

Surface/atmosphere exchange of ammonia over grazed pasture

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PROEFSCHRIFT

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Stellingen

behorende bij het proefschrift

"Surface/atmosphere exchange of ammonia over grazed pasture"

van M.A.H.G. Plantaz

1. Het resultaat van emissie geschat met in het ammoniakbeleid toegepaste emissiefactoren en depositie berekend volgens de 'Big Leaf' benadering uit het OPS-model geeft alleen op jaarbasis een redelijke schatting van de netto-uitwisseling tussen begraasd weiland op veengrond en de atmosfeer. Overschatting van emissie in het weideseizoen wordt dan gecompenseerd door overschatting van depositie in de stalperiode.
Dit proefschrift; OPS model: zie J.A. van Jaarsveld (1995) 'Modelling the long-term atmospheric behaviour of pollutants on various spatial scale'.
2. Emissiefactoren voor ammoniak uit mest-aanwending zijn waarschijnlijk te hoog voor veengrond. Deze emissiefactoren zullen mogelijk regionaal gedifferentieerd moeten worden rekening houdend met grondsoort en/of pH.
Dit proefschrift.
3. Emissie uit de stomata van het gras levert een niet verwaarloosbare bijdrage aan de uitwisselingsflux van ammoniak tussen beweid grasland op veengrond en de atmosfeer. Deze uitwisseling kan daarom met het canopy compensation point-model ('bladerdak-compensatiepunt-model') van Sutton en Fowler beter beschreven worden dan met de in transport-modellen gangbare 'Big Leaf'-beschrijving.
Dit proefschrift. Canopy compensation point model: zie M.A. Sutton and D. Fowler (1993) 'A model for inferring bi-directional fluxes of ammonia over plant canopies' In: WMO/GAW-91, WMO Geneve.
4. Vorming of dissociatie van NH_4NO_3 kan door beïnvloeding van de gradiënten van NH_3 , HNO_3 , en NH_4NO_3 tot foutieve fluxberekening van deze componenten leiden. In ammoniak-emissiegebieden zijn de gradiënten van NH_3 op molaire basis echter veel groter dan die van beide andere componenten zodat fluxen van NH_3 daar weinig vertekend zullen worden.
Y. Zhang, H. ten Brink, S. Slanina, and G.P. Wyers (1995) 'The influence of ammonium nitrate equilibrium on the measurement of exchange fluxes of ammonia and nitric acid' In: Studies in Environmental Science 64., RIVM Bilthoven; zie ook dit proefschrift.

5. Het 'Besluit chemische waterrijen milieubeheer' geeft in de praktijk onvoldoende bescherming aan bewoners van woningen boven waterrijen tegen het doorlekken van tetrachlooretheen ('PER'), omdat de voorgeschreven dampdichtheid van scheidingswanden en -plafonds niet nader is omschreven noch van toetsingscriteria is voorzien.
(Besluit chemische waterrijen milieubeheer, 1990; cf. T.Fast, GG en GD Amsterdam (1993) De blootstelling aan tetrachlooretheen (PER) van omwonenden van chemische waterrijen voorzien van een gesloten systeem; en recent, nog te publiceren onderzoek in Rotterdam door de DCMR Milieudienst Rijnmond.).
6. De door voortvarende bestuurders vaak gehekelde bloei van het 'nimby' (not in my back-yard)-principe duidt erop dat de burgers de slogan 'een beter milieu begint bij jezelf' vooral als een toezegging betreffende hun persoonlijke adres zijn gaan zien.
7. Het kunnen ontstaan van het millennium-probleem suggereert dat veel software-producenten beschikken over een gering anticipatievermogen of over een apocalyptische toekomstvisie. In beide gevallen is op de elektronische snelweg goed uitkijken geboden.
8. Wanneer over beperking van vliegtuiglawaai rond Schiphol wordt gedebatteerd, bedekt men in Zuid-Limburg, Rotterdam en Eindhoven alvast veiligheidshalve de oren.
9. Milieuproblemen zijn doorgaans een kwestie van verstoorde evenwichten. Overeenkomstig hiermee is er meestal een onbalans tussen het aantal opgeleide milieudeskundigen en het aantal beschikbare banen.
10. Behalve als manifeste bron van milieuproblemen dient het automobiel toch ook eens genoemd te worden als onmisbaar hulpmiddel bij veel milieu-onderzoek.
11. Wie de droge depositie van ammoniak wil meten gaat een turbulente fase tegemoet.
12. Gebruik van de trein voor het bijhouden van vakliteratuur kan tot ernstige omwegen aanleiding zijn.
(Cf. T. van Vliet (1995), stelling bij 'Intestinal absorption and cleavage of β -carotene in rat, hamster and human models': "zij die moeite hebben hun vakliteratuur bij te houden kan worden geadviseerd zoveel mogelijk per trein te reizen").

Wageningen, 2 september 1998

List of errata

in "Surface/atmosphere exchange of ammonia over grazed pasture"
by M.A.H.G Plantaz

page	line	error	should be replaced by
ii	4	dr. E.Adema	dr. E.H. Adema
xv	32	$\text{mol l}^{-1} \text{Pa}^{-1}$	-
3	19	(Borrell, 1989)	(Borrell, 1993)
6	23	(Van Elzakker <i>et al.</i> 1994)	(Van Elzakker <i>et al.</i> 1995)
7	27	(Erisman, 1993b)	(Erisman 1993)
9	31	(Erisman <i>et al.</i> , 1995)	(Erisman and Draaijers, 1995)
11	2	(Wouters, 1994)	(Wouters <i>et al.</i> 1994)
19,22	9/33	(Van Hove <i>et al.</i> 1989)	(Van Hove, 1989)
	13	(Van Hove and Adema, 1995)	(Van Hove and Adema, 1996)
24	28	Table E.2	Table E.1
28	29	1.2.4	1.2.3
40	21	From eqs. 2.5, 2.8, 2.10 and 2.11	From eqs. 2.6, 2.9, 2.11 and 2.13
42	7	see 2.2.3	see 2.2.2.
45	21	[subscripts above eq. 2.31]:	z_0/z_s
53	13	[below eq. 2.39] cf. eq.2.27...	cf. eq. 2.37...
60	3	see also 3.4...	see also 3.2.1...
61	1	Fowler and Duyzer, 1990	Fowler and Duyzer, 1989
64	4	3.2.3	3.2.2
66	6	chapter 6	chapter 7
	27,33	Beljaars <i>et al.</i> 1990	Beljaars <i>et al.</i> 1989
66,67	38/2	4.2.1	4.2.2
71	4	0.03"	0.003"
79	16	chapter 7	chapter 8
	31	(Press <i>et al.</i> 1989)	(Press <i>et al.</i> 1990)
80	10	see 3.3.2	see 3.2.2
81	16	see 3.4.3.4	see 4.1.1
118	2,17	(eq. A.3)	(eq. A.2)
127	29	[last sentence:] see 2.4	see 2.5
170	31	[2nd ref. Chamberlain], A.C.(1966)	, A.C. (1968).
172		Add: Gravenhorst G. and Breiding, H.(1990). NH_3 transfer between the atmosphere and coniferous trees. In: Beilke, S. and Millan, M. (Eds.) Field measurements and interpretation of species derived from NO_x , NH_3 and VOC emissions in Europe, Air Pollution Research Report 25, p.118-146.	

Voor mijn moeder

Voorwoord

Dit voorwoord biedt mij een gelegenheid enkele persoonlijke woorden toe te voegen aan het proefschrift en aan het daarin beschreven onderzoek. Niet alleen de resultaten van het onderzoek zelf tellen in zo'n promotietijd! Daarom neem ik hier volop de ruimte om instituten en personen te danken die naar mijn gevoel direct of indirect een belangrijke betekenis hebben gehad voor mijn werk aan dit proefschrift. De volgorde van vernoeming is daarbij niet maatgevend voor een ieders betekenis.

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Het Regionaal Onderzoeks Centrum voor de Melkveehouderij (*ROC*) te Zegveld stond ons welwillend toe op het terrein van hun proefboerderij te meten. Met name *Joop Verheul* en *Karel van Houwelingen* wil ik daarvoor bedanken. Zij leverden mij ook alle gewenste gegevens over de bedrijfsvoering van de proefboerderij. Voor zijn advies voor het maken van emissieschattingen op basis van die gegevens dank ik *Klaas van der Hoek* van het RIVM. Het RIVM dank ik ook voor het mogen gebruiken van de portocabine van hun landelijk meetnet luchtverontreiniging (LML) voor onze computer, en als warme (!) schuilplaats tegen weer en wind tussen onze acrobatie op de meetsteiger door. *Jan Willem Erisman* (RIVM, ECN) en *Bernard van Elzakker* (RIVM) dank ik voor gegevens van het LML voor Zegveld (en Jan Willem ook voor zijn kritische commentaar op concept-delen van het proefschrift en voor zijn opbeurende woorden).

Voor hun directe wetenschappelijke begeleiding bij de uitvoering, interpretatie en verslaglegging van mijn onderzoek wil ik mijn beide promotoren, *Eep Adema* (LUW) en *Sjaak Slanina* (LUW/ECN), en *Paul Wyers* (ECN) en *Peter Hofschreuder* (LUW) uitgebreid bedanken. Hun allen dank ik voor hun adviezen en voor alle energie, tijd en geduld die zij hebben gestoken in onze bespreking en in het doorwerken van al mijn stukken en concepten. Eep droeg mij indertijd aan ECN voor als kandidaat-promovendus voor dit onderzoek. Dat vertrouwen is voor mij -naast Eeps inzet en belangrijke inhoudelijke inbreng-, altijd een grote stimulans gebleven om dit onderzoek ook met een goed proefschrift, als zijn promovendus af te ronden.

Sjaak was tevens mijn groepsleider (Milieu-onderzoek) bij ECN. Hij nam vooral later in de interpretatiefase en bij de verslaglegging en afronding de meest directe, 'dagelijkse' begeleiding voor zijn rekening. Zijn voortvarende en heldere benadering van complexe zaken waren zeer vormend voor mijn aanpak. Meer dan enig ander trainde Sjaak mij erin om grote en

kleine dilemma's in de interpretatie altijd vanuit een positieve houding te blijven benaderen, echter met de blik strak gericht op beantwoording van de *hoofdvragen*. In onze vele gesprekken werd aldus menige knoop krachtig en met zwier doorgemaakt, -met wetenschappelijke argumenten. Deze vaardigheid is beslist essentieel voor de voortgang van projectgebonden onderzoek (vrijwel alle onderzoek), en ik bedank Sjaak daarom hier ook nog eens voor zijn krachtige 'scholing'.

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Symbols and abbreviations

Symbols

c_0	Air concentration at surface height (surface concentration), or equivalent gas concentration in equilibrium with the surface.	$\mu\text{g m}^{-3}$
c_{0c}	Canopy compensation point	$\mu\text{g m}^{-3}$
c_{0st}	Gas concentration in the stomata = stomatal compensation point	$\mu\text{g m}^{-3}$
c_{ow}	(equivalent) gas concentration in equilibrium with water layer	$\mu\text{g m}^{-3}$
c_r	Air concentration (at reference height r)	$\mu\text{g m}^{-3}$
C_p	Specific heat of air	$(\approx 1.01) \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1}$
CV	variation coefficient	-
d	Displacement height of profile	m
D_i	Molecular diffusion coefficient of compound i	$\text{m}^2 \text{ s}^{-1}$
DF_{30}	Value of R_c (etc) which would lead to a 30% higher or lower inferred flux (than the 'best fit' value')	s m^{-1}
E	Evaporation rate	$\text{g m}^{-2} \text{ s}^{-1}$
ER_{SE}	Error derived from the propagation of SE values of average parameters from which another parameter is calculated.	-
F	Flux (without subscript: flux of pollutant)	$\text{ng m}^{-2} \text{ s}^{-1}$
F_{atm}	Net exchange flux with the atmosphere	$\text{ng m}^{-2} \text{ s}^{-1}$
F_{st}	Exchange flux through the stomata	$\text{ng m}^{-2} \text{ s}^{-1}$
F_w	Exchange flux with water layers on the leaf surface	$\text{ng m}^{-2} \text{ s}^{-1}$
F_x	Flux of any scalar property of air other than momentum	variable
g	Acceleration due to gravity	m s^{-2}
G	Ground (soil) heat flux	W m^{-2}
h	Vegetation height	m
H	Sensible heat flux	W m^{-2}
k	Von Karmann constant (0.41)	-
k_b	Alkalinity constant	-
K_e	Equilibrium constant for a given equilibrium reactions	-
k_H	Henry constant	$\text{mol l}^{-1} \text{ Pa}^{-1}$
K_i	(Eddy)- diffusivity (turbulent diffusion constant) of air property i	$\text{m}^2 \text{ s}^{-1}$
l	mixing length	m
L	Monin-Obukhov stability length scale	m
LE	Latent heat flux	W m^{-2}
L_v	Latent heat of vaporization	J g^{-1}
m	Momentum (as a scalar: in the direction of the main wind so that $m=p_s U$)	$\text{g m}^{-2} \text{ s}^{-1}$
n	Number of measurements	-
N	Number of profile heights	-
P	Production of compound within the atmosphere	$(e.g.) \text{ g s}^{-1}$
Pr	Prandtl number	(≈ 0.72)
q	Absolute humidity	g m^{-3}
q_0	Absolute humidity at surface level	g m^{-3}
q_*	Turbulent scale of absolute humidity	g m^{-3}
q_{sat}	Absolute humidity at saturation point	g m^{-3}
Q	Global radiation	W m^{-2}
R_{prof}	Regression coefficient of c versus the $\ln$ of stability corrected height	-
RH	Relative humidity	%

R_a	Aerodynamic resistance	$s\ m^{-1}$
R_b	(Quasi-)laminar boundary layer resistance	$s\ m^{-1}$
R_c	Surface resistance	$s\ m^{-1}$
R_{cu}	Cuticle resistance	$s\ m^{-1}$
R_{ef}	Effective surface resistance	$s\ m^{-1}$
R_{ext}	External leaf surface resistance	$s\ m^{-1}$
R_i	Minimum stomatal resistance for water vapour	$s\ m^{-1}$
R_{mt}	Mesophyl-transfer resistance	$s\ m^{-1}$
R_{so}	Soil resistance	$s\ m^{-1}$
R_{st}	Stomatal resistance	$s\ m^{-1}$
R_w	Water layer resistance	$s\ m^{-1}$
R_{net}	Net radiation	$W\ m^{-2}$
S	Heat storage in soil layer	$s\ m^{-1}$
Sc	Schmidt number	-
SD	Standard deviation	-
SE	Standard error	-
SVP	Saturation vapour pressure	kPa
t	Time	s
T	Temperature	$^{\circ}C, K$
T_0	Temperature at surface level	$^{\circ}C, K$
T_*	Turbulent temperature scale	$^{\circ}C, K$
T_{leaf}	Leaf temperature	$^{\circ}C, K$
T_{soil}	Soil temperature	$^{\circ}C, K$
T_{surf}	Surface temperature ($\approx T_0$)	$^{\circ}C, K$
u	Horizontal (longitudinal) wind velocity component	$m\ s^{-1}$
u_*	Friction velocity	$m\ s^{-1}$
U	Wind speed	$m\ s^{-1}$
v	Horizontal (lateral) wind velocity component	$m\ s^{-1}$
v_d	Deposition velocity	$m\ s^{-1}$
w	Vertical wind velocity component	$m\ s^{-1}$
WD	Wind direction	$^{\circ}$
x	horizontal distance (along the main wind)	m
X	Any property of air (not momentum): e.g. mass (concentration), heat (temperature), humidity)	variable
X_*	Turbulent scale of property X of air (not momentum)	variable
z	Height above the surface	m
z_0	Roughness length for momentum	m
z_s	Height of the surface for other properties than momentum	m

Greek symbols

θ	Potential temperature	$^{\circ}C, K$
θ_v	Virtual potential temperature	$^{\circ}C, K$
θ_*	Turbulent scale of potential temperature	$^{\circ}C, K$
κ	Thermal diffusivity of air	$m^2\ s^{-1}$
ν	Kinematic viscosity of air	$m^2\ s^{-1}$
ρ_a	Air density	$g\ m^{-3}$
τ	Shearing stress = flux of momentum	$N\ m^{-2}$
Φ_H	Dimensionless gradient ('stability correction') for sensible heat	-

Φ_m	Dimensionless gradient ('stability correction') for momentum	-
Φ_x	Dimensionless gradient ('stability correction') for air property X (not momentum)	-
Ψ_H	Integrated stability correction for sensible heat	-
Ψ_m	Integrated stability correction for momentum	-
Ψ_x	Integrated stability correction for air property X (not momentum)	-

Abbreviations

AMANDA	Ammonia Measurement by ANnular Denuders with online Analysis
AMOR	Ammonia MONitoR
BIATEX	Biosphere-ATmosphere EXchange of pollutants and trace substances
CBS	Central Bureau for Statistics
DLO	Department of Agricultural Research (Dienst Landbouwkundig Onderzoek)
ECN	Netherlands Energy Research Foundation (Energie onderzoeksCentrum Nederland)
EMEP	European Monitoring and Evaluation Program
EUROTRAC	European Experiment on the Transport and Transformation of Environmentally Relevant Trace Constituents in the Troposphere over Europe.
DEADM	Dutch Empirical Acid Deposition Model
DPPA	Dutch Priority Programme on Acidification
IMAG-DLO	Institute of Agricultural and Environmental Engineering (Instituut voor Mechanisatie, Arbeid en Gebouwen)
KNMI	Royal Dutch Meteorological Institute (Koninklijk Nederlands Meteorologisch Instituut)
LEI-DLO	Agricultural Economics Research Institute (Landbouw Economisch Instituut)
LML	National Air quality Monitoring Network (Landelijk Meetnet Luchtverontreiniging)
LUW	Landbouw Universiteit Wageningen (=WAU, Wageningen Agricultural University)
OPS	Operational model for Priority Substances.
RIVM	National Institute of Public Health and the Environment (Rijks Instituut voor Volksgezondheid en Milieuhygiëne)
ROC	Regional Research Centre for Cattle Farming (Regionaal Onderzoeks Centrum melkveehouderij).
TD	Thermodenuders

Summary

This thesis deals with the exchange of ammonia between the atmosphere and grazed pasture in an area of intensive livestock breeding. The term exchange is used because gaseous ammonia can be taken up (dry deposition) as well as released (emission) by this type of surface.

Ammonia exchange fluxes over the grass pasture of a research farm for dairy cattle breeding at Zegveld (the Netherlands) were measured continuously from July 1992 until July 1994. The main objective was to investigate the long term values and general patterns of the net contribution to atmospheric ammonia provided by exchange with such pastures. This is important for assessments of the export of ammonia from emission regions to natural areas that are sensitive to eutrophication and acidification.

The first chapter gives an introduction to the background and aims of the research. Some general aspects about ammonia and about its role in acidification and eutrophication are summarized; emission from slurry, fertilizer and urine patches in a pasture is treated in some more detail. Then the relevant knowledge on ammonia exchange is reviewed, and the importance of research of the exchange over grazed pasture is explained. Finally the aims and approach of the research are given.

Chapter 2 gives a summary of common mathematical descriptions of vertical transport and exchange processes in terms of resistance modelling. First the 'Big leaf' resistance framework is explained, which is commonly used to describe deposition to a surface; the resistance of the surface to uptake of ammonia is expressed in the surface resistance R_s , neglecting the surface concentration. If emission can occur from the same surface (bi-directional exchange), the resistance model is adapted to include the surface concentration. For stomatal exchange, this surface concentration may be estimated from the so-called compensation point (chapter 1). Finally the 'canopy compensation point' model by Sutton and Fowler (1993) is summarized, which describes simultaneous bidirectional exchange via the stomata and deposition to the leaf surface of vegetation.

In chapter 3 the experimental set up is described. First the location and relevant features of the site are reported. The soil type of the pasture was woody peat, with a soil pH of 4.5-5.3, and an estimated availability of nitrogen to the grass that corresponds to fertilization with about $300 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of nitrogen. Next, possible methods of flux measurement are discussed leading to the choice of the micrometeorological flux-gradient technique for the present research. The third section describes the instruments applied in the flux measurement system. Vertical profiles of NH_3 , NH_4NO_3 and HNO_3 were measured by thermodenuders; those of SO_2 by a pulsed fluorescence monitor; profiles of NH_3 were temporarily measured also by continuous flow denuders (AMANDA).

Chapter 4 reports the data processing and evaluates the uncertainty in measurements and conclusions. The procedure of flux calculation is described briefly, followed by an overview of criteria and results of selection procedures to reject unreliable measurements. In the uncertainty evaluation, first the uncertainty in a single, typical flux measurement is estimated at about 30%-35%, dominated by the random error in the concentration gradient. The uncertainty in a typical R_c is much higher according to standard error propagation rules (up to 80-100%), but in practice an uncertainty of 25-40% is appropriate. If average parameters over longer periods of time are used, random errors will partly average out; in that case the standard error of the mean is used as a measure of uncertainty. A fitting procedure to estimate representative R_c -values for a set of measurements is explained. Finally the uncertainty due to possible *biases* in average fluxes (and R_c) caused by the applied selection criteria is estimated at $\pm 25\%$.

In chapter 5, the measurements of ammonia concentrations and fluxes are used to derive the annual values and general patterns of ammonia concentrations and exchange. The mean annual concentration was $10\text{--}11 \mu\text{g m}^{-3}$ of NH_3 with clear seasonal variations (dependent on seasonal emissions in the whole region). Clear diurnal concentration patterns were also found, mainly due to diurnal variations in wind speed, atmospheric stability and mixing layer height.

The measured annual net emission of ammonia at Zegveld was relatively low, about $4.5 \text{ kg ha}^{-1} \text{ NH}_3$, as the result of net emission of $5.4\text{--}6.7 \text{ kg ha}^{-1}$ in the grazed half year (May-October) and net deposition of $0.8\text{--}1.8 \text{ kg ha}^{-1}$ in the ungrazed half year. In the grazed season, the dominant diurnal pattern of exchange consisted of net emission at daytime and net deposition at night. In the ungrazed season, deposition generally dominated both day and night. However, after slurry spreading (late winter/early spring) some periods with considerable emission occurred also in the ungrazed season.

In periods when mainly net deposition was measured and no slurry had been spread recently, the efficiency of the deposition of NH_3 was low (with high surface resistances of $35\text{--}105 \text{ s m}^{-1}$). This deposition proceeds mainly to (water layers on) the leaf surface. The high resistances are probably caused by a high pH at the leaf surface, due to the high loads of ammonia in this region.

In chapter 6 the mechanisms behind the observed bidirectional patterns of NH_3 exchange are analysed. The regular emission at daytime in the grazed season was also observed when no slurry had been applied recently and was not clearly related with actual grazing. As a first possibility, a dominant role of the leaf surface in both deposition and emission is evaluated. A compensation point approach is tested, as well as an analysis of emission as a function of previous deposition. Then the contribution of other sources than the leaf surface to the emissions is evaluated, especially the soil and the stomata. The conclusion is that the stomata play a very important role in the ammonia emission, probably due to a high nitrogen content of the grass as a result of the fertilization.

In chapter 7, the measured net emission of NH_3 from the pasture is compared with volatilization of ammonia from slurry, fertilizer and urine patches, estimated from current emission factors and farm management data for the same terrain. In the grazed season the calculated emission is two times higher than the measured emission. In transport models, the contribution of the estimated emission from pastures to atmospheric ammonia is compensated partly by the estimated deposition to the same pastures. Applying a similar approach to Zegveld, a better agreement between measured and estimated exchange can be achieved. However, this requires assumption of a too low surface resistance, and overestimation of emission in one season is then compensated by overestimation of deposition in another season. The current emission factors for ammonia appear too high for pasture on peat soil, probably due to the low soil pH of 4.8. This is important for environmental policy studies and transport models that use emission estimates based on these factors. The net contribution of this type of pasture to the ambient NH_3 concentration therefore may be overestimated. It is concluded that possibly, a regional differentiation in emission factors would be necessary.

In chapter 8 the effects of SO_2 , NH_4NO_3 and HNO_3 on ammonia exchange are investigated.

SO_2 showed efficient deposition with an average deposition velocity of 1.14 cm s^{-1} ; the mean surface resistances varied between -5 and 20 s m^{-1} (during frost: 40 s m^{-1}). The deposition proceeds mainly to the (wetted) leaf surface, and is probably enhanced by the high ammonia loads in this region causing a high pH at the leaf surface. This favours SO_2 deposition and reduces NH_3 deposition. In the grazed season, NH_3 is present in excess over SO_2 in the air (molar ratio NH_3/SO_2 of about 6), while in the ungrazed period, the molar ratio is about 4:3. This coincides with an increase in deposition efficiency for NH_3 and a (weaker) decrease in deposition efficiency for SO_2 . These relations between both compounds can be interpreted in terms of so-called co-deposition. However, no such relations could be found on shorter time scales (one or more days).

Measurements of NH_4NO_3 aerosol and HNO_3 during 15 months showed a very low average deposition velocity of NH_4NO_3 (0.12 cm s^{-1}) and an extremely high deposition velocity of HNO_3 (3.4 cm s^{-1}), higher than physically possible. Both values may reflect an influence of reaction of HNO_3 with locally emitted NH_3 to form NH_4NO_3 . The gradients of HNO_3 and NH_4NO_3 may have been biased by this reaction, leading to over-estimation of the deposition velocity of HNO_3 and underestimation of the deposition velocity of NH_4NO_3 . Because NH_3 concentrations and gradients are much higher on molar base than those of HNO_3 and NH_4NO_3 , gradients of NH_3 are not biased as much by this reaction.

In chapter 9 a parameterization of the exchange at Zegveld, based on the 'canopy compensation point model' is tested. The model parameters are fitted to periods without

influence of slurry spreading. Best results are achieved by the assumption of a concentration within the stomata (stomatal compensation point) of $19 \mu\text{g m}^{-3}$ at 20°C and values of the leaf surface resistance that depend on the surface humidity of the leaves. By application of the same parameterization to periods after slurry spreading, the measured exchange can be corrected for the contribution of canopy exchange. Evaluating the remaining emission, it is concluded that current emission factors for slurry application are probably too high for this type of soil and/or for soils with low pH, in accordance with chapter 7.

In chapter 10 the main conclusions from the research are drawn.

Samenvatting

Dit proefschrift gaat over de uitwisseling van ammoniak (NH_3) tussen de atmosfeer en begraasd weiland in een gebied met intensieve veehouderij. De term 'uitwisseling' wordt gebruikt omdat ammoniakgas niet alleen door een oppervlak kan worden opgenomen uit de atmosfeer (depositie) maar ook door hetzelfde oppervlak aan de atmosfeer kan worden afgestaan (emissie).

Tussen juli 1992 en juli 1994 werden de uitwisselings-stromen ('fluxen') van ammoniak tussen grasland en de atmosfeer continu gemeten op het terrein van een proefboerderij (melkveehouderij) te Zegveld. Het voornaamste doel was na te gaan hoe groot de netto-bijdrage is van zulke weilanden aan het ammoniak in de atmosfeer, en volgens welke patronen dat verloopt. Deze kennis is ondermeer van belang voor het maken van schattingen van de export van ammoniak van emissie-gebieden naar natuurgebieden. Daar kan het deponeren en schade aanrichten door *eutrofiëring* (toevoer van extra stikstof aan 'arme' ecosystemen, waardoor aan andere voedingsstoffen weer tekorten ontstaan) en *verzuring* (na omzetting in salpeterzuur in de bodem).

De volgende aspecten van de uitwisseling van ammoniak tussen grasland en atmosfeer werden onderzocht:

- totale netto-uitwisseling per jaar en per seizoen
- regelmatig optredende flux patronen en de achterliggende mechanismes
- vergelijking van gemeten uitwisseling met schattingen op basis van procedures die in modellen en emissie-inventarisaties worden toegepast.
- invloed van zwaveldioxide (SO_2), ammoniumnitraat (NH_4NO_3) en salpeterzuur (HNO_3) in de lucht op de uitwisseling van ammoniak.
- parametrisatie (eenvoudig modellering) van het uitwisselingsproces.

Het *eerste hoofdstuk* geeft een algemene inleiding over de achtergronden en doelstellingen van het onderzoek. Eerst worden een aantal algemene aspecten van ammoniak en zijn rol in verzuring en eutrofiëring samengevat. Dan wordt de emissie van ammoniak uit drijfmest, kunstmest en urineplekken in een weiland uitgebreider behandeld. Vervolgens wordt een overzicht gegeven van de bestaande kennis over de uitwisseling van ammoniak. Er wordt ondermeer uitgelegd dat ammoniak depositie op de vegetatie meestal plaatsvindt in water(lagen) op de bladeren, en/of in de stomata (huidmondjes). Ammoniak deponeert gemakkelijker als het oppervlak zuur is, maar dit oppervlak wordt door diezelfde depositie juist basischer. Op den duur kan ammoniak-depositie zichzelf daardoor gaan afremmen. Zwaveldioxide maakt een oppervlak zuurder, en deponeert juist op een minder zure oplossing beter. Door depositie in de juiste verhouding (2:1) kunnen NH_3 en SO_2 elkaars pH-effect waarschijnlijk neutraliseren en elkaars depositie versterken (co-depositie).

Voorts wordt uitgelegd welke lacunes er zijn in de kennis over ammoniak-uitwisseling. Tenslotte worden de doelstellingen en de algemene opzet van het onderzoek beschreven.

Hoofdstuk 2 geeft een samenvatting van een veel gebruikte modelmatige beschrijving van verticaal transport en van uitwisselingsprocessen in termen van weerstanden. Eerst wordt het algemeen toegepaste 'Big Leaf' weerstands model beschreven. In dat model worden de eigenschappen van een oppervlak die de snelheid regelen waarmee ammoniak wordt opgenomen gezamenlijk uitgedrukt in een oppervlakte weerstand R_c . Als behalve *depositie naar* het oppervlak ook *emissie vanaf* datzelfde oppervlak mogelijk is (bi-directionele uitwisseling), moet in het weerstandsmodel ook de oppervlakte-concentratie in aanmerking worden genomen. In de praktijk is ammoniak op/in het oppervlak goeddeels in oplossing (als ammonium) aanwezig. De oppervlakte-concentratie is dan de bij de samenstelling van die oplossing horende evenwichts-concentratie van ammoniak in de gasfase. Vooral bij uitwisseling via stomata (huidmondjes) van vegetatie wordt de oppervlakte concentratie (in dit geval in de stomatale holte) vaak aangeduid als het compensatie punt. Dat is de concentratie in de lucht waarbij geen netto-uitwisseling plaatsvindt tussen een (vegetatie)oppervlak en de atmosfeer, omdat zij gelijk is aan de oppervlakteconcentratie. Er is dan 'evenwicht' tussen oppervlak en atmosfeer.

Tenslotte wordt het bladerdak-compensatie punt -model van Sutton en Fowler (1993) uitgelegd. Dit model beschrijft het gelijktijdig optreden van bidirectionele uitwisseling via de stomata en depositie naar het bladoppervlak van vegetatie. Hiertoe wordt een compensatiepunt voor het bladerdak als geheel gedefinieerd dat afhankelijk is van beide routes van uitwisseling tezamen.

In hoofdstuk3 wordt de opzet van het experiment beschreven. Eerst worden de plaats en relevante details van de meetlocatie beschreven. De grondsoort was veengrond, met een bodem pH tussen 4.5 en 5.3. De geschatte beschikbaarheid van stikstof voor het gras kwam overeen met een (gangbare) bemesting met ongeveer 300 kg stikstof per hectare per jaar. Vervolgens worden mogelijke methoden om fluxen te meten besproken, en wordt de keuze voor de micrometeorologische flux-profiel methode gemotiveerd. De derde paragraaf geeft een beschrijving van de instrumenten in de meetopstelling. Verticale concentratieprofielen van de gassen NH_3 en HNO_3 en van NH_4NO_3 in aerosol (deeltjes) werden gedurende twee jaren gemeten met thermodenuders. Profielen van SO_2 werden gedurende 4 maanden gemeten, met een fluorescentie monitor. Profielen van ammoniak werden -ter vergelijking met de thermodenuders- tijdelijk ook gemeten met zeer gevoelige en nauwkeurige continue natte denuders (AMANDA's).

Hoofdstuk 4 beschrijft de dataverwerking en geeft een evaluatie van de onzekerheid in de metingen en in de conclusies. Voor de dataverwerking werden eerst fluxen berekend.

Vervolgens werden onbetrouwbare metingen verworpen op basis van een aantal criteria. Het gaat daarbij om omstandigheden waaronder de methode van flux-berekening niet zondermeer mag worden toegepast of waaronder de instrumenten niet betrouwbaar kunnen meten. Na de strenge selectie bleven nog ruim voldoende metingen over voor een statistische analyse van de fluxen in relatie tot seizoenen invloeden, dagpatronen en andere factoren.

In de onzekerheids analyse wordt de onzekerheid in een enkele, typische fluxmeting geschat op 30-35%, gedomineerd door de toevallige fout in de concentratie gradiënt bepaald uit de profielmetingen. De onzekerheid in een typische R_c waarde is veel hoger volgens standaardregels van fouten-voortplanting (tot 80-100%). In de praktijk blijkt het voldoende met een onzekerheid van 25-40% rekening te houden.

Als gemiddelde waarden van metingen over een langere periode worden gebruikt, middelen toevallige fouten goeddeels uit. In dat geval wordt de 'standaard fout van het gemiddelde' gebruikt als maat voor de onzekerheid. Berekening van een 'gemiddelde' R_c levert allerlei problemen op; daarom wordt een alternatieve procedure voor het bepalen van representatieve waarden voor gemeten sets van R_c 's uitgelegd.

Tenslotte wordt de onzekerheid door mogelijke *systematische* fouten in gemiddelde fluxen en R_c -waarden geschat op circa $\pm 25\%$.

In hoofdstuk 5 worden uit de metingen van concentraties en fluxen de jaarlijkse waarden en patronen van de concentratie en uitwisseling van ammoniak tussen grasland en atmosfeer afgeleid. De jaargemiddelde concentratie was $10-11 \mu\text{g m}^{-3} \text{NH}_3$ met duidelijke variaties tussen seizoenen (laag voornamelijk in het najaar en vroege winter; hoog in vroege voorjaar t/m zomer). Deze zijn afhnakelijk van emissies per seizoen in de hele regio. Dagelijkse patronen in het concentratie verloop werden ook gevonden; deze worden vooral veroorzaakt door variaties in wind snelheid, atmosferische stabiliteit en menglaaghoogte.

De jaarlijkse netto-emissie van ammoniak was vrij laag te Zegveld, ongeveer $4.5 \text{ kg ha}^{-1} \text{jr}^{-1}$ (als NH_3), als het eindresultaat van een netto-emissie van $5.4-6.7 \text{ kg ha}^{-1} \text{jr}^{-1}$ in het weideseizoen (mei-oktober) en een netto-depositie van $0.8-1.8 \text{ kg ha}^{-1} \text{jr}^{-1}$ in de stalperiode. In het weideseizoen was het dominante dagelijkse patroon dat van netto-emissie overdag en netto-depositie 's nachts. In de stalperiode domineerde depositie zowel overdag als 's nachts. Niettemin kwamen ook in de stalperiode na mest-applicaties (late winter, vroege lente) enkele periodes met aanzienlijke emissies voor.

In perioden waarin vooral netto depositie werd gemeten en er niet kort geleden mest was toegediend, was de efficiëntie waarmee ammoniak deponeerde gering (met hoge oppervlakteweerstanden R_c van $35-105 \text{ s m}^{-1}$). Deze depositie vindt hoofdzakelijk plaats op (waterlagen op) het bladoppervlak. De hoge weerstanden zijn waarschijnlijk het gevolg van een hoge pH van het bladoppervlak, als gevolg van een voortdurende belasting met ammoniak. Die is het gevolg van de voortdurend relatief hoge ammoniak concentraties in deze regio.

In hoofdstuk 6 worden de mechanismes achter de waargenomen bi-directionele uitwisselingspatronen van NH_3 geanalyseerd. Het reguliere patroon van emissie overdag / depositie 's nachts in het weideseizoen werd ook waargenomen indien er geen recente drijfmest-applicatie had plaatsgehad, en toonde geen duidelijk verband met feitelijke begrazing van een perceel. Als eerste verklaring wordt de mogelijkheid onderzocht dat het bladoppervlak zowel bij depositie als bij emissie de uitwisseling domineert. Een benadering uitgaande van een compensatiepunt wordt geprobeerd, evenals een analyse van de emissie als functie van de accumulatie van NH_3 op het oppervlak door depositie sinds de laatste regenbui. Vervolgens wordt de bijdrage van andere bronnen dan het bladoppervlak aan de emissie geëvalueerd, in het bijzonder van de bodem en van de stomata. De conclusie is dat de stomata een zeer belangrijke rol spelen in de ammoniak-emissie, mogelijk door een hoog stikstofgehalte van het gras tengevolge van de bemesting.

In hoofdstuk 7 wordt de uit de metingen berekende netto-emissie van ammoniak vanaf de weilanden vergeleken met de geschatte vervluchtiging van ammoniak van drijfmest, kunstmest en urineplekken. Deze laatste wordt geschat met behulp van de gangbare emissiefactoren voor ammoniak, toegepast op de door de leiding van de proefboerderij verstrekte gegevens over hun bedrijfsvoering. In het weideseizoen blijkt de aldus geschatte emissie tweemaal zo hoog als de gemeten waarde.

In transportmodellen wordt de bijdrage van de geschatte emissie vanaf weilanden aan de atmosferische ammoniakconcentratie gedeeltelijk gecompenseerd door een geschatte depositie op dezelfde weilanden. Wordt eenzelfde benadering gevolgd voor Zegveld, dan kan een betere overeenstemming tussen gemeten en geschatte uitwisseling worden bereikt. Daartoe moet dan echter van een veel te lage oppervlakte weerstand worden uitgegaan, en dan wordt overschatting van emissie in het weide seizoen in feite gecompenseerd door een overschatting van de depositie in de stalperiode. De huidige emissiefactoren blijken derhalve te hoog voor grasland op veengrond, waarschijnlijk door de lage bodem pH van ongeveer 4.8. Dit is belangrijk voor milieubeleids-studies en transportmodellen die emissieschattingen gebaseerd op deze factoren gebruiken. De netto-bijdrage van dit type grasland aan de ammoniak concentratie in de lucht kan daardoor worden overschat. De conclusie is dat mogelijk een regionale differentiatie in de emissiefactoren moet worden aangebracht.

In hoofdstuk 8 worden de effecten van SO_2 , NH_4NO_3 en HNO_3 op de uitwisseling van ammoniak onderzocht. SO_2 vertoonde een efficiënte depositie met een gemiddelde depositiesnelheid van 1.14 cm s^{-1} ; representatieve waarden voor de oppervlakte-weerstand varieerden tussen -5 en 20 s m^{-1} (bij vorst: 40 s m^{-1}).

De depositie vindt hoofdzakelijk plaats op het (vochtige) bladoppervlak, en wordt waarschijnlijk versterkt door de hoge ammoniak belasting in deze regio die een hoge pH van het oppervlak veroorzaakt. Dit bevordert SO_2 -depositie en remt NH_3 -depositie. In

het weideseizoen bevat de lucht in dit gebied een overmaat aan NH_3 in verhouding tot SO_2 (in een molaire verhouding $\text{NH}_3 / \text{SO}_2$ van ongeveer 6:1). In de stalperiode is deze verhouding slechts 4:3. Dit seizoensverschil valt samen met een toename van de depositie-efficiëntie voor NH_3 en een afname van de efficiëntie van de depositie van SO_2 . Hieruit kan een zekere relatie tussen de beide componenten worden afgeleid in termen van co-depositie. Een overmaat NH_3 bevordert de depositie van SO_2 ; een ondermaat is juist gunstiger voor depositie van NH_3 . Dergelijke relaties konden echter niet worden gevonden op kortere tijdschalen (één of meer dagen).

Uit de metingen van NH_4NO_3 -aerosol en van HNO_3 volgde een zeer lage gemiddelde depositie snelheid van het NH_4NO_3 (0.12 cm s^{-1}) en een extreem hoge depositie snelheid van HNO_3 (3.4 cm s^{-1}), hoger dan fysisch mogelijk. Beide waarden weerspiegelen mogelijk een invloed van reactie van HNO_3 met lokaal geëmitteerd NH_3 tot NH_4NO_3 . De gradiënten van HNO_3 en NH_4NO_3 kunnen daardoor verschoven zijn, zodanig dat de depositiesnelheid van HNO_3 wordt overschat en die van NH_4NO_3 wordt onderschat. Omdat de NH_3 concentraties en gradiënten op deze lokatie veel groter zijn (op molaire basis) dan die van beide andere componenten, worden de gradiënten van NH_3 hier veel minder sterk beïnvloed.

In hoofdstuk 9 wordt een parametrisatie van de uitwisseling te Zegveld uitgetest die is gebaseerd op het model van Sutton en Fowler. De model-parameters worden afgeleid (via 'fitting') uit de metingen gedaan in periodes waarin geen invloed van drijfmest-applicatie op de uitwisseling te verwachten is.. De beste resultaten blijken te worden verkregen als een concentratie van ammoniak in de stomata (stomataal compensatiepunt) van $19 \mu\text{g m}^{-3}$ bij 20°C wordt verondersteld, en waarden van de oppervlakteweerstand van het bladoppervlak die afhangen van het al of niet vochtig zijn van het bladoppervlak. Met deze parameterkeuzen blijkt het waargenomen patroon goed gereproduceerd te kunnen worden. Een dergelijk model biedt dus goede perspectieven voor de beschrijving van bidirectionele uitwisseling met grasland.

Wordt het model met die parameter-waarden toegepast op perioden waarin juist wel drijfmest-applicatie heeft plaatsgehad, dan kan daarmee een correctie worden berekend voor de bijdrage van uitwisseling met de vegetatie aan de totale gemeten uitwisseling in die periode. De overblijvende emissie kan dan geheel worden toegeschreven aan de drijfmest-applicatie. Uit de berekende waarden voor deze emissie uit drijfmest blijkt opnieuw dat de huidige emissiefactoren voor drijfmest-applicatie waarschijnlijk te hoog zijn voor dit bodemtype (veengrond) en/of voor bodems met zo'n lage pH. Dit is in overeenstemming met de conclusies uit hoofdstuk 7.

In hoofdstuk 10 tenslotte worden de conclusies genoemd die in deze samenvatting al zijn verwerkt.

Chapter 1

Introduction

1.1 General introduction

This thesis describes the results of field measurements of dry exchange (deposition and emission) fluxes of ammonia over grazed pasture. The principle aim of this research was to investigate how much and by which patterns such pastures contribute to atmospheric ammonia that is exported from an intensive livestock breeding area to sensitive receptor areas.

Deposition of ammonia is an important contributor to acidification and eutrophication of sensitive areas. These processes are responsible for a number of damaging effects, such as decline of forests, disappearance of sensitive natural ecosystems, damage to buildings and monuments. To abate ammonia deposition, governmental policies and measures have been developed that are aimed at reduction of emission of ammonia. To develop and evaluate these measures, the transport of ammonia from emission regions to sensitive natural areas is estimated by transport models. An important uncertainty in these models concerns the deposition to grazed pastures within the emission region.

Grazed pastures in areas of intensive livestock breeding usually are a significant source of ammonia during some periods, especially shortly after application of slurry to the pasture. In other periods however, deposition of ammonia to the pasture may occur. As a result, part of the ammonia emitted in a region of intensive livestock breeding will be removed from the air by deposition in the same area, before it can be transported to other (more sensitive) regions. In widely used transport models in the Netherlands (such as OPS) estimated emission due to pastures and other sources is included in the source strength which is used as input to the model. Deposition is calculated independently from this emission estimate, by a simplified surface resistance parameterization.

To evaluate this modelling approach and the applied parameterization of deposition, measurements of the exchange fluxes over pasture are necessary that cover both emission periods and deposition periods. However, so far almost all such measurements over pasture were focussed on volatilization of ammonia from slurry application and from urine excreted during grazing; only emission was quantified. There are no adequate direct measurements available of the deposition to those pastures and of the net-result of deposition and emission.

Therefore in the research reported in this thesis, continuous exchange measurements of ammonia exchange over pasture were carried out during a period of two full years. In

this way the influence of all land treatments and of most of the possible weather and surface conditions could be investigated.

Measurements of SO_2 , ammonium nitrate and nitric acid were also carried out because these compounds may influence ammonia exchange.

In the rest of this chapter the background of the experiment will be elucidated. First the emission, transport and deposition of ammonia and its consequences will be summarized (1.2). Then emission of ammonia due to land treatments in agriculture is discussed in more detail (1.3). The present knowledge on the exchange of ammonia is reviewed in section 1.4, including the gaps in knowledge that need to be filled in by the present research. The aims and general approach of the research is summarized in 1.5, followed by a thesis plan (1.6).

1.2 Ammonia in the environment

1.2.1 Overview

In the next subsections, relevant aspects of ammonia in the environment will be summarized, from its emission (release into the atmosphere), via transport, to its deposition (transfer to the surface) and the resulting environmental effects. Finally governmental measures to abate ammonia emissions are summarized very briefly. A general overview of the main processes to be treated is given in figure 1.1, for anthropogenic ammonia (from Hey and Schneider, 1991).

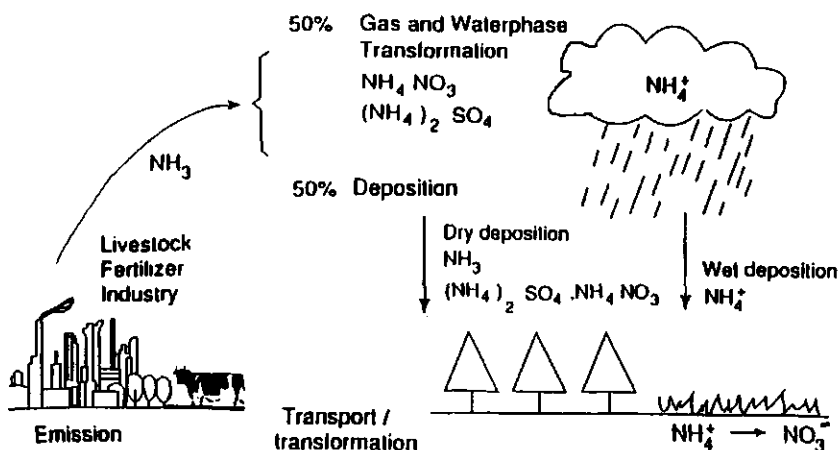


Fig 1.1. Overview of the cycle of emission, transport and deposition of ammonia.

As is shown in the figure, NH_3 is converted into NH_4^+ by several reactions; some of these are equilibria. Because of this, it is not always relevant or even not possible to make a distinction between these two reduced nitrogen compounds. Then they are usually referred to (together) as NH_x . Amines (NH_2R) constitute another group of reduced nitrogen compounds, but their ambient concentration is very low and hence their contribution to acidification is very minor.

Much of the current knowledge on the environmental behaviour of NH_x has been acquired in projects of two large air pollution research programs:

In the Netherlands, much of the research on the subject of acidification (and eutrophication) has been coordinated in the Dutch Priority Programme on Acidification (DPPA). This covered a very wide variety of research projects, including extended measurements of quantities and effects of acid deposition and eutrophication to forests and heather. An overview of the projects, results and conclusions is given by Hey and Schneider (1991). Because of the large contribution of NH_x to acidification and eutrophication in the Netherlands, DPPA spent much attention to ammonia.

Another framework in which much research on acidification, eutrophication and photo-oxydantia took place was the joint European research program EUROTRAC (e.g. Borrell, 1989), an environmental project of the EUREKA program. EUROTRAC (1985-1995) is an abbreviation for the European Experiment on the Transport and Transformation of Environmentally Relevant Trace Constituents in the Troposphere over Europe. The troposphere is the lowest layer (about 20 km) of the atmosphere in which most processes relevant to air pollution take place.

Many Dutch research groups of various disciplines took part in EUROTRAC and/or in the DPPA. The research reported in this thesis was a contribution to the EUROTRAC subproject BIATEX (BIosphere ATmosphere EXchange of pollutants and trace substances), which was dedicated to obtain better quantitative descriptions of exchange in Europe (Slanina, 1997).

1.2.2 Sources

NH_x plays a role in several metabolic processes in living organisms, especially as an intermediate in the protein metabolism.

In the soil it is produced during the microbiologic mineralisation of organic matter. During this process, organic nitrogen is first transformed into (mainly) NH_4^+ . This ammonification process is usually followed by oxidation to nitrate by other micro-organisms (nitrification, see 1.4) and therefore generally emissions into the atmosphere as ammonia are limited.

In the metabolism of animals, however, large amounts of NH_x are produced, because the food contains more nitrogen than is used by the animal for production of animal proteins (meat, milk). This is especially the case for livestock: about 81% of the nitrogen taken up by dairy cows is not used (Tamminga, 1992). The excess nitrogen is excreted mainly

as urea. Decomposition of urea produces NH_4^+ , which is emitted partly as NH_3 to the atmosphere.

