be incomplete wash-off of dry deposition. Perhaps part of the dry deposition accumulated in the canopy (e.g. at the bottom of needles) is difficult to reach by rainwater and will only be washed off very slowly. Moreover, dry deposition may still be effective during the rain event which causes the ion pools to be replenished even when it is raining. Dry deposited material will most probably be easier absorbed to the surfaces when the canopy is wet. Additionally, wind speeds are generally relatively high during rain events favouring dry deposition. To test this hypothesis dry deposition of SO_x and NH_x was estimated for the events which were sampled sequentially and where deposition data from micrometeorological measurements were available. In all cases, however, dry deposition was (by far) not large enough to explain the gap between throughfall and precipitation concentrations at the near end of the events when throughfall concentrations are lowest.

Finally, leaching may be the reason for the remaining difference between throughfall and precipitation concentrations. At the end of long lasting events concentrations in the needles are relatively high compared to concentrations in the water layer covering the needles thereby introducing leaching through diffusion. This would suggest that canopy exchange can be a highly dynamic process with uptake in the initial stages and leaching of the same ion at the end of (long-lasting) events. The chemical exchange rate in the initial phase of an event in this case strongly depends on the amount of dry deposition accumulated in the antecedent

dry period. This explanation would be in accordance with findings of Wilson (1992) who found foliar uptake and release of N in pine shoots depending on the concentration gradient between rain solution and either symplast or apoplast.

As already stated in chapter 2, K^+, Ca^{2+} and Mg^{2+} in throughfall are considered the result of both dry deposition and leaching from plant tissue. To obtain more insight in the process of canopy leaching, ratios of these cations to Na^+ were calculated as Na^+ is considered to be solely the result of sea salt deposition. Results for some sequentially sampled throughfall events are presented in Figure 3. The contribution of K^+ to throughfall relative to Na^+ decreased in the first 2 mm of the event after which the ratio increased during the rest of the event. The corresponding ratios of Ca^{2+} and Mg^{2+} to Na^+ generally declined steadily (Figure 3). The initial decline in the ratio of K^+ to Na^+ is obtained because the sequential K^+ curve is steeper than the Na^+ curve, suggesting that there is a large pool of K^+ and/or that the K^+ which is dry deposited is washed off more easily in the initial stage of the event and/or that Na^+ perhaps is better bound to external ion pools in the foliage. When the contribution of K^+ to throughfall relative to Na^+ starts to increase the sequential curve for Na^+ becomes more steep than the K^+ curve. K^+ is known to be very mobile within the plant tissue (Tukey, 1970), but the internal ions must penetrate the plant cuticle to enter into the throughfall which might delay the leaching process (Hansen et al., 1994). In contrast to K^+, the constant decline in the Ca^{2+}/Na^+ and Mg^{2+}/Na^+ ratios indicates that these ions were released in larger amounts in the beginning of the event compared to later. A late leaching of Ca^{2+} and Mg^{2+} which generally are regarded as more mobile within the foliage in comparison to Na^+ (Tukey, 1970; Schaefer & Reiners, 1990), could contribute to the decline in the ratios. Shortage of Ca^{2+} and Mg^{2+} in the foliage as a result of the low soil nutrient status at Speuld (de Visser et al, 1994) might also influence the slower release of internal ions (Hansen et al., 1994).

4.4. Deposition estimates from micrometeorological measurements and inferential modelling

Summed for the period 23 November 1992 - 10 May 1993, the dry and fog deposition estimate for NO_y is approximately twice as large as the net throughfall flux of NO_3^- (Table III). Dry and fog deposition estimates for SO_x, NH_x, Na^+, Cl^- and Mg^{2+} are not significantly different from corresponding net throughfall fluxes (paired t-test, one tailed, $\alpha = 0.05$). For K^+ and Ca^{2+}, dry and fog deposition estimates are significantly smaller (89% and 36%, respectively) than corresponding net throughfall fluxes. This is probably the result of the contribution of canopy leaching to the net throughfall flux of K^+ and Ca^{2+}. If net throughfall fluxes of base cations are corrected for canopy exchange using the canopy exchange model of Ulrich (1983) and Van der Maas & Pape (1991), very reasonable agreement is found with dry and fog deposition estimates (Table III). Corrected net throughfall fluxes of Ca^{2+} and Mg^{2+} were somewhat smaller than corresponding dry and fog deposition estimates (Table III),

which is probably due to the overestimation of the contribution of canopy leaching to the net throughfall fluxes of Ca^{2+} and Mg^{2+} by the exchange model.

For the 16 individual throughfall collections performed between 23 November 1992 and 10 May 1993 no significant relationships are found when comparing dry and fog deposition estimates derived from micrometeorological measurements and inferential modelling with the corresponding net throughfall fluxes. To a large extend this can be explained by incomplete wash off of dry deposition from the canopy by rain, through which no independent samples are obtained. Moreover, in several periods concentration measurements have a relatively small time coverage through which dry deposition estimates are subject to large potential error. Four periods can be distinguished in which complete wash off of dry deposition could be guaranteed (Van Leeuwen & Bleuten, 1994). For these periods the SO_x dry and fog deposition estimate relates significantly (r=0.997; p=0.002) to the net throughfall flux of SO_4^{2-}. For other components no significant relationships are found.

