

Review and parameterisation of bi-directional ammonia exchange between vegetation and the atmosphere

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Abstract. Current deposition schemes used in atmospheric chemical transport models do not generally account for bi-directional exchange of ammonia (NH_3). Bi-directional exchange schemes, which have so far been applied at the plot scale, can be included in transport models, but need to be parameterised with appropriate values of the ground layer compensation point (χ_g), stomatal compensation point (χ_s) and cuticular resistance (R_w). We review existing measurements of χ_g , χ_s as well as R_w and compile a comprehensive dataset from which we then propose generalised parameterisations. χ_s is related to Γ_s , the non-dimensional ratio of $[\text{NH}_4^+]_{\text{apo}}$ and $[\text{H}^+]_{\text{apo}}$ in the apoplast, through the temperature dependence of the combined Henry and dissociation equilibrium. The meta-analysis suggests that the nitrogen (N) input is the main driver of the apoplastic and bulk leaf concentrations of ammonium ($\text{NH}_4^+_{\text{apo}}$, $\text{NH}_4^+_{\text{bulk}}$). For managed ecosystems, the main source of N is fertilisation which is reflected in a peak value of χ_s a few days following application, but also alters seasonal values of $\text{NH}_4^+_{\text{apo}}$ and $\text{NH}_4^+_{\text{bulk}}$. We propose a parameterisation for χ_s which includes peak values as a function of amount and type of fertiliser application which gradually decreases to a background value. The background χ_s is based on total N input to the ecosystem as a yearly fertiliser application and N deposition (N_{dep}). For non-managed ecosystems, χ_s is parameterised based solely on the link with N_{dep} .

For R_w we propose a general parameterisation as a function of atmospheric relative humidity (RH), incorporating a minimum value ($R_{w(\text{min})}$), which depends on the ratio of atmospheric acid concentrations (SO_2 , HNO_3 and HCl) to

NH_3 concentrations. The parameterisations are based mainly on datasets from temperate locations in northern Europe making them most suitable for up-scaling in these regions (EMEP model for example). In principle, the parameterisations should be applicable to other climates, though there is a need for more underpinning data, with the uncertainties being especially large for tropical and subtropical conditions.

1 Introduction

Ammonia (NH_3) is a major atmospheric acid-neutralising agent that plays an important role in aerosol formation (Finlayson-Pitts and Pitts, 1999). Aerosols impact on human health, decrease visibility, and affect atmospheric radiative forcing (Adams et al., 2001; Ramanathan et al., 2007). Once deposited, NH_3 contributes to soil acidification and species and habitat loss due to excess nutrient loading (Sutton et al., 1993c; Krupa, 2003; Sutton et al., 2009c). Biological processes in soils enriched by reduced nitrogen (NH_x) can lead to emissions of NH_3 , NO_x and also of nitrous oxide (N_2O), a greenhouse gas (Mosier et al., 1998). The use of NH_x as a fertiliser in agriculture has dramatically increased over the past century and the trend is expected to continue with an increasing demand for biofuels and to simply meet the nutritional requirements of an increasing global population (Galloway et al., 2003; Erisman et al., 2008). The impacts of human activity on the nitrogen cycle have prompted active research into the parameterisation of NH_3 emissions and deposition in air quality models for determining sound regulatory scenarios for human exposure to particulates, ecosystem nutritive loading and climate change (Sutton et al., 2008).



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Direct flux measurements over the past 20 years have shown that vegetation can be a source or a sink of atmospheric NH_3 (e.g., Farquhar et al., 1980; Sutton et al., 1995b). The direction and magnitude of the exchange depends on the concentration gradient between the canopy and the atmosphere. The canopy compensation point (χ_c) is the atmospheric NH_3 concentration for which the flux between the surface and the atmosphere switches from emission to deposition (or vice versa) (Farquhar et al., 1980). χ_c is the net effect of different exchange pathways with the ecosystem and includes contributions from the plant (stomata and cuticle), leaf litter and soil (Sutton et al., 1995b). The cuticles are mainly a sink for NH_3 (van Hove et al., 1989). As ammonia is soluble, it can deposit rapidly to leaf cuticles (Sutton et al., 1993a; Duyzer, 1994), though cuticular uptake tends to saturate at high atmospheric NH_3 concentrations (Jones et al., 2007b), and can be enhanced in the presence of atmospheric acids (van Hove et al., 1989; Erisman and Wyers, 1993; Nemitz et al., 2001). The consequence is that the resistance for NH_3 deposition to plant surfaces are controlled by many factors including the availability of moisture, leaf area and atmospheric chemistry. It should be noted that cuticular emissions can also occur as a consequence of desorption when leaf water layers dry out (Flechard et al., 1999). This tends to be a transient process which cannot be sustained over long periods. By contrast, the stomatal flux is typically bi-directional, depending on the concentration gradient of NH_3 between the sub-stomatal cavity (stomatal compensation point: χ_s) and the canopy air. χ_s is the NH_3 air concentration in the leaf sub-stomatal cavity that is in equilibrium with ammonium ($[\text{NH}_4^+]_{\text{apo}}$) concentrations in the apoplast (Farquhar et al., 1980; Schjoerring et al., 1998a). It can be calculated from the ratio of apoplastic $[\text{NH}_4^+]_{\text{apo}}$ to $[\text{H}^+]_{\text{apo}}$ concentrations (the emission potential Γ_s), corrected by a thermodynamic temperature function (Nemitz et al., 2001). Γ_s depends on the plant nitrogen (N) metabolism as well as influxes and outfluxes of various N forms to the leaf (Massad et al., 2008). Its value therefore depends strongly on land-use and management as well as growth stage throughout the season (Riedo et al., 2002).

Despite the recognition of these dynamics with leaf tissues and surfaces, current deposition schemes used in regional and global models tend to be rather simplified and out of date. For example, in many models such as CHIMERE (Vautard et al., 2001) or CMAQ (Byun and Schere, 2006), dry deposition of NH_3 is calculated according to the parameterisation scheme of Wesley (1989) or related approaches. This is based on look-up tables of the deposition velocity ($V_d = \text{flux}/\text{atmospheric concentration}$) and canopy resistance components (R_c) for different ecosystems and climatic/seasonal conditions. It does not account for bi-directional exchange and there is no dependence of cuticular NH_3 uptake on leaf wetness (except for fully wet canopies).

The testing of bi-directional exchange schemes in transport models is rather limited (Sorteberg and Hov, 1996;

Vieno, 2006). Recent improvements in the understanding of the underlying processes involved in vegetation-atmosphere NH_3 exchange thus need to be included in regional and global models. Efforts are being made to derive a generalised parameterisation for bi-directional exchange of NH_3 to be included in chemistry and transport models: Zhang et al. (2010) in AURAMS (A Unified Regional Air-quality Modelling System, developed by Environment Canada) and Cooter and Bash (2009) in CMAQ (Community Multiscale Air-Quality Modeling System, developed by the US Environmental Protection Agency). This is essential as a basis for surface-atmosphere exchange modules to respond to changes in climate, chemical composition and vegetation status, as well as to evaluate the success of air pollution mitigation strategies (Sutton et al., 2003; Bleeker et al., 2009). The Unified EMEP model (Simpson et al., 2003, 2006) is the reference atmospheric dispersion model used in supporting the development of air quality policies under the EU Commission. Along with other large-scale models, the EMEP model generally under-estimates NH_3 concentrations, especially close to source areas (e.g., van Pul et al., 2009). This is likely due to an inability to resolve large vertical gradients of NH_3 near source areas, as well as the lack of a bi-directional approach as discussed in this study. It should be noted that over forested areas the EMEP model has been found to over-estimate NH_3 concentrations in one study (Simpson et al., 2006).

In this paper, we first review recent progress in elucidating the mechanisms driving the air-surface exchange of ammonia at the plot scale, as represented in existing bi-directional exchange modelling approaches. Here, the key parameterisations, specific to NH_3 , needed by these models are those of Γ_s and χ_s , as well as the resistance to NH_3 deposition to the leaf cuticle (R_w). We then compile data from existing measurements, highlighting current understanding of the physical, chemical and biological processes that control surface/atmosphere exchange. Finally, based on the measurements reviewed, we propose a new operational parameterisation for integrating bi-directional NH_3 exchange into chemical transport models and earth system models.

2 Review of existing modelling approaches

Field-scale NH_3 exchange models that account for bi-directional stomatal exchange and cuticular deposition were developed and adapted in a number of applications (e.g., Sutton and Fowler, 1993; Sutton et al., 1995b; Sutton et al., 1998b; Nemitz et al., 2001). In the single-layer (or ‘big-leaf’) version of these models (Fig. 1a), plant-atmosphere exchange of NH_3 is governed by two main parallel pathways: deposition to leaf surfaces and bi-directional exchange with the leaf apoplast through the stomata. A two-layer model can be developed by adding NH_3 exchange with the soil surface (Fig. 1b) (Nemitz et al., 2001). A multi-layer model

including soil emissions together with different layers in the plant canopy (inflorescences, bottom senescing leaves, etc.) has also been developed (Nemitz et al., 2000b). While this may be useful for assessing cycling processes in specific canopies at the plot scale, the multi-layer model requires a very large number of parameters and therefore represents a higher degree of complexity than is merited for integration into large scale models considering several ecosystem types.

Exchange of NH_3 with the soil is most important after fertilisation, but may also be important for barren land and in highly senescent plant canopies where leaf litter on the soil surface contributes to emissions (e.g. Nemitz et al., 2000a; Sutton et al., 2009a). Currently, ammonia emissions from leaf litter, though understood in principle, remain very uncertain due to the limited number of studies (Sarwar et al., 2005; David et al., 2009). For short semi-natural vegetation and agricultural vegetation during the growth stage, any soil emissions are expected to be largely recaptured by the overlying canopy (cf. Nemitz et al., 2000a). This is different in drier desert climates or for recently cut vegetation (Personne et al., 2009; Sutton et al., 2009a). In this work we focus on reviewing and deriving generalised parameterisations for the two-layer model, although, it is not always possible to include the soil/litter surface layer which requires further assessment before it can be incorporated into the model in all situations. Coupling a suitable litter decomposition module to canopy level ammonia exchange represents a future priority (Sutton et al., 2009a).

In order for a two layer model to be applied at large scales, generalised parameterisation of the resistances (R_a , R_b , R_{ac} , R_{bg} , R_s and R_w) as well as the stomatal (χ_s) and the ground layer (χ_g) compensation points are required. The two-layer model simplifies into the single-layer model if the in-canopy resistance (R_g) is set to infinity. Detailed parameterisations of atmospheric and in-canopy resistances are given in Sects. 4.2 and 4.3.

2.1 Stomatal resistance (R_s)

The stomatal resistance also governs the exchange of water, CO_2 and O_3 and has been well researched and tabulated (e.g., Jarvis, 1976; Wang and Leuning, 1998; Dewar, 2002). If values derived for other gases are applied for NH_3 , they need to be adjusted for differences in the molecular diffusivity:

$$R_{s\text{NH}_3} = R_{sx} \times \frac{D_x}{D_{\text{NH}_3}} \quad (1)$$

where R_{sx} and D_x are the stomatal resistance and diffusivity in air of the derived gas, respectively. D_{NH_3} varies with temperature and can be determined from the equation proposed by Massman (1998) at 1 atm atmospheric pressure where T is the temperature in $^\circ\text{K}$:

$$D_{\text{NH}_3}(T) = 0.1987 \times \left(\frac{T}{273.13} \right)^{1.81} \quad (2)$$

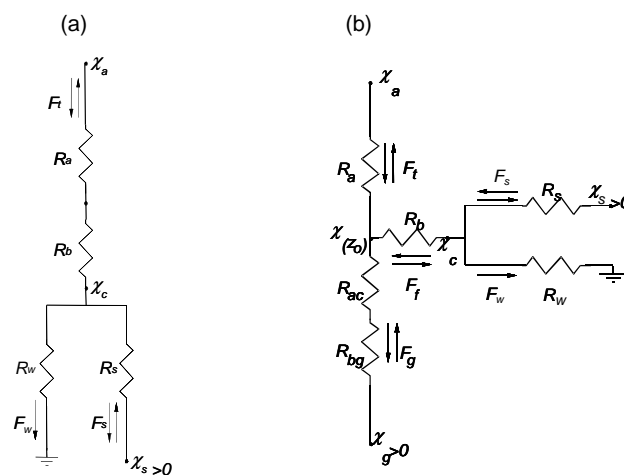


Fig. 1. Big leaf (a) and two layer (b) resistance scheme for bi-directional NH_3 exchange between the vegetation and the atmosphere from Sutton et al. (1995b). F_i , F_s , F_w and F_g are the total, stomatal, cuticular and ground layer fluxes of NH_3 respectively; R_a , R_b , R_w , R_s , R_{ac} and R_{bg} are the aerodynamic, leaf boundary layer, cuticular, stomatal, in canopy aerodynamic and ground boundary layer resistances to exchange; χ_a is the atmospheric NH_3 concentration; χ_c , χ_s and χ_g are the canopy, stomatal and ground layer NH_3 compensation points respectively.

2.2 Cuticular resistance (R_w)

The cuticular resistance is one of the key parameters in modelling bi-directional NH_3 exchange and cannot be derived from parameterisations for other chemical species. It is mainly influenced by the wetness of the surface and its pH (van Hove et al., 1989; Sutton et al., 1995a; Wyers and Erismann, 1998). A simple dynamic model of ammonia adsorption and desorption with the cuticular water pool was developed by Sutton et al. (1998a), which was dependent on specifying set leaf surface pH, as may be established from dew chemistry measurements. Flechard et al. (1999) extended this concept to develop a more detailed mechanistic approach that accounts for inorganic chemistry interactions on the leaf surface, using a chemical model to simulate the temporal pH dynamics in response to the air concentration and simultaneous exchange of several trace gases, aerosols and wet deposition. Although such dynamic models can successfully simulate NH_3 fluxes at the plot scale (e.g. Neiryneck and Ceulemans, 2008; Burkhardt et al., 2009), they require excessive computing time to be integrated in large scale models, such as chemical transport or deposition models (e.g., requiring many iterations, short time-steps and a large number of input parameters). Simpler empirical approaches are therefore needed, such as that investigated by Wichink-Kruit et al. (2010) who examined the potential for a non-zero cuticular concentration to depend on atmospheric ammonia concentrations.

Exchange of ammonia between plant cuticles and the atmosphere depends on the amount of atmospheric acids present and, in particular, on the thickness and chemical composition of the leaf-surface water-layer. A frequent simplification in models is to assume that the ammonia concentration at the leaf surface is zero, thereby defining a resistance for cuticular deposition (R_w), for transfer between the canopy air space (represented by χ_c) and the leaf surface (Sutton and Fowler, 1993; Sutton et al., 1995a; Nemitz et al., 2001). Although there is no way to measure R_w directly, it can be derived from night-time measurements. In this approach, it is assumed that stomata are effectively closed at night so that stomatal exchange is negligible (van Hove et al., 1989), and R_w can be approximated by the bulk canopy resistance (R_c) (Sutton et al., 1995b; Wyers and Erisman, 1998; Spindler et al., 2001).