Emissions of pollutants are generally expressed in terms of source strength per category of sources and time. Emission inventories for a pollutant (per country or per area) can be made from (geographical) data on the source distribution and known or estimated values of the emission rate per individual source or per source type (emission factors). Table 1.1, based on an ammonia emission inventory by v.d. Hoek (1994), gives a summary of the contribution of various types of anthropogenic sources to the emission of ammonia in the Netherlands. Natural sources (wildlife, sea) are generally considered to be negligible compared to the anthropogenic sources in this country.

Table 1.1. Estimated source contribution to anthropogenic ammonia emissions in 1992 in the Netherlands (from v.d. Hoek, 1994; expected effects of governmental emission abatement measures are included).

Source of NH_3	Emission (million tons of NH_3)	Fraction of total emission (%)
Animal manure	146	86
=> animal houses and manure stores	88.5	52
=> grazing (meadow)	14.5	8.5
=> application (manure)	43	25.5
Fertilizer application	9.5	5.5
Industrial processes	4.5	2.5
Households	10.5	6
Total	171	100

From these figures it is clear that animal wastes produced in livestock breeding deliver by far the most important contribution to total ammonia emissions (86%). The contribution of another (mainly) agricultural source, fertilizer application, is much lower. Grazed pastures can contribute to the emissions not only by animal wastes

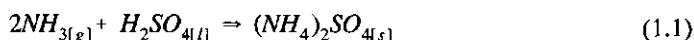
deposited of during grazing, but also via application to the land of wastes excreted in the animal houses and via fertilizer application. In this way they can be important sources of ammonia in periods during and after these treatments. Therefore emissions from grazed pasture are discussed in more detail in a separate section (1.3)

The ammonia emissions from households and industrial processes are small compared to those from agricultural activities, though not negligible. Industrial processes consist mainly of fertilizer, sugar and stark industries and the production of compost for mushroom cultivation.

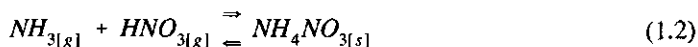
1.2.3 Atmospherical transport

During transport the emitted ammonia is primarily dispersed as a function of a variety of meteorological factors. In addition ammonia can be transformed or produced by chemical reactions and/or removed from the atmosphere by deposition to the surface.

Chemical reactions of ammonia in the atmosphere concern mainly reactions with acids, for example with acid aerosols containing H_2SO_4 . Then stable ammonium sulphate is formed:



NH_3 may also react with gaseous HNO_3 or HCl . The reaction with HNO_3 is:



Unlike $(NH_4)_2SO_4$, NH_4NO_3 and NH_4Cl are unstable salts under ambient conditions. This means that they can dissociate again if the concentration product of NH_3 and HNO_3 (resp. HCl) falls below the respective equilibrium values K_e . In this way these salts -if present in aerosol- may locally lead to production of NH_3 in the atmosphere. K_e depends on temperature and (for aerosol in droplet shape) relative humidity; higher temperatures and humidities favour dissociation (see *e.g.* Seinfeld 1986).

Most NH_4^+ present in the atmosphere is a product of such atmospheric reactions of ammonia. Therefore the composition of aerosol, as far as ammonium is concerned, depends on the available acids in the atmosphere. Generally $(NH_4)_2SO_4$ and NH_4NO_3 are dominant.

Estimated annual average NH_3 - concentrations for 1990, in remote areas of Europe are 0.1 to $2 \mu g m^{-3} NH_3-N$, and $0.5 - 3 \mu g m^{-3} N$ for NH_4^+ (Asman and Van Jaarsveld, 1990). Compared with these, the country average ambient concentrations for the Netherlands are estimated much higher: about $6.4 \mu g m^{-3}$ for NH_3 and $5.1 \mu g m^{-3}$ for NH_4^+ in aerosol,

at 4 m height (Erisman and Draaijers, 1995). The influence of large agricultural emissions of ammonia is clear.

The spatial variation in ammonia concentrations is high due to an unequal distribution of sources and due to a short residence time in the atmosphere, which precludes mixing over larger time scales. The short residence time is caused by the quite rapid removal of ammonia by atmospherical conversion to NH_4^+ (at an estimated rate of $0.5\text{--}1.0 \times 10^{-4} \text{ s}^{-1}$; Erisman *et al.*, 1988) and by deposition. As a result the travelling distance of ammonia is low, -of an order of 100 km. Typical *annual* average concentrations in areas with intensive livestock breeding such as De Peel and Gelderland can be as high as $19 \mu\text{g m}^{-3}$ and $33 \mu\text{g m}^{-3} \text{NH}_3$ (at Vredepeel and Lunteren, respectively, Boermans and Erisman, 1993, for 1991-1992). Temporarily, values up to more than $300 \mu\text{g m}^{-3} \text{NH}_3$ can occur locally. This is generally due to manure-spreading or plumes from manure stores and animal houses.

Ammonium aerosols are hardly emitted into the atmosphere directly (eventually by seawater spraying, and by some chemical industries), and the travelling distance is much higher (of an order of 1000 km or more), due to a slower deposition rate. Hence long range transport is much more important for NH_4^+ than for NH_3 , and the spatial variations are much less extreme. Generally the highest concentrations of NH_4^+ are found in continental air masses.

In monitoring networks over Europe a variety of pollutants is measured on regular basis. In the Netherlands, this is done in the National Air Quality Monitoring Network, referred to as LML. Ammonia is measured at 8 locations of this LML (Van Elzakker *et al.*, 1994), ammonium-aerosol at 6 locations.

Because the spatial variability in the concentrations of ammonia is so high, it is not possible to make detailed maps of concentration (and deposition) over the Netherlands. For this aim use is made of transport-models such as the EMEP model (Seland *et al.*, 1995) and OPS (for some years a version of the OPS was applied under the name of TREND; Van Jaarsveld, 1995). In these models, mechanistical knowledge on horizontal transport, deposition and atmospherical reactions of pollutants has been integrated. So transport models describe the link between emissions in certain regions and air quality and deposition in other regions. In this way present or projected effects of policies concerning air pollution can be evaluated.

1.2.4 Deposition

Deposition refers to the transfer of pollutants from the atmosphere to the surface.

The total deposition of a pollutant consists of wet deposition, dry deposition and occult deposition. *Occult deposition* refers to the uptake of pollutants from clouds or fog that come(s) into contact with the surface. The precise contribution of occult deposition is not known, because it is difficult to measure. However, it is generally considered to be relatively unimportant in the Netherlands (of an order of a few %; for example 3% over

forest, Erisman and Draaijers, 1995). *Wet deposition* refers to deposition via uptake in rain, snow or hail. It can be measured relatively easily, by analysing the chemical composition of collected precipitation. A large number of national and international networks of wet deposition measuring stations exists all over Europe. In the Netherlands, wet deposition is measured at 14 locations (RIVM, 1993). For ammonia, 30-35% of the total NH_x deposition proceeds by wet deposition (Erisman and Draaijers, 1995).

Dry deposition refers to direct deposition of gases and aerosols from the atmosphere to the surface. It is much more difficult to monitor than wet deposition, and it is generally derived from measured or modelled air concentration, meteorological conditions (especially turbulence) and surface characteristics. Dry deposition of NH_x contributes for about 65-70% to total NH_x deposition; the estimated country-average total deposition (dry+wet) of NH_x for the Netherlands is about 28-30 $\text{kg ha}^{-1} \text{ yr}^{-1}$ of $\text{NH}_x\text{-N}$ (Erisman and Draaijers, 1995).

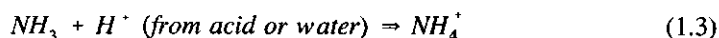
Ammonia is deposited in considerable amounts to natural terrains, depending on the atmospheric concentration. Annual (dry) deposition estimates based on field measurements were 28 to 44 $\text{kg ha}^{-1} \text{ yr}^{-1}$ of $\text{NH}_3\text{-N}$ for a Dutch coniferous forest (Duyzer *et al.*, 1994); 8 $\text{kg ha}^{-1} \text{ yr}^{-1}$ of $\text{NH}_3\text{-N}$ for Dutch heathlands (Duyzer, 1994); and 2.9 and 10 $\text{kg ha}^{-1} \text{ yr}^{-1}$ of $\text{NH}_3\text{-N}$ for two British moorlands (Sutton *et al.*, 1992). By far most of this deposition is intercepted by the canopy of the vegetation. Part of this ammonia will be taken up via the leaves. Finally rain will wash a large part of the dry deposited ammonia to the soil below the vegetation.

Deposition maps are often made by use of regional or long-range transport models (OPS, EMEP). For more detailed estimates of deposition, special deposition models can be applied, *e.g.* DEADM (Erisman, 1992; Erisman 1993b). This model uses concentration fields calculated by transport models and/or measured concentrations as input.

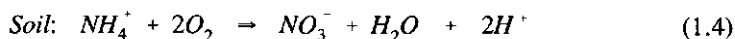
1.2.5 Effects

Ammonia concentrations in air are generally far too low to cause acute toxic effects. Deposition of air pollutants however can cause a wide range of long term damage effects to eco-systems and to materials and monuments. The final results are probably the most visibly reflected in die-back of forests and damage to sculptures and buildings. In some cases, *e.g.* the K  llner Dom, this damage is large scale and spectacular, in many other cases however the damage processes are proceeding more gradually. Most of these effects can nowadays be explained by processes known as acidification and eutrophication. Ammonia is an important contributor to both processes.

Acidification means that a surface becomes more acid (its pH is reduced), or that its capacity to neutralize acid is reduced. This can be caused by deposition of strong acids (H_2SO_4 , HNO_3 , HCl) or other compounds that are transformed into strong acids at the surface after deposition, for example when dissolving in water ($\text{SO}_2 \Rightarrow \text{H}_2\text{SO}_3$, which is partly oxidized to H_2SO_4). Based on the atmospherical reactions of ammonia with acids, ammonia was originally regarded mainly as an acid neutralizer. Indeed ammonia 'binds' one proton to form NH_4^+ when reacting with acids in the air or when dissolving in rain drops or in water-layers on a humid surface:



However, Van Breemen *et al.* (1982) pointed at the microbiological oxidative conversion (nitrification) of NH_4^+ by soil bacteria:



In this way, deposition of one ammonia molecule leads to a net addition of one proton to the ecosystem; deposition of one NH_4^+ -ion from the atmosphere leads to the addition of two protons: one from previous reaction with acid (or from water in precipitation), one from the nitrification. For more detailed proton balances for ammonia in acidification processes see *e.g.* Nihlgard, 1985; Binkley and Richter, 1987. Through nitrification in the soil, the high deposition of ammonia in the Netherlands leads to a high contribution of ammonia to the total acid deposition in this country, estimated 46% for 1993 (Erisman and Draaijers, 1995).

Many mechanisms by which acidification finally affects organisms are related to the increased dissolution of several compounds at lower pH. Examples are weathering of stone; leaching of plant materials; mobilization of toxic metals and aluminium in soil and water bodies. Changes in ratios among ions in the soil due to the acidification may result in nutrient imbalances in organisms causing growth irregularities.

Such nutrient imbalances may also be caused by *eutrophication*. This term refers to changes in an eco-system caused by an increased availability of nutrients. This may be harmful to species which are adapted to conditions of low nutrient availability, such as heather and moorlands. Other species are not sensitive to or even profit from the higher nutrient availability and gradually replace the original species. The input of ammonia and NH_4^+ -salts via deposition from the atmosphere contributes significantly to the total available nitrogen in natural areas.

Furthermore it has become clear that many effects attributed to deposition of air pollution are caused by *combinations* of stress factors (Hey and Schneider, 1991) rather than by one dominating mechanism. Species affected by acidification and/or eutrophication will be less able to resist natural stress factors (*e.g.* frost, plagues, illnesses) or to compete with other organisms. The latter may even profit from changed nutrient conditions and from *e.g.* better light that passes a damaged canopy. In the Netherlands, replacement of heather vegetation by grasses and changes in the undergrowth of forests are examples of processes caused by multiple stress factors (for an overview see Hey and Schneider, 1991).

In addition to the important contribution of NH_x to the general acidification and nitrogen-eutrophication effects, increased ammonium concentrations (or NH_4^+/K^+ ratios) inhibit the uptake of other nutrients (Hey and Schneider, 1991). Leaching of plant ions (K^+) in exchange for ammonium may also contribute to the damage.

From the mechanisms behind acidification and eutrophication processes, it is clear that the time-integrated deposition flux of the involved pollutants is the appropriate criterion for environmental measures (and not primarily their atmospheric concentration). This is accounted for in the modelling concept of the *critical load*. The critical load is defined as 'a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge' (Nilsson and Grennfeldt, 1988). Based on criteria for specific effects, maximum concentrations for the soil solutions are derived (see *e.g.* De Vries 1994; Hettelingh *et al.* 1991). Then the critical load is calculated as the maximum input rate of pollutant to the soil at which the ion on which the criterion is based remains below the critical concentration or below a critical ratio to specific other ions. For example: for the Speulder forest, the critical acid load for inhibition of uptake, is based on the criterion that the ratio of Al^{3+} to basic cations ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+$) should not exceed 1.0 mole mole⁻¹, leading to a critical load of 2760 mol ha⁻¹ yr⁻¹ of acid. Similarly, the critical load for NH_3 for the same effect and forest is 2460 mol ha⁻¹ yr⁻¹ of NH_3 , based on the criterion that the molar ration of NH_4^+/K^+ should not exceed a value of 5 (Erisman *et al.*, 1995). Critical loads refer to average input rates over long periods (*e.g.* ten years or more).

The *exceedance* of such critical loads is often used as a parameter to evaluate effects of emission reduction policies. Exceedances are determined by estimating the difference between actual loads and critical loads for the time and scales for which the critical loads were estimated. The actual load refers to the net input of the depositing compound(s) to the (soil of) the eco-system that occurs at present (or according to a modelled scenario, giving a projected load). Both dry and wet deposition are included.

With respect to acidification, the total of the acid contribution of all acidifying compounds is important. This is usually estimated from the total *potential acid*

deposition load. The acid contribution of compounds that are transformed into strong acids after deposition is set equal to the acidifying potential of this strong acid. So all SO_x (H_2SO_4 , H_2SO_3 , SO_2) is assumed to produce 2 mole eq. of H^+ per mole deposited; all NO_y (HNO_3 , NO , NO_2) are assumed to produce 1 mole eq. H^+ per mole deposited. In case of NH_x , gaseous ammonia and particulate or dissolved ammonium are both set to produce 1 mole eq. per mole deposited NH_x . This is done so because the anion associated with the depositing NH_4^+ is accounted for separately as if it were the original acid (NH_4NO_3 corresponds to $1\text{NH}_x + 1\text{NO}_y$).

In practice this potential acid deposition load represents a maximum possible value of the acidifying effect of the depositing compounds. Especially the acid formation from deposited NH_x is often much less efficient than theoretically possible. Part of the NH_x is removed or fixated by uptake by plants, denitrification and humification (Heij *et al.*, 1991). As a result, the actual contribution of NH_x to acidification in the Netherlands is currently estimated to be only half the potential contribution (Heij and Erisman, 1997). Furthermore, estimates of the potential deposition usually refer to deposition to the canopy (or net-removal from the atmosphere). Then interaction with the canopy ('canopy exchange': e.g. leaching, uptake) before the pollutant reaches the soil must be taken into account to calculate the actual load from deposition estimates. A *direct* estimate of the load of NH_x and other pollutants to the soil can be derived from throughfall analyses. Throughfall is precipitation water that drips from the leaves, transporting previously deposited pollutants from the leaves to the soil. For the Speulder forest, a reasonable agreement has been found between throughfall fluxes of NH_4^+ corrected for canopy exchange, and atmospheric deposition of NH_x derived from measurements and models (Erisman and Draaijers, 1995). This is an indication that despite the complexity of the mechanisms involved in canopy exchange, the most relevant processes can be described sufficiently well. This is important, because it means that actual loads can be derived from modelled atmospheric deposition, and hence, via transport models, can be linked to emissions and emission reductions.

1.2.6 Measures to reduce ammonia emissions

Because transport and deposition of pollutants can hardly be influenced, reduction of emissions is necessary to prevent acidification and eutrophication. Almost all of the NH_x that deposits in the Netherlands is emitted in the country itself (85%, Erisman and Draaijers, 1995), mainly in regions of intensive livestock breeding. Therefore national legislation was developed, aiming at a reduction of the ammonia emissions in the Netherlands by 50 %, until the year of 2000 (compared to 1980; see 'Notitie derde fase mest- en ammoniakbeleid, 1993'; for a brief overview, see also Monteny, 1994). Legal measures give technical and quantitative prescriptions concerning the production, storage and land application of animal wastes. For example, covering of manure storage tanks is now obligatory. Slurry application is forbidden from October until January; in the rest of the year the application of low emission techniques is obligatory. Such

techniques reduce the volatilization of NH_3 by up to 80% (injection even >95%) compared to conventional surface spreading (Wouters, 1994). As a result of the (partial) introduction of these measures, emissions from slurry application were estimated to diminish by more than 50% in 1992 compared to 1991. For 1991 the estimated emission from slurry application was still 89.5 million ton NH_3 (V.d. Hoek, 1994) or 41% of total ammonia emission.

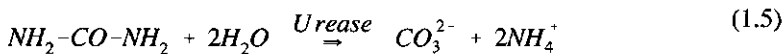
However, in case of injection (and comparable methods) more ammonium may penetrate into the soil to be converted there to nitrate. This may harm ground water quality, which is also threatened by other compounds in slurry such as phosphates. Hence legal prescriptions concern also the quantity of manure (and of the minerals in it) produced and disposed of per farm. The possibilities to reduce the nitrogen in the fodder and/or to achieve a more efficient N-conversion by the animal are an important subject of research.

1.3 Ammonia emissions from grazed pastures

Ammonia emissions from pastures in intensive livestock breeding areas are generally assumed to be caused by three types of agricultural land treatments: slurry application, grazing by cattle and fertilizer application. Relevant aspects of the emission from each of these treatments will be summarized in the next three sections, followed by an explanation of the estimation of emissions in emission inventories.

1.3.1 Emissions from slurry application

Slurry is a mixture of faeces and urine diluted by the water used to rinse the stable floor. The urine contains urea, which is hydrolysed to form ammonium (and (bi)-carbonate:



This reaction is catalysed by the enzyme urease, which is produced by bacteria present in faeces and in soil. If the produced ammonium (solution) is in good contact with the atmosphere, part of it may volatilize as NH_3 . On the floor of animal houses, the urease concentration is usually very high (faeces), and so the hydrolysis can start almost immediately after the excretion of the urine. As a result, considerable amounts of ammonia can be emitted directly from the stable floor and from slurry collected under it. After some time the slurry is usually pumped to manure storage tanks. During this storage the hydrolysis continues; especially since covering the manure storage tanks is obligatory, ammonia emissions during this storage are relatively small. At the time that the slurry is applied to the land, most of the urea has been decomposed. Hence the

solution contains a very high concentration of ammonium, which volatilizes quite rapidly as NH_3 once the slurry is exposed to the air during and after application to arable land or pasture. As a result the pasture can be a very strong source of ammonia during several days following slurry application.

Almost all measurements of ammonia fluxes over pastures were part of investigations to quantify the emission of NH_3 involved in agricultural activities to enable estimation of their contribution to atmospheric ammonia concentrations. Especially the NH_3 -volatilization after slurry spreading was investigated. To do so, typically the ammonia emission from a piece of land (pasture) treated with slurry was measured during a certain period after slurry spreading. Generally the micrometeorological mass balance method (see chapter 3) was applied. Usually after 2-4 days no significant emission was observed anymore. Most of these measurements therefore lasted only 4-5 days (De Winkel, 1988; Van der Molen *et al.*, 1989; Bussink, *pers. comm.*, Huijsmans, *pers.comm.*). Then the total integrated emission was calculated and expressed as a fraction of the nitrogen content of the slurry (volatilization fraction).

The variation in measured volatilization fraction in case of conventional surface spreading of slurry is very high (less than 20 to almost 100% of the $\text{NH}_4\text{-N}$; Wouters *et al.*, 1994). Apart from the composition of the slurry, the meteorological conditions, soil parameters and type and height of vegetation are important factors that determine the actual fraction in a given situation (Wouters *et al.* 1994; Van Faassen *et al.*, 1990). Most of the ammonia volatilization after conventional slurry spreading takes place before the slurry has infiltrated into the soil. Partly due to this, 50% of the emission occurs in the first 6 hours after application (Hey and Schneider, 1991). The rate of infiltration depends strongly on soil porosity and soil humidity, on the occurrence of rain after application, and on the composition of the slurry (dry matter content) and the height of the vegetation (sticking of slurry to leaves). Meteorological conditions that influence the volatilization rate (turbulence, temperature) will be most important in this short period too. After infiltration, soil processes affecting the composition of the slurry (*e.g.* pH-buffering, cation-exchange, nitrification), and relatively slow gas transport within the soil strongly reduce the volatilization of ammonia to the atmosphere.

So far, the untangling and quantification of the influence of the most relevant parameters that determine NH_3 -emission from spread slurry or from urine patches during grazing still poses difficulties. The main aim of many emission measurements was to compare alternative techniques of slurry application to the conventional method. Then both techniques were applied simultaneously on neighbouring plots, so that conditions were the same. In this approach, the relative differences in measured fluxes between both plots give a good indication of the effectivity of the measures. Under these conditions measurements of other parameters than those necessary to calculate the fluxes were often considered less relevant and hence they were not measured. Recently the institute

of IMAG-DLO carried out a large number of measurements of ammonia volatilization after slurry application on various soil types and by various techniques. Here also, the primary aim was to compare methods (reported in Mulder and Huijsmans, 1994), but a wide variety of meteorological and soil parameters was measured. A statistical (regression) analysis of the influence of these parameters on the volatilization is presently being carried out (Huijsmans, *pers. comm.*).

1.3.2 Emissions from urine excreted during grazing

During grazing, urine is excreted in patches that are more or less randomly distributed over the pasture. The emission usually occurs during a longer period (up to 10-20 days, Van der Molen *et al.*, 1989, Jarvis *et al.*, 1989) than in case of slurry application. This is because now the urea in the excretes must be hydrolysed first, under influence of urease in the soil. The rates of this process, -and of the transport to the soil surface and transfer into the atmosphere-, depend on a mixture of meteorological and soil conditions. As a result the volatilization proceeds much more slowly and gradually than in case of slurry.

Measurements over pasture during and after grazing by dairy cattle were carried out by Bussink *et al.* (1990). In this experiment, mainly the volatilization of ammonia from urine excreted during grazing was measured. For fertilization rates of 250 and 550 kg ha⁻¹ N, the derived annual emissions were about 10 and 45 kg ha⁻¹ of NH₃, respectively. The corresponding volatilization percentages were 3 and about 8 % (kg NH₃-N emitted per kg N excreted).

Other relevant measurements of this type were carried out by Jarvis *et al.* (1989), for grazing by sheep and young steers. Reported annual NH₃ emissions were 11.4 and 30.1 kg ha⁻¹ NH₃ for fertilizations of 210 and 420 kg ha⁻¹ N, with volatilization percentages of 4.5 and 6%.

Vertregt and Rutgers (1988) investigated the volatilization of NH₃ from (artificial) urine, applied to small model plots. They found volatilization percentages between 4 and 17 % for sandy soil (average 10.5 %, 12 experiments). Two measurements on peat soil gave percentages of 6 and 13%.

Roughly, in these three experiments the average ammonia volatilization percentages from urine excreted during grazing ranged from 3 to 10.5 %. Lower fertilization leads to lower volatilization percentages.

1.3.3 Emissions due to fertilizer application

Most plant species can take up ammonium directly by the roots as a source of nitrogen. For this reason, most fertilizers contain an ammonium salt or synthetic urea. After application to the land, a fraction of the ammonium may volatilize as NH₃. For urea fertilizers, the volatilization can be quite high (up to 12% of the nitrogen). In the

Netherlands urea is hardly used; most commonly ammonium nitrate (with added calcium-carbonate) is applied. This CAN (Calcium Ammonium Nitrate) fertilizer has a very low loss by NH_3 -volatilization (estimated about 2% of the nitrogen, Van der Hoek, 1994). Still the contribution of this source to total ammonia emission was significant (see 1.2.2, table 1.1.). This is because the total amount of fertilizer-N applied to pastures and arable land is high.

Over other crops, periods of deposition and periods of emission have frequently been found to alternate (see overview in Sutton, 1990 or Sutton *et al.*, 1993b). This phenomenon is attributed to the emission of biogenic ammonia by the vegetation itself, as a result of a high nitrogen level inside the plant. The latter is due to the high fertilization compared to natural vegetation.

Because grazed pastures generally are also strongly fertilized, such biogenic ammonia emissions might also play a role over this type of terrain (Sutton, 1990; Bussink, 1996). In this way fertilizer might contribute indirectly to ammonia emission from pasture.

1.3.4 Estimating ammonia emissions from grazed pasture.

Several mainly theoretical models for volatilization after slurry application (or from urine patches during grazing) have been developed. A model for slurry application by Van Faassen *et al.* (1990), has been very useful to increase the insight into the importance of several parameters. This model was used to evaluate the effects of changes in the method of application of the slurry. However, such volatilization models are quite complex and their prediction in individual situations is very uncertain. For this reason they are not able to make more realistic or more detailed quantitative estimates of ammonia emission from a specific area than the current approach followed in making emission inventories.

Emission inventories -including ammonia emission from pastures and other sources- are basically calculated from emission factors. These give average values of the ammonia volatilization (directly, as an average quantity of NH_3 or as a volatilization percentage of the involved total nitrogen), for average Dutch weather and farming practice. Emission factors are detailed according to various classifications, *e.g.* per animal of a certain species and age category, per land treatment or per source type (*e.g.* De Winkel, 1988). Emission inventories per municipality are produced by the LEI-DLO (Dutch abbreviation for Dutch Agricultural Economics Research Institute). They are derived, partly by extrapolation, from the (type of) experiments described above. From statistics about the farms per municipality the nitrogen production per relevant type of source is calculated. By application of the appropriate emission factors, the total (annual) emission per municipality is estimated. Effects of legal regulations are taken into account, as well as estimates of transport of slurry between municipalities (V.d.Hoek, 1994). After addition of contributions from industrial sources and households

-calculated also from emission factors-, these emissions per municipality are interpolated to grids of 5x5km by RIVM (V.d. Hoek, 1994).

1.4 Deposition and bidirectional exchange of ammonia

1.4.1 Introduction

At the surface, in principle both emission and deposition of a pollutant can occur. If it is not on beforehand clear whether deposition to or emission from a surface occurs, usually the term *surface/atmosphere exchange* is used, or -more briefly- *surface exchange* or *exchange*. Vertical transport in the atmosphere that accompanies the actual transfer is considered to be part of the exchange process. In this section, as well as in the rest of this thesis, the focus is on *dry (surface/atmosphere) exchange* processes. This means that wet and occult deposition are not taken into account; neither are emissions from other sources than the surface included (unless mentioned explicitly). So *e.g.* point sources of ammonia such as animal houses and manure stores are not included.

Dry exchange can take place with various types of surfaces or surface elements, *e.g.* with water surfaces (*e.g.* lakes, seas), with the soil, with the leaves of vegetation. A leaf can provide three possible sites of exchange: the cuticle, water on the cuticle and the stomata (see fig. 1.2, next page).

The *cuticle* is a more or less rigid, waxy structure, produced by the outer tissue of the leaf, the epidermis. It provides a wall between the atmosphere and the inner leaf tissues. Generally it is assumed that the cuticle is almost impermeable for most depositing water soluble compounds and that for most of these compounds adsorption to the cuticle itself is negligible if the leaf surface is dry. *Moisture on the leaf surface* however may provide a much more important substrate for exchange. The *stomata* are openings in the cuticle, through which exchange of gases between the inner leaf tissues (the mesophyll) and the atmosphere can take place. This exchange concerns mainly evaporation of water and release/uptake of gases involved in the photo-assimilation (O_2 and CO_2 , respectively), but other gases can follow the same pathway. The stomata can be closed by two specialized cells, *e.g.* when no assimilation takes place (dark, cold) or when drying out of plant tissues may occur (very dry and hot conditions). The mesophyll cells that surround the cavity below the stomatal opening are covered with moisture, with which they can exchange dissolved compounds. This moisture is part of the apoplast fluid. The apoplast is the system of intercellular cavities and vessels through which water, nutrient-ions and gases can be transported -basically from the root to other plant parts-, going around the cell plasma and cell membranes.

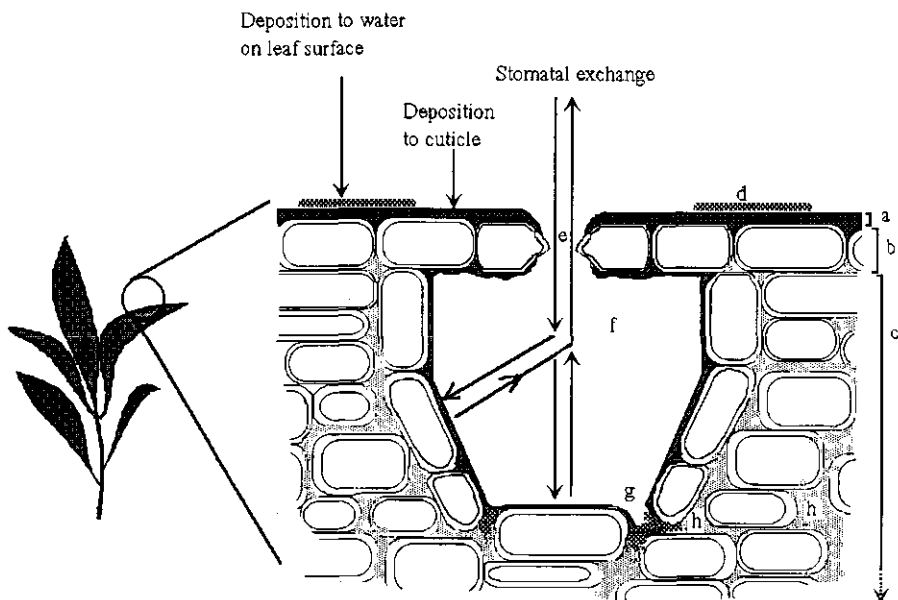


Fig 1.2. *Pathways of exchange with leaves of vegetation. Schematic representation of part of the leaf, showing: a) cuticle; b) epidermis; c) part of the mesophyll; d) water on cuticle; e) stoma (entrance); f) stomatal cavity; g) moisture on cell-walls bordering stomatal cavity; h) intercellular cavities.*

The exchange of a compound is quantified by its flux (density) in units of mass per unit of area and per unit of time (e.g. $\text{ng m}^{-2} \text{s}^{-1}$). Fluxes directed towards the surface ('downward' fluxes, indicating deposition to the surface) are given a negative sign by convention. Correspondingly 'upward' fluxes (indicating emission) are positive.

Exchange is basically induced by differences in concentration of a compound between the atmosphere and a surface. If the concentration at the surface is lower than in the atmosphere, deposition is favoured. If the concentration at the surface is higher, emission can occur. The actual exchange flux depends on the sign and magnitude of the concentration difference, as well as on the efficiency of all mechanisms involved in the transport and transfer.

Various processes can lead to effective removal or transformation of a compound on or in a surface *after* uptake from the atmosphere, so that the concentration at the surface remains negligible. In that case only deposition takes place; e.g. HNO_3 is taken up very

efficiently by almost any surface because it dissociates readily into H^+ and NO_3^- . In case of SO_2 , oxidation leads to removal of the dissolved SO_2 by transformation into SO_4^{2-} (see also 1.4.4).

In such situations with negligible surface concentration the deposition flux is only dependent on the concentration in the air. Now a deposition velocity (v_d) can be defined, relating the flux (F) and the ambient concentration (c) at height z :

$$F = -v_d(z) \cdot c(z) \quad (1.6)$$

On the basis of deposition velocities, the efficiency of deposition under different conditions can be compared, independent from the ambient concentration. Alternatively, based on estimated deposition velocities, the flux can be inferred from measured or modelled air concentrations.

In the next subsections -after a brief summary of the historical development of ammonia exchange measurements in 1.4.2- mechanistical knowledge on the exchange of ammonia will be summarized. In many situations, surface exchange of ammonia can be interpreted in terms of deposition and be approximated by use of the deposition velocity concept (1.4.3). However, the deposition to a surface may be limited because a surface may become saturated with ammonia (1.4.4). In some cases both emission and deposition occurs from the same surface (1.4.5). In 1.4.6 the description of these processes in transport models will be evaluated briefly (the often applied concept of resistance modelling is treated in detail in chapter 2). Finally an evaluation of gaps in knowledge that should be filled in by research is given in 1.4.7.

1.4.2 History of measurements of ammonia exchange

Most research on the dry exchange of NH_3 is quite recent, from the last 15-20 years and started after the recognition of its role in acidification and eutrophication in the early eighties. Much earlier however, -starting from the mid 19th century-, atmospheric ammonia and ammonium in rain were already subject of research to determine their contribution to the nitrogen supply of plants. Later, ammonia volatilization from fertilizer and manure was investigated mainly as a cause of losses of nitrogen in agriculture. For a review of these early measurements and relevant references, see *e.g.* Sutton (1990). In most of the early measurements of atmospheric ammonia, no distinction was made between gaseous ammonia and particulate ammonium. This makes interpretation in terms of dry exchange very difficult as both compounds have a quite different transport behaviour. Only few results on dry deposition were reported. The main reason was that analysis techniques for ammonia and ammonium often were not accurate enough for reliable determination of the small concentration differences (of an order of a few percent) that are usually involved in flux measurements in the field (for

a general overview of flux measurement techniques see chapter 3). Ammonia concentrations in laboratory measurements were often so high that it is very questionable if the exchange behaviour found in those experiments will also occur in the field, where concentrations are much lower.

Only since quite recently developments of especially denuder techniques (reviewed *e.g.* by Slanina, De Wild and Wyers (1992), see also 3.3.3) have provided analysis techniques that are both precise and sensitive enough for field measurements of gaseous NH_3 and particulate NH_4^+ separately, on routine basis, including application for exchange measurements.

Even up until a few years ago, all of the knowledge of exchange of ammonia was derived from extrapolation of results of relatively short experiments (of typically a few days or weeks) to much longer periods, as it was impossible to monitor exchange fluxes for longer periods due to inadequate or very labourious measurement techniques.

At present, continuous measurements of fluxes of ammonia and NH_4^+ over extended periods have become possible by use of thermodenuder (3.3.3.1) and wet denuder systems (3.3.3.2). These systems were applied in the research for this thesis, because they enable the very high degree of automation necessary for long term flux measurements.

1.4.3 Deposition of ammonia

As mentioned in section 1.2.4, considerable amounts of ammonia deposit to natural terrain. In measurements over such terrain, deposition predominated, generally with high efficiency (*e.g.* Duyzer *et al.*, 1987; Andersen *et al.*, 1993; Duyzer, 1995; Erisman and Wyers, 1993; Sutton, 1990; Sutton *et al.*, 1992; Wyers *et al.*, 1992). Reported deposition velocities are often not much smaller than the maximum value that would be possible if the exchange were determined by transport within the atmosphere only (v_{dmax}). This means that the actual transfer to the surface is no limiting factor to the deposition velocity.

This efficient deposition is generally attributed to the dissolution of ammonia in aqueous solutions at the surface. Via the stomata, ammonia can dissolve into the apoplast fluids inside the plants. Like the case for many other compounds (*e.g.* SO_2), the stomata are therefore considered to be an important pathway for ammonia deposition to vegetation. However, it was also observed that the deposition of compounds like NH_3 and SO_2 was frequently more efficient than could be explained by stomatal uptake. Even when the stomata are (almost) closed (*e.g.* at night) considerable deposition fluxes of NH_3 or SO_2 were observed. Because of this, the leaf surface is supposed to be also an important sink for ammonia. As mentioned in 1.4.1, the cuticle is assumed to be hardly permeable to water-soluble compounds due to its waxy structure. Therefore it is assumed that deposition of NH_3 to the leaf surface proceeds mainly to water on this surface. After rain and when dew or guttation occurs, the presence of this water is obvious and visible.

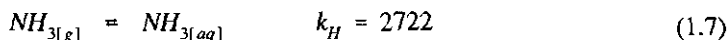
However, even in absence of visible water, the leaf surface is often a relevant sink for NH_3 and SO_2 , e.g. Van Hove *et al.*, 1989 (bean and poplar leaves, see below); Vermetten *et al.*, 1992 (forest), Vermetten and Hofschreuder, 1994; Duyzer *et al.*, 1994 (forest). It is generally assumed that this is because still water is present in thin, microscopic layers or in micropores of the cuticle. The involved quantity of water ('water layer thickness') may vary with relative humidity (Van Hove, 1989).

In fact, the actual form and origine of such microscopic water layers is a point of discussion. In leaf chamber experiments, Van Hove *et al.* (1989) measured the ammonia adsorption to the leaf surface of *Phaseolis Vulgaris* (bean) and *Populus Euramericana* (poplar) as a function of air humidity (RH 50-90%). From this, they derived an equivalent thickness of the assumed water layer of about 50-400 μm . Van Hove and Adema (1995) however weighed volumes of water that adsorb to dead leaves of various species. They found that these volumes are too small to explain the high adsorption of ammonia just by uptake in superficial water. They postulated that the cuticle has a variable permeability, which decreases with decreasing humidity. In this way ammonia could be absorbed by the interstitial fluids of the plant even when the stomata are closed. A different mechanism has been suggested by Burkhardt and Eiden (1994) and Burkhardt (1995). They measured the (electrical) conductivity at the surface of coniferous needle in relation to ammonia deposition. They derived that water layers may exist even at low ambient RH due to deliquescence of hygroscopic salts. They observed that those salts were especially concentrated close to the stomata. There local RH is high when the stomata are open, so that the salts may easily deliquish to form solutions. Additionally, Burkhardt and Eiden suggest that salts close to the stomata may have a 'wick' effect by attracting water from inside the stomata. As a result thin water films through the stomatal opening might connect water films on the leaf surface with the apoplast fluids, enabling an almost continuous feeding of the leaf surface water layers as long as the stomata are not completely closed.

1.4.4 Saturation effects

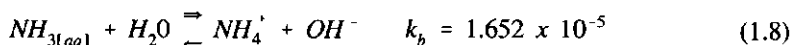
In principle, after ammonia has deposited to a humid surface or to water in the stomata, its dissolution is subject to two chemico/physical equilibrium reactions.

In presence of water, gaseous ammonia dissolves until Henry equilibrium is reached, according to:



with k_H being the Henry constant for the dissolution of ammonia (value at 15°C).

Next the dissolved ammonia may be protonized:



where k_b is the alkalinity constant of NH_3 (value at 15 °C).

Combining both equilibria and expressing their temperature dependence yields (for diluted solutions):

$$c_0 = (NH_3)_g = f \cdot \frac{[NH_4^+]}{[H^+]} \quad (Pa) \quad (1.9)$$

$$f = 1.026 \cdot 10^{-6} \cdot \exp\left(-10378 \cdot \left(\frac{1}{T} - \frac{1}{298.15}\right)\right) \quad (Pa)$$

(after Asman, 1992, after conversion of C_0 and f into Pascal units).

The combined equation (1.9) makes clear that in addition to temperature, the pH has a strong influence on the equilibrium ratio between gaseous ammonia and an ammonium solution. Very generally speaking, a solution with a low pH (*e.g.* below 6.5) will much more easily take up NH_3 from the atmosphere than the same solution at a high pH (*e.g.* over 8).

The equilibria are generally considered to be established instantaneously. As a result of these reactions, for any wet surface with a given concentration of NH_4^+ and H^+ and a given temperature, an equivalent concentration in the gas phase immediately above this surface can be calculated. This equilibrium gas phase concentration can be seen as the potential gas phase concentration of ammonia at the surface of this wet surface. It will be referred to further as the surface concentration of gaseous ammonia; in line with eq. 1.9 it will be denoted as c_0 . As long as the actual air concentration above the solution is higher than this surface concentration, atmospheric ammonia can still dissolve in the solution at the surface and deposition can proceed. If the actual air concentration is lower than c_0 , volatilization of NH_3 may occur from the surface, leading to emission. If the actual gas phase concentration in the atmosphere above the solution equals this (potential) surface concentration, the solution is in chemical equilibrium with the atmosphere above it, and no exchange takes place (saturation of the surface).

The role of pH and Henry-equilibrium in the deposition of ammonia over a water layer was investigated in a small scale wind tunnel by Adema *et al.* (1986), Heeres and Adema

(1989) and Adema and Heeres (1995). After deposition during a certain period, saturation of the water layer occurred. The quantity of NH_3 that could be absorbed depended on the pH of the solution. If the water layer was not buffered, the deposition of NH_3 caused an increase of pH (eq. 1.7-1.9), fastening saturation. The efficiency of ammonia deposition was high at a pH below 7.5-8, but decreased rapidly at higher pH values.

Adema and coworkers did the same experiments with SO_2 . Reactions involved in the dissolution of SO_2 are the following:



In most cases a large part of the dissolved SO_2 may be oxidized (by O_3 , H_2O_2 or O_2), leading to sulphate formation and production of 2H^+ . There is discussion whether the oxidation of SO_2 is a metal catalysed reaction, taking place in the bulk of the water layer, as is generally assumed. Adema and Heeres (1995) concluded from the wind tunnel experiments that uncatalysed oxidation by O_2 in the boundary layer between water and atmosphere is the dominant process. However, this mechanistical question is considered to be beyond the scope of this thesis.

Adema and coworkers also observed clearly, that SO_2 deposited efficiently at a pH above 5. Below this value the deposition decreased rapidly and finally stopped. Hence over unbuffered water layers SO_2 deposition finally inhibited itself, like the case for NH_3 (but with opposite relations to pH).

From mixtures of NH_3 and SO_2 , much higher amounts of both gases could deposit. A certain "steady state" situation occurred, in which NH_3 and SO_2 deposited almost continuously in a ratio of 2:1 on molar base. This indicates that the deposition of both compounds is mutually adjusted so that at the surface they neutralize each others pH effect. This mutual relation between the deposition rates of two compounds is often referred to as "co-deposition". Of course the relation is only indirect, via the pH of the surface. The deposition of one compound facilitates the deposition of the other, but no in-air interaction takes place (Adema *et al.* 1986).

The mentioned experiments concerned mainly the saturation effects caused by NH_3 (and SO_2) equilibria. Adema and Heeres (1995) argued that the deposition of NH_3 might be reversible or irreversible, depending on the compounds that deposited together with NH_3 . Due to changes in air concentration or surface conditions, water layers might become over-saturated and previously deposited NH_3 might in principle be emitted again. If NH_3 deposits together with SO_2 , solutions containing stable ammonium sulphate salt will be produced. This deposited NH_3 will not be emitted again. Significant volatilization of ammonia would require that the H^+ resulting from the dissociation of NH_4^+ be taken up by the sulphate anion. This does not occur due to the very weak alkaline properties of this anion. Hence in such a case the NH_3 deposition is irreversible. In absence of SO_2 (or other pollutants with sufficient acidity), the pH effect of deposition of NH_3 to clean water will partly be neutralized by deposition of CO_2 , resulting in ammonium(bi)-carbonate solutions. Unlike the sulphate, ammonium(bi)carbonate is unstable. The Henry constant of CO_2 and the alkaline properties of HCO_3^- and CO_3^{2-} are such, that -according to Adema and co-workers-, the deposition process can be reversed quite easily. This may occur when temperature increases, air concentration decreases or when the water evaporates. Then simultaneous volatilization of NH_3 and CO_2 may proceed until equilibrium between air and solution is re-established again for both compounds. In this case the deposition is reversible (Adema and Heeres, 1995).

It is still unclear how well laboratory results on saturation effects, co-deposition of SO_2 and NH_3 , or the theoretical concepts of reversible and irreversible deposition can be extrapolated to field conditions. On natural surfaces, water layers may have a much more complex composition. Various compounds excreted by the leaves and deposition of strong acids such as HNO_3 , HCl and H_2SO_4 may partly neutralize the pH effect of NH_3 deposition. In dew on grass, Arends and Wyers (1991) generally found a pH close to 5. At this low pH, saturation of the dew with ammonia is not expected to occur soon.

Confirmation that results of Adema on saturation effects and co-deposition are applicable to real leaves -though under laboratory conditions, in leaf chambers-, can be found in the work of Van Hove and co-workers. They found that leaves of bean and poplar acted as a capacitance for NH_3 , dependent on humidity. They suggested to represent it as such in deposition models (Van Hove *et al.* 1987). They partly followed a capacitor approach in their calculations of water layer thicknesses (1.4.3). These were derived from the observed absorption of ammonia (Van Hove *et al.* 1989).

When they applied mixtures of NH_3 and SO_2 , they found that absorption of both gases was enhanced considerably (Van Hove *et al.* 1989), as occurred in the wind tunnel of Adema and co-workers.

Field measurements in canopy throughfall by Van Breemen *et al.* (1982, forest) and by Bobbink *et al.* (1992, heathland) support the occurrence of co-deposition. They found a

2:1 ratio between NH_4^+ and SO_4^{2-} in the throughfall water. Erisman and Wyers (1993) however found mean ratios of NH_3 and SO_2 deposition much larger than 2 for heathland.

1.4.5 Bidirectional exchange.

Over many types of terrain periods of emission are observed to alternate with periods of deposition. Over crops and grazed pastures, significant emission occurs frequently. Even over natural terrains, in many experiments short periods with gradients indicating emission are observed from time to time (e.g. Duyzer *et al.*, 1992; Wyers *et al.* 1992), though the effect on the net-exchange (deposition) over long periods is usually considered insignificant in such cases.

Varying per type of terrain, bidirectional exchange behaviour can be explained by one or more of three main mechanisms: reversible deposition, stomatal exchange and volatilization due to land treatments.

Reversible deposition.

Emissions of ammonia may occur when ammonia that has previously been deposited to the leaf surface volatilizes again. This mechanism was already discussed, as reversible deposition, in 1.4.4. Extension of the concept of the surface as a capacitor may be possible (Sutton *et al.* 1995, Sutton *et al.* 1998). Dissociation of deposited ammonium-nitrate in aerosol may also contribute to emissions of ammonia (Wyers *et al.* 1993). For natural terrains, the short and weak emissions might eventually be explained largely by reversible deposition. For other terrains, it might contribute for some part to the emissions, but other processes are likely to be involved too.

Stomatal exchange

In measurements over crops, often alternating periods of emission and of deposition were observed (e.g. Morgan and Parton, 1989; Schjørring and Byskov-Nielsen, 1991; Sutton *et al.*, 1993a). On annual basis such crops may often be net emitters of NH_3 , which is generally attributed to emission via the stomata. This is opposite to the stomatal deposition which is usually observed over natural vegetation.

The main theory to explain this different stomatal exchange behaviour is that fertilization, via metabolic processes, increases the ammonium content of the apoplast fluid (e.g., Sutton *et al.* 1993ab) in crops. The ammonia concentration inside the stomatal cavity may be assumed to be in equilibrium with this apoplast ammonium concentration and pH (Farquhar, 1980). As a result, stomatal ammonia concentrations in crops may often exceed the ambient concentration, causing emission when the stomata are open. In natural vegetation the much lower N-supply causes lower stomatal ammonia concentrations, so that stomatal deposition dominates.

So the concentration inside the stomata can be interpreted as a surface concentration; therefore it will be denoted here as c_{st} . When the actual pH and ammonium

concentration of the apoplast fluid are known or can be estimated, c_{ost} can be calculated from the Henry- and protonization equilibrium relations (for the given temperature; eq. 1.7-1.9). This was first demonstrated by Farquhar (1980); see also *e.g.* Sutton, 1990. However, measurement of the composition of apoplast fluids without contamination by other (cell)fluids has long been difficult to realize technically. At present it has become possible to sample leaf apoplast fluid even on routine basis, by a vacuum extraction technique developed by Schjørring and co-workers. In the extract, pH and NH_4^+ concentration of the leaf apoplast fluid can be measured; contamination is very small (Husted and Schjørring, 1995).

A more indirect estimate of c_{ost} has often been derived from flux measurements by determination of the so-called compensation point. The compensation point is the ambient concentration at which equilibrium is observed between ambient concentration and surface concentration and hence where no net exchange with the surface is observed. At air concentrations higher than the compensation point, deposition occurs while at lower concentrations emission is found. According to this reasoning, a measured compensation point for stomatal exchange with vegetation may provide an estimate of c_{ost} . On the other hand, a calculation of c_{ost} from the composition of the apoplast fluids can be interpreted as an estimate of the stomatal compensation point.

The use of compensation points for these aims implies in practice that the assumption is made that the compensation point is either constant or can be parameterized in a straightforward manner. Generally it is assumed that c_{ost} is independent from the ambient air concentration, because the ammonium concentrations and pH of the apoplast fluid in (contact with) the stomatal cavity are controlled mainly by metabolic processes. However, these processes and hence c_{ost} may vary as a function of other, biological variables (*e.g.* plant species and variety, growth stage, fertilization (Schjørring, 1991)).

Indeed measurements of compensation points show a large variation. Table E.2 (appendix E) gives an overview of experiments in which compensation point values (or apoplast pH and NH_4^+ concentration) were determined.