	SOx	NOy	NHx	Na	Cl	Ca	K	Mg
gas	663	356	1443	0	0	0	0	0
aerosol	216	414	645	599	885	101	34	118
cloud water	34	23	96	2	4	1	1	0
total	913	793	2184	599	889	102	35	118
	SO4	NO3	NH4	Na	Cl	Ca	K	Mg
netTF	924	394	1728	692	802	159	305	138
netTF cor.	924	394	1983	692	802	86	35	98

Table III Deposition estimates for the Speulder forest from micrometeorological measurements and inferential modelling for the period 23 November 1992 - 10 May 1993 (in $mol.ha^{-1}.a^{-1}$). Net throughfall estimates for this time period are presented as well. Moreover, net throughfall fluxes corrected for canopy exchange by the exchange model of Ulrich (1983) and Van der Maas & Pape (1991), are presented.

Observed differences between dry and fog deposition estimates from micrometeorological measurements and inferential modelling on the one hand and net throughfall fluxes on the other hand can not be regarded exclusively due to canopy exchange but may also be the result of measuring artifacts. Dry deposition estimates from micrometeorological measurements and inferential modelling are uncertain through errors in the air concentration measurements (Arends et al., 1994), their sometimes small time coverage (Erisman et al., 1994) and the uncertainties associated with the parametrization of the dry deposition velocities (Erisman et al., 1994; Ruijgrok et al, 1994). Especially dry deposition estimates of NO_y are subject to relatively large uncertainty (Erisman et al., 1994). Uncertainties in fog deposition estimates are associated with the estimation of water fluxes and the measurement of the

average chemical composition of the fog droplets (Vermeulen et al., 1994). Uncertainties associated with the throughfall method when used for estimating dry and fog deposition include the dry deposition to the forest floor and understorey vegetation, dry deposition directly onto the throughfall gutters, the representatively of the throughfall sampling, the wet deposition estimate, the stemflow contribution and canopy exchange processes (Draaijers & Erisman, 1993). With canopy exchange processes being the only exception, mentioned factors probably contributed only to a very small extent to the uncertainty in the throughfall dry and fog deposition estimates in this study.

4.5. Surface wash experiments using Douglas-fir and artificial twigs

From laboratory experiments it was concluded that the rinsing method used removed on average 89% and 86% of the accumulated material from the Douglas-fir and artificial twigs, respectively (Römer & Te Winkel, 1994). Rinsing should ideally be performed after dry periods of several days, but only three such periods could be distinguished. In the seven other measurement periods needle wetness occurred as a result of (light) drizzle and/or fog (Römer & Te Winkel, 1994). Generally, the amount of material accumulated on the twigs was found to increase with height in the canopy (Römer & Te Winkel, 1994). Significant relationships ($p< 0.05$) are found between the amount rinsed from Douglas-fir twigs and artificial twigs, K^+ being the only exception (Figure 4). Averaged over all measurement periods and integrated over the whole canopy (using LAI per canopy stratum), the amount of K^+ and Ca^{2+} rinsed from Douglas-fir twigs is 52% respectively 23% larger than the amount rinsed from artificial twigs (Figure 5a). For all other ions no significant differences are found between the amount rinsed from Douglas-fir and artificial twigs, respectively (paired t-test, one tailed, $\alpha = 0.10$). When only measurement periods with dry conditions are considered, for all ions (except Ca^{2+}) significantly larger amounts are rinsed from Douglas-fir twigs in comparison to artificial twigs (Figure 5b). For measurement periods with drizzle and/or fog, significantly larger amounts of K^+ and Ca^{2+} and significantly smaller amounts of SO_4^{2-}, NO_3^-, NH_4^+, Na^+ and Cl^- are rinsed from Douglas-fir twigs (Figure 5c).

During dry periods, the migration of substances in the transpiration stream may result in an accumulation on the surface of Douglas-fir needles. Under dry circumstances gaseous deposition will mainly (except for HNO_3) be controlled by stomatal uptake (Erisman et al., 1994) which will only be relevant for real twigs. The fate of gases adsorbed to foliar tissues is uncertain as they may be permanently retained (through incorporation into amino-acids and/or translocation to other parts of the tree), leached (through diffusion and/or ion-exchange) or re-emitted to the atmosphere. When gases are permanently retained or re-emitted to the atmosphere, they will not be measured in the rinsing solution of Douglas-fir twigs. Particle deposition may differ as a result of differences in wettability, stickiness and/or surface geometry of Douglas-fir and artificial twigs, respectively. However, the amount of material