R_w estimated during night-time by this approach is reported to have a clear relationship to surface relative humidity (RH), because invisible water films form on leaf cuticles, stems and other non-stomatal surfaces in the canopy, and their thickness is controlled by RH (van Hove and Adema, 1996). These water layers provide efficient sinks for atmospheric NH_3 (Sutton et al., 1995b; Flechard et al., 1999). Other factors that have been reported to affect R_w include the following:

- Interactions with acid gases. Rates of ammonia dry deposition to leaf surfaces can be enhanced or suppressed by the presence of acid or basic agents, respectively. Thus, while the deposition of ammonia leads to alkalisation of the leaf surface, simultaneous deposition of SO_2 would neutralise the deposited NH_3 . The specific interaction between ammonia and SO_2 is well known and has been termed “co-deposition”, the idea being that the presence of both NH_3 and SO_2 would tend to decrease R_w and increase the deposition rate for both gases (van Hove et al., 1987; Erisman and Wyers, 1993; Sutton et al., 1994; Fowler et al., 2009). Co-deposition of SO_2 and NH_3 was suspected in some field experiments (Flechard and Fowler, 1998; Wyers and Erisman, 1998). Firm field evidence has always proven difficult to obtain because of the interaction of several factors influencing NH_3 fluxes (RH, stomatal flux, etc.), even with the observation that SO_2 rich acidic plumes can deplete NH_3 concentration promoting NH_3 emissions (Sutton et al., 1994). However, the synergistic effect of SO_2 and NH_3 in promoting deposition has been successfully modelled (Flechard et al., 1999; Burkhardt et al., 2009) and implied through the comparison of field observations (Nemitz et al., 2001). The co-deposition effect of SO_2 on NH_3 deposition has been implemented in the EMEP model as the reciprocal of the effect of NH_3 co-deposition on SO_2 deposition, which can be seen in field measurements (H. Fagerli et al., personal communication, 2010; Fowler et al., 2009). It should

be noted that leaf surface chemistry can also be influenced by the deposition of other atmospheric acids such as HCl or HNO_3 , which, following the decline of SO_2 emissions make an increasingly large relative contribution to the acid loading, at least in Europe and North America.

- Very high concentrations of ammonia. It has been known for a long time that very high concentrations of ammonia tend to saturate leaf cuticular water pools, potentially reducing deposition velocities, because under these conditions the neutralising effect of the acids becomes negligible (Sommer and Jensen, 1991; Sutton et al., 1993c). However, until recently there were few data specifically generated to quantify the dependence of R_w on atmospheric ammonia concentrations. Jones et al. (2007a, b) studied this phenomenon over a wide concentration range and reported an increase in R_w with increasing NH_3 concentration in the atmosphere for a range of heathland species.
- Temperature. Temperature is one of the major controllers of NH_3 gaseous exchange. Temperature affects NH_3 thermodynamics via the $\text{NH}_3/\text{NH}_4^+$ dissociation equilibria and the Henry constant (Farquhar et al., 1980; Nemitz et al., 2001). Temperature also plays a role via its effect on RH especially through the relationship of R_w on RH. A more explicit way of seeing this effect is by looking at R_w as a function of vapour pressure deficit (VPD) instead of RH (e.g., Nemitz et al., 2004). Recently, Flechard et al. (2010) derived a parameterisation of R_w as a function of both RH and temperature for measurements made over a grassland in Switzerland, with an exponential increase of R_w with surface temperature for non-freezing conditions.
- Leaf surface area and properties. The effective leaf surface area on which NH_3 can be deposited influences R_w . The leaf area index (LAI) was accounted for in parameterisation of R_w by Zhang et al. (2003). Different leaf surface characteristics also affect R_w and might be the explanation for differences between different plant species. Rudich et al. (2000) discuss the dependence of the formation, growth and fate of water films on organic surfaces on the chemical composition and corrugation degree of the surface. For example, Klemm et al. (2002) and Wichink-Kruit et al. (2008) show that water stays longer on grass leaves compared with forest leaves. Furthermore, water film development on leaf surfaces is influenced by salts and solutes originating from atmospheric deposition of aerosols and other gases, as well as by cuticular leaching and the deposition of calcareous soil particles (Sutton et al., 1993c; Burkhardt et al., 2009).

Table 1. Compiled data of R_w as a function of RH¹.

Type	Specifications	$R_{w(\min)}$ s m ⁻¹	a	conditions	[NH ₃] _{atm} μg m ⁻³	LAI <i>one sided</i> m ² m ⁻²	Average temperature °C	Reference	Total acid/NH ₃ ² molar ratio	Reference	
1	arable	oilseed rape	0.93	0.369		1.03	6.5	15	(Nemitz et al., 2001)	1.79	(Sutton et al., 2000)
2	arable	Soybean	172	0	wet	5.5	6	30	(Walker et al., 2006)	0.57	(Walker et al., 2006)
3	arable	Soybean	230	0	dry	5.5	6	30	(Walker et al., 2006)	0.57	(Walker et al., 2006)
4	arable	wheat	5	0.143		3.09	4	10	(Sutton et al., 1996a)	0.73	EMEP model ³
5	arable	wheat	2	0.083		3.5	3	8	(Sutton and Fowler, 1993)	1.96	(Sutton et al., 1995a)
6	forest	conifers	3.2	0.050	NH ₃ /SO ₂ > 5	2.3	3	15	(Neiryck and Ceulemans, 2008)	3.48	(Neiryck et al., 2007)
7	forest	conifers	24	0.020	1 < NH ₃ /SO ₂ < 5	4	3	15	(Neiryck and Ceulemans, 2008)	1.40	(Neiryck et al., 2007)
8	forest	conifers	71	0.010	NH ₃ /SO ₂ < 1	4.2	3	15	(Neiryck and Ceulemans, 2008)	0.82	(Neiryck et al., 2007)
9	forest	Douglas Fir	26	0.029	1994	4.5	4	12	(Wyers and Erisman, 1998)	0.99	(Wyers and Erisman, 1998)
10	forest	Douglas Fir	9.1	0.050	1993	5.6	4	11	(Wyers and Erisman, 1998)	0.84	(Wyers and Erisman, 1998)
11	grassland	agricultural	30	0.143		5	3	15	(Personne et al., 2009)	0.19	(Sutton et al., 2009b)
12	grassland	agricultural	5	0.143		1.9	2	15	(Milford et al., 2001b)	0.55	(Milford et al., 2001b)
13	grassland	agricultural	20	0.008		3	2	10	(Fowler et al., 2007)	0.16	UK monitoring network
14	grassland	agricultural	10	0.110		3.13	2	10	(Flechard et al., 2010)	0.44	(Flechard et al., 2010)
15	grassland	semi-natural	30	0.143		3.23	2	11	(Sutton et al., 1997)	0.38	(Sutton et al., 1997)
16	grassland	semi-natural	1	0.074	summer	1.45	0.75	20	(Horvath et al., 2005)	0.63	(Horvath et al., 2005)
17	grassland	semi-natural	30	0.369	winter	1.84	2	8	(Horvath et al., 2005)	0.67	(Horvath et al., 2005)
18	grassland	semi-natural	1	0.209	autumn	2.62	3.5	10	(Horvath et al., 2005)	0.43	(Horvath et al., 2005)
19	grassland	semi-natural	1	0.381	spring	3.02	4	12	(Horvath et al., 2005)	0.30	(Horvath et al., 2005)
20	semi-natural	dry heathland	19	0.048		5.2	2.5	15	(Nemitz et al., 2004)	0.39	(Nemitz et al., 2004)
21	semi-natural	dry heathland	24	0.069	RH < 81.3%	5.2	2.5	15	(Erisman et al., 1994)	0.71	EMEP model ³
21	semi-natural	dry heathland	1	0.278	RH > 81.3%	5.2	2.5	15	(Erisman et al., 1994)	0.71	EMEP model ³
22	semi-natural	bog heathland	0.5	0.083		0.26	2.5	11	(Milford et al., 2001a)	1.41	UK monitoring network
23	semi-natural	bog heathland	20	0.045		0.95	2	12	(Flechard et al., 1999)	1.80	(Flechard et al., 1999)

¹ $R_{w \min}$ and a are parameters of the following equation for R_w as a function of RH: $R_w = R_{w(\min)} \times \exp^{a(100-RH)}$.

² Total acid/NH₃ ratio (AR) is calculated using the following equation where concentrations are in M: total acid/NH₃(AR)=(2[SO₂]+[HNO₃⁻]+[HCl])/[NH₃].

³ EMEP modelled concentrations were obtained from the model run for the year the measurements were conducted in (1990) and for the grid where the measurement site is situated (Simpson et al. 2003, 2006).

The parameterisations found in the literature for R_w are generally an exponential curve function of relative humidity having the following form:

$$R_w = R_{w(\min)} \times e^{a \times (100-RH)} \quad (3)$$

where $R_{w(\min)}$ is the minimum cuticular resistance in s m⁻¹, RH is the relative humidity in % and a is an empirical factor (Sutton and Fowler, 1993).

Table 1 summarises 22 different functions of R_w for various ecosystem types proposed in the literature.

$R_{w(\min)}$ was previously found to decrease with increasing SO₂ to NH₃ ratio in the atmosphere (Nemitz et al., 2001), whereas a is expected to increase with a decrease in plant surface hygroscopicity and aerosol deposition and thus change with plant species. We therefore choose to subdivide ecosystem types for R_w parameterisation as a function of leaf characteristics. Consistent with the detail of land-cover information typically available to atmospheric transport models, we distinguish the four following ecosystem types: forests, arable crops, short semi-natural (mostly heathlands) and grassland (managed and unmanaged).

The major factors reported to affect R_w are temperature, relative humidity and co-deposition with acidic compounds. Sulphur dioxide (SO₂) was the main acidic gas in the atmosphere in the 1980's. Major efforts for reducing emissions were successful (Fowler et al., 2005) and now it is important to consider HCl, HNO₃ and SO₂ together when accounting for acid gases. Flechard et al. (2010) suggest an effect

of temperature (average study reported temperature) on R_w while Zhang et al. (2003) suggest an effect of LAI (one-sided – m² m⁻²). We combine the two equations of Flechard et al. (2010) and Zhang et al. (2003) into equation 4 below and apply it to correct R_w :

$$R_{w(\text{corr})} = \frac{R_w \times e^{0.15 \times T}}{(LAI)^{0.5}} \quad (4)$$

$R_{w(\text{corr})}$ is the corrected cuticular resistance and R_w the cuticular resistance as reported by the literature in s m⁻¹. Figure 2 shows the different $R_{w(\text{corr})}$ curves as a function of RH at height $d+z_0$. We note the important scatter in the dataset and no clear relationship either between R_w and RH or R_w and the acid ratio. One of the reasons for this might be the use of water vapour and NH₃ concentrations at a height z_0 instead of leaf level which could be significantly different. This information however was not available for all the collected dataset and we therefore chose to consider measurements done at z_0 for consistency. We also note that R_w curves as a function of RH are in general flatter for forests than other types of ecosystems particularly for conifers. This might be the result of the needle shape and waxy surface of the leaves that would retain less water at high relative humidity than other types of plants and therefore have a higher R_w . This highlights the importance of accounting for leaf surface characteristics while studying R_w .

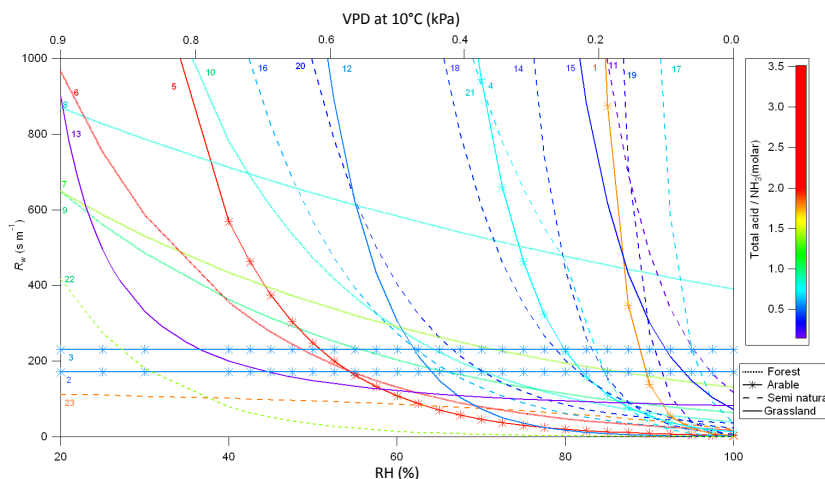


Fig. 2. Compilation of cuticular resistance ($R_{w(\text{corr})}$) as a function of relative humidity (RH) at height z_0 separated according to ecosystem type. Dotted lines represent forest ecosystems, short dashed lines represent short semi-natural ecosystems, solid lines represent grasslands and star marked lines represent arable crops. The top x-axis represents the corresponding vapour pressure deficit (VPD) for the primary x-axis at a temperature of 10°C . Different colours represent the corresponding molar ratio of total acid/ NH_3 (AR). Numbers correspond to Table 1.

2.3 Stomatal compensation point (χ_s)

The stomatal compensation point (χ_s) is expected to be dependent on the nitrogen status of the plant, which in return is related to the influx of N based compounds (N fertilisation or atmospheric deposition) (Mattsson et al., 1998; van Hove et al., 2002). χ_s is further influenced by the developmental stage and may peak at senescence (Francis et al., 1997; Hill et al., 2002; Mattsson and Schjoerring, 2003). Several attempts have been made to model the dynamics of χ_s mechanistically, for example in relation to environmental conditions, agricultural practices, plant metabolism and/or exchange with the atmosphere (Riedo et al., 2002; Wu et al., 2009; Massad et al., 2010). While N input is likely to be the first order driver, values of χ_s have been found to differ significantly between different plant species growing in the same sward (Mattsson et al., 2009b). Our understanding of the plant physiological controls of χ_s is still too rudimentary to explain this inter-species variability.

One of the major challenges in quantifying vegetation-atmosphere fluxes of NH_3 is the measurement of χ_s . Three methods were developed so far that allow its estimation.

1. *Micrometeorological flux measurements.* Inference of the stomatal compensation point from fluxes over large fields and concentrations in the atmosphere (e.g., Flechard, 1998; Spindler et al., 2001). This technique allows estimation of χ_c for conditions where the flux is zero (e.g., flux changing in time from deposition to emission or *vice versa*). In situations where R_w is thought to be very large (e.g., dry canopy, low relative humidity) and R_s and the flux are small, χ_c will approach χ_s . In other studies, χ_s values have been de-

rived by fitting diurnal cycles of the modelled flux to measured values, based on prior parameterisation of R_w (Sutton and Fowler, 1993; Sutton et al., 1995b; Sutton et al., 1998a).