Farquhar (1980) found values of $1.5\text{--}4\ \mu\text{g m}^{-3}\ \text{NH}_3$ over several species (beans, mays, amaranthus, eucalyptus) in growth chambers. Compensation points of $1.4\text{--}2.1\ \mu\text{g m}^{-3}\ \text{NH}_3$ were found by Dabney and Bouldin (1990) over alfalfa (field conditions). Much higher values were reported by Morgan and Parton (1989) over wheat: $16\text{ to }28\ \mu\text{g m}^{-3}\ \text{NH}_3$, during grain ripening and senescence (laboratory conditions). The latter may be explained by a shift in the balance between NH_4^+ producing and consuming reactions within the plant. In the later growth stages, NH_4^+ producing reactions become more important leading to higher intercellular NH_4^+ concentrations (Morgan and Parton, 1989; Schjørring, 1991).

At present, much research on biological and other factors influencing compensation points, both from direct analysis of apoplast fluids and from flux measurements, is being done by Husted, Schjørring and co-workers (see table E.1).

In practice, exchange with crops may not be limited to the stomata. Deposition to the leaf surface may also occur. It is even the most probable explanation of deposition during the night, when the stomata are closed. At daytime, both pathways of exchange may compete with each other: ammonia emitted from the stomata may be deposited again to the leaf surface. Sutton, Fowler and co-workers showed that the net-exchange resulting from these competing mechanisms could be understood and described quite well by the assumption of a surface concentration for the canopy as a whole. This 'canopy compensation point' can further be interpreted or modelled as the result of stomatal and leaf surface exchange (e.g. Sutton, 1990; Sutton and Fowler, 1993; Sutton *et al.* 1995, Sutton *et al.* 1998).

Ammonia volatilization due to land treatments; pastures

Slurry spreading, grazing (urine patches) and -to a lower extent- fertilizer application can result in a considerable volatilization of ammonia and hence in periods of emission. Measurements of this volatilization of ammonia due to land treatments were already discussed in section 1.3. It was also pointed out there that only emission was measured. However, by the followed approach the possibility was neglected that even if no emission occurs any longer, the surface may still be influenced by the treatment. This might e.g. lead to a reduced ability of the surface to absorb ammonia and so to a lower deposition efficiency.

On the other hand, even during the experiments, emission may not have occurred continuously; it may have alternated with periods of deposition. The micrometeorological mass balance method cannot be used to quantify deposition fluxes. This deposition could be relevant, however, for the net amount of ammonia transferred from the plot to the atmosphere as a result of the land treatment.

Due to this focussing on emission only, it is also hardly possible to derive information on the contribution of bidirectional exchange via the stomata (and eventually reversible emission) to the net-exchange of such intensively managed pastures. From a few available measurements over pastures that had only be treated with fertilizer it follows that a pasture may show behaviour that is comparable with other crops:

Sutton (1990) measured ammonia fluxes over an ungrazed pasture (mixed grass species, mainly Italian ryegrass) during three days in June 1988. The pasture had only been treated with fertilizer (ammonium nitrate based; 150 kg ha^{-1} of N), 8 weeks before the (flux-gradient) measurements. At daytime, mainly significant emission was observed, especially under dry conditions. In the beginning of the night, weak deposition occurred.

The measurements were not continued all night long, so that the net daily exchange cannot be derived. From in-canopy profiles, Sutton established that the daytime emission originated from the canopy, not from the soil. Assuming that this was probably due to stomatal emissions, he derived stomatal compensation points under dry conditions within the range of 2-7 $\mu\text{g m}^{-3}$ of NH_3 . Ambient concentrations were generally below 1 $\mu\text{g m}^{-3}$ of NH_3 .

In flux-gradient measurements by Bussink *et al.* (1996; see also the companion paper on these measurements by Harper *et al.*, 1996) over ungrazed pasture (perennial ryegrass), emission occurred mainly at daytime during one or two days after fertilizer applications. This was attributed to stomatal emissions due to excessive uptake of N from fertilizer. At daytime of other days (and generally at night) however, deposition dominated, with sometimes periods of weak emissions which were attributed to evaporation of dew. The measurements were distributed over the growing season, during which the pasture received about 400 kg ha^{-1} of N from calcium nitrate fertilizer in several applications, generally shortly after mowing of the grass. This fertilization rate was much higher than in Sutton's measurements. As a result, the derived compensation points (for the crop as a whole) were high: in the range 13-18 (seasonal average 14) $\mu\text{g m}^{-3}$ NH_3 . Because average ambient concentrations were even higher (Harper *et al.* 1996), the pasture was still a net-absorber of NH_3 from the atmosphere. The compensation point was related to grass N concentration (related partly to fertilization), soil water content, and mowing. Some caution should be taken in the interpretation of these measurements by Bussink and co-workers, because in fact gradients of total NH_x were measured. The ammonia was sampled in gas-washing-bottles, and no filters were used to discriminate between particulate and gaseous NH_x (Bussink *et al.* 1996).

It follows from both experiments, that uptake and release of ammonia by the grass may play a relevant role in ammonia exchange over intensively managed pastures. Compensation points, actual flux-patterns and the resulting long-term net-exchange vary considerably. More measurements over this type of terrain are necessary to investigate that variation.

1.4.6 Descriptions of ammonia exchange in transport-models.

General aspects of transport models

In long-range or regional transport models, the concentration of a pollutant in an air parcel (EMEP) or theoretical plume (OPS) is recalculated at regular distances (the points in a horizontal grid) relative to the source. The size of the applied grid determines the resolution of these transport models (EMEP model: 150x150km (Seland *et al.* 1995); OPS: 5x5km for the Netherlands; 50x50km for Europe (Van Jaarsveld, 1995). Effects of dispersion, emissions, deposition and chemical reactions are calculated per grid square. Measured concentrations at monitoring stations can also be taken into account. In this

way maps of concentration and deposition can be made, as well as budget studies of in- and export of pollutants per country. Also the origin (main source areas) responsible for the deposition to specific areas can be identified. In the Netherlands, for policy development purposes, OPS is the most important transport model.

Special deposition models such as DEADM (Erisman, 1992; Erisman 1993) describe only the deposition process; as input they need either measured concentrations or concentrations calculated by transport models.

Estimates of emission in transport models

The OPS model uses estimates of annual ammonia emission on a 5x5 grid as basic input. These estimates are derived from emission inventories as described in section 1.3.4. To derive (theoretical) hourly emissions from these annual values, statistically derived, average seasonal (monthly) and diurnal patterns (*e.g.* from Asman, 1992) can be applied.

Descriptions of deposition

In most transport- and deposition models, the deposition flux is basically parameterized from a deposition velocity and concentration. Sometimes fixed values of deposition velocity are used. Often however, including OPS, the EMEP-model and DEADM, the deposition velocity is calculated by a parameterization based on resistance modelling. The concept and theory of resistance modeling will be treated in detail in chapter 2 of this thesis. Very generally spoken, efficiency of transport through the atmosphere and of the actual uptake by the surface are separated and expressed in different resistances. The resistance to transport through the atmosphere is derived from relatively simple parameterizations and meteorological parameters. The surface resistance is derived from parameterizations with a variable degree of detailing: one fixed average value; classified values (per type of surface, season, day or night, meteorological condition), or subdivided into a number of parameterized subresistances.

In OPS, for a long time one fixed average surface resistance for all surfaces and conditions was used. In DEADM, variation in the surface was implemented according to type of terrain, season, day/night and wetness of the surface (Erisman *et al.* 1994). Since recently, these more detailed parameterizations of DEADM have been implemented in OPS too (Erisman, *pers. comm.*).

1.4.7 Weaknesses of estimates of exchange

In combination with the critical load concept, transport- and deposition models play a crucial role in the development of deposition abatement policies. They can be used to estimate how (present or optional) specific emission reductions contribute to the prevention or reduction of exceedance of critical loads in (specific) natural areas.

Therefore it is very important that their parameterizations of net-exchange are accurate. In practice, some shortcomings may influence the estimates:

Resolution of models

Although a resolution of 5x5 km for OPS and DEADM is quite high compared to the resolution of other models, it is still quite coarse given the high spatial variability of ammonia concentrations (and hence deposition). This may limit the accuracy of loads to ecosystems, especially in case of typical small scale ecosystems (e.g. lakes).

Parameterization of deposition of ammonia in general

Generally spoken, the correctness of the parameterization of deposition of ammonia in transport models is quite uncertain. So far, no parameterizations have been implemented to account directly for processes such as saturation of the leaf surface, co-deposition with SO_2 and bi-directional stomatal exchange. The mechanistical knowledge regarding these processes has increased strongly due to research frameworks such as DPPA and BIATEX. However, it turns out to be difficult to derive parameterizations that can be applied in models. This is mainly because surface equilibrium concentrations (c_0) of ammonia can be very variable, as a function of many factors. Examples are factors that determine the composition of the apoplast fluids (stomatal exchange) and eventual interactions between the leaf surface and the inner plant environment. Even as far as the influences of these factors are understood in general, it seems that many additional measurements are necessary to quantify the relevant parameters for specific types of vegetation and conditions.

Apart from these problems in the description of the exchange, an additional uncertainty concerns measurements of fluxes of ammonia that are used to derive such parameterizations. In some situations, the ammonia gradients that are measured to derive fluxes may be influenced by atmospheric reactions with HNO_3 to form NH_4NO_3 (1.2.4), or by the dissociation of previously produced NH_4NO_3 (see 1.2.4). An analysis by Zhang *et al.* (1995) showed that often no equilibrium exists and that gradients of HNO_3 and NH_4NO_3 may be affected seriously by decomposition of NH_4NO_3 . In an analogous way formation of NH_4NO_3 due to reaction of HNO_3 with NH_3 emitted from the surface may bias the measured gradients.

Exchange over grazed pasture

The rather large uncertainty in estimates of exchange over grazed pasture is related both to the resolution of the models and to uncertain parameterizations. If strong emissions occur within a grid, in principle a high deposition to the same grid may be calculated if emission and deposition are calculated independently from each other. In the documented versions of OPS (under the name of TREND, Van Jaarsveld 1995) indeed deposition was parameterized completely independent from the emission, with a

constant surface resistance for all surfaces. At least in periods that pastures are an important source for ammonia, this representation is at least unrealistic, because a surface cannot be a net-source and a net-absorber at the same time. Of course, in most cases this modeling result represents the situation that ammonia emitted by one pasture is deposited to another, within the same grid, which will occur quite frequently in practice. However, even if no slurry spreading, fertilizer gift or grazing occurs, pasture in emission regions is exposed to relatively high concentrations of ammonia. This might also reduce the sink efficiency of the leaf surface to deposition. Due to the dissolution of NH_3 in the water layers at the leaf surface, pH will increase and NH_4^+ will accumulate, so that the water layer finally may become saturated with NH_3 . Apart from this, instead of deposition, stomatal emission might also occur as a result of the high N-supplies to pastures.

By the recent adaption of parameterizations from DEADM (Erisman, pers. comm), the OPS model may distinguish between ungrazed and grazed pastures in summer and winter season, with different surface resistance parameterizations. However, validation with net-exchange measurements over grazed pasture so far has not yet been possible.

For pastures the ammonia exchange with the atmosphere is not very relevant, compared to the high direct supplies of NH_x via fertilizer and slurry. But it is important however, as a factor determining the net-transport of ammonia to other, more sensitive areas. Therefore it is necessary to evaluate if the current modeling approach still leads to correct estimates of the contribution of pastures to ammonia transport. This requires an extended set of measurements of the net-ammonia exchange over a pasture terrain undergoing all usual agricultural treatments (including periods without actual treatment). As explained in 1.4.5, no net-exchange measurements over a grazed pasture are available that could be used for that aim, because focus was on emission only and/or measurement periods were too short.

1.5 Aims and general approach of the experiment

The primary aim of this study was to investigate the net-contribution of pastures in an intensive livestock breeding area to the export of ammonia from this area to sensitive receptor areas. In this framework a quantitative and mechanistical analysis of the net exchange of ammonia over grazed pasture was made. The following aspects of ammonia exchange were investigated:

- Total net-exchange on annual and seasonal scales
- Regular flux patterns and controlling mechanisms
- Compatibility of measured exchange with estimates according to the procedures followed in models and emission inventories

- Influence of SO_2 , NH_4NO_3 and HNO_3 on ammonia exchange
- Parameterization of the exchange process.

To acquire the necessary data, the net ammonia exchange over a pasture was measured continuously during two full years, with high time resolution (1 hour). In this way the measurements covered all usual treatments of the pasture, and seasonal as well as diurnal patterns could be analysed. Also, errors due to lack of representativeness with respect to meteorological and biological conditions were avoided by this approach as best as possible. The exchange was measured by the aerodynamic gradient method. Only dry exchange was measured; deposition via rain was not included. Neither were emissions from other sources than pasture included, such as animal houses, manure stores or stacks.

To study possible effects of SO_2/NH_3 co-deposition, and to evaluate the influence of HNO_3 and NH_4NO_3 on the exchange of ammonia, gradients of these compounds were measured simultaneously with those of NH_3 during 8 and 15 months respectively.

1.6 Thesis plan

This chapter 1 gives an introduction to the background, aims and general approach of the research reported in the thesis, and gives an overview of current knowledge on ammonia exchange.

Chapter 2 gives a summary of mathematical descriptions of vertical transport and exchange processes in terms of resistance modeling. The theory of vertical transport through the atmosphere is summarized and simple resistance models to describe deposition, bidirectional exchange and simultaneous exchange with stomata and leaf surface (respectively) are elucidated.

In *chapter 3* the experimental set up is described. This includes the location and relevant features of the site, the choice of the techniques to be applied and a description of the actual set-up and the applied instruments.

Chapter 4 reports the data processing, including flux calculation and selection of reliable flux measurements, and evaluates the uncertainty in measurements and conclusions drawn from them.

In *chapter 5*, the main results of ammonia concentration and exchange measurements are summarized and annual, seasonal and diurnal patterns are derived. Also, typical surface resistances are estimated for periods in which deposition dominated.

In *chapter 6* the mechanisms behind observed bidirectional patterns of NH_3 exchange are analysed. Explanations assuming an overall compensation point for the leaf surface, reversible leaf surface deposition or emission from soil or stomata are evaluated subsequently.

In *chapter 7* a comparison is made between the net-exchange derived from the measurements and estimates based on emission factors applied to the treatments of the pasture.

In *chapter 8* the effects of SO_2 , NH_4NO_3 and HNO_3 on ammonia exchange are discussed. The general patterns of SO_2 concentration and deposition efficiency are summarized and compared with those for NH_3 to find evidence for co-deposition effects. Observed high deposition velocities of HNO_3 and the frequent upward gradients of NH_4NO_3 are explained as results of reaction of HNO_3 with emitted ammonia close to the ground. It is concluded however, that these effects do not influence NH_3 fluxes significantly at this location because NH_3 gradients are much larger on molar basis than those of both other compounds.

In *chapter 9* a parameterization of the exchange at Zegveld, based on the 'canopy compensation point model' by Sutton and Fowler (1993) is tested. The model parameters are fitted to periods without influence of slurry spreading. Then this parameterization is used to estimate the contribution of slurry spreading to the net exchange.

In *chapter 10* the main conclusions from the research are drawn.

Chapter 2

Resistance modelling of dry exchange

2.1 General approach of resistance modelling

In chapter 1 the deposition velocity has been introduced as a parameter to express the efficiency of transfer from atmosphere to surface. However, the deposition velocity just reflects the resulting efficiency of *all* mechanisms involved in the exchange of a compound. In practice dry exchange can be considered to proceed in several subsequent stages, with different main transport mechanisms. Describing transport of a pollutant through the atmosphere to the surface, at least three (notional) layers can be distinguished. In the aerodynamic layer the vertical transport is driven by turbulence, by means of eddies in the atmosphere. Very close to the surface there is a thin layer into which eddies can not penetrate, because the vertical air movement is blocked by the surface. As a result, the flow very close to surface elements is about laminar. Pollutants cross this quasi-laminar boundary layer mainly by molecular diffusion.

The third stage of transport is the actual uptake or release by the surface. Here several different mechanisms can be involved, depending on the type of surface and the compound.

The deposition velocity provides no direct information on each individual stage of transport. This makes analysis of the effects of meteorological and surface parameters very difficult. Sometimes classification of measurements according to turbulence parameters can help to distinguish between variations related to atmospheric transport and variation caused by other processes. However, factors that influence turbulence often affect other transport stages as well. Therefore where possible, in more detailed analyses of exchange generally use is made of the framework of *resistance modelling*.

In resistance models of surface exchange, an analogy is drawn between the flux in exchange processes and a current in electricity (which was in turn modelled by analogy with heat transfer). The flux is determined by a resistance (R) and the concentration difference (Δc) across it, according to:

$$F = - \frac{\Delta c}{R} \quad (2.1)$$

The resistance analogy enables subdivision of the exchange into a number of processes with respective resistances. It is often applied in models for exchange with vegetation (e.g. Thom, 1975). Generally the canopy of vegetation as a whole is treated as one 'big

leaf'. In such 'Big Leaf' resistance models usually at least the three main transport 'layers' are distinguished. They are assigned an aerodynamic (R_a), (laminar) boundary layer (R_b) and surface resistance (R_c) (e.g. Garland, 1977; see fig. 2.1).

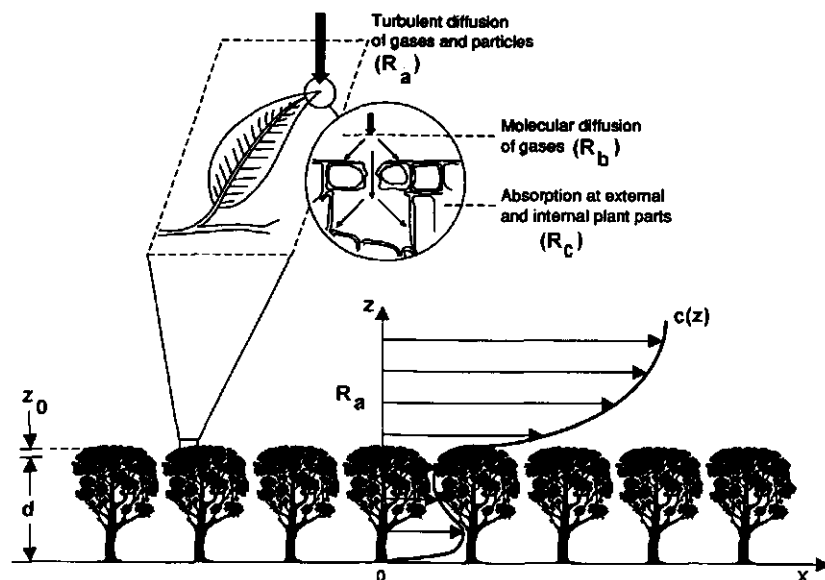


Fig. 2.1 The resistance model of the dry deposition process (from Erisman and Draaijers, 1995). Z_0 = aerodynamic roughness length and d = zero plane displacement height (see 2.2); $c(z)$ = concentration at height z .

In 'Big Leaf' resistance models, generally the assumption is made that the surface concentration is negligible. Then the concentration difference between the surface and the atmosphere is determined by the concentration in the atmosphere only. In that case the flux can be expressed by the ambient concentration at reference height (c_r) and the (serial) sum of the resistances in subsequent layers:

$$F = \frac{-c_r}{R_a + R_b + R_c} \quad (2.2)$$

The serial sum of the resistances is equivalent to the reciprocal of the deposition velocity. R_a and R_b for given measurement conditions can be parameterized from relatively simply meteorological parameters, so that the influence of surface

characteristics on the flux can be studied much more specifically on basis of R_c than from v_d . Likewise, resistance modelling enables more detailed estimation of fluxes from measured or modelled concentrations, because the influences of surface characteristics and of meteorological conditions can be accounted for separately.

Starting from the basic form, more detailed Big Leaf models have been developed (*e.g.* Wesely, 1989; Hicks, *et al.*, 1989 and many others). Different processes involved in the uptake of pollutant at the surface are represented as individual (parallel or serial) pathways ('subcircuits') each with their own resistance (see section 2.3). Especially for forests this has resulted in quite complex resistance models. However validation of the description of individual pathways in such models is often very difficult. In many situations only the overall, net exchange between a surface and the atmosphere can be measured with sufficient accuracy. In section 3.2, a number of techniques for measurement of total exchange are described briefly. Often micrometeorological techniques are applied; in many of these, the uptake (or release, see below) of pollutant by the surface is derived from vertical transport of pollutant within the atmosphere above the surface. This is only possible if the vertical flux at the measurement height equals the actual exchange flux at the surface (constant flux requirement), or can be corrected for changes of flux with height. Non-constant fluxes can be caused by processes of advection, storage, or production or decomposition of pollutant within the atmosphere. These possible error sources to exchange measurements will be explained further in chapter 3.

In the next sections, resistance modelling of transport will be worked out in more detail. In section 2, the vertical transport through the atmosphere to the surface is described. First a summary is given of relevant theory of vertical atmospheric transport, which serves also as a basis for the treatment of micrometeorological measurement techniques in chapter 3. Subsequently resistance parameterizations are given for the transport through the aerodynamic layer and through the quasi-laminar layer. In section 3 the actual transfer process to the surface is worked out according to conventional 'Big Leaf' modelling. As mentioned, this implies that the assumption is made that the surface concentration is negligible. This may not always be correct in practice, but in many situations the mathematical parameterization given by Big Leaf models yields acceptable results for general analyses and flux estimates. However, if significant emission occurs, the surface concentration cannot be negligible. In this situation, -and eventually when the absorbing solution approaches saturation-, the resistance model should be adapted so that a non-zero surface concentration can be accounted for. Parameterization of such bidirectional exchange processes will be treated in section 4. Finally, in section 5 the canopy compensation point model by Sutton and Fowler (1993) will be summarized. This model enables the description of net-exchange between a crop

canopy and the atmosphere as a result of simultaneous bidirectional exchange with the stomata and with the leaf surface.

2.2 Transport through the atmosphere

2.2.1 Summary of the theory behind aerodynamic vertical transport

The aerodynamic transport is the first stage in the vertical transport of a pollutant to the surface. The equivalent 'layer' extends from the top of the atmospheric boundary layer to very close to the surface, where the (quasi)laminar boundary layer begins. Meteorological conditions have a strong influence on this transport stage and so on the whole exchange process. To understand these effects and of its parameterization in resistance modelling, some generally accepted theory of transport in this stage is summarized here. The summary is based on much more detailed descriptions of micrometeorological theory given by Thom (1975) and Stull (1988). Most equations were adapted from these works. In some cases rearranged versions of the basic equations were adapted from summaries by Van Pul (1992), Erisman (1992) and Sutton (1990).

Generally the vertical flux F of a property X is given by the average product of vertical wind velocity w and the value of X in the displaced air:

$$F = \overline{wX} \quad (2.3)$$

It is obvious that vertical transport occurs if the vertical component of the main wind is not zero on average. Property X is then carried upward or downward according to the net-direction of the main wind. However, in practice turbulent eddies in the atmosphere cause fluctuations of air movement relative to the main wind in all directions, including the vertical. These vertical fluctuations can cause net vertical transport of properties of the air although the average vertical wind velocity is zero. With mass (pollutant concentration) as an example, -and simplifying the real processes considerably-, this

can be explained as follows. Figure 2.2 shows air moving upward and downwards as a result of vertical eddies.

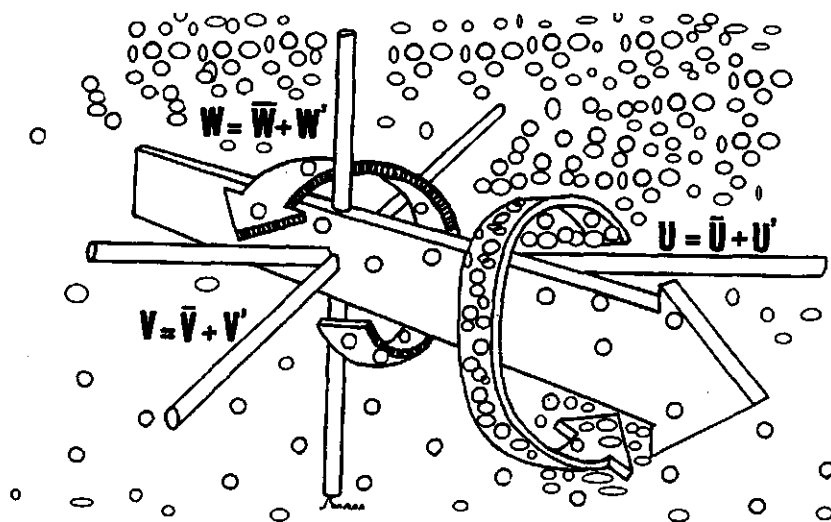


Fig 2.2 Vertical transport by eddies that cause fluctuations (u', v', w') relative to the average longitudinal, lateral and vertical wind components $(\bar{u}, \bar{v}, \bar{w})$ respectively), see text.

The total volume of air moving in both directions is equal, because the net air movement is horizontal (main wind). However, the downward moving air contains a higher concentration of pollutant than the upwards moving air. Therefore as a net result, pollutant is displaced downwards. Similarly, if the concentration in the downward moving air was the lower one, net upward transport would be the result. The differences in concentration between air parcels moving in opposite directions may be the result of interaction with the surface when air parcels touch (or come near) this surface. If the surface takes up pollutant from the air, the upward moving air parcels will be depleted with pollutant. Contrarily, if the surface releases pollutant, the upward moving air parcels will be enriched. Such net displacement of pollutant as a result of differences between upward and downward moving air parcels takes place at all heights in the aerodynamic boundary layer. The eddies vary largely in size; so that air parcels (also of

variable sizes) are displaced over variable distances. As a result, pollutant released from the surface is mixed over the whole aerodynamic layer leading to a net upward transport of pollutant. Analogously, uptake of pollutant by the surface finally results in downward transport of pollutant in the atmosphere.

Other properties (*e.g.* sensible heat, momentum) are transported in a similar way.

It turns out (*e.g.*, Stull 1988) that as an approximation, the effect of wind fluctuations due to eddies on the transport of property X can be split up as follows:

$$F_X = \overline{w \cdot X} + \overline{w' \cdot X'} \quad (2.4)$$

Here the first term accounts for the transport due to the mean vertical displacement of air, while the second term accounts for the (remaining) transport due to instantaneous deviations from the mean value in the vertical wind and in the value of X (indicated by the accents).

In most situations the mean vertical air movement is negligible ($\overline{w} = 0$), so that:

$$F_X = \overline{w' X'} \quad (2.5)$$

In the technique of eddy correlation the vertical transport flux in the atmosphere is derived from direct measurements of upward and downward air movements and the involved fluctuations of a transported property of the air (see chapter 3).

This description of vertical transport of mass (concentration) and other properties in the aerodynamic layer resembles the molecular diffusion process. Instead of the Brownian movement of molecules, turbulence is the driving force of the transport. Therefore aerodynamic vertical transport is often described in an analogous way. The vertical flux and the gradient of a property are assumed to be related by a turbulent diffusion coefficient, the 'diffusivity' K . The vertical flux of momentum (F_m) is equal in magnitude to the shearing stress τ , which is the drag force per unit area of level ground caused by horizontal air motion (Thom, 1975). Unlike the sign convention for fluxes, τ is usually denoted positive for downward transport of momentum. For momentum transport, 'K-theory' or gradient theory yields:

$$\tau = (-)F_m = K_m(z) \frac{\partial(\rho_a U)}{\partial z} \quad (2.6)$$

Here U is the wind speed, K_m is diffusivity for momentum, ρ_a is the air density, and z is height.

Similarly, for the sensible heat flux (H):

$$H = -K_H(z) \frac{\partial(\rho_a C_p \theta)}{\partial z} \quad (2.7)$$

Where C_p is the specific heat of air at constant pressure and θ is the potential temperature; K_H is the diffusivity of heat.

And finally for mass flux (F):

$$F = -K_c(z) \frac{\partial c}{\partial z} \quad (2.8)$$

where c and K_c are the air concentration and diffusivity of the transported compound (analogous to the equation for water vapour transport by Thom (1975)).

In the theory of exchange often use is made of scaling parameters. Very important is the friction velocity u_* , scaling the eddy velocity. It is defined as:

$$u_*^2 \equiv \overline{|w' u'|} = \frac{\tau}{\rho_a} \quad (2.9)$$

with u being the horizontal wind speed component (in line with the mean wind direction). Next, scaling parameters for (other) properties of the air can be defined (see e.g. Thom, 1975; and Stull, 1988):

$$X_* \equiv - \frac{\overline{(w' X')}}{u_*} \quad (= - \frac{F_X}{u_*}) \quad (2.10)$$

X_* quantifies the turbulent fluctuations in the value of property X within the boundary layer in much the same way that u_* quantifies the turbulent velocity fluctuations in the air flow itself (Thom, 1975).

Turbulence is caused by friction with the earth surface (mechanical effects) and by buoyancy effects. The efficiency of transport by turbulence depends on turbulence intensity, as well as on the ability of the eddies to transport a property. For momentum transport, expressed in terms of u_* , this can be written as:

$$u_* = l \frac{\partial U}{\partial z} \quad (2.11)$$

The proportionality with $\partial U / \partial z$ reflects the effect of the friction caused by the surface on wind speed, inducing turbulence. The mixing length l is a notional 'effective eddy size'; it reflects the ability of the eddies to transport momentum. The presence of the surface limits the size of eddies at a given height. Under neutral conditions, l is proportional to height:

$$l = k z \quad (2.12)$$

where k is the Von Karmann constant (0.41).

However, in a non-neutral atmospheric stability may reduce or enlarge the vertical eddy size as follows. A relatively warm air parcel will tend to move upwards; upward moving air expands and cools down. Similarly cold air will move downwards and heat up. In a neutral, adiabatic atmosphere the mean air temperature decreases by 1 degree per 100 m (adiabatic lapse rate). This has no influence on vertical movement of air parcels. In an unstable atmosphere (lapse rate larger than adiabatic) vertical air movement leads to an increase of the temperature difference between an air parcel and its surroundings; the vertical movement is enforced. Contrarily, in a stable atmosphere the temperature gradient (lapse rate) is less than adiabatic (or even of opposite sign: inversion) and vertical air movements are reduced. As a result, $l > k z$ in an unstable atmosphere, and $l < k z$ in a stable atmosphere. This can be expressed by a dimensionless gradient Φ (e.g. Thom, 1975):

$$l = \frac{k z}{\Phi_m} \quad (2.13)$$

The 'stability function' Φ has a value larger than one in a stable atmosphere; and smaller than one in an unstable atmosphere.

From eqs. 2.5, 2.8, 2.10 and 2.11, the diffusivity for momentum can now be written as:

$$K_m = \frac{k z u_*}{\Phi_m} \quad (2.14)$$

Analogous formulas relate the diffusivity of other properties with corresponding Φ functions:

$$K_x = \frac{k z u_*}{\Phi_x} \quad (2.15)$$

The stability corrections for mass (and other properties except for momentum) turn out to be equal to those for heat under all stability conditions ($\Phi_x = \Phi_h$). For momentum, Φ_m

only equals Φ_H under stable and neutral conditions: under unstable conditions a different stability correction must be applied.

The height dependent diffusivity K is seldomly used directly; the use of the scaling parameters u_* and X_* is more convenient, so that from eqs. 2.11 and 2.13:

$$u_* = \frac{kz}{\Phi_m} \frac{\partial U}{\partial z} \quad (2.16)$$

and from 2.15, 2.7/2.8 and 2.10, and substituting Φ_H for Φ_x :

$$X_* = \frac{kz}{\Phi_H} \frac{\partial X}{\partial z} \quad (2.17)$$

On the other hand, from the definition of X_* (eq. 2.10) it follows that if X_* and u_* are known, the flux F_X can be calculated from:

$$F_X = -u_* X_* \quad (2.18)$$

The stability corrections Φ are usually expressed as functions of the ratio between height and a scaling length for stability, the Monin-Obukhov length L , which is often approximated by:

$$L = \frac{-\overline{\theta_v} u_*^3}{kg w' \overline{\theta_v'}} \quad (2.19)$$

(e.g. Stull, 1988). One physical interpretation of L is that it is proportional to the height above the surface at which buoyant factors first dominate over mechanical (shear) production of turbulence (Stull, 1988). Small positive values of L (below 1 to about 100 m) indicate a stable atmosphere; in an unstable atmosphere L has negative values in a similar range. Under neutral conditions L has large positive or negative values ($|L| \rightarrow \infty$). θ_v is the virtual potential temperature, in which density fluctuations due to humidity fluctuations are taken into account. Neglecting the effect of humidity fluctuations leads to an error in L of an order of $LE/H^*7\%$ of L , see e.g. van Boxtel, 1986; LE is the latent heat flux due to water vapour transport. Over land, this generally results in only small errors in stability corrections (and for low heights, $T \approx \theta$), and L is often approximated by:

$$L \approx \frac{-T u_*^3}{k g w_* \theta_*} = \frac{-T u_*^3}{k g u_* \theta_*} = \frac{-\rho_a C_p T u_*^3}{k g H} \quad (2.20)$$

For resistance parameterizations as well as in measurement techniques the infinite, height dependent gradients $\partial U/\partial z$ and $\partial X/\partial z$ are inconvenient. Generally integrated profile equations are preferred, derived by integration of eqs. 2.16 and 2.17 between a reference height z and the roughness length z_0 . The parameter z_0 is the (theoretical) height above the ground level of the surface where the wind speed approaches zero ($U(z_0) = 0$). It represents a notional bottom of the aerodynamic layer: below z_0 , the flow is assumed to be (about) laminar without vertical momentum transport (see 2.2.3). The value of z_0 depends on the spatial distribution and height of obstacles on a terrain. It can be derived from tables classifying terrain types (*e.g.* Wieringa 1993). Mathematically, it can be derived from extrapolation of the wind speed profile. Alternatively z_0 is often estimated as 0.1 times the mean obstacle height h . In case of vegetation, the relevant surface for exchange (the canopy) has a certain depth (*e.g.* the crop or tree height). Finite wind speeds occur in and below the canopy (see fig 2.1), caused by intermittent turbulent transport that is not described by common gradient theory. As a net-effect, the ground plane for the exchange (the relevant surface) is 'elevated'. Therefore z_0 and the profile are often defined relative to a displacement height d (about 0.7 times the canopy height). The reference height z (above soil!) is adjusted accordingly. Now the integration yields for the wind speed profile:

$$U(z) = \frac{u_*}{k} \left\{ \ln\left(\frac{z-d}{z_0}\right) - \Psi_m\left(\frac{z-d}{L}\right) + \Psi_m\left(\frac{z_0}{L}\right) \right\} \quad (2.21)$$

The Ψ -functions are the integrated stability corrections (see below).

Other properties than momentum usually do not approach a zero value in $z_0(+d)$. Equivalent extrapolated 'zero-value heights' for *e.g.* heat (temperature) or mass (concentration) cannot be used in a formula for turbulent transport: they are not determined by turbulent processes alone. Therefore profiles of temperature or concentration are integrated starting at z_0 as well. Implicitly it is assumed that turbulent transport of other properties (effectively) ends or starts at the same height as turbulent transport of momentum. Though this assumption is difficult to verify this approximation is widely applied (including this thesis).

Hence the integrated profile equation for other properties than momentum, temperature or concentration (X) can be formulated as :

$$X(z) = X(z_0) + \frac{X_s}{k} \left\{ \ln\left(\frac{z-d}{z_0}\right) - \Psi_H\left(\frac{z-d}{L}\right) + \Psi_H\left(\frac{z_0}{L}\right) \right\} \quad (2.22)$$

Widely use is made of the stability corrections functions derived empirically by Dyer and Hicks (1970). Slightly adapted parameterizations, given by Holtslag and De Bruijn (1988; see also Beljaars *et al.* 1989) have been used in this thesis:

- for $z/L < 0$ (**unstable** atmosphere):

$$\Psi_m\left(\frac{z-d}{L}\right) = 2 \cdot \ln\left(\frac{1+\xi}{2}\right) + \ln\left(\frac{1+\xi^2}{2}\right) - 2 \cdot \arctan(\xi) + \frac{\pi}{2}$$

$$\text{with } \xi = (1-16)\frac{z-d}{L}^{\frac{1}{4}} \quad (2.23)$$

$$\Psi_H\left(\frac{z-d}{L}\right) = 2 \cdot \ln\left(\frac{1+\beta}{2}\right)$$

$$\text{with } \beta = (1-16 \cdot \frac{z-d}{L})^{\frac{1}{2}} \quad (2.24)$$

- and for $z/L > 0$ (**stable** atmosphere):

$$\Psi_m\left(\frac{z-d}{L}\right) = -0.7 \left(\frac{z-d}{L}\right) - 0.75 \left(\frac{z-d}{L} - 10.72\right) \exp(-0.35 \left(\frac{z-d}{L} - 10.72\right))$$

$$(2.25)$$

$$\Psi_H = \Psi_m$$

If the reference height is sufficiently larger than z_0 ($z \gg z_0$), the values of the Ψ -functions for z_0/L are small compared to those for z/L and can be neglected.

The similarity between transport of momentum and other properties and the profile equations (2.21 and 2.22) are widely applied in the micrometeorological gradient (or flux-profile) technique of flux measurement (see chapter 3).

To find a resistance parameterization for this aerodynamic layer, the aerodynamic resistance for momentum ($R_{a,m}$) can be derived by application of eq. 2.1 to momentum and momentum flux, between heights z and the surface height for momentum z_0 :

$$R_{a,m}(z) = \frac{\rho_a U(z) - \rho_a U(z_0)}{\rho_a (\overline{w' u'})} = \frac{\rho_a U(z) - \rho_a U(z_0)}{\rho_a u_*^2} = \frac{U(z)}{u_*^2} \quad (2.26)$$

For other properties (X) such as heat or mass, stability effects on transport may be different from those for momentum. From equation (2.1) and (2.18) and the flux-profile-relation (2.22) we find for R_a of property X :

$$R_{a,X}(z) = \frac{X(z) - X(z_0)}{u_* X_*} = \frac{1}{k u_*} \left[\ln\left(\frac{z-d}{z_0}\right) - \psi_H\left(\frac{z-d}{L}\right) + \psi_H\left(\frac{z_0}{L}\right) \right] \quad (2.27)$$

Or, neglecting stability corrections at z_0 and replacing the $\ln\{(z-d)/z_0\}$ term using the flux-profile relation for momentum (eq. 2.21):

$$R_{a,X}(z) = \frac{U(z)}{u_*^2} - \frac{\psi_m\left(\frac{z-d}{L}\right) - \psi_H\left(\frac{z-d}{L}\right)}{k u_*} \quad (2.28)$$

(Garland, 1977).

2.2.2 The (quasi-)laminar boundary layer resistance (R_b)

Turbulence is assumed to dominate atmospheric transport only in the layer above z_0 . Below this level a thin (quasi)-laminar layer is assumed to exist, where molecular diffusion is the main driving force of transport. This layer is crossed by heat and mass, but not by momentum; momentum is not transported by molecular diffusion. The equivalent resistance R_b of this layer therefore quantifies additional resistance against transport of heat and mass (compared to momentum) through the atmosphere very close to the surface. The depth of this layer can be expressed as the height difference between z_0 and the site where the actual uptake or release by the surface takes place (z_s). Then a formula similar to eq. 2.27 might be derived (Monteith and Unsworth, 1990):

$$R_b = \frac{\ln\left(\frac{z_0}{z_s}\right) - \psi_H\left(\frac{z_0}{L}\right)}{k \cdot u_*} \quad (2.29)$$

However, z_s can hardly be determined directly. Its magnitude may also depend on how and into which detailing the actual uptake/release by the surface is modelled (e.g. a single leaf or a whole canopy). In fig 2.1 it was also shown how the borders of R_c and R_b in the Big Leaf model are generalized from the situation for one leaf. R_c 'begins' where a pollutant dissolves in a water layer on the leaf surface respectively at the entrance of a stoma. However, the combination of leaves constituting a canopy may lead to quite different flow patterns and thicknesses of the (quasi)laminar boundary layer than a single leaf.

Various parameterizations for R_b exist: e.g. Garland (1977), Brutsaert (1982), Hicks *et al.* (1987), Chamberlain (1966, 1968), Monteith and Unsworth, (1990). Most of them were based on theory of molecular diffusion and/or wind tunnel research of heat or mass transfer to fibrous surfaces. Generally they estimate a sublayer Stanton number B from which R_b is calculated by:

$$R_b = (B u_*)^{-1} \quad (2.30)$$

From a comparison by Sutton (1990), it follows that for short vegetation, results of R_b parameterizations of different authors are relatively small. In accordance with many transport models (e.g. EMEP, OPS), in this thesis the formulation by Hicks *et al.* (1987) has been chosen. Hicks *et al.* (1987) assume a fixed value of B for a given compound. This was based on field studies on heat and water vapour transfer to vegetation, where $k u_* R_b$ attained a limiting value of about 2 (Wesely and Hicks, 1977). They proposed to correct only for the diffusive properties of the compound compared to heat. Hence their R_b formulation is independent from z_0 and z_s (see eq. 2.29; z_0/z_s becomes constant):

$$R_b = \frac{2}{k u_*} \left(\frac{\kappa}{D_i} \right)^{\frac{2}{3}} = \frac{2}{k u_*} \left(\frac{Sc}{Pr} \right)^{\frac{2}{3}} \quad (2.31)$$

Here κ is the thermal diffusivity of dry air; D_i is the molecular diffusion coefficient of compound i in air. Usually Sc and Pr are used, where the Schmidt number $Sc = \nu/D_i$, with ν is the kinematic viscosity of dry air ($0.15 \text{ cm}^2 \text{ s}^{-2}$). Pr is the Prandtl number: $Pr = \nu/\kappa$ (≈ 0.72).

2.3 Uptake by the surface (R_c)

The surface resistance R_c is often calculated as a residual resistance, representing the excess of total resistance R_t (given by the reciprocal of the deposition velocity) over the sum of R_a and R_b :

$$R_c = R_t - [R_a + R_b] = \frac{1}{v_d} - R_a - R_b \quad (2.32)$$

As a result of this way of calculation of R_c , this parameter usually shows a very high scatter, because all errors in v_d , R_a and R_b accumulate in the calculated R_c . Nevertheless it is often possible to derive parameterizations of R_c from measurements of v_d via eq. 2.32.

R_c is often subdivided into a number of sub-resistances, to account for the various processes at or in the surface that influence the uptake of the pollutant. If deposition takes place via two different pathways, they are represented by two parallel resistances. If in a single pathway two processes are involved subsequently, this is represented by two resistances in series. Eq. 2.33 gives a general example of the application of this principle in a surface resistance parameterization of deposition to the canopy of vegetation:

$$\frac{1}{R_c} = \frac{1}{R_{\text{stom. uptake}}} + \frac{1}{R_{\text{ext}}} = \frac{1}{R_{st} + R_{mt}} + \frac{1}{R_{cu}} + \frac{1}{R_w} \quad (2.33)$$

R_{st} and R_{mt} are resistances associated with two subsequent processes in stomatal uptake of a pollutant: the passage through the stomatal opening and the transfer to the mesophyll, respectively. Deposition to the external leaf surface (quantified by R_{ext}) may proceed via the cuticle (R_{cu}) and/or via uptake in water layers on the cuticle (R_w). In the next passages, each resistance will be treated in more detail.

Stomatal resistance R_{st}

The transport from the leaf surface into the stomatal cavity is driven by (molecular) diffusion. The stomatal resistance refers only to the passage through the stomatal opening, as the diffusive transport through the quasi-laminar layer just above the leaf surface is accounted for separately in R_b .

Values of R_{st} can be derived from the stomatal resistance for water. This can in turn be derived from measured gradients of temperature and water vapour. The calculation procedure is summarized in appendix A. However, the resistance calculated by this method refers to the total transport of water vapour. For a dry vegetation at daytime in the growing season, stomatal evaporation will dominate the water vapour transport. Under many other conditions, evaporation of rain and formation/ evaporation of dew (in the morning and evening) may pay a significant contribution to the water vapour flux. Direct evaporation from a relatively wet soil can also be relevant. Especially from late autumn until early spring, when stomatal activity of plants is low, these contributions to water vapour transport may cause severe errors in stomatal resistances derived by this method.

Alternatively the bulk stomatal resistance for water can be parameterized *e.g.* according to Wesely (1989):

$$R_{st,H_2O,bulk} = R_i \left[1 + \left(\frac{200}{Q + 0.1} \right)^2 \frac{400}{T_{surf}(40 - T_{surf})} \right] \quad (2.34)$$

This parameterization was derived from a much more detailed scheme provided by Baldocchi *et al.* (1987). R_i indicates a minimal stomatal resistance for water vapour per type of terrain and season, tabulated by Wesely (1989). T_{surf} is the surface temperature, which can be measured or derived from extrapolation of measured temperature gradients (see also appendix A); Q is the global radiation. The term bulk stomatal resistance indicates that the average behaviour of all stomata in the canopy is modelled.

To derive the stomatal resistance for a pollutant S from the stomatal resistance for water, a correction for differences in molecular diffusivity in air between water and S must be applied, according to:

$$R_{st,i} = R_{st,H_2O} \frac{D_{H_2O}}{D_i} \quad (2.35)$$

In this formula, $D_{NH_3} = D_{H_2O}$; $D_{SO_2} = D_{HNO_3} = 0.53 \cdot D_{H_2O}$.

Resistance to transfer into the mesophyll R_{mi}

After the passage through the stomatal opening, transfer of pollutant must take place between the gas phase of the stomatal cavity and the apoplast fluids. Parameterizations for R_{mi} usually include a dependency on the Henry constant of the compound (*e.g.*, Wesely, 1989). However, many water soluble compounds, such as HNO_3 and SO_2 are assumed to dissolve easily into the apoplast fluid due to a high or moderate (respectively) Henry coefficient and/or efficient conversion and transport after dissolution. Therefore R_{mi} for HNO_3 and SO_2 is generally assumed to be negligible (*e.g.* Voldner, 1986; Wesely, 1989; Erisman *et al.*, 1994). For NH_3 , R_{mi} is usually also set to zero. This approximation may be well acceptable for unfertilized vegetation. However, it may be too far from realistic if fertilization causes a high ammonium content in the apoplast (see 1.4.4) leading to frequent and significant emissions. In that case, it may be necessary to account for R_{mi} , unless the concentration in the stomata is estimated or calculated directly as a compensation point (see 2.4).

Cuticle resistance R_{cu}

For most water soluble, gaseous atmospheric pollutants, including NH_3 , the cuticle is generally assumed to be almost impermeable. Reported values of R_{cu} are generally higher than 1000 s m^{-1} (*e.g.* for NH_3 and SO_2 , in the range $2000\text{--}40000 \text{ s m}^{-1}$; Van Hove,

1989). This includes adsorption to the cuticle matrix itself under conditions of low RH (<65%). An exception is HNO_3 , which adsorbs -as mentioned before- readily to almost every surface, because of its high polarity.

It is generally assumed that at higher RH deposition to the external leaf surface proceeds mainly to thin water films on (or associated with) the cuticle (see below). An alternative explanation may be that the cuticle becomes more permeable at higher RH; see 1.4.3).

Water layer resistance R_w

As mentioned in 1.4.3, a wet canopy is generally observed to be an efficient sink to compounds such as NH_3 and SO_2 , which means that resistances are close to zero (e.g., Erisman and Wyers, 1993, Duyzer 1994, Duyzer *et al.* 1994). Frost may cause R_c to increase: over a pasture which was wet from melting snow Sutton (1990) measured R_c values for NH_3 that were close to zero; when frost occurred, R_c became significantly higher (up to 80 s m^{-1}).

For the situation that the surface is not visibly wet (and not frozen), R_w has been found to be related with relative humidity (lower resistance at higher relative humidity, see 1.4.3, e.g. Van Hove 1989). Parameterizations of R_c (without explicit subdivision into R_w and R_{st}) for Douglas fir forest, classified on basis of surface wetness and RH have been derived by Vermetten *et al.* (1992; SO_2), Vermetten and Hofschreuder (1994; NH_3 , SO_2 , O_3), and Duyzer *et al.* (1994; NH_3 ; dry/wet status surface). In an R_c parameterization for NH_3 deposition to heathland (Duyzer, 1994), effects of surface wetness and of temperature were included.

A general functional relationship between R_w for NH_3 and RH has been derived empirically by Sutton and Fowler (1993), based on literature data from various experiments. Erisman *et al.* (1993) parameterized R_{ext} for SO_2 over heather as a function of leaf wetness (due to rain), RH and frost. R_{ext} for NH_3 was parameterized by Erisman *et al.* (1994) for classes of dry/wet, land-use category, day/night and season. Assuming that deposition to or via the cuticle itself is negligible, R_w is about equal to R_{ext} .

Application of Big Leaf models under conditions that the surface equilibrium concentration is not negligible.

Especially for ammonia, saturation of the leaf surface may be possible (see 1.4.4). If this occurs, the surface equilibrium concentration is no longer negligible, and the assumptions of the Big Leaf resistance model are violated. So in that situation, the exchange mechanism is no longer described in a (physically) correct way.