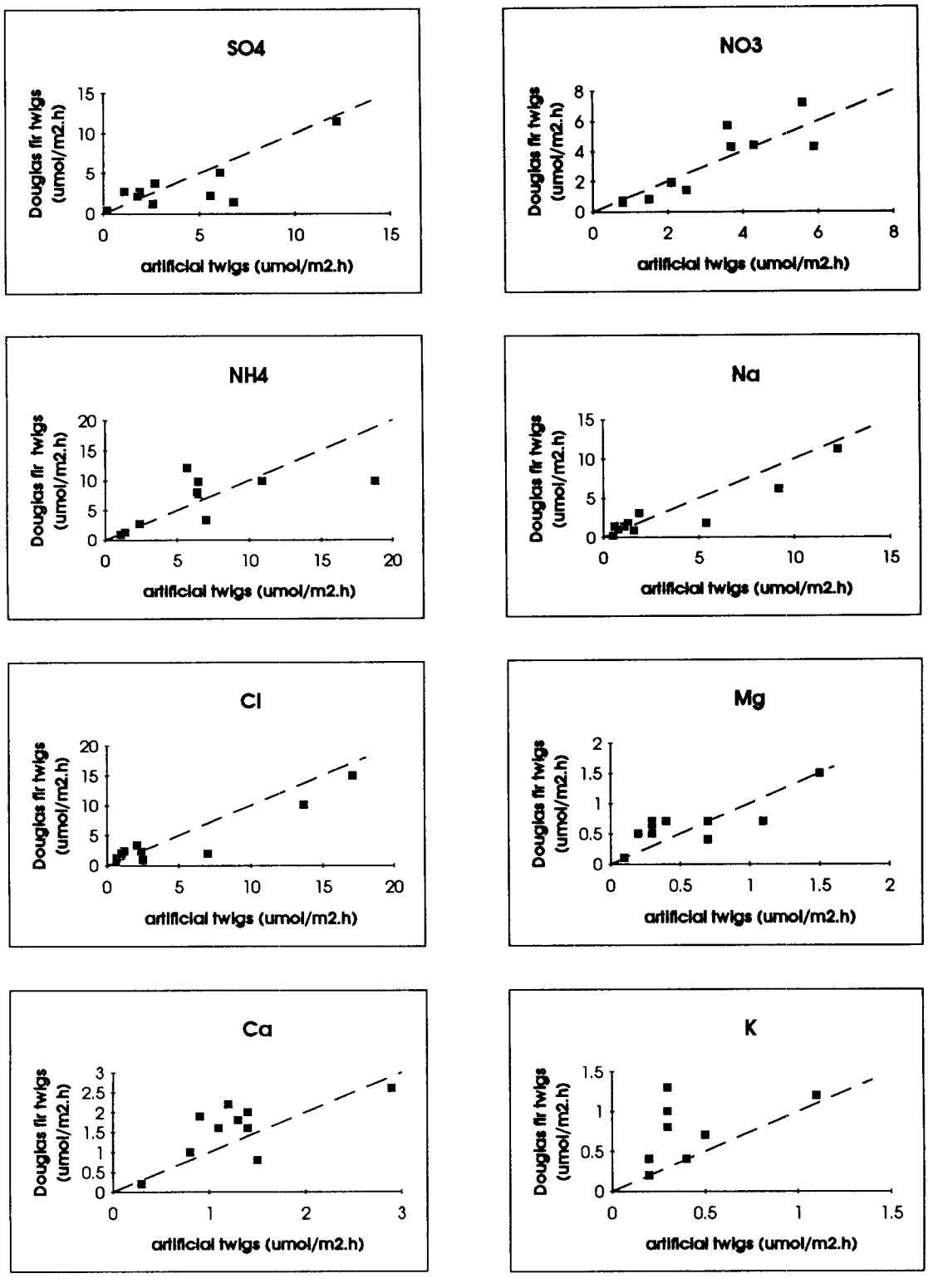
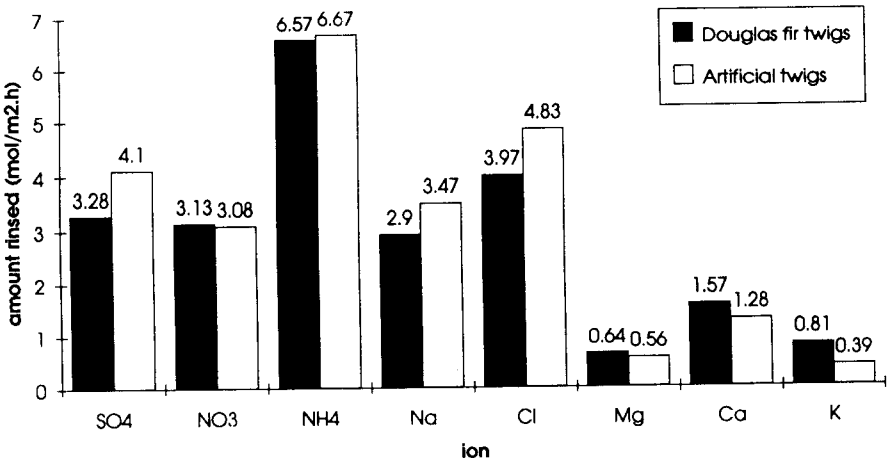
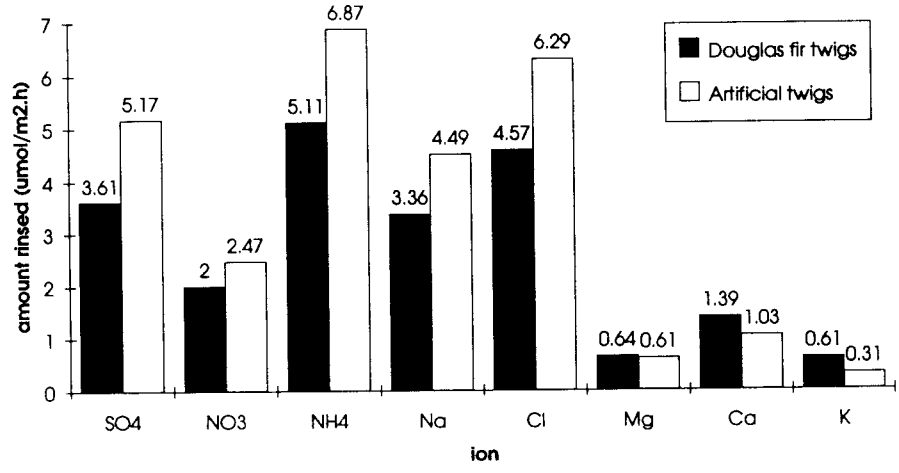