2. *Controlled gas exchange measurements.* Calculation of χ_c for plants enclosed in a cuvette by varying the NH_3 concentration at the entrance of the cuvette and finding the concentration at which the total flux is zero (e.g., Farquhar et al., 1980; Husted and Schjoerring, 1995a; Schjoerring et al., 1998a; Hill et al., 2001). Measurements are typically made during light conditions with open stomata and low RH (large R_w). However, fluxes measured in the dark in this approach can also be used to estimate the role of cuticular exchange. Errors related to chamber measurements include separation of the cuticular and stomatal fluxes and the calculation of total resistance to NH_3 exchange (calculation of R_a and R_b) within the cuvette, especially at higher RH (Massad et al., 2009).
3. *Apoplastic extraction.* Direct determination of leaf apoplastic $[\text{NH}_4^+]_{\text{apo}}$ concentration and pH by means of extraction of the apoplastic fluid with successive vacuum infiltration and centrifugation of leaf segments (Husted and Schjoerring, 1995b). This technique has been applied to several plant species in the field (Husted et al., 2000a; Herrmann et al., 2009; Mattsson et al., 2009a; Mattsson et al., 2009b). However, the extraction technique is subject to uncertainties regarding potential regulation of apoplastic pH and $[\text{NH}_4^+]_{\text{apo}}$ by the plant during the extraction, buffering effects and potential local gradients of pH and $[\text{NH}_4^+]_{\text{apo}}$ in the apoplast

but also inter-species gradients of χ_s (Hill et al., 2001; Loubet et al., 2002; Schjoerring et al., 2002, Sutton et al., 2009a). Systemic differences between apoplast extraction and the gas exchange techniques were reported (Hill et al., 2001, Massad et al., 2009), these are attributed to errors in both methods and should be further investigated.

The ratio of $[\text{NH}_4^+]_{\text{apop}}$ to $[\text{H}^+]_{\text{apop}}$ concentration in the apoplast (Γ_s), can be calculated from extraction measurements as well as from flux measurements. The equation relating χ_s to Γ_s according to Nemitz et al. (2001) is:

$$\chi_s = \frac{161\,500}{T_l} \times 10^{\frac{-10\,380}{T_l}} \times \Gamma_s \quad (5)$$

where T_l is the leaf temperature. Γ_s therefore represents a useful parameter for comparison between the three estimation techniques, as it is unitless and temperature independent (from a chemical thermodynamic perspective). Γ_s reflects the physiological state of the vegetation, while χ_s also depends on meteorological parameters (temperature). For this reason we base our parameterisation on values of Γ_s directly rather than on χ_s .

2.4 Ground layer compensation point (χ_g)

Similar to the leaf apoplast solution, the equilibrium between gaseous NH_3 in the soil pore space and NH_4^+ in the soil solution establishes a soil compensation point (χ_g) (Nemitz et al., 2001). A soil emission potential (Γ_g) can be calculated from χ_g using the same approach as in leaf apoplast or by applying Eq. (5). The ground layer compensation point can be attributed to the litter or to the soil, or both. There are few reported measurements of ground layer emission potentials (Γ_g) especially for bare soils and litter. Nemitz et al. (2001) modelled the litter emission potential based on measurements of $[\text{NH}_4^+]/[\text{H}^+]$ ratio in bulk tissue extracts and on the mineralization and nitrification rates to simulate the NH_3 cycling within an oilseed rape canopy. Concerning the soil emission potential, one should differentiate between fertilised and non-fertilised soils. Unfertilised soils have seldom been shown to have a Γ_g larger than Γ_s (Schjoerring et al., 1993; Sutton et al., 1993b; Nemitz et al., 2000a), whereas fertilised soils have very high emission potentials especially in the days following fertiliser application. These include direct emissions from the mineral or organic fertilisers. Nemitz et al. (2000b) report measurements over a wheat stubble estimating a Γ_g value of 630 which corresponds to the ratio of $[\text{NH}_4^+]$ to $[\text{H}^+]$ measured in the soil solution. Numerous models exist that account for the physico-chemical processes controlling NH_3 emission from fertilisers and their interactions with the soil (e.g. Générumont and Cellier, 1997; Cooter et al., 2010) and are being integrated into atmospheric transport models (Cooter et al., 2010).

A recent comparison of Γ values for different plant and soil compartments in a managed cut grassland showed val-

ues ranging over four orders of magnitude, with the smallest values being for Γ_s (Sutton et al., 2009a). That analysis indicated that, following cutting, when litter elements are exposed and well connected to the atmosphere, Γ_{litter} would be a better descriptor of net exchange than Γ_s , warranting further efforts into the parameterisation of litter dynamics.

3 Review of compensation point published datasets

Table 2 summarises 60 values of Γ_s for non-managed ecosystem types (short semi-natural and forest) ranging between 3 and 5604, with a mean of 502 and a median of 190, while Table 3 summarises 96 values of Γ_s for managed ecosystems (arable and grassland) outside fertilisation events ranging between 16 and 5233, with a mean of 782 and a median of 416. The highest Γ_s value was derived for a forest ecosystem whereas the lowest value corresponds to non-managed grassland. However, Sutton et al. (1997) report a Γ_s value of 10 000 for a managed grassland, which occurred two weeks after a fertilisation event. The surprisingly high Γ_s value for the forest ecosystem is attributed to Wyers and Erisman (1998). This value was probably subject to a contribution from cuticular desorption rather than just reflecting stomatal emission, consistent with more recent interpretations by Neiryck and Ceulmans (2008) over a similar forest. This value apart, the highest Γ_s is reported for arable crops. For the compiled data, none of the three measurement methods gave a tendency towards higher or lower values compared with the other. However, the gas exchange measurements seem to give higher Γ_s values for semi-natural vegetation but this is probably due to measurements being done in high N input semi-natural ecosystems. Figure 3 presents the assembled data relative to each ecosystem type: arable (mainly wheat, barley, oilseed rape and maize), grassland (managed), short semi-natural vegetation (unmanaged grassland, heathland, etc.) and forest. Data are also grouped according to measurement technique.

Elevated values of Γ_s have been derived for Dutch and Belgian semi-natural ecosystems, which are subject to considerable N deposition, and fertilised vegetation tends to have larger values of Γ_s than non-fertilised vegetation. This confirms that the likely key factor affecting Γ_s appears to be the N input to the ecosystem, and this is also consistent with existing ecosystem models that attempt to predict Γ_s . The N input is dominated by atmospheric deposition of reactive nitrogen (N_{dep}) in natural ecosystems surrounded by highly polluted areas (Sutton et al., 1994; Dijk et al., 2009) or N fertilisation in agricultural ecosystems (Mattsson and Schjoerring, 1996; Mattsson et al., 2009a). Field fertiliser application results in a peak in Γ_s in the days following the application and usually returns to the pre-fertilisation value one to two weeks later depending on meteorological conditions (Milford et al., 2001b; Mattsson and Schjoerring, 2002).

Table 2. Compiled data of Γ_s values for unmanaged ecosystem types.

Type	Species	X_s ppb	Γ_s	$[\text{NH}_4^+]_{\text{bulk}}$ $\mu\text{mol g}^{-1}$ FW	Temp. $^{\circ}\text{C}$	N input $\text{kg ha}^{-1} \text{yr}^{-1}$	N status source	Equi. N fertiliser $\text{kg ha}^{-1} \text{yr}^{-1}$	Growth stage	Growth condition	Meas. tech.	Ref.
forest	Spruce	0.27±0.16	27±16		~20	13.56	EMEP			field	ext.	12
forest	Spruce	0.43±0.13	61±34		~20	27.60	EMEP	no fertilisation		field	ext. & curv.	24
forest	Mixed pine	0.80	141		3–22	6.30	meas.	no fertilisation		field	micromet	26
forest	Spruce	0.72±0.58	290±102		1–12	16.41	EMEP	no fertilisation		field	micromet	1
forest	Beech	3.00	373		20–17	23.71	EMEP	0.5 mM NH_4^+ + 1 mM NO_3^-		g-house	curv.	8
forest	Beech	3.50±1.70	616±299		~20	23.71	EMEP	no fertilisation		g-house	curv.	8
forest	loblolly pine	13.2	1300		~20	14.00	meas.	no fertilisation		field	micromet	36
forest	Mixed coniferous	23.7	2338±1925		~20	35.00	meas.	no fertilisation		field	micromet	39
forest	Coniferous	31.9±26.30	5604±4628		~20	49.40	meas.	no fertilisation		field	micromet	54
s. natural	Luzula sylvatica	0.51	3	3.41	> 10°C	3.74	b. tissue	2 kg N ha ⁻¹ y ⁻¹ NH_4NO_3		vegetative	ext. & curv.	16
s. natural	Luzula sylvatica	0.60±0.20	3±20	3.22	> 10°C	3.59	b. tissue	100 kg N ha ⁻¹ y ⁻¹ NH_4^+		vegetative	ext. & curv.	16
s. natural	Luzula sylvatica	0.70±0.40	4±40	4.93	> 10°C	4.91	b. tissue	2 kg N ha ⁻¹ y ⁻¹ NH_4^+		vegetative	ext. & curv.	16
s. natural	Luzula sylvatica	0.59	5	2.84	> 10°C	3.27	b. tissue	50 kg N ha ⁻¹ y ⁻¹ NH_4NO_3		vegetative	ext. & curv.	16
s. natural	Arrhen. Elatius	0.04±0.59	7±104		18–12		b. tissue	0.4g N kg ⁻¹ soil		vegetative	ext. & curv.	10
s. natural	Luzula sylvatica	0.60±0.10	10±10	4.17	> 10°C	4.34	b. tissue	20 kg N ha ⁻¹ y ⁻¹ NH_4^+		vegetative	ext. & curv.	16
s. natural	Calluna vulgaris	0.10±0.00	14		~15		b. tissue	no fertilisation		g-house	curv.	43
s. natural	Luzula sylvatica	0.57	15	2.84	> 10°C	3.27	b. tissue	100 kg N ha ⁻¹ y ⁻¹ NH_4NO_3		vegetative	ext. & curv.	16
s. natural	Luzula sylvatica	0.94±0.09	21±9	6.56	> 10°C	6.07	b. tissue	200 kg N ha ⁻¹ y ⁻¹ NH_4NO_3		vegetative	ext. & curv.	16
s. natural	Luzula sylvatica	0.64	24	2.77	> 10°C	3.21	b. tissue	20 kg N ha ⁻¹ y ⁻¹ NH_4NO_3		vegetative	ext. & curv.	16
s. natural	Echinochloa crus-galli	0.14±0.14	25±25		15–20		b. tissue	medium N status		vegetative	ext.	29
s. natural	Triplet. inodorum	0.14±0.14	25±25		15–20		b. tissue	medium N status		g-house	ext. & curv.	29
s. natural	Luzula sylvatica	0.70±0.10	25±10	5.87	> 10°C	5.60	b. tissue	50 kg N ha ⁻¹ y ⁻¹ NH_4^+		g-house	ext. & curv.	16
s. natural	headland	0.16±0.01	50±2		9–23	7.14	EMEP	no fertilisation		field	micromet	34
s. natural	Bromus erectus	0.32±0.58	56±102		18–12	4.25	meas.	0.4g N kg ⁻¹ soil		vegetative	ext. & curv.	10
s. natural	tropical pasture	0.65±0.40	64±69		20–25	10.87	b. tissue	no fertilisation		field	micromet	51
s. natural	Lolium perenne	5.00	78±19		~20		b. tissue	3 mM NH_4^+		vegetative	ext. & curv.	32
s. natural	Luzula sylvatica	1.10±0.10	8±10	14.40	> 10°C	9.12	b. tissue	200 kg N ha ⁻¹ y ⁻¹ NH_4^+		vegetative	ext. & curv.	16
s. natural	Bromus erectus	6.80	8±40	12.60	~20	9.84	b. tissue	3 mM NO_3^-		vegetative	ext. & curv.	32
s. natural	Calluna vulgaris	0.58±0.29	102±253		8–18	9.13	EMEP	no fertilisation		field	curv.	22
s. natural	Lolium perenne	5.80	105±25	9.00	~20	7.68	b. tissue	3 mM NO_3^-		hydr.	ext. & curv.	32
s. natural	Calluna vulgaris	0.05	109		~2	12.58	EMEP	no fertilisation		field	micromet	49
s. natural	Arrhen. Elatius	0.78±0.95	137±168		18–12		b. tissue	1.6 mM NO_3^- + 1.6 mM NH_4^+		hydr.	ext. & curv.	10
s. natural	Arrhen. Elatius	0.85±0.47	149±83		18–12		b. tissue	1.6 mM NO_3^- + 1.6 mM NH_4^+		hydr.	ext. & curv.	10
s. natural	Arrhen. Elatius	0.95±0.41	166±72		18–12		b. tissue	1.6 mM NO_3^- + 1.6 mM NH_4^+		hydr.	ext. & curv.	10
s. natural	Bromus erectus	9.00	179±76	23.40	~20	15.56	b. tissue	3 mM NH_4^+		hydr.	ext. & curv.	32
s. natural	moorland	1.82	180		0–14	9.55	EMEP	no fertilisation		field	micromet	6
s. natural	Mixed	1.14±0.60	200±300		~20	9.20	meas.	no fertilisation		field	micromet	17
s. natural	Chenopodium album	1.29±0.29	228±51		17–20		meas.	medium N status		g-house	ext.	29
s. natural	Solanum nigrum	1.29±0.14	228±25		15–20		meas.	medium N status		g-house	ext.	29
s. natural	tropical pasture	2.50±1.50	247±296		30–36	4.25	meas.	medium N status		field	micromet	51
s. natural	Bromus erectus	1.44±0.71	253±125		18–12		b. tissue	1.6 mM NO_3^- + 1.6 mM NH_4^+		hydr.	curv.	10
s. natural	Arrhen. Elatius	1.44±1.31	253±230		18–12		b. tissue	1.6 mM NO_3^-		hydr.	ext. & curv.	10
s. natural	Bromus erectus	1.46±1.02	256±180		18–12		b. tissue	1.6 mM NO_3^-		hydr.	ext. & curv.	10
s. natural	Bromus erectus	1.47±0.71	259±124		18–12		b. tissue	1.6 mM NO_3^-		hydr.	ext. & curv.	10
s. natural	Bromus erectus	1.76±0.48	310±84		18–12		b. tissue	1.6 mM NO_3^- + 1.6 mM NH_4^+		hydr.	ext. & curv.	10
s. natural	Deschampsia flexuosa	3.00±1.10	332±122		~19		b. tissue	no fertilisation		g-house	curv.	43
s. natural	Lolium perenne	1.19	339±76	52.20	~20	28.18	b. tissue	6 mM NH_4^+		hydr.	ext. & curv.	32
s. natural	headland	1.44±	460		3–23	40.03	EMEP	no fertilisation		field	micromet	3
s. natural	Eriophorum vaginatum	6.90±4.00	510		~23	12.58	EMEP	no fertilisation		field	micromet	50
s. natural	Lolium perenne	2.85±2.15	564±851		~15	17.00	EMEP	no fertilisation		field	micromet	45

Table 2. Continued.