Nevertheless, R_c values calculated by a Big Leaf approach will still scale the efficiency of the actual uptake by the surface. The lower solubility of ammonia in a partly saturated solution will decrease the deposition flux to this solution. As a result, a higher value of R_c will be calculated. In many cases, it is not relevant -given other uncertainties in parameterizations- to make a detailed distinction between the influence of saturation and the influence of other surface conditions on the deposition efficiency. Then

parameterizations on basis of a 'Big Leaf' approach may enable estimation of fluxes with acceptable results. In the analogous case of stomatal uptake when the concentration of NH_4^+ in the apoplast fluid is not negligible, R_{mt} may account for saturation effects.

The influence of NH_3/SO_2 co-deposition on the surface resistances of SO_2 and NH_3 so far has not yet been included in parameterizations. For situations that one compound is present in excess to the other, a table of measured average R_{ext} values for NH_3 and SO_2 by Erisman and Wyers (1993) might be used. This table included a classification of R_{ext} according to the ratio between ambient NH_3 and SO_2 concentrations. If the NH_3 concentrations exceeded those of SO_2 by far (ratio > 3), R_c for NH_3 increased; in the opposite situation (ratio < 1), the surface resistance of SO_2 increased.

For more detailed mechanistical analyses and descriptions of the influence of chemical processes at the surface on the deposition, it may be necessary to include the non-zero surface concentration as a separate parameter in a bidirectional resistance model. This will be discussed in the next section.

When emission occurs, the Big Leaf model in eq. 2.2. will calculate negative values of R_c (positive F , while R_a , R_b and c_r are always positive).

This complicates interpretation, especially if average values of R_c should be calculated for a set of measurements containing emission and deposition events. Additionally, negative R_c values are also calculated when measured v_d is higher than $v_{d\text{max}}$ ($=1/(R_a+R_b)$). The latter is often caused by errors in the measured gradients or in R_a or R_b in situations that R_c is negligible and so when there is an efficient uptake by the surface. Especially the parameterization of R_b is quite uncertain which is important if R_c as well as R_a are very small, as is often the case for forests. Both more or less contradicting conditions in which negative signs of R_c are calculated (emission and strong deposition) should be distinguished in interpretation, e.g. by the sign of the flux.

In parameterizations a negative R_c could be ambiguous in a similar way.

Instead of using a negative R_c , Erisman *et al.* (1994) parameterize emission fluxes by reversing the sign of the general resistance equation (2.2) to:

$$F_{\text{em}} = \frac{c_r}{R_a + R_b + R_c} \quad (2.36)$$

This emission is calculated only under specific conditions and only if ambient concentration is below $2 \mu\text{g m}^{-3}$ of NH_3 .

This parameterization will not be used in this thesis. It may yield acceptable results as part of parameterizations for long term exchange estimates if emission is relatively unimportant compared to deposition in other periods. It is clear however, that the gradient between surface and atmosphere that actually drives the emission cannot be

estimated from the concentration in the air alone. Therefore, if considerable emission by a surface occurs frequently, as in the present research (see chapter 5), inclusion of a surface concentration in the resistance parameterization is inevitable.

2.4 Bi-directional resistance model

To describe both emission and deposition by one resistance model, the conventional Big Leaf model must be adjusted to account for the surface concentration c_0 . Assuming that the resistance analogy holds for the processes that control the actual uptake or release of ammonia at the surface, this yields:

$$F = \frac{c_0 - c_r}{R_a + R_b + R_c} \quad (2.37)$$

This will be referred to in this thesis as the 'bi-directional (resistance) model'. It can in principle be used to describe bidirectional stomatal exchange, as well as saturation effects and volatilization from slurry and excreta. However, in practice estimating c_0 poses many difficulties.

Stomatal exchange

The best possibilities to estimate c_0 probably exist for stomatal exchange, where a compensation point can be determined. Filling in equation 2.37 confirms that at the compensation point, where $c_0 = c_r$, the flux should be zero; while $c_0 > c_r$ results in positive fluxes (emission), and $c_0 < c_r$ yields negative fluxes (deposition).

Methods to derive c_{0st} according to the compensation point theory were already discussed in section 1.4.5. Summarizing briefly, the most direct way to estimate the stomatal compensation point is by analysis of the ammonium concentration and pH in the liquid in the stomatal cavity or in the apoplast fluid nearby. Then via eq. 1.7-1.9 the compensation point can be calculated. Alternatively, the compensation point can be derived from measurements (in the field or laboratory) of the exchange flux as a function of ambient concentration.

Once a value of the compensation point has been derived for a given temperature, the compensation point at other temperatures can be estimated from eq. 1.9. Then the assumption must be made that the ratio between NH_4^+ and H^+ concentrations remains constant.

Once a stomatal compensation point has been derived, the stomatal exchange flux can be estimated using the bi-directional resistance model and parameterizations for R_s and other resistances given in the previous section. No R_{mi} needs to be added to the stomatal

resistance. If an estimate of the net-exchange with the canopy is required, the derived parameters may be used, together with estimates of R_w , in the canopy compensation point model (see 2.5).

Saturation of the leaf surface and reversible deposition.

Accumulation of ammonium and increasing pH due to deposition of ammonia, increase of temperature, decrease of ambient concentration and evaporation of the water layers are all factors that may cause saturation or even over-saturation of the leaf surface with ammonia (1.4.4). In case of stomatal exchange the assumption could be made that the composition of the liquid inside the stomatal cavity was more or less independent from the exchange with the atmosphere (steady state). This may not be the case for a water layer on the surface. As a result, to estimate the influence of saturation, the composition of the water layer must be calculated stepwise in time. The exchange during each period depends partly on the exchange during the previous period, which increases or decreases the degree of saturation of the solution. This can be compared to the situation of charging and discharging a capacitance in electricity (Van Hove, 1987). Recently Sutton *et al.* (1995, 1998) formulised this interpretation of the leaf surface as a capacitance into a model. They described the variation of the composition of the water layers on the leaf surface in dependency of previous deposition- or emission fluxes, thickness of the water layer, capacity and resistance of the capacitor. Their application of this model to observed flux patterns over a crop yielded encouraging results. However, the model still needs further development, and knowledge of several necessary parameters in the existing model is still inadequate. This concerns *e.g.* the time-constant and/or charging resistance of the capacitor; the pH at the leaf surface and its course during exchange, and parameters describing net-removal of ammonium by uptake into the leaves or by rinsing by rain.

Emission from slurry, urine and fertilizer

In section 1.3 some problems of modelling emissions from land treatments were already discussed. It was explained there, that mechanistical models of volatilization after slurry spreading (*e.g.* Van Faassen *et al.*, 1990) are not yet accurate enough to make reliable quantitative estimates for a particular situation. In terms of resistance modelling, the main difficulty is not the atmospheric transport after the volatilization of ammonia due to the treatment, but the calculation of the relevant surface concentration c_0 . This changes continuously due to the volatilization itself as well as due to the infiltration of slurry into the soil which is followed by a complex variety of chemical, biological and transport processes in the soil.

Similar difficulties are met in modelling volatilization from excreta (urine) during grazing and from fertilizer application. In case of excreta, additionally the decomposition rate of ureum must be estimated, making the model even more complex.

Because of the low volatilization from the CAN fertilizers applied in the Netherlands, detailed modelling of fertilizer volatilization is generally not relevant anyhow, given the high uncertainty and the relatively small emission fluxes involved.

2.5 The canopy compensation point model

Sutton and Fowler (1993) proposed a resistance model for ammonia exchange with plant canopies that accounts for parallel bidirectional exchange through the stomata and deposition to the leaf surface. In this model, the contributions of both pathways to the net-exchange with the atmosphere are expressed in terms of a single surface concentration for the canopy as a whole, instead of in an overall R_c . Sutton and Fowler refer to this representative surface concentration as the canopy compensation point, denoted here as c_{oc} . It may be considered as the net potential for NH_3 emission from the canopy (e.g. Sutton *et al.* 1998).

The model will further be referred to in this thesis as the 'canopy compensation point model' (ccp-model).

Figure 2.3 shows how the canopy compensation point is defined in relation to the flux between canopy and atmosphere, the flux through the stomata and the deposition flux to the leaf surface.

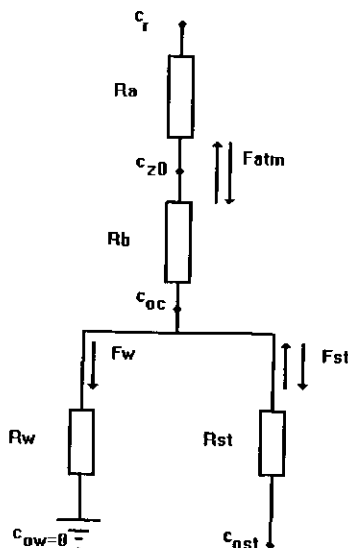


Fig. 2.3 Schematic representation of the canopy compensation point model by Sutton and Fowler (1993) (see text).

F_{atm} is the total (net) exchange flux between the canopy and the atmosphere. Because fluxes must be constant with height (see 2.1), F_{atm} must equal the sum of the actual uptake or release of ammonia via the stomata (F_{st}) and the actual uptake by (and eventual release from) the leaf surface (F_w):

$$F = F_{atm} = F_{st} + F_w \quad (2.38)$$

As shown in fig. 2.3, Sutton and Fowler took the notional bottom of the laminar boundary layer as the reference point for c_{oc} . The laminar boundary layer and the aerodynamic layer that a pollutant has to cross in the exchange process are assumed to be the same for exchange with the stomata and with the leaf surface. This is acceptable, as the diffusive transport during passage of the opening of the stomata is accounted for separately in the stomatal resistance. Then, according to resistance modelling:

$$F_{atm} = \frac{c_{oc} - c_r}{R_a + R_b} \quad (2.39)$$

The term canopy compensation point was chosen by analogy with the use of the stomatal compensation point as the relevant surface concentration in case of purely stomatal exchange (see 2.4; cf. eq. 2.27 and 2.39). In practice the main analogy is the fact that there is no net exchange with the atmosphere when $c_{oc} = c_r$ (see also Sutton *et al.* 1998). Canopy compensation points derived from field measurements of fluxes (eq. 2.39) are often quite variable. This is because the fluxes via stomata and to the leaf surface can both vary strongly and more or less independently of each other. Therefore fluxes can hardly be parameterized directly from average or typical values of canopy compensation points. The importance of this concept however is that it provides the tool to couple the two parallel, exchange processes at the canopy level to the net exchange process with the atmosphere in a resistance model. Now the processes at canopy level can be worked out as follows:

The deposition to (water films on) the leaf surface may basically be described by the gradient between the concentration in equilibrium with the ammonium concentration in the water layer (c_{ow}) and c_{oc} and by the surface resistance of the moist leaf surface R_w :

$$F_w = \frac{c_{ow} - c_{oc}}{R_w} \quad (2.40)$$

In the basic ccp-model, Sutton and co-workers only accounted for deposition to the leaf surface (see below). If the approximation is made that c_{ow} remains negligibly small (or

that saturation effects are accounted for in an R_w parameterization), this deposition can be described by:

$$F_w = \frac{-c_{0c}}{R_w} \quad (2.41)$$

The exchange with the stomata is determined by the gradient between the concentrations inside the stomata (the stomatal compensation point (c_{0st})) and c_{0c} , and by the stomatal resistance R_{st} :

$$F_{st} = \frac{c_{0st} - c_{0c}}{R_{st}} \quad (2.42)$$

Like other resistance models, the ccp-model can be used either for interpretation of measured fluxes or to estimate fluxes from a limited set of other measured parameters. In the latter case, by combination of eq. 2.38, 2.39, 2.41 and 2.42, c_{0c} can be expressed in R_{st} , R_w , c_{0st} , R_a and R_b :

$$c_{0c} = \frac{\frac{c_r}{R_a + R_b} + \frac{c_{0st}}{R_{st}}}{\frac{1}{R_a + R_b} + \frac{1}{R_{st}} + \frac{1}{R_w}} \quad (2.43)$$

Subsequently the net-flux can be estimated from (2.39) using the measured or modelled ambient concentration and common parameterizations of R_a and R_b .

This ccp-model will be tested to describe and analyse flux patterns observed over grazed pasture in the research of this thesis. A limitation of the summarized parameterization is, that exchange with the leaf surface is described only by a simplified deposition parameterization. In practice, saturation of the leaf surface and even emission from the leaf surface may be possible. Incorporation of the capacitor model (e.g. Sutton *et al.* 1995, 1998) into the ccp-model (to estimate c_{0w} in 2.40) might in theory give a more accurate mechanistical description of the exchange with the vegetation. However, the capacitor model introduces a number of extra parameters that can -sofar- only be estimated with considerable uncertainty (see 2.4).

Therefore at this moment, implementation of the capacitor concept can hardly reduce the present uncertainties in fluxes that are estimated by the ccp-model for a terrain like the grazed pasture. Furthermore, calculations in chapter 6 will show, that emission from the leaf surface probably played only an unimportant role compared to other sources at

the pasture. Saturation of the leaf surface can be accounted for sufficiently via proper values of R_w .

Chapter 3

Experimental setup

In this chapter a description is given of the experimental setup of this research project. First an overview of the characteristics of the location of the experiments is given in section 1. Next the applied micrometeorological techniques are described in section 2. The instrumental setup is described in section 3.

3.1 Site description

3.1.1 Location and soil type

The measurements were performed near the village of Zegveld, about 30 km South of Amsterdam. This location is part of a region of flat, humid polder land with peat soil. The land is mainly used as pasture for (intensive) dairy farming. The region extends for about 3 km North of Zegveld and for about 10-30 km in other directions (see fig 3.1).

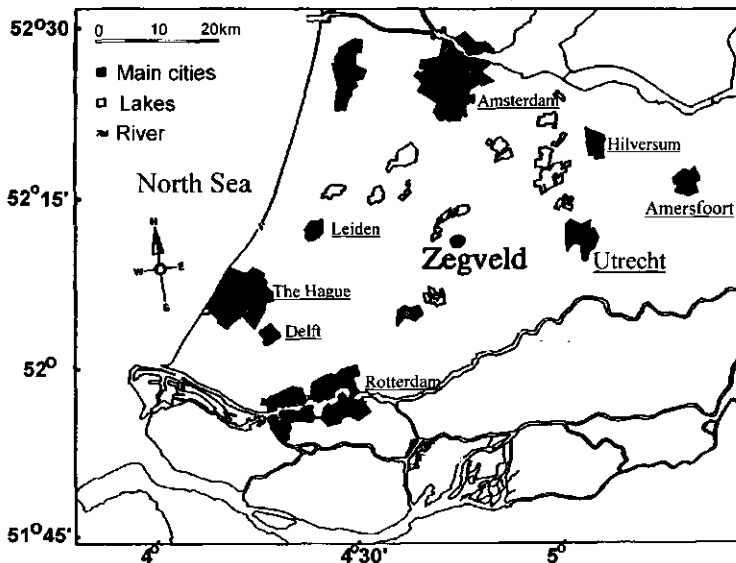


Fig 3.1: Location of Zegveld in the Netherlands.

The measurement site was located on the pasture (about 62 ha) of the Regional Research Centre for Cattle Farming (ROC-Zegveld); figure 3.2 gives a map of the ROC-terrain.

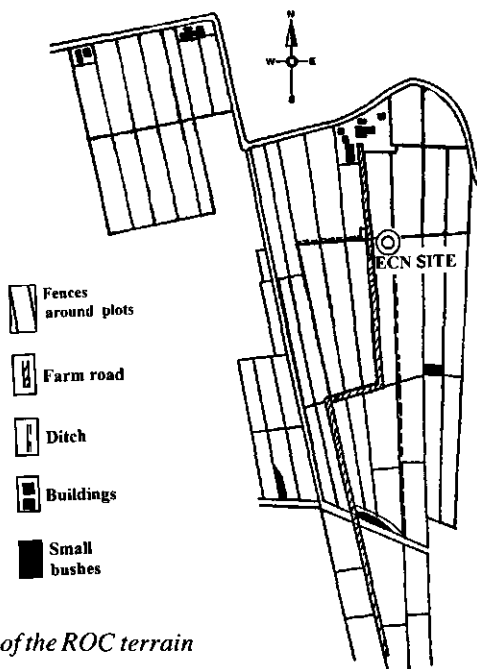


Fig 3.2: *Plan of the ROC terrain*

The terrain was virtually free of obstacles over a distance of at least 500 m in the wind sector 90-270° (see overview pictures in Appendix B). Wind from other directions can be disturbed severely by farm buildings or other obstacles and hence flux measurements were disregarded under these conditions. By doing so, measurements disturbed by plumes from nearby animal houses and manure stores were also avoided. The measurement equipment was mounted -pointing to the South- on a scaffold on a small plot. This was separated from the rest of the terrain by a fence of wire netting.

The soil type was drained woody peat (pH-KCl between 4.5 and 5.3). In the Netherlands a considerable part (30%) of the grassland is on drained peat soil. It is mainly used for intensive dairy cattle breeding. This use is quite typical for the Netherlands; in the rest of Europe, this soil type is mainly covered by natural vegetation.

The water table in the ditches of the ROC terrain is regulated at 30-90 cm below the surface. Consequently humidity near the surface is high, and at night and in the early morning often radiation fog occurs. The height of the grass varied little (5-25 cm), except shortly before mowing for ensilage or haymaking.

3.1.2 Agricultural treatments of the terrain around the site

Agricultural treatments of the terrain mainly consisted of mowing, grazing and applications of organic manure slurry and fertilizer. These treatments were carried out rotationally over the 66 plots into which the ROC terrain was subdivided. Detailed day-by-day information about the treatments of each plot was available by courtesy of the ROC.

From February until October 1992 and from February until August 1993 each plot was treated one or more times with fertilizer and/or slurry. The fertilizer consisted of calcium ammonium nitrate (CAN), which is commonly used in the Netherlands. The average annual supply of nitrogen by fertilizer was $100 \text{ kg ha}^{-1}\text{yr}^{-1}$ of N.

Slurry was applied mainly by the technique of band spreading by trailing feet. In this technique the slurry is applied in small bands (about 3 cm) on the soil, at the bottom of the grass shoots. This method reduces ammonia volatilization with 50 to 80% compared to conventional surface spreading in a broad fan (Wouters *et al.*, 1994). The fertilization effect of the slurry applications is comparable to that of $60 \text{ kg ha}^{-1}\text{yr}^{-1}$ of fertilizer-N. For several plots, the ROC varied the total annual fertilization (*e.g.* $60\text{--}200 \text{ kg ha}^{-1}\text{yr}^{-1}$ N) or the partition between N supplied by fertilizer and by slurry (*e.g.* only fertilizer or partly slurry).

(Net) conversion of organically bound nitrogen in the peat material to anorganic compounds (net mineralisation) makes extra nitrogen available to the plant roots. This net mineralization is estimated to provide an extra source of nitrogen of (up to) $150 \text{ kg ha}^{-1}\text{yr}^{-1}$ N. As a result, the total average supply of available nitrogen to the grass is in the order of about $300 \text{ kg ha}^{-1}\text{yr}^{-1}$ N.

Grazing by dairy cattle took place roughly from May until October. In the rest of the thesis that period will be referred to as the grazing season. This distinction is made because the excreta are expected to influence exchange patterns. It is obvious that the grazing season coincides with the growing season of the grass. In the rest of the year, referred to as the ungrazed season, some sheep remained in the pastures. Their contribution to the nitrogen load however is only small compared to that of the dairy cattle.

The grazing occurred in 7 or 8 groups on average: milch cows (3 groups: 20, 20 and 40 animals), 'dry' cows (variable, 6 to 20), heifers (40), calves (25, together with 50 lambs), and sheep (80, in one or two groups). A dry cow is a cow that is temporarily not producing milk (shortly before calving). A heifer is a young cow that has not yet had a calf. A group of 40 milch cows were in the pasture only at daytime during the whole grazing season. The other cows were in the pasture both day and night, except for very early and very late in the season, when they were kept inside the animal houses at night.

The rotational system of management of the terrain, and the variations in fertilizer and slurry doses imply that on the short term (days) differences in treatment between individual plots can be large (see also 3.4 and chapter 7).

The ROC management has stated that their management of the pasture can be considered to be representative for dairy farming on peat soil in the Netherlands. Feeding experiments that might cause some deviations in nitrogen excretion concern only a small fraction of the cattle. The band spreading technique for slurry application, however, was not yet common practice in the region in the years of our experiment (1992-1994). If the estimated contribution of net mineralization is taken into account, the total N-supply to the ROC pasture ($300 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of N) seems roughly comparable to common values in the Netherlands for other soils (about $300 \text{ kg ha}^{-1} \text{ yr}^{-1}$ N on average for sandy and clay soils). However comparison of N doses with other farms or regions is difficult because the true contribution of net mineralisation is uncertain and variable. Neglecting net mineralization, the N-supply by fertilizer and slurry is lower for the ROC terrain ($150 \text{ kg ha}^{-1} \text{ yr}^{-1}$ N) than common for peat soils (about $240 \text{ kg ha}^{-1} \text{ yr}^{-1}$ N). Indeed the ROC has slightly reduced the supply of N by fertilizer and slurry during the last years. An optimal use of nitrogen supplies was aimed at by better adjustment of the moments of fertilizer application to the needs of the grass.

For analysis of the results of the measurements it is relevant to subdivide the ungrazed period into two periods: in the rest season (November and December 1992, November 1993-January 1994) no grazing by cattle or other land treatments took place. In the pre-season, no grazing occurred, but the terrain was prepared for the growing season by relatively large doses of slurry and fertilizer. This concerns the periods of January-April 1993 and February-April 1994.

3.2 Techniques of flux measurement at Zegveld

3.2.1 Comparison of possible techniques

Exchange can be measured directly by a number of techniques, that can be grouped into surface accumulation techniques, enclosure methods and micrometeorological techniques. In the so-called inferential method, fluxes are not measured directly but derived from resistance modelling and measurements of concentration and meteorological parameters.

The main principles of these techniques and some of their main advantages and disadvantages as far as relevant for their use in the present experiment can be

summarized as follows (partly after Erisman and Draaijers, 1995; Fowler and Duyzer, 1990).

Surface accumulation techniques

In these techniques, the deposition of a compound is measured directly from its accumulation at or in the surface. In the throughfall method, this accumulation of a compound is measured from its uptake in rainwater that, during passage through the canopy, has washed the compound from the leaves. The technique is relatively simple and cheap, and the exchanging surface is not influenced by the measurement itself as the throughfall is collected below the canopy. However, time resolution is low: it is determined by the length of periods between rain events and often the wash-off is only partial, complicating interpretation. Also, the concentration of a compound in throughfall may be influenced by uptake and excretion by the leaves and (other) interactions with leaf tissues. Therefore the method is especially useful to monitor the actual *soil loads* of a compound as a final result of deposition over longer periods.

Alternatively, surrogate surfaces can be used (petri dishes, water layers on artificial surfaces). It is very difficult to develop surrogate surfaces that are sufficiently representative for vegetation. Experiments with artificial water layers in wind tunnels (e.g. Adema *et al.*, 1986, Adema and Heeres, 1995, see 1.4.4) enabled detailed mechanistical studies of physical and chemical processes involved in deposition to wet surfaces. However, water layers on artificial surfaces (in laboratory or field (dew)) lack potentially relevant influences of plant excretes and other interactions with leaf tissues. Therefore generalization to vegetation remains difficult and uncertain.

Surface accumulation techniques are not fit to monitor bi-directional exchange with vegetation in the field. Only the net accumulation is measured and/or contributions to the exchange of other surface elements than the leaf surface (e.g. stomata) are not included.

Enclosure methods

In enclosure methods, the exchange is derived basically from the enrichment or depletion of a compound in a volume of air enclosed above (or around) a surface(element). Many variations to this principle exist: naturally or artificially ventilated tunnels; open top chambers; growth chambers for potted plants; leaf chambers (leaf cuvettes) covering one branch or leaf, etcetera. For field measurements typically boxes or tunnels are used that cover an area of less than one to a few square metres.

Enclosure methods enable the study of the exchange behaviour of different plant species or of a different plant component (leaf), under very accurately controlled conditions (growth or leaf chambers). Time resolution generally is no limit for application of this technique. Hardly any restrictions apply to the surroundings of the enclosure, as only the exchange of the enclosed surface or object is measured. However, the latter is often

rather a disadvantage in case of field measurements. Very local conditions of plants and soil may dominate the result of a single measurement. To allow generalization, a large number of duplicate measurements may be necessary. Furthermore the flow and other conditions of the enclosed atmosphere and surface (e.g., temperature, humidity) may be altered by the enclosure itself. The method is very useful for mechanistic studies but has proven to be hazardous to assess absolute fluxes.

Micrometeorological methods

In micrometeorological methods, the dry exchange between surface and atmosphere is derived from measurement of the transport within the atmosphere above the surface. In these methods, the measurements are representative for the exchange over a certain distance upwind of at least a few tens of metres. So they do not influence the exchange, (as the instruments are downwind from the exchanging surface) and they give an average exchange for a larger area than enclosure methods. The fluxes can be measured with a time resolution which is sufficiently high to relate them to diurnal patterns in meteorological and surface conditions. A disadvantage of these techniques is that concentrations in the air must be measured with high precision and/or with very high time resolution. Furthermore most of these techniques rely on the existence of a surface layer where the turbulent transport in the atmosphere is in equilibrium with the surface, so that the flux is constant with height. This requires that atmospheric and surface conditions are sufficiently constant both in time (during a measurement) and over a certain distance upwind from the measurement. As a rule of thumb the surface should be homogeneous over a distance of about 100 times the measurement height (the "fetch"). However, as long as the surface type and its aerodynamic roughness (d , z_0) do not change abruptly, micrometeorological methods are much less sensitive to very local surface variations than enclosure methods. A further requirement is that the measurements should be carried out well above the surface ($z \gg d + z_0$), so that individual surface elements do not influence the measurement. This is hardly a problem over pastures with relatively low grass height, but it may be relevant in the case of forests.

Inferential technique

In the inferential technique (e.g., Hicks, 1987), fluxes are estimated by resistance modelling (see 2.1) using relatively simply measurable meteorological parameters and air concentrations as input. For this indirect method, monitoring stations can be much simpler and cheaper than for direct flux measurements; data from routine weather stations and concentration monitoring networks can be used. However, the quality of the flux estimation by inferential techniques at a specific location depends highly on the availability of an adequate resistance parameterization. For bi-directional exchange, resistance-based parameterizations so far are very uncertain (see 2.4).

Choice among the basic techniques of flux measurement

Which technique for exchange measurement is most appropriate for a specific experiment depends on a large number of factors; among these are the following:

- The aim and (in relation to this) the duration of the experiment (*e.g. trend analysis*, which generally requires continuous monitoring over long periods; *mechanistical studies*, which require measurement of a number of additional parameters that influence the exchange process and /or which are often carried out only under specific, well defined conditions).
- The studied compound and its (expected) exchange behaviour (mainly deposition, emission or both).
- The site and surrounding terrain of the experiment (homogeneity of the site and surrounding terrain).
- The availability of appropriate instruments to measure a compound by a given technique (adequate time resolution, adequate precision and accuracy).
- Necessary degree of automation (depending on duration and continuity of the measurements; available personnel; vicinity of the site).
- all in relation to the available budget.

For the present experiment, both trends and mechanisms of the exchange in relation to atmospheric and surface conditions were to be studied. Parameterizations applied in inferential techniques are based on existing mechanistical knowledge; to evaluate and improve these parameterizations, direct exchange measurements were necessary. Long term measurements were needed, but the time resolution should be sufficient for analysis of diurnal patterns. The main compound studied was ammonia, for which bi-directional exchange was expected to occur; other pathways of exchange than the leaf surface were expected to be involved (stomata, soil). Hence surface accumulation techniques were not adequate either. A high degree of automation was necessary (continuous measurements to cover all relevant conditions). The exchanging surface should not be influenced by the measurements themselves. A high variability in exchange on a scale of a few metres was expected (*e.g. urine spots*) while a representative average for a whole pasture terrain was needed.

The only type of techniques that could satisfy all these requirements sufficiently were micrometeorological methods. As an extended flat terrain of only pasture was available for the measurements, fetch requirements put no restraints to application of methods of this type.

Different micrometeorological techniques

The three most important micrometeorological techniques are the aerodynamic flux-profile method, the eddy-correlation technique, and the micrometeorological mass balance method.

In the *aerodynamic flux-profile method*, fluxes are derived from average vertical concentration profiles within the atmosphere. The relation between flux and profile of a compound is derived from measured flux-profile relations for momentum (see also 3.2.3). An advantage of this method over eddy-correlation is that only averages of the variables are needed, so that a much lower time resolution is necessary (averaging times are typically 10 minutes to several hours). However, small concentration differences between the different heights of the profile must be measured with high precision (better than 5%). Furthermore, stability corrections must be applied to correct for differences in transport between momentum and mass in stable or unstable atmospheres. For these, estimates are needed of the heat and momentum fluxes. If the heat flux is derived from profile measurements, recursive procedures may be necessary.

In the *eddy-correlation technique* the fast fluctuations of concentration and of vertical wind velocity caused by turbulent eddies (see 2.2.1) are measured directly. From the covariance between concentration and vertical wind the (local) flux in the atmosphere is calculated. Provided that constant flux requirements are met, the measured vertical flux equals the exchange flux with the surface. Over sufficiently homogeneous terrain the flux will be the same over the fetch distance upwind. If constant flux requirements are violated severely, measured fluxes may only be representative for the exact position (location and height) of the sensor.

The theoretical principle behind the method is simple and basic; the vertical transport is measured directly. However, the main disadvantage is posed by the high instrumental requirements of the method. A large part of the transport takes place by small eddies, meaning that measurements of wind speed and of concentration must be possible with high time resolution (typically 0.1 second) and sufficient precision.

The *micrometeorological mass balance method* differs from the previous two in that it does not assume a fully developed atmospheric "surface layer" in which the concentration profile has become adapted to the exchange with the underlying surface. Instead, the flux is derived rather from the change in concentration profile after passage of the air over a piece of emitting terrain. The deviation of the downwind profile from the background profile upwind is ascribed to the exchange with the surface; in fact a plume measurement is carried out. This method is very often applied to determine the emission from (spread) slurry or from excreta during grazing over small pieces of terrain (a few tens of metres in diameter). This is possible because in this method the relevant exchanging area is defined well as the terrain between the upwind and downwind measurement. No homogeneity requirements apply to the terrain further upwind. So much smaller experimental terrains can be used than for eddy-correlation or for the aerodynamic flux profile method. However, to derive fluxes accurately, the measured profile should cover (almost) the whole vertical plume extension. Over large terrains (and generally in case of deposition) this is practically not possible. Furthermore, two

measurement points should always be sufficiently aligned according to the wind direction.

Choice of the best micrometeorological technique for this research

In principle eddy correlation is considered to be the most direct technique of flux measurement, but for ammonia (and for NH_4NO_3 and HNO_3) no analysing techniques with sufficient time resolution were available for continuous field application. Contrarily, for the measurement of average concentration profiles-requiring much lower time resolutions-, adequate techniques existed. These could be well integrated in an automatic monitoring system for all studied compounds. From profiles, fluxes can be derived by the micrometeorological mass balance method or by the aerodynamic flux-profile method. The mass balance method might in principle be preferred if strong surface emissions of ammonia from small areas occur, as may be the case after slurry spreading on an individual plot. However, in this experiment it could not be used for long term monitoring of the exchange because it is not applicable when deposition dominates. Furthermore this method would require constant alignment of the upwind and downwind measurement along with the wind direction. This was not possible at this site in an automated, continuous system. Also the measurements would practically be limited to a too small area (a single plot), while it was preferred to measure an average flux over a larger terrain. For all these reasons, it was decided to measure the pollutant fluxes in this experiment from the concentration profiles according to the aerodynamic flux-profile method. Only by this technique would it be possible to monitor patterns of deposition and emission continuously over a representative area of pasture.

Influence of treatments of specific plots on fluxes measured by the flux profile method

In practice, representativeness of measured fluxes for a larger area also had some disadvantages. It complicated analyses of the relation between land treatments and measured exchange. Given the dimensions of the plots at Zegveld (generally rectangular and quite narrow), it is likely that most measured ammonia profiles were influenced by the exchange over several plots at the same time. It would be very labourious, -if even possible with sufficient accuracy- to derive the contribution of each relevant plot to an actually measured flux value.

Also, it had to be taken into account that sometimes, requirements of surface homogeneity would be violated due to agricultural treatments of single plots (or groups of plots), especially shortly after slurry application. It was decided that this problem could be overcome by an adequate data selection (see 4.1) and by the use of average diurnal exchange patterns over sufficiently long periods where possible. It seems acceptable to assume that effects of temporary, local inhomogeneity on the flux measurements remaining after the data selection average out largely over longer periods (season, year).

Some concern could arise that in certain directions relative to our site, the terrain might receive a different land treatment on seasonal basis, as a result of agricultural experiments of the ROC. This could cause a consistently different surface exchange behaviour in those directions. For several plots, the ROC varied the annual nitrogen fertilization (e.g. 60-200 kg ha⁻¹ yr⁻¹ N) or the way of N application (e.g. only fertilizer or partly slurry). However, calculations in chapter 6 will show that differences in seasonal treatment per wind sector (30°) over the distance that is relevant to the flux measurements (about 300-500m) were small. Therefore seasonal averages of exchange can be compared to the average treatment of the terrain as a whole, without weighing per wind direction.

3.2.2 Aerodynamic flux-profile measurements

The aerodynamic flux-profile method is based on the assumption of an analogy between vertical atmospheric transport by turbulence and transport at molecular level by molecular diffusion. The underlying "gradient" theory to describe exchange and the relevant parameters and formulas were already explained in more detail in chapter 2. Briefly summarizing, fluxes of momentum, heat and pollutant are related to the vertical profiles of the respective properties via diffusivity coefficients K (eqs. 2.6, 2.7 and 2.8). The diffusivities for mass and for heat are assumed to be equal. In the aerodynamic flux-gradient method they are derived from K for momentum, taking different effects of stability to momentum transport into account. In practice the flux-profile relations are usually expressed in terms of scaling parameters (u_* , T_* , c_* , see eqs. 2.16, 2.17) and the diffusivities are often not calculated explicitly.

For the measurements at Zegveld, the integrated profile equations 2.21 and 2.22 were used, with stability corrections by Beljaars *et al.* (1990). For the necessary meteorological parameters of u_* and L , values measured by eddy-correlation were used. As mentioned earlier, pollutant fluxes could not be measured by this method, but it could be applied well to derive fluxes of momentum and heat.

Actually, these parameters were also derived according to the flux profile method from profiles of wind speed and temperature which were also monitored continuously. In this, a recursive calculation procedure described (e.g.) by Beljaars *et al.* (1990) was followed, because to calculate L in the stability corrections, u_* and H must be estimated first.

The values of u_* and L by eddy-correlation were preferred principally, as this method is more direct without stability corrections and recursive procedures. Furthermore, as will be shown in section 4.2.1, our values of u_* by eddy correlation agreed very well with values found by RIVM. This institute temporarily measured exchange fluxes simultaneously with the ECN measurements, on the same site. Our *profile*

measurements of wind speed and temperature yielded slightly higher values of u_* (11% on average, see 4.2.1) than those found by eddy-correlation. Though in fact this is still a quite good agreement for these two very different methods, eddy-correlation values were preferred for the analyses in this thesis.

The profiles of the pollutants were measured at 2, 3 or 4 heights (see also 3.3.3). For calculations, it is convenient to rearrange equation (2.22) into the form of a straight line, yielding for the concentration profile:

$$c(z) = \frac{c_*}{k} [\ln(z-d) - \Psi_H(\frac{z-d}{L})] + \{c(z_0) - \frac{c_*}{k} \ln(z_0) + \Psi_H(\frac{z_0}{L})\} \quad (3.1)$$

Now c_* may be approximated by the slope (c_*/k) of the line found by least square fitting of $c(z)$ as a function of $[\ln(z-d) - \Psi_H(\frac{z-d}{L})]$, the 'stability corrected height'.

The offset of equation 3.1 is provided by three terms that include the roughness length z_0 (or the concentration at this notional height). It can be seen that in calculations of fluxes from profiles of two or more heights z , these terms will cancel out. Nevertheless the magnitude of z_0 was evaluated, because the method requires that measurements take place well above the surface. The average value of z_0 for the Zegveld terrain determined by Erisman (1993) was about 1 cm. In our research we measured mean values between about 0.5 and 3 cm according to the method applied to derive z_0 . The most common method consists of extrapolation to zero wind speed of measured profiles under (near) neutral conditions. This yielded average values of z_0 close to 2 cm, with no clear influence of the season. The lowest height of concentration measurement of SO_2 was 53 cm, and for all other compounds the lowest height was 1.00 m. This means that indeed, $z \gg z_0$, so that the method was applicable. Furthermore, it means that the stability corrections for z_0 can be neglected in profile and resistance (R_a) calculations.

Contrarily to z_0 , the displacement height d does not cancel out in profile and flux calculations. For Zegveld a d -value of 16 cm was derived. This resulted from a comparison of heat fluxes calculated from the temperature profile with heat fluxes measured directly by eddy-correlation (see appendix C). It is slightly higher than generally calculated by other parameterizations in literature (about 0.6-0.8 times the vegetation height: Brutsaert, 1975; Wieringa, 1993). Possibly the flow was slightly obstructed downwind the instruments. It could be the case that boxes, boards of a fence, and the pump (and tall grass surrounding it) together lifted up the streamlines slightly.

3.2.3 Eddy-correlation technique

In chapter 2 it was explained how differences in concentration of pollutant (or other properties) in upward and downward moving air parcels result in net transport. It was also explained that the resulting vertical transport of a property could be derived from eq. 2.4. The second term of this relation is the covariance of w and X . Under conditions of steady state and homogeneity of surface and atmosphere, and a sufficiently long averaging time (for example, more than 5 minutes) the average vertical wind velocity $\bar{w}$ approximates zero. In that case the flux equals the covariance of w and X , according to eq. 2.5.

In the micrometeorological technique of eddy-correlation the relevant covariances are measured almost directly. Wind velocity in vertical direction is measured simultaneously with other air properties in the same point, at a high frequency (>5 Hz). The fluctuations are calculated with respect to the running average values of w and X :

$$w' = w - \bar{w} \quad (3.4)$$

$$X' = X - \bar{X} \quad (3.5)$$

In this way the sensible heat flux can be derived from fast measurements of w and θ :

$$H = \overline{w'(\rho_a c_p \theta')} = \rho_a c_p \overline{(w' \theta')} \quad (3.8)$$

In an analogous way, u_* can be derived from fast measurements of the wind velocity in vertical and horizontal direction (the latter along with the mean wind direction):

$$u_* = \sqrt{\overline{|w' u'|}} \quad (3.9)$$

which is equivalent with the definition of u_* in eq. 2.9.

The vertical alignment of the wind velocity measurements should be better than 1° if possible, to prevent w from being influenced by the horizontal wind components (u and v). If all three wind components (u, v, w) are measured, correction for eventual misalignments is possible by coordinate rotation (McMillen, 1986). In this procedure

the axes are redefined in such a way that the u -axis is parallel to the average wind vector and the averages of v as well as of w are equal to zero.

3.3 Instrumental setup at Zegveld

3.3.1 General setup

The measurements at Zegveld included measurements of meteorological parameters and of profiles of the compounds of NH_3 , NH_4NO_3 , HNO_3 and SO_2 . Figure 3.3 on the next page gives a schematic representation of the complete flux monitoring system applied at Zegveld.

In the next section the measurements and relevant data-preprocessing steps to derive the meteorological parameters are discussed briefly. Most of the meteorological instruments were commercial products that are very commonly applied in this type of research. The systems used to measure the pollutant profiles were much more specific for this experiment, and therefore they are discussed in more detail, in section 3.3.3. They were based mainly on analytical techniques developed by ECN.

A list of all measured parameters and of the applied instruments is given in appendix D.

3.3.2 Measurements of meteorological parameters

For the eddy-correlation measurements of u , H and L , a sonic anemometer (Applied Technologies, k-probe) was used for high speed measurements (10 Hz) of the *wind velocities* in the three orthogonal directions (u, v, w) and of *temperature*. A 'sonic' derives the wind velocity along each axis from the travelling time of a sound pulse between two transducers. This also yields the speed of sound, from which the air temperature can be calculated. This 'sonic' air temperature is close to the virtual temperature, and θ , derived from its fluctuations can be used to calculate the Monin-Obhukov length L very accurately according to eq. 2.19.

Coordinate rotation was applied to correct for eventual misalignments of the probe. In practice, analysis of actually applied rotation angles showed that the vertical misalignments were very small ($< 1.5^\circ$) during the whole experiment.

The raw (10 Hz) data of wind and temperature measured by the sonic anemometer were passed to a central computer for further processing. This processing implied the calculation of running mean values (with time constant 200 sec) and fluctuations of u , v , w and θ . Per 20 (later 10) minutes period, coordinate rotation was applied followed by calculation of the relevant variances and covariances (wu , $w\theta$, etc.), the mean *wind speed* U and *wind direction* WD , u , H , L and several additional parameters. All raw data were backed up on tape to enable later reprocessing.

Research site Zegveld

Instruments

- a: Solarimeter
- b: Net-radiation meter
- c: Rain sensor
- d: Thermocouple (air)
- e: Cup anemometer
- f: Wind vane
- g: Inlet dewpoint hygrometer
- h: Sonic 3d-anemometer
- i: Fog sensor
- j: Soil heatflux plates
- k: Soil thermocouples
- L: SO₂ monitor (pulsed fluor.)
- m: NH₃-thermodenuder
- n: NH₄NO₃/HNO₃ thermodenuder
- o: NH₃ continuous flow denuder
- p: Dewpoint hygrometer

Inlet gas sampling

- 1 : NH₃ (f.d.)
- 2 : HN₄NO₃/HNO₃
- 3 : SO₂
- 4 : NH₃ (c.f.d.)

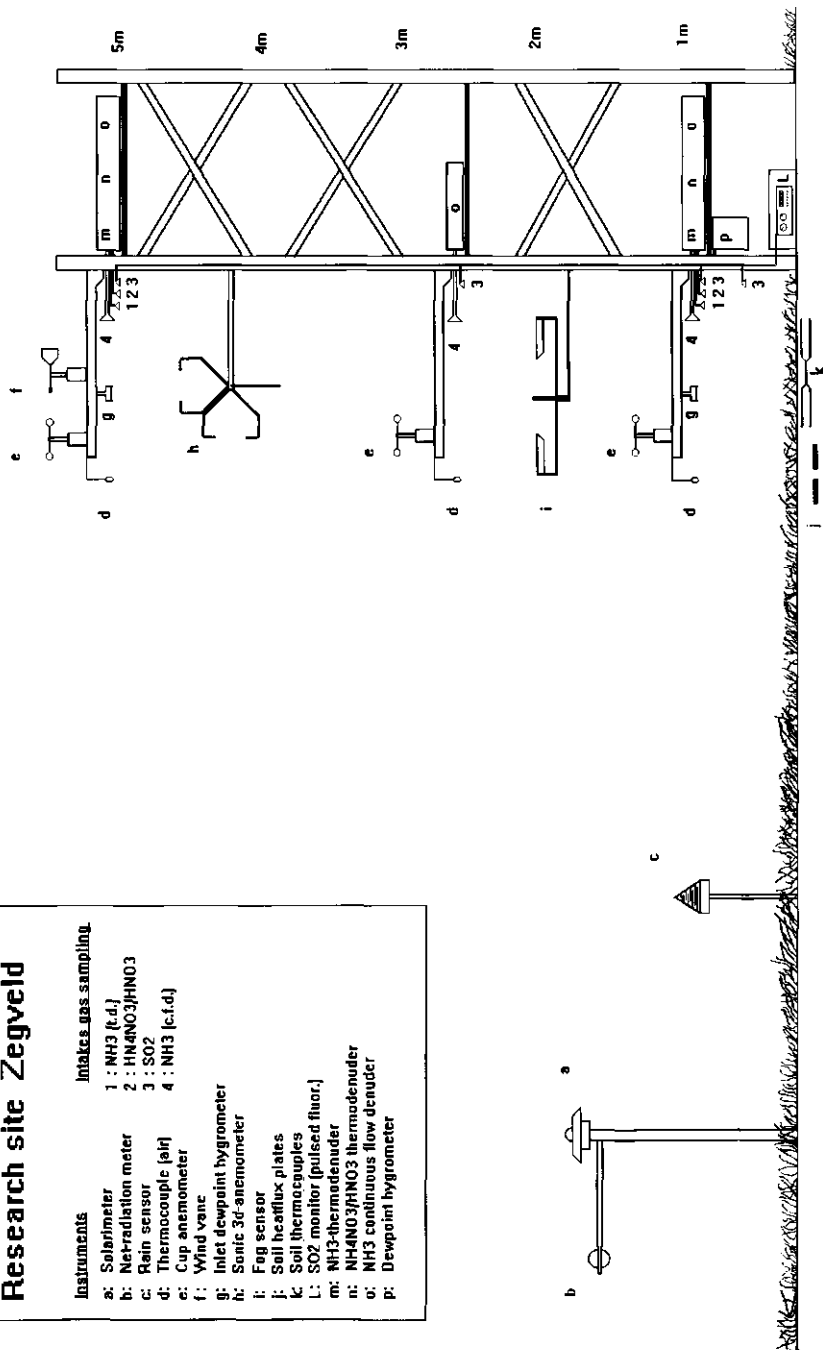


Fig 3.3 Schematic overview of the flux monitoring system at Zegveld

To enable the derivation of u_* and L by the *profile* method, profiles were measured of temperature, wind speed and humidity. Sensitive cup anemometers at three heights were used for the *wind speed* profiles. *Temperatures* were measured at three heights using very fine (0.03"), non-shielded chromel-constantane thermocouples. *Dewpoints* were measured at two levels by a cooled mirror dewpoint system. Air samples from the two levels were passed alternatingly over the mirror. From the dewpoints, the respective saturation vapour pressures (*SVP*) were calculated using an approximating polynomial derived by Lowe (1976). From the values of *SVP* and the air temperatures measured by the thermocouples, the profiles of absolute humidity (q) were calculated (assuming a standard air pressure of 100 kPa). *Relative humidity RH* was calculated from *SVP* at the dewpoint and at the actual air temperature.

Several additional meteorological parameters were measured, to monitor as accurately as possible the conditions of surface and atmosphere during the flux measurements. The wind direction *WD* was measured directly by a wind vane (in addition to the wind direction derived from sonic measurements). An ECN *rain* detector indicated the occurrence of rain. This detector signalled the increased conductance between electrodes on its surface caused by rain droplets. This surface was heated so that it dried up again within a minute if the rainfall ceased.

An ECN *fog* detector indicated occurrence of fog. In this instrument, a small bar interrupts a light beam between an infra-red lamp and an IR-sensitive cell opposite to it. If the IR-light is deflected by fog particles, part of it reaches the cell causing a response of the detector. Sometimes cob-webs caused erroneous responses.

To enable determination of the daytime period and parameterization of the stomatal resistance R_s , the *global radiation* (incoming shortwave radiation, Q) was measured by a solarimeter. Later this sensor was replaced by a *PAR* (*photosynthesis active radiation*) sensor; global radiation was parameterized as $Q = 2 * PAR$. The *net radiation* R_n (the net result of incoming and outgoing long- and short-wave radiation) was also measured. Q and R_n were measured by thermopile-based pyranometers.

The *soil heat flux* G was measured using flux-platelets (two) at 10 cm below the soil surface. The average *soil temperature* T_{soil} in the soil layer above the flux-plates was measured by thermocouples (chromel-constantane) at 2 and 8 cm. The *heat storage* S in this layer was derived from the change of T_{soil} with time.

Except for those derived from the 'sonic' measurements, the meteorological parameters were sampled at a frequency of 0.1 Hz (wind speed, radiation) or 1 Hz (others). The average values of these observations were calculated and stored per 20 minutes period (rain and fog: total duration in seconds per 20 min period).

3.3.3 Measurements of the profiles of pollutants

NH₃ concentrations at two heights (1 and 5m) were measured by use of two simultaneously sampling NH₃-thermodenuders. Similarly two NH₄NO₃/HNO₃ thermodenuders sampled NH₄NO₃ and HNO₃ at these heights. These measurements were continued during the whole experiment (July 1992-July 1994). Both thermodenuder systems will be described in the next subsection.

Profiles of SO₂ were measured from mid-August 1993 until mid-January 1994, by a single (pulsed fluorescence) SO₂ monitor that sampled subsequently from 4 heights (see 3.3.3.3).

From July until October 1993 and from January until March 1994 the profiles of NH₃ were also analysed by a gradient system of three continuous flow denuders (see 3.3.3.2). These measurements were carried out partly to test and improve the application of the continuous flow denuder technique to monitor gradients over low vegetation. They are used in this thesis to check the performance of the NH₃-thermodenuders.