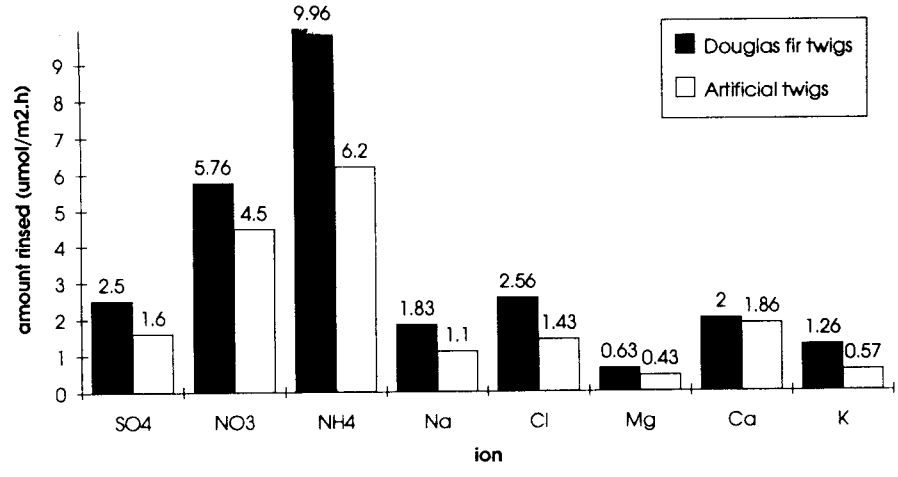
Figure 4 Relationship between the amount rinsed from Douglas-fir and artificial twigs, respectively. Amounts are integrated over the whole canopy (in $\mu mol/m^2$ ground area. hour). The dashed line represents the 1:1 relationship.



(a)



(b)



(c)

Figure 5 The amount rinsed from Douglas-fir and artificial twigs, respectively, averaged for (a) all measurement periods, (b) averaged for periods with dry conditions and (c) averaged for periods with light drizzle and/or fog. Amounts are integrated over the whole canopy (in μmol/m^2 ground area. hour).

rinsed from artificial twigs during measurement periods with dry conditions corresponded very well with modelled dry deposition (Ruijgrok et al., 1994), suggesting that under these circumstances artificial twigs represent real Douglas-fir twigs reasonably well.

During periods with needle wetness, canopy leaching will be relatively intense (Schaefer & Reiners, 1990), explaining the large amounts of K^+ and Ca^{2+} rinsed from Douglas-fir twigs in comparison to artificial twigs (Figure 5c). Moreover, some uptake of NH_4^+ and probably NO_3^- in solution may be expected (see chapter 2.2). Gaseous deposition will mainly take place in the water layer covering the surface and, for this reason, will not be different for Douglas-fir and artificial twigs unless their wettability differs. Field observations showed that after fog, rain or dew formation artificial twigs remained wet for a considerable longer time period than did Douglas-fir twigs. As a consequence gaseous deposition amounts on artificial twigs will be relatively large, which may explain the relatively large accumulation of acidifying compounds on artificial twigs in comparison to Douglas-fir twigs during periods with drizzle and/or fog. Moreover, the retention of (sea salt) particles will be more efficient on artificial twigs, which may explain the relatively large amounts of Na^+ and Cl^- rinsed from artificial twigs. For Mg^{2+}, increased leaching from Douglas-fir twigs probably counterbalanced the more efficient retention of Mg^{2+} containing particles on artificial twigs, resulting in no significant difference between the amount rinsed from Douglas-fir and artificial twigs, respectively, during periods with drizzle and/or fog (Figure 5c).

The rinsing experiments had a time coverage of only 25% and were made mainly in the winter period when the vegetation in physiologically less active and usually covered with a waterfilm. Differences between real and artificial twigs may therefore not be representative for the whole year or even the measurement period.