Type	Species	χ_s ppb	Γ_s	$[\text{NH}_4^+]_{\text{bulk}}$ $\mu\text{mol g}^{-1}$ FW	Temp. $^{\circ}\text{C}$	N input $\text{kg ha}^{-1} \text{yr}^{-1}$	N status	Equi. N fertiliser $\text{kg ha}^{-1} \text{yr}^{-1}$	Growth stage	Growth condition	Meas. tech.	Ref.
s. natural	Calluna vulgaris	5.30 ± 1.80	739 ± 251		~ 15		no fertilisation		2 years	g-house	cuv.	43
s. natural	Mixed	4.50 ± 3.00	792 ± 528		~ 15	22.07	no fertilisation	EMEP		field	micromet	15
s. natural	Calluna vulgaris	6.20 ± 2.00	864 ± 279		~ 15		no fertilisation		2 years	g-house	cuv.	43
s. natural	Agropyron repens	5.00 ± 1.00	880 ± 352		~ 18		no fertilisation			field	micromet	27
s. natural	Bromus erectus	18.3	1167 ± 256	77.40	~ 20	37.71	12 mM NH_4^+	b. tissue	vegetative	hydr.	ext. & cuv.	32
s. natural	heathland	12.1	1200		~ 20	33.41	no fertilisation	EMEP		field	micromet	38
s. natural	blanket bog	7.20	1267		~ 15		no fertilisation			field	micromet	46
s. natural	dry heathland	8.15 ± 7.70	1434 ± 1355		~ 15	33.41	no fertilisation	EMEP		field	micromet	55
s. natural	Luzula sylvatica	10.9	1918		~ 15		no fertilisation			field	cuv.	47
s. natural	dry heathland	16.7 ± 7.70	2930 ± 1355		~ 15	33.41	no fertilisation	EMEP		field	micromet	55

s. natural: short semi-natural; b. tissue: bulk tissue extracts; meas.: measured; g. house: grown in a glass house; hydr.: grown in hydroponics; cuv.: cuvette measurement technique; ext.: extraction measurement technique; micromet.: micrometeorological measurement technique.

(1) Andersen et al 1999; (3) Duyzer, 1994; (6) Flechard et al 1998; (8) Gessler et al., 2000; (10) Hanstein et al., 1999; (12) Hartmann, 2005; (15) Hesterberg et al 1996; (16) Hill et al., 2001; (17) Horvath et al 2005; (22) Jones et al 2007; (24) Kesselmeier et al., 1993; (26) Langford and Fehsenfeld, 1992; (27) Lemon and Van Houtte, 1980; (29) Manderscheid et al., 2005; (32) Mattsson and Schjoerring, 2002; (34) Milford et al., 2001; (36) Neiryck & Ceulemans 2008; (38) Nemitz et al., 2004; (39) Nemitz et al., unpublished; (43) Schjoerring et al. (1998b); (45) Spindler et al., 2001; (46) Sutton et al. (1996a); (47) Sutton et al. (1996b); (49) Sutton et al., 1992; (50) Sutton et al., 1993a; (51) Trebs et al., 2005; (54) Wöyers and Erisman, 1998; (55) Erisman et al., 1994.

Measurements further suggest that Γ_s is affected by the plant's stage of growth. This is especially true for agricultural crops where senescent and mature leaves have a high potential for NH_3 emission (Mattsson and Schjoerring, 2003). In grassland ecosystems cutting as well as grazing are reported to affect Γ_c . Due to additional remobilisation from urine and dung, grazing can be considered as an additional N source for the grassland as regards ammonia emission. By contrast, cutting seems to affect Γ_c because it (i) prevents the recapture of NH_3 emitted from the litter (Sutton et al., 2009a), (ii) exposes the litter to higher temperatures (David et al., 2009; Personne et al., 2009; Sutton et al., 2009a) and (iii) alters the metabolism of the plant, possibly affecting emissions through injuries to the leaves (Milford et al., 2009) and reducing consumption of substrate N into structural N in the plant (Riedo et al., 2002).

3.1 Relationship between Γ_s and bulk foliar ammonium concentrations

Given the complexity of determining Γ_s from bioassays (Husted and Schjoerring, 1996; Hill et al., 2001; Massad et al., 2009), there is significant interest in using bulk foliar $[\text{NH}_4^+]$ concentration ($[\text{NH}_4^+]_{\text{bulk}}$) as a simpler proxy bioassay of the compensation point. Bulk tissue $[\text{NH}_4^+]$ is easier to measure than apoplastic $[\text{NH}_4^+]_{\text{apo}}$ and may be an easier way to estimate NH_3 exchange between the vegetation and the atmosphere. Mattsson et al. (2009b) found a linear relationship between $[\text{NH}_4^+]_{\text{bulk}}$ and Γ_s across grass species growing within a single sward. The larger dataset compiled here allows the relationship between Γ_s and $[\text{NH}_4^+]_{\text{bulk}}$ to be assessed more comprehensively. Figure 4a shows the data for managed ecosystem types. Using the full range of data, there appears to be an exponential rather than a linear relationship between the two variables, where Γ_s tends to increase much more than $[\text{NH}_4^+]_{\text{bulk}}$. This can be explained by the biological regulation of cytoplasmic $[\text{NH}_4^+]$ which is well buffered as compared to physical and chemical regulation of apoplastic $[\text{NH}_4^+]$ (Nielsen and Schjoerring, 1998). The exponential fitted equation to these data is:

$$\Gamma_s = 19.3 \times e^{(0.0506 \times [\text{NH}_4^+]_{\text{bulk}})} \quad (6)$$

where $[\text{NH}_4^+]_{\text{bulk}}$ is in $\mu\text{g g}^{-1}$ tissue fresh weight and Γ_s is unitless. The difference between the linear regression proposed by Mattsson et al. (2009b) and the exponential equation proposed in this study can partly be explained by the difference in landuse type. The Mattsson et al. (2009b) data is for grasslands whereas the fitted equation in this study is derived for both arable land and grassland data; with grassland data being more scattered and corresponding to lower $[\text{NH}_4^+]_{\text{bulk}}$.

For semi-natural vegetation there are far fewer direct paired measurements of Γ_s and $[\text{NH}_4^+]_{\text{bulk}}$ (Fig. 4b). However, Pitcairn et al. (2004) proposed a relationship between

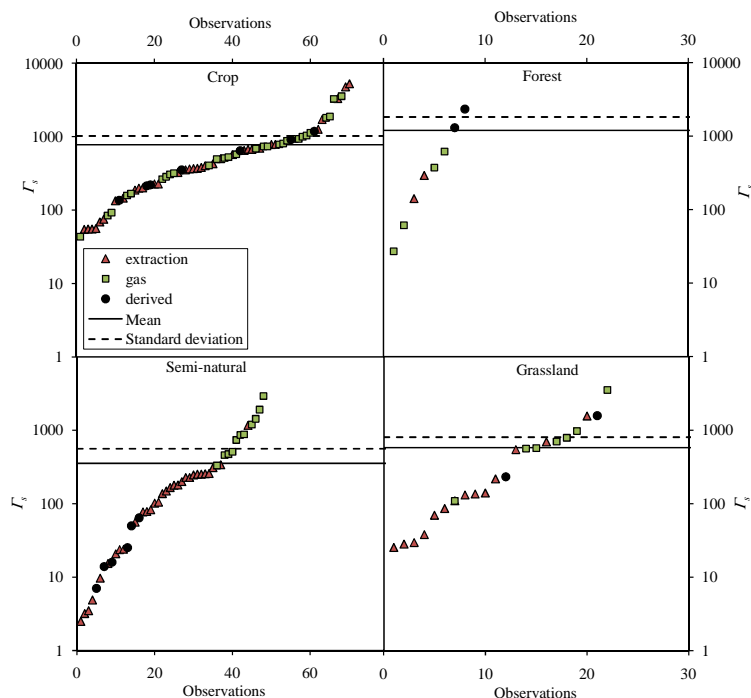


Fig. 3. Summary of stomatal ammonia emission potential (Γ_s) from different studies (see Tables 2 and 3) as reported in the literature (means or single measurements) separated according to ecosystem type. Round symbols represent values derived from modelling, triangles represent values measured by the apoplast extraction technique and squares represent values measured by the gas exchange method. Full lines represent the mean and dashed lines the standard deviation around the mean per ecosystem type.

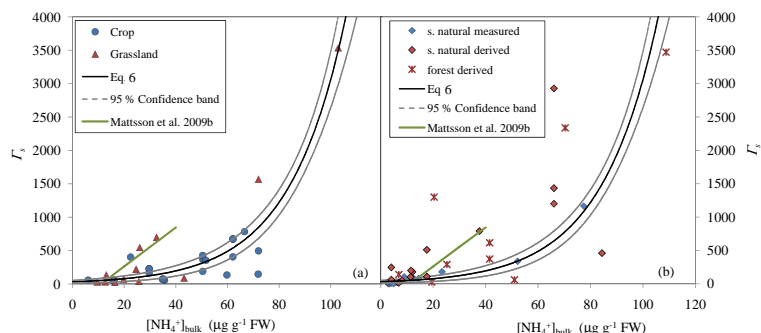


Fig. 4. (a) Compiled stomatal ammonia emission potential (Γ_s) for managed ecosystem types as a function of measured bulk tissue $[\text{NH}_4^+]_{\text{bulk}}$ concentrations. Round symbols represent arable crops and triangle symbols represent grasslands. The black line is the best fit exponential curve derived by minimisation of the least square method and the dashed line is the 95% confidence band. The green line is the linear function previously derived by Mattsson et al. (2009b) between Γ_s and $[\text{NH}_4^+]_{\text{bulk}}$ for different grass species. (b) Compiled stomatal ammonia emission potential (Γ_s) for un-managed ecosystem types as a function of bulk tissue $[\text{NH}_4^+]_{\text{bulk}}$ concentrations. Red symbols represent $[\text{NH}_4^+]_{\text{bulk}}$ derived from N deposition values according to Eq. (7) while blue symbols represent measured concentrations. Asterisks represent forests and diamonds represent short semi-natural ecosystem types. The full, dashed and green lines are similar to (a).

$[\text{NH}_4^+]_{\text{bulk}}$ and total N deposition, which may be inverted to estimate $[\text{NH}_4^+]_{\text{bulk}}$ for additional measurements, for which an N deposition estimate is available:

$$N_{\text{dep}} = 1.51 \times ([\text{NH}_4^+]_{\text{bulk}})^{0.739} \quad (7)$$

Here, N_{dep} is the total atmospheric N deposition in $\text{kg ha}^{-1} \text{yr}^{-1}$ and $[\text{NH}_4^+]_{\text{bulk}}$ is in $\mu\text{g g}^{-1}$ tissue fresh weight. These additional, derived data have been added to Fig. 4b to see how they compare to managed ecosystems. This figure shows estimated and measured $[\text{NH}_4^+]_{\text{bulk}}$ for unmanaged ecosystems as a function of Γ_s . We note that although there is

a larger uncertainty in $[\text{NH}_4^+]_{\text{bulk}}$ estimates coming from both N_{dep} values and applying a site and species specific derived equation (Eq. 7), they compare well to the fitted relationship for managed ecosystems. In particular, these additional values also support the choice of the non-linear fitted function type.

These results imply that the relationship between Γ_s and $[\text{NH}_4^+]_{\text{bulk}}$ is relatively robust across a wide range of plant species. The relationship of Eq. (6) enables us to extend the application of ecosystem or dynamics crop models to sites where only information is available on the plants N status, but not on Γ_s . The use of this equation in atmospheric chemistry and transport models is more problematic, because spatial input fields of N status are not generally available. It is more convenient to link Γ_s to a more accessible variable.

3.2 Dependence of long term Γ_s values on N inputs

As discussed above, in most non-agricultural ecosystems, the major source of N is atmospheric deposition (N_{dep}). Figure 5a and c show the plot of compiled Γ_s values versus total N input for forest and short semi-natural ecosystems on a linear and logarithmic scale, respectively. We notice that Γ_s increases considerably with N input (power function). Atmospheric deposition represents an estimate of wet and dry deposition of reduced and oxidized forms of N. For field studies, N_{dep} was derived either from direct measurements or taken from the results of a European atmospheric transport model (EMEP Unified model run for the year the Γ_s measurements were made for, N_{dep} values on a grid basis, Simpson et al., 2003, 2006). Nitrogen deposition values on a grid basis are significantly different from ecosystem specific values in some cases and are an additional source of uncertainty in this study. For many laboratory experiments, total N input had to be estimated from $[\text{NH}_4^+]_{\text{bulk}}$ according to Eq. (7). The values are listed in Table 3, together with their mode of calculation. With the exception of two studies (16: Hill et al., 2001; 32: Mattsson and Schjoerring, 2002), the total N input is in the form of atmospheric deposition. We notice that the laboratory experiments clearly differentiate from the rest of the data points which could be due to the large uncertainty resulting from the calculation of total N input. The lack of correlation can also be explained by the fact that:

- These data points are in the majority semi-natural vegetation that was transposed to the laboratory and watered with high N solution for a short time interval. One can think that in the case of semi-natural vegetation an adaptation time is required for the high N input to be reflected in Γ_s .
- These data points are for a range of different plant species and as shown by Mattsson et al. (2009), there is an important interspecies variability in Γ_s .

- On top of the uncertainty in the estimation of the total N input to the experimental setup there is an uncertainty in the measurement of Γ_s especially that this was done with different methods (gas exchange vs. apoplast extraction).

We therefore chose to exclude the data points concerning laboratory conducted experiments where N input to the ecosystem was derived from $[\text{NH}_4^+]_{\text{bulk}}$ from the parameterisation. The best fit equation to the measured data is the following power curve:

$$\Gamma_s = 246 + (0.0041) \times (N_{\text{in}})^{3.56} \quad (8)$$

where N_{in} is in $\text{kg N ha}^{-1} \text{ yr}^{-1}$.