3.3.3.1 Profiles of NH₃, NH₄NO₃ and HNO₃ by thermodenuders

Principle of analysis

Denuder techniques are widely used to measure atmospheric pollutants. An overview of different types of denuders has been given by Slanina *et al.* (1992). Denuders are used primarily to separate gaseous from particulate compounds. The separation results from the principle that molecular diffusion is much slower for particles than for gases. Sample air is drawn, -in a *laminar flow*-, through a tube which is coated with an effective absorbent for a pollutant. During the passage through the tube, gaseous compounds will diffuse laterally towards the coated wall where they are absorbed. Particles will also diffuse laterally, but much more slowly than gases. So in an adequate combination of sampling rate and length and diameter of the denuder tube, particles will have passed the tube before they can reach the wall. If the denuders consist of such a simple tube, in practice only relatively low sample flow rates are possible. In an annular denuder, the sample air is drawn through the space (ring or annulus) between two concentric tubes with only a small difference in diameter. In this way the distance to be crossed by diffusion towards the coated walls of the annulus can remain short while higher sampling rates are possible.

After a sampling period, the quantity of the compound that has been absorbed by the denuder coating is analysed. In ordinary denuders for this aim usually the absorbent is dissolved, meaning that a new coating must be applied for each measurement.

In the *thermodenuder* technique, the denuder is coated with a material that releases the absorbed gas (or a conversion product) again if the coated wall is heated. The desorbed compound can be analysed by common gas analysis techniques. After cooling down, the

coating regains its absorbing capacity, so that the denuder is immediately ready for a new measurement. Thermodenuders are well applicable in continuous, automated monitoring systems.

In this research, the thermodenuders for NH_3 (see figure 3.4) were coated with V_2O_5 . After sampling, the analysis of the absorbed NH_3 started by placing a hot tubular furnace (700 °C) over the denuder. At this high temperature, the NH_3 was oxidized and desorbed as nitrogen oxides. These were led to a common (chemiluminescence) NO_x -monitor and measured.

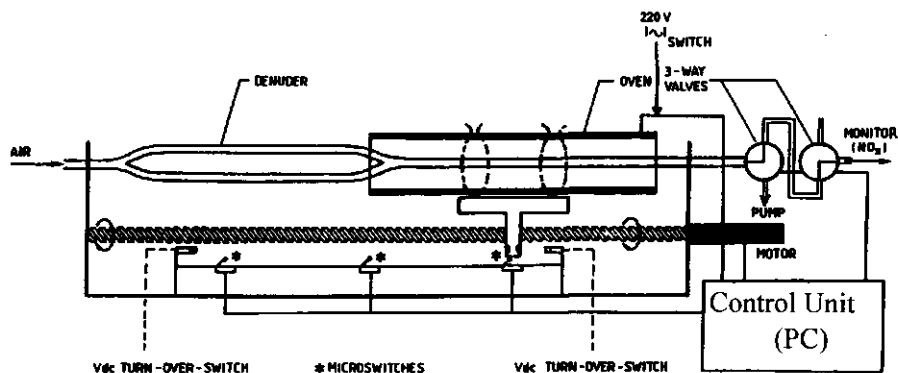


Fig 3.4 Thermodenuder for the measurement of ammonia

In the HNO_3 / NH_4NO_3 -thermodenuders, the coating consisted of magnesium sulphate which absorbs HNO_3 . Simultaneously NH_4NO_3 could be measured by making use of the dissociation of this compound into HNO_3 (and NH_3) at elevated temperatures. During sampling two different temperature zones were maintained in the denuder (see fig.3.5).

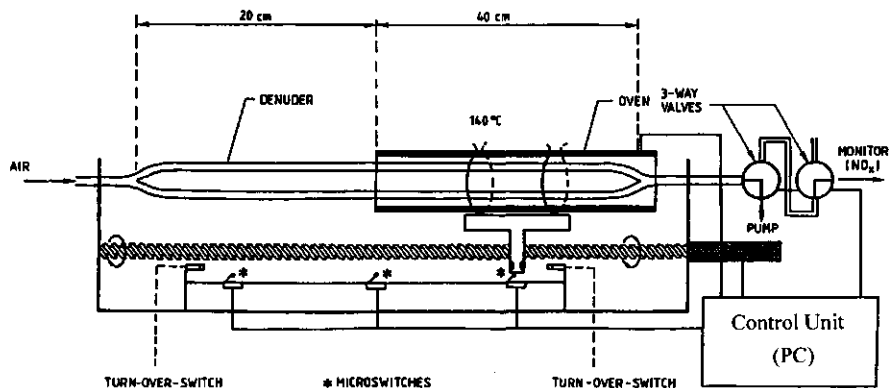


Fig 3.5 Thermodenuder for the simultaneous measurement of NH_4NO_3 and HNO_3

The first part of the denuder was not heated; here the coating absorbed the HNO_3 from the sampled air. The NH_4NO_3 aerosol however passed into the second zone, where a temperature of 130°C caused its dissociation. The HNO_3 gas resulting from this reaction was adsorbed by the coating in this part of the denuder.

After the sampling period, the HNO_3 absorbed in each section was analysed subsequently by heating to 700°C . This caused the reduction of the HNO_3 into nitrogen oxides which were measured by a chemiluminescence NO_x -monitor. For a more detailed description see Klockow *et al.* (1989).

Application at Zegveld

At Zegveld, the four thermodenuders (one NH_3 denuder and one $\text{HNO}_3/\text{NH}_4\text{NO}_3$ denuder for each of both heights) were connected to a single NO_x -monitor. Periods of sampling, heating and analysing were fitted into a two hours cycle. In this cycle, both NH_3 denuders sampled (simultaneously) during one 20 minutes period per hour (flow rate 10 l min^{-1}). NH_4NO_3 and HNO_3 were sampled during 40 minutes once per two hours period (flow rate 2 l min^{-1}).

The reported precision of the thermodenuders is 2% for NH_3 and 3-5% for HNO_3 and NH_4NO_3 (Slanina and Wyers, 1994).

The practical performance of the NH_3 thermodenuders in these flux measurements in the field was very good in general. Only if too high ambient concentrations were sampled ($>25 \mu\text{g m}^{-3} \text{NH}_3$), the coating approached saturation and sampling efficiency decreased. Then the precision became too uncertain to derive reliable gradients. At concentrations below $0.75 \mu\text{g m}^{-3} \text{NH}_3$, a small zero drift sometimes might have reduced the precision too. For these reasons, NH_3 -profiles containing concentrations below $0.75 \mu\text{g m}^{-3}$ or over $25 \mu\text{g m}^{-3}$ were rejected for flux-calculation.

With respect to NH_4NO_3 and HNO_3 , this experiment showed that it had become possible to monitor fluxes of these compounds on continuous basis, with high time resolution, during an extended period. As far as known, this was the first experiment in which during such a long period continuous flux measurements of these compounds were realized. It illustrates the progress in the development of flux measurement techniques of the last decade. Nevertheless, the $\text{NH}_4\text{NO}_3/\text{HNO}_3$ thermodenuders may need some improvements to make them less sensitive to adverse (humid) weather conditions. At Zegveld, the precision of these instruments (3-5%) may not always have been achieved. These values were actually obtained in field measurements under conditions different from those in the present experiment. At Zegveld, the sampled air contained much more moisture, which affected the coatings of the denuders and of the air inlets. Resulting offsets of the measured concentration between denuders sometimes became considerable and in some (mainly humid) periods quite large random variations were observed. Quantitative interpretation of these measurements in terms of fluxes is therefore more uncertain than in the case of NH_3 and SO_2 measurements.

To reduce the uncertainty of the measured profiles of HNO_3 and NH_4NO_3 , several measures were taken:

- the denuders were replaced when visual checks or instrumental parameters indicated poor quality of the coating of the denuders;
- the data before such a replacement in which the denuders might already have been affected were rejected in an extra screening.
- starting April 1993 denuders of both heights were interchanged regularly so that offsets in sampling efficiency would be largely compensated.

The same procedures were applied to the NH_3 measurements, but in this case deterioration of the coating caused hardly any problems.

3.3.3.2 NH_3 profiles by continuous flow denuders.

Principle of analysis

The continuous flow denuder is a version of the so-called wet denuder. In wet denuders, the coating consists of a thin film of liquid absorbent. This film is maintained by a

continuous rotation of the (annular) denuder around its length axis. In ordinary wet denuders, for each measurement a volume of absorbent is injected (automatically) into the annulus. After the sampling period the absorbent is collected again in test tubes for later analysis in the laboratory. In a continuous flow denuder however fresh absorbent is supplied continuously to one end of the annulus. As the film covering the wall of the annulus the absorbent gradually flows to the other end of the denuder. From there it is carried off to a detector cell for on-line analysis (see fig 3.6). In this way, uninterrupted, direct monitoring of pollutant concentrations is possible.

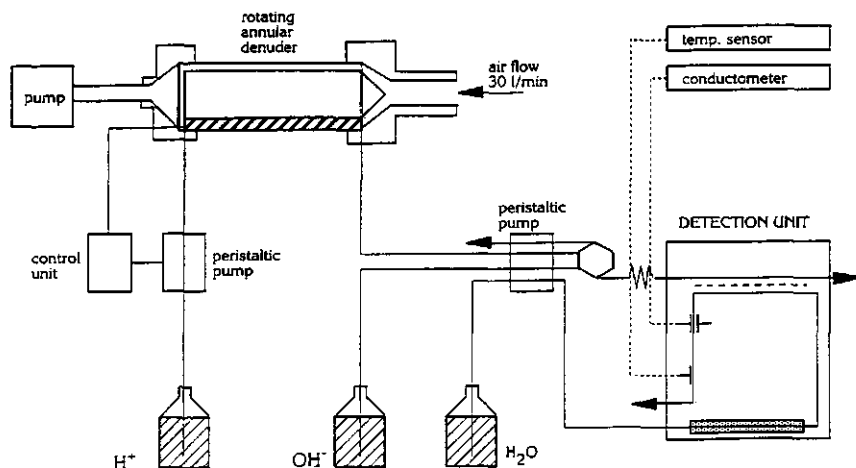


Fig 3.6. Continuous flow denuder system (AMANDA) for ammonia measurements

Continuous flow denuders have been developed by ECN for ammonia measurements. The type 'AMANDA' and its successor 'AMOR' are applied *e.g.* by RIVM in the LML air quality network (Van Elzakker *et al.* 1995). The absorbent in this instrument is water, buffered by addition of KH_2SO_4 at a pH of about 4, so that NH_3 dissolves well to form NH_4^+ . The detection is based on conductivity measurement. In the detector unit the pH of the absorbent flow is raised by addition of NaOH, causing a shift of the $\text{NH}_4^+/\text{NH}_3$ equilibrium (eq. 1.7-1.9) towards NH_3 . The NH_3 passes a membrane and is taken up in a second (counter)flow of pure demineralised water. The conductivity of this water is measured by two electrodes and compared with calibration standards, corrected for temperature variations.

A more detailed description of the continuous flow denuder is given by Wyers *et al.* (1993), who also reported a precision of 1% with a time resolution of 1 minute, and a detection limit of about 50 PPT.

Application at Zegveld.

At Zegveld temporarily a profile system based on ECN continuous flow denuders of the type AMANDA was added to the thermodenuder (TD) profile system. It consisted of three continuous flow denuders (at 1, 2.5 and 5 m height) that shared a single detection unit. By this construction, eventual offsets due to drift between different detector units were avoided. Absorbent from each denuder was led through the detector for analysis during two minutes per denuder. Tubing lengths between the denuders and the detector were adapted to create delay-loops, so that analysed volumes of absorbent from all three heights reflected the same sampling period. The measurement of a complete profile took 6 minutes. The air was sampled at a flow of 30 l min^{-1} .

These AMANDA measurements at Zegveld were carried out primarily to check the performance of the thermodenuder gradient system. In principle, this AMANDA gradient system had better specifications for profile measurements than the thermodenuder system at Zegveld. As mentioned above, the precision of continuous flow denuders (1%) is higher than the precision of the thermodenuder for NH_3 (2%). The time resolution of the AMANDA gradient system is much better: (6 minutes vs 1 hour for the TD-system). Finally the concentration range that can be measured with high precision is much larger (AMANDA: <0.01 up to over $300 \mu\text{g m}^{-3}$; TD at Zegveld: 0.75 to $25 \mu\text{g m}^{-3} \text{NH}_3$). This is very relevant in emission areas with strong concentration fluctuations. An important disadvantage is that AMANDA systems cannot measure under frost conditions. Thermodenuders do not have this restriction; furthermore they require much less routine maintenance than AMANDA.

The AMANDA measurements covered about 8 months in total. In this period several modifications of the AMANDA system were tested which caused some loss of data. Due to an error in the autorange routines of the control program of the AMANDA system at Zegveld, during a considerable period no concentrations higher than 15 to $30 \mu\text{g m}^{-3} \text{NH}_3$ could be measured. Finally no AMANDA measurements were possible during a few frost periods in these months. Nevertheless a considerable data set is available to allow a comparison between both gradient systems. This will be done in 4.2.2, where an evaluation is made of the uncertainty in the measurements at Zegveld.

For the actual analyses of ammonia exchange patterns in this thesis, only the thermodenuders were used because these covered a very long period (two years) including all seasons and a wide variety of conditions. It was decided not to combine results from two different measurement systems in the data set used for interpretation.

3.3.3.3 SO₂ profiles

Profiles of SO₂ were measured from the end of August until the mid-December 1993. The system developed for this purpose was partly comparable to one developed by RIVM (Mennen, 1992). It consisted of a TSI 43S pulsed fluorescence SO₂-monitor that sampled sequentially from 4 heights via (FEP) tubing. The precision of the SO₂ analyser was 1%. Every 24 hours, a zero signal control was carried out by sampling over active carbon. The concentrations at the four profile heights were scanned in a 30 minutes cycle. Air at each height was sampled during 7.5 minutes, then sampling switched to the next profile height.

The use of one instrument for all four heights has the important advantage that systematic errors in the profile due to offsets among instruments are prevented. However, if profiles are derived from subsequent sampling at the different heights, the concentration (at each height) should in principle remain constant during the complete scan. Otherwise part of the concentration difference between heights may result from changes of the concentration with time that actually occurred in the whole profile. To enable correction for such concentration variations with time during a scan, a second 'reference' monitor sampled continuously at the top height. However, this reference monitor had a lower precision than the profile monitor and it showed too much drift. Corrections derived from these reference measurements did not improve the log-linearity of the profiles. Therefore the measurements of this reference monitor were not used and in the data-processing another detrending procedure was applied (see 4.1).

Chapter 4

Data processing and evaluation of sources of uncertainty in the fluxes

This chapter first gives a summary of the data processing from the raw measurements to a reliable data set that can be subjected to analysis of exchange patterns in the next sections. This includes the calculation of exchange parameters from the basic, measured parameters and a selection procedure to identify and reject unreliable measurements. In the second part of this chapter an evaluation is made of the different sources of uncertainty in the measurements and in the conclusions derived from them.

The described selections and the uncertainty evaluation apply to the measurements of NH_3 and SO_2 . The NH_4NO_3 and HNO_3 measurements require a different approach which will be treated separately in chapter 7.

4.1 Data-processing prior to analysis of flux patterns

4.1.1 Calculation of fluxes and other exchange parameters

Before the calculation of fluxes started, the measurements of the individual instruments were validated. Results that were unreliable due to traceable instrumental failures were removed from the set of input data for the flux calculations.

As mentioned in 3.3.3.3, the reference SO_2 -monitor was too unprecise and showed too much drift to use its results to correct the SO_2 -profiles for concentration changes during a full scan. Therefore another detrending procedure was applied. The course of concentration between to subsequent measurements at the same height (available with an interval of 30 minutes) was estimated by interpolation. A fitting curve was calculated through the four intervals of 7.5 minutes spanned by each original 30 minutes interval.

The fitting curves were calculated by cubic spline interpolation (Press *et al.*, 1989). In that procedure, not only pairs of measurements between which must be interpolated are taken into account, but also adjacent measurements. This yields smoother, probably more realistic curves than simple linear interpolation.

Such a curve was calculated for each height separately. In this way SO_2 profiles for every 7.5 minutes interval were estimated. Finally these were averaged to one hour mean profiles which were used for the flux calculations.

The concentration profiles that passed the validation were combined with the corresponding values of the relevant meteorological parameters. For NH_3 measured by

thermodenuders, in principle one 20 minute average per hour was available (see 3.3.3.1). This was combined with the corresponding 20 minute values of u_* and other parameters. To allow a comparison with the thermodenuders, AMANDA measurements in the same intervals were also added, averaged to 20 minute mean values. The detrended SO_2 profiles were processed as one hour mean values and so combined with hour-averaged meteorological parameters.

The fluxes, deposition velocities and resistances were calculated from the concentration profiles and eddy-correlation ('sonic') values of u_* , L and U . First c_s was calculated from the profile (based on eq. 3.1, see 3.3.2), with $d=16$ cm) and L from eddy-correlation. Then the flux was calculated as the product of c_s and u_* . Values of v_d and R_a (both at 5m), and R_b and R_c for each compound were calculated according to eqs 1.6, 2.28, 2.31, and 2.32, respectively.

By analogous procedures, the temperature profiles and eddy-correlation u_* and L were used to calculate (profile derived) values of T_s , H , and R_a and R_b for heat. From these, the extrapolated temperature at the surface (at canopy height, $T_s = T_0$) was derived according to eq. A.2 (appendix A). From T_0 and Q , R_{st} of the compounds was parameterized according to Wesely (1989), by eq. 2.34.

Within the period of 17628 hours (about two years) spanned by the NH_3 measurements, fluxes could be calculated for 8313 hours (47%). In the other hours one or more basic input parameters necessary to calculate or interpret fluxes had not been measured or had not passed the validation of correct functioning of the individual instruments. In case of the SO_2 measurements (spanning 2880 hours) fluxes became available for 2303 hours (80%).

4.1.2 Selection of reliable flux-measurements

4.1.2.1 Overview

After the calculation of exchange parameters as described in the previous subsection, the sets of all available flux measurements of NH_3 (by thermodenuder, $n=8313$) and of SO_2 ($n=2303$) were screened by a number of selection criteria. The selection criteria were defined in order to avoid artifacts by conditions which are outside the domain where micrometeorological methods are applicable. They concern the precision of the concentration profiles, meteorological conditions during the measurement, and advection and storage effects of plumes. Each group will be discussed briefly below. If all these criteria are met, the flux-profile method is applicable and results are reliable.

4.1.2.2 Criteria on profile precision

To reject unreliable profiles of the pollutant concentrations, a selection was made on:

- *Concentration.* All specifications of the chemical measurements (3.3) are sufficient for reliable analysis of vertical concentration differences, given the concentration change as function of height and the large number of observations. However, at concentrations above $25 \mu\text{g m}^{-3}$ NH_3 , NH_3 profiles measured by the thermodenuders were rejected, as the denuder coating then approaches saturation (3.3.3.1). A lower limit of $0.75 \mu\text{g m}^{-3}$ NH_3 has been chosen based on practical experience in the field with the given configuration. The same applies to the lower limit of $2 \mu\text{g m}^{-3}$ chosen for SO_2 .
- *Correlation coefficient and variation coefficient of the profile.* In case of SO_2 , concentrations were measured subsequently at 4 heights. The (log)-linearity of the profiles after the application of stability corrections and spline correction (see 3.4.3.4) was tested. This was used primarily as a check on the effectiveness of the spline procedure to correct for changes in the mean concentration during a scan over the 4 heights. Implicitly it provides an indirect test on eventual advection and storage errors (see 4.1.2.3).

Primarily the correlation coefficient R was tested. However to prevent unfounded rejection of measurements with small gradients (with usually small R), also the variation coefficient of the regression coefficient (cv_{prof}) was considered. Data were accepted if R^2 exceeded 0.3 provided that $cv_{prof} < 1$, or if R^2 was smaller than 0.3 provided that cv_{prof} was smaller than 0.3.

4.1.2.3 Criteria on adverse meteorological conditions

The following meteorological parameters were used to reject conditions with poor fetch or uncertain flux-profile relations:

- *Wind direction,* to satisfy fetch requirements. As mentioned in 3.1, the terrain was free of relevant obstacles over a distance of 500 m or more in the wind sector between 90 and 270 degrees. No relevant influence of the nearby ditch (see fig 3.2 and appendix B.) was observed so this was neglected.
- *Wind speed.* At low wind speeds, the validity of flux-profile relations becomes uncertain. In a stable, nocturnal atmosphere, at low wind speeds, transport is often dominated by very large eddies with long intervals which may be described less accurately by flux-profile relations. The same applies if at low wind speeds in an unstable atmosphere, convective transport completely dominates the transport. Partly for this reason, it is common practice in similar experiments to reject flux

Table 4.1. Selection results for NH_3 starting from the 8313 available flux measurements.

Criterion	Rejected from total		Rejected from remainder after previous criterion		
	n	%	n	% from remainder	% from total
$0.75 < c < 25$ ($\mu\text{g m}^{-3} \text{NH}_3$)	884	10.6	884	10.6	10.6
$90 < WD < 270$ ($^\circ$)	3348	40.3	3106	41.8	37.4
$U(1\text{m}) > 0.8 \text{ ms}^{-1}$	1034	12.4	294	6.8	3.5
$L < -10\text{m}$ or $L > 5\text{m}$	1725	20.8	482	12.0	5.8
No rain	1658	20.0	804	22.7	9.7
$F_{\text{soil}}/F_{\text{meas}} < 0.50$ (or < 1 if $F_m < 1 \text{ ng m}^{-2} \text{s}^{-1}$)	1467	17.6	179	6.5	2.2
$CV_{\text{RNM}} < 0.20$ (or not available)	503	7.1	72	2.8	0.9
Remaining for analysis			2492	(30.0%)	

Table 4.2. Selection results for SO_2 , starting from 2303 available flux measurements

Criterion	Rejected from total		Rejected from remainder after previous criterion		
	number	%	number	% from remainder	% from total
$c < 2 \mu\text{g m}^{-3} \text{SO}_2$	770	33.4	770	33.4	33.4
$90^\circ < WD < 270^\circ$	1238	53.8	669	43.6	29.0
$U(1\text{m}) > 0.8 \text{ m s}^{-1}$	409	17.8	90	10.4	3.9
$L < -10\text{m}$ or $L > 5\text{m}$	467	20.3	41	5.3	1.8
No rain	461	20.0	179	24.4	7.8
$R^2 > 0.3$ and $CV_{\text{pred}} < 1$ or $R^2 < 0.3$ and $CV_{\text{pred}} < 0.3$	269	11.7	68	12.3	3.0
$F_{\text{soil}}/F_{\text{meas}} < 0.50$ (or < 1 if $F_m < 1 \text{ ng m}^{-2} \text{s}^{-1}$)	285	12.4	21	4.3	0.9
Remaining after selection			465	(20.2%)	

Most of the rejected measurement periods concerned wrong wind directions, rain, extreme stability and -especially in case of SO_2 - too low concentrations. Finally, 2492 measurements of NH_3 passed all criteria. This is well sufficient to allow a statistical analysis of the annual and seasonal patterns of NH_3 exchange including further stratifications for specific conditions.

Slightly different percentages of unfavourable (weather) conditions are found for SO_2 , because this experiment was much shorter. Because estimating annual fluxes was no aim of the SO_2 measurements, representativeness for a whole year was not required. In the covered period of two months in the grazed season and two months in the rest season, 465 measurements passed the selection. This set is sufficient to analyse major trends in SO_2 exchange in these seasons and to compare them with seasonal differences in the exchange behaviour of NH_3 .

4.2 Evaluation of sources of uncertainty

4.2.1 Introduction

The uncertainty in conclusions based on the selected measurements can in principle originate from several sources. A primary source of uncertainty is provided by errors in the individual measurements of fluxes. In section 4.2.2 an evaluation will be made of the errors in the individual parameters in a flux calculation and their propagation in the resulting values of fluxes and resistances. In this way information is acquired which parts of the flux measurements and -calculations contribute most to the uncertainty in the final results.

Where available, comparisons with other instruments or methods will be used to estimate the error in a specific parameter or in the total flux.

In practice, the analyses in this thesis are based on average values of the measured fluxes over longer periods. This reduces the influence of instrumental errors in individual measurements considerably. On the other hand it is necessary to have a measure for the variability that occurred in the measured parameter due to variation in measurement conditions, so that the representativeness of the average value can be evaluated. As an approximation, the variability around such a mean value will be treated as a random error, estimated by the standard error. This subject and some general difficulties that occur when mean values of R_c must be derived will be discussed briefly in section 4.2.3

In section 4.2.4, eventual biases (systematical errors) due to the selection of reliable measurements are discussed. The selection criteria could lead to the rejection of conditions in which a specific, non-average exchange pattern occurs. Generalisation of such selected results therefore involves a risk that conclusions are biased ('selection

thermodenuder measurement were averaged. It may be assumed that generally, average profiles during 18 minutes differ very little from 20 minute averages. Fluxes from profiles by both systems were calculated using the same values of u_* and L . Only measurements in which no traceable malfunctioning in either of both systems had occurred were taken into account. In table 4.3 the average values of the fluxes and concentrations measured simultaneously by both systems are compared. This is done for two data sets, viz. the sets before and after selection by the criteria for reliable flux measurements (section 4.1).

Table 4.3. Comparison of average fluxes and other parameters derived from NH_3 profile measurements by thermodenuders and by an AMANDA profile system.

Parameter	Before selection (n=1148)			After selection: n=197		
	TD	AMANDA	Deviation TD from AMANDA	TD	AMANDA	Deviation TD from AMANDA
Flux in $\mu\text{g m}^{-2}\text{s}^{-1}$	-15.0	-12.8	17 %	-5.4	0.8	See text
c_* in $\mu\text{g m}^{-3}$	-0.52	-0.52	0 %	-0.039	-0.044	-11 %
$c(5\text{m})$ in $\mu\text{g m}^{-3}$	7.3	8.0	-9 %	6.9	7.9	-14 %

Before selection, the thermodenuder measurements yielded a 17% higher flux (stronger deposition) than those by the AMANDA system. The difference in c_* is negligible. The concentration by thermodenuders is about 9% lower than by AMANDA.

After selection, the deviations are larger, which can partly be explained by a larger influence of random errors at a smaller number of measurements. Especially the difference between the average fluxes would be very large on relative basis. This is mainly due to the fact that the average flux is so small; however this average flux is the mean result of positive and negative fluxes that are generally much larger. The order of magnitude of average fluxes in periods of emissions as well as in periods of deposition is about ± 40 to $60 \mu\text{g m}^{-2}\text{s}^{-1}$ of NH_3 . In view of this, the difference between both systems in the average flux (as well in c_*) is even quite small.

The concentrations after selection are again lower for the thermodenuders than for the AMANDA. Probably at least part of this difference is systematical, because at 1 m height deviations of similar magnitude in the same direction occurred. If concentrations at both heights of the profile show the same bias, the influence on c_* is limited. This was already confirmed by the low average deviation in c_* between both systems.

As followed from the propagation of errors in the individual parameters, it may be assumed that the error in the concentration profile dominates the uncertainty of a flux

measurement. Other parameters -kept constant in the above comparison of different methods of profile measurement- will be much less important. Therefore it can be concluded from this comparison that the earlier derived uncertainty of about 30% in a typical NH_3 flux measurement is a realistic, probably even quite 'safe', estimate.

Errors in parameters derived from the flux measurements

Starting from the derived uncertainties in u_* , stability corrected heights, fluxes and concentrations the errors in v_d and R_a can be derived in a straightforward manner. For v_d :

$$\frac{\Delta v_d}{v_d} = \sqrt{\left[\frac{\Delta F}{F}\right]^2 + \left[\frac{\Delta c_r}{c_r}\right]^2} \quad (4.9)$$

With estimated values of relative error in fluxes and reference concentrations of about 30 and 2% for NH_3 , the relative error in v_d is dominated by the error in the flux and so typically also about 30%. An eventual systematical deviation in concentrations at both levels will cancel out because it will affect flux and reference concentration about equally.

In a similar way the typical uncertainty in v_d for SO_2 will be about equal to the uncertainty in its flux (35%).

Based on eq. 2.27 the *relative* error in R_a can be estimated by:

$$\frac{\Delta R_a}{R_a} = \sqrt{\left[\frac{\Delta u_*}{u_*}\right]^2 + \left[\frac{\Delta f(z, d, \Psi)}{f(z, d, \Psi)}\right]^2} \quad (4.10)$$

where $f(z, d, \Psi)$ is similar to eq. 4.7, substituting z_0 for z_2 . In practice, in the calculations in this thesis R_a was derived from eq. 2.28, in which z_0 has cancelled out. For the estimation of the error, eq. 2.27 is much more practical and it may be expected that the error by both formulas is about identical.

In similar calculations as used to estimate the error in $f(z, d, \Psi)$ in c_* turned out that the effect of errors in d on R_a is negligible. Halving or doubling z_0 caused a difference of about $\pm 12\%$ in $f(z, d, \Psi)$, (ranging between $\pm 7\%$ and $\pm 16.5\%$ under stable or unstable conditions, respectively). Errors of 32% in L caused a variation that was generally less than $\pm 6\%$ in $f(z, d, \Psi)$; only under moderately stable conditions ($L > 30\text{m}$) a value of $\pm 10\%$ is more representative. Based on these calculations, and taking an uncertainty of 10% in u_* into account, the typical uncertainty in R_a is estimated to be about 18% ($\sqrt{(10^2 + 12^2 + 10^2)}$).

The (relative) random error in R_b is equal to the error in u , so about 10%. However, in case of R_b , the uncertainty about the correctness of the parameterization is high, so that a considerable systematical error may be possible. It will be shown below, that R_c is not very sensitive to errors in R_b so that this possible systematical error is neglected here.

Taking into account that the relative error in R_i equals the relative error in v_d (as $R_i = 1/v_d$), the absolute error in R_c is given by:

$$\Delta R_c = \sqrt{\left[\frac{\Delta v_d}{v_d}\right]^2 v_d^2 + [\Delta R_a]^2 + [\Delta R_b]^2} \quad (4.11)$$

Now by this equation, and by using mean values of v_d , R_a and R_b , an estimate can be made of the contribution of errors in each of these parameters to the uncertainty in R_c . For ammonia deposition at Zegveld, typical values are 0.0062 m s^{-1} for v_d , and 70 and 20 s m^{-1} for R_a and R_b respectively. These values are halfway between medians and averages of these parameters in the selected data (section 4.1), for periods with deposition fluxes only. Substitution of these values and the derived relative errors into eq. 4.11 results in $R_c = \sqrt{(2341 + 159 + 4)}$, which is about 50 s m^{-1} . This means that the error in R_c is determined almost completely by the error in the flux (or in v_d). For this reason, often the approximation is made that $\Delta R_c \approx \Delta R_v$. It implies also that under most conditions, an eventual systematical error in R_b will have very little effect on the uncertainty in R_c at this location.

From the mean values of v_d , R_a and R_b , a typical value of $R_c = 70 \pm 50 \text{ s m}^{-1}$ is found. Clearly, according to error propagation, the uncertainty in a typical measurement of R_c for NH_3 is quite large.

SO_2 at Zegveld showed much higher mean values of v_d (0.0114 m s^{-1}), leading to an error in R_c of about 30 s m^{-1} . However, the large v_d is mainly due to values of R_c close to zero ($R_c = 15 \pm 30 \text{ s m}^{-1}$), so that the relative error is even higher as for ammonia..

Estimation of R_c from scatter under constant conditions.

An alternative way to acquire some estimate of the order of magnitude of errors in R_c is to evaluate the random variation of R_c in series of subsequent measurements (time series). Preferably, for this aim a long period with only small variation in surface condition should be taken. In practice such periods are difficult to find, because several processes, e.g. growth (or evaporation) of water layers, take place on timescales of a few hours. To make a best approximation, a number of periods were chosen in which both atmospheric and surface conditions were as constant as possible or at least changed only gradually. Only periods with deposition fluxes were chosen, and only

measurements that had passed the criteria for reliable flux measurements. No large changes in atmospheric conditions should occur because interest was mainly in the uncertainty due to errors in the measured gradients. A selection was made of periods with moderate, typical values of R_a and R_b , and no large variations in the sum of these parameters. Concentration at 5m should also have moderate, typical values, with only slow variations within a total range of a factor two or less. Too high concentrations or sudden decreases might lead to saturation effects. Within the first few hours after rain, atmospheric conditions are often either stagnant or very inhomogeneous so that such periods were rejected. Periods with a strong increase of temperature (possibly causing fast evaporation of water layers and/or relevant stomatal activity) were also avoided. Finally four periods were chosen, in which changes in surface conditions probably proceeded only gradually, so that scatter in R_c attributed to measurement errors could be distinguished from any general trend due to surface processes. This separation was done by estimating a linear regression line of R_c as a function of time. Though the actual trend may be much more complicated, this approximation may suffice for the present aim. An example of such a period is given in fig 4.4.

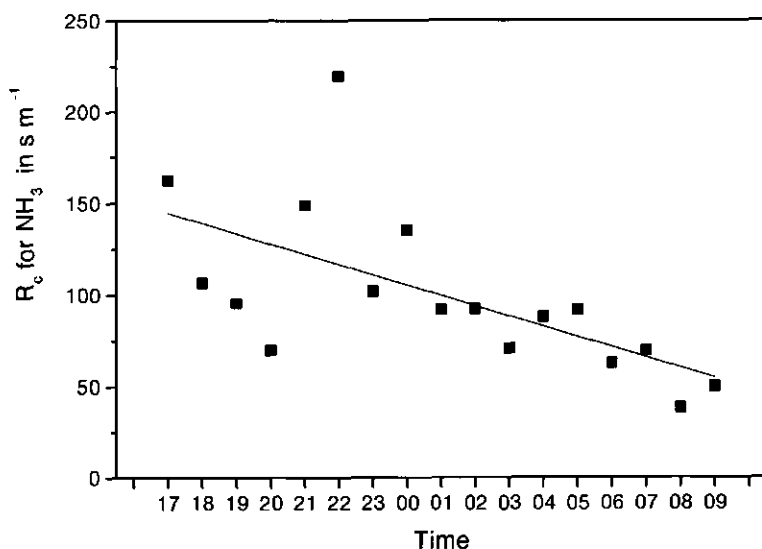


Fig 4.4 Scatter of R_c for ammonia around a line that estimates a mean change of R_c in the shown period; Zegveld, 16-17 January 1993. (Sd of fit) / $\text{avg } R_c = 36\%$.

In this case, the mean of the fluctuations around the trend line was 36%. This percentage was calculated from the standard deviation of the Y estimate of the regression line (36 s m^{-1}) divided by the mean level of R_c (100 s m^{-1}).

estimated R_c . The sum of all inferred fluxes in the selection is compared to the sum of all measured flux values in the selection. Iteratively, the estimate of R_c is improved until the sum of the parameterized fluxes equals the sum of the actually measured fluxes.

The advantage of this 'best fit' method is, that the different sensitivity of inferred fluxes to variations of R_c under different conditions (c , R_a , R_b) is weighed in the derived representative values of R_c . The relative importance of R_c to a flux estimate depends e.g. on the magnitude of R_c relative to that of R_a and R_b (see eq. 2.32). In addition, inferred fluxes are proportional to concentration; therefore long term average fluxes will generally be more sensitive to errors in the resistance in periods of high concentration than in periods of low concentration, if total resistance is about the same. These effects are not weighed properly if median or average R_c values are used. Therefore the 'best fit values' may be expected to give more representative R_c values, especially if these are to be used in flux parameterizations.

In practice, best fit values generally turned out to be closer to median R_c values (generally somewhat lower) than to either the harmonic or arithmetic averages.

A disadvantage of this procedure is that it provides no measure of the uncertainty of this 'best fit' R_c . This may be especially relevant if flux parameterizations are to be derived from such representative R_c -values.

Therefore the best fit R_c -values will be given together with the values for which the sum of parameterized fluxes would be 30% higher and 30% lower than the sum of the measured fluxes. These values will be noted between brackets and will be referred to as ' DF_{30} ' values (deviation of flux 30%).

4.2.4 Uncertainty from biases due to the data selection

4.2.4.1 Effect of validation prior to flux calculation

In this section on biases due to data selection, focus is aimed at the selection of reliable flux measurements by the criteria summarized in 4.1. In principle however, the validation of parameters measured by the individual instruments *prior* to flux calculation could also cause a bias. In case of ammonia, for about 50% of the number of hours covered by the experiment no fluxes could be calculated (SO_2 : 20%, in an experiment spanning 4 months). However, it is assumed that the remaining hours still cover all relevant conditions in a representative way. Unlike in the selection *after* flux calculation, in the validation of the raw data no criteria were applied yet that were based on meteorological conditions or concentrations. Therefore no relevant bias is expected in the resulting input data set for the flux calculations. This was confirmed by a comparison of the distribution of wind directions and wind speeds before and after the

validation, which showed no relevant changes. This comparison could be made because unlike other parameters, wind speed and wind direction as well as rain duration were available for (almost) every hour of the experiments. The fraction of periods with rain decreased slightly as an indirect effect of the validation (25% to 20%). This is because most failures of the sonic anemometer were caused by rain drops on the probe. Because in the subsequent selection of reliable flux measurements periods with rain were rejected anyhow, this small effect of the validation is considered irrelevant.

4.2.4.2 Qualitative evaluation of combined effects of selection criteria

In the actual selection of reliable flux measurements, many criteria were directly related to atmospheric conditions. Therefore contrarily to the validation of the input data for the flux calculations, this selection might cause significant biases that have to be evaluated. Combinations of criteria may sometimes enforce and sometimes compensate each others biasing effect. To evaluate such relations between criteria in a qualitative way, columns 3 and 5 of tables 4.1 and 4.2 (section 4.1.2.5) were compared. These columns give the rejected fractions when a criterion is applied to the whole data set and when it is applied in a subsequence.

The most relevant relations among selection criteria are the following:

- For SO_2 , the percentage of measurements from wind sector 90-270 decreased after the concentration criterion (54 to 44%); very low concentrations occurred more often in winds from the rejected sectors.
In case of NH_3 , background concentrations from these directions were also relatively low, but this was 'compensated' by plumes from nearby animal houses and slurry stores. As an overall result, high concentrations of NH_3 occur about as frequently in the rejected sectors as in winds from the other directions.
- As explained in section 4.1, extreme stability or instability often coincides with periods of low wind speed. Indeed, without previous selection on concentration or wind direction, rejection of low wind speeds diminished the fraction of periods with extreme (in)stability by about 50% (not shown in the tables).
- Reduced vertical transport under stable conditions favours higher concentrations of NH_3 and lower concentrations of SO_2 close to the ground (see also 5.1 and 8.1). In case of NH_3 , in practice mainly high concentrations are rejected by the concentration criterion; for SO_2 only low concentrations are rejected. As a result, previous selection on concentration reduces the fraction of low wind speeds or stable conditions in column 5 of the tables.
- In case of SO_2 , the fetch criterion also contributed significantly to the reduction of stable conditions with low wind speeds (regardless of the concentration). Such

A similar procedure was followed to derive a selection bias for SO_2 . In the less strict selection, the concentration only had to exceed a value of $0.375 \mu\text{g m}^{-3}$; the other criteria were the same as for NH_3 . Now 9% of the SO_2 measurements in the wind sector $90\text{--}270^\circ$, without rain, were rejected (only 1.9% due to low concentration). Results are shown in table 4.5. For this compound, the actual flux was less important to the present research, because focus was on the exchange effectiveness parameters v_d and R_c . Unlike the case for NH_3 , emission of SO_2 was negligible, so that these parameters could be used without restriction in this estimation of the selection bias. Median values of R_c instead of best fit values were used because the purpose was only comparison of selections and not parameterization.

Table 4.5 Comparison of average concentration, flux and deposition velocity and of median R_c values of SO_2 in three selections: the actual selection for analysis, a selection by less strict criteria (see text) and all measurements; each including and excluding rain periods.

Selection	Rain periods excluded					Rain periods included				
	n	c $\mu\text{g m}^{-3}$	F $\mu\text{g m}^{-2}\text{s}^{-1}$	V_d m s^{-1}	R_c s m^{-1}	n	c	F $\mu\text{g m}^{-2}\text{s}^{-1}$	V_d m s^{-1}	R_c s m^{-1}
Actual	465	12.4	-137	1.14	13.1	596	11.8	-136	1.23	10.6
Less strict	786	10.1	-99	0.91	12.6	1010	9.5	-100	1.00	9.5
All meas.	1842	7.9	-67	0.68	15.4	2303	7.3	-66	0.75	11.8

According to table 4.5, average SO_2 concentrations in the actual selection are much higher (up to 45%) than in the original data. Part of this difference is due to the selection on wind sector; as mentioned earlier, this leads to indirect rejection of lower concentrations. In the less strict selection, the average concentration is still 23% higher than without any selection. Rain has only a relatively weak influence on the average concentration. The further increase of the average concentration in the actual selection is mainly due to the partly overlapping effects of criteria on concentration, wind speed and stability.

Differences in average flux have about the same order of magnitude as those in average concentration. However, the same pattern is found in the average v_d values. Obviously the differences in average flux are not caused by the shifts in concentration, but by variations in the effectiveness of either the atmospheric transport or the uptake by the surface.

Table 4.5 shows that the R_c values vary only weakly, so that the distribution of surface conditions is not severely biased by the selection. The inclusion of rain periods causes a small shift towards lower R_c , probably due to wetness of the surface. Obviously the much higher v_d after selection is mainly due to rejection of conditions that reduce atmospheric transport. Indeed average values of R_d (not shown) were 50 to 80% higher in the preselection. This bias is not relevant for the present analysis as long as the influence of surface conditions is derived mainly from R_c . Taking the highest and lowest values in the table as limits, the uncertainty in R_c caused by eventual selection biases is estimated to be about $\pm 25\%$.

5.2 Concentration patterns

The annual average concentration at reference height (5m) was $10.2 [0.1] \mu\text{g m}^{-3} \text{NH}_3$. In the pre-season and grazed season, concentrations are significantly higher than in the rest season. This is caused mainly by contributions of emissions from pastures. In the pre-season the highest concentrations are found, caused by very intensive manure spreading in the whole region. In this period the farmers apply most of the manure stored during the winter period to the pastures. It is relevant to realize that the ambient concentrations at Zegveld are determined by processes on a much larger scale than only the ROC terrain. It depends on emissions by pastures as well as cattle houses and manure storages from a large area upwind, but of course is the influence of nearby sources stronger. Incidentally, use by the ROC of the conventional technique of manure spreading (broad fan) caused some high concentration peaks in the pre-season. (In a few measurements, values of over $100 \mu\text{g m}^{-3}$ occurred; however these were exceptions).

The concentration also depends strongly on dilution and dispersion of the ammonia after its release by the surface or by other low level sources. This is reflected in the average diurnal patterns of concentration variations, shown in fig. 5.1 for the three distinguished seasons. These diurnal patterns were derived by averaging (per season) of all concentrations that were measured at the same hour of the day. The error bars in fig. 5.1 show the average of the corresponding 24 SE values per diurnal pattern.

At night, during periods of low wind speed, low mixing layer heights and stable atmosphere, dilution and vertical mixing of ammonia emitted close to the surface with clean air is poor. Consequently concentrations close to the surface remain high. During daytime, wind speed and turbulence increases as well as the mixing layer height. Stronger dilution and vertical mixing of the emitted ammonia with cleaner air now results in lower concentrations. In the rest season this diurnal pattern seems less outspoken than in the other seasons, though on relative scale (e.g. compared to the average value over all 24 hours) the diurnal variation is not much smaller than in the pre-season. The weaker diurnal variation -especially compared to the grazed season- is mainly caused by generally higher wind speeds and turbulence at night (autumn). To a lower extent, perhaps the absence of nocturnal emissions from pastures (no slurry spreading) may also play a role.

As explained in 5.1, the average *concentration* values in table 5.1 and in this section, were calculated from all available, validated concentration measurements. Because at concentrations over $25 \mu\text{g m}^{-3} \text{NH}_3$ the sampling efficiency of the thermodenuders decreases gradually (chapter 3), it was anticipated that the long term average concentrations might be slightly too low. It was deduced from simultaneous measure-

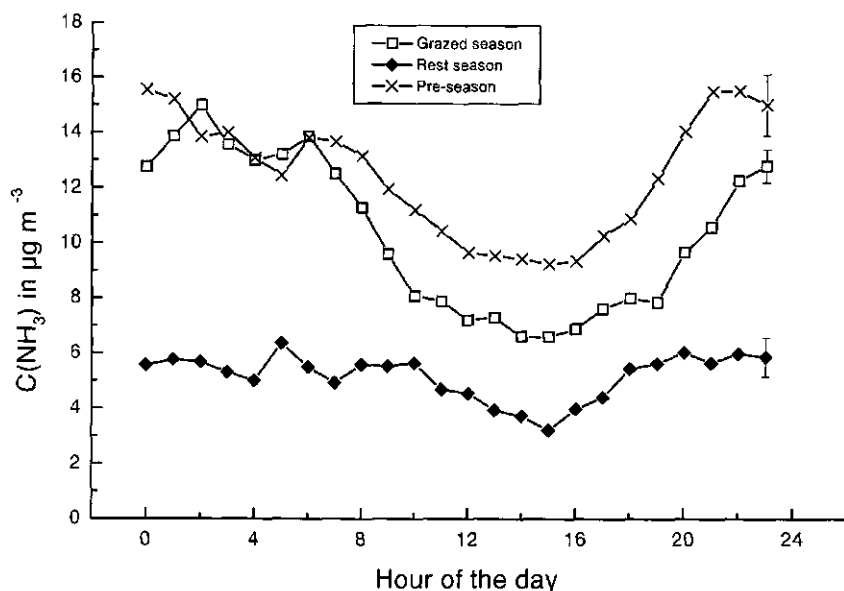


Fig. 5.1 Average diurnal pattern of ammonia concentration at Zegveld (July 1992-July 1994), per season. Error bars denote average SE.

ments by the thermodenuders and by a continuous flow denuder of RIVM, that this resulted in an underestimation of about 10% of the annual average concentration.

Corrected for this underestimation, the measured annual average concentration at Zegveld is about $11 \mu\text{g m}^{-3} \text{NH}_3$. This value is high compared to the annual average for the Netherlands in 1993 which was $6.4 \mu\text{g m}^{-3}$, as estimated by OPS (Erisman and Draaijers, 1995; this value refers to a height of 4m).

The NH_3 concentration at Zegveld is high, but not quite so high as values in two other areas with intensive livestock breeding in the Netherlands such as De Peel (Vredepeel: $19 \mu\text{g m}^{-3} \text{NH}_3$) and Gelderland (Lunteren: $33 \mu\text{g m}^{-3} \text{NH}_3$), as reported for 1991-1992 by Boermans and Erisman (1993). The diurnal and annual patterns at Zegveld are roughly comparable to those observed in the latter two regions.

In an additional analysis, the concentration patterns in fig. 5.1 were compared to those that would be derived if only the data selected for analysis of fluxes ($n=2492$) were used. The main patterns in NH_3 concentration are identical, so that eventual relations with flux variations can be investigated properly. However the average concentrations and the

diurnal variations are smaller after the application of selection criteria for flux measurements. Fortunately most of the difference between selected and unselected data sets is due to removal of only a relatively small number of nocturnal peak concentrations. These are rejected when the concentration is higher than $25 \mu\text{g m}^{-3}$ or at low wind speeds and/or high stability. Exchange fluxes are relatively small under these conditions, so that the derived long term average exchange will not be influenced severely by this selection. Furthermore, on most individual days in the selected set, the diurnal pattern is well conserved. Therefore the selection will not introduce serious artifacts in parameterizations that are derived from the remaining data set.

5.3 Exchange patterns

5.3.1 Total exchange per year and per season

The average of all measured fluxes (after selection; $n=2492$) over the period July 1992 to July 1994, was a net emission flux of $21 [3] \text{ ng m}^{-2}\text{s}^{-1} \text{ NH}_3$. In the grazed season the average flux indicated net-emission, whereas an average deposition flux resulted for the rest season. In the pre-season the average measured flux was close to zero.

Assuming that the distribution of the selected measurements is representative for each season, the annual net exchange can be estimated on basis of averages of the measured fluxes. Two methods were employed to account for missing values in the derivation of seasonal and annual fluxes, the 'equal weight method' and the 'interpolation method'.

In the first method, *equal weight* was given to each available measurement (per season) in straightforward averaging. So the sum of all measured fluxes per season was divided by the number of measurements to yield an average flux in $\text{ng m}^{-2}\text{s}^{-1}$. The total exchange (kg ha^{-1}) per season was calculated by time integration of this average flux over the number of days (per year, on average) covered by that season. Results per season and per year are shown in table 5.2; the annual exchange follows from summation of the contributions of each season.

The *interpolation method* is based on the diurnal patterns and monthly variations within a season. The applied procedure leads to virtually the same result as when missing values would be replaced by average values of the available measurements at the same hour of the day in the same month.

First all available flux measurements of identical hours of the day in a month are averaged. For each month, this yields diurnal patterns, consisting of the average flux per hour of the day in that month. These patterns were time integrated over all 24 hours, to find the average total exchange per day in each month. Integration over the days of each month covered by a season (on average, per year) yielded the average total exchange per

season (see table 5.2). The average annual exchange was again calculated from the sum of the contributions of the individual seasons to the annual exchange.