4.6. S^{35} nutrition experiment

The specific activities of needles and water-leachable sulphur were found about equal and showed similar trends with time (Wyers et al., 1994). This indicated that isotopic equilibrium was obtained, i.e. that the specific radioactivity was about equal for the total and the water-leachable sulphur pool in the needles. The relative contribution of foliar leaching of root-derived sulphate to sulphate in throughfall calculated from the ratio of the ^{35}S specific activity of sulphate and the water-leachable sulphur from the canopy is presented in Figure 6. The contribution of leaching of root-derived sulphur to sulphate in throughfall equals on average approximately 3%. Only during one occasion (November 1993), the relative contribution is found larger than 10%. These results are similar to those obtained for Red Maple and Yellow Poplar trees in the USA (Garten et al., 1988) and Scotch pine trees in Scotland (Cape et al., 1992). No significant effect of doubling of the annual deposition of ammoniumsulphate on root-derived sulphur leaching is found (Wyers et al., 1994).

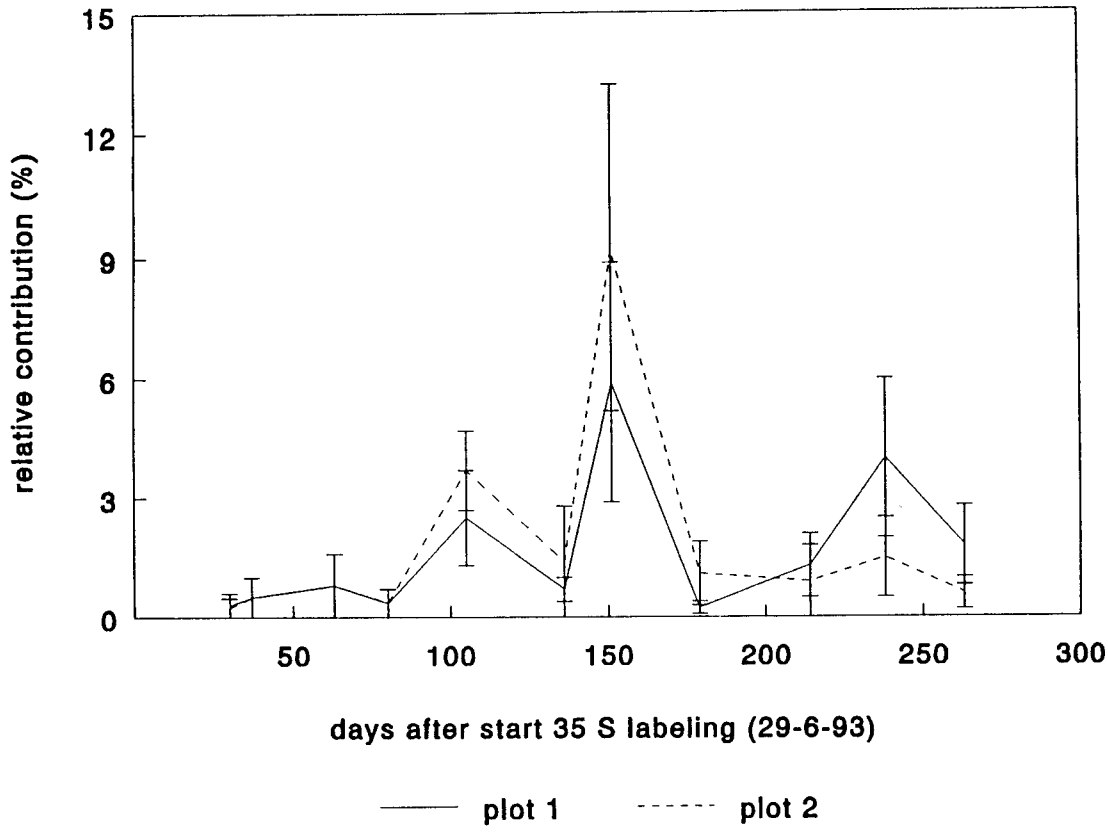


Figure 6 Contribution of leaching of soil-derived sulphate to the throughfall flux of SO_4^{2-} expressed as the ratio of the ^{35}S specific activity of sulphate in throughfall and the water-leachable sulphur from the canopy at any time after the start of the ^{35}S labelling (in %). Plot 1 received an amount equal to the yearly mean deposition of ammonium and sulphate, whereas plot 2 was fertilized with twice this amount.

It was assumed that by soaking freshly collected needles for 24h in water, the 'leachable' portion of root-derived sulphur was extracted from the needles (Wyers et al., 1994). Most likely, the water extract will also contain some dry deposited SO_2 and SO_4^{2-} aerosols, resulting in some dilution of the root-derived ^{35}S labelled 'leachable' sulphate with unlabelled dry deposited sulphur. If so, the specific activity of sulphate measured in the extract is not representative for the root-derived leachable sulphate. This effect will increase if sampling of needles is preceded by long dry periods. The relative contribution of foliar leaching to sulphate in throughfall as presented in Figure 6 should therefore be regarded as upper limit for leaching of root-derived sulphur (Wyers et al., 1994). It is currently under investigation if better results are obtained if the soaking of the needles for 24h is preceded by washing for a few seconds or minutes, thereby removing a considerable part of the dry deposition on the needles (Wyers et al., 1994).