With the exception of the period right after fertilisation events, Γ_s in managed ecosystems should also be related to the average N status which is mainly related to the long-term (e.g., annual) fertiliser input. Figure 5b and d show the relation between Γ_s and total N input to the ecosystem (annual N fertilisation rate plus atmospheric N input values derived from Eq. 7). It should be noted that data points for which both of those variables (N input and N fertilisation rate) could not be derived were not accounted for in the parameterisation. The major N source for most of those studies is the fertiliser application; therefore the uncertainty resulting from the estimation of atmospheric N deposition is negligible. The data for managed ecosystem may be described by:

$$\Gamma_s = 66.4 + (0.0853) \times (N_{\text{in}})^{1.59} \quad (9)$$

where N_{in} is the total N input to the ecosystem (fertilisation and atmospheric deposition) in $\text{kg ha}^{-1} \text{ yr}^{-1}$. As with the data on the unmanaged ecosystems, this relation does not explain the entire scatter in the data (adjusted $R^2 = 0.36$). One of the possible reasons is linked to the uncertainties in estimating total yearly fertiliser N application from hydroponics and pot experiments where N addition are not expressed as $\text{kg N ha}^{-1} \text{ yr}^{-1}$. But it is also consistent with the interspecies variability within a single grass sward as reported by Mattsson et al. (2009b).

Comparison of Fig. 5a and b demonstrates clearly that for managed ecosystems an almost 10 times larger N input is required to generate the same Γ_s . This suggests that semi-natural vegetation may be less adapted to using large supplies of nitrogen and becomes nitrogen saturated at lower levels, whereas arable crops and agricultural grassland species have been genetically selected to have a higher N use efficiency resulting in lower soluble $[\text{NH}_4^+]_{\text{bulk}}$ both in the apoplastic fluid and in the total bulk tissue.

3.3 Dynamics in Γ_s after fertilisation

While Γ_s was found to be linked to annual N input for periods outside of the first 2–3 weeks following a fertilisation event, it is likely that directly after fertilisation it is more linked to the amount and type of fertiliser of the event itself,

Table 3. Compiled data of Γ_s values for managed ecosystem types.

Type	Species	χ_s ppb	Γ_s	$[\text{NH}_4^+]_{\text{bulk}}$ $\mu\text{mol g}^{-1} \text{FW}$	Temp. °C	N_{input} $\text{kg ha}^{-1} \text{yr}^{-1}$	N status source	Equiv. N fertiliser $\text{kg ha}^{-1} \text{yr}^{-1}$	Growth stage	Growth condition	Meas. tech.	Ref.
arable	Oilseed rape	0.44±0.30	43±30	16.02	~25	11.76	b. tissue	70	vegetative	g. house	curv.	42
arable	Oilseed rape	0.31±0.29	55±51	35.66	20–18	21.26	b. tissue	22	vegetative	hydr.	ext.	30
arable	Oilseed rape	0.44±0.30	55±30	16.02	~25	11.76	b. tissue		vegetative	g. house	ext. & curv.	19
arable	Oilseed rape	0.44±0.30	55±6	16.02	~20	11.76	b. tissue		vegetative	g. house	ext. & curv.	31
arable	Oilseed rape	0.32±0.20	56	6.08	~20	5.74	b. tissue	0	35 days	g. house	ext.	5
arable	Oilseed rape	0.39±0.38	69±66	34.84	20–18	20.89	b. tissue	44	vegetative	hydr.	ext.	30
arable	Barley	5.02±0.79	75±78	35.10	~17	21.01	b. tissue		vegetative	g. house	curv.	33
arable	Oilseed rape	0.48±0.10	84±18		20–18		b. tissue	0	vegetative	hydr.	curv.	30
arable	Oilseed rape	0.53±0.08	93±14		20–18		b. tissue	0	vegetative	hydr.	curv.	30
arable	Oilseed rape	0.76±0.31	134±55	59.77	20–18	31.14	b. tissue	44	vegetative	hydr.	ext.	30
arable	Eucalyptus	3.00	137		N/A		High NO_3^-	22	20–40 days	g. house	curv.	4
arable	Oilseed rape	0.83±0.39	146±68	71.90	20–18	35.71	b. tissue	0	vegetative	hydr.	ext.	30
arable	Barley	0.90	158		~17		N limitation		after anthesis	hydr.	curv.	20
arable	Oilseed rape	1.70±0.90	168±89	29.70	~25	18.56	b. tissue	140	vegetative	g. house	curv.	42
arable	Oilseed rape	0.54	187±239	50.40	~15	27.45	b. tissue	55	maturity	Field	ext.	21
arable	Barley	2.01	199±12		~17		0.5 mM NH_4^+	11	vegetative	hydr.	ext.	31
arable	Barley	2.03	200±15		~17		2.5 mM NO_3^-	0	vegetative	hydr.	curv.	31
arable	Amaranthus	4.70	214		N/A		High NO_3^-		20–40 days	g. house	curv.	4
arable	Common bean	2.50±0.13	221±11		N/A		High NO_3^-		20–40 days	g. house	curv.	4
arable	Oilseed rape	1.72±0.87	227±86	29.70	~25	18.56	b. tissue		vegetative	g. house	ext. & curv.	19
arable	Oilseed rape	1.70±0.87	227±18	29.70	~20	18.56	b. tissue		vegetative	g. house	ext. & curv.	31
arable	Oilseed rape	1.50±0.16	264±28		20–18		10 $\text{NO}_3^- + 5 \text{ mM NH}_4^+$	110	vegetative	hydr.	curv.	30
arable	Oilseed rape	1.62±0.30	285±53		20–18		10 $\text{NO}_3^- + 2 \text{ mM NH}_4^+$	44	vegetative	hydr.	curv.	30
arable	Oilseed rape	1.74±0.22	307±38		20–18		10 $\text{NO}_3^- + 2 \text{ mM NH}_4^+$	44	vegetative	hydr.	curv.	30
arable	Oilseed rape	1.80±0.37	317±65		20–18		10 $\text{NO}_3^- + 5 \text{ mM NH}_4^+$	110	vegetative	hydr.	curv.	30
arable	Oilseed rape	5.30±0.80	325±79	135.72	~25	57.13	b. tissue		anthesis	g. house	ext. & curv.	19
arable	Maize	4.00±1.90	353±335		N/A		High NO_3^-		20–40 days	g. house	curv.	4
arable	Barley	8.32±0.60	354±59	51.66	~17	27.96	b. tissue		47%GS	g. house	curv.	33
arable	Oilseed rape	2.60±0.50	364±49	180.36	~25	70.51	b. tissue	55	maturity	g. house	ext. & curv.	19
arable	Oilseed rape	1.12	367±239	50.40	~15	27.45	b. tissue		maturity	g. house	ext.	21
arable	Oilseed rape	3.32±0.90	371±89	141.12	~25	58.81	b. tissue		anthesis	g. house	ext. & curv.	19
arable	Oilseed rape	0.90	381	104.40	~25	47.05	b. tissue		senescing	g. house	ext.	5
arable	Oilseed rape	2.28±1.01	402±310	22.50	~20	15.12	b. tissue	220	35 days	g. house	ext.	42
arable	Oilseed rape	4.10±0.20	405±20	62.10	~25	32.04	b. tissue	231	vegetative	g. house	curv.	21
arable	Oilseed rape	1.32	426±239	50.40	~15	27.45	b. tissue	55	maturity	field	ext.	21
arable	Barley	5.00±4.00	494±791	72.00	~20	35.74	b. tissue	160	maturity	field	ext.	21
arable	Oilseed rape	5.08	503	219.78	~25		b. tissue		anthesis	g. house	ext. & curv.	19
arable	Barley	2.91±0.64	512±112		~17		N limitation	0	before anthesis	hydr.	curv.	20
arable	Barley	3.00±0.40	528±70		~17		N limitation		after anthesis	hydr.	curv.	20
arable	Oilseed rape	3.24	569		~20		0.4 g N kg ⁻¹ soil		leaf 8–10	g. house	ext.	18
arable	Barley	3.27±0.73	576±128		~17		N limitation		maturity	hydr.	curv.	20
arable	Glycine	6.50±1.50	642±296		~23		N limitation		maturity	field	micromet	27
arable	Oilseed rape	3.68	648		~20		0.4 g N kg ⁻¹ soil		leaf 6–9	g. house	ext.	18
arable	Oilseed rape	4.10±0.20	672±20	62.10	~25	32.04	b. tissue		vegetative	g. house	ext. & curv.	19
arable	Oilseed rape	4.10±0.20	672±10	62.10	~20	32.04	b. tissue		vegetative	g. house	ext. & curv.	31
arable	Barley	3.91±0.69	688±122		~17		N limitation		grain filling	hydr.	curv.	20
arable	Oilseed rape	3.96	696		~20		0.4 g N kg ⁻¹ soil		leaf 12–16	g. house	ext.	18
arable	Oilseed rape	4.18±0.62	736±109		20–18		5 mM NH_4^+	110	vegetative	hydr.	curv.	30
arable	Barley	4.20±0.30	739±53		~17		N limitation	0	vegetative tillering	hydr.	curv.	20

Table 3. Continued.

Type	Species	X_s ppb	Γ_s	$[\text{NH}_4^+]_{\text{bulk}}$ $\mu\text{mol g}^{-1}$ FW	Temp. °C	N input $\text{kg ha}^{-1} \text{yr}^{-1}$	N status	Equi. N fertiliser $\text{kg ha}^{-1} \text{yr}^{-1}$	Growth stage	Growth condition	Meas. tech.	Ref.
arable	Barley	11.8±0.41	782±41	66.60	~17	33.74	b. tissue		66%GS	g.house	cuv.	33
arable	Oilseed rape	4.45	783		~20		0.4g N kg ⁻¹ soil		leaf 15–21	g.house	ext.	18
arable	soybean	19.9	785		23–32	13.90	poultry litter			field	micromet	53
arable	Barley	4.58±0.20	806±35		~17		N limitation		before anthesis	hydr.	cuv.	20
arable	Wheat	5.00±1.00	880±352		5–20	14.40	200 kg ha ⁻¹ NH ₄ NO ₃	200		field	micromet	56
arable	Barley	5.30±0.10	933±18		~17		N limitation	0	maturity	hydr.	cuv.	20
arable	Barley	5.30±0.80	933±141		~17		N limitation	0	grain filling	hydr.	cuv.	20
arable	soybean	11.5	996		23–32	13.90	poultry litter			field	micromet	53
arable	soybean	18.1	1037		23–32	13.90	poultry litter			field	micromet	53
arable	Barley	6.40±1.10	1126±194		~17		N limitation		tiltering	hydr.	cuv.	20
arable	Maize	12.0±4.00	1186±395		~20	8.00	N limitation			hydr.	micromet	11
arable	Barley	12.7	1258±364		~17		1mM NH ₄ ⁺	22	vegetative	hydr.	ext. & cuv.	31
arable	Oilseed rape	17.3	1712	215.64	~25		0.15 mol N 0.0025m ⁻³		senescing	g.house	ext. & cuv.	19
arable	Oilseed rape	10.2±2.63	1802±463		20–18		5 mM NH ₄ ⁺	110	vegetative	hydr.	cuv.	30
arable	Wheat	19.0	1878		20–14		~5mM NO ₃ ⁻	0	grain filling	g.house	cuv.	35
arable	Wheat	33.0	3261		20–14		~5mM NO ₃ ⁻	0	grain filling	g.house	cuv.	35
arable	Barley	33.3	3289±411		~17		2.5mM NH ₄ ⁺	55	vegetative	hydr.	ext.	31
arable	Wheat	36.0	3558		20–14		~5mM NO ₃ ⁻	0	maturity	g.house	cuv.	35
arable	Barley	48.2	4764±878		~17		10mM NH ₄ ⁺	220	vegetative	hydr.	ext.	31
arable	Barley	52.9	5233±606		~17		5mM NH ₄ ⁺	110	vegetative	hydr.	ext.	31
grass	Bromus mollis	0.24±0.04	24±4	16.47	10–30	12.00	100 kg N ha ⁻¹	100		field	ext.	57
grass	Holcus ianatus	0.29±0.04	28±4	9.57	10–30	8.03	100 kg N ha ⁻¹	100		field	ext.	57
grass	Phleum pratense	0.30±0.03	30±3	12.64	10–30	9.87	100 kg N ha ⁻¹	100		field	ext.	57
grass	Lolium perenne	0.85±0.20	38±64	25.72	9–16	16.69	65 kg N ha ⁻¹ NH ₄ NO ₃	65		field	ext.	28
grass	Trifolium repens	0.40±0.57	70±99	19.80	20–15	13.75	4.5 mM NH ₄ ⁺	88	60 days	field	ext.	13
grass	Lolium perenne	0.87	86	43.20	10–30	24.50	100 kg N ha ⁻¹	100		field	ext.	14
grass	Mixed	0.31	100		8–16		after grazing			field	micromet	23
grass	Poa pratensis	1.33±0.29	132±28		10–30	17.10	100 kg N/ha	100		field	ext.	57
grass	Lolium multiflorum	1.37±0.56	136±55	13.10	10–30	10.13	100 kg N ha ⁻¹	100		field	ext.	57
grass	Lolium perenne	1.42	140	47.20	10–30	44.63	100 kg N ha ⁻¹	100		field	ext.	14
grass	Mixed	0.55	200		6–18	7.50	EMEP grazed	0		field	micromet	37
grass	Lolium perenne	2.21±0.37	218±56	24.66	10–30	16.18	100 kg N ha ⁻¹	100		field	ext.	57
grass	Medicago sativa	2.10±0.70	233±78		9–32	14.30	no fertilisation	0	cut grass	field	micromet	2
grass	Lolium perenne	1.63	520		~20		Slurry			field	ext.	9
grass	Dactylis glomerata	5.53±0.51	546±51	26.04	10–30	16.85	100 kg N ha ⁻¹	100		field	ext.	57
grass	Lolium perenne	3.25±2.50	572±897		0–25	28.90	~200 kg ha ⁻¹ yr ⁻¹	200		field	ext.	52
grass	Mixed	2.06±1.37	659±439		5–20	15.00	meas.	0		field	micromet	7
grass	Festuca pratensis	7.05±0.67	697±66	32.55	10–30	19.87	100 kg N ha ⁻¹	100		field	ext.	57
grass	Trifolium repens	4.00	704		20–15		no fertilisation	0	60 days	field	cuv.	13
grass	Mixed	2.50	800		8–16		after grazing			field	micromet	23
grass	Mixed	2.74±1.96	875±625		5–20	15.00	meas.	200	After fertilisation	field	micromet	7
grass	Lolium perenne	15.8±1.01	1566±100	72.00	10–30	35.74	100 kg N/ha			field	ext.	14
grass	Lolium perenne	20.1	3537	102.85	9–16	46.54	65 kg N ha ⁻¹			field	ext.	28
grass	Mixed	12.5	4000		8–16		Grazed			field	micromet	23
grass	alpine tundra	0.16	16		~19	6.30	no fertilisation			field	micromet	41
grass	Lolium perenne	7.00	976		20–12	27.45	no fertilisation			field	micromet	25
grass	Lolium perenne	27.0	4751		10–20	35.00	slurry			field	micromet	40

b. tissue: bulk tissue extracts; meas.: measured; g. house: grown in a glass house; hydr.: grown in hydroponics; cuv.: cuvette measurement technique; ext.: extraction measurement technique; micromet.: micrometeorological measurement technique.