Table 5.2. *Estimates of seasonal and annual net-exchange of ammonia at Zegveld derived from flux measurements (July 1992-1994). Missing measurements were accounted for via two different methods. Negative signs denote deposition; between square brackets: ER_{sc} (see text, 4.2.3)*

	Net exchange by 'equal weight' method	Net exchange by 'interpolation' method
	kg ha ⁻¹ of NH ₃	kg ha ⁻¹ of NH ₃
Rest season	-1.7 [0.1]	-1.6 [0.1]
Pre-season	-0.1 [0.3]	0.8 [0.4]
Grazed season	6.7 [0.6]	5.4 [0.5]
Year	4.9 [0.7]	4.6 [0.6]

In a relative sense, table 5.2 shows a considerable difference between the net-exchanges calculated for the pre-season by both methods. This is caused by a few measurements shortly after slurry spreading that have more importance for the net result in the interpolation method. However, both methods give overall comparable results in view of the variability of measured fluxes, and the quite different way in which the available measurements are weighed in the final exchange estimates. A similar agreement between results of both methods was found if the net exchanges during the night and during the day were calculated separately. This gives an indication that the distribution of the selected data, with respect to hour of the day or month of the year is only a limited contributor to the overall uncertainty due to selection biases. It also means that both procedures can be used for analysis of the observed exchange patterns.

In 4.2.3, the overall uncertainty due to selection biases was estimated to be about $\pm 25\%$. Combining this value with the random uncertainty derived from the standard errors (about 14%), the total most probable uncertainty in the annual exchange is estimated to be $\pm 28\%$. The final estimate of the total exchange (taking the average of both methods) then becomes $4.8 \pm 1.3 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of NH₃.

A range of 12-55 kg ha⁻¹ yr⁻¹ of NH₃ is given by Hassink *et al.* (1994) as an estimate for the emission from grazed pasture in the Netherlands. The net emission at Zegveld derived from the measurements of $4.8 \pm 1.3 \text{ kg ha}^{-1} \text{ yr}^{-1}$ NH₃ is much smaller. The mentioned literature range however, refers only to the emission from excreta produced during grazing, and it does not take eventual deposition during periods without grazing

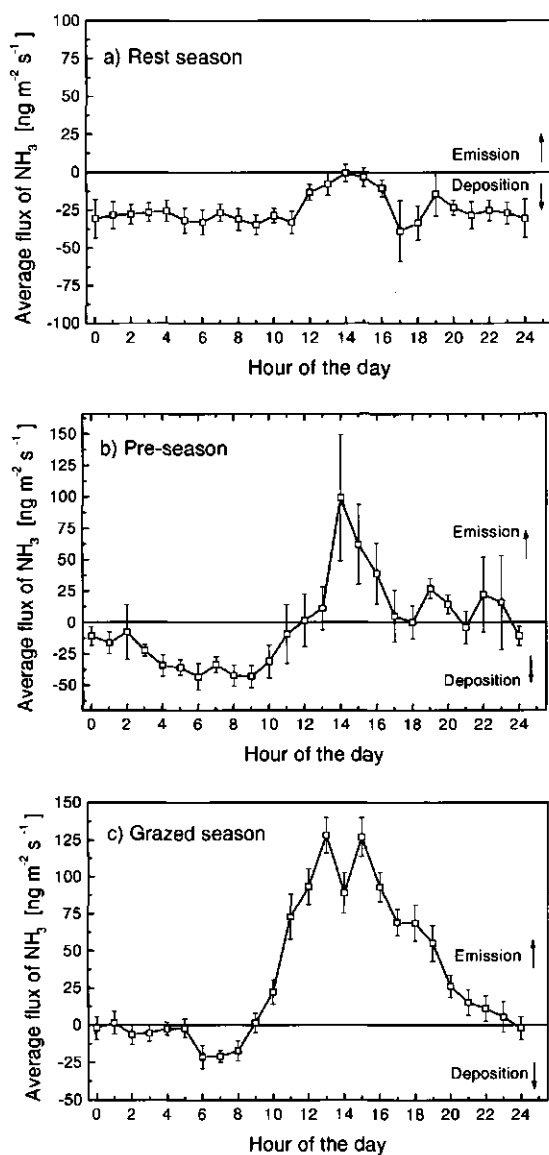


Fig. 5.2 Average diurnal pattern of ammonia exchange fluxes at Zegveld (July 1992-July 1994) per season. Error bars denote ER_{SE} .

into account. Therefore comparison between this literature estimate and our measured averages is difficult. The availability of information on the agricultural treatments of the ROC terrain enables a more detailed estimate of the emission for the Zegveld location. In chapter 6 such an estimate will be made, based on the land treatments and currently used emission factors.

5.3.2 Main diurnal patterns of NH_3 exchange

Differences in average exchange between day and night are obvious from table 5.1. These variations are presented in more detail in fig. 5.2, giving the average diurnal flux patterns per season. These were derived by averaging the diurnal flux patterns of the respective months. The error bars indicate the error following from propagation of the standard errors of the mean fluxes per hour of the day per month.

These average diurnal flux patterns were evaluated qualitatively by comparison with flux variations on individual days, leading to the following conclusions:

- * In the *rest season*, on most days deposition occurred during the whole day. This is reflected in the average diurnal pattern of fig. 5.2a showing consistent deposition. Still, in some afternoons net emissions were observed. These emission events lower the average deposition for this time of the day. Their influence on the average net flux over the whole season was much smaller however than in the pre-season and grazed season.
- * In the *pre-season*, the dominating direction of the net exchange of NH_3 on most days was also deposition to the pasture. However, the average diurnal pattern (fig. 5.2b) shows clear net emission in the afternoon and evening. This average net emission is strongly influenced by a small number of slurry spreading events by the conventional method (fan) and is therefore very uncertain. Apart from this, like in the rest season, on a few days periods of net emissions were observed that could not be attributed to recent manure applications.
- * In the *grazed season*, the overall exchange of the season is dominated by net emission during daytime and in the evening (fig. 5.2c). In the average diurnal pattern, the emission starts early in the day and then increases rapidly; in the evening it fades out quite gradually. In the late night a small mean deposition is observed. A contribution of manure spreading to this diurnal pattern may be expected, similar to the one described for the pre-season. From study of fluxes on individual days, it follows that a basic pattern for the grazed season exists of deposition at night and emission during daytime. During periods after manure spreading, this pattern is disturbed, with a shift towards a higher net emission. In such periods also some emission may occur at night.

Summarizing, the exchange at Zegveld can be described roughly by two regular patterns: alternating deposition and emission in the grazed season and consistent deposition during the rest of the year. Manure spreading is the main cause of a shift from these regular patterns towards higher net-emission (and weaker deposition), in the grazed season and pre-season.

5.4 Typical surface resistances during deposition

The fact that at Zegveld both emission and deposition occur indicates that the surface concentration (c_o) is not always zero. Therefore in principle analysis of the exchange in terms of a big leaf resistance model would require the use of a version that accounts for bi-directional exchange (see 2.4).

However, net deposition dominates in certain periods, especially during the rest season and at night. It will be shown later that (unless slurry has been spread recently) emission only occurs if the stomata of the grass are open. This phenomenon allows a separate estimate of the exchange parameters for deposition and emission. It is assumed that emissions from the pasture are insignificant at night (obviously excluding periods with manure spreading) and thus an 'effective surface resistance' (R_{ce}) can be derived from deposition fluxes measured in these periods.

Periods within five days after slurry application were excluded from the calculations, as it was assumed that emission would always take place during these periods. Furthermore in the pre-season and the grazed season, nocturnal emissions were considered to be an indication that the surface was somehow influenced by slurry application. Days on which a significant number of nocturnal emissions were found were therefore also excluded from the measurements.

At daytime emission occurred much more frequently than at night, and even after the exclusion of periods with slurry spreading a considerable number of emission events remained. These emissions were probably due to stomatal activity, as will be shown later in this chapter. To have at least an indication of the minimum value of R_{ce} at daytime, which will e.g. be used in the parameterization in chapter 8, only measurements that showed net deposition were considered. It should be stressed that for these daytime periods, except for the rest season, the representativeness of the R_{ce} -values is very uncertain.

The 'mean' R_{ce} -values were derived by the simple fitting procedure described in 4.2.3. The resulting values of R_{ce} are given in table 5.2. They are representative for the effective surface resistance under conditions when net deposition occurs (see remarks

made above with respect to daytime results). The '30% deviation range', given between brackets, refers to values of R_{ce} that would yield a 30 % higher and 30% lower (respectively) sum of parameterized fluxes than the 'best fit' value (see 4.2.3).

Table 5.3. 'Best fit' values and DF_{30} ranges (see text, 4.2.3) of R_{ce} for ammonia in $s\ m^{-1}$, during deposition. Zegveld, 1992-1994. Periods with recent manure spreading are not included.

	Rest season	Pre-season	Grazed season
R_{ce} at night	35 (12; 81)	100 (56; 183)	80 (35; 160)
R_{ce} at daytime	65 (31; 130)	105 (64; 180)	95 (54; 167)

The obtained values of R_{ce} are rather high; the pasture obviously is an inefficient receptor to ammonia.

Some mechanistic information may be derived from the variations of R_{ce} . Because deposition is generally more efficient at night and in the rest period, stomata are apparently less important for the deposition of ammonia than the leaf surface. The grass covers the soil completely during the whole year, so NH_3 is probably deposited mainly to the leaf surface. It is generally accepted that the leaf surface can play an important role in the dry deposition of several compounds including SO_2 and NH_3 . This is usually ascribed to the presence of water on the cuticle. This water will often be present in droplets on the leaves (rain, dew, guttation). As mentioned in 1.4.3, even under relatively dry conditions still water may be present, in micropores of the cuticle (Van Hove, 1989) or in deliquescent salts on the cuticle (Burkhardt, 1995).

From a separate analysis it was found that relative humidity at canopy height (RH_{50}) is generally over 95% if RH at 1 m height above canopy is over 85%. This means that water layers are frequently present at the leaf surface at Zegveld, so that indeed an important contribution of this pathway of deposition is likely to occur. The availability of water on the leaf surface for deposition of compounds at Zegveld will be confirmed in chapter 8, by results for SO_2 . Moreover, it will turn out there that at this location, the leaf surface is a much more efficient recipient to deposition of SO_2 than of NH_3 . Previous experiments (Adema *et al.*, 1986) have indicated that water layers are good sinks for SO_2 and NH_3 as long as the pH of this layer is not too much influenced by deposition (1.4.4). The high load of NH_3 probably creates conditions in Zegveld in which the pH of the water layers is high. Hence these water layers are no longer absolute sinks for NH_3 , while SO_2 may be efficiently deposited.

Only at lower relative humidities, some influence of the water layer *thickness* is observed; R_{ce} values at Zegveld were clearly higher when RH (at 1m) was below 85% than when it was higher than 85%. This difference was found both for daytime measurements (87 versus 66 s m⁻¹) and nighttime measurements (71 versus 41 s m⁻¹), and in all seasons. However at night the number of measurements at RH below 85% is only small; as a result on average R_c is higher at daytime than at night. This is most obvious in the rest season (see table 5.3). Probably this is related to the lower ambient concentrations in this season than in the other seasons. As a result, the pH and/or ammonium concentration of the water layers may only increase far enough to reduce the deposition efficiency of NH_3 after evaporation at daytime. In the other seasons, the generally higher loads of NH_3 will more easily affect the deposition efficiency even without the evaporation effect.

From the analysis of R_{ce} values it can be concluded that the effective surface resistance for this pasture was relatively high compared to surface resistances derived from similar measurements over semi-natural terrains. As mentioned in 2.3, the latter are generally close to zero (Duyzer *et al.*, 1994, Duyzer, 1994, Sutton *et al.*, 1992, Erisman and Wyers, 1993). In the pre-season and grazed season R_{ce} is higher than in the rest season. This might be expected, because even when no manure has been spread over the ROC pastures, the ambient concentrations and hence the loads of NH_3 in these seasons are also higher.

Chapter 6

Mechanistic analysis of diurnal patterns of deposition and emission of ammonia

6.1 Introduction

In chapter 5, a regular pattern of deposition at night and emission during daytime was found for the grazed season. Generally speaking, possible sources for ammonia emission at the pasture are the vegetation and the soil. It has been established earlier that deposition probably proceeds mainly to (water on) the leaf surface. As a first step to find an explanation for the regular diurnal pattern in the grazed season, mechanisms will be evaluated in which also the leaf surface could be the main source of ammonia (6.2). According to the (bi-directional) resistance model (2.4) the (sign of) the difference between the ambient concentration (c_a) and the concentration at the surface (c_o) must determine the flux direction. Two options are investigated:

- a more or less constant c_o , so that the actual value of c_a determines the flux direction and compensation points reflect c_o ;
- Variability of both c_o and c_a , where c_o could be dependent on previous deposition of ammonia from the atmosphere.

In a second step, contributions of other sources than the leaf surface, such as the soil and the stomata will be evaluated (6.3).

6.2 Role of the leaf surface in the daytime emission

The high effective surface resistances derived in the previous section suggest that in the water layers often considerable concentrations of ammonium are present. In terms of resistance modelling this means that c_o is not necessarily zero. c_o is the concentration of (gaseous) NH_3 that is in equilibrium with the concentration of dissolved NH_4^+ at the surface (1.4.5).

The first possible explanation of the diurnal change of flux direction could be that the emission occurs at daytime mainly because ambient concentrations then decrease to below c_o . At first sight, a comparison of diurnal patterns of concentration (fig. 5.1) and flux (fig. 5.2c) in the grazed season seems to support this mechanism. Emission at

daytime concurs with lower concentrations; deposition concurs with higher nocturnal concentrations.

If the ambient concentration is the main factor that determines the diurnal variation of the flux direction then compensation points will give an indication of c_0 . The underlying assumption is of course that c_0 of the leaf surface is more or less constant (1.45), e.g. due to some buffering mechanism for ammonium and for pH. Otherwise c_0 will change continuously so that transitions between deposition and emission (interpreted as compensation points) can occur over a broad range of ambient concentrations.

Compensation points were detected in three different ways:

In the first method, it was attempted to derive a representative value of the compensation point from a scatter plot (fig. 6.1) between net flux and ambient concentration, by determining the concentration where the net flux approaches zero and changes sign.

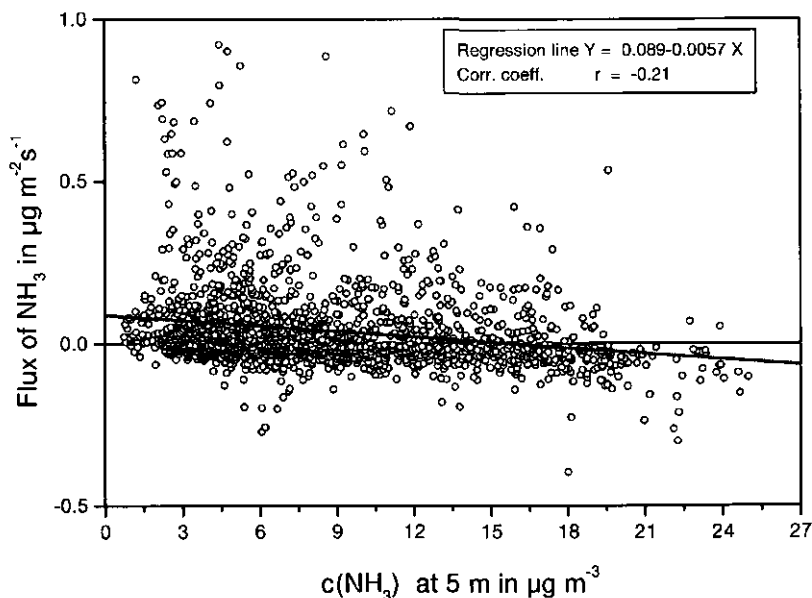


Fig. 6.1 Variation of exchange fluxes of ammonia with ammonia concentration ($z=5\text{m}$) at Zegveld in the grazed season.

A linear regression line between flux and concentration crosses the zero flux line at a concentration of $15.5 \mu\text{g m}^{-3} \text{NH}_3$. However, it can be seen directly from the figure that the correlation between flux and concentration is very weak ($R=-0.213$). Obviously the influence of other parameters (turbulence, stability) dominates the magnitude of the

flux. Accordingly, small fluxes are found over a large range of concentrations. Therefore this approach is not suitable to derive a compensation point at Zegveld.

The second approach is based on the fact that the direction of the flux is not dependent on turbulence. Therefore if ambient concentration is higher than the assumed compensation point, deposition should dominate and if it is lower, mainly emission should be observed. The variation of the distribution between emission and deposition with concentration is not clear from fig. 6.1, and was therefore studied in more detail. Per class of concentration the ratio was calculated between the number of emission fluxes and the total number of measurements in that class. If a more or less constant value of the compensation point exists, the ratio should decrease strongly above this concentration value. Figure 6.2 shows that this is not the case. The decrease in the ratio is rather gradual over a large range from 6 to 18 $\mu\text{g m}^{-3}$.

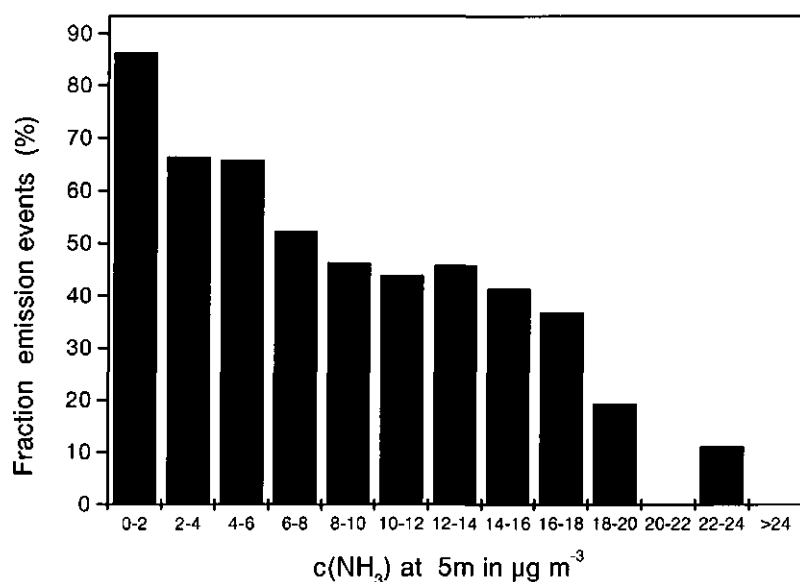


Fig. 6.2 *Frequency fraction of emission (= ratio between the number of measurements showing a positive (upward) ammonia gradient to the total number of measurements per class) per concentration class ($z=5\text{m}$) in the grazed season. (Zegveld, 1992-1994).*

If the solution on the leaves has a more or less constant composition, c_0 depends on temperature only (chapter 2). According to eq. 1.9, c_0 will double when temperature

increases by 6 degrees. To see if this explains the variability of the compensation point at Zegveld, concentrations were normalised for the estimated (eq. A.3) temperature at the surface T_s (fig. 6.3). In this normalisation based on eq. 1.9, it was assumed that the concentration ratio $[\text{NH}_4^+]/[\text{H}^+]$ was independent of temperature.

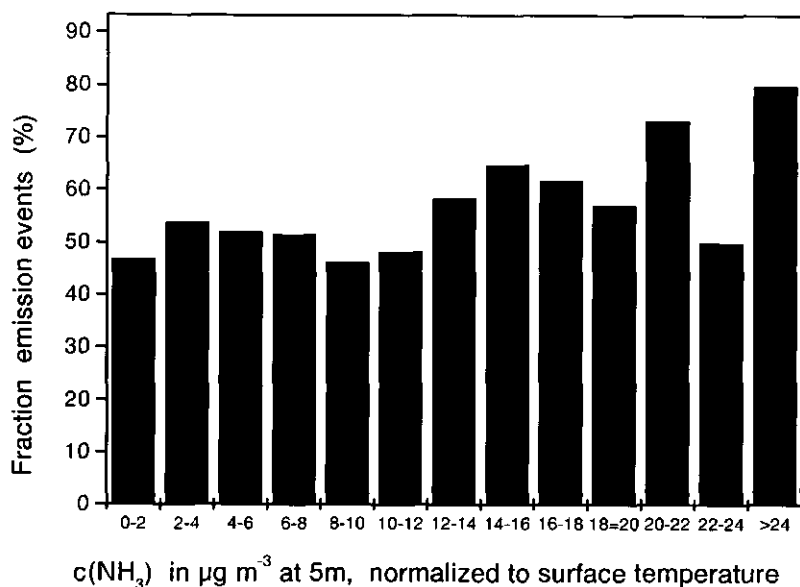


Fig. 6.3 *Frequency fraction of emission (see explanation in fig. 6.2) per class of temperature-normalized concentration. Normalization for surface temperature according to Henry and protonisation equilibria.*

Clearly, the frequency distribution is even flatter than if temperature is not taken into account. If influences of temperature were accounted for by stratification into temperature classes, no dominating values of the compensation point could be found either.

Several variations to the analyses of fig. 6.1 to fig. 6.3 were also tested, including the use of the concentration at 1m instead of c_r ($z=5\text{m}$), and analogous analyses of the extrapolated concentration at surface level (c_s). In the latter case, c_s was estimated analogously to eq. A.3, from the flux, R_a , R_b and c_r (and hence mathematically identical to the 'canopy compensation point', cf eq. 2.39). Furthermore, the same analyses were applied to a selection of periods without recent manure spreading. In no case an approximately constant value for a compensation point could be derived.

Finally, compensation points were estimated per day, by linear interpolation between two subsequent flux measurements with opposite sign, indicating a transition from deposition to emission and vice versa. The purpose was to investigate eventual regular variations in the compensation point which could be the reason why the previous two methods did not yield a representative value of the compensation point. It turned out that these compensation points followed quite closely the variation of the mean daily average concentration during the season. In figure 6.4 the frequency distribution of these compensation points is plotted together with the frequency distribution of all measured concentrations.

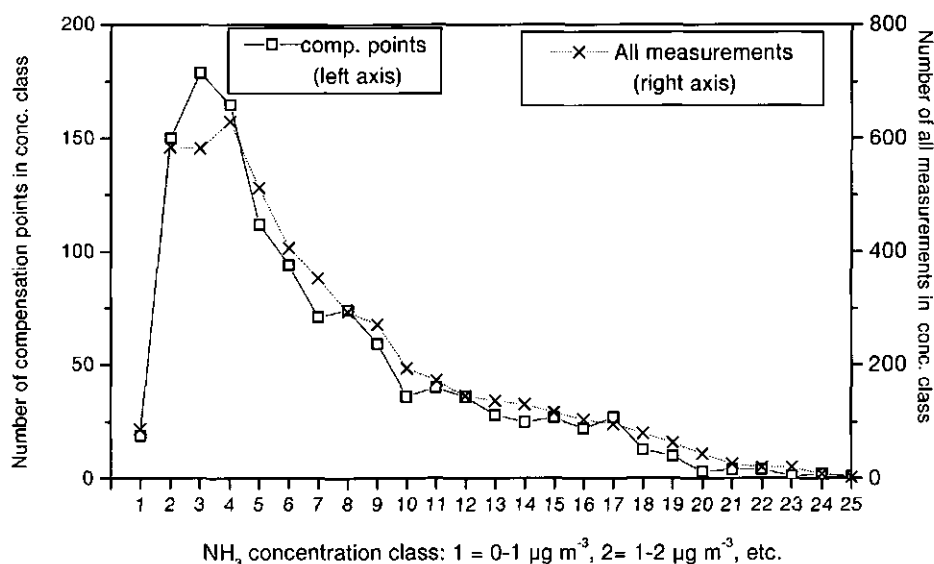


Fig. 6.4 Frequency distribution of compensation point values and of all measured concentrations ($z=1\text{m}$). The compensation points were derived from interpolation between concentration values before and after a switch of flux direction.

Both distributions differ little; this implies that the compensation points are not independent from ambient concentration. Therefore the compensation point theory is not appropriate to describe the diurnal flux patterns at Zegveld. These patterns obviously are not determined by changes in ambient air concentration and a more or less constant surface concentration.

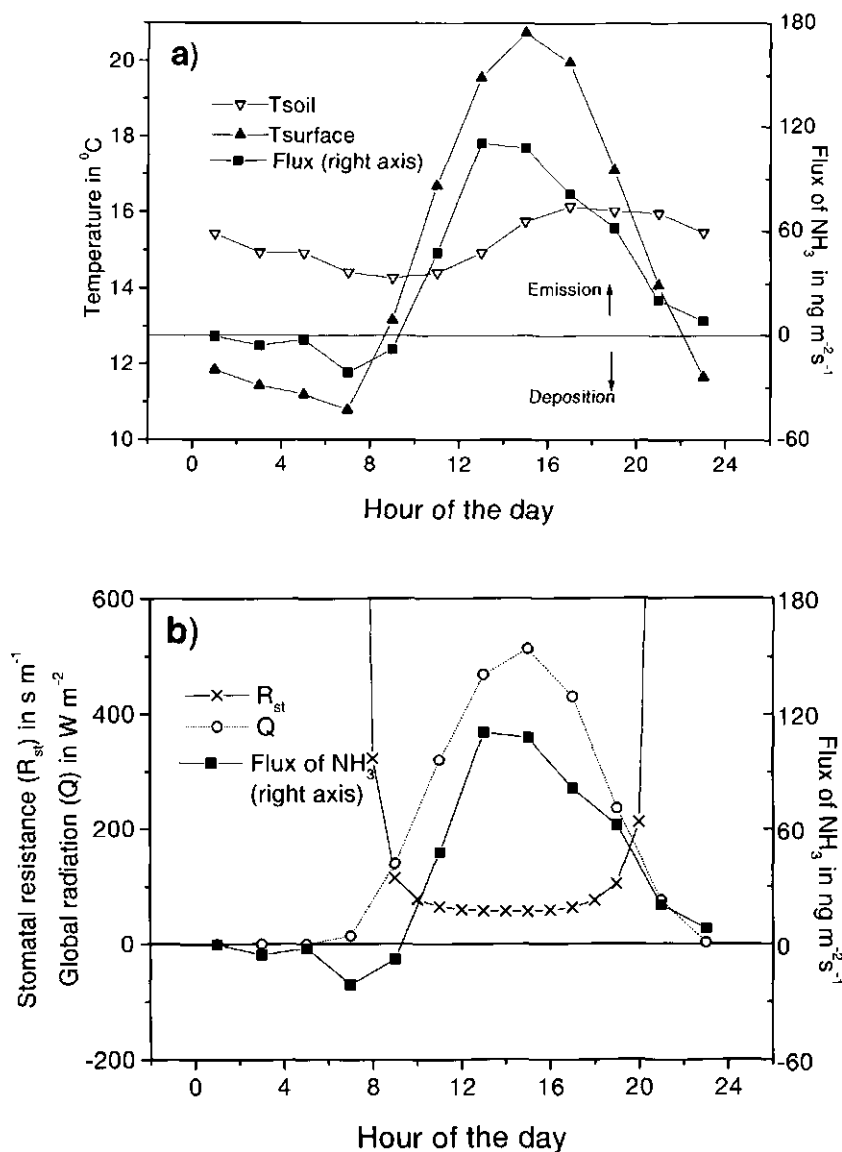


Fig. 6.7 Average diurnal pattern of ammonia flux and a) soil temperature (2-8 cm depth) and (profile-derived) surface temperature, and b) stomatal resistance (Wesely, 1989) and global radiation, at Zegveld, in the grazed season.

Early in the morning the flux increases rapidly, while soil temperature (T_{soil}) is still low (fig. 6.7a). The relatively weak influence of the land treatments on the emission patterns is probably caused by the low pH of the soil at Zegveld (pH-KCl= 4.8). This low pH will reduce the volatilization of ammonia once urine and slurry have infiltrated into the soil. Eventual local increases of pH in the soil top layer in urine patches (as reported *e.g.* by Vertregt and Rutgers, 1988) are probably too weak to maintain an efficient volatilization of NH_3 .

For these reasons, it must be assumed that the regular emission patterns in the grazed season at Zegveld are caused mainly by emission from the vegetation, and not from the soil. The stomata provide the only other source of ammonia of the vegetation if the contribution of the leaf surface to the emission is minor. The importance of the stomata is in agreement with the quick response of the emission to both global radiation and surface temperature. These parameters are the main factors determining the stomatal resistance, as is expressed *e.g.* in eq. 2.34. The mean pattern of R_{st} estimated according to this parameterization by Wesely (1989) is included in fig. 6.7b. The stomatal resistance could eventually be derived also from water vapour profiles (see appendix A), but those profiles were missing or not reliable for too many measurements. Furthermore, as explained in 2.3, for several conditions R_{st} derived by this method may not be representative for evaporation by the stomata alone. By comparison of parameterized R_{st} and R_{st} from water vapour profiles measured under 'reliable' conditions, a value of 50 s m^{-1} for the minimal stomatal resistance R_{st} in eq. 2.34 was found to be suitable.

It can be seen in fig. 6.7b that indeed the transition to emission virtually coincides with the opening of the stomata. Fertilization is assumed to be the reason why many fertilized crops often show considerable (stomatal) emission, while natural vegetation usually shows deposition (see 1.4.5). The nitrogen availability for the Zegveld grassland ($300 \text{ kg ha}^{-1}\text{yr}^{-1} \text{ N}$, including also net-mineralization) is quite normal for pasture (3.1), but high compared to natural conditions. Therefore it seems not unlikely that for a well fertilized, grazed grassland, also substantial stomatal emissions may occur, as was found for ungrazed fertilized grassland *e.g.* by Sutton (1990).

In the analysis of compensation points in the previous section, quite frequently emission was observed at concentrations over $15 \mu\text{g m}^{-3} \text{ NH}_3$. To have an idea of the order of magnitude of the stomatal compensation point, the distribution between deposition and emission events was studied again. In this case only daytime measurements were taken into account, because at night stomata are closed. The ratio between the number of concentration profiles indicating emission and the total number of measurements was calculated per concentration class. The set of unselected concentrations (see section 5.1) was used, as this results in a larger data set with a much wider range of concentrations. For this limited purpose, use of this set can be assumed to be acceptable, as only the direction of the gradients is evaluated. Violation of the selection criteria may imply a

greater risk that profiles are disturbed, and over $25 \mu\text{g m}^{-3} \text{NH}_3$ the gradients may be less reliable, but in most cases this will not go as far as to a complete reversal of the sign of the gradient.

Periods after slurry spreading were excluded as under these condition emissions from the soil and vegetation surface can take place. Results are plotted in figure 6.8. Unlike figure 6.2, it shows a clear decrease in the share of emission events at increasing concentration. It turns out that in periods without recent slurry spreading, daytime concentrations over $20 \mu\text{g m}^{-3} \text{NH}_3$ do not occur frequently. However, extrapolation of the plot results in a maximum for the stomatal compensation point of about $25\text{--}30 \mu\text{g m}^{-3} \text{NH}_3$.

In chapter 9 it will be shown that a temperature dependent stomatal compensation point corresponding to $19 \mu\text{g m}^{-3} \text{NH}_3$ at 20°C is a good estimate for use in parameterizations. These values are quite high; appendix E gives a table of stomatal compensation points reported in the literature. For most other crops, reported stomatal compensation points are much lower than in the present research (*e.g.* Farquhar *et al.*, 1980, Dabney and Bouldin, 1990). However, similarly high values as derived for Zegveld (13 to $>25 \mu\text{g m}^{-3}$ for wheat) were reported by Morgan and Parton (1989).

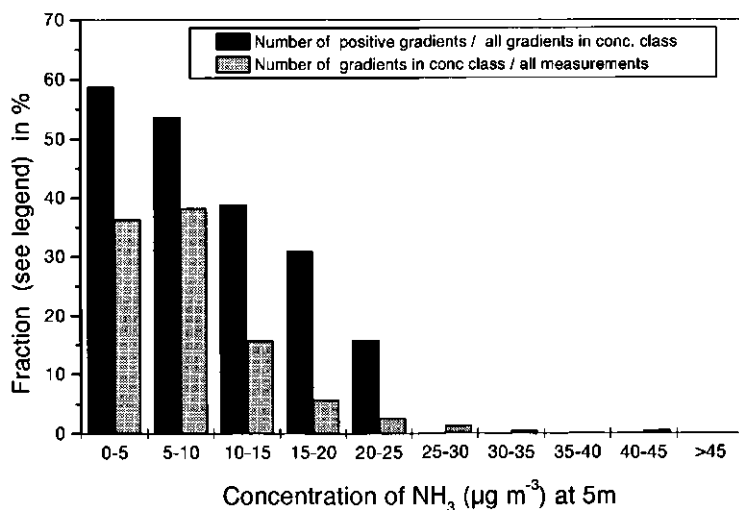


Fig. 6.8 Frequency fraction of emission (see fig. 6.2) per concentration class, at daytime and on days without recent manure spreading (see text). No selection for reliable flux measurements. Also shown is the frequency distribution of all measurements over the concentration classes.

The grass mixture of the ROC pasture consisted for 40% of perennial ryegrass (*Lolium Perenne*), and for the rest of several other grass species (20% meadow-grass, *Poa spp.*). Quite few literature data on compensation points for such grasses are available. For a more or less comparable, fertilized perennial ryegrass pasture, Harper *et al.* (1996) reported compensation points for the crop as a whole in a range of 13-18 (average: 14) $\mu\text{g m}^{-3}$ of NH_3 ; see 1.4.5. In their experiments usually deposition dominated at night as well as at daytime. This was due to a constantly high ambient concentration. Emission (attributed to stomatal activity) occurred mainly after fertilizer application. The exchange during the rest of the time was ascribed to exchange with the leaf surface, including uptake via the cuticle and also some ammonia volatilization from evaporating dew. So at this point conclusions for Zegveld are different. Sutton (1990, see also 1.4.5) derived much lower compensation points (2-7 $\mu\text{g m}^{-3}$ of NH_3). Because ambient concentrations in his experiment were generally lower, he frequently observed emission at daytime.

At Zegveld, diurnal variations in concentration are considerable. For the derived values of the stomatal compensation point this means that in most cases, the beginning and end of a net emission event will not be caused by variations in the ambient concentration. It is probably the result of the opening or closure of the stomata. The compensation points derived earlier from changes of flux sign therefore are no real compensation points. They are just spurious ambient concentrations coinciding with the moments that the stomata open or close. These 'compensation points' do therefore not provide any information on c_o .

The main conclusion from this chapter is that the regular pattern of the exchange in the grazed season of this pasture is dominated by two mechanisms: deposition to the leaf surface, and emission by the stomata. A parameterization of this exchange therefore should be based on a combination of these two pathways. In chapter 9 the canopy compensation point model by Sutton and Fowler (1993, see 2.4) will be tested for use in the Zegveld situation.

Chapter 7

Comparison of measured ammonia exchange to emission estimates from land-use

7.1 Introduction

One of the aims of this research was to evaluate estimates of the contribution of ammonia exchange over pastures to atmospheric ammonia that are used as a basis for environmental policy discussions. A first step was already set in 5.3 where the annual ammonia exchange at Zegveld was compared with a range of values for ammonia release from grazed pasture mentioned in the literature. The exchange values measured at Zegveld turned out to be much lower, but as pointed out already in 5.3, care should be taken in this comparison. The literature values do not include the contribution to the exchange of slurry application (including this, the literature values would even be higher). On the other hand, the measurements of net-exchange at Zegveld include also deposition to the same pasture, which is not accounted for in the mentioned literature values.

The latter is a consequence of the general approach followed in the estimation of ammonia emissions in emission inventories. As explained in 1.3.4, such estimates are based on emission factors. In this, the contribution of a pasture to the atmospheric ammonia concentration is quantified by the volatilization of ammonia from the different land treatments applied to that pasture. As a result, almost all measurements of ammonia exchange over pastures so far were focussed on emission due to volatilization of ammonia from spread slurry or from urine excreted by grazing cattle (see overview in 1.3). The set-up of those experiments (micrometeorological mass balance method, relatively short duration) was adequate in view of this aim, but led to the consequence that net-exchange in periods of deposition to the same pasture was neglected (1.4.5). Only in very few experiments ammonia fluxes over fertilized pasture were measured by the profile method (measuring both emission and deposition). However, these did not include periods of grazing or slurry application to the same pasture and they covered relatively short periods (Harper *et al.* 1996; Sutton, 1990). These results so far have not been accounted for in emission factors.

Because emission factors play such a crucial role in estimates of the contribution of pastures to atmospheric ammonia, in the next sections the measured net-exchange at

Zegveld will be compared with the estimated release of ammonia from the same terrain based on emission factors. First the procedure and results of the application of emission factors to the ROC terrain will be elucidated (7.2). Next the results will be compared with the measured exchange; the effect of accounting for deposition to the pasture will also be shown (7.3). In 7.4 the comparison is evaluated.

7.2 Application of emission factors to the Zegveld pasture

As mentioned in 3.2.1, the measurements at Zegveld were not designed to examine the volatilization due to a specific treatment of a specific part of the terrain. Only long term averages of the exchange over the terrain could be determined reliably. Comparison of the measured exchange after a specific treatment of a plot, with the estimated volatilization according to the respective emission factor is not possible. Such a comparison would be very uncertainty anyhow, because emission factors give average values for a wide range of conditions (seasonal or annual average). Therefore the average volatilization per ha for the whole terrain was estimated on seasonal (and annual) basis.

Van der Hoek (1994) describes the emission factors (actually volatilization percentages) and calculation procedures that are used by the LEI (Dutch Agricultural Economics Institute) and by RIVM to estimate the ammonia emission in the Netherlands for the years of 1990-1992 (see *e.g.* RIVM (1993)). The same volatilization percentages (or updates, see below) and procedures were applied to the ROC terrain, for the year of 1993.

First the total-nitrogen supplied to the pasture per type of treatment was calculated from detailed day-by-day information made available by the ROC. This information contained doses of total-nitrogen involved in each event of slurry or fertilizer application per plot, and the number and type of animals that were grazing on each plot. The excretion during grazing was calculated by application of average excretion factors for 1993 per category of animal (Van Eerd, 1995). In this procedure, also the grazing system (all day or only at daytime) was taken into account. The average N-supply per ha over the whole ROC terrain was calculated by dividing the sum of the N-supplies of all plots (in kg) by the total area (ha) of all plots.

To see if relevant differences per wind sector existed, an equivalent procedure of averaging was followed for the plots within each wind sector. Only plots within a distance of 500m from the measurement site were taken into account. This distance

limits the area upwind for which the measured fluxes are representative (derived from estimates by Gash (1986)). It is an acceptable average for the Zegveld conditions; the actual limit may vary between about 200m (very unstable) and >1000m (stable). Stable conditions occur at night, when volatilization can be expected to be relatively small due to lower temperatures (and reduced turbulence). Therefore no large error in the total volatilization is expected from contributions of plots farther than 500m during such stable conditions. The total area of the ROC terrain is 62 ha; the plots within 500m from the measurement site span 50 ha. In figure 7.1 the calculated N-supplies per year are plotted for the respective areas.

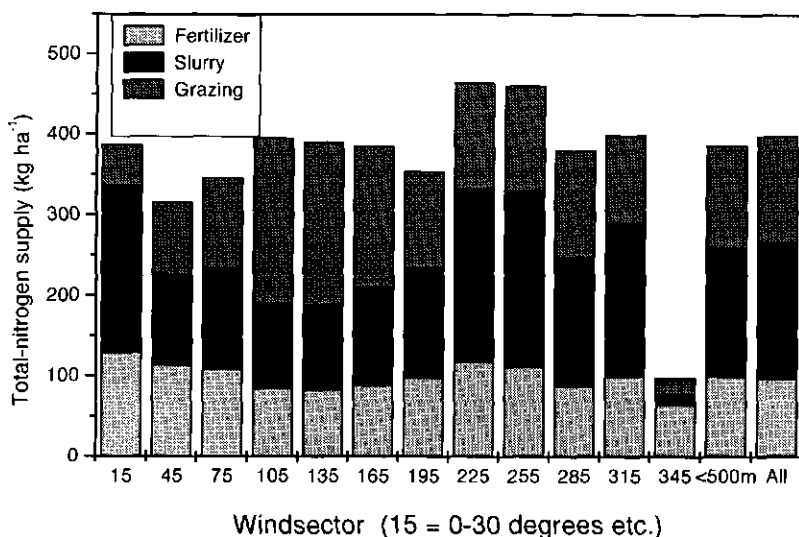


Fig. 7.1 Annual total-nitrogen supply to the pastures of the ROC due to land treatments. Values show (area-)averages per wind sector, for all wind sectors within 500m (see text), and for the whole ROC terrain ('all').

It should be noted that these calculated N-supplies, required as the basis for the estimation of the NH_3 volatilization, refer to all nitrogen that is excreted in or applied to the pasture. This includes also the (organic) nitrogen that is not available for uptake by the plants on the short run. For slurry, only about 50% of the total nitrogen is in mineral form (e.g. v.d. Hoek, 1994), part of which volatilizes after spreading. Therefore to calculate the contribution of slurry to the fertilization of a terrain, (e.g. in chapter 3), fertilization efficiency indices must be applied. The indices for slurry applied by the conventional (fan) and trailing feet technique are 25 and 40% , respectively (of total-N;

fertilizer=100%). In such fertilization estimates, the return of nitrogen via urine and faeces excreted in the pasture during grazing is -by convention- not considered as fertilization.

Based on the estimated total-N supplies shown in figure 7.1, the volatilization of NH_3 can be estimated. The applied volatilization percentage for fertilizer is 2%, for excreta 8%, and for slurry application 25% of total-N (Van der Hoek, 1994). The volatilization from slurry is reduced by 50-80% if the band spreading technique by trailing feet is applied (Wouters *et al.*, 1994); therefore in that case a volatilization percentage of 9% was used. The percentages refer to the fraction of the total nitrogen that volatilizes as ammonia-nitrogen. Therefore they must be multiplied by 17/14 to yield the actual emission of ammonia. The estimated ammonia volatilization according to these calculations is shown in figure 7.2.

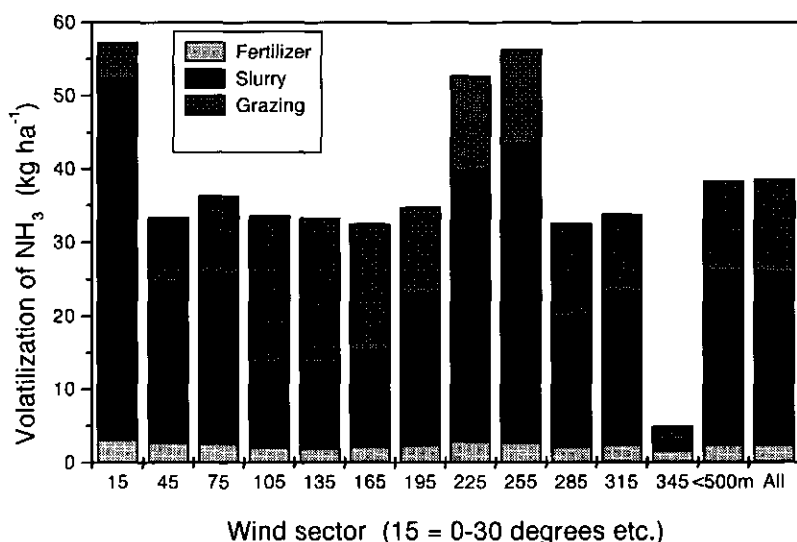


Fig. 7.2 Volatilization of ammonia from the ROC pastures due to land treatments. Values derived from total-N supplies (fig. 7.1) applying volatilization percentages (see text).

From figures 7.1 and 7.2 it can be seen that overall, the variation over the different wind sectors is not very large. However, four sectors show significant deviations from the average. Two of these, the Northern sectors 345 and 15, are not relevant as they are not

included in the flux measurements (see chapter 3). The higher volatilization in the sectors 225 and 255 is caused by a short period of slurry spreading by conventional technique in the pre-season. In the grazed season no significant differences occur among the relevant wind sectors. Fig. 7.1 and 7.2 indicate also that the average N-supply and the volatilization over a distance up to 500m are equal to those over all plots. Additional calculations showed that the same is true if only plots within a distance of 300m were considered.

It can be concluded that on the long term the differences in N-supply and NH_3 volatilization per plot average-out sufficiently. This is essential because it allows a comparison with measured seasonal or annual exchange without taking notice of the wind direction or of (the stability and) the distance to the measurement site.

7.3 Comparison of measured exchange with estimates from emission factors

Figure 7.3 (next page) visualizes a comparison for 1993 between the estimated volatilization from the ROC terrain using emission factors and the net exchange derived from the measurements. The values of the latter were derived from average diurnal patterns per month as described in 5.3.1. ('interpolation method'), now for the year of 1993 only. Figure 7.3 makes clear that the estimated input to the atmosphere is much higher than the actually measured exchange in the same period. The difference between estimated and measured exchange is largest in the pre-season: about 15 instead of $0.5 \text{ kg ha}^{-1} \text{ NH}_3$ (see table 7.1, below). One reason for this may be that a relatively large part of the volatilization in this season was not measured because the wind did not pass over treated terrain during a proportional part of time. Especially if this happened after slurry spreading by the conventional method, considerable differences in estimated and measured exchange may occur. Only a few days with slurry spreading by the conventional technique were responsible for a large part of the total estimated volatilization in this season.

As explained earlier (1.4.5) the volatilization factors have been derived from the (integrated) emission in a limited period during and after a treatment. Therefore, if treatments take place more regularly, estimates based on volatilization factors for these treatments will be more comparable with continuous measurements of surface exchange over the same period. Therefore it is better to focus on the grazed season. Partly due to the regular grazing, treatments were spread much more equally over the season than in case of the pre-season. Even in the grazed season however, a large difference remains between the estimated volatilization and the net flux derived from the measurements (about 23 instead of $6.9 \text{ kg ha}^{-1} \text{ NH}_3$, see table 7.1 below).

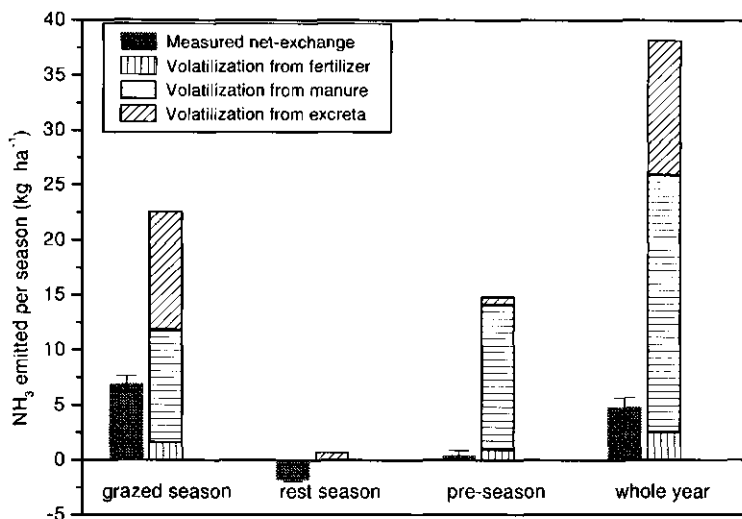


Fig. 7.3 Comparison of net ammonia exchange at Zegveld per season derived from flux measurements to emission estimated from data on land treatments using current volatilization factors. Error bars denote ER_{se} .

Correction for deposition

As follows from section 7.1, a possible explanation of the difference between the estimate from emission factors and the measured net exchange is that deposition to the same terrain is neglected when applying emission factors. In most *transport models* deposition is accounted for in the calculations of the plume development. They do not use or estimate the net exchange directly, but emission (source strength) and deposition are accounted for separately in the calculation of the concentration per grid (1.4.6/1.4.7). In many of those models the deposition is calculated by use of a resistance model (eq. 2.2). In the currently documented versions of OPS, a fixed value for R_c (30 s m^{-1}) is applied for NH_3 over all surfaces (Van Jaarsveld, 1995). Specific surface conditions of grazed pastures (high surface resistance, high average concentrations) are not taken into account in the calculation of this deposition.

The resistance module in such models is applied to the modelled concentrations. It is outside the scope of this research to include detailed model calculations for Zegveld and its surrounding area. However, the concentrations over the pasture were measured directly and can in principle be used to estimate the deposition component of the net exchange that would be calculated by OPS. Figure 7.4 shows again the comparison of

fig. 7.3, but now the estimate of emission based on land-use has been corrected for deposition.

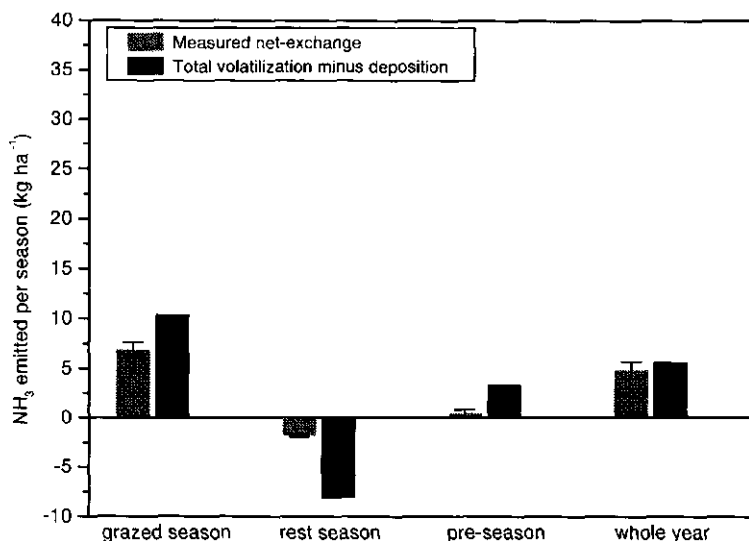


Fig. 7.4 Comparison of measured net ammonia exchange at Zegveld with estimated emission from emission factors, corrected for deposition according to TREND ($R_c = 30 \text{ s m}^{-1}$). Error bars denote ER_{se} .

