



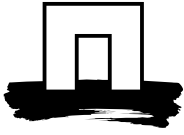
# Ammonia emission from standing crops and crop residues

Contribution to total ammonia emission in the Netherlands

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# Table of contents

	page
Preface	1
Summary	3
1. Introduction	5
2. Methodology for estimating ammonia emissions from standing crops and crop residues	7
2.1 Introduction	7
2.2 Ammonia emissions from standing crops	7
2.2.1 Introduction	7
2.2.2 Calculation of the ammonia emission from a crop	8
2.3 Ammonia emission from crop residues	11
2.3.1 Introduction	11
2.3.2 Arable crops	11
2.3.3 Green manure crops	14
2.4 Ammonia emission from grassland	15
2.4.1 Pasture topping	16
2.4.2 Cutting, drying and collection	16
2.4.3 Grassland renovation	16
3. Areas of agricultural crops in the Netherlands	19
4. Estimated ammonia emission from crops and crop residues in the Netherlands	23
4.1 Emissions from crops	23
4.2 Emissions from crop residues	26
5. Discussion	29
5.1 Ammonia emission from crops	29
5.2 Ammonia emission from crop residues	30
5.3 Relative contribution to national ammonia emissions from agricultural activities	32
Conclusions	33
References	35
Appendix I. Evaluation of gammas	6 pp.
Appendix II. Measured compensation points	15 pp.
Appendix III. Literature data on crop residues and their N content	3 pp.
Appendix IV. Field period of crop residues	3 pp.
Appendix V. Land use class dependent parameters within DEPAC	3 pp.



## Preface

Standing crops and crop residues may contribute to ammonia emission, but sufficient information on their contribution to ammonia emission in the Netherlands is up till now lacking. The Ministry of Infrastructure and Environment asked Plant Research International of Wageningen UR (PRI-WUR) and the National Institute for Public Health and Environment (RIVM) to assess the contribution of crops and crop residues to the national ammonia emission. In this study RIVM focused on the emission from standing crops and PRI-WUR focused on the emission from crop residues. Results of both emission sources were combined with cropped areas, crop residue management and ambient ammonia concentrations. This report describes the results of this study and an estimation of the ammonia emission from crops and crop residues in the Netherlands.





## Summary

Major sources for emission of ammonia are animal housing, manure storage, handling and use of livestock manure and fertilizers in agricultural fields. Standing crops and crop residues may also contribute to ammonia emission, but sufficient information on their contribution to ammonia emission in the Netherlands is up till now lacking. To assess the contribution of crops and crop residues to the national ammonia emission, emission measurements and literature data were combined with cropping areas, information on the crop residue management and ambient ammonia concentrations.

The ammonia emission from a crop is defined as the integral of the exchange of ammonia over the entire growing season of the crop, i.e. between planting or sowing and crop harvest. In the literature, experimental ammonia emission factors of standing crops vary between large emission and deposition values per growing season. Obviously, these differences are related to the intensity of agricultural activities. The large emission values were found when crops had received a high N-input by fertilization, or after cutting of a crop. In addition to these agricultural activities, emission is affected by plant parameters, meteorological conditions and by ambient ammonia concentration levels. For calculation of the ammonia volatilization of standing crops in this study, a resistance model (DEPAC model) was used in which the regional differences in weather conditions and the atmospheric concentrations of ammonia in the Netherlands was taken into account.

Crop residues are the plant parts that remain on the field after crop harvest. After the plant parts are cut, the protein in the plant tissue will degrade and nitrogen is released. Part of the nitrogen is emitted as ammonia if crop residues are left on the soil surface. If residues are incorporated into the soil, ammonia volatilization will stop. The amount of crop residue that remains on the field after harvest and its N content depends on production goal of the crop, time of production within a growing season, soil fertility level and fertilization. Ranges in the amount of crop residues (in kg ha<sup>-1</sup>) and the N content (in g kg<sup>-1</sup> dry matter) were derived from literature to estimate ammonia volatilization from crop residues. An estimation was made on the degree in which crop residues are incorporated into the soil. Residues that are incorporated within days after harvest do not contribute to the ammonia emission.

The contribution of crops and crop residues (excl. grazed grassland) to total ammonia volatilization in the Netherlands was estimated at 1.5 million kg NH<sub>3</sub>-N from standing crops, with a range of 0 to 6 million kg NH<sub>3</sub>-N and 1.9 million kg NH<sub>3</sub>-N from crop residues, with a range between 0.3 and 3.8 million kg NH<sub>3</sub>-N. In total, the ammonia emission from standing crops and crop residues together lies between 0-10 million kg NH<sub>3</sub>-N with the best estimate being about 3.4 million kg NH<sub>3</sub>-N.

Ambient ammonia concentration has a large effect on ammonia emission from standing crops. Below a concentration of 5 µg NH<sub>3</sub>-N/m<sup>3</sup> standing crops in the Netherlands always emit ammonia and above 15 µg/m<sup>3</sup> ammonia is always deposited. Between these two boundaries, depending on local circumstances, there can be either emission or deposition. The uncertainty in the calculation of the emissions from standing crops is quite large and mainly due to the large uncertainty in the estimates of the ammonium levels (compensation point) of the plants.

Ammonia volatilization from crop residues can be reduced by quicker incorporation of crop residues. However, ammonia volatilization from residues cannot completely be prevented as e.g. time remains required for haulm killing of potato and losses of grass during cutting, drying and collection for silage cannot be prevented. The N content of residues has a large effect on calculated ammonia volatilization, as variation in N content of the residues affects both the % of total N that volatilizes as NH<sub>3</sub> and the total N in the residues.

Within the Netherlands, the emissions from standing crops are small (< 5%) compared to the direct emissions of ammonia by animal housings and manure application, but about 15% of the contribution by fertilizers and in the same order as emissions during grazing. This also counts for crop residues. The estimated ammonia emission from crops and crop residues together are more than the contribution by manure storage and about twice as much as the estimated ammonia emission by grazing.



# 1. Introduction

To protect the environment, the European Union (EU) has adopted the National Emission Ceilings (NEC) directive (EC, 2001). This directive sets national limits for amongst others ammonia ( $\text{NH}_3$ ) emissions. Velthof *et al.* (2012) developed a new model for national emission registration in the Netherlands called NEMA (National Emission Model for Ammonia). This model adds up the emission from the various sources. Major sources for emission of ammonia are animal housing, manure storage, handling and use of livestock manure and fertilizers in agricultural fields. Standing crops and crop residues may also contribute to ammonia emission, but sufficient information on their contribution to ammonia emission in the Netherlands is up till now lacking. Transferring the crop emission estimate in Denmark (NERI, 2007) to practices in the Netherlands, however, yields an estimate of 4,8 million kg ammonia which is about 4% of the Dutch agricultural emission (Van Pul *et al.*, 2008).

Various measurements and literature reviews show that standing crops and crop residues may emit ammonia (see references under Section 2.2. and 2.3). To assess contribution of crops to the national ammonia emission, the measurements and literature data need to be combined with cropping areas and information on the residue management. This report describes the method used to estimate the emission from crops and crop residues in the Netherlands.

Chapter 2 gives the background on the processes of ammonia volatilization and the way how to parameterize these processes. Whilst the processes and their parameterizations are considered to be universally valid, the focus lies on the application for the Netherlands. Chapter 3 gives information on what crops are considered and their cultivation areas in the Netherlands. Chapter 4 integrates all available data into an estimate of the national ammonia volatilization by crops and crop residues. A discussion on the results and conclusions are given in Chapter 5 and 6.



## 2. Methodology for estimating ammonia emissions from standing crops and crop residues

### 2.1 Introduction

Standing crops and crop residues may emit ammonia. The amount of ammonia that is released depends on some plant physiological and environmental conditions. This chapter gives a brief overview of literature on ammonia volatilization from crops and crop residues, and subsequently the way how the emission is determined.

The chapter is split into sections on emissions for standing crops (Section 2.2) and crop residues (Section 2.3). Grassland is considered separately (Section 2.4) due to the fact that grass is a perennial crop with quite different management regimes compared to annual arable crops.

Section 2.2 focusses on the emission that originates from standing crops during the growing season till harvesting. So emissions occurring from application of manure before the growing season are not considered. The emissions after harvesting, i.e. that originate from crop residues, are estimated and discussed in Section 2.3.

### 2.2 Ammonia emissions from standing crops

#### 2.2.1 Introduction

Laboratory work has demonstrated that living plants can absorb  $\text{NH}_3$  from the air (=deposit) (Farquhar *et al.*, 1980; Hutchinson *et al.*, 1972) and also that plants may desorb (=emit) ammonia to the air (Farquhar *et al.*, 1980; Hooker *et al.*, 1980; Odeen & Porter, 1986; Schjoerring & Mattsson 2001). Also, field studies have shown crops may both loose to and gain ammonia from the ambient air (Denmead *et al.*, 1978; Harper *et al.*, 1987). The direction of this exchange of  $\text{NH}_3$  between plant and atmosphere depends on the difference between ammonia concentration in the ambient air and the concentration within and at the leaves. While at relatively high ambient concentrations  $\text{NH}_3$  is absorbed by plants, at low concentrations plants will release  $\text{NH}_3$ . The turning point depends on the ammonia concentration in the plant that is to say it depends on its fertilization and growing state. At the so-called 'NH<sub>3</sub> compensation point' (Farquhar *et al.*, 1980), emission and deposition are in balance or compensate for each other. For many crops periods of emission and deposition of ammonia will alternate on a daily and seasonal basis, so it is appropriate to consider the net crop-atmosphere exchange of ammonia (Wichink Kruit, 2010).

Over the last decades the exchange of ammonia of various crops with the atmosphere has been measured; e.g. managed grassland (Harper *et al.*, 1996), unmanaged grassland (Wichink Kruit 2010), corn (Meyers *et al.*, 2006), wheat, barley (Schjoerring & Mattsson, 2001), oil seed rape (Sutton *et al.*, 2000). The magnitude of the  $\text{NH}_3$  exchange between the atmosphere and crops was found to vary from crop to crop and to depend on growing conditions and agricultural management.

The effect of agricultural management on ammonia exchange processes was found in a large field experiment with grassland, where emissions increased after grass cutting and after N-fertilization compared with before the cutting (Milford *et al.*, 2009; Sutton *et al.*, 2009). Variation between crops can be caused by differences in leaf drop and senescence. In a standing crop, senescing leaves and leaf litter are a major source of  $\text{NH}_3$  (Sutton *et al.*, 2000).  $\text{NH}_3$  emission from maturing plant stands was measured by Mannheim *et al.* (1997) under simulated environmental conditions with the wind tunnel method.

Growing conditions vary over the year. Harper *et al.* (1996) measured the net effect of  $\text{NH}_3$  exchange in a heavily fertilized grassland during a period of 40 days. They found a net  $\text{NH}_3$  absorption of  $2.3 \text{ kg N ha}^{-1}$  in spring and  $3.9 \text{ kg N ha}^{-1}$  in summer. Plantaz (1998) measured a net annual emission of ammonia of grazed grassland on peat soil in the Netherlands of about  $3.7 \text{ kg NH}_3\text{-N ha}^{-1}$  as the result of net emission of  $4.4\text{-}5.5 \text{ kg ha}^{-1}$  in the grazed half year (May-October) and net deposition of  $0.7\text{-}1.5 \text{ kg ha}^{-1}$  in the ungrazed half year. The source of the emission was mainly manure, and in this research, the acidity of the peat soil may have limited  $\text{NH}_3$  emission from all sources, i.e. soil, manure and decaying residues.

Schjoerring *et al.* (1993) and Schjoerring & Mattsson (2001) measured ammonia fluxes above a number of crops (winter wheat, spring barley, winter oilseed rape, field pea) in Denmark. Over the growing season net emission fluxes were found ranging from  $0.5\text{-}5 \text{ kg N ha}^{-1}$  with an average of about  $3 \text{ kg N ha}^{-1}$ .

Asman (2009), Massad *et al.* (2010) and Zhang *et al.* (2010) give overviews of the exchange of ammonia from various vegetation types as measured during the last decades.

In the literature, more experimental ammonia emission factors of standing crops can be found. These factors vary between large emission and deposition values of several  $\text{kg N per ha per growing season}$ . Obviously, these differences are related to the intensity of agricultural activities. The large emission values were found when crops had received a high N-input by fertilization, or after cutting of a crop. In addition to these agricultural activities, emission is affected by environmental conditions, i.e. meteorological conditions and finally by ambient ammonia concentration levels. Therefore, it is hard to evaluate an emission factor based on the collected literature data alone. However, in a number of papers the measurement data is used to derive parameters which model the exchange of ammonia between atmosphere and vegetation. In this way emissions can be calculated that go together with deviating conditions. This will be further elaborated in Section 2.2.2.

## 2.2.2 Calculation of the ammonia emission from a crop

The emission of ammonia from vegetation is among others a function of plant parameters, meteorological conditions and the ammonia concentration in air. The processes of the exchange of ammonia between the atmosphere and the underlying surface are often described using a resistance model. These models are also regularly used in studies on the deposition of substances and are thus used to derive parameters from measurements of the emission and deposition fluxes (e.g. Sutton *et al.*, 1995). In essence, these models describe the transport of a substance to or from the surface using three resistances:

1. a resistance  $R_a$  models the atmospheric transport by turbulence between the ambient air to a level just above the canopy surface,
2. a resistance  $R_b$  models the transport from this level to the canopy surface,
3. a resistance  $R_c$  models the transport from the canopy surface and the canopy itself (that is in the stomata, in water layers on leaves, to the soil surface).

An implementation of such a resistance model is made in the DEPAC-module (Van Zanten *et al.*, 2010 and Figure 2.1-left). The canopy resistance  $R_c$  may be considered as the result of a number of resistances representing transport processes in and at the canopy. The basic model with the canopy resistance  $R_c$  split up in resistances is given in Figure 2.1-right. The physical unit of the resistances is  $[\text{s/m}]$ . Physically, they are the inverse of the exchange – deposition or emission - velocity.