(2) Dabney and Bouldin, 1990; (4) Farquhar et al., 1980; (5) Finneman and Schjoerring, 1999; (7) Flechard et al., 2010; (9) Sutton et al., 2002; (11) Harper and Sharpe, 1995; (13) Hermann et al. 2002; (14) Hermann et al. 2009; (18) Husted and Schjoerring (1995b); (19) Husted and Schjoerring (1996); (20) Husted et al. (1996); (21) Husted et al. (2000); (23) Fowler et al., 2007 (Keenley-Kruit et al., 2007; (27) Lemon and Van Houtte, 1980; (28) Loubet et al., 2002; (30) Massad et al. 2009; (31) Mattson et al. (1997); (33) Mattsson et al. (1997); (35) Morgan and Parton, 1989; (37) Fowler et al., 1997 (Easter Bush); (40) Plantaz et al. 1996; (41) Rattray and Sievering, 2001; (42) Schjoerring et al. (1998a); (44) Schjoerring et al., 1993; (52) Van Hove et al., 2002; (53) Walker et al., 2006; (56) Yamulki et al., 1996; (57) Mattsson et al., 2009a.

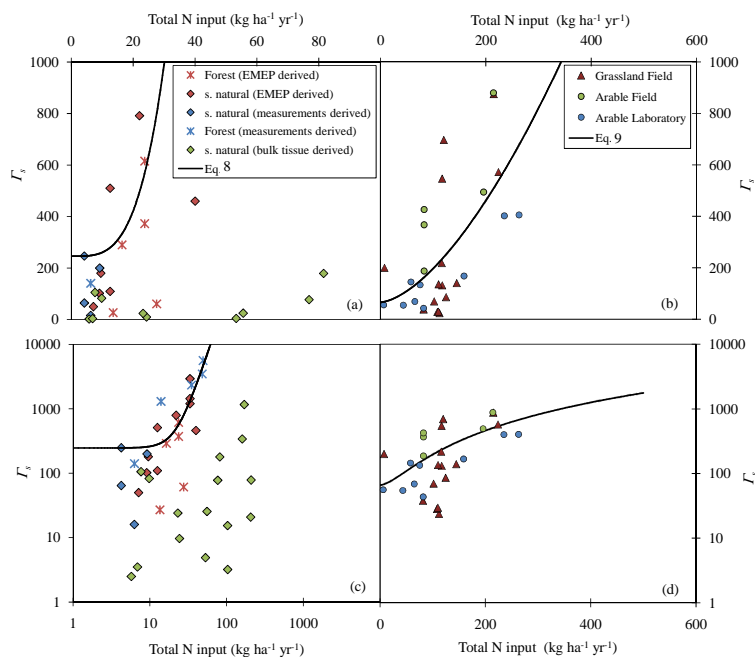


Fig. 5. (a) and (c) Compiled stomatal ammonia emission potential (Γ_s) for non-managed ecosystem types as a function of total N input to the ecosystem on a linear and logarithmic scale respectively. Data are separated according to the data source of the N_{in} value (EMEP model estimated, site-based measurements and bulk tissue derived values according to Eq. 7). Red and blue symbols have only atmospheric deposition as an N source and green symbols have atmospheric deposition as well as fertiliser as N source. The line is the best fit power function derived by minimisation of the least square method excluding data for laboratory based experiments (green symbols) (refer to text). (b) and (d) Compiled stomatal ammonia emission potential (Γ_s) for managed ecosystem types as a function of total N input on a linear and logarithmic scale respectively. The black line is the best fit equation to the data points. Red triangles represent field grassland measurements, green and red circles represent field based and laboratory based measurements on arable crops respectively. Approximated fertiliser N input values for laboratory based experiments are given in Table 3.

the application technique and soil and weather conditions. Measurements including fertiliser application include plants grown in soil and those grown in hydroponic solution. It is worth noting that the data analysed for Γ_s directly following fertilisation events are only for measurements done using the apoplast extraction technique since the flux measurement technique would give Γ_c for the whole canopy (plant and soil). Figure 6a shows Γ_s versus fertiliser application (primary x-axis) the first day after application and $[\text{NH}_4^+]$ concentration in the nutritive solution (secondary x-axis). We note a linear relation between Γ_s and the amount of fertiliser applied for both plants grown in soil and in hydroponics. Some of the Γ_s values for plants grown in hydroponics have a different slope than the others (Mattsson et al., 1998). In that particular study, the higher Γ_s values for plants grown with 5 mM NH_4^+ in the nutritive solution relative to those grown with 10 mM NH_4^+ are due to a lower pH and not to higher $[\text{NH}_4^+]_{\text{apop}}$ concentrations in the apoplast. We also note that for plants grown in hydroponics, Γ_s is more strongly correlated to the NH_4^+ concentration in the nutritive solution than the NO_3^- concentrations (Mattsson et al., 1998; Massad et al., 2009). If we assume for the compiled Γ_s data that plants

grown in hydroponics respond in the same way as plants grown in the field to N application then we can equate the two linear regressions (between Γ_s and $[\text{NH}_4^+]$ in the nutritive solution on one hand and Γ_s and total N in the fertiliser applied on the second). One mM NH_4^+ in the nutritive solution can then be approximated to 22 kg ha⁻¹ of applied N fertilisation. Although significant uncertainties lie around this approximation, it is a useful practical approach for grouping laboratory and field based experiments.

Γ_s dynamics after fertilisation were measured in several studies. These measurements are shown in Fig. 6b. We notice a return to pre-fertilisation Γ_s values in the 10 days that follow fertiliser application. The only exception in the compiled data was the study on the Dutch GRAMINAE site (Sutton et al., 2002) where the peak in Γ_s only appeared 2 days later. This could be explained by the fact that in this case the fertiliser applied was in the form of manure which can take time to become available to the plant.

3.4 Dynamics in Γ_g after fertilisation

Table 4 summarises existing values of Γ_g for ground layer measurements. Those include bare soil, leaf litter and soil

Table 4. Compiled data of Γ_g values.

Type	Species	Specifications	χ_g ppb	Γ_g	Average temp. °C	N status	Meas. tech.	Reference
grassland	Mixed	Cut grassland	434	85 800	19	300 kg ha ⁻¹	ext.	David et al., 2009
grassland	Mixed	Tall Grassland	313	61 900	19	300 kg ha ⁻¹	ext.	David et al., 2009
grassland	Mixed	Cut grassland, with hay	429	84 900	19	300 kg ha ⁻¹	ext.	David et al., 2009
grassland	Mixed	Bare soil	530	104 900	19	300 kg ha ⁻¹	ext.	David et al., 2009
grassland	Mixed	Bare soil and litter	384	76 000	19	300 kg ha ⁻¹	ext.	David et al., 2009
grassland	Mixed	slurry	4900–36 000	8.5×10^5 – 6.3×10^6	20		ext.	Flechard et al., 2010
grassland	Mixed	Bare soil	2	360	19	no fertilisation	ext.	David et al., 2009
arable	Brassica napus	litter	10	3431	14	285 kg ha ⁻¹ yr ⁻¹	ext.	Husted et al., 2000
arable	Soybean/wheat/maize		74	13 000	20	no fertilisation	ext.	Walker et al., 2008
arable	Soybean/wheat/maize		9	1514	20	swine manure	ext.	Walker et al., 2008
arable	wheat stubble		8	1450	20	no fertilisation	micromet.	Nefel et al., 1998
arable	wheat stubble		2	630	15	no fertilisation	model	Nemitz et al., 2001
arable	wheat		44	7742	20	no fertilisation	extr.	Fang et al., 2006
arable	Brassica napus		17–74	3000–13 000	20	285 kg ha ⁻¹ yr ⁻¹	model	Nemitz et al., 2000b
semi-natural	Lolium perenne	<i>senescing excised</i>	142	25 000	20	no fertilisation	extr.	Mattsson and Schjoerring, 2003
semi-natural	Lolium perenne	<i>leaves after 4 days</i>	188	33 000	20	3 mM NO ₃ ⁻	extr.	Mattsson and Schjoerring, 2003
semi-natural	Lolium perenne	<i>in darkness</i>	347	61 000	20	6 mM NO ₃ ⁻	extr.	Mattsson and Schjoerring, 2003
forest	–		0.1	20	20	no fertilisation	extr.	Walker et al., 2008

ext.: extraction measurement technique; micromet.: micrometeorological measurement technique.

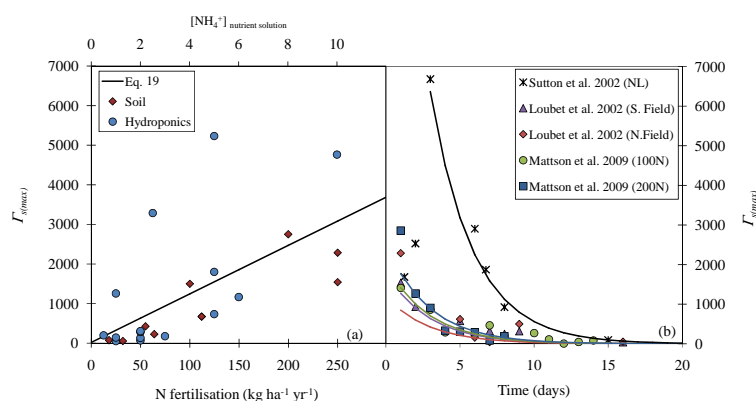


Fig. 6. (a) Compiled maximal stomatal ammonia emission potential ($\Gamma_{s(\max)}$) for managed ecosystem types (i) the first day after fertilisation (red diamonds) as a function of applied fertilisation rate (primary x-axis) or (ii) grown in hydroponics (blue circles) as a function of $[\text{NH}_4^+]$ concentration in the nutritive solution (secondary x axis). The line is the best fit linear function derived by minimisation of the least square method for the two series (hydroponics and soil). One mM of NH_4^+ in the nutritive solution was approximated to be equal to 22 kg N ha⁻¹. (b) Dynamics of Γ_s in the days following N fertiliser application (symbols) and adjusted functions (curved lines) according to Eq. (20).

after slurry or fertiliser application. Very few measurements exist for ground layer NH_3 emissions. Most of the existing data from flux measurements are for the whole canopy and therefore do not differentiate between ground layer emissions, canopy emissions and NH_3 cycling within the canopy. Nemitz et al. (2000a) estimate values of Γ_g for oilseed rape litter based on within-canopy NH_3 gradient measurements to range between 3000 and 13 000. David et al. (2009) measured much larger values based on chamber measurements in the field for an uncut grassland (140 000) and a cut grassland (260 000). Furthermore, David et al. (2009) report bare soil to have large Γ_g (50 000–100 000) in field conditions and a study above the Mojave desert reported relatively high emis-

sions above a bare natural desert soil without fertiliser application (McCalley and Sparks, 2008).

Milford et al. (2001b) estimated values for Γ_s and Γ_g from flux measurements. They fitted a bi-directional model to measured night time fluxes to estimate Γ_g , while measured day time fluxes are used to estimate values of Γ_s .

Ground-layer emissions after slurry spreading are usually very high and reflect emission from the slurry itself (e.g. Générumont and Cellier, 1997; Flechard et al., 2010). Γ_g in the case of slurry can be calculated as the ratio of total ammoniacal nitrogen (TAN) content to H^+ content of the slurry.

Table 5 shows Γ_g values calculated from TAN and pH values given by Provolo and Martinez-Suller (2007) for

Table 5. Mean and standard deviation of total ammoniacal nitrogen (TAN) content and pH of different slurry types from Provalo and Martinez-Suller (2007) and calculated Γ_g values.

Animal type	Pigs			Cattle	
	Finisher	Farrowing sows	Integrated farrow-to-finish	Dairy cows	Calves
pH	7.41±0.33	7.46±0.5	7.55±0.47	7.34±0.42	7.28±0.33
TAN (kg N m ⁻³)	2.03±0.8	1.76±0.94	1.61±0.66	1.12±0.59	1.62±0.4
Γ_g (NH ₄ ⁺ /H ⁺)	3 727 074±3 140 234	3 625 640±6 123 501	4 080 354±4 936 463	1 750 209±2 425 068	2 204 890±1 163 944

different slurry types. This derived Γ_g is within the range measured for the canopy Γ_c by Flechard et al. (2010) following six events of slurry spreading.

Ground layer emissions after mineral fertiliser application depend on the type and quantity of fertiliser applied, but also on soil properties as reflected by its pH buffering and water holding capacities. Concerning pH, Harrison and Webb (2001) conclude that for urea, hydrolysis greatly increases pH of the soil and is therefore relatively unaffected by the soil pH itself. For other fertilisers, such as ammonium sulphate (AS) or di-ammonium phosphate (DAP), which increase dissolution of calcium carbonate, solution pH will be greater on calcareous soils. For ammonium nitrate (AN), which form readily-soluble salts with calcium, solution is unaffected by soil pH.

3.5 Interactions between Γ_s and grazing

Concerning grazing, Γ_s is expected to depend on the amount of grass eaten and excreted on the field, which is related to the number of animals (in terms of livestock units) present on the field; however, few data are available in a form suitable to calculate Γ values. Although the impact of grazing also depends on whether animals are fed solely on grass within the field or whether the animals are also fed concentrates and other forage on site or in the stable, the major impact on NH₃ emissions originates from the remobilisation of plant N into urine and dung. During recent measurements over grazed pasture in the UK, Γ_s values dropped from 4000 when there were around 6.5 sheep ha⁻¹ (~1 LU ha⁻¹) to around 100 two weeks after the sheep were moved (Fowler et al., 2007). Milford (2004) also estimated a Γ_s value of 4000 for a grazed pasture with a density of 200 sheep ha⁻¹ (~30 LU ha⁻¹) and the same value was confirmed during more recent measurements at the same site (Fowler et al., 2007).

4 Proposed model and parameterisation

Resistance models are appropriate to be integrated in chemistry and transport models as they incorporate the key elements of process understanding while being efficient in cal-

culaton. The key issues to which these model parameterisations should respond are the following:

- Capture dynamics of NH₃ exchange with key variables (N input, temperature, etc.).
- Rely on variables or outputs of chemistry and transport models (EMEP, UKCA, etc.).
- Allow response to global change variables (temperature, land use, atmospheric composition, etc.).
- Be easily implemented in global scale models.