5 SYNTHESIS

5.1. Canopy exchange estimates for the Speulder forest

No significant differences were found between the dry and fog deposition estimates of SO_x and the net throughfall fluxes of SO_4^{2-}. Moreover, no significant differences were found between the amount of SO_4^{2-} rinsed from Douglas fir and artificial twigs, respectively. The S^{35} nutrition experiment indicated that leaching of soil-derived sulphur contributed about 3% (80 $mol.ha^{-1}.a^{-1}$) to the throughfall flux of SO_4^{2-} at the Speulder forest. Using a stomatal uptake model developed by Bouten & Bosveld (1992), stomatal uptake of SO_2 was estimated to constitute 5% (36 $mol.ha^{-1}.a^{-1}$) of the total dry deposition of SO_2 (Erisman et al., 1994). When opposed to the total atmospheric deposition of sulphur, it may be concluded that at the Speulder forest sulphur behaves more or less conservative, with SO_2 uptake balancing leaching of soil-derived sulphur (Table IV).

Differences found between NO_y dry and fog deposition estimates and NO_3^- net throughfall fluxes would suggest that approximately 50% (399 $mol.ha^{-1}.a^{-1}$) of the total NO_y deposition is irreversibly retained within the canopy (Table IV). Canopy foliage is, in principle, capable to absorb and incorporate gaseous NO_2, HNO_2 and HNO_3, as well as NO_3^- in solution. At the Speulder forest, stomatal uptake as estimated with the model of Bouten & Bosveld (1992) was found to constitute 100%, 11% and 0% of the total NO_2, HNO_2 and HNO_3 dry deposition, respectively (Erisman et al., 1994). The sum of the stomatal uptake of these compounds equalled 128 $mol.ha^{-1}.a^{-1}$. No significant differences were found between the amount of NO_3^- rinsed from Douglas-fir and artificial twigs, respectively, indicating uptake of NO_3^- in solution of no or only little importance. This leaves an inexplicable gap of 270 $mol.ha^{-1}.a^{-1}$ between the NO_y dry and fog deposition estimate and the NO_3^- throughfall flux.

Differences found between the dry and fog deposition estimates of NH_x and the net throughfall fluxes of NH_4^+ were statistically not significant. According to the canopy exchange model of Ulrich (1983) and Van der Maas & Pape (1991) canopy uptake of NH_4^+ at the Speulder forest amounts 255 $mol.ha^{-1}.a^{-1}$. This is larger than the amount of NH_3 estimated to deposit through stomatal uptake, 139 $mol.ha^{-1}.a^{-1}$, i.e. 10% of the total dry deposition of NH_3 (Erisman et al., 1994). The difference (116 $mol.ha^{-1}.a^{-1}$) is assumed to be due to uptake of NH_4^+ in solution although results from the rinsing experiments indicate that at the Speulder forest this process is of limited importance: no significant differences were found between NH_4^+ amounts rinsed from Douglas-fir and artificial twigs, respectively.

Dry and fog deposition estimates of Na^+, Cl^- and Mg^{2+} were found not significantly different from corresponding net throughfall fluxes. Moreover, no significant differences existed between the amounts of Na^+, Cl^- and Mg^{2+} rinsed from Douglas-fir and artificial twigs, respectively. The canopy exchange model of Ulrich (1983) and Van der Maas & Pape

(1991) suggests that Mg^{2+} leaching equals 41 mol.ha^{-1}.a^{-1} but the model is assumed to slightly overestimate the real leaching amount of Mg^{2+} at the Speulder forest. In all, it may be concluded that at the Speulder forest canopy exchange of Na^+ and Cl^- is negligible and canopy leaching of Mg^{2+} small (< 40 mol.ha^{-1}.a^{-1}) (Table IV).

At the Speulder forest leaching of K^+ is considerable. A comparison with dry and fog deposition estimates has revealed that 89% (270 mol.ha^{-1}.a^{-1}) of the net throughfall flux of K^+ results from canopy leaching. This is in good agreement with the leaching of K^+ calculated with the canopy exchange model of Ulrich (1983) and Van der Maas & Pape (1991) (270 mol.ha^{-1}.a^{-1}). Somewhat lower K^+ leaching was calculated with the multiple regression model of Lovett & Lindberg (1984) (190 mol.ha^{-1}.a^{-1}), perhaps the result of the exudation of K^+ which appears as dry deposition in the model. Surface wash experiments indicate a K^+ leaching amount of only 104 mol.ha^{-1}.a^{-1}. This large deviation from the other estimates (around a factor of 2.5) is probably due to the relatively small time coverage of these experiments through which results are not representative for the whole measurement period.