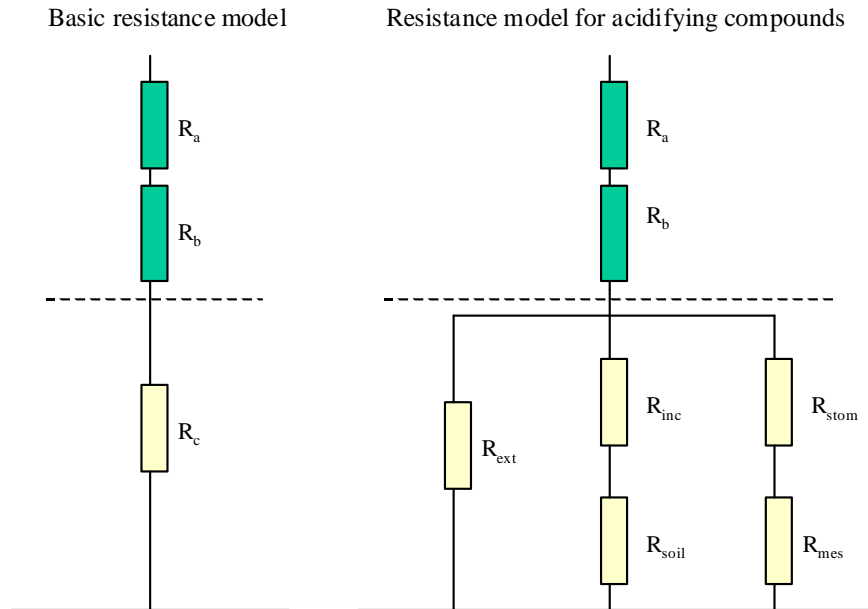


Figure 2.1. Resistance model with sub-resistances for the canopy resistance  $R_c$ . See text for explanation of symbols. Crop emissions are calculated by considering the pathway described by  $R_a$ ,  $R_b$ , and  $R_{stom}$  only.

In this model  $R_{stom}$  and  $R_{mes}$  represent the stomatal and mesophyll resistances of leaves respectively. Mesophyll tissue, in plant anatomy, consists of cells that lie between the upper and lower epidermis layers of a leaf. It contains the apoplast, where plants transport water and solutes.  $R_{inc}$  and  $R_{soil}$  are resistances representing in-canopy vertical transport to the soil, which bypasses leaves and branches, and transport into the soil.  $R_{ext}$  is an external resistance, which represents transport to and from leaf and stem surfaces, especially when these surfaces are wet. The DEPAC module contains parameters for each of the resistances given in Figure 2.1 for various land-use types and for various gaseous components. Furthermore, a seasonal distinction is made in the values of some of the resistances. The resistance modeling uptake via the stomata,  $R_{stom}$ , is calculated according to Emberson *et al.* (2000). The exchange of a substance is obtained by calculating the resistances and the concentration potential between the atmosphere and the surface.

For the computation of the standing crop emission only the air-stomata-mesophyll exchange has been considered. So, the pathways containing  $R_{ext}$ ,  $R_{inc}$ , and  $R_{soil}$  were disconnected. This implies that the net ammonia emission from soil and wet cuticula parts has been ignored.

The stomata of a plant are the pores on its leaves and stems that control its gas exchange. Through these openings air containing carbon dioxide enters the plant, while oxygen and water vapor exit. Also ammonia can pass through. The direction of this flow depends on the concentration difference between the ammonia in the free air and the mesophyll. So, the emission of ammonia ( $E$ ) from a crop can be calculated from the stomatal compensation point ( $\chi_s$ ) the atmospheric concentration ( $\chi_a$ ) and the resistances determining the transport from the crop stomata to the atmosphere according to:

$$E = -\frac{(\chi_a - \chi_s)}{R_a + R_b + R_s}. \quad [1]$$

More details on the atmospheric resistances and the stomatal resistance and how they are calculated can be found in Van Zanten *et al.* (2010).

The stomatal compensation point of ammonia has been determined for several vegetations in various types of experiments: in the laboratory, in closed chambers and in the field. Stomatal compensation points of ammonia vary from low values ( $< 1 \mu\text{g}/\text{m}^3$ ) in non-managed ecosystems to high values ( $> 10 \mu\text{g}/\text{m}^3$ ) for well managed and fertilized crops.

The stomatal compensation point depends on the ratio between the ammonium concentration and the pH in the apoplast of the mesophyll, following the equilibrium  $\text{NH}_3 + \text{H}^+ \leftrightarrow \text{NH}_4^+$  (see Appendix I). This ratio is denoted by  $\Gamma_s$ . The stomatal compensation point ( $\chi_s$ ) is a linear function of  $\Gamma_s$  and an exponentially increasing function of temperature ( $T_s$ ) (e.g. Wichink Kruit, 2010):

$$\chi_s = \frac{2.75 \cdot 10^{15}}{T_s + 273.15} \exp\left(\frac{-1.04 \cdot 10^4}{T_s + 273.15}\right) \cdot \Gamma_s \quad [2]$$

At high temperatures the stomatal compensation point can reach high values (see Figure 2.2).

Values for the ratio  $\Gamma_s$  vary with plant types and growing conditions. For a natural vegetation, the ratio  $\Gamma_s$  generally is as low as a few tenths, but for agricultural crops the ratio  $\Gamma_s$  can be as high as several thousands. However the uncertainty in the ratio  $\Gamma_s$  values is quite high.

Values for the ratio  $\Gamma_s$  and compensation points [ $\chi_s$ ] were obtained from literature and are discussed in detail in Appendix I and Appendix II. For a number of agricultural crops, potatoes and sugar beet, grown in the Netherlands no  $\Gamma_s$  values were found. For these crops, default conservative values were used. For the most important agricultural crops in the Netherlands the  $\Gamma_s$  values are presented in Table 2.1. Since the uncertainty in the  $\Gamma_s$  values is large also a range is presented.

*Table 2.1. Most important crops in The Netherlands (according to area) and proposed  $\Gamma_s$  values quantifying its fertilization status. Default values for potatoes and sugar beet.*

Crop	Area (in 1000 ha)	$\Gamma_{\text{lower}}$	$\Gamma_{\text{medium}}$	$\Gamma_{\text{upper}}$
Grassland intensively managed, not grazed	523	500	2000	4000
Maize grain+ silage + corn cob mix	262	200	1500	4000
Potatoes	154	500	1000	2000
Cereal crops Wheat (of which 3/4 winter wheat), Barley	191	500	2000	4000
Sugar beet	76	500	1000	2000
Total area (in 1000 ha)	1206			

Figure 2.2 explores the impact of high temperatures and high ammonia-hydrogen ratios  $\Gamma_s$  on the stomatal compensation point  $\chi_s$ . Eq 2 and Table 2.1 imply that compensation points may rise to values well over the ambient atmospheric concentration and hence, the crop will emit ammonia.

The net exchange of ammonia between crops and the ambient air can be calculated using eq. 2 along with measurements of the average atmospheric ammonia concentration. This is elaborated further in Section 4.1.



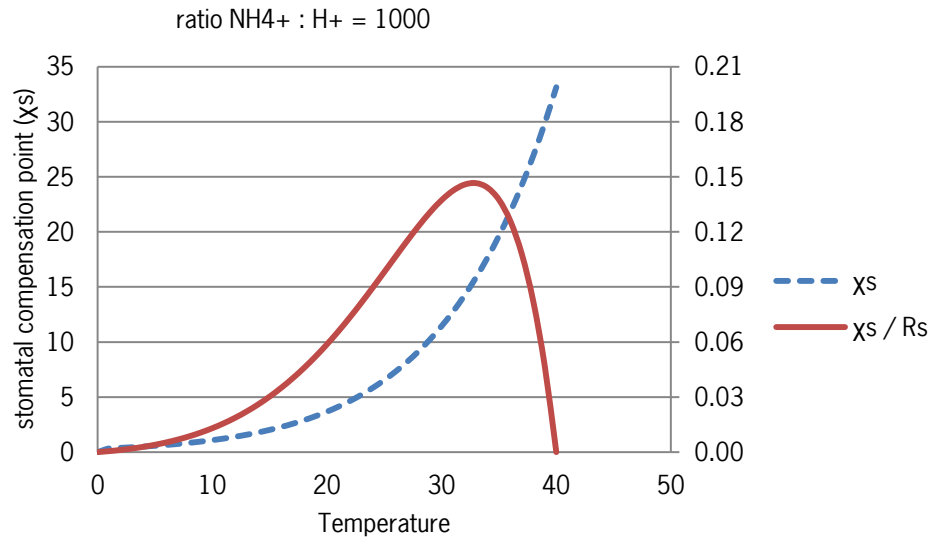


Figure 2.2. The stomatal compensation point  $\chi_s$  ( $\mu\text{g NH}_3/\text{m}^3$ ) for increasing temperature ( $^{\circ}\text{C}$ ) and mesophyll ammonia-hydrogen-ratio  $\Gamma_s$  of 1000. Also, the combined impact of temperature on stomatal compensation point and the stomatal resistance  $R_s$  (s/m) is also shown. At high temperatures the exchange effectively decreases to zero as at high temperature the stomata close.

## 2.3 Ammonia emission from crop residues

### 2.3.1 Introduction

Crop residues are the plant parts that remain on the field after crop harvest. After the plant parts are cut, the protein in the plant tissue will degrade and nitrogen is released (Marstorp, 1995; Mohr *et al.*, 1998). Part of the nitrogen is emitted as ammonia if crop residues are left on the soil surface. If residues are incorporated into the soil, ammonia volatilization will stop (De Ruijter *et al.*, 2010; Janzen and McGinn, 1991; Mohr *et al.*, 1998). In De Ruijter and Huijsmans (2012), an overview of measured data of ammonia volatilization from surface applied crop residues is given, and a relationship between ammonia volatilization (expressed as fraction of the N content of the residues) and N content of the residues was derived. When the N content is below 12.7 g/kg the ammonia emission equals zero.

The regression model of De Ruijter and Huijsmans (2012) is valid for crop residues that remain on the soil surface for a period long enough to expect all ammonia to be volatilized. When crop residues are incorporated earlier, the fraction of the calculated ammonia volatilization needs to be estimated (Chapter 4.2).

### 2.3.2 Arable crops

Within a crop, the amount of crop residue that remains on the field after harvest and its N content depends on production goal, time of production within a growing season, soil fertility level and fertilization. An example of the effect of production goal is most clear with carrot, where entire plants are harvested for the production of bunch carrot, and where foliage remains on the field for the production of washed carrot. The amount and N content of some vegetables can also be affected by harvest time (early or late in the growing season), as well as by soil fertility and vigor of growth (Feller *et al.*, 2011). N fertilization affected the total N load (amount and N content) of crop residues in sugar beet: at an N application of 120 kg ha<sup>-1</sup> the N content of crop residues was 88 kg ha<sup>-1</sup>, whereas at an N application of 190 kg ha<sup>-1</sup> the N content was 124 kg ha<sup>-1</sup> (Van Geel *et al.*, 2008).

Ranges in the amount of crop residues (in  $\text{kg ha}^{-1}$ ) and the N content (in  $\text{g kg}^{-1}$  dry matter) are given in literature and are presented in Appendix III. For the present study, single average values are derived that are used in estimating ammonia volatilization from residues of arable crops (Table 2.2). For potato, a further distinction was made into seed potatoes, ware potatoes and starch potatoes, in analogy to the registration of cultivated areas by Statistics Netherlands (see Chapter 3).

Experts were consulted on the degree in which crop residues are incorporated into the soil. Residues that are incorporated within days after harvest do not contribute to the ammonia emission. When residues are incorporated after a longer time being left at the soil surface, their contribution to ammonia volatilization is based on the field period of crop residues after crop harvest and mixture with soil at harvest (Appendix IV). The contribution of crop residues to the ammonia volatilization is expressed by a fraction. This fraction is based on the field period of crop residues after crop harvest (incorporation within a few days after harvest means no contribution; fraction=0) and mixture with soil at harvest (covering half of the residues with soil means a fraction of 0.5). Total ammonia volatilization (fraction = 1) is described by the regression equation derived from literature data (De Ruijter & Huijsmans, 2012).

Table 2.2. Averaged values of N content of crop residues based on literature data (Appendix III) and for each crop the fraction of residues that contribute to ammonia volatilization in the Netherlands (Appendix IV).