This deposition was inferred (eq. 2.2) from the measured concentration c_r , the measurement-derived R_a and R_b (eqs. 2.28 and 2.31, as in OPS), and the standard value in OPS for R_c of 30 s m^{-1} . From the results, the deposition component of the total exchange in each season was estimated, again using the 'interpolation method' of 5.3.1. The exchange estimates with and without deposition, as well as values derived from the flux measurements, are also summarized in table 7.1.

Comparison of fig. 7.4 and fig. 7.3, -or the corresponding columns in table 7.1-, shows that in the grazed season, the inferred deposition compensates most of the difference between the estimated emission and the measured net exchange. In the pre-season this difference is also reduced but is still very large. As mentioned above, the representativeness of the measurements is less certain here than in the other seasons. Contrarily, in the rest season inclusion of parameterized deposition leads to an estimated net-uptake by the pasture that is much larger than derived from the flux measurements.

Table 7.1 *Net ammonia exchange at Zegveld (1993) derived from measurements, or estimated from emission factors excluding or including estimated deposition (assuming $R_c=30 \text{ s m}^{-1}$ as in OPS). Exchange given in kg ha^{-1} of NH_3 . Between square brackets: ER_{SE} .*

Period	Measured exchange	Exchange estimate from emission factors	
		without deposition	including deposition
Grazed season	6.9 [0.8]	22.6	10.4
Rest season	-1.8 [0.2]	0.8	-8.2
Pre-season	0.5 [0.4]	14.8	3.4
Year	4.6 [0.9]	38.2	5.6

7.4 Evaluation

The results in the previous section show clearly that for a location such as the Zegveld pasture, the net exchange is overestimated by far if it is derived from land-use and current emission factors only. Only if deposition to the same terrain is included separately in the estimate, as in OPS, a better approximation of the measured net exchange is found.

One interpretation of this result could be that local deposition is the main reason for the difference between the emission estimates from emission factors and the actually measured net exchange. Following this assumption an attempt will be made to derive the local deposition as a percentage of the emission from the pasture. This would enable a relatively easy correction of emission estimates based on emission factors only.

Another possibility is that the emission factors themselves are too high. This will also be evaluated.

First an attempt is made to derive a re-deposition factor. This factor must express the fraction of the NH_3 emitted by the pasture which is re-deposited within a short range (say within a few km, to similar terrain).

The net exchange derived from the measurements at Zegveld is 70% lower than the estimate based on land-use (grazed season). However, this does not mean that 70% of

the NH_3 emitted by the pasture re-deposits again locally. The measured total net exchange includes also deposition of NH_3 emitted by other sources. At night net deposition is mostly observed over the pasture. It may be assumed that the ROC terrain is representative for grasslands in the region. Therefore this nocturnal net deposition must concern mainly NH_3 emitted by other sources than pasture. Hence it is difficult to derive which fraction of the difference between estimated emission and measured net exchange is really due to re-deposition of NH_3 emitted by pasture. A very rough approximation may be achieved by extrapolation of emissions by the ROC. Therefore the emission from animal houses and slurry stores of the ROC was calculated by use of a similar procedure as used to estimate the emission by the pasture. The nitrogen excretion by the cattle disposed of in the animal houses (and transported to the slurry stores) was calculated from management data put available by the ROC (part of total animals per category that was grazing per period; grazing regime) and excretion factors given by Van Eerd (1995). These were multiplied by volatilization factors given by v.d. Hoek (1994). These volatilization factors are expressed on annual basis (percentage of total nitrogen that volatilizes per year). As an approximation, it is assumed here that this volatilization is more or less constant during the year. In practice, higher temperatures in the summer half year compared to winter may favour volatilization of NH_3 of all agricultural sources (eq. 1.7-1.9). Bogaard and Hofschreuder (1996) found that in emission regions, the monthly average (overall) ammonia emission correlates well with the monthly average temperature. However such temperature effects are likely to differ considerably in magnitude between the different types of sources, and net consequences for the above mentioned ratio can hardly be quantified with current knowledge.

Another point is, that in 1993 most other farms in that region may not have used reduced emission techniques for slurry application (they were not yet obligatory for that region). So generally the mentioned ratio may be lower (due to a larger relative contribution by the pastures) and therefore a value of about 1 is likely to be more realistic. The difference between estimated (land-use) and measured net exchange was about 15 kg ha^{-1} of NH_3 . Assuming that this difference is fully due to net deposition, and that half of this concerns ammonia from pastures, the (maximal) re-deposition would be about $7.5 \text{ kg ha}^{-1} \text{ NH}_3$, or about 30% of the estimated emission.

Due to the lack of data on the actual origin of the depositing NH_3 , this value of 30% is very uncertain. More certainty about the role of re-deposition could perhaps be achieved by application of models for short range transport (such as SLAM, see Boermans and Van Pul, 1993) to this region. Then a better estimate of the contribution of each type of source to the ammonia that deposits to the ROC terrain can be found. However this is beyond the scope of this thesis.

Another explanation for the difference between the measured exchange and the exchange calculated from emission factors for Zegveld might be that the emission factors are too high. Indeed application of the R_c value of 30 s m^{-1} of OPS in combination

with the emission estimate from emission factors resulted in an annual net exchange of similar magnitude as measured. However it is unlikely that such a strong deposition is realistic. In section 4.4 considerably higher values than 30 s m^{-1} (2-3 times higher) were derived for R_{ce} even under conditions where net deposition occurred. Only at night in the rest season R_{ce} values of similar magnitude (35 s m^{-1}) were found. However figure 7.4 shows that the deposition is clearly overestimated even in this season. Because the deposition module of the OPS model also assumes that the surface concentration is negligible, its R_c parameter is fully comparable to our R_{ce} .

As mentioned already in 1.4.6, at present a newer version of OPS has been developed in which the resistance parameterization of DEADM has been adopted (Erisman, *pers. comm.*). As this version has not been documented yet, it has not been used in the comparison. According to the description of the parameterization used in DEADM (Erisman, 1993; Erisman *et al.* 1994), obviously a considerably higher surface resistance (and even some emission) is now assumed for grazed pasture. Hence it may be expected that the new parameterization of OPS estimates a lower deposition to grazed pasture than the old one. For fig. 7.4 this would result in a higher estimated net-exchange (more positive).

Due to the low efficiency of NH_3 deposition that was actually measured at Zegveld, local deposition cannot explain the large difference between estimated volatilization and measured net exchange. Therefore the volatilization of NH_3 calculated for the ROC pasture from emission factors is probably an overestimate. This could well be related to properties of the peat soil, especially the low pH (4.8). Once urine, slurry or (dissolved) fertilizer come(s) into contact with the soil, the low pH may virtually inhibit the volatilization of NH_3 . Additionally the cation exchange capacity of peat soil is high, comparable to clay. This may cause efficient adsorption of NH_3 (as NH_4^+) to the soil.

Summarizing, a large difference was found between estimated emissions based on land-use and emission factors and the measured net exchange of ammonia. If the difference is attributed to local re-deposition, it would mean that about 30% of the emission from the pasture deposits again within a short distance (of an order of a few km). However, deposition is probably not the main reason for the difference between estimated and measured emission. Given the measured concentrations, the surface resistance should be unrealistically low to make sufficient deposition possible. Therefore the currently used volatilization percentages are probably too high for pasture on peat soil. Only if the overestimation of emission by current emission factors is compensated by an overestimated deposition to the same terrain, a realistic net exchange is calculated. This is the case if OPS is applied to terrains like the Zegveld pasture.

If the emission factors are indeed too high in case of peat soil, it may be necessary to evaluate whether emission factors should be specified per region or per soil type.

Chapter 8

Effects of SO_2 , HNO_3 and NH_4NO_3 on ammonia exchange

8.1 General pattern of SO_2 deposition

Summary of the results

The measurements of SO_2 dry deposition were carried out from 18 August 1993 until 17 December 1993. The main objective was to study mutual relations between SO_2 and NH_3 deposition. Patterns of exchange of NH_3 were already treated in chapter 5 and 6. The calculation of the exchange parameters for SO_2 and the selection of reliable flux measurements has been described in 4.1.2.

Table 8.1 (next page) gives an overview of average values of measured deposition velocities and concentrations and 'best fit' values (see 4.2.3) of R_c , classified per period and parameterized surface condition. The classification was carried out as follows:

- * Frost was assumed to have occurred when the surface temperature was below -1°C ; these measurements (all in the rest period) were not subdivided further.
- * The classification of measurements according to season and day/or night period was the same for all compounds (grazed 1993: until 15 October; day: $Q > 10 \text{ W m}^{-2}$).
- * The surface was assumed to be *dry* at relative humidity below 85%, if it had not been raining in the preceding 5 hours (grazed season: 3 hours). At night it was assumed that 2 hours more were necessary for the surface to dry. In all other situations the surface was assumed to be *wet*.
- * The class 'wetness unknown' refers to measurements (no frost) for which relative humidity was not available and no classification could take place on basis of the period after rain only.

Concentrations of SO_2

The average concentration during the measurement period ($12.4 [0.5] \mu\text{g m}^{-3}$ of SO_2) is somewhat higher than the annual average measured over the Netherlands in 1993 ($9 \mu\text{g m}^{-3}$, Erisman and Draaijers, 1995). Of course, part of this difference may be explained by unrepresentativeness of the measurements in this research (covering 4 months) for a whole year. Differences in measurement height (Erisman: 4m) may also explain some of the difference in average concentration (less than 10%). Regional variations among average concentrations of O_2 are probably not important; these are

Table 8.1 Average values of deposition velocity (v_d) and concentration (c_r) and best fit values of surface resistance (R_c) for SO_2 at Zegveld, August - December 1993. Between square brackets: SE; between brackets DF_{30} range (see text, 4.2.3).

Period	Selection	v_d (5m) [cm s ⁻¹]	R_c [s m ⁻¹]	c_r (5m) [µg m ⁻³]
Grazed season	Night, Wet	1.12 [0.06]	-5.5 (-23; 29)	7.5 [0.4]
	Night, Dry	1.27 [0.05]	11 (-7.5; 45)	10.8 [2.4]
	Day, Wet	1.49 [0.08]	-1.5 (-15; 25)	11.0 [0.7]
	Day, Dry	1.17 [0.07]	15 (-2; 48)	8.0 [0.6]
Rest season	Night, Wet	1.06 [0.06]	19 (0; 56)	14.3 [1.1]
	Night, dry	1.28 [0.20]	13 (0; 29)	6.2 [0.8]
	Day, Wet	1.11 [0.10]	8 (-14; 51)	14.7 [1.5]
	Day, Dry	1.29 [0.14]	7 (-10; 40)	16.1 [2.4]
Wetness unknown		1.13 [0.07]	5 (-12; 38)	10.3 [0.9]
Frost	$T_{\text{surf}} < -1^\circ\text{C}$	0.65 [0.04]	37 (11; 90)	23.6 [1.9]

generally quite small, contrarily to the case for NH_3 . However, the difference can also be due to a bias in the average concentration for Zegveld, caused by the selection of reliable flux measurements. In 4.2.4 it was derived that this may lead to an overestimation of the concentration of 23 to 45%. Without any selection, the average would be $7.9 \mu\text{g m}^{-3} \text{SO}_2$ which is closer to the country average.

Apart from during rain, SO_2 concentrations below the rejection criterion of $2 \mu\text{g m}^{-3}$ were frequently measured at night. Hence as a result of the selection, the difference between the average concentrations at daytime and at night in table 8.1 is smaller than would be the case without selection. However on most individual days, a significant diurnal variation in concentration is still obvious in the selected measurements. Fig. 8.1 gives a typical time series of the concentration of SO_2 . For comparison, the variation of NH_3 on the same days is also shown.

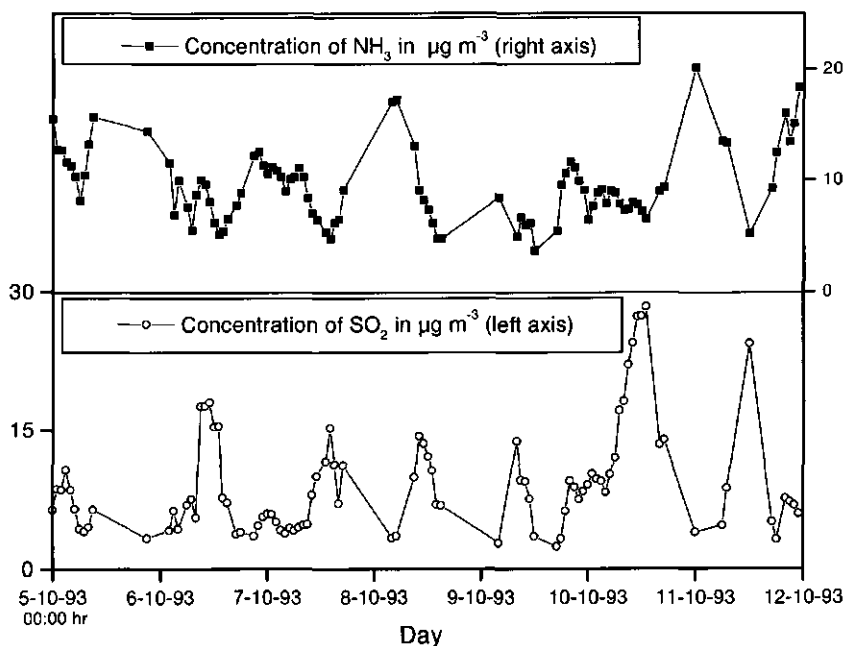


Fig. 8.1 Time series of the measured concentrations of NH_3 and SO_2 ($z=5\text{m}$) at Zegveld, October 1993.

The patterns often show an anti-correlation between both compounds. This can be explained by opposite effects of weak vertical mixing and low wind speeds at night on the concentrations of both compounds. For NH_3 , which is emitted close to the ground and relatively close to the measurement site, these effects result in lower concentrations at daytime than at night (see 5.2). Most SO_2 however is emitted by sources at a higher level, and at larger distance from the site. Low wind speed and stable conditions with low mixing layer height will now prevent replenishing of SO_2 that has been removed from the lower layers of the atmosphere by deposition. When the nocturnal ground inversion has been broken down at daytime, inflow of SO_2 from higher layers occurs, and the higher wind speeds at daytime facilitate transport of SO_2 emitted at larger distances. Consequently the SO_2 concentration at the measurement height is generally higher at daytime than at night, opposite to the pattern for NH_3 .

According to table 8.1, the SO_2 concentrations are much higher in the rest season (=autumn/winter) than in the grazed season (=summer). The influence of higher energy consumption on SO_2 emissions in winter is obvious. In addition, winds from Eastern

directions -advecting air that is heavier polluted with SO_2 - occurred more frequently in the rest season.

Exchange parameters

Mean levels of v_d and R_c

The deposition of SO_2 at Zegveld was moderately efficient. The average deposition velocity was $1.14 [0.03] \text{ cm s}^{-1}$ over the whole period of the measurements ($n=465$). The 'best fit' value for R_c was $11.3 (-7; 45) \text{ s m}^{-1}$.

The observed deposition velocities are similar to annual average values derived by Erisman (1992) from measurements by RIVM at the same location in 1987-1989 ($1.2 \pm 0.3 \text{ cm s}^{-1}$). Correspondingly the observed R_c -values are also of the same order of magnitude (RIVM: -1 to 21 s m^{-1} , depending on conditions of dry/wet and day/night).

In 4.2.4 (table 4.5), it was shown that the selection of reliable flux measurements leads to a considerable shift in v_d towards higher values. This is mainly caused by rejection of conditions that reduce the transport through the atmosphere. The shown values of v_d therefore should be interpreted as maximum values, especially at night (stable conditions).

However, in this part of the research at Zegveld, focus was aimed on the effect of surface conditions on the efficiency of the deposition of SO_2 (and of NH_3); this efficiency is best analysed on basis of R_c . The uncertainty in this parameter due to possible selection biases was only moderate (about $\pm 25\%$, 4.2.4) so that the selected data set can be used safely for that purpose.

R_c in the grazed season

Table 8.1 shows a variation of R_c with the (parameterized) surface wetness in the grazed season. R_c of the 'dry' surface is higher than R_c of the 'wet' surface. It should be noticed that at night conditions fulfilling the 'dry' criterium were hardly encountered at Zegveld; the mentioned values are based on a very small number of observations ($n=3$). Probably the grass is nearly always moist at night. The occurrence of relatively efficient deposition at night, when the stomata are closed, indicates that the (wetted) leaf surface plays an important role in the deposition of SO_2 .

Between measurements at daytime and at night under *wet* surface conditions a small, probably insignificant difference was found (-5.5 vs. -1.5 s m^{-1}).

Under *dry* surface conditions also some difference between day and night is found, but here the comparison is very uncertain due to the mentioned small number of observations of dry condition at night introduces additional uncertainty.

Figure 8.2 shows a representative time series of R_c for the same week as figure 8.1.

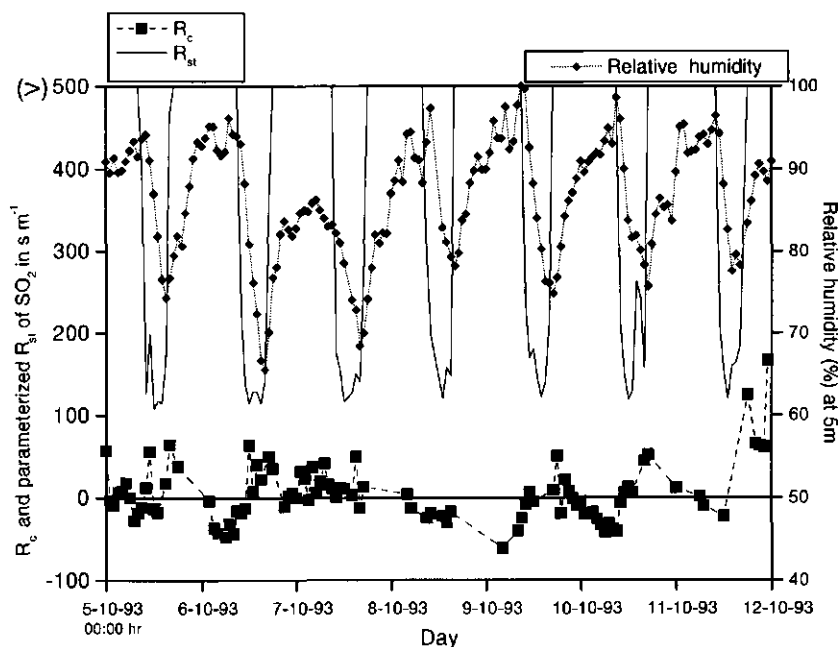


Fig. 8.2 Time series of surface resistance (R_c) and stomatal resistance (R_{stom}) of SO_2 and of relative humidity (RH) at 5m at Zegveld, October 1993. R_{stom} has been parameterized according to Wesely (1989).

R_c usually reaches its highest value in the afternoon; there is a clear anti-correlation with relative humidity. Under humid conditions even negative values of R_c occur, indicating extremely efficient deposition. These negative values (which are physically not possible) may result from an overestimation of R_b while the true R_c is negligibly small. The chosen R_b -parameterization by Hicks *et al.* (1987) is widely used, but the validity of this or other parameterizations (*e.g.* by Garland (1977) or Monteith and Unsworth (1990)) is hard to verify in the field.

In figure 8.2, also the parameterized stomatal resistance (eq. 2.35) is shown. It has been corrected for the lower molecular diffusivity of SO_2 compared to water ($D_{\text{H}_2\text{O}}/D_{\text{SO}_2} = 1.83$). Generally R_c remains well below the minimum stomatal resistance, even if an eventual underestimation of R_c due to errors in R_b is taken into account. Therefore it can safely be concluded that the diurnal variation of R_c is determined almost completely by the exchange with the (wet) leaf surface.

The enhancement of SO_2 deposition by wetness of the leaf surface due to rain or high relative humidity agrees with observations in other field experiments (see *e.g.* Fowler and Unsworth, 1979; Vermetten *et al.*, 1992; Vermetten and Hofschreuder, 1994; Erisman and Wyers, 1993; Erisman, 1992) and in leaf chamber experiments (Van Hove, 1989). At this point NH_3 and SO_2 show similar behaviour. The measurements at Zegveld give no further information on the exact mechanism by which water associated with the cuticle facilitates deposition at higher RH (see 1.4.3: permeable cuticles, proposed by Van Hove, 1989; Van Hove and Adema, 1996; deliquescent salts, possibly even causing connections between substomatal fluid and water on the leaf surface: Burkhardt and Eiden, 1994). For simplicity, in this thesis an eventual increased permeability of the cuticle at high RH is considered to be a form of wetness of the leaf surface. This is in line with common practice in current deposition modelling. It is obvious however, that both mechanisms could have important consequences for the composition of the actual substrate to which 'leaf surface' deposition takes place. Interactions between leaf surface water and plant fluids may be much stronger and much more direct than is generally accounted for in resistance models. More detailed mechanistic research at this point will be required in future.

R_c in the rest season

In the rest season, the variation with surface wetness is absent or weak. Probably the leaf surface is wet most of the time because solar radiation is too weak to cause effective evaporation of this water. Diurnal variations in relative humidity are much smaller than in the grazed season. (RH generally over 85% except for frost periods).

This season contained a frost period of about 3 weeks. A clearly elevated value of R_c during frost is found of about 40 s m^{-1} on average; occasionally the freezing of the water on the leaf surface can result in R_c values exceeding 500 s m^{-1} (fig. 8.3).

In the afternoon, thawing occurs and the surface resistance is low during a few hours, until freezing starts again. An increased surface resistance for SO_2 during frost is consistent with observations reported in the literature (Onderdelinden *et al.*, 1984; Erisman and Wyers, 1993).

Table 8.1 also indicates that in the rest season values of R_c are lower during daytime than at night. This is mainly the case for wet conditions, where the nocturnal value is clearly higher. The reason for this is not yet clear. One possibility is that fog occurred more often in this season. Under fog conditions sometimes increased values of R_c were observed both for NH_3 and SO_2 . This has also been reported by Erisman and Wyers (1993).

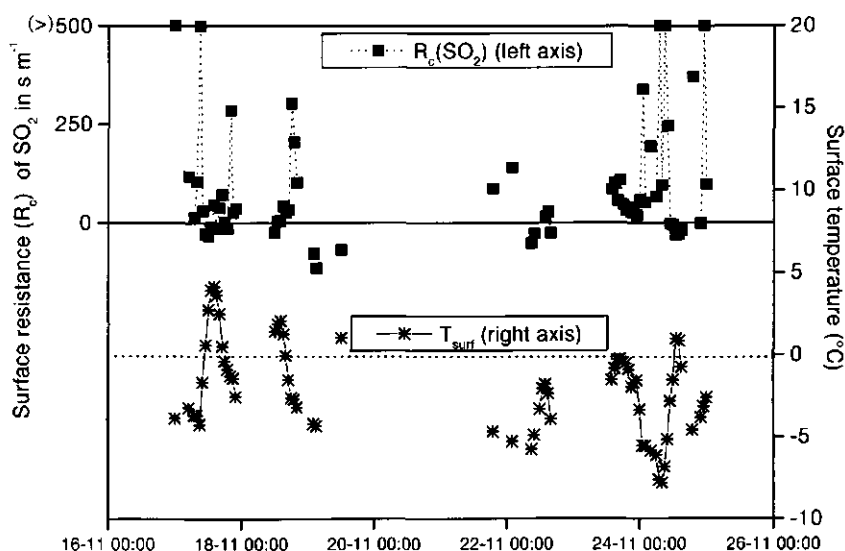


Fig. 8.3 Time series of the surface resistance (R_c) of SO_2 and of the surface temperature at Zegveld, November 1993.

8.2 Co-deposition of SO_2 and NH_3

From a comparison of table 8.1 (SO_2) and 5.1 (NH_3) it can be seen, that the deposition efficiency of both compounds shows an opposite seasonal variation.

For SO_2 , the mean value of R_c was higher in the rest season than in the grazed season, even when the surface was wet. Generally values of R_c were too low for the stomata to play an important role in this seasonal difference (minimal R_s for SO_2 is about 90 s m^{-1}). Additionally, the shift in R_c was also found between nighttime selections of both seasons, in which stomata play no role.

For NH_3 higher mean R_{ce} -values were found for the grazed period than for the rest season (table 5.1). However, generally the R_{ce} values of ammonia were considerably higher than those of SO_2 .

Seasonal concentration variations of both compounds were also opposite: concentrations of NH_3 were highest in the grazed season, those of SO_2 were highest in the rest season.

These opposite variations in R_c of both compounds may possibly be explained by SO_2 - NH_3 co-deposition. The term co-deposition is used to denote the phenomenon that these two compounds enhance each others deposition via opposite effects on the pH of the surface. This was observed *e.g.* in wind-tunnel experiments by Adema and co-workers (1.4.4). Implicitly, co-deposition can also be interpreted as a mutual dependency (via the processes at the surface). Proportional deposition of each of both compounds is necessary to compensate the pH effect of the deposition of the other compound. So if one compound is available in excess, its deposition efficiency will decrease until deposition rates of both compounds are in balance. From this point of view, an optimal molar air concentration ratio of NH_3 to SO_2 would be about 2, for the formation of solutions of $(\text{NH}_4)_2\text{SO}_4$. A molar ratio well above that value will favour a high pH at the surface (and inhibit NH_3 deposition), while molar ratios well below that value will favour a low pH at the surface (and inhibit SO_2 deposition). A dependence of the surface resistances of both compounds on their molar ratio in the atmosphere was indeed observed by Erisman and Wyers (1993).

On average, NH_3 in the air at Zegveld is present in excess over SO_2 with an average molar concentration ratio ($\text{NH}_3:\text{SO}_2$) of about 4. As a result of this, a high pH may be found at the leaf surface, which is favourable for SO_2 deposition and unfavourable for NH_3 deposition. In this respect the lower R_c for SO_2 than for NH_3 could be interpreted as a general effect of co-deposition.

In the period in which both compounds were measured, this molar ratio was much higher on average in the grazed season (6:1) than in the rest season (4:3). Figure 8.4 shows the average diurnal patterns of the molar ratios between both compounds in each season (calculated from average diurnal concentration patterns per compound). For this figure, the measurements were not subjected to the selection criteria of section 4.1; only rain periods were rejected.

Clearly NH_3 is present in excess during all parts of the day in the grazed season. In the rest period, the molar ratio is much smaller, on average even below the optimum of 2, with only a limited diurnal variation.

It may be assumed that per season, the ratio was about similar in periods in which only one of both compounds was measured. Based on this, the difference in molar ratio may explain why going from the grazed season to the rest season, $R_{c,e}$ of NH_3 (table 5.1) decreases considerably (by up to 50%; deposition velocity (not shown) increased by 30%). Explained in terms of co-deposition, the low deposition efficiency in the grazed season results from the obvious excess of NH_3 over SO_2 , causing a high leaf surface pH. In the rest season, the lower NH_3 concentration and higher availability of SO_2 cause a decrease of the pH at the leaf surface, which is more favourable to NH_3 deposition.

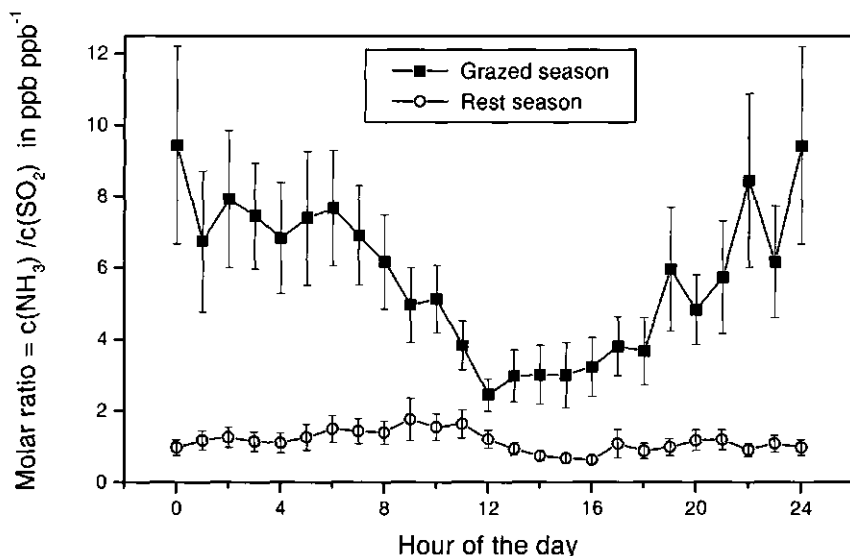


Fig. 8.4 Average diurnal patterns of the molar concentration ratio of NH_3/SO_2 at Zegveld, during simultaneous measurements of both compounds in the grazed season and rest season of 1993. Error bars indicate SE.

Accordingly, the surface resistance for SO_2 increases, (table 8.1), though the effect is weaker than for NH_3 , and the deposition of SO_2 remains quite efficient on average. Possibly the pH at the leaf surface, despite a certain decrease, remains relatively high so that restraints to uptake of SO_2 remain weak.

In 5.4 the seasonal variation of the deposition efficiency of NH_3 was already attributed to a higher surface pH in the grazed season, without taking relations to SO_2 deposition into account. As shown above, a relative shortage of SO_2 in the grazed season provides a good explanation why pH can increase to higher values in that season. It should be considered, that possible influences of other factors than the NH_3 - SO_2 molar ratio cannot be eliminated in such analyses of long term average effects. Simultaneous deposition of other acidifying compounds (*e.g.* strong acids) and (other) buffering mechanisms may also influence the pH at the leaf surface. This may reduce the importance of SO_2 availability to the deposition efficiency of NH_3 . Furthermore, high ambient concentrations of NH_3 -regardless of the SO_2 concentration-, will also favour accumulation of NH_4^+ at the leaf surface. This may contribute to the higher R_{ex} in the grazed season, especially if pH is already high. At present no adequate quantitative

knowledge is available on the rate of removal of leaf surface NH_4^+ by microbiological conversion and by interactions with the leaf tissues (*cf.* Sutton *et al.*, 1998).

In case of SO_2 the net-conversion to well-soluble sulphate by oxidation (1.4.4) will generally prevent a strong accumulation of HSO_3^- at the surface; pH-effects will generally be much more important than actual accumulation of HSO_3^- . Of the simultaneously depositing compounds, NH_3 is most likely to be the dominant alkaline species to compensate the decrease of pH due to SO_2 deposition. Therefore especially the mentioned characteristics of the deposition efficiency of SO_2 (in relation to the NH_3/SO_2 molar ratio) give a strong indication that the deposition efficiency of both compounds is interrelated via co-deposition.

It was investigated whether co-deposition could be observed on a smaller than seasonal timescale, *e.g.* in daily variations. As follows from the generally opposite concentration patterns of both compounds, their molar ratio changes also with the hour of the day. The average diurnal patterns in fig. 8.4 show that this variation is considerable, especially in the grazed season. However, in the grazed season the excess of NH_3 remains high even at daytime, which may explain why the diurnal variation of SO_2 deposition is only small on average and is dominated by variation in surface wetness (*cf.* fig. 8.2). Correspondingly the surface resistance (R_{ce}) for NH_3 remains high at daytime. In the rest season, the average diurnal variations of the ratio are much smaller than in the grazed season. No large excess of one compound to the other occurs. The remaining diurnal variation in concentration ratio does not explain why in this season a lower resistance is found at daytime than at night.

In addition to these analyses on basis of long term average parameters, several analyses were made of individual measurements of the deposition efficiencies and molar ratios of both compounds, when they were measured simultaneously. However, patterns of R_c values of both compounds during deposition gave no further evidence of co-deposition. No consistent relations with the molar ratio of ambient concentrations were found. The same applies to analyses of patterns of v_d and fluxes. Here, variations in turbulence often dominated the patterns of both compounds. After stratifications to eliminate the correlation via the turbulence intensity, no clear correlation remained. Extension of the analyses to include periods with ammonia emission gave no evidence of mutual effects either.

It is concluded, that on the short term, effects of co-deposition on the deposition efficiency of both compounds are probably minor compared to variations caused by other factors. It should be noticed that at this location, the molar ratio between both compounds often fluctuates quite strongly on hourly basis. The changes are probably too rapid to allow a strong shift of pH in either direction. Possibly the leaf surface has a

certain buffering capacity so that its pH is not too easily affected by short term fluctuations of the molar ratio. Per season, those variations may average-out largely so that only the effects of more structural differences in concentration ratio are observed.

Summarizing, it is concluded that NH_3 - SO_2 co-deposition probably plays a role at Zegveld as one of the factors determining the *long term average* deposition efficiency of each of both compounds. On average SO_2 deposition at Zegveld is quite efficient (low R_c), while R_{cc} for NH_3 is quite high on average. In terms of co-deposition, this is because in the air, NH_3 is generally present in excess over SO_2 . In a similar way seasonal differences in deposition efficiency for each compound are in agreement with a much higher molar ratio of NH_3 to SO_2 in the grazed season than in the rest season.

On shorter timescales however, co-deposition seems to have no relevant effect on the deposition efficiency of either compound.

8.3 Main patterns of NH_4NO_3 and HNO_3 exchange

Because the $\text{NH}_4\text{NO}_3/\text{HNO}_3$ denuders were regularly interchanged between both sampling heights only after March 1993 (see 3.3.3.1), earlier measurements were not used for interpretation. As a result of this regular interchange, systematic differences between the two denuders average-out over long periods. So if average diurnal patterns are calculated for the concentration profiles and gradients of both compounds, these will be considerably less sensitive to large systematic errors than without the interchange.

Average diurnal patterns of the profiles of HNO_3 and NH_4NO_3 are given in figure 8.5 (next page). In general, according to the profiles, both compounds were deposited, which is in accordance with expectations. As mentioned earlier, it is generally accepted that HNO_3 deposits even very efficiently to almost every surface. Particles are not emitted by a surface (re-suspension is not considered as emission, but as a factor reducing the efficiency of deposition of particles).

The average measured concentrations of HNO_3 and NH_4NO_3 at 5m height are 1.25 and 4.3 $\mu\text{g m}^{-3}$ respectively. These values are roughly in accordance with mean values over the Netherlands (for HNO_3 0.9 $\mu\text{g m}^{-3}$, for particulate NO_3^- 5 $\mu\text{g m}^{-3}$ (RIVM, 1994)). It is

assumed that most particulate NO_3^- is present as NH_4NO_3 . Furthermore it is clear that the gradients of NH_4NO_3 are only very small, while the gradients of HNO_3 are large.

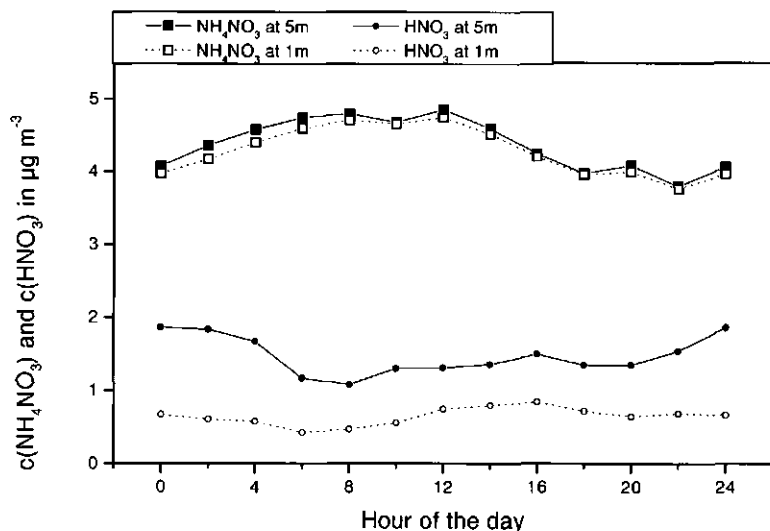


Fig. 8.5 Average diurnal patterns of the concentrations of NH_4NO_3 and HNO_3 . Results for both measurement heights (1 and 5m) are shown.

To have an indication of the average deposition velocities of both compounds these were estimated from average diurnal patterns of concentration gradients and of meteorological data. This was done to maximize the reduction of uncertainty in the gradients, achieved by the regular interchange of the denuder tubes (see above). The average v_d for each hour of the day was calculated from the average values of that hour for u_* , c , and c_z . This method was applied earlier by Erisman (1992).

Normally calculation of fluxes and deposition velocities for individual measurements is preferred, because the concentration is not independent from meteorological variations. To see if this method can yield reliable estimates of the deposition velocity at Zegveld, it was tested for SO_2 . In figure 8.6 the average of the hourly determined v_d of SO_2 is compared with the mean v_d calculated from the average u_* , heat flux and concentration profile. The comparison is very good, and therefore this method was applied also to the data for HNO_3 and NH_4NO_3 .

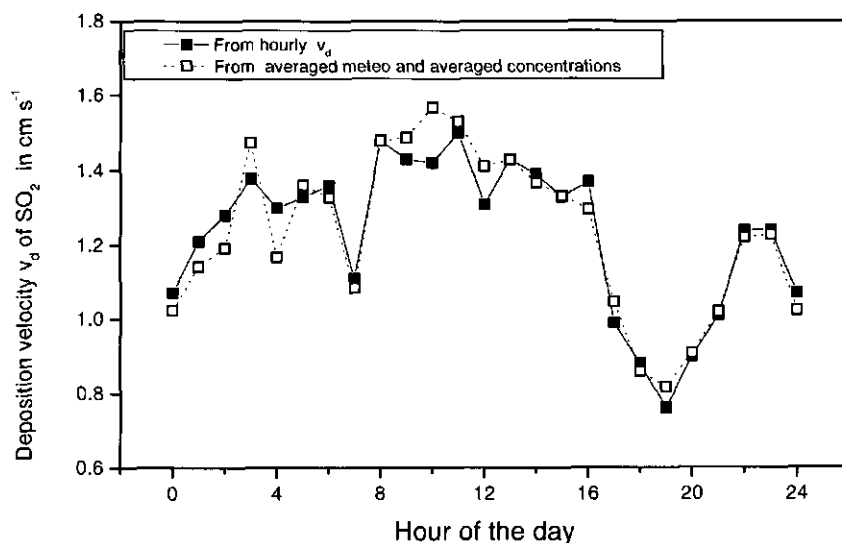


Fig. 8.6 Comparison of methods to derive average diurnal patterns of the deposition velocity (v_d) of SO_2 ; averaging of values of v_d calculated per individual measurement versus calculation of v_d from average diurnal patterns of u_* , heat flux (H) and concentration profiles.

To preserve a large number of measurements for calculation of the averages, missing values of u_* and L from eddy-correlation were replaced by values derived from wind speed and temperature profiles. If these were not available either, u_* was parameterized according to $u_*/U(5\text{m}) = 0.07$, and L was calculated using a fixed value of sensible heat flux of 6 W m^{-2} . This parameterization had been derived from the set of available u_* and heat flux measurements. It may be expected that the error in this parameterization is small compared to the error in individual measurements of concentration gradients.

The resulting average diurnal patterns of the deposition velocities of NH_4NO_3 and HNO_3 are shown in figure 8.7.

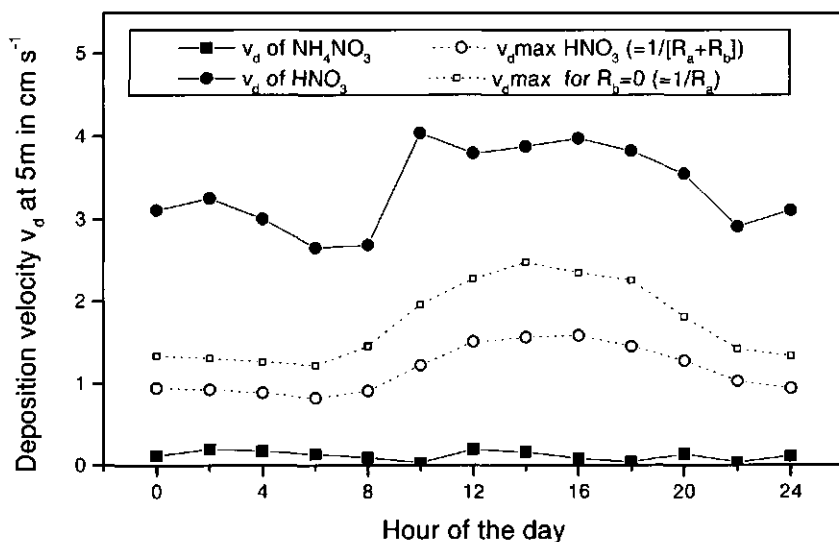


Fig. 8.7 Average diurnal patterns of deposition velocities of NH_4NO_3 and HNO_3 , derived from diurnal patterns of meteorological parameters and of concentration profiles. Also shown: maximum deposition velocities HNO_3 for $R_c=0$ ($v_{d,\text{max}}$) and for $R_b=R_c=0$ ($v_{d,\text{max},R_b=0}$).

The daily average deposition velocity of NH_4NO_3 is 0.12 cm s^{-1} . This is within the range reported for deposition of aerosol over low vegetation (about $0.07 - 0.22 \text{ cm s}^{-1}$ (Wesely *et al.*, 1985; Nicholson and Davies, 1987; Duyzer, 1995).

Contrarily, the deposition velocity of HNO_3 is very high (3.4 cm s^{-1} on average). High deposition velocities of HNO_3 are commonly reported, *e.g.* by Müller *et al.* (1993) over wheat (2.2 cm s^{-1}). It is generally assumed that the surface resistance to HNO_3 deposition is zero, so that its deposition velocity is equal to $v_{d,\text{max}}$, given by $(1/(R_a+R_b))$. Figure 8.7 shows that $v_{d,\text{max}}$ for HNO_3 at Zegveld was about 1.2 cm s^{-1} , so it was exceeded by more than a factor two by the measured v_d for HNO_3 .

Because theoretically v_d values above $v_{d,\text{max}}$ are impossible, often systematical errors in the parameterization of R_a and especially of R_b are held responsible. For low vegetation, the error in R_a can be assumed to be small. The estimation of R_b is much more uncertain; an overestimation of R_b was already mentioned in 8.1 as a possible explanation for negative R_c -values for SO_2 . However, R_b is generally small at Zegveld, and a systematical error should be very large in a relative sense to have a relevant influence on

calculated R_c or v_{dmax} (cf. 4.2.1). If R_b for HNO_3 is set to zero, an absolute limit to v_{dmax} is found (figure 8.7). This parameter is often used as a reference v_{dmax} for aerosol, as for aerosol the R_b concept is hardly applicable. The measured v_d of HNO_3 is still much larger than this $v_{dm(Rb=0)}$, so that an error in R_b is not the main cause of the high v_d for this compound. This was already derived theoretically in chapter 4; generally R_b is only small at Zegveld so that large relative errors remain unimportant in an absolute sense over this type of terrain.

This means that the measured gradients must be too large. It may be assumed that systematical errors in the profiles have been reduced considerably by the use of average diurnal patterns over a long period. Therefore the gradients of HNO_3 must have been affected by other processes (additional to deposition), probably formation of NH_4NO_3 by reaction of HNO_3 with NH_3 . This effect will be explained further in the following section.

8.4 Influence of NH_4NO_3 on gradients of HNO_3 and NH_3

Although on average downward gradients of NH_4NO_3 and HNO_3 were found (figure 8.5), individual measurements often showed upward gradients. For NH_4NO_3 even about 25 % of all gradients were reversed; for HNO_3 this percentage was much lower, about 10% of all measurements.

Formation of NH_4NO_3 by reaction of HNO_3 with NH_3 near the surface will lead to exaggeration of the HNO_3 gradient and to a NH_4NO_3 gradient that is too small or even reversed. Underestimation of HNO_3 deposition or apparent HNO_3 emission, together with overestimation of NH_4NO_3 deposition, suggests decomposition of NH_4NO_3 near the surface.

It was investigated (Zhang, 1995) to what extent equilibrium exists among the three compounds HNO_3 , NH_3 and NH_4NO_3 in the air at several locations, including Zegveld. He focussed on periods with high numbers of upward gradients of HNO_3 . He analysed the products of measured concentrations of HNO_3 and NH_3 (K_m) and compared these to the theoretical values (K_e). At equilibrium, $K_m = K_e$. The equilibrium constant K_e depends on temperature and relative humidity. Due to diurnal variations in these parameters, K_e shows a diurnal variation with a peak in the afternoon and low values at night. A more or less anti-correlating diurnal pattern is found for K_m . K_m is mainly determined by the diurnal pattern of the NH_3 concentration, as HNO_3 varies less strongly. It was found that strong deviations from equilibrium occur at night, with K_m/K_e

up to 100. At daytime generally equilibrium was approached or K_m/K_e was slightly lower than unity.

Kinetic constraints to the reactions may be much larger at night (because of the lower temperature and higher relative humidity). Therefore, if the equilibrium among the compounds is disturbed, especially at daytime, influences to the gradients may be expected. If the timescale of reactions to accommodate to the equilibrium (formation or decomposition of NH_4NO_3) is similar to the timescale of the turbulent transport, the vertical concentration gradients will be affected significantly.

If NH_3 (like HNO_3) is removed efficiently from the lower level of the atmosphere by deposition, K_m will fall below K_e close to the surface. Consequently, NH_4NO_3 will decompose in order to accommodate to the equilibrium requirement that $K_m=K_e$. This leads to the production of NH_3 and HNO_3 in the lowest level of the atmosphere, in a 1:1 molar ratio. So as a net effect the downward gradients of these two compounds will be reduced and may even change sign. From the obvious change in HNO_3 gradients (compared to a situation with normal, efficient HNO_3 deposition), the corresponding effect to the NH_3 gradient was calculated (Zhang, 1995), and it was found that the NH_3 gradient could be affected severely in conditions where the NH_3 flux is small.

However, upward gradients of HNO_3 were not observed very frequently at Zegveld. In fact v_d was too high on average, so that the downward gradients are higher than if they were determined by vertical transport only. This observation is in agreement with the fact that on average a significant upward gradient of NH_3 is observed at daytime, which is shown in fig. 8.8.

The net supply of ammonia from the surface leads to a net reaction with HNO_3 to NH_4NO_3 to accommodate to the equilibrium requirement. Consequently HNO_3 is removed from the lowest level of the atmosphere by this reaction and not only by deposition. This results in the very large HNO_3 gradients that were actually measured.

The eventual impact of these reactions on NH_3 gradients at Zegveld should be evaluated. In figure 8.8, the average diurnal gradients are shown on molar basis (nmole m^{-3}). It is clear that the concentration gradients of NH_3 generally exceed those of NH_4NO_3 and HNO_3 by far. As in production or decomposition of NH_4NO_3 equal amounts of NH_3 and HNO_3 are involved, it is clear that at Zegveld the resulting bias of measured gradients of ammonia is of minor importance, while HNO_3 gradients may be affected much more easily.

The net formation of NH_4NO_3 in turn may lead to a reduction of the downward gradient,

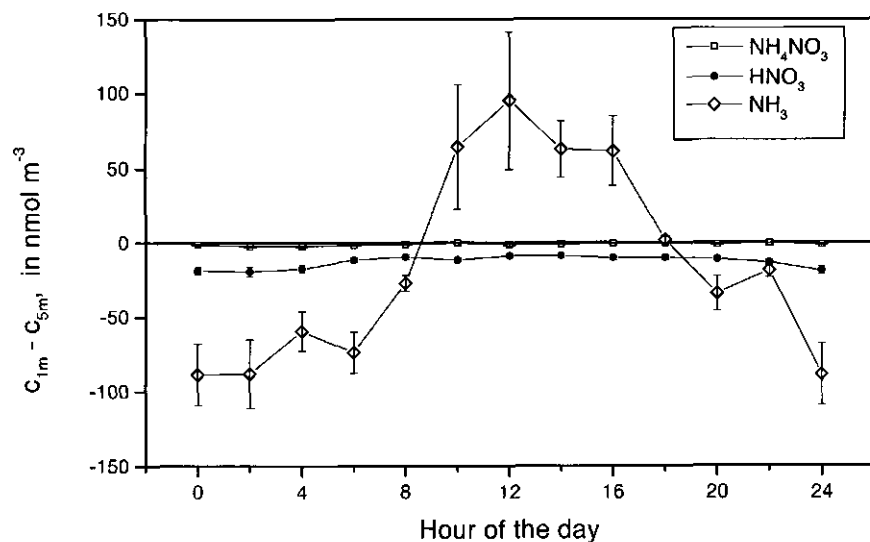


Fig. 8.8 Average diurnal patterns of the vertical gradients of NH_4NO_3 , HNO_3 and NH_3 at Zegveld, April 1993-June 1994, plotted as concentration differences between both measurement heights on molar basis. Error bars indicate SE.

or even to upward gradients for this compound. Therefore the average deposition velocity of NH_4NO_3 may in reality be larger than was derived from the measured gradients. Similarly the relatively high number of upward gradients may partly be due to this net formation of NH_4NO_3 .