Comparing dry and fog deposition estimates with net throughfall fluxes has revealed that 36% (57 mol.ha^{-1}.a^{-1}) of the net throughfall flux of Ca^{2+} may be the result of canopy leaching. This corresponds reasonably well with the Ca^{2+} leaching amount calculated with the model of Ulrich (1983) and Van der Maas & Pape (1991) (73 mol.ha^{-1}.a^{-1}), especially taken into account that this model slightly overestimates the real leaching amount of Ca^{2+} at the Speulder forest. As for K^+, the Ca^{2+} leaching amount calculated from surface wash experiments (30 mol.ha^{-1}.a^{-1}) is probably too low. Canopy leaching of Ca^{2+} at the Speulder forest may then be assumed to range between 50 and 75 mol.ha^{-1}.a^{-1}.

Canopy retention of H^+ as estimated with the exchange model of Ulrich (1983) and Van der Maas & Pape (1991) (181 mol.ha^{-1}.a^{-1}) agrees well with the H^+ canopy uptake calculated with the multiple regression model of Lovett & Lindberg (1984) (200 mol.ha^{-1}.a^{-1}).

	SO4	NO3	NH4	Na	Cl	Mg	Ca	K	H
Model Van der Maas & Pape (199	x	x	-255	x	x	41	73	270	-181
Model Lovett & Lindberg (1984)	x	x	x	x	x	x	x	190	-200
Model Bouten & Bosveld (1992)	-36 a)	-128 b)	-139 c)	x	x	x	x	x	x
Dry+fog dep. versus net throughfal	nil	-399	nil	nil	nil	nil	57	270	x
Rinsing experiments	nil	nil	nil	nil	nil	nil	30	104	x
S-35 experiment	80	x	x	x	x	x	x	x	x

a) stomatal uptake of SO2
b) stomatal uptake of NO2, HNO2 and HNO3
c) stomatal uptake of NH3
x = no information

Table IV Canopy exchange rates for the Speulder forest derived from different field experiments and canopy exchange models performed during the period 23 November 1992 and 10 May 1993 (in mol.ha^{-1}.a^{-1}). '+' denotes leaching, '-' denotes uptake.

Comparing results given in Table III with canopy exchange rates presented in Table IV, it becomes apparent that at the Speulder forest differences observed between soil loads and deposition fluxes to a major extent are the result of canopy exchange. For closing the gap between the soil load of NO_3^- and the deposition flux of NO_y, however, additional research is necessary. Further knowledge on canopy exchange may be obtained by e.g. using tracers (^{15}N) in ecosystem studies. At the same time, NO_2, HNO_2, HNO_3 and NO_3^- dry deposition estimates from micrometeorological measurements and inferential modelling need to be improved (Erisman et al., 1994).

The total above-ground uptake of inorganic nitrogen compounds at the Speulder forest amounted 385 $mol.ha^{-1}.a^{-1}$. This is only slightly larger than uptake amounts reported by e.g. Ivens (1990) and Johnson & Lindberg (1992) for locations receiving considerably less N deposition. The moderate behaviour of the Speulder forest with respect to above-ground N uptake may be due to *i)* the relatively high N content of the foliage at the Speulder forest through which passive diffusion of NH_4^+ and NO_3^- from the rain solution to either symplast or symplast will be relatively small (Wilson, 1992), and/or *ii)* re-emission of previously deposited N compounds. Erisman & Wyers (1993), for example, observed significant re-emission of NH_3 from stomata at the Speulder forest. In their study, NH_3 emission was measured during dry conditions (relative humidity below 70% and no precipitation for at least eight hours) at day time (global radiation above 350 $W.m^{-2}$), with NH_3 air concentrations smaller than 2-8$\mu g/m^3$. If forests receiving large N loads from the atmosphere are able to regulate to some extent their above-ground N uptake, this may have important consequences for our risk assessment of direct effects near local sources (e.g. intensive animal husbandries and highways).

5.2. *Generalisation of measurement results*

Field experiments at the Speulder forest were mainly performed in the winter period (November until May) when the vegetation is physiologically less active and frequently wet. By scaling measurement results to one year (Table IV), stomatal uptake is probably underestimated. The effect of measuring only in the winter period on uptake and leaching in solution is more difficult to assess. The more frequent occurrence of waterfilms in the winter period may to some extent have counterbalanced the effect of the low physiological status of the vegetation. Leaching of K^+, Ca^{2+} and Mg^{2+} as estimated with the canopy exchange model of Ulrich (1983) and Van der Maas & Pape (1991) (Table I) was 38%, 46% and 34%, respectively, smaller than leaching amounts found for the Speulder forest by Van der Maas & Pape (1991), using the same model but now for a three year measurement period (March 1987 up to March 1990). The canopy uptake estimated for NH_4^+ was 58% smaller and the uptake of H^+ 91% larger than the uptake amounts reported by Van der Maas & Pape (1991). Differences in canopy uptake were, in part, the result of the larger ratio of canopy uptake

efficiency between H^+ and NH_4^+ used in this study ($CU_H/CU_{NH4} = 6$) compared to the one used by Van der Maas & Pape (1991) ($CU_H/CU_{NH4} = 1$). During the measurement period no episodes with winter smog, frost, drought or an insect plague occurred. Such stress factors may intensify canopy exchange processes considerably.