Group	Crop name	Residue	N-content	N in crop	Fraction <sup>1</sup>
		dry matter		residue	
		(kg ha <sup>-1</sup> )	(g/kg dry matter)	(kg/ha)	
Arable crops	wheat	5000	9	45	-
	barley	3150	6	19	-
	grain maize	6250	9	56	0.1
	green pea	1900	25	47	1.0
	marrowfat pea	1800	22	40	1.0
	dry bean	2650	6	16	-
	field beans	1500	13	19	-
	rapeseed	4000	10	40	-
	caraway	3000	9	27	-
	poppy seed	1400	15	21	1.0
	linseed/flax	200	5	1	-
	chicory	2700	22	59	0.25
	hemp	1500	15	23	1.0
	potatoes	1700	18	31	
	- seed potatoes	2700	32	85	0.75
	- ware potatoes	2100	15.5	31.5	0.75
	- starch potatoes	2100	15.5	31.5	0.75
	sugar beet	4600	26	120	0.27
	fodder beet	3500	26	92	0.27
	Vegetable crops	strawberry - open field	1100	17	19
Leaf and stem vegetables	endive	1400	29	40	0.25
	asparagus	900	29	27	1.0
	Florence fennel	3050	33	100	0.25
	leek	2650	31	82	0.50
	celery	600	23	14	0.25
	head lettuce	650	34	22	-
	lettuce - iceberg	1300	35	45	0.25
	spinach	700	43	30	0.1
Root and tuber crops	bunch & washed carrot	600	15	9	0.15
	celeriac	3100	24	75	0.25
	red beet	3800	25	95	0.25
	salsify	2550	18	46	0.25
	onion	2700	7	19	-
	winter carrot	3100	21	65	0.15
Cabbage crops	cauliflower	3700	36	132	0.6
	kale	3450	25	86	1.0
	broccoli	4200	37	156	0.6
	Chinese cabbage	2000	35	71	0.5
	red cabbage	4800	28	135	0.6
	green cabbage	4800	29	140	0.6
	Brussels sprouts	8100	21	170	1.0
	white cabbage	4600	24	111	0.6

Group	Crop name	Residue dry matter	N-content	N in crop residue	Fraction <sup>1</sup>
		(kg ha <sup>-1</sup> )	(g/kg dry matter)	(kg/ha)	
Leguminous crops	pea	5900	29	170	0.25
	green bean	3000	26	77	0.33
	field beans	1250	13	16	-
Fruit vegetables	zucchini	4000	38	150	0.25
Other vegetables		2900	23	67	0.25

<sup>1</sup> *The fraction expresses the part of the residue that contributes to ammonia volatilization, based on the field period of crop residues after crop harvest. There is no contribution (fraction = 0) when incorporation takes place within a few days after harvest or when the N content of the residues is below 12.7 g/kg dry matter. Mixture with soil at harvest covering half of the residues with soil means a fraction of 0.5. No incorporation means total ammonia volatilization (fraction = 1).*

### 2.3.3 Green manure crops

Green manure crops produce ammonia volatilizing residues when they are killed by frost or by herbicides. The amount of dry matter and N content of green manure crops can vary between growing conditions. In 2002, most common green manure crops in the Netherlands were fodder radish, yellow mustard and Italian ryegrass, covering almost 80 percent of the area grown with green manure crops (Table 2.3). The green manure crops indicated in Table 2.3 were grown following arable crops but not after maize.

Since 2006, the total area grown with green manure crops increased as growing a green manure crop after maize on sand and löss soils became obligatory in the Netherlands. On these sandy soils and löss, all grain maize is grown and 75 percent of the total national area of silage maize. Together this is an area of 196000 ha where mostly winter rye and Italian ryegrass are sown as green manure crop. Dry matter production of these green manure crops is low because of the late sowing date after harvest of the maize. In experiments with different green manure crops after maize, above-ground dry matter in January of rye and Italian ryegrass sown after maize harvest was 821 and 1143 kg ha<sup>-1</sup> (Hilhorst & Verloop, 2009). In farmers' practice, average dry matter production of green manure crops after maize is estimated at about 500 kg ha<sup>-1</sup> for crops that are killed by herbicides in February/March (pers.comm. H. van Schooten, WUR-ASG). During growth of a crop, the N content (%) gradually decreases (Greenwood *et al.*, 1990). As green manure crops sown after maize have limited growth, their N content (%) will be higher than presented values in Table 2.3. For the present study, an N content of 39 g kg<sup>-1</sup> is used, based on the average of autumn sown rye and Italian ryegrass (Hilhorst & Verloop, 2009).

Ammonia volatilization from green manure crops is calculated by distinguishing between crops that have no contribution to ammonia volatilization (fraction = 0) and crops that fully contribute (fraction = 1). Crops with frost sensibility 1-3 are expected to be killed by frost when they are on the field in winter. Part of the green manure crops is incorporated before frost occurs and has no ammonia emission. About half of the area of frost sensitive crops is expected to contribute to ammonia volatilization. Frost tolerant green manure crops are generally incorporated by plowing. When the green manure crop is well developed, plowing is preceded by a harvest or by destruction with a disc harrow. Estimates for the area of frost tolerant green manure crops that is killed by herbicides vary between 10-15% (pers.comm. H. van Schooten, WUR-ASG) and 25% (pers.comm. B. Aasman, DLV Plant). In the present study, an average estimate of 19% is used for the part of the area of frost tolerant green manure crops that contribute to ammonia volatilization.

Table 2.3. Characteristics of green manure crops grown in the Netherlands (Timmer et al., 2003). In addition, 196000 ha of Italian ryegrass and winter rye are grown after maize.

Crop	Total area (ha)	Frost sensibility	dry matter (ton/ha)	N content (% of dm)	N content (kg/ha)
Fodder radish	32050	3	3 (1-6)	2.3 (2.0-3.0)	50 (30-150)
Yellow mustard	18500	1	2 (1-4)	2.1 (2.0-3.0)	40 (30-80)
Brassica	375	5	3 (2-6)	2.1 (2-2.5)	100 (50-120)
Perennial ryegrass	5525	7	1.5 (1-2)	2.8 (2.0-3.5)	45 (30-60)
Italian ryegrass	20000	5	2 (1-4)	2.2 (1.5-2.5)	45 (20-80)
'Westerwolds' ryegrass	1000	5	2 (1-2)	2.2 (2.0-2.5)	40 (40-45)
Winter rye	6200	9	3 (2-4)	3.2 (2.0-4.0)	100 (50-130)
Red clover	100	3	3 (2-4)	3.2 (3-3.5)	100 (60-140)
White clover	100	5	2 (1-3)	3.5 (3-4)	80 (50-120)
Persian clover	100	3	4 (3-5)	3 (2.5-3.5)	120 (100-175)
Vetch	500	3	3 (2-5)	4 (3-4.5)	120 (90-200)
Facelia	500	1	4 (2-5)	3.1 (2.5-4.0)	120 (60-200)
Tagetes patula	400	1	8 (4-15)	1.9 (1.5-2.5)	140 (70-170)
Green manure crops after maize <sup>1</sup>	196000	5	0,5	3.9	19.5

<sup>1</sup> See text for further specification.

## 2.4 Ammonia emission from grassland

For grassland estimating the ammonia emission is more complex compared to arable crops and green manure crops due to the fact that grassland is intensively managed over the year. This makes it difficult to separate emissions that are already included in the calculation of national emissions such as from application of manure, fertilizer and grazing on one hand and from ammonia emissions that are not directly linked to an agricultural activity on the other hand. For the calculation of the national emission it is important to know what is and what is not already included in the emission factors.

The emissions from grassland already included in the calculation of national emissions are:

- a) the emissions after application of manure and fertilizer;
- b) the emissions during grazing.

The emissions under a) reflect for manure application the emissions during the first four days after application. The emissions under b) reflect all types of emissions during the growing season while grazing. In the calculation of national emissions, emission factors for grazing are derived from Bussink (1992), who mentions that emissions from grazed grassland were relatively large in some grazing periods possibly due to topping of the sward after grazing. Therefore it may be concluded that the grazing emission factor includes topping of the grass.

Emissions that are not yet included are:

- 1) the emissions from non-grazed grassland in the period from application of manure and fertilizer till the next application. In the present study, these emissions are included in the emissions from standing crops taking into account a specific compensation point or gamma for grassland.
- 2) the emissions from crop residues related to management activities such as mowing and grassland renovation. Emissions may result from crop residues that remain on the field after mowing when not all herbage is removed. Furthermore, crop residues that may contribute to ammonia volatilization arise when grassland is killed by herbicides for grassland renovation or for follow up by another crop.

The specific emissions per management activity for grass are discussed in the following sections.

### 2.4.1 Pasture topping

Ammonia emission from pasture topping is likely included in the emission factors for grazing within the calculation of national emissions, based on Bussink (1992) who mentioned that emissions from grazed grassland were relatively large in some grazing periods possibly due to topping of the sward after grazing. Therefore, in the present study ammonia emission from residues after pasture topping is not included in the calculations. However, as the practice of pasture topping is changing over time, information on the contribution of pasture topping is given in this report. This information may be used if a re-evaluation of the emission factor for grazing is desired.

Pasture topping is decreasing in the Netherlands, and general advice is to alternate mowing and grazing. This way, seed heads and stalks that may have developed in rejected areas around feces and urine patches are mown and removed and become part of the grass silage. Most farms manage to alternate grazing and mowing their fields and will not top their pastures. Farms that keep their cows in the stable all year round also have no pasture topping. If alternating grazing and mowing is not possible, pasture topping is advised after two times grazing. About 15 to 20 percent of the cattle farms are expected to use pasture topping (pers. comm. G. Holshof, WUR-ASG; G.J. Hilhorst, WUR-ASG and D.Z. van der Vegte, WUR-ASG). Generally these farms have a smaller acreage than average. For calculations in the present study, a single event of pasture topping is expected to be carried out on 15 percent of the total grassland area. Because in current practice first harvest of all fields is by cutting, first pasture topping is around Mid-June.

The amount of grass residues that is left behind after pasture topping is estimated between 200 and 500 kg dry matter per hectare. When higher amounts of dry matter are present, no pasture topping will be carried out but the grass will be harvested and used for silage. Calculations with the Farm Budget Program for Cattle (BBPR, [www.bbpr.nl](http://www.bbpr.nl)) also showed amounts of crop residues between 250 and 500 kg dry matter per hectare (pers. Comm. G. Holshof). These losses include trampling losses. For the present study, an average estimate of 350 kg dry matter per hectare per topping will be used for crop residues after pasture topping.

The N content of topped grass may be lower than normal grass that is cut because of development of stalks and seed heads. On the other hand, this grass develops around feces and urine patches and has more N available. Estimations by experts of the N content of topped grass varied between 27-28 g kg<sup>-1</sup>, 33 g kg<sup>-1</sup> and 35-36 g kg<sup>-1</sup> dry matter. In the present study, a value of 30 g kg<sup>-1</sup> will be used. This is in accordance with Vellinga and Hilhorst (2001) who give average values of 29.3 g kg<sup>-1</sup> for silage cuts and 33.3 g kg<sup>-1</sup> for grazing cuts.

### 2.4.2 Cutting, drying and collection

During cutting, drying and collection, part of the grass dry matter is lost and remains on the field. In field experiments with cut grass, Corporaal (1993) measured losses of dry matter of 3.9% for grassland and 8.8% for grass/clover mixtures, equaling 120 and 251 kg dry matter per hectare per cut. For five cuts per year, this amounts to 600 and 1255 kg ha<sup>-1</sup>. Herbage losses of cut grassland are also described in Farmmin, a model to simulate nutrient flows on a mixed dairy farm ([www.farmmin.wur.nl](http://www.farmmin.wur.nl)). A loss of 10% of total dry matter can be estimated for cut grassland (pers. comm. F.W. van Evert, WUR-PRI). Together with an average yield of grassland in the Netherlands of 10.2 ton ha<sup>-1</sup> (Aarts *et al.*, 2008), this means an input of residues of 1020 kg dry matter ha<sup>-1</sup>. For the present study, an average loss of 1000 kg dry matter ha<sup>-1</sup> year<sup>-1</sup> is used for cut grassland with an N content of 30 g kg<sup>-1</sup>.

### 2.4.3 Grassland renovation

To maintain or increase productivity of grassland, swards are occasionally ploughed and reseeded. Grassland renovation or resowing is necessary when the quality of the grassland is decreased. In the Netherlands, grassland on sand, clay and peat soils is renovated every 5, 10 and 30 years, respectively (Schils *et al.*, 2007). It is generally recommended to kill the old sward with glyphosate, to kill couch grass and to prevent old sward rests from

regrowing (Hoving and De Boer, 2004). Between 1990 and 2005, on average 12 percent of the grassland area was newly sown (Table 2.4). This amount varied between years, partly due to weather conditions.

Time of killing the grass vegetation is restricted by legislation in the Netherlands, and varies between soil type and the type of crop that follows (Table 2.5). On sand, the grass can only be killed in spring or before cultivation of flower bulbs. On peat and clay soil, killing the grass is also possible in autumn and winter if crops other than grass follow.

Grass that is killed by herbicide will not be incorporated within a few days and contributes to ammonia volatilization. About 90% of the grassland that is renovated by resowing or sod seeding is killed by herbicides (pers.comm. D.Z. van der Vegte, WUR-ASG). Herbicides are used less frequently when another crop than grass follows, and it is assumed that half of this grassland area is killed by herbicides. Using average values over the period 1990-2005 (Table 2.4), 90% of the area resown and sod seeded plus 50% of the area grass sown after another crop gives 84484 ha of grassland that is killed by herbicides.

When grassland renovation is carried out in spring, a first cut before herbicide application is not advised. It takes too much growing time for sufficient production, and for good germination sowing should be as early as possible to avoid dry weather in May and June (Hoving and Velthof, 2006). Measurements of the amount of dry matter at the time of killing are scarce. Of grassland swards, the amount of organic matter of grassland and its N content varied between age of a sward, between cutting and grazing, and were affected by N fertilization (Whitehead *et al.*, 1990). The average amount of above-ground organic matter (stubble plus leaf litter) of two swards of 8 and 15 years old in the UK was 3500 kg ha<sup>-1</sup> with an N content of 23.5 g kg<sup>-1</sup> (Whitehead *et al.*, 1990). This value is comparable with measurements in the Netherlands of the amount of dry matter of stubble in March just before renovation of on average 3360 kg ha<sup>-1</sup> dry matter with an N-content of 24.5 g kg<sup>-1</sup> (Van Dijk *et al.*, 1996). Grassland experts estimated the amount of above-ground dry matter of grassland in spring before spraying between 1800-2000 kg ha<sup>-1</sup> (pers. comm. G. Holshof, WUR-ASG). A value of 3000 kg ha<sup>-1</sup> of above-ground dry matter (including stubble) with an N content of 24.0 g kg<sup>-1</sup> will be used in the present study.

Table 2.4. Grassland renovation on cattle farms in the Netherlands (Statistics Netherlands, 2007).