Chapter 9

Parameterization of ammonia exchange over grazed pasture

9.1 Introduction

According to chapter 6 the regular alternation between deposition of NH_3 at night and emission during daytime can be described best by emission from the stomata and deposition to the leaf surface. At night stomata are closed, and the exchange consists mainly of deposition to the leaf surface. During daytime in the grazed season, emission from the stomata dominates the exchange, although some deposition may occur simultaneously to the leaf surface. Stomatal compensation points are high, so that only occasionally stomatal uptake of ammonia may take place. These high stomatal compensation points are probably the result of the high N-input at this site.

In the rest season and pre-season stomatal resistance is high, so that hardly any stomatal emission occurs and exchange with the leaf surface dominates the NH_3 flux during day and night.

This regular diurnal exchange pattern is disturbed mainly by slurry spreading events. They cause a general shift towards more positive net fluxes (higher emission, weaker deposition). Current estimates of the volatilization from land treatments, including slurry spreading, overestimate emission. Only if low surface resistances are used to estimate deposition to the same terrain (*e.g.* by OPS with $R_c \approx 30 \text{ s m}^{-1}$) the net exchange over the pasture is approximated. In practice such low resistances occur only at night in the rest season; in all other periods the (effective) surface resistance is at least a factor two higher, even if no slurry has been spread recently. In addition, the applied simplified resistance model does not account for net emission by the stomata of the vegetation.

Sutton and Fowler (1993) have derived a suitable parameterization for simultaneous exchange with the stomata and deposition to the leaf surface for crops. This model, denoted in this thesis as the 'canopy compensation point' (ccp)-model, has been described in 2.5. The ccp-model is not yet commonly applied in transport models for ammonia. Neither has it been used so far to describe exchange of ammonia over grazed pasture. However such an application seems well possible to describe the exchange in periods without slurry spreading. Therefore in this chapter, this model will be applied to the Zegveld data.

In the next section, first a brief evaluation is made whether there are principal obstructions to the use of the ccp-model for Zegveld. Then it is tested whether the basic parameters of the ccp model can be fitted so that they give a suitable description of the *regular* daily emission/deposition pattern in periods without influence of slurry spreading. In 9.3, this parameterization will be used, instead of a simple deposition model, to correct emission estimates from emission factors in a comparison similar to those made in chapter 7. In this way the volatilization percentage will be estimated that should be used to correct results of the parameterization in case of slurry application.

9.2 Fitting of model parameters of the ccp-model to conditions without recent slurry application

Applicability of the ccp-model to the Zegveld pasture.

The ccp-model assumes that there are situations in which equilibrium between the atmosphere and the vegetation as a whole occurs, so that the net exchange is zero. Then the emission from the stomata is completely balanced by deposition to the leaf surface. In chapter 6 it was shown that such equilibrium conditions are hardly ever found at Zegveld. Transitions from deposition to emission were observed over a large range of concentrations. It was concluded that the transition from deposition to emission is mainly determined by the opening of the stomata. Consequently it could be argued that the exchange behaviour of the Zegveld pasture is different from the situation for which the ccp-model was developed. However, the ccp-model is in fact a consequent combination of (bi-directional) resistance models for two pathways of exchange (stomata and leaf surface). The same result would be found without the notion that the net exchange must be zero if the ambient concentration equals the concentration at the bottom of the laminar boundary layer. Consequently the actual occurrence of this 'compensation' situation is not required for the formulation to be valid. Therefore the ccp-model can safely be tested for the Zegveld situation.

Fitting of the model parameters to the measurements

The input parameters of the model were fitted to the regular pattern of exchange at Zegveld. For this aim only those days were taken into account on which no slurry has been applied.

R_w in the ccp-model was replaced by an effective resistance (R_{wef}) derived from the measurements by the 'best fit' procedure described in 4.2.2. Only days without recent slurry spreading were used, and only periods showing net deposition. Three different surface conditions were distinguished per season: dry, wet or frozen. The parameteri-

zation of these conditions was the same as used for SO_2 (see 8.1). At night dry conditions were very rare because relative humidity then generally exceeded 85%. Frost in the grazed season was negligible.

An influence of NH_3/SO_2 -co-deposition was not accounted for explicitly in this R_{wef} parameterization. However, it was concluded in 8.2 that co-deposition probably only leads to relevant effects on the long term, on seasonal scale (for this location). Because the R_{wef} values in this parameterization were derived *per season*, a seasonal variation due to co-deposition is de facto included.

For R_{st} , again the parameterization according to Wesely (1989) was used (see chapter 6).

The parameterization of c_{ost} was derived from the measurements because no literature values of stomatal compensation points of pasture grasses under comparable conditions were found. Neither were sufficient data available on the composition (ammonium concentration and pH) of the apoplast fluid of ryegrass or other pasture grasses under these conditions, to estimate the compensation point according to eqs. 1.7-1.9. Estimation of these parameters based on the flux measurements was preferred to extrapolation of c_{ost} from literature data on other plant species (*e.g.* Husted and Schjör-ring, 1995).

Therefore representative values of c_{ost} were derived by fitting the model to the data, in a procedure similar to the 'best fit' procedure for R_{wef} . In this case, for each flux measurement the corresponding parameterized flux was estimated from eqs. 2.43 and 2.39 using the c_{ost} value to be tested, the measured concentration at reference height and parameterized values of R_a , R_b , R_{wef} and R_{st} . The average of the measured fluxes was again compared with the average of the corresponding parameterized fluxes, and the estimate of c_{ost} was adapted accordingly until both averages agreed.

When the surface is wet and values of R_{st} are high, the parameterized flux is dominated by F_w and hence by variations and errors in R_{wef} . Such conditions occur quite frequently (*e.g.* at night and early in the morning, and late or early in the year often also at full daytime). To avoid that errors in the parameterization of F_w had a disproportional influence on the estimate of c_{ost} , only measurements in the grazed season were considered, and initially only those in the afternoon, more than 3 hours since last rainfall. From this, it turned out that the fit between parameterized and measured fluxes improved significantly if c_{ost} was parameterized as a function of temperature instead of when a fixed value for all temperatures was used. From equation 1.9 it follows that if the ratio between the (logarithm of) the ammonium concentration and the pH in the apoplast is constant, c_{ost} will be a function of temperature only. Hence this equation was included in the calculation of the parameterized flux. To substitute for pH in the equation, a fixed value of the apoplastic pH of 6.8 (Farquhar, 1980) was assumed.

In this way finally an ammonium concentration inside the stomatal cavity of $775 \mu\text{M}$ was derived as a best fit value for all measurements in the grazed season without recent slurry spreading. This corresponds to a c_{ost} of $19 \mu\text{g m}^{-3} \text{NH}_3$ at 20°C .

The resulting parameterization is summarized in table 9.1.

Table 9.1 Summary of best estimates of input parameters for application of the ccp-model to Zegveld.

R_{wef} effective leaf surface resistance	variable per period of the year and dry/wet/frost conditions of the surface, according to: (in s m^{-1})								
	Rest season			Pre-season			Grazed season		
	wet	dry	frost	wet	dry	frost	wet	dry	
	33	55	105	110	135	130	80	135	
C_a stomatal compensation point	variable with temperature; corresponding to $19.0 \mu\text{g m}^{-3}$ at 20°C .								
R_s stomatal resistance:	According to Wesely; (minimal $R_{si}(R_s)$ is 50 s m^{-1})								

The values of R_{wef} are in line with the variations of R_{ce} described in chapter 5. The value of c_{ost} at 20° is high, but not beyond the range of values mentioned in the literature. For higher ambient temperatures indeed values of up to $25\text{--}30 \mu\text{g m}^{-3}$ could be reached. The level of the derived compensation point was already discussed in 6.5.

The derived ammonium concentration in the apoplast is also within the range of literature values (for other plant species); ammonium concentrations up to 2 mM were measured by Schjørring and co-workers (see table E.1, appendix E). However, their recent measurements seem to indicate that the commonly used value of 6.8 for the pH in the apoplast, may be too high for many plant species. They found values close to 6 (see table E.1). If similar pH values occur in the grasses at Zegveld, the corresponding ammonium concentration should be estimated at about 3 mM to yield the same compensation point.

The sensitivity of the calculated fluxes to the c_{ost} estimation was also tested. The average flux over the grazed season would be parameterized higher or lower by about $5 \text{ ng m}^{-2} \text{ s}^{-1}$ if the ratio of H^+ to NH_4^+ varied by $\pm 10\%$. Roughly spoken, this corresponds to an overestimation or underestimation of the total exchange in this season by 0.7 kg ha^{-1} .

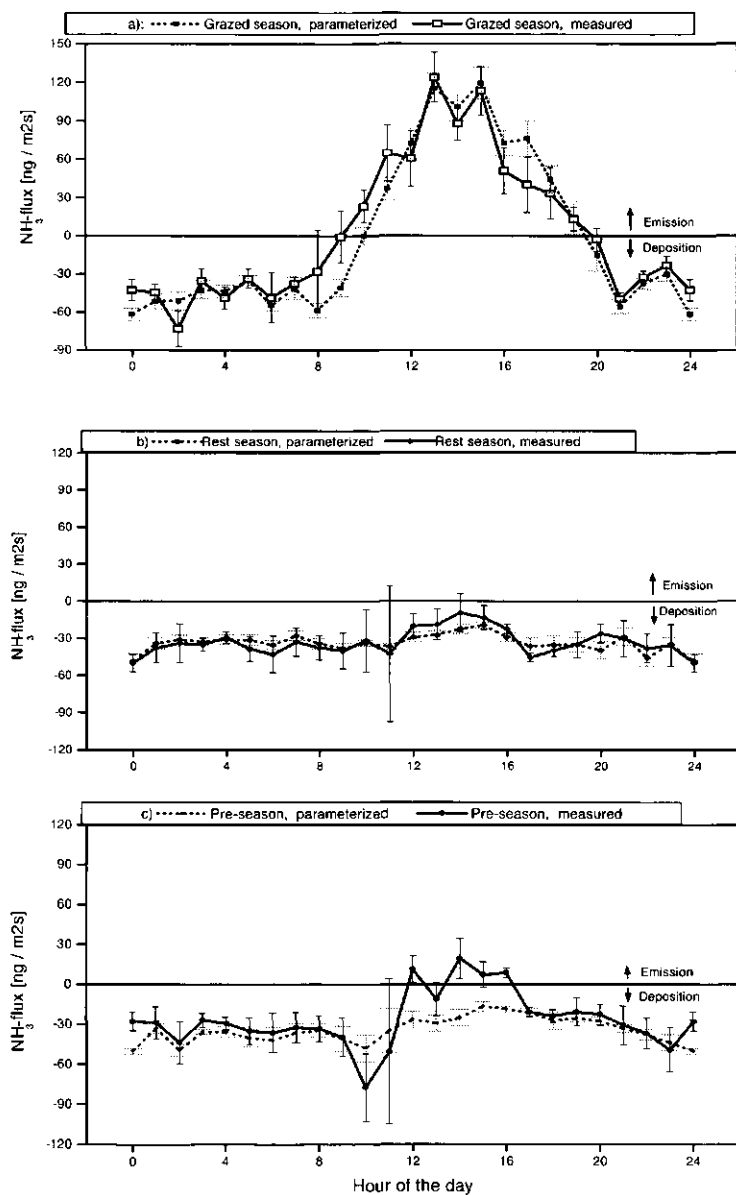


Fig. 9.1 Average diurnal patterns of parameterized and measured ammonia exchange at Zegveld, 1992-1994, in the grazed season, in the rest season and in the pre-season. Only days without recent slurry spreading. Error bars indicate ER_{SE} .

Evaluation of the performance of the model

Because long term average exchange fluxes have been used to derive the shown parameter values, the averages of the corresponding parameterized fluxes cannot be used to evaluate the performance of the ccp-model for derivation 'ab initio' of the exchange. However, in the fitting procedure the distribution of the fluxes over the day was not weighed directly, so that we can still evaluate the parameterization with respect to its description of the diurnal patterns. The average diurnal patterns of the measured and parameterized fluxes are shown in fig. 9.1. Error bars indicate the standard error of the mean.

Overall, the daily variations of emission and deposition are represented well. Only in the pre-season the emission in the afternoon is not predicted.

In practice emission in this period occurred only on a few days. The inaccuracy of the parameterization on these days may be due to overestimation of R_{st} by the Wesely parameterization in this season.

Alternatively, a higher ammonium content or pH in the apoplast than in the grazed season may play a role. The assumption of a stomatal compensation point that only varies with temperature, at a fixed (ratio of) apoplast pH and NH_4^+ concentration, is probably quite a simplification. In practice the pH and NH_4^+ concentration may vary, especially with growth stage and fertilization. This was confirmed by measurements by Schjørring and coworkers for other plant species (see also 1.4.5). Despite this simplification the ccp-model enables a quite good description of the mean diurnal flux pattern over this pasture in the grazed (=growth) season.

Because for most days in the pre-season, the parameterization in table 9.1 gave good results too, it was maintained without adaptations of the description of c_{ost} or R_{st} for this season.

Effects of variations of the thickness of water layers on the leaf surface are only incorporated in a very simplified way in the parameterization. Only a difference between 'dry' or 'wet' leaf surface is made; eventual saturation of the leaf surface is only accounted for implicitly, as far as it contributes to the higher mean value of R_{wet} under dry conditions. Re-emission from the leaf surface is not implemented in the model.

If such effects strongly influenced the measured diurnal emission/deposition pattern, the modelled flux would show an underestimation in the morning but an overestimation (too positive) in the evening. The comparison in fig. 9.1a (grazed season) indicates indeed some underestimation of the emission flux in the morning, but in the evening the estimate is good or slightly too low. This suggests that re-emission of deposited ammonia does not play a major role as already pointed out in chapter 6.

Based on the analyses in the same chapter, it was assumed that the net exchange is only slightly influenced by direct volatilization from fertilizer and excreta of grazing cattle.

Periods after fertilizer application and/or during and after grazing were not excluded from the selection from which the parameter values in table 9.1 were derived in 9.2.

This implies that eventual contributions of such direct volatilization to the exchange are included in the derived values of c_{0st} (and eventually in R_{wej}). However, the good performance of the ccp-model in describing the average diurnal flux pattern indicates that the emission is regulated largely by the stomatal resistance, which would not be the case for direct volatilization. This confirms again that direct volatilization from excreta and fertilizer probably plays a minor role compared to stomatal exchange.

The *indirect* influence of all treatments via uptake and stomatal emission by the grass is probably the main cause of the relatively high c_{0st} .

It can be concluded that with the derived values of the model parameters, both the total exchange and its average daily variation in periods without recent slurry spreading are estimated very well. This means that the ccp-model, with these parameter values, can be considered well suitable to describe the *regular pattern of exchange* at Zegveld. Therefore it can be used to estimate the contribution of this regular pattern to the total exchange if additional sources (slurry spreading) are involved (see next section).

More in general, this section demonstrates that the ccp-model is very promising as a basis for the description of the exchange with grazed pastures. As such it may provide an alternative for the simplified 'Big leaf' deposition parameterizations by which this exchange usually is described in transport models.

9.3 Influence of slurry spreading

Slurry spreading causes a shift in the diurnal flux patterns towards more positive fluxes, i.e. a larger net emission or weaker net deposition. Under these conditions the parameterized regular pattern must be corrected to find the actual exchange flux. Current volatilization percentages probably overestimate the volatilization after land treatments (chapter 7) and cannot be used as such to estimate the necessary correction. A better estimate of the volatilization percentage can be derived from analysis of the measured fluxes in periods with slurry spreading. However, as pointed out in 3.2.1, such an analysis must be based on long-term averages. If only occasional events of slurry spreading are studied, conditions are too variable to derive a representative average with the aerodynamic gradient technique. Also local advection may play too strong a role.

Therefore a comparison was made between the parameterized and measured fluxes for all measurements where an influence of slurry spreading was expected. In practice this concerns the data that were rejected for the parameterization of the regular diurnal

pattern described above. Of course only the data that had passed the criteria for reliable flux measurements were taken into account. The parameterized fluxes yield the exchange with the stomata and the leaf surface; the difference with the measured fluxes represents the effects of slurry spreading. Results are shown in figure 9.2 a and b (1992-1994) for the grazed season and pre-season. In the rest season no slurry spreading occurred and hence this period is not included in the figures.

First, these patterns can be compared to those for the days that were selected for absence of slurry spreading (figure 9.1). The measured fluxes are much more positive than in figure 9.1. As expected, this shift is not reproduced in the parameterized fluxes, as it is caused by the influence of slurry spreading which is not accounted for in the parameterization.

The total exchange fluxes of NH_3 after slurry spreading per season, derived from the parameterization and from the flux measurements, are summarized in table 9.2. For the pre-season only results for 1993 are shown, because in the pre-season of 1994 too few measurements with recent slurry spreading were available to derive a representative exchange value.

Table 9.2 Average values of parameterized and measured fluxes per season (in kg ha^{-1} of NH_3) at Zegveld in periods with recent slurry spreading.

	Pre-season	Grazed season	
	1993	1993	1992 to 1994
Measured	0.8 [0.3]	6.5 [0.7]	5.5 [0.5]
Parameterized	-2.1 [0.1]	0.0 [0.5]	0.1 [0.3]
Difference	2.9 [0.4]	6.5 [1.2]	5.4 [0.8]

The table confirms that the measured exchange flux is considerably higher (more emission) than predicted by the parameterization. The parameterization was derived for periods without influence of recent slurry spreading. So the difference with measured exchange must be attributed mainly to effects of this type of land treatment.

According to calculations described in chapter 7, summarized in fig. 7.2, the volatilization due to slurry spreading was about $22 \text{ kg ha}^{-1} \text{ NH}_3$ in 1993. About one half of this ($12 \text{ kg ha}^{-1} \text{ NH}_3$) occurred in the grazed season, the rest in the pre-season. These estimates of the volatilization from slurry application were calculated using volatilization percentages of 9% (band spreading) and 25% (broad fan). From table 9.2 it follows that these estimates and thus the applied volatilization percentages must be too high by a factor of about 2 (grazed season) to 3.5 (pre-season). Because the representa-

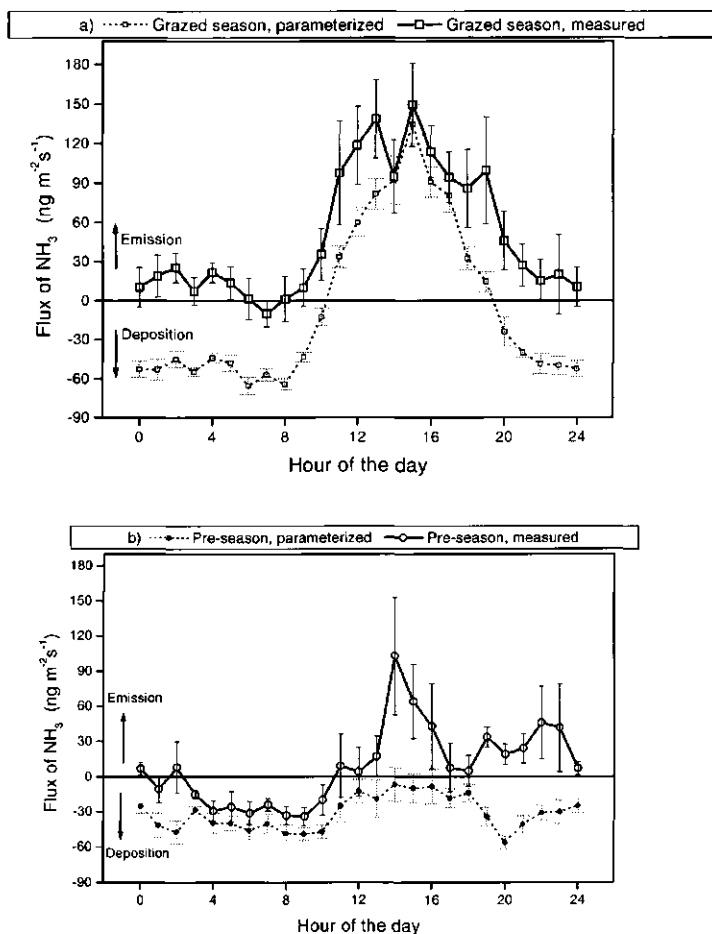


Fig. 9.2 Average diurnal patterns of parameterized and measured ammonia exchange at Zegveld, 1992-1994, in the grazed season (a) and in the pre-season (b). Only periods with expected influence of slurry application. Error bars indicate ER_{SE} .

tiveness of the measurements is less certain in the pre-season, a factor 2 seems to be a safe estimate. An overestimation of the exchange flux of the same order of magnitude is found if the comparison for the grazed season is extended to the period July 1992 - July

1994. The difference in table 9.2 for 1992-1994 ($5.4 \text{ kg ha}^{-1} \text{ NH}_3$) represents an average over the grazed seasons of each year. There were no relevant changes in farm management. Therefore the estimated volatilization due to slurry spreading per grazed season is about the same in each year: $12 \text{ kg ha}^{-1} \text{ NH}_3$. Hence corrected volatilization percentages are estimated at 5% for band spreading and 13% for conventional (fan) spreading.

In table 9.2, the standard errors of measured and parameterized exchange were added to find a maximum value in the difference. This leads to a (random) uncertainty of about 20% in the part of the exchange that might be attributed to volatilization from slurry.

It is hardly possible to estimate the possible bias in the parameterization that results from errors in the estimates of the individual model parameters. However, we expect the effect on the finally estimated total of the parameterized exchange to be small. This because the description of the regular diurnal pattern was quite good, and the parameters had been fitted to reproduce the total exchange in periods without slurry spreading, but with otherwise similar conditions and in the same season.

The possible bias in long term average fluxes due to the selection of reliable flux measurements was estimated at $\pm 25\%$ in chapter 4. It is assumed here that a similar value applies to the (sub)selection of periods with recent slurry spreading. Because measured and parameterized exchange in table 9.2 refer to the same subselection, the eventual selection bias in each of them will have the same direction. Therefore it is not likely that the selection bias in the difference between measured and parameterized exchange will exceed the bias in the measured flux.

Based on these considerations, the uncertainty in the contribution of slurry application to the total exchange is estimated to be of an order of 20-50%.

Overall, it is concluded here that the exchange with grazed pasture on peat soil can be parameterized successfully as a combination of deposition to the leaf surface and emission (or bi-directional exchange) by (with) the stomata. The farm management of the ROC is representative for this type of farms, hence it is expected that the ccp-model, with similar parameter values, is applicable to other grazed pastures on (acid) peat soil as well.

However, if slurry is spread over the pasture, a correction must be made to account for volatilization of ammonia from the slurry. This correction can be calculated from the N-supply involved in slurry spreading and a volatilization percentage of 5% (band spreading) or 13% (broad fan). The applicability of this parameterization and the low value of the volatilization percentage imply that currently used emission factors tend to be too high for this type of pasture on peat soil, although they may be just within the limit of uncertainty of this research.

Chapter 10

Conclusions

This experiment has provided two years of continuous data on surface exchange of ammonia over grazed grassland on peat soil. The availability of nitrogen to the pasture, including N from fertilizer, slurry and net-mineralization, was equivalent to a supply of about $300 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of fertilizer-N.

Fluxes could be measured with an uncertainty of about 30% in a typical flux measurement. Due to criteria necessary to select conditions under which fluxes can be measured reliably, a possible bias in long term total exchange values of about $\pm 25\%$ must be taken into account.

The terrain is a small net producer of ammonia ($4.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of NH_3). Clear seasonal and diurnal patterns of the net exchange could be derived, showing that emission dominates in the grazed season during daytime, while deposition dominates at night and in the ungrazed season.

Deposition of NH_3 proceeds mainly to the wet leaf surface, with high surface resistances of 35 to 105 s m^{-1} . The high surface resistances are probably due to accumulation of ammonium and a relatively high pH on the leaf surface.

A regular pattern of emission at daytime and deposition at night was observed for ammonia in the grazed season, even when no recent land treatment had occurred. Slurry spreading caused a general shift towards higher net emission and lower net deposition.

The regular alternation between deposition and emission in the grazed season could not be described solely by exchange with the leaf surface. Neither a compensation point approach nor descriptions of emission as a function of deposition in previous periods were suitable to describe the exchange as a process in which only the leaf surface is involved.

The main source behind the regular patterns of emissions at daytime is opening and closing of the stomata. The stomatal compensation point can be as high as $25\text{--}30 \text{ } \mu\text{g m}^{-3}$ NH_3 . Short-term influence of the soil after grazing or fertilizer application seems to be relatively weak; slurry spreading causes temporary deviations from the regular emission patterns.

Comparison of the measured exchange with estimates of emission from such terrain based on land-use and emission factors indicates that currently used volatilization percentages overestimate the emission by a factor two. If deposition to the same terrain is

accounted for by use of the procedures followed in the OPS model, the calculated annual flux approaches the measured net exchange flux, but this transport model assumes an unrealistically low surface resistance of 30 s m^{-1} , and thus overestimates deposition in the case of Zegveld.

Probably the volatilization from land treatments is overestimated for this type of soil, which could be related to the low soil pH of 4.8.

A parameterization based on combined exchange with the leaf surface and the stomata, developed by Sutton and Fowler (the canopy compensation point model), was fitted to the ammonia measurements over the pasture. This exercise confirmed that the stomatal compensation point is probably rather high (corresponding to about $19 \mu\text{g m}^{-3} \text{ NH}_3$ at 20°C). The parameterization was very well able to describe the regular diurnal pattern of the exchange at Zegveld. In case of slurry spreading, a correction must be made for volatilization of NH_3 due to slurry spreading. The currently used volatilization percentage for this type of land treatment may be too high by a factor of about two for this type of terrain (pasture on peat soil). This was derived from a comparison between the parameterized and measured exchange in periods after slurry spreading.

Evidence for co-deposition of SO_2 and NH_3 was found in seasonal differences of concentrations and surface resistances (and v_d) of both compounds. The surface resistance of NH_3 is higher and the surface resistance of SO_2 is lower in the grazed season compared to the rest season. The v_d of SO_2 is on average 1.14 cm s^{-1} , with representative R_c -values ranging between zero (-5) and 20 s m^{-1} . During frost, R_c -values were higher (up to 500 s m^{-1} , on average 40 s m^{-1}).

HNO_3 was found to deposit with a v_d of 3.4 cm s^{-1} , which is larger than allowed by aerodynamic resistance; the deposition velocity of NH_4NO_3 was only weak (0.12 cm s^{-1}). The extremely high value of v_d for HNO_3 as well as the frequently observed upward gradients of NH_4NO_3 are probably due to the reaction of emitted NH_3 with HNO_3 to form NH_4NO_3 . The gradients of ammonia were much larger on a molar basis than those of HNO_3 and NH_4NO_3 . Therefore measured NH_3 gradients were not biased significantly by these reactions. The HNO_3 gradients however become considerably larger (steeper) due to the reaction, giving an overestimation of v_d . The gradients of NH_4NO_3 become smaller and are sometimes even reversed, leading to an underestimation of v_d or apparent emission.

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Appendix A

Stomatal resistance from humidity profiles

The stomatal resistance to gaseous pollutants is usually derived from the stomatal resistance to water vapour R_{st, H_2O} . The stomatal resistance to water vapour can be estimated from evaporation measurements over vegetation, using a Big Leaf resistance model for bi-directional exchange (like eq. 2.37). The resistance depends on the water vapour flux (evaporation rate E) and the concentration difference of water vapour inside and outside the stomata:

$$R_{st, H_2O, bulk} = \frac{q_0 - q_{sat}(T_{leaf})}{E} \quad (A.1)$$

Inside the stomata, the water vapour concentration will be saturated for the leaf temperature [hence it is denoted as $q_{sat}(T_{leaf})$]. The leaf temperature can be approximated by T_0 , to be calculated from the measured heat flux and temperature at reference height:

$$T_0 = T(z) - \frac{H}{\rho_a C_p} [R_a(z) + R_{b, heat}] \quad (A.2)$$

(assuming that a negligible temperature gradient exist over the stomatal opening).

R_b for heat can be calculated from (see also 2.2.3):

$$R_{b, heat} = \frac{2}{k u_*} \quad (A.3)$$

Outside the stomata, the value of q is the value at the leaf surface (q_0 , at the entrance of the stomata); this can be estimated from:

$$q_0 = q(z) - E [R_a(z) + R_{b, H_2O}] \quad (A.4)$$

Appendix B

Overview of the ROC terrain

Figure B.1 and B.2 (next pages) give an impression of the terrain features in the wind direction 90-270 degrees. Only flux measurements with winds coming from these directions were accepted for analysis of exchange patterns.

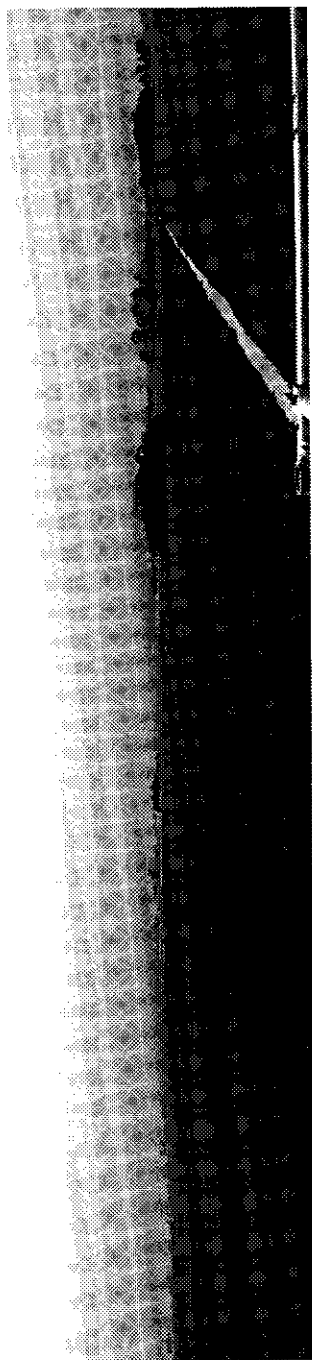


Fig. B.1 Overview of the ROC terrain in the directions 100-190 degrees upwind from the measurement site.

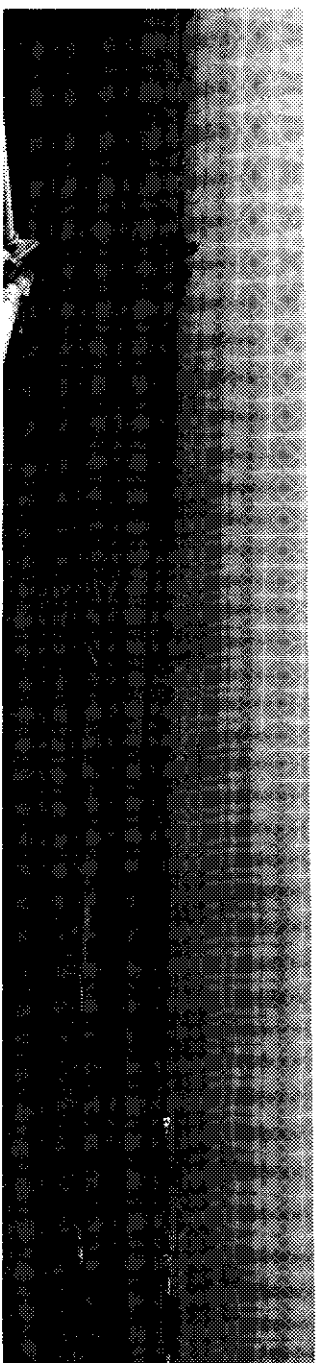


Fig. B.2 Overview of the ROC terrain in the directions 190-270 degrees upwind from the measurement site.

Appendix C

Estimation of the displacement height for the Zegveld pasture

Over vegetation, usually a certain displacement of the profiles relative to the zero plane (ground) occurs. As a result, the relation between wind speed (temperature, concentration etc.) and the natural logarithm of the stability corrected height is not exactly linear but shows a curvature. This effect is corrected for by the displacement height d in the flux-profile relations and in the calculation of R_a (cf. eqs. 2.21, 2.22, 2.28, 3.1).

Often the d -value for a terrain is parameterized as 0.6-0.8 times the vegetation height (and z_0 as 0.1 times the vegetation height (e.g., Brutsaert, 1975; Wieringa, 1993)). For Zegveld this would yield values of d varying between 4 and 20 cm, as grass height generally varied between about 6 and 25 cm. This variation is considerable, and is preferable to try to derive a typical d -value from the measurements themselves.

A common procedure to estimate the displacement height from measurements is to test different values of d until optimal linearity of the profile is achieved. Usually neutral conditions are chosen so that no uncertainty is introduced by stability corrections (and calculation procedures are much simpler). If at least three profile heights (e.g., of wind speed) are available, d -values can be solved by iteration from:

$$\frac{u(z_1) - u(z_2)}{u(z_1) - u(z_3)} = \frac{\ln(z_1 - d) - \ln(z_2 - d)}{\ln(z_1 - d) - \ln(z_3 - d)} \quad (\text{C.1})$$

(e.g., Monteith and Unsworth, 1990).

In practice, usually profiles of four or preferably even five or more heights are required to achieve reliable estimates of the displacement height. Otherwise random errors and relatively small biases in the measurements at the individual heights have too much influence on the derived d -value. This turned out to be also the case when d was calculated from profiles of wind speed measured at three heights at Zegveld. The derived displacement heights scattered considerably between small negative values and values of 50 cm and more. Classification per wind-direction or per season (grass height) did not reveal clear trends (except for rejected sectors with poor fetch). The d -values could not be derived from *temperature* profiles under neutral conditions, because then per definition differences between heights are small so that very small measurement

errors become very important. Extension of these analyses to measurements under non-neutral conditions (including stability corrections in eq. C.1 or in its equivalent for temperature) did not yield a dominating value of d either.

The measured *concentration* profiles were expected to be too uncertain for derivation of d because the profiles might be influenced by advection (NH_3 by AMANDA) or concentration changes during a measurement cycle (SO_2).

Because direct derivation from profiles yielded poor results, another approach was chosen to estimate a 'typical' d -value for Zegveld. In our flux calculations the displacement height is only necessary to correct the concentration profile in the calculation of c_* , because u_* and H (and hence L) were measured directly by eddy-correlation. Information on the required profile correction might therefore be derived from comparison of fluxes calculated by this procedure with directly measured (eddy-correlation) fluxes. The latter were not available for pollutants, but the sensible heat flux was measured directly by eddy-correlation and could also be calculated from (potential) temperature profiles over three heights and eddy-correlation u_* . In principle, the same applies to momentum flux and wind speed profiles. Generally the same d -value is used for momentum, heat and mass, but in practice differences in transfer mechanisms and main sinks (and sources) at the surface might cause differences in displacement heights. In that case, closer similarity may be expected between transfer (and d -values) for mass and heat than for mass and momentum. Therefore use of sensible heat fluxes and temperature profiles was preferred.

Values of θ_* were calculated from the measured temperature profiles for a range of d -values. In the stability corrections L from eddy-correlation was used. This θ_* was multiplied with C_p and ρ_a and with u_* from eddy-correlation to yield the sensible heat flux H_{prof} . These were compared with the values of H measured directly by eddy-correlation. Selection criteria were applied accounting for undisturbed fetch (WD 90 - 270°), no rain, no extreme (un)stability ($L > 5$ or $L < -10$); $U > 1 \text{ m s}^{-1}$. By regression analysis, the d -value that gave the best fit between the sensible heat fluxes via both methods was calculated. In this way a d -value of 16 cm was derived; a scatter plot between H_{prof} and H from eddy-correlation is given in fig. C.1. This value of 16 cm was finally used in the flux-profile relations in this thesis.

It should be considered, that the uncertainty in this d -value is quite large, mainly because H_{prof} is not very sensitive to this parameter. For d -values of 0 and 32 cm, H_{prof} would be calculated 10% higher and 16% lower, respectively ($R^2 = 0.82$). Fortunately, variation of d within these limits leads to an uncertainty in c_* of pollutants that is generally less than 10% (see 4.2.1).

If u_* is derived from profiles of wind speed and temperature, the use of a d -value of 16 cm also in the *wind speed profile* gives a quite good agreement with u_* from eddy-correlation (see 4.2.1). Therefore in the calculation of R_a (eq. 2.28) this value was applied both in Ψ_m and in Ψ_H .

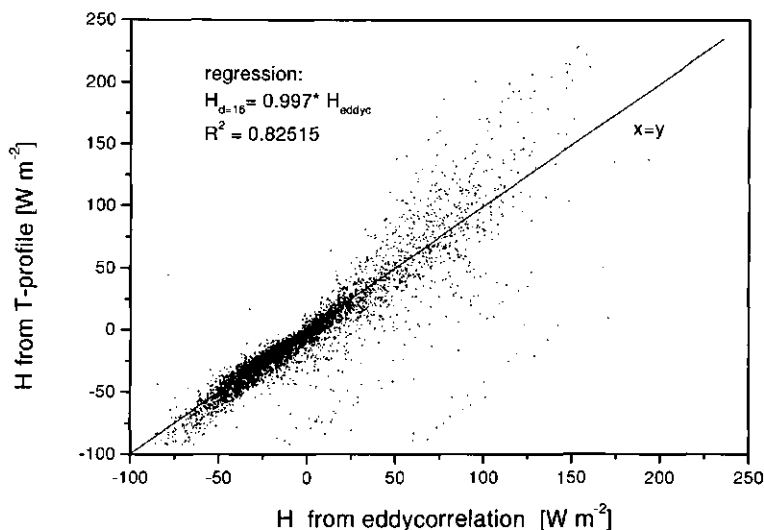


Fig. C.1 Comparison of sensible heat fluxes measured directly by eddy-correlation, with those calculated by combining u_* from eddy-correlation and θ_* from temperature profiles corrected with a displacement height of 16 cm (Zegveld, July-December 1993).

Appendix D

List of measured parameters and applied instruments

Table D.1 (next pages) gives a summary of parameters that were measured at Zegveld, and of the applied instruments. Also some features are given about measurement height and periods for which parameters are available or missing.

List of parameters measured at Zegveld, between 3 July 1992 and 7 July 1994.

Parameter	technique <i>Manufacture</i> (and type)	measurement heights	Time resolution	covered period	Availability: hourly measure- ments available in covered period (%)	Remarks	Major missing periods
Air temperature (T_{air}),	thermocouple (E-type) 0.003" Campbell Scientific (TCBR-3)	three: 1, 2.3 and 5m	20 minutes	03-07-92 to 07-07-94	>90%	2 heights (1 and 5m) until 27-10-92; After that in several short periods only 2 heights when one ther- mocouple was defect and during calibration ex- periments.	Less than 2 heights available; 18-02-92 to 08-03-92; and 16-12-93 to 11-01-94;
Soil temperature (T_{soil})	thermocouple (E-type) Campbell Scientific TCAV	avg of 0.02-0.08 cm below surface	20 minutes	03-07-92 to 07-07-94	>95%		18-02-92 to 08-03-92
Soil heat flux (G)	flux platelets (thermopile) Radiation and Energy Balance Systems (HFT 1)	0.10 cm below surface	20 minutes	03-07-92 to 07-07-94	>95%		18-02-92 to 08-03-92

List of parameters measured at Zegveld, between 3 July 1992 and 7 July 1994.

Parameter	technique <i>Manufacture</i> (and type)	measurement heights	Time resolution	covered period	Availability: hourly measure- ments available in covered period (%)	Remarks	Major missing periods
Horizontal wind speed (U_{cup})	cup anemometers <i>Vector</i> <i>Instruments</i> (A101 ML, R30 rotor (3 cups))	three 1.3, 2.6, and 5.3 m	20 minutes	03-07-92 to 07-07-94	>95% (includ- ing stalling periods)	Only two heights (1.3 and 5.3) until 27-10-92. Also two heights (1.3 and 2.6 m) during two calibration experiments	18-02-92 to 08-03-92
Dew point and abso- lute humidity (q) and relative humidity (RH)	dew point hygro- meter; <i>General Eastern</i> (Dew-10, modified by Campbell Scientific) q and RH derived from dewpoint and air temperature (thermocouples)	two: 1 and 5 m	20 minutes	03-07-92 to 03-04-94	With sufficient accuracy for humidity gra- dients: 50% Including approximate values (RH>95%): 70%	Short data gaps (<1-5 days) due to dirty mirror or condense in tubing. Longer data gaps due to sensor repairs. Only approximate values if RH > 95%	(longer than 5 days) 13-01-93 to 08-03-93 11-03-93 to 06-04-93 15-06-93 to 24-06-93 25-07-93 to 04-08-93 11-08-93 to 02-09-93 16-12-93 to 11-01-93 (1 height partly available) 18-02-94 to 28-02-94

List of parameters measured at Zegveld, between 3 July 1992 and 7 July 1994.

Parameter	technique <i>Manufacture</i> (and type)	measurement heights	Time resolution	covered period	Availability: hourly measure- ments available in covered period (%)	Remarks	Major missing periods
Wind direction	Wind vane <i>Vector</i> <i>Instruments</i> (W200P)	one: 5.3 m	20 minutes	03-07-93 to 07-07-94	> 90% (threshold wind speed not taken into account)	Less reliable below threshold wind speed of 1 m/s	18-02-92 to 08-03-92; 16-12-93 to 11-01-94
3-dimensional wind speed components (u, v, w) and 'sonic' (= 'virtual') air tem- perature (T_{sonic})	sonic anemometer <i>Applied</i> <i>Technologies</i> (SWS-211/3, k-probe, 15cm path length)	one: 2.6m, later 4.0m	0.1 second	03-07-92 to 17-01-94 and 19-04-94 to 07-07-94	≈ 70%	Unreliable during rain; preselection of data necessary. Repair of ATI sonic be- tween 17/01 and 19/04 of 1994. Measurements of other sonic (Solent, of SREMP system) might be used between 09/03 and 18/04.	

List of parameters measured at Zegveld, between 3 July 1992 and 7 July 1994.

Parameter	technique Manufacture (and type)	measurement heights	Time resolution	covered period	Availability: hourly measure- ments available in covered period (%)	Remarks	Major missing periods
Mean horizontal wind speed (U_{hor}), wind direction (WD), 'sonic' (= 'virtual') air temperature (T_{sonic}); friction velocity (u_*); eddy temperature scale and sensible heat flux (T , SH);	Calculated from fast sonic measurements of u , v , w and T	one: 2.6m, later 4.0m	20 minutes; later 10 minutes	03-07-92 to 17-01-94 and 19-04-94 to 07-07-94	$\approx 70\%$	Unreliable during rain; preselection of data necessary. Repair of ATI sonic be- tween 17/01 and 19/04 of 1994.	
Net radiation (long and short wave) (R_{net})	Net-radiometer (thermopile) REBS (Q'6)	one: 1.5m	20 minutes	03-07-93 to 07-07-94	$>95\%$		18-02-92 to 08-03-92
Global radiation (Q)	solarimeter Casella (W6500)	one: 1.5m	20 minutes	12-03-93 to 5-10-93	$>95\%$	before 12-03-93: values of nearby KNMI weather station (Cabauw). after 5-10-93 derived from $Q=2 \cdot \text{PAR}$	

List of parameters measured at Zegveld, between 3 July 1992 and 7 July 1994.

Parameter	technique <i>Manufacture</i> (and type)	measurement heights	Time resolution	covered period	Availability: hourly measure- ments available in covered period (%)	Remarks	Major missing periods
Photosynthesis active radiation (PAR)	par- radiometer <i>LICOR</i> (LI-190SA)	one: 1.5m	20 minutes	10-06-93 to 07-07-94	>95%		
Rain (occurrence)	rain sensor <i>ECN</i>	one: 0.75m	seconds of rain per 20 minutes	03-07-92 to 07-07-94	>90%	missing periods generally shorter than 2 days	
Fog (occurrence)	fog sensor <i>ECN</i>	one: 2 m	seconds of fog per 20 minutes	03-07-92 to 13-03-94	>80%, but interference by cobwebs not accounted for	frequent interference by cob-webs	09-03-93 to 31-03-93 12-10-93 to 02-11-93
NH ₃ concentration	thermo-denuder <i>ECN</i> NO _x monitor: <i>TECAN</i> (CLD 700 AL)	two: 1 and 5m	20 minutes per cycle of one hour	03-07-92 to 07-07-94	60 % reliable gradients; (78 % concentra- tions of 1 or 2 heights includ- ing >25 µg/m ³)	unreliable gradients at concentrations > 25 µg/m ³ .	06-08-93 to 26-08-93 (no or only one height) 27-09-93 to 05-10-93

List of parameters measured at Zegveld, between 3 July 1992 and 7 July 1994.

Parameter	technique Manufacture (and type)	measurement heights	Time resolution	covered period	Availability: hourly measure- ments available in covered period (%)	Remarks	Major missing periods
NH ₄ NO ₃ and HNO ₃ concentration	thermo-denuder ECN Same NO _x -monitor as for NH ₃	two: 1 and 5 m	48 min. per cycle of 2 hours	01-04-93 to 07-07-94	about 40%, but individual mea- surements less reliable for gradient interpretation.	Measurements were easily affected by very humid air and fog. Also measured between 03-07-92 and 01-04-93, but instruments were still being developed then and tubes were not interchanged regularly.	29-09-93 to 05-10-93
NH ₃ concentration	continuous flow denuder ECN (AMANDA)	three: 1 m, 2.3 m and 5 m	6 minutes (2 min per cy- cle of 6 min)	21-06-93 to 24-10-93 and 23-12-93 to 10-04-94	Reliable gra- dients: about 60%; (2 or 3 heights); (66% at least one height)	No measurements during frost periods; until 08-09-93 high concentrations "cut off" (upper limit between about 13 and 25 µg/m ³) due to auto-range pro- blems	23-07-93 to 28-07-93; 14-02-94 to 25-02-94 (frost); 25-02-94 to 02-03-94.

Table E. 1 Compensation point values reported in the literature

Reference	Species	Compensation points [$\mu\text{g m}^{-3} \text{NH}_3$]	Apoplast [NH_4^+] (in mM) and pH	Type of measure- ments
Husted and Schjørring, 1995	Oilseed Rape (<i>Brassica Napus</i>)	from pH and NH_4^+ : 3.1-4.1 From measured fluxes.: 3.7 $\pm$ 2.5	pH: 5.8 NH_4^+ : 1.1 to 1.3	growth chambers
Husted <i>et al.</i> 1996	Barley	<0.7 - 4.5; dependent on cultivar and growth stage	-	growth chambers
Husted and Schjørring, 1996	Oilseed rape	From measured fluxes: 0.3 - 5.4, (at 25°) increasing with N-supply; varying with growth stage. Comp. point is strongly dependent on temperature in accordance with NH_4 equilibria. Comp. point from pH and NH_4^+ : 0.3- 4.6	Mean pH: 5.7 $\pm$ 0.1 Independ-ent of N-status and plant ontogeny NH_4^+ : 0.3 - 2.0 increasing with N-supply, also dependent on growth stage	Growth chamber
Harper <i>et al.</i> 1996; (see also Bussink <i>et al.</i> 1996)	Ryegrass (fertilized)	14 seasonal average crop compensation point	-	Field (micromet.)
Yamulki <i>et al.</i> 1996	Wheat	3-4	-	Field (micromet.)

Table E. 1 Compensation point values reported in the literature

Reference	Species	Compensation points [$\mu\text{g m}^{-3} \text{NH}_3$]	Apoplast [NH_4^+] (in mM) and pH	Type of measure- ments
Schjørring <i>et al.</i> 1998	Heather Wavy Hair Grass (<i>Deschampsia</i> <i>Flexuosa</i>)	<0.07 early in season- (8°) 4.2 later in season (22°), (corresp. to 0.6 at 8°!) 2.1 at 24° (~0.31 at 8°)		Growth Chamber

Curriculum Vitae

Marcus Antonius Hendricus Gertruda Plantaz werd geboren op 9 augustus 1961 te Maastricht. Hij bezocht de lagere school (Sint Martinus) in het dorpje Gronsveld. In 1979 behaalde hij zijn VWO-diploma (atheneum-b) aan het Stedelijk Lyceum en HAVO te Maastricht. In september van dat jaar startte hij zijn studie Milieuhygiëne aan de Landbouwwuniversiteit Wageningen. Zijn doctoraal-programma ('oude stijl') omvatte de twee hoofdvakken Bodemverontreiniging en Luchtverontreiniging, en een extra vak Agrarisch recht (milieurecht). Zijn stages voor beide hoofdvakken doorliep hij respectievelijk bij de Provincie Limburg te Maastricht en bij DSM te Geleen. In september 1988 rondde hij deze studie af met het doctoraaldiploma.

Tussen die datum en januari 1990 werkte hij ongeveer 10 maanden bij de Vakgroep Luchthygiëne en -verontreiniging, in diverse projecten en functies. Ook behaalde hij in augustus 1989 zijn propaedeuse Nederlands recht aan de Rijksuniversiteit te Utrecht. Vanaf januari 1990 tot juli 1994 was hij als promovendus in dienst bij ECN, voor het verrichten van het hier beschreven onderzoek. Tussen september 1997 en heden heeft hij gedurende ongeveer 6 maanden gewerkt aan verschillende projecten bij de DCMR Milieudienst Rijnmond te Schiedam.