Canopy exchange rates for the Speulder forest can not directly be considered representative for other forests in the Netherlands. Canopy exchange is found to depend on tree species and ecological setting. Table V presents canopy exchange estimates for thirty forest stands at 'de Utrechtse Heuvelrug' growing on dry sandy soils, low in exchangeable base cations and low in acid neutralizing capacity (after Draaijers, 1993). Estimates are based on throughfall measurements and results of the canopy exchange model of Ulrich (1983) and Van der Maas & Pape (1991). A considerable variability can be observed, leaching of Mg^{2+}, Ca^{2+} and K^+ varying between -4 and 104 $mol.ha^{-1}.a^{-1}$, 82 and 187 $mol.ha^{-1}.a^{-1}$, and 168 and 1086 $mol.ha^{-1}.a^{-1}$, respectively. Uptake of H^+ and NH_4^+ was found to vary between 78 and 755 $mol.ha^{-1}.a^{-1}$, and 48 and 454 $mol.ha^{-1}.a^{-1}$, respectively. Comparable canopy exchange rates were found for Douglas-fir and Scots pine stands, respectively, while Pedunculate oak stands revealed significantly larger exchange rates. As already suggested by Smith (1981), deciduous forests experience larger canopy exchange in comparison to coniferous forests. With Ca^{2+} and NH_4^+ being the only exceptions, canopy exchange rates calculated for the Speulder forest are within the range of exchange rates derived for the nine Douglas-fir forests at de Utrechtse Heuvelrug (Table V). In general, Dutch forests will experience nil canopy exchange of SO_x, Na^+ and Cl^-.

		Mg	*Ca*	*K*	*H*	*NH4*
Douglas	mean	22	119	392	-264	-171
(n=9)	stdev	15	20	156	68	44
	min	-4	99	193	-95	-63
	max	50	162	658	-318	-209
Pine	mean	11	106	297	-168	-103
(n=10)	stdev	8	21	97	81	51
	min	-4	82	168	-78	-48
	max	25	141	531	-307	-193
Oak	mean	68	124	749	-631	-374
(n=11)	stdev	18	25	170	74	47
	min	45	94	519	-535	-305
	max	104	187	1086	-755	-454
Speuld	mean	41	73	270	-181	-255

Table V Canopy exchange rates for nine Douglas-fir, ten Scots pine and eleven Pedunculate oak stands at the Utrechtse Heuvelrug derived from throughfall measurements during the period 17 May 1990 and 30 April 1991, in combination with the canopy exchange model of Ulrich (1983) and Van der Maas & Pape (1991) (in $mol.ha^{-1}.a^{-1}$). '+' denotes leaching, '-' denotes uptake. The exchange rates for the Speulder forest are presented as well.

The climatic conditions during the measurements did not favour the application of the multiple regression model of Lovett & Lindberg (1984). Moreover, the simple formulation of the model was found subject to a number of caveats. In contrast, the model of Ulrich (1983) & Van der Maas & Pape (1991) has proven to be a useful tool for determining the impact of canopy exchange on throughfall fluxes at the Speulder forest. The combination of throughfall measurements and this model resulted in deposition estimates which were similar to deposition estimates derived from micrometeorological measurements and inferential modelling. Unfortunately, several basic assumptions in the model of Ulrich (1983) and Van der Maas & Pape (1991) are not properly evaluated under different environmental conditions (ecological setting, pollution climate). This limits the models utility up to now to forest stands growing on dry and sandy, nutrient poor podzolic soils under current air pollution levels. The model can be improved by taken into account the different mass median diameters of Mg^{2+}, Ca^{2+} and K^{+} containing particles compared to Na^{+} containing particles in the calculation of the dry deposition factors. Moreover, stomatal uptake of NO_2 and HNO_2 has to be included in the model.

If the model of Ulrich (1983) and Van der Maas & Pape (1991) is evaluated for different environmental conditions, the 'throughfall method' will become an increasingly attractive tool for *i)* process oriented studies on deposition (e.g. studies on the spatial variability of atmospheric deposition and the impact of complex terrain), *ii)* the validation of deposition models like DEADM (Erisman, 1992) and EDACS (Van Pul et al., 1994; Erisman et al., 1994), and *iii)* the monitoring of atmospheric deposition. Within the framework of the UN/ECE International Cooperative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP-forests), a throughfall monitoring network is being set up with the aim to monitor atmospheric deposition at 300 forest sites scattered over Europe (Landmann, 1993). An important advantage of the throughfall method is the allowance of long-term continuous monitoring of a wide range of elements (sulphur, nitrogen, base cations) at relatively low costs. This makes the throughfall method well suited for monitoring deposition at a large number of sites, provided that canopy exchange rates can be quantified. Deposition estimates from micrometeorological measurements and inferential modelling can be used for validation purposes. Specific sampling criteria should be met to obtain useful results from throughfall measurements (Beier & Rasmussen, 1989; Kostelnik et al., 1989; Ivens, 1990; Draaijers, 1993).

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