Year	Total area grassland (ha)	Area sown	Resown	Sod seeding	Sown after another crop than grass <sup>1</sup>
1990	1004000	127000	61000	14000	52000
1993	965000	88000	45000	13000	31000
1996	958000	153000	59000	50000	44000
1999	913000	131000	67000	9000	55000
2002	929000	100000	48000	5000	46000
2005	980000	87000	34000	6000	46000
Average	958167	114333	52333	16167	45667

<sup>1</sup> This area is assumed to equal the area of grass followed by another crop.

Table 2.5. Time period when grassland can be killed. Additional requirements include soil sampling before application of fertilizer and requirements for the following crops ([www.derogatie.nl](http://www.derogatie.nl); accessed Sept. 5, 2011).

Period	Sand/löss	Peat	Clay
1 - 31 Jan	Not allowed		
1 Feb - 31 May	Allowed, soil sampling required, only crops with high N demand		
1 June - 15 Sept	Not allowed	Allowed, soil sampling required, only crops with high N demand	
16 Sept - 31 Oct	Only allowed before flower bulb crops, no soil sampling required		
1 Nov - 30 Nov	Only before flower bulbs, no soil sampling required		Allowed before all crops except grass, no soil sampling required
1 Dec - 31 Dec	Not allowed		



### 3. Areas of agricultural crops in the Netherlands

Cultivated areas per crop were retrieved from Statistics Netherlands (2011). Most recent data for grassland were from 2009, for arable crops from 2010 and for vegetable crops from 2009 (provisional data). Areas are based on the 'Landbouwtelling'. As areas may vary over years due to market mechanisms, the average area over the years 2007, 2008 and 2009 is used in the present study (Table 3.1).

Data on cultivated areas per crop are based on total area where the crop is planted or sown. On fields, multiple crops per year can be grown, especially in horticulture. For such fields, the cultivated area of each crop is taken into account. Excluded are the crops that are grown in greenhouses: eggplant, cucumber, paprika, radish, tomato. Some crops are grown both in greenhouses, and on the field: zucchini, endive, head lettuce, iceberg lettuce, spinach, strawberry. For simplicity it is assumed that half of the area of these crops refers to cultivation in greenhouses, and half to open fields.

The area of green manure crops is not given by Statistics Netherlands and is taken from Timmer *et al.* (2003). Cultivated areas with green manure are given in Table 2.3.

Grassland can be grazed or cut. Statistics Netherlands (2011) give both the area cultivated with grassland (982 333 ha) and the cut area (2 358 500 ha). This means that on average each hectare is cut 2.4 times.

Table 3.1. Area (ha) of crops grown in the Netherlands (average of 2007-2009; Statistics Netherlands, 2011).

Crop	Specification	Area (ha)
<b>Grassland</b>	total area	982333
	area cut	2358500
<b>Arable crops</b>		
wheat		149604
	winter wheat	131313
	spring wheat	18291
winter barley		4602
spring barley		42296
rye		2427
oats		1593
triticale		3274
grain maize		20124
silage maize		234501
corn cob mix		7481
green pea		507
capucijner pea		498
dry bean		1130
field beans		292
rapeseed		2831
caraway		56
poppy seed		674
linseed/flax		2746
chicory		3471
hemp		435

Crop	Specification	Area (ha)
ware potatoes		70762
	on clay	50575
	on sand or peat	20187
plant potatoes		37135
	on clay	33815
	on sand or peat	3321
starch potatoes		46861
sugar beet		75653
fodder beet		337
onion		19993
<b>Vegetable crops</b>		1382
strawberry - open field		
leaf and stem vegetables		14830
	endive	787
	asparagus	2091
	Florence fennel	173
	leek	3133
	celery	141
	head lettuce	708
	lettuce - iceberg	2633
	spinach	1946
	chicory	3217
root and tuber crops		37861
	carrot (bunch and washed)	3192
	carrot (winter)	5617
	celeriac	1315
	red beet	397
	radish	110
	salsify	1115
	onion	26115
cabbage crops		11886
	cauliflower	2625
	kale	700
	broccoli	1917
	Chinese cabbage	330
	green cabbage	140
	red cabbage	659
	green cabbage	517
	Brussels sprouts	3317
	white cabbage	1682
leguminous crops		13761
	pea	6266
	green bean	6641
	field beans	853
fruit vegetables (incl eggplant, cucumber, paprika, tomato)		3789
	zucchini	223
other vegetables		1747

For calculation of ammonia volatilization of standing crops, the DEPAC model (chapter 2.2) uses regional differences in weather and in concentrations of atmospheric ammonia. Provinces of the Netherlands are shown in Figure 3.1. Information on grassland is registered by Statistics Netherlands (2013) as total grassland area and the area mown, specified for four major grassland areas, largely covered by the provinces as indicated in Table 3.2. The area of ungrazed grassland was calculated from the total area of mown grassland and the assumption of five cuts per year. The distribution of major arable crops over the Dutch provinces is shown in Table 3.3.



Figure 3.1. Location of the provinces in the Netherlands.

Table 3.2. Major grassland regions in the Netherlands, the linkage with provinces as used in this report and the area (1000 ha) with ungrazed grassland (derived from Statistics Netherlands, 2013).

Major grassland region (Dutch name)	Related provinces	Area ungrazed (1000 ha)
North (Noordelijk weidegebied)	Groningen, Friesland, Drenthe, Overijssel	147.6
Eastern and central (Oostelijk en centraal veehouderijgebied)	Drenthe, Overijssel, Gelderland, Utrecht	135.0
Western (Westelijk weidegebied)	Utrecht, Zuid-Holland, Noord-Holland	73.2
Southern (Zuidelijk weidegebied)	Noord-Brabant, Limburg	62.8
Other	Flevoland, Zeeland, and grassland areas within major arable regions of other provinces	104.6

Table 3.3. Area (ha) cropped with major agricultural crops in 2011, specified for the 12 provinces of the Netherlands (Statistics Netherlands, 2013).

	Groningen	Friesland	Drenthe	Overijssel	Flevoland	Gelderland	Utrecht	Noord-Holland	Zuid-Holland	Zeeland	Noord-Brabant	Limburg	Total <sup>1</sup>
Cereal crops	41159	9259	15037	4774	17522	10668	798	11492	16232	36376	16644	10643	190604
Maize crops	10510	18949	21164	42643	3804	46092	6678	4986	5099	6023	64922	21465	252335
Potato (total)	26270	8185	29859	6698	19238	4835	70	9723	10758	18690	18352	7007	159685
Sugar beet	10473	2457	10628	1800	9507	2618	77	4826	4714	10577	8864	6789	73330
Total area <sup>1</sup>	88412	38850	76688	55915	50071	64213	7623	31027	36803	71666	108782	45904	675954

<sup>1</sup> Total area is the total agricultural area of major agricultural crops per province, covering almost 90 percent of total arable area.

## 4. Estimated ammonia emission from crops and crop residues in the Netherlands

### 4.1 Emissions from crops

The emission of ammonia from crops was calculated using the methodology described in Section 2.2. The hourly ambient air concentrations of ammonia were taken from the National Air Quality Network (Mooibroek *et al.*, 2012). Values of stomatal ratio between  $\text{NH}_4^+$  and  $\text{H}^+$ , denoted by  $\Gamma_s$ , are taken from Table 2.1; other parameter values such as assumptions about the growth functions for crops are given in Appendix V. The emission fluxes were calculated on an hourly basis using the weather data for the year 2003 and 2008. 2003 being representative for a year with high temperatures in summer with low amounts of rainfall; while the summer of 2008 was more average in temperature but with somewhat higher amounts of rainfall.

The exchange between the crops and the ambient air was calculated for the five types of crops from Table 2.1: ungrazed grassland, maize, potatoes, wheat and sugar beet. For wheat the calculations were split into the summer and winter variety to take into account the different meteorological conditions during growth, so six crops were considered. The emission was calculated for the medium  $\Gamma_s$  value and the lower and upper values for each crop and eight locations in the Netherlands. All eight locations of the National Air Quality Network were taken to obtain a good representation of the ammonia levels in the Netherlands.

The ammonia emission from a crop is defined as the integral of the exchange of ammonia over the entire growing season of the crop, i.e. between planting or sowing and crop harvest, expressed in  $\text{kg NH}_3$  per ha. A negative value denotes a net deposition of ammonia. In Figure 4.1, the emission of ammonia as an average of the six crops for these eight locations for the years 2003 and 2008 is depicted. Also the ensemble of the lower and upper estimates are presented. Results of the calculations are presented in Table 4.1.

Figure 4.1 and Table 4.1 show that the flux depends on the atmospheric ammonia concentration and the ratio  $\Gamma_s$ . At locations with lower air concentrations, such as De Zilk, the flux is positive which means net emission of ammonia over the growing season. Conversely, the flux at the locations with higher air concentrations, such as Vredepeel, is negative which means a deposition of ammonia. The variation caused by meteorology (compare 2003 with 2008) is small compared to the effect of the atmospheric ammonia concentration or the variation between crops. The variation in emission between crops at a location for 2003 or 2008 lies in the order of a few  $\text{kg NH}_3$  per ha and falls well within the range of the emissions calculated with the lower and upper values of the ratios  $\Gamma_s$ . Hence, the emission were considered from crops using the average emission and ranges (as in Figure 4.1) and not the individual emission per crop type.

The emission from the crops on average on the sites with relatively low concentrations, less than  $5 \mu\text{g NH}_3 / \text{m}^3$ , lies between 1 and 4 kg N per ha with an average of about 2.5 kg N per ha. The upper range of the emission estimate (with the upper  $\Gamma_s$  value) lies between 5 and 10 kg N per ha with an average of 7.8 kg  $\text{NH}_3$  per ha. At sites with concentrations higher than about  $5 \mu\text{g NH}_3 / \text{m}^3$ , deposition takes place on the crops. However, up to about  $12 \mu\text{g NH}_3 / \text{m}^3$  emissions are calculated with the higher estimate of gamma, being on average 2.5 kg N per ha for concentration levels between about 5 and  $12 \mu\text{g NH}_3 / \text{m}^3$ .

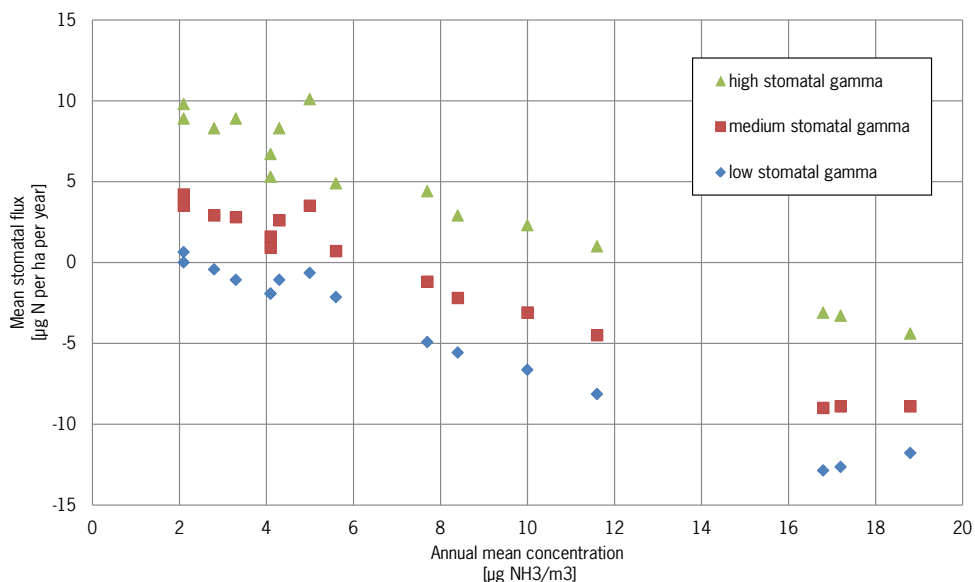


Figure 4.1. Emission (positive values) or deposition (negative values) ( $\text{kg N ha}^{-1} \text{ year}^{-1}$ ) versus atmospheric ammonia concentration. Data points give average values over all crops.

It is clear from Figure 4.1 that the ambient atmospheric ammonia concentration is the dominant parameter in describing the variation of the emission from a crop over the Netherlands. This means that for a national estimate of the total ammonia emission from standing crops, the variation in ammonia concentration over the country has to be taken into account.

Figure 4.2 maps the variation of the averaged ammonia concentration over the Netherlands for the years 2003 and 2008. The maps have been used to estimate the area per province that is exposed to an average concentration of less than 5, between 5 and 12, and more than 12  $\mu\text{g NH}_3 / \text{m}^3$ , respectively. These estimates in combination with the cropped area per province (Tables 3.2 and 3.3) provide an estimate of the extent of the area emitting ammonia. It was calculated that about 600.000 ha of cropped area in the Netherlands is exposed to an ammonia concentration of less than 5  $\mu\text{g NH}_3 / \text{m}^3$ . Another 480.000 ha is exposed to a concentration between 5 and 12  $\mu\text{g NH}_3 / \text{m}^3$  and about 120.000 ha is exposed to concentrations higher than 12  $\mu\text{g NH}_3 / \text{m}^3$ .

Combining these results, the national emission is estimated at  $600.000 \times 2.5 = 1.5$  million kg N for medium gamma values and  $600.000 \times 7.8 + 480.000 \times 2.5 = 5.9$  million kg N for high gamma estimates. With the low gamma estimates no emissions are calculated. Accordingly, an overall rough estimate of the ammonia emission by crops is about 1.5 kton with a range from 0 up to about 6 million kg N.

Table 4.1. Emission (positive sign) or deposition (negative sign) of ammonia ( $\text{kg N ha}^{-1} \text{ year}^{-1}$ ) for six crops at eight locations in the Netherlands using weather data for 2003 (top half) and 2008 (bottom half). Results are shown from calculations using the average and the upper estimates of the gamma value (Table 2.1). Averages over crops are shown in Figure 4.1.