The three types of resistance models (single layer, two-layer and multi-layer) (Nemitz et al., 2000b) previously described can theoretically all be integrated in chemistry and transport models. However, the multi-layer resistance model adds much complexity in parameterisation and calculation. The two-layer model for NH₃ exchange has the advantage of capturing the soil and litter emissions. These emissions can be particularly important after fertilisation for grassland and arable ecosystems, after cutting for grassland and in case of a crop that has senescent leaves during its maturation like oilseed rape (Nemitz et al., 2000a; Sutton et al., 2009a). It can be argued however that in case of a single layer model scheme, the value of Γ_s attributed to a managed ecosystem after fertilisation or cutting is not a stomatal Γ_s but a canopy Γ_c . Thus the Γ value used in single layer models integrates emissions from the litter and or soil and subsequent recapture by the above canopy.

We recommend using a two-layer model since it better captures the dynamics of NH₃ exchange in the case of managed ecosystems. The bottom layer of the model can be switched off for non-managed ecosystems (values of Γ_g are small and uncertain) by setting the in-canopy resistance (R_g) to infinity.

Based on the preceding review and data compilation, we here propose parameterisations for a bi-directional NH₃ exchange scheme applying the two-layer steady state model of Nemitz et al. (2001): Γ_s , Γ_g , and R_w . For completeness, we first describe the approaches for the atmospheric and canopy scale turbulent and boundary layer resistances.

4.1 Summary of overall concept of the two layer model

The two-layer NH_3 exchange model as described by Nemitz et al. (2001) contains bi-directional exchange with the leaf stomata, deposition to the leaf cuticle and a ground emission potential (Fig. 1b).

The total flux of ammonia (F_t) is calculated according to the following equation:

$$F_t = -\frac{\chi_a - \chi(z_0)}{R_a} \quad (10)$$

where χ_a is the air ammonia concentration, $\chi(z_0)$ is the concentration at height $d + z_0$ and R_a is the aerodynamic resis-

tance between the air and $d + z_0$ that describes the vertical turbulent diffusive transport through the atmosphere between a reference height (z) and displacement height ($d + z_0$), which, for a closed canopy, usually equals about 0.63 times the canopy height (h_c) (Monteith, 1973).

$\chi(z_0)$ is calculated from the canopy ammonia concentration χ_c which is the resultant of the stomatal flux (F_s), cuticular flux (F_w) and ground layer flux (F_g) (for more details refer to Nemitz et al., 2001). The equations for $\chi(z_0)$ and χ_c are as follows:

$$\chi(z_0) = \frac{\chi_a \times R_a^{-1} + \chi_g \times R_g^{-1} + \chi_c \times R_b^{-1}}{R_a^{-1} + R_g^{-1} + R_b^{-1}} \quad (11)$$

$$\chi(c) = \frac{\chi_a \times (R_a \times R_b)^{-1} + \chi_s \times \left[(R_a \times R_s)^{-1} + (R_b \times R_s)^{-1} + (R_g \times R_s)^{-1} \right] + \chi_g \times (R_b \times R_g)^{-1}}{(R_a \times R_b)^{-1} + (R_a \times R_s)^{-1} + (R_a \times R_w)^{-1} + (R_b \times R_g)^{-1} + (R_b \times R_s)^{-1} + (R_b \times R_w)^{-1} + (R_g \times R_s)^{-1} + (R_g \times R_w)^{-1}} \quad (12)$$

where R_b , R_s , R_g and R_w are the quasi laminar boundary layer, stomatal, canopy and cuticular resistances respectively and χ_s and χ_g are the stomatal and ground layer compensation points, respectively.

4.2 Parameterisation of atmospheric and boundary layer resistances

The total resistance to exchange between a reference height and the canopy is the sum of the aerodynamic resistance (R_a) and the quasi laminar boundary layer resistance (R_b). These resistances are usually parameterised through meteorological parameters (wind speed: u , friction velocity: u_* , surface roughness length: z_o , and Obukhov stability length: L) (Monin and Obukhov, 1954; Sutton et al., 1993a; Högström, 1996). The boundary layer resistance (R_b) accounts for the diffusion through the quasi-laminar boundary layer at the surface of the vegetation. R_a and R_b are usually calculated in chemistry and transport models from easily measurable meteorological parameters (e.g. R_a : Garland, 1977; Monteith and Unsworth, 1990; R_b : Jensen and Hummelshøj, 1995, 1997). The commonly used equations are given below:

$$R_{a(z)} = \frac{u(z-d)}{u_*^2} - \frac{\psi_H \times \left(\frac{z-d}{L}\right) - \psi_M \times \left(\frac{z-d}{L}\right)}{k \times u_*} \quad (13)$$

$$R_b = \frac{\nu}{D_{\text{NH}_3}} \times \left[\frac{c}{(\text{LAI})^2} \times \left(\frac{l \times u_*}{\nu}\right) \right]^{1/3} \quad (14)$$

where u is the windspeed, u_* is the friction velocity, L is the Obukhov length, ψ_H and ψ_M are the integrated stability functions for entrained scalars and momentum respectively, ν is the kinematic viscosity of air ($\sim 1.56 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ at 25 °C), D_{NH_3} is the molecular diffusivity of NH_3 in air ($\sim 2.32 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ at 25 °C, Massman, 1998), c is an empirical constant of order one, k the von Karman constant

($k = 0.41$), and l is the length scale over which the viscous sub-layers are permitted, which is a typical leaf width. Leaf area index values for different ecosystem types and canopy heights are usually calculated or tabulated in chemistry and transport models. Simpson et al. (2003) propose a variation of LAI as well as h_c between a minimal and maximal value for different growth periods.

4.3 Parameterisation of the in-canopy resistance

The in-canopy transport resistance to the ground (R_g) is the sum of the aerodynamic resistance within the canopy (R_{ac}) and the soil boundary layer resistance (R_{bg}). In general, the in-canopy resistance is defined as a turbulent transport resistance and is therefore modelled as the integral of the inverse of the eddy diffusivity (K_H) between the ground surface and the roughness height ($d + z_o$). K_H can be deduced according to Raupach et al. (1989) and depends on the standard deviation of the wind component (σ_w), u_* and the canopy height (h_c). Shuttleworth and Wallace (1985) defined R_{ac} via an exponentially decaying function of σ_w , while Wesely (1989) specified a constant in-canopy aerodynamic resistance for forest canopies and Erisman et al. (1994) suggested a formula dependent on canopy height and u_* . By contrast, Zhang et al. (2003) calculated R_{ac} as a function of u_* , LAI, and the vegetation specific minimum in-canopy aerodynamic resistance. R_{bg} is not explicitly considered in all studies.

Nemitz et al. (2000b) suggested using the following equation where R_{ac} is inversely proportional to u_* :

$$R_{ac(d+z_0)} = \alpha_{(d+z_0)} \times u_*^{-1} \quad (15)$$

z_0 is the vegetation roughness and is usually equal to 0.13 times vegetation height (h_c), whereas α can be derived from Shuttleworth and Wallace (1985) as:

$$\alpha_{(d+z_0)} = \frac{1}{k} \times \frac{h_c}{n(h_c - d)} \times \left(e^n - e^{n \times \left(1 - \frac{d+z_0}{h_c}\right)} \right) \quad (16)$$

where n is the exponential decay constant (Monteith, 1973). Lafleur and Rouse (1990) suggest to calculate n according to the following equation:

$$n = y \times (\text{LAI})^x \quad (17)$$

where $y = 2.6$ and $x = 0.36$. The minimal value of n is to be set to 1.87 and the maximal value to 3.62.

As for the ground boundary layer resistance (R_{bg}), Nemitz et al. (2001) suggest to calculate it according to Schuepp (1977):

$$R_{bg} = \frac{v/D_{\text{NH}_3} - \ln(\delta_0/z_1)}{ku_{*g}} \quad (18)$$

where δ_0 is the distance above ground where the eddy diffusivity is equal in magnitude to the molecular diffusivity of NH_3 , z_1 is the upper height of the logarithmic profile that forms above the ground and u_{*g} is the friction velocity at ground level. If at height z_1 , we consider that the vertical wind speed ($u_{(y)}$), the eddy diffusivity (K_H), and the slope of K_H are equal between the exponential and the logarithmic profiles above and below z_1 respectively, then we can derive an expression for u_{*g} and z_1 as a function canopy height (h_c), the exponential decay constant (n) and the eddy diffusivity (K_H). In case LAI and h_c values are not provided by the model calculations, Table 6 summarises proposed default parameter estimates according to ecosystem type and season to be used in Eqs. (13), (14), (15) and (16).

4.4 Parameterisation of χ_s for non-agricultural ecosystems

We propose to use Eq. (8) to parameterise Γ_s for both forest and short semi-natural ecosystems because there does not appear to be a significant difference in the response of Γ_s to the N_{dep} between those two ecosystem types. The fitted equation represents rather well the data with an adjusted R^2 value of 0.75. There is however variability in Γ_s which is not explained by N_{dep} especially for low Γ_s values. This is likely to reflect uncertainties in our N_{dep} estimate (for example N fixation and organic N deposition are not considered as an N source), but also reflects differences between species. For example, Mattsson et al. (2009b) found that values of Γ_s ranged from 25 to 700 between grass species growing within the same sward (and thus receiving the same N deposition). These uncertainties reflect the limitations of our current understanding in the controls of Γ_s .

4.5 Parameterisation of χ_s and χ_g for agricultural ecosystems

In the case of managed ecosystems, Γ_s and Γ_g are reported to depend on the N input via fertilisation or grazing. Time series measurements of Γ usually show a peak after fertilisation events (e.g. Loubet et al., 2002; Mattsson et al., 2009a). This high Γ after fertilisation or during grazing usually decreases when the cattle are removed from the field or in the week following fertiliser application. These high measurements reflect ground (soil/fertiliser and or litter) emissions as well as stomatal exchange. We propose a parameterisation that distinguishes background Γ_s values (i.e. before fertilisation) and values of Γ_s and Γ_g after management events such as fertiliser application.

In our parameterisation we only use the ground layer (Γ_g) for the periods following management events. This is done for two main reasons: (i) very few data are available on ground layer emissions from background, (ii) ground layer emissions are expected to be small and recaptured by the overlying canopy, except following management events and in the case of senescing arable canopies, where bottom layers emit considerable amounts of NH_3 (Nemitz et al., 2000a) and (iii) most of the compensation point measurements for this type of ecosystems are measurements which often do not differentiate clearly between Γ_s and Γ_g and therefore reflect in some of the cases a measurement of Γ_c . Therefore proposing a big leaf model in those cases might be a way to limit the uncertainty both related to the quality of the measurements and the lack of data. A special case to be considered is managed bare soil (tilled land outside the growing season). In this case we might assume that Γ_g is different from zero since some plant litter remains on the soil surface. Nemitz et al. (2001) estimated a Γ_g over a wheat stubble equal to 630. We therefore suggest using $\Gamma_g = 500$ for managed tilled land outside the vegetation season.

– Background Γ_s

Agricultural ecosystems receive N in two major forms: fertiliser application and N input through atmospheric deposition. We propose to use Eq. (9) to estimate Γ_s from total N input to the ecosystem (fertiliser application and N_{dep}) as a parameterisation for managed background Γ_s .

– Temporal dynamics in Γ_s after fertilisation

In the days following fertiliser application, there is usually a peak in Γ which is due to emission from the fertiliser or slurry itself but also from the plant canopy. The dependence of the maximal Γ_s values after fertilisation on the amount of fertiliser applied (kg N ha^{-1}) or $[\text{NH}_4^+]$ concentration in the nutritive solution (Fig. 6a) reveals a linear relationship which can be approximated by:

$$\Gamma_{s(\text{max})} = 12.3 \times N_{\text{app}} + 20.3 \quad (19)$$

Table 6. Parameters used for the calculation of aerodynamic and boundary layer resistances above (R_a and R_b) and within canopy (R_{ac}), respectively.

Ecosystem type	Season	LAI ($\text{m}^2 \text{m}^{-2}$)	l (m)	h_c (m)	z_0 (m)	d (m)	n	α
Temperate/boreal coniferous forests	winter	3.4	0.005	20	2.6	12.6	3.62	65.24
	spring	4	0.005	20	2.6	12.6	3.62	65.24
	summer	4.5	0.005	20	2.6	12.6	3.62	65.24
	autumn	4	0.005	20	2.6	12.6	3.62	65.24
Temperate/boreal deciduous forests	winter	3.5	0.05	20	2.6	12.6	3.62	65.24
	spring	4.2	0.05	20	2.6	12.6	3.62	65.24
	summer	5	0.05	20	2.6	12.6	3.62	65.24
	autumn	3.9	0.05	20	2.6	12.6	3.62	65.24
Mediterranean needleleaf forests	winter	3.5	0.005	15	1.95	9.45	3.62	65.24
	spring	3.5	0.005	15	1.95	9.45	3.62	65.24
	summer	3.5	0.005	15	1.95	9.45	3.62	65.24
	autumn	3.5	0.005	15	1.95	9.45	3.62	65.24
Mediterranean broadleaf forests	winter	3.5	0.05	15	1.95	9.45	3.62	65.24
	spring	3.5	0.05	15	1.95	9.45	3.62	65.24
	summer	3.5	0.05	15	1.95	9.45	3.62	65.24
	autumn	3.5	0.05	15	1.95	9.45	3.62	65.24
Temperate Crops	winter	0	0.02	0	0	0	1.87	17.78
	spring	2.5	0.02	0.6	0.08	0.378	3.62	65.04
	summer	3.5	0.02	1	0.13	0.63	3.62	65.24
	autumn	0	0.02	0	0	0	1.87	17.78
Mediterranean Crops	winter	0	0.03	2	0.26	1.26	1.87	17.78
	spring	2	0.03	2	0.26	1.26	3.34	52.45
	summer	3	0.03	2	0.26	1.26	3.62	65.24
	autumn	0	0.03	2	0.26	1.26	1.87	17.78
Root Crops	winter	0	0.04	0	0	0	1.87	17.78
	spring	2.5	0.04	0.5	0.065	0.315	3.62	65.04
	summer	4.2	0.04	0.5	0.065	0.315	3.62	65.24
	autumn	2	0.04	0	0	0	3.34	52.45
Seminatural/Moorland	winter	2	0.01	0.5	0.065	0.315	3.34	52.45
	spring	3	0.01	0.5	0.065	0.315	3.62	65.24
	summer	3	0.01	0.5	0.065	0.315	3.62	65.24
	autumn	2	0.01	0.5	0.065	0.315	3.34	52.45
Grassland	winter	2	0.01	0.3	0.039	0.189	3.34	52.45
	spring	3	0.01	0.3	0.039	0.189	3.62	65.24
	summer	3.5	0.01	0.3	0.039	0.189	3.62	65.24
	autumn	2	0.01	0.3	0.039	0.189	3.34	52.45
Mediterranean shrub	winter	2.5	0.02	2	0.26	1.26	3.62	65.04
	spring	2.5	0.02	2	0.26	1.26	3.62	65.04
	summer	2.5	0.02	2	0.26	1.26	3.62	65.04
	autumn	2.5	0.02	2	0.26	1.26	3.62	65.04
Wetlands	All year	1	0.01	0.5	0.065	0.315	2.60	30.14
Tundra	All year	1	0.01	0.5	0.065	0.315	2.60	30.14
Desert/Bare soil	All year	0	0	0	–	–	–	–

Table 7. Soil water content (θ_s in %) at field capacity and permanent wilting point according to soil type from Lambers et al. (2008).

	sand	loam	Clay
Field capacity	10	20	40
Permanent wilting point	5	10	20

This $\Gamma_{s(\max)}$ reflects mineral fertiliser application. We only have one dataset where manure application was coupled with apoplast extraction measurements (Sutton et al., 2002 (NL)). We notice a similar response to mineral N application with respect to the peak value of Γ_s , however, dynamics in this case is different. Organic fertiliser application should be treated with caution due to the shortage of data.