Location	Average annual concentr.	Calculations using the average estimates of the gamma value						Calculations using the upper estimates of the gamma value								
		Average	Grassland	Maize	Spring wheat	Winter wheat	Potatoes	Sugarbeet	Average	Grassland	Maize	Spring wheat	Winter wheat	Potatoes	Sugarbeet	Average
2003																
De Zilk	2.1	4.5	3.9	6.1	4.8	2.5	3.0	4.2	9.9	11.7	13.3	11.3	5.6	6.8	9.8	
Huijbergen	3.3	3.4	2.9	4.4	3.4	1.5	1.3	2.8	9.4	11.2	12.4	10.5	4.7	5.4	8.9	
Vatthermond	4.3	3.1	2.4	4.2	3.3	1.4	1.4	2.6	8.6	9.7	11.5	10.4	4.3	5.1	8.3	
Zegveld	5.0	4.2	2.9	6.1	4.9	1.5	1.6	3.5	10.7	11.9	14.4	12.3	5.0	5.9	10.1	
Wieringerwerf	5.6	1.5	0.8	1.8	0.4	0.1	-0.3	0.7	5.7	6.4	7.1	5.3	2.1	2.6	4.9	
Eibergen	10.0	-1.8	-2.3	-2.4	-4.4	-3.1	-4.7	-3.1	3.4	4.7	4.5	2.5	-0.3	-1.1	2.3	
Wekerom	16.8	-6.6	-8.9	-8.1	-9.2	-9.0	-12.4	-9.0	-0.9	-1.0	-0.5	-2.1	-5.9	-8.4	-3.1	
Vredepeel	18.8	-6.3	-7.3	-9.7	-11.3	-8.1	-10.5	-8.9	-2.1	-1.8	-3.8	-5.5	-5.8	-7.5	-4.4	
2008																
De Zilk	2.1	3.9	3.4	5.1	4.4	2.0	2.1	3.5	8.9	10.7	12.0	10.6	5.0	6.0	8.9	
Huijbergen	2.8	3.3	3.0	4.3	3.6	1.7	1.7	2.9	8.2	10.3	11.1	9.8	4.7	5.4	8.3	
Wieringerwerf	4.1	2.4	1.7	2.7	2.1	0.5	-0.1	1.6	7.3	8.4	9.5	8.3	3.3	3.6	6.7	
Vatthermond	4.1	1.6	1.0	1.7	1.2	0.1	-0.4	0.9	5.8	6.6	7.4	6.4	2.5	2.8	5.3	
Zegveld	7.7	0.5	-0.9	0.0	-0.9	-2.3	-3.5	-1.2	5.7	6.7	7.2	5.7	0.9	0.5	4.4	
Eibergen	8.4	-0.6	-1.5	-1.7	-2.6	-2.8	-4.2	-2.2	4.1	5.5	4.9	3.5	0.1	-0.6	2.9	
Wekerom	11.6	-2.2	-4.0	-3.7	-4.5	-5.4	-7.3	4.5	2.9	3.4	3.4	2.0	-2.3	-3.5	1.0	
Vredepeel	17.2	-5.9	-7.6	-8.8	-9.3	-8.9	-13.0	-8.9	-0.6	-0.1	-1.5	-2.6	-5.7	-9.1	-3.3	

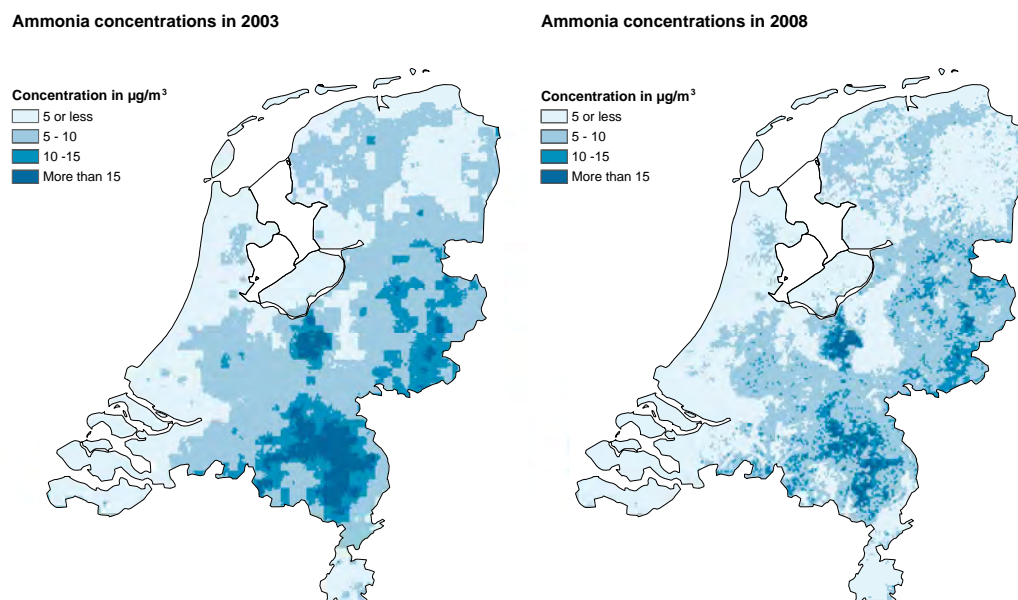


Figure 4.2. Annual averaged concentration of ammonia over the Netherlands. Concentrations are a combination of calculated ammonia concentrations and measurements from the National Air Quality Network ([www.compendiumvoordeleefomgeving.nl](http://www.compendiumvoordeleefomgeving.nl)).

## 4.2 Emissions from crop residues

Ammonia volatilization from crop residues in the Netherlands was calculated per crop by multiplication of:

- Area grown (average of 2007-2009; Chapter 3)
- N in residues ( $\text{kg ha}^{-1}$ ; Chapter 2)
- Volatilization (% of total N in  $\text{kg ha}^{-1}$ ) calculated from N content ( $\text{g kg}^{-1}$  dry matter) by the regression equation derived from literature (Chapter 2)
- Fraction of the residues that contributes to ammonia volatilization.

Total ammonia volatilization from crop residues in the Netherlands was calculated at 1.9 million  $\text{kg NH}_3\text{-N}$ . Largest contribution is from grassland, and especially the losses from mowing (Figure 4.3-left). Ammonia volatilization from residues of arable crops and during grassland renovation also have a large contribution to total volatilization. Potatoes are responsible for almost half of the ammonia volatilization of arable crop residues (Figure 4.3-right). Other large contributions are from sugar beet and cabbage crops. Ammonia emission from freezing or herbicide killing of green manure crops is a little higher than the emission from sugar beet residues. Almost two third of the ammonia volatilization from green manure crops is from crops that are killed by herbicides, of which 80% is from green manure crops after maize.

The large contribution from losses from mowing is mainly caused by the large area of grassland. Per hectare of cut grassland (5 cuts per year), ammonia volatilization from residues is  $2.1 \text{ kg NH}_3\text{-N}$ . For comparison, average ammonia volatilization is  $4.8 \text{ kg ha}^{-1} \text{ NH}_3\text{-N}$  from residues of seed potatoes,  $0.3 \text{ kg ha}^{-1} \text{ NH}_3\text{-N}$  from ware and starch potatoes and  $1.7 \text{ kg ha}^{-1} \text{ NH}_3\text{-N}$  for sugar beet residues. Cabbage crop residues have a high average ammonia volatilization per hectare, varying between  $2.9 \text{ kg NH}_3\text{-N ha}^{-1}$  for white cabbage and  $8.9 \text{ kg NH}_3\text{-N ha}^{-1}$  for broccoli. For specific fields without incorporation and where crop residues remain on top of the soil for a long period, volatilization per hectare is higher than these average values.



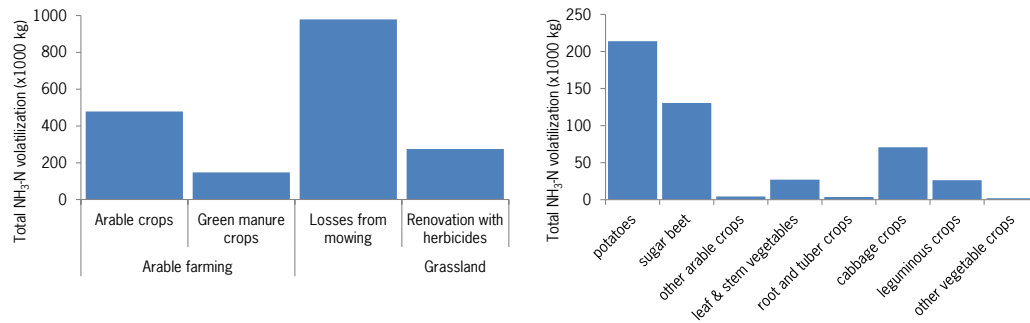


Figure 4.3. Total ammonia volatilization in the Netherlands from arable crops, green manure crops and grassland (left), and specification of ammonia volatilization from arable crops (right).

Uncertainty in input data gives large ranges in calculated values of total ammonia volatilization from crop residues in the Netherlands. When the 90% confidence band is used (De Ruijter and Huijsmans, 2012), total ammonia volatilization varies between 0.3 and 3.8 million kg NH<sub>3</sub>-N. Other uncertainties are the N content of the crop residues and the contribution of the crop residues to ammonia volatilization as estimated from the mixture with soil during harvest and the field period between harvest and incorporation.



## 5. Discussion

In this report estimates are made for the contribution of standing crops and crop residues to total ammonia volatilization in the Netherlands. These estimates are additional to those already included in the national emissions calculations. In these calculations, emissions after application of manure and fertilizer and emissions during grazing are already included. For grassland therefore only the emissions from non-grazed grassland and from crop residues after mowing were included.

Emissions from standing crops were calculated using an inference type of modeling assuming stomatal compensation points for typical crops in the Netherlands. Crop residues were defined as residues that remain and decay on the field after management operations such as harvest and spraying with herbicides, and after freezing in winter time.

### 5.1 Ammonia emission from crops

The range given in the calculated emission from standing crops of 0 to 6 kton is quite large. Two parameters dominate the process of ammonia exchange and the resulting emission or deposition: the ambient ammonia concentration and the stomatal compensation point (Figure 4.1). The uncertainty in the ambient concentration is small (< 10%) compared with the uncertainty in the stomatal compensation point. As can be seen from Table 2.1 the range between the lower and upper estimate of the values of the  $\text{NH}_4^+$  to  $\text{H}^+$  ratio  $\Gamma$ 's (from which the compensation point is calculated) can amount up to a factor of ten. This range is much larger than the range of gamma values between the distinguished crops. This makes the estimates of the emission by standing crops very rough and hence the estimates should be considered as indicative.

The large range also puts the uncertainty of all other parameters used in the calculations into perspective, that is, their uncertainties are all small compared with the uncertainty in the ratio  $\Gamma$ 's values or compensation point. So the effect of taking only 2003 and 2008 data in the calculations and not making an exact match between the location of the crops or the ambient concentration (as could have been done using a GIS-application) are relatively small.

For two crops, potatoes and sugar beets, no information was found for its  $\text{NH}_4^+$  to  $\text{H}^+$  ratio  $\Gamma$ 's and low – conservative - values were used as default. Nevertheless, the emissions from these crops were used in the – arithmetically, so not crop area weighed - averaged estimate of the emission from crops (as in Figure 4.1). Therefore, choosing conservative default values takes effect on the overall estimate. If higher estimates would have been chosen, the average emission factor would have been about 10 to 20% higher and consequently the overall emission estimate would have been larger as well.

Notwithstanding the fact that emission calculations are uncertain, there are two regimes that can be determined from Figure 4.1:

1. Below an ambient concentration of about  $5 \mu\text{g}/\text{m}^3$  all crops emit ammonia, whereas above  $15 \mu\text{g}/\text{m}^3$  the crops always absorb ammonia (i.e. deposition).
2. In between 5 and  $15 \mu\text{g}/\text{m}^3$  both emission and deposition are possible which is strongly dependent on the value of the compensation point.

The estimate of the emission using the upper value of the compensation point of 6 kton indicates what will be the typical maximal value for these emissions.

The strong effect of ambient ammonia concentration on ammonia emission from crops explains the large variation in emission factors (expressed in  $\text{kg N ha}^{-1}$ ) that is found in literature. This clearly illustrates that estimates of crop emissions should take into account the ambient concentration. For example, estimates of the emissions from crops in Denmark (wheat, barley) are reported typically to be in the range of 1 to 5  $\text{kg N/ha}$  (Schjoerring & Mattsson,

2001). These values are also found for the Netherlands, but only in areas with low ambient concentrations levels (i.e. areas with ambient ammonia levels as high as those common in Denmark). This suggests that emission factors derived in one country cannot be used directly for estimates of the crop emission totals in another country and that at least the ambient ammonia level should be taken into account.

Reducing the emission in animal houses and the emission after manure application will both effectively lead to lower concentrations in the ambient air. However, these lower concentrations will consequently lead to higher emissions of standing crops, thus resulting in a negative feedback on emission reduction. There appears to be a climate effect as well. Higher temperatures lead to higher compensation points and thus to larger crop emissions. Still higher temperatures restrict this effect, as stomata will close, the plant-air exchange stops and the emission is blocked.

It is clear from the above discussion on the emission calculations that the major item for improvement of the calculations lies in better estimates of the gamma value or compensation point of crops and its seasonal variation. The range in the gamma values also reflects differences in agricultural management (N fertilization). As the agriculture in the Netherlands is intensive – uses large fertilizer inputs - the question rises whether the gamma values from literature are valid for the Netherlands. Only few Dutch measurements are available (e.g. Volten *et al.*, 2012). These measurements indicate though that in the Netherlands the gamma values are more likely to lie towards the upper than to medium value of the range as derived from literature in this study.

Another indication for – temporary - high compensation points comes from a study by Van Pul *et al.* (2008) in which it was estimated that during the three week heat wave of August 2003 alone about 1 kton of ammonia could have been emitted by standing crops on a national scale. This implies that the lower value for gamma is not very realistic for the Netherlands and also that the estimate of 1.5 kton based on average gamma values may be considered as conservative.

Besides the necessity of measurements, a way forward would be to couple the compensation point or gamma to the nitrogen content in the plant which is somewhat easier to measure. And by coupling the nitrogen content to the nitrogen balance of a plant a parameterization of the compensation point or gamma could be obtained.

## 5.2 Ammonia emission from crop residues

From crop residues, a total contribution to Dutch national ammonia emission was calculated of 1.9 million kg  $\text{NH}_3\text{-N}$ , varying between 0.3 and 3.8 million kg  $\text{NH}_3\text{-N}$  when the broad confidence band of the regression equation of De Ruijter and Huijsmans (2012) is used. The calculations were carried out for the current situation with variation in the degree of incorporation into the soil during harvest or with variation in the amount of time that crop residues remain on top of the soil after harvest. The variations depend on crop type and farming practice. Changes in farming practice may have impact on ammonia volatilization from crop residues. To indicate the maximum effects, three scenarios were calculated:

1. All residues remain on the soil surface, indicating a maximum contribution
2. Current situation, based on the degree of mixing with soil at harvest and the duration between harvest and incorporation (Chapter 2)
3. Maximum reduction of ammonia volatilization, based on technical possibilities to prevent or reduce ammonia volatilization from crop residues

Scenario 1 is included to give the ammonia volatilization potential of all crop residues. Scenario 3 is a combination of the following strategies to achieve maximum mitigation:

- Prevention of ammonia volatilization by incorporation of crop residues within one week after harvest (except potato) and incorporation of green manure crops within one week after freezing;
- Potato crop residues have to remain for at least two weeks on the field because of the required time between haulm killing and harvest. Collection of dead potato haulm stems after harvest may reduce the emission factor from 0.75 to 0.5;

- Reduction of the time between spraying and incorporation of dead plants (grassland or green manure crops) to a minimum of two weeks that is required for sufficient dying of the plants. This may reduce the emission factor from 1 to 0.5.

Ammonia volatilization from losses during cutting, drying and collection for silage cannot be prevented. As this volatilization from grassland contributes about half of the total ammonia volatilization from crop residues, the mitigation practices of scenario 3 have a modest impact (Table 5.1).

Table 5.1. Ammonia volatilization from crop residues in the Netherlands ( $10^3$  kg  $NH_3$ -N) for three scenarios of residue management.

	Scenario 1 All residues on top	Scenario 2 Current situation	Scenario 3 Maximum mitigation
Arable crops	1053	479	143
Green manure crops	607	148	48
Losses from cutting	979	979	979
Renovation with herbicides	275	275	137
<b>TOTAL</b>	<b>2914</b>	<b>1881</b>	<b>1307</b>
<i>Arable crops contribution</i>			
potatoes	285	214	143
sugar beet	483	130	0
other arable crops	11	4	0
leaf & stem vegetables	45	27	0
root and tuber crops	20	4	0
cabbage crops	104	71	0
leguminous crops	97	27	0
other vegetable crops	8	2	0

The regression equation used to calculate ammonia volatilization from crop residues is valid for crop residues left on the soil surface for a period of time long enough to allow maximum cumulative ammonia volatilization (De Ruijter & Huijsmans 2012). Generally, a number of days is required after harvest before crop residues start to emit ammonia, followed by a peak in volatilization rate between 1-4 weeks (De Ruijter *et al.*, 2010; Glasener & Palm, 1995; Mohr *et al.*, 1998). After these peak rates, volatilization can continue at a slow rate for many weeks (De Ruijter *et al.*, 2010; Whitehead *et al.*, 1988). Temperature plays a role when peak rates of ammonia volatilization occur and when volatilization ceases (Whitehead *et al.*, 1988). This variation also occurs in farming practice where crop residues arise during harvest in summer or in autumn, and where crop residues can be incorporated shortly after harvest or after several weeks or months. Freezing of green manure crops occurs in winter when temperatures are low. Herbicides to kill green manure crops or grassland are generally used in autumn or spring. In calculating the contribution of crop residues to national ammonia volatilization, part of this variation is included in the regression equation, and part is accounted for by estimating the fraction of each crop that contributes to ammonia volatilization. These fractions are based on interviews with field experts. More detailed insight in the field period of crop residues requires surveys among farmers.

Ambient ammonia concentration has an effect on ammonia emission from crops (see 5.1), and it may also affect ammonia emission from crop residues, However, the effect on emission of crop residues is expected to be limited, as ammonia emission from decaying residues is more pronounced and within a shorter time period than from standing crops. The regression equation that describes ammonia emission in relation to N content of crop residues

is supposed to be representative for Dutch conditions, as data points from measurements in the Netherlands are above the average (De Ruijter & Huijsmans, 2012), indicating that the relatively high ambient ammonia concentrations of the Netherlands have had no systematic lowering effect on the degree of ammonia emission.

Crop residues that have the largest contribution to ammonia volatilization at the national scale are those from mowing of grassland. The amount of residues that arises during mowing is difficult to measure. Experimental data therefore are scarce and estimates for the amount of residues remain based on expert knowledge. Trend in current practice in the Netherlands is that grazing is decreasing, and cows are increasingly fed in the stables. This results in a shift from losses from grazing to losses from mowing. Grass that is cut and collected at the same time will give limited amounts of residues as the fresh grass is easily picked up. Cutting and drying for silage gives larger losses, partly due to breaking into small fragments that cannot be collected. Therefore, the other trend to minimize the field period of grass cut for direct feeding may also reduce losses and ammonia volatilization from these residues.

Grassland for seed production was absent in the overviews of cropping areas and crop residues. However, no ammonia emission is expected from these crop residues as the N-content of grass straw is 11.2 g/kg dry matter (Kempe *et al.*, 2005) and crop residues after collection of the straw will have similar N content. This N content is below the value of 12.7 g/kg where the calculated ammonia emission is equal to zero. Grassland for seed production was grown on 12680 ha in 2010 (Statistics Netherlands, 2013).

Potato haulms show the largest contribution of the arable crops. In the calculations, this is mainly derived from seed potatoes where the haulms are killed by herbicides. Because of the time of 2-4 weeks between spraying and harvesting, a contribution of 0.75 was used. This may be an underestimation, as in alfalfa senescence by herbicides caused earlier and higher ammonia volatilization than crop termination by tillage (Mohr *et al.*, 1998). Mannheim *et al.* (1997) measured ammonia volatilization from freshly cut potato haulms, and almost all ammonia volatilization took place within the first three weeks. However, they found this also for sugar beet tops, whereas De Ruijter *et al.* (2010) found ammonia volatilization of sugar beet tops over a period of more than three months. Because of the large contribution of potato in the calculations, it is recommended to measure ammonia volatilization from herbicide treated potato haulms under conditions representative to the field situation.

Ammonia volatilization was estimated by the relationship between  $\text{NH}_3\text{-N}$  volatilization (as % of N in residues) and the N content (in  $\text{g kg}^{-1}$  dry matter). When the amount of residue dry matter is assumed to remain stable, variation in N content of the residues affects both the % of total N that volatilizes as  $\text{NH}_3$  and the total N in the residues. Therefore, a reduction in N content of the residues has a more than proportionate effect on ammonia volatilization. Reducing the N content from 40 to 36  $\text{g kg}^{-1}$  (10%) reduces ammonia volatilization (in  $\text{kg NH}_3\text{-N ha}^{-1}$ ) by 23%. At lower N content this effect is even larger: from 20 to 18  $\text{g kg}^{-1}$  (10%) reduces ammonia volatilization by 35%. As crop fertilization determines the N content of the foliage, decreasing fertilizer inputs may therefore have a large impact on ammonia volatilization from crop residues. Based on information of BLGG-Agroexpertus and calculations of Statistics Netherlands, N contents of grass are decreasing (Tamminga *et al.*, 2009). To what degree N contents of arable crop residues in farmers practice have decreased in recent years is not known. This, and possible effects by further reductions because of fertilizer regulations deserves further study.

### 5.3 Relative contribution to national ammonia emissions from agricultural activities

Van Bruggen *et al.* (2013) show the calculated ammonia emission from animal manure and fertilizers for the Netherlands. The emissions from standing crops are small (< 5%) compared to the direct emissions of ammonia by animal housings and manure application, but about 15% of the contribution by fertilizers and in the same order as emissions during grazing. This also counts for crop residues. The estimated ammonia emission from crops and crop residues together are more than the contribution by manure storage and about twice as much as the estimated ammonia emission by grazing.

## Conclusions

- The contribution of crops and crop residues (excl. grazed grassland) to total ammonia volatilization in the Netherlands was estimated at:
  - 1.5 million kg  $\text{NH}_3\text{-N}$  from standing crops, with a range of 0 to 6 million kg  $\text{NH}_3\text{-N}$ ; This range is obtained by using low and high estimates of the ammonia compensation points of crops found in literature and reflect the large uncertainty in the compensation point values;
  - 1.9 million kg  $\text{NH}_3\text{-N}$  from crop residues, with a range between 0.3 and 3.8 million kg  $\text{NH}_3\text{-N}$  based on the 90% confidence band of the regression equation that describes  $\text{NH}_3$  volatilization in relation to N content of the residues;
  - in total the ammonia emission from standing crops and crop residues together lies between 0-10 million kg  $\text{NH}_3\text{-N}$  with the best estimate being about 3.4 million kg  $\text{NH}_3\text{-N}$ .
- Ambient ammonia concentration has a large effect on ammonia emission from standing crops. Below a concentration of  $5 \mu\text{g NH}_3/\text{m}^3$  standing crops in the Netherlands always emit ammonia and above  $15 \mu\text{g}/\text{m}^3$  ammonia is always deposited. Between these two boundaries, depending on local circumstances, there can be either emission or deposition.
- The uncertainty in the calculation of the emissions from standing crops is quite large and mainly due to the large uncertainty in the compensation point of crops. Therefore the range in the estimate for ammonia volatilization from standing crops can mainly be narrowed by improving the assessment of the compensation point values.
- Ammonia volatilization from crop residues can be reduced by quicker incorporation (within one week) of crop residues. However, ammonia volatilization from residues cannot completely be prevented as eg. time remains required for haulm killing of potato and losses of grass during cutting, drying and collection for silage cannot be prevented. Maximum mitigation of ammonia volatilization from crop residues is estimated to reduce emission from 1.9 to 1.3 million kg  $\text{NH}_3\text{-N}$ .
- The N content of residues has a large effect on calculated ammonia volatilization, as variation in N content of the residues affects both the % of total N that volatilizes as  $\text{NH}_3$  and the total N in the residues. As a result from fertilizer regulations, N contents of crops and crop residues may decrease with a relatively larger effect on ammonia volatilization. The actual effect of fertilizer regulations on crop N status, however, requires further study.
- The estimated ammonia emission by crops and crop residues is about twice the contribution by grazing and also higher than by manure storage.





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# Appendix I.

## Evaluation of gammas

### 1. Introduction

The gamma values used in the emission calculations are based on values found in literature. In this appendix we will elaborate how we get to the gamma values as used in Table 2.1.

The gamma,  $\Gamma$ , can be given for the whole canopy (including the soil and the litter) and is then denoted by  $\Gamma_c$  or it can be given for different parts of the plant-soil complex (leaves, different parts of leaves, litter). When it is the  $\Gamma$  for leaves only (i.e. the stomata) it is denoted by  $\Gamma_s$ .

$\Gamma$  is not measured itself, but can be calculated from the following measurements:

- The  $\text{NH}_3$  compensation point and the temperature. The measurements can take place in the field as well in the laboratory, but are usually done in the laboratory. The  $\text{NH}_3$  compensation point is usually determined when the plant (parts) are in cuvettes or chambers. This method gives the most accurate results. It can also include soil, but usually litter is not included and in many cases only the leaves are investigated. In the literature this method is mostly used to give  $\Gamma_s$ .
- The  $\text{NH}_4^+$  concentration and the pH in the apoplast of the leaves. These values can be applied in the laboratory as well as in the field. The result is a  $\Gamma_s$  value. In theory  $\Gamma_s$  calculated from these data should give the same result as from the compensation point and the temperature, but simultaneous measurements with both methods show that the results obtained can be different (Hill *et al.*, 2001).
- The airborne  $\text{NH}_3$  concentration at the time where the flux direction changes during non-stable conditions during daytime. This gives  $\Gamma_c$ . This method is not used very often.

The  $\Gamma_c$  can be inferred from model calculations, where different parameters, such as  $\Gamma_s$  are fitted to give an optimal agreement with the measurements. It is not always clear how this is done and whether different combinations of parameter values could lead to a similar result (Horvath *et al.*, 2005).

$\Gamma$  values are likely to vary with time, growth stage, nutrient level, weather (e.g. drought) and are influenced by fungal diseases. Different plant varieties do not necessarily give the same  $\Gamma$  values.

In general there are limited numbers of measurements of  $\Gamma$  values for one species. For that reason the uncertainty in  $\Gamma$  values can be very large and can change in the future when more data become available.

There are relatively few projects where  $\Gamma$  values have been determined for a season or a year. If  $\Gamma$  values are determined during a typical field campaign period (a few weeks), this is often done when the plant is in a growth stage where higher  $\Gamma$  values can be expected, i.e. values that are not representative of a whole year.

The literature survey presented here was finished in August 2012 and was to a large extent based on the work reported by Asman (2009). Asman (2009) focused on the compensation point, however, whereas this survey focuses on the gamma values. All results presented here are based on the original articles and included only direct or indirect (by fitting model results with measurements) measurements. All literature presented in the surveys by Zhang *et al.* (2010) and Massad *et al.* (2010) was also taken into account, but only if the reported data be found in the original literature (this was not always the case for the survey of Massad *et al.*, 2010) and were based on measurements.

There are different measures for the airborne  $\text{NH}_3$  concentration. Conversion between these measures was made using Equation (10) in Section 2.

Where the authors mentioned  $\Gamma$  values, they were used. In some, mostly older, publications  $\text{NH}_3$  compensation points are given. If the temperature was also given the compensation point was calculated from Equation (9) in Section 2. In other publications the apoplastic  $\text{NH}_4^+$  concentration and pH were given and subsequently the compensation point was calculated from Equation (7) in Section 2, assuming that the influence of the ionic strength can be neglected.

In Section 2 the theory behind the calculation of the compensation point and the conversion between different ways to express the concentration is treated. In Section 3 values and ranges for  $\Gamma$  values for different crops are given.

## 2. Conversion and calculation of the gamma $\Gamma$

Ammonia is normally emitted from aqueous solutions in manure, fertilizer/soil or plants. The emission rate of  $\text{NH}_3$  generally increases with temperature because the  $\text{NH}_3$  vapor pressure over an aqueous solution of  $\text{NH}_3/\text{NH}_4^+$  increases exponentially with temperature. In this section the relation between the different measures of the concentration as well as methods to calculate the gamma  $\Gamma$  is described.

The  $\text{NH}_3$  concentration in the air is in equilibrium with the dissolved  $\text{NH}_3$  concentration in a solution ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ), which again is determined by the  $\text{NH}_4^+$  and  $\text{H}^+$  concentration. The equilibrium between the  $\text{NH}_3$  concentration in the air and in the solution can be described by:



A measure for the solubility of a gas is the Henry's law coefficient  $H_{\text{NH}_3}$ , which relates the  $\text{NH}_3$  concentration in air to the concentration in water at equilibrium (Dasgupta and Dong, 1986):

$$H_{\text{NH}_3} = \frac{[\text{NH}_3 \cdot \text{H}_2\text{O}]}{[\text{NH}_3(\text{air})]} = 5.60 \times 10^1 \exp\left(4092 \left(\frac{1}{T} - \frac{1}{298.15}\right)\right) \text{ mol l}^{-1} \text{ atm}^{-1} \quad (2)$$

T is the temperature in K.

$\text{NH}_3 \cdot \text{H}_2\text{O}$  associates in the solution with  $\text{H}^+$  to form  $\text{NH}_4^+$  (and  $\text{H}_2\text{O}$ ):



The equilibrium constant  $K_{\text{NH}_4}$  for this reaction is (Bates and Pinching, 1950):

$$K_{\text{NH}_4} = \frac{[\text{NH}_3 \cdot \text{H}_2\text{O}][\text{H}^+]}{[\text{NH}_4^+]} = 5.67 \times 10^{-10} \exp\left(-6286 \left(\frac{1}{T} - \frac{1}{298.15}\right)\right) \text{ mol l}^{-1} \quad (4)$$

The  $\text{NH}_3$  concentration in air in equilibrium with the  $\text{NH}_4^+$  and  $\text{H}^+$  concentrations in solution can be found by combining (2) and (4).

$$[\text{NH}_3]_{\text{air}} = f \frac{[\text{NH}_4^+]_{\text{dissolved}}}{[\text{H}^+]_{\text{dissolved}}} = f \Gamma \quad (\text{atm}) \quad (5)$$

where:

$$f = \frac{K_{\text{NH}_4}}{H_{\text{NH}_3}} = 1.013 \times 10^{-11} \exp\left(-10378 \left(\frac{1}{T} - \frac{1}{298.15}\right)\right) \quad \text{atm} \quad (6)$$

and

$$\Gamma = \frac{[\text{NH}_4^+]_{\text{dissolved}}}{[\text{H}^+]_{\text{dissolved}}} \quad (7)$$

Both  $K_{\text{NH}_4}$  and  $H_{\text{NH}_3}$  are functions of the temperature in such a way that  $[\text{NH}_3]_{\text{air}}$  doubles approximately for each 5° C increase in temperature. This strong temperature dependence plays an important role in the emission and dry deposition processes for  $\text{NH}_3$ : the  $\text{NH}_3$  emission rate from manure, fertilizer and plants increases with temperature as does the emission rate associated with the  $\text{NH}_3$  compensation point of vegetation and seawater. In the case of concentrated solutions such as seawater or humidified particles on leaves some corrections have to be made for the ionic strength.

As can be seen from (5), the  $\text{NH}_3$  concentration in air increases, when the  $\text{H}^+$  concentration decreases, i.e. when the solution becomes more alkaline. It should be noted that the ratio  $[\text{NH}_4^+]/[\text{H}^+]$  itself usually does not depend very much on temperature and is called the gamma  $\Gamma$  and sometimes referred to as emission potential.

The gas-phase  $\text{NH}_3$  concentration in the sub-stomatal cavities of plants is called the stomatal compensation point and is related to the  $\text{NH}_4^+$  and  $\text{H}^+$  concentration in the apoplast according to (5).

In older literature the value of  $\Gamma$  is often not given but the compensation point ( $\text{NH}_3$  concentration in air at equilibrium) and often also the temperature.

Equation (5) can also be used to calculate  $\Gamma$  from the gas-phase concentration and the temperature:

$$\Gamma = \frac{[\text{NH}_3]_{\text{air,atm}}}{f} \quad (8)$$

If the  $\text{NH}_3$  concentration is in ppb ( $10^{-9}$  atm) then the following expression should be used:

$$\Gamma_s = \frac{[\text{NH}_3]_{\text{air,ppb}} 10^{-9}}{f} \quad (9)$$

where  $[\text{NH}_3]_{\text{air,ppb}}$  is the concentration in ppb.

Sometimes the air concentration is in  $\mu\text{g NH}_3 \text{ m}^{-3}$ .

Using the gas law the following expression can be found (Seinfeld and Pandis, 1998):

$$[\text{NH}_3]_{\text{air},\mu\text{g}/\text{m}^3} = \frac{10^{-3} \text{ pM}}{RT} [\text{NH}_3]_{\text{air,ppb}} \quad (10)$$

where in this case:

$$[\text{NH}_3]_{\text{air},\mu\text{g}/\text{m}^3} = \text{concentration } (\mu\text{g NH}_3 \text{ m}^{-3})$$

p	= pressure (atm); in this case p = 1 atm
M	= molecular mass (g mol <sup>-1</sup> ); the molecular mass of NH <sub>3</sub> is 17.03 g mol <sup>-1</sup>
R	= gas constant (8.2057x10 <sup>5</sup> m <sup>3</sup> atm mol <sup>-1</sup> K <sup>-1</sup> )
T	= temperature (K)
[NH <sub>3</sub> ] <sub>air,ppb</sub>	= concentration (ppb)

From (9) and (10) the following expression can be found:

$$\Gamma = \frac{RT[\text{NH}_3]_{\text{air,ug/m}^3} 10^{-6}}{pMf} = \frac{8.2057 \times 10^{-5} \cdot 10^{-6} T [\text{NH}_3]_{\text{air,ug/m}^3}}{1 \cdot 17.03 \cdot f} =$$

$$4.818 \times 10^{-12} \frac{T [\text{NH}_3]_{\text{air,ug/m}^3}}{f} \quad (11)$$

### 3. $\Gamma$ values for different crops

#### 3.1 Grass

There are many grass species that are being used as a crop. There is often more than one species in a grass field. It has been shown that different species within one grass field can have  $\Gamma_s$  values that are a factor of 30 different at the same time (Mattsson *et al.*, 2009b). For that reason it is important to know which grass species are present as well as their abundance. Moreover, it is important to know whether the grassland is managed intensively (applying manure/mineral fertilizer) or whether it is managed extensively without any nitrogen added. It is also important to know whether animals are grazing or not. It should be noted that when decaying litter is present, the  $\Gamma$  value from the litter can be much higher than the  $\Gamma_s$  value from grass itself, up to 400,000 (David *et al.*, 2009) and therefore 'overwhelm' the contribution from  $\Gamma_s$  for shorter time periods.

For The Netherlands there are long-term measurements for both intensively and extensively managed grassland.

##### 3.1.1 Intensively managed grassland

Plantaz (1998) found for a grassland in Zegveld, The Netherlands, a rather high  $\Gamma_c$  value of 4751.

Van Hove *et al.* (2002) found for a grassland at Wageningen, The Netherlands using the results from apoplast extraction an average  $\Gamma_s$  value of 1156 for temperatures less than 12°C and a value of 588 for temperatures larger than 12°C.

The average  $\Gamma_c$  value for a 16 month period for an intensively managed grassland in Switzerland was 620 (Flécharde *et al.*, 2010).

##### 3.1.2 Extensively managed grassland

Wichink Kruit (2010) and Wichink Kruit *et al.* (2007) found an average  $\Gamma_c$  value of 2200±1600 for a grassland at Wageningen using a micrometeorological method. This is grassland that has not received any manure or mineral fertilizer, recently. This is a higher value than van Hove *et al.* (2002) found for intensively managed grassland, whereas the contrary would be more logical. This difference could be due to the fact that van Hove *et al.* (2002) found the  $\Gamma$  from the pH and NH<sub>4</sub><sup>+</sup> concentration in the apoplast, which does not include the soil and the litter as sources.

### 3.1.3 Intensively and extensively managed grassland

Flécharde *et al.* (2010) did not find a significant difference in  $\Gamma_c$  between intensively and extensively managed grassland. This does not mean that there is no difference between the two types of grassland, only that the scatter in the data is so large that this could not be deduced.

Taking into account the uncertainty in the measurements it would for the moment be reasonable to adopt the same value for  $\Gamma_c$  values for both systems: 500 (lower estimate), 2000 (medium estimate) and 4000 (upper estimate).

Wichink Kruit *et al.* (2010) found from collection of literature values that  $\Gamma_c$  and  $\Gamma_s$  increased with the long-term  $\text{NH}_3$  air concentration. This information could perhaps be used to differentiate between different sites within The Netherlands. It would also be useful if  $\Gamma$  values could be measured at locations in the Netherlands with a much lower background concentration than the sites where the measurements have been made so far.

Furthermore larger  $\Gamma_s$  values (van Hove *et al.*, 2002) and  $\Gamma_c$  values (Wichink Kruit *et al.*, 2010) were found at lower temperatures and the relation with the temperature found by Wichink Kruit (2010) could be used to find  $\Gamma_c$  as function of the time of the year.

## 3.2 Maize

Five publications give information on the compensation point and/or  $\Gamma_s$  value. Two of them give only the compensation point without any usable information on the temperature and therefore  $\Gamma_s$  cannot be calculated. Two of the remaining publications give measurements of the compensation point itself in the laboratory (Farquhar *et al.*, 1979) leading to  $\Gamma_s$  values of 182 and 575. Another publication (Bash *et al.*, 2010) gives  $\Gamma_s$  values ranging from 40-429 with an average of 221 measured in North Carolina, USA, from 6 July through 1 August 2007. The canopy reached a peak leaf area index (single-sided) of  $2.9 \pm 0.6 \text{ m}^2 \text{ m}^{-2}$  and a maximum canopy height of 2.2 m near 15 July and had fully senesced by 21 August. There was no real trend in the  $\Gamma_s$  value during the measurement period. Also low  $\Gamma_s$  values were observed at the end. It should be noted that the plant variety was different from the varieties used in The Netherlands and the climate is certainly different.

Loubet *et al.* (2006) mention the following: 'Based on measurements of the stomatal compensation point for maize receiving different amounts of nitrogen (Loubet, personal communication; according to the methodology of Loubet *et al.* (2002)) and on the knowledge of the field management,  $\Gamma$  was set to 3000.' This indicates that much higher values for  $\Gamma$  are also found for maize.

Recently Volten *et al.* (2012) reported gamma values for long term measurements above maize of 3200 with a range of 2400-4200. Measurements were carried out above a tall variety of corn (over 3 m). These results are in line with the findings of Loubet *et al.* (2006).

Taking into account the uncertainty in the measurements it would for the moment be reasonable to adopt the following  $\Gamma_s$  values: 200 (lower estimate), 1500 (medium estimate), 4000 (upper estimate).

## 3.3 Potatoes

No data at all are available for potatoes.

### 3.4 Wheat

Winter wheat and spring wheat are different wheat varieties and for that reason it can be expected that their  $\Gamma_s$  values are different. The seasonal behavior is certainly different. Winter wheat is sown in autumn and harvested in summer, whereas spring wheat is sown in spring and harvested in autumn. There are no long-term measurements of  $\Gamma$  values for wheat. Moreover, it is not always specified which type of wheat it is. The few existing  $\Gamma$  values vary from 631 to 3786.

Taking into account the uncertainty in the measurements it would for the moment be reasonable to adopt the following  $\Gamma_s$  values: 500 (lower estimate), 2000 (medium estimate), 4000 (upper estimate).

### 3.5 Sugar beet

No data at all are available for sugar beet.

### 3.6 Summary

Table 1 shows the best available estimates for the gamma  $\Gamma$ . For Potatoes and sugar beets no literature values could be found and conservative default values were chosen.

*Table 1. Estimated  $\Gamma$  values for the most important crops.*

Crop	Type of $\Gamma$	$\Gamma$ , lower	$\Gamma$ , medium	$\Gamma$ , upper
Grassland (intensively and extensively managed)	$\Gamma_c$	500	2000	4000
Maize	$\Gamma_s$	200	1500	4000
Potatoes <sup>a)</sup>	$\Gamma_s$	500	1000	2000
Wheat	$\Gamma_s$	500	2000	4000
Sugar beet <sup>a)</sup>	$\Gamma_s$	500	1000	2000

<sup>a)</sup> *No data available; default values were used.*

## **Appendix II.**

### **Measured compensation points**

The values for gamma from Appendix I are based on measurements of compensation points. In this Appendix an overview of the literature on compensation point measurements is presented.

Table Appendix II. Measured compensation points, air concentrations and  $\Gamma$ -values crops from literature.

Vegetation	Location	Conditions	Comp. point (various units)	Comp. point ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Conc. air ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Temp. (C)	NH <sub>4</sub> <sup>+</sup> conc. Apoplast (mM)	pH apoplast	$\Gamma$ (dim.less)	References
Amaranthus edulis	Laboratory	1 plant	4.7 nbar	3.2		32			206 <sup>b)</sup>	Farquhar <i>et al.</i> (1980)
Barley (Hordeum vulgare)	Howmuir, UK	Ear emergence, 0.45 m tall, LAI=4.9	0.57-1.69 $\mu\text{g NH}_3 \text{ m}^{-3}$ (stomatal) 0.6-7.4 $\mu\text{g NH}_3 \text{ m}^{-3}$ (canopy)	0.57-1.69 (stomatal) 0.6-7.4 (canopy)	0.47-1.30 (1 m)	4-21			-	Sutton <i>et al.</i> (1993a)
Barley (Hordeum vulgare)	Laboratory	Intact shoots used of wild type; other types of barley mentioned are not used as crops	5.0 nmol mol <sup>-1</sup>	3.7	-	25			456 <sup>b)</sup>	Mattsson <i>et al.</i> (1997)
Barley (Hordeum vulgare)	Laboratory	Nonsenescent leaves used of wild type	0.75 nmol mol <sup>-1</sup>	0.52	-	25	0.36	5.32	75 <sup>c)</sup>	Mattsson <i>et al.</i> (1997)
Barley (Hordeum vulgare Golf)	Laboratory	Intact shoots, tillering	6.4±1.1 nmol mol <sup>-1</sup> air	4.7	-	25			632 <sup>b)</sup>	Husted <i>et al.</i> (1996)
Barley (Hordeum vulgare Golf)	Laboratory	Intact shoots, before anthesis	4.7±0.3 nmol mol <sup>-1</sup> air	3.4	-	25			464 <sup>b)</sup>	Husted <i>et al.</i> (1996)
Barley (Hordeum vulgare Golf)	Laboratory	Intact shoots, after anthesis	3.0±0.4 nmol mol <sup>-1</sup> air	2.2	-	25			296 <sup>b)</sup>	Husted <i>et al.</i> (1996)
Barley (Hordeum vulgare Golf)	Laboratory	Intact shoots, mid grain filling	4.0±0.6 nmol mol <sup>-1</sup> air	2.9	-	25			395 <sup>b)</sup>	Husted <i>et al.</i> (1996)
Barley (Hordeum vulgare Golf)	Laboratory	Intact shoots, maturity	5.3±0.1 nmol mol <sup>-1</sup> air	3.9	-	25			523 <sup>b)</sup>	Husted <i>et al.</i> (1996)
Barley (Hordeum vulgare Golf)	Laboratory	N-limited conditions, 59 days after emergence	4.6±2.9 nmol mol <sup>-1</sup> air	3.3±2.0	-	20			822 <sup>b)</sup>	Husted and Schjoerring (1995a)
Barley (Hordeum vulgare Golf)	Laboratory	Root medium 0 mM NH <sub>4</sub> <sup>+</sup>					0.04±0.003	6.70±0.18	200 <sup>c)</sup>	Mattsson <i>et al.</i> (1998)
Barley (Hordeum vulgare Golf)	Laboratory	Root medium 0.5 mM NH <sub>4</sub> <sup>+</sup>					0.05±0.003	6.60±0.11	251 <sup>c)</sup>	Mattsson <i>et al.</i> (1998)
Barley (Hordeum vulgare Golf)	Laboratory	Root medium 1 mM NH <sub>4</sub> <sup>+</sup>					0.38±0.11	6.52±0.05	1258 <sup>c)</sup>	Mattsson <i>et al.</i> (1998)



Vegetation	Location	Conditions	Comp. point (various units)	Comp. point ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Conc. air ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Temp. (C)	$\text{NH}_4^+$ conc. Apoplast (mM)	pH apoplast	$\Gamma$ (dim.less)	References
Barley ( <i>Hordeum vulgare</i> Golf)	Laboratory	Root medium 2.5 mM $\text{NH}_4^+$					1.04 $\pm$ 0.13	6.50 $\pm$ 0.22	3444 <sup>d</sup>	Mattsson <i>et al.</i> (1998)
Barley ( <i>Hordeum vulgare</i> Golf)	Laboratory	Root medium 5 mM $\text{NH}_4^+$					1.90 $\pm$ 0.22	6.44 $\pm$ 0.09	5233 <sup>d</sup>	Mattsson <i>et al.</i> (1998)
Barley ( <i>Hordeum vulgare</i> Golf)	Laboratory	Root medium 10 mM $\text{NH}_4^+$					2.28 $\pm$ 0.42	6.32 $\pm$ 0.14	4764 <sup>d</sup>	Mattsson <i>et al.</i> (1998)
Barley ( <i>Hordeum vulgare</i> Laevigatum)	Laboratory	Intact shoots, tillering	4.2 $\pm$ 0.3 nmol mol <sup>-1</sup> air	3.0	-	25			415 <sup>b</sup>	Husted <i>et al.</i> (1996)
Barley ( <i>Hordeum vulgare</i> Laevigatum)	Laboratory	Intact shoots, before anthesis	2.9 $\pm$ 0.6 nmol mol <sup>-1</sup> air	2.1	-	25			286 <sup>b</sup>	Husted <i>et al.</i> (1996)
Barley ( <i>Hordeum vulgare</i> Laevigatum)	Laboratory	Intact shoots, after anthesis	0.9 $\pm$ 1.7 nmol mol <sup>-1</sup> air	0.7	-	25			89 <sup>b</sup>	Husted <i>et al.</i> (1996)
Barley ( <i>Hordeum vulgare</i> Laevigatum)	Laboratory	Intact shoots, mid grain filling	5.3 $\pm$ 0.8 nmol mol <sup>-1</sup> air	3.9	-	25			523 <sup>b</sup>	Husted <i>et al.</i> (1996)
Barley ( <i>Hordeum vulgare</i> Laevigatum)	Laboratory	Intact shoots, maturity	3.3 nmol mol <sup>-1</sup> air	2.4	-	25			326 <sup>b</sup>	Husted <i>et al.</i> (1996)
Barley ( <i>Hordeum vulgare</i> Laevigatum)	Laboratory	N-limited conditions, 59 days after emergence	4.2 $\pm$ 2.8 nmol mol <sup>-1</sup> air	3.0 $\pm$ 2.0	-	20			751 <sup>b</sup>	Husted and Schjoerring (1995a)
<i>Eucalyptus pauciflora</i>	Laboratory	1 plant	3 nbar	2.0		32			132 <sup>b</sup>	Farquhar <i>et al.</i> (1980)
Grass, <i>Agrostis</i> spp. (Bent-grass), <i>Poa</i> spp. (Meadow-grass) etc.	Harwell, UK	Calcareous grassland, pH 8.4	$\mu\text{g NH}_3 \text{ m}^{-3}$ (canopy)	1.01 (canopy)	1.77	8			1108 <sup>b</sup>	Sutton <i>et al.</i> (1993b)
Grass, <i>Arrhenatherum elatius</i> (an European meadow grass)	Laboratory	Different N treatments	0.04 nmol mol <sup>-1</sup> (highest treatment) or < 0.16 nmol mol <sup>-1</sup> (other)	0.03 (highest treatment) or < 0.12 (other)		20			7 or < 29 <sup>b</sup>	Hanstein <i>et al.</i> (1999)

Vegetation	Location	Conditions	Comp. point (various units)	Comp. point ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Conc. air ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Temp. (C)	$\text{NH}_4^+$ conc. Apoplast (mM)	pH apoplast	$\Gamma$ (dim.less)	References
Grass, <i>Bromus erectus</i> (an European meadow grass)	Laboratory	Different N treatments	0.32 nmol mol <sup>-1</sup> (highest treatment) or < 0.16 nmol mol <sup>-1</sup> (other)	0.23 nmol mol <sup>-1</sup> (highest treatment) or < 0.12 nmol mol <sup>-1</sup> (other)	-	20			57 and < 29 <sup>b)</sup>	Hanstein <i>et al.</i> (1999)
Grass, <i>Bromus erectus</i>	Laboratory				-	-			237 <sup>a)</sup>	Sutton <i>et al.</i> (2001)
Grass, <i>Deschampsia flexuosa</i> (L.) Trin	Laboratory	5 months old	0.45 nmol mol <sup>-1</sup> air	0.33	-	8			364 <sup>b)</sup>	Schjoerring <i>et al.</i> (1998b)
Grassland	Devon, UK	Long grass (1.5 cm) fert.: 300 kg N ha <sup>-1</sup> yr <sup>-1</sup>	-	-	-	-			3000 <sup>a)</sup>	Fowler <i>et al.</i> (1998) cited in Spindler <i>et al.</i> (2001)
Grassland	Devon, UK	Short grass (5 cm) fert.: 300 kg N ha <sup>-1</sup> yr <sup>-1</sup>	-	-	-	-			13000 <sup>a)</sup>	Fowler <i>et al.</i> (1998) cited in Spindler <i>et al.</i> (2001)
Grass, <i>Lolium perenne</i> (ryegrass)	Laboratory		-	-	-	-			477 <sup>a)</sup>	Sutton <i>et al.</i> (2001)
Grass, <i>Lolium perenne</i> , <i>Traxacum officinale</i> , <i>Leontodon autumnales</i>	Melpitz, Germany	Semi-natural grassland, fert: 70 kg N ha <sup>-1</sup> yr <sup>-1</sup>	0.5-3.5 $\mu\text{g NH}_3 \text{ m}^{-3}$ (stomatal) 0.2-1 $\mu\text{g NH}_3 \text{ m}^{-3}$ (canopy)	0.5-3.5 $\mu\text{g NH}_3 \text{ m}^{-3}$ (stomatal) 0.2-1 (canopy)	-	-			1000 <sup>a)</sup>	Spindler <i>et al.</i> (2001)
Grass, <i>Luzula sylvatica</i> (Huds.) Gaud.	Laboratory	2 methods, no agreement	Gas exchange: 0.51-1.10 $\mu\text{g NH}_3 \text{ m}^{-3}$ Apoplast extracts: 0.017-0.54 $\mu\text{g NH}_3 \text{ m}^{-3}$	Gas exchange: 0.51-1.10 Apoplast extracts: 0.017-0.54	-	-			18.7 (mean) 2.5-78.4 (range) 101.1 (mean) 73.7-159.0 (range)	Hill <i>et al.</i> (2001)

Vegetation	Location	Conditions	Comp. point (various units)	Comp. point ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Conc. air ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Temp. (C)	NH <sub>4</sub> <sup>+</sup> conc. Apoplast (mM)	pH apoplast	$\Gamma$ (dim.less)	References
Grass, <i>Luzula sylvatica</i> (Huds.) Gaud.	Laboratory	Apoplastic extraction					0.032	6.63	1.37 (younger leaves) 7 (older leaves)	Hill <i>et al.</i> (2002)
Grass: <i>Lolium</i> multiflorum, <i>Phleum pratense</i> etc.	Bush, UK	Intensively managed grassland. Nearing anthesis, 0.85 m tall, LAI=6	-0.02-1.82 $\mu\text{g NH}_3 \text{ m}^{-3}$ (stomatal) -0.9 to 7.3 $\mu\text{g NH}_3 \text{ m}^{-3}$ (canopy)	-0.02-1.82 (stomatal) -0.9 to 7.3 (canopy)	0.0 - 0.96	14-21	0.026	5.41	-	Sutton <i>et al.</i> (1993a)
Grass: <i>Lolium</i> multiflorum, <i>Phleum pratense</i> etc.	Bush, UK	Intensively managed grassland. Snow and wet grass, 0.07 m tall	-0.26-0.42 $\mu\text{g NH}_3 \text{ m}^{-3}$ (canopy)	-0.26-0.42 (canopy)	0.54-3.14	0-3			-	Sutton <i>et al.</i> (1993a)
Grass: <i>Lolium perenne</i> L. (ryegrass)	Swifterbant, The Netherlands	Intensively managed grassland	14 $\mu\text{g NH}_3 \text{ m}^{-3}$ (canopy)	14	>14	-			-	Harper <i>et al.</i> (1996)
Grass: <i>Lolium perenne</i> L. (ryegrass)	North Wyke, UK	Wind tunnel measurements grass sward with artificial urine	1.0-2.3 $\mu\text{g NH}_3 \text{ m}^{-3}$ (canopy)	1.0-2.3 (canopy)	-	14			518-1192 <sup>a)</sup>	Ross and Jarvis (2001)
Grass: <i>Lolium perenne</i> L. (ryegrass)	Scotland, UK	Intensively managed grassland, 270 kg N ha <sup>-1</sup> yr <sup>-1</sup>	-	-	-	-			precut:630 postcut: 6000 post fertilizing: 40000 <sup>a)</sup>	Milford <i>et al.</i> (2001)

Vegetation	Location	Conditions	Comp. point (various units)	Comp. point ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Conc. air ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Temp. (C)	$\text{NH}_4^+$ conc. Apoplast (mM)	pH apoplast	$\Gamma$ (dimless)	References
Grass: Lolium perenne L. (ryegrass)	Laboratory	Different $\text{NO}_3^-$ and light level							Attached senescing leaves: 20-300 Excised senescing leaves: < 1000	Mattsson and Schjoerring (2003)
Grassland	Burrington Moor, UK	intensively managed grassland							Long grass: 3150 Short grass: 12600 (model fitted to measure- ments)	Asman <i