The temporal decrease in $\Gamma_{s(\max)}$ after a fertilisation event can be adjusted to an exponential function as shown in Fig. 6b. The exponential equation is of the following form:

$$\Gamma_s = \Gamma_{s(\max)} \times e^{(-t/\tau)} \quad (20)$$

where $\Gamma_{s(\max)}$ is from Eq. (19), τ is the e-folding time constant of the decay and is set to 2.88 days, and t is the time in days. This type of parameterisation can be applied the day following fertiliser application since the peaks in Γ_s values are directly observed in most of the cases. We propose using Eqs. (19) and (20) to parameterise Γ_s dynamics after a fertilisation event.

– Temporal dynamics in Γ_g after fertilisation and/or grazing

We suggest using the same Γ dynamics equation for the ground layer as for the plant layer (Eq. 20). Given that in the days following slurry spreading or fertiliser application, most of the emissions are from the slurry or fertiliser itself, we propose using $\Gamma_{g(\max)}$ equal to Γ_g of the slurry or fertiliser used. As for τ we propose to use a value of 2.88 days similar to the value used for Γ_s parameterisation.

In the case of slurry, $\Gamma_{g(\max)}$ is calculated from TAN content and pH of the slurry. Typical values for different organic fertiliser types are given in Table 5.

For mineral fertiliser application, we propose to estimate a Γ value for the fertiliser in the top 5 cm of the ground layer. If we suppose that the applied N fertiliser is dissolved in the soil water content in the top 5 cm of the ground layer then we can approximate $\Gamma_{g(\max)}$ by the following equation:

$$\Gamma_{g(\max)} = \frac{N_{\text{app}}/\theta_s \times M_N \times l_s \times h_m}{10^{-\text{pH}}} \quad (21)$$

where N_{app} is the N content of the applied fertiliser in kg-N ha^{-1} , θ_s is the soil percentage water content, M_N is the molar mass of nitrogen (14 g mol^{-1}), l_s is the soil layer where fertiliser is applied (typically 0.05 m), h_m is to convert hectares to m^2 ($=10\,000 \text{ m}^2$) and pH is the pH of the soil solution after fertiliser application. Soil water content depends on meteorological conditions as well as soil type. Rough values for θ_s are given in Table 7 for different soil types. Concerning pH, we propose to use a pH value of 7.5 for urea based fertilisers and AS or DAP based fertilisers in calcareous soils and a pH value of 7 for AS and DAP fertilisers in acidic soils and AN fertilisers. In the case of significant rainfall, nitrate N might be lost in leaching; this can also trigger soil microbiology therefore altering Γ_g . Very few measurements exist under these conditions. Equation (21) is a rough approximation of fertiliser emissions and should be better evaluated and tested.

For grazing, one could assume that it depends on the intensity or the number of live units of cattle per hectare. The few data available show similar Γ values for fields extensively or intensively grazed (Milford, 2004; Fowler et al., 2007). We therefore propose to use a constant Γ_g for grazed grasslands equals to 4000 until the animals are removed from the field.

One should note, however, that usually emissions of NH_3 from fertiliser application and grazing are accounted for as biogenic emissions derived from inventories in several models (EMEP, CHIMERE, etc.). Therefore when integrating the bi-directional exchange scheme described here corrections to avoid double counting are necessary.

4.6 Proposed parameterisation for R_w

The cuticular resistance (R_w) clearly depends on air relative humidity as expressed in Eq. (3). From Fig. 2 it is difficult to see a pattern in the data as a whole. However, there is a relationship between $R_{w(\text{corr})}$ at 95% RH and AR, the molar ratio of total acid/ NH_3 in the atmosphere, as shown in Fig. 7. The functions per ecosystem type of $R_{w(\text{corr})}$ at 95% RH versus AR are also shown, which is an expansion of the analysis by Nemitz et al. (2001). The data as divided per ecosystem seem rather scattered. We therefore propose to use the power fit (Eq. 22 below) for all ecosystems as a parameterisation of

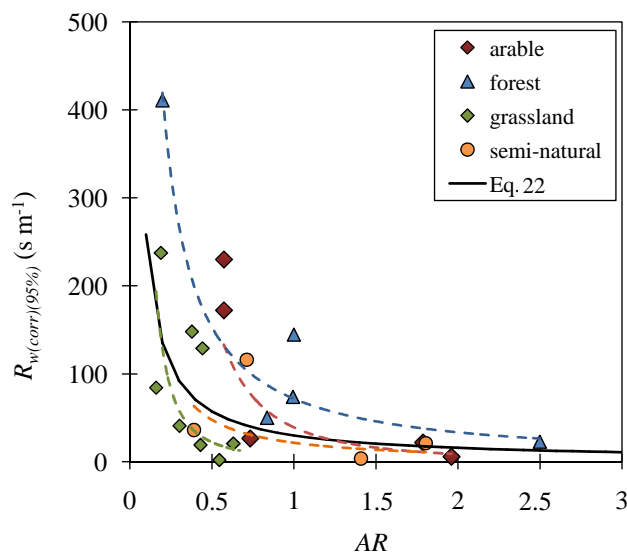


Fig. 7. Cuticular resistance at 95% relative humidity ($R_{w(\text{corr})}(95\%)$) as a function of the ratio of total acid/ NH_3 ($\text{AR}) = (2[\text{SO}_2] + [\text{HNO}_3^-] + [\text{HCl}]) / [\text{NH}_3]$ in the atmosphere separated according to ecosystem type. $R_{w(\text{corr})}(95\%)$ is corrected for LAI and temperature. Dotted lines represent the corresponding fitted power curves to the data by ecosystem type. The solid line represents the fitted power curve to all ecosystem types.

$R_{w(\text{corr})}(95\%)$. It is worth noting that $R_{w(\text{corr})}(95\%)$ is corrected for LAI and temperature according to Eq. (4).

$$R_{w(\text{corr})}(95\%) = 29.9 \times (\text{AR})^{-1} \quad (22)$$

If we consider that the relation between RH and $R_{w(\text{corr})}$ is linear for relative humidity values between 95 and 100% then:

$$R_{w(\text{corr})(\text{min})} = R_{w(\text{corr})(100\%)} = 31.5 \times (\text{AR})^{-1} \quad (23)$$

Thus combining Eq. (3) and Eq. (23) above we obtain the following equation which we propose as a parameterisation for R_w :

$$R_{w(\text{corr})} = 31.5 \times (\text{AR})^{-1} \times e^{a(100-\text{RH})} \quad (24)$$

Concerning the parameter a , deriving a generalised parameterisation for it seems much more challenging because its biological or physical significance is not fully understood. We could not find any relation between values of the parameter a for the compiled data and reported dependencies of R_w such as aerosol burden or leaf wetting potential. We therefore suggest using the average values per ecosystem type of the parameter a for the compiled R_w data.

- Forest: $a = 0.0318 \pm 0.0179$ (st. dev.)
- Grassland: $a = 0.176 \pm 0.126$ (st. dev.)
- Short semi-natural: $a = 0.120 \pm 0.107$ (st. dev.)
- Arable: $a = 0.148 \pm 0.113$ (st. dev.)

5 Limitations of the approach

The parameterisation of the bi-directional exchange model presented here provides a basis for integrating ammonia exchange processes into large scale chemical transport and earth system models. One of its major advantages as compared to the parameterisation proposed by Zhang et al. (2010) is the mechanistic linkage between Γ and atmospheric N deposition but also between Γ and agricultural practices. This approach therefore allows ecosystems to dynamically respond to changes in emissions and deposition patterns but also to land management events. It has, however, several limitations.

- *Uncertainties.* The parameterisation derived here relies on measurements of Γ_s and atmospheric N deposition, both of which are subject to uncertainties. There is no absolute reference method for estimating Γ_s , while N deposition rates were extracted from sources of varying quality. As for R_w , as stated earlier, we do not have a direct measurement technique and can only derive values for it by making certain assumptions. Furthermore, the relationships established between different variables are far from perfectly correlated. This is especially true for example for the maximum Γ_s values as a function of mineral N fertiliser application (Fig. 6a). These particular data are very scattered, probably due to the different conditions specific to each experiment and the different types of fertiliser applied (nitrate, ammonium or ammonium nitrate). There is currently a lack of measurements for Γ_s with organic fertiliser (manure, slurry and

Table 8. Summary of the proposed parameterisation of a two-layer NH₃ bi-directional exchange model.

			Γ		R_w	
			Γ_s	Γ_g	R_{wmin}	a
Un-managed			$\Gamma_s = 246 + (0.0041) \times (N_{in})^{3.56}$	N/A ($R_g = \infty$)	$R_w = R_{w(min)} \times e^{a \times (100 - RH)}$	<ul style="list-style-type: none"> • Forest: 0.0318±0.0179 • Semi-natural 0.120±0.107 • Arable: 0.148±0.113 • Grassland 0.176±0.126
Managed	Background	Without vegetation	N/A (R_s and $R_w = \infty$)	$\Gamma_g = 500$		
		With vegetation	$\Gamma_s = 66.4 + (0.0853) \times (N_{in})^{1.59}$	N/A ($R_g = \infty$)		
	Management events	Mineral fertilisation	$\Gamma_s = \Gamma_{s(max)} \times e^{(-t/\tau)}$ $\Gamma_{s(max)} = 12.3 \times N_{app} + 20.3$ $\tau = 2.88$ days	$\Gamma_g = \Gamma_{g(max)} \times e^{(-t/\tau)}$ $\Gamma_{g(max)} = \frac{N_{app} / (\theta_s \times M_N \times l_s \times h_m)}{10^{-pH}}$ $\tau = 2.88$ days		
		Organic fertilisation		$\Gamma_g = \Gamma_{g(max)} \times e^{(-t/\tau)}$ $\Gamma_{g(max)} = \frac{TAN_{slurry}}{10^{-pHslurry}}$ $\tau = 2.88$ days		
	Grazing	$\Gamma_g = \Gamma_{g(max)} \times e^{(-t/\tau)}$ $\Gamma_{g(max)} = 4000$ $\tau = 2.88$ days (after cattle are removed from field)	$R_{w(min)} = 31.5 \times (AR)^{-1}$			

Γ is unitless; t and τ are in days; $R_{w(corr)}$ is in $s\ m^{-1}$;

N_{in} and N_{app} are the total N input to the ecosystem ($N_{app} + N$ deposition) and N applied as fertiliser respectively in $kg\ ha^{-1}\ yr^{-1}$.

urea) application events. Nevertheless, the parameterisation proposed here provides a first attempt to move from a static offline emission inventory approach to the dynamic modelling of emissions, at least for fertilised land. This simple approach takes into account the effect of temperature on the emission and, to some extent, precipitation, but leaves scope for future refinement. There is also a significant scatter in $R_{w(min)}$ as a function of the ratio of total atmospheric acid to NH₃ concentrations for arable and short semi-natural ecosystems.

– *Applicability.* The stomatal ammonia compensation point is not only driven by N input to the ecosystem, it is a strongly regulated process that depends on plant metabolism and environmental conditions (Riedo et al., 2002; Massad et al., 2008). The parameterisation proposed here would therefore not capture the dynamics of Γ_s at a field or plant scale. For example, Mattsson et al. (2009b) observed high variability of Γ_s between different grass species in the same sward (and thus subjected to the same N_{dep}). It should also be noted that R_w is set as a function of RH, NH₃ and total acid concentrations measured at a reference height above the canopy, when in fact, R_w will more closely respond to the values at the leaf surfaces. This is a necessary simplification, since surface concentrations are highly dependent on the fluxes, so that accounting for this would make the calculations much more complex. Finally, the

data available for Γ_s as well as R_w values are limited mainly to Northern European ecosystems. Very few data are available covering other geographical regions (especially tropical and subtropical climates). While the parameterisations are expected to be reasonably robust in very cold climates (with freezing conditions increasing R_w), the uncertainties are much larger for application to warmer climates, for example where soil and litter decomposition processes may have a larger effect on net ammonia fluxes. In addition, N fixation, not quantified in most chemistry and transport models becomes a large fraction of the N input at many tropical sites.

– *Scaling.* The parameterisation proposed here requires land use data as well as agricultural practice data to be integrated at sub-grid level in large scale models. This limits the model to situations where accurate agricultural practice data are accessible, while sub-grid resolution should be defined in accordance with land use data available and type of model used. Another important limitation is the availability of NH₃ concentrations and acid ratios at sub-grid level (by landuse type). NH₃ concentration for example over an agricultural area will be much greater than over a semi-natural area.

- *Circularity*. There remains the issue of circularity in solving the model, since the parameterisation proposed requires the use of atmospheric N deposition and NH₃ concentration data as a basis to infer NH₃ fluxes. This issue can be addressed by spinning up the model with the same year several times, so that it converges to a constant N deposition value. Once an initial model time series is available, N deposition rates data from previous years are appropriate to use in the parameterisation of Γ_s .

6 Conclusions

A complete parameterisation for estimating bi-directional exchange of NH₃ suitable for atmospheric chemistry and transport models is presented. The parameterisation includes newly developed specifications for the cuticular resistance and the stomatal compensation point. A summary is presented in Table 8. Currently, most regional models only treat dry deposition of ammonia, and do not address bi-directional exchange. Incorporating this effect can be expected to improve the estimation of NH₃ atmospheric concentrations and total atmospheric N deposition over ecosystems. Nevertheless, there are relatively limited measurements of the key model parameters: the temperature normalized stomatal compensation point (Γ_s) and the resistance for deposition to plant surfaces (R_w), with most data available for temperate, European conditions. Although in the absence of other measurements, the principles of this parameterisation can be expected to apply for other climates, the uncertainties are expected to be largest in sub-tropical and tropical conditions, where background soil mineralization processes may have a larger effect on net ammonia fluxes. Future steps should include a thorough validation by integrating the parameterisation in a large scale system model and comparing the output to point measurements, previous model outputs and other simulation models. Further model developments, beyond that presented in this paper would rely heavily on the future availability of more extensive and detailed ammonia flux measurements but also on more sophisticated sub-grid treatments in chemistry and transport models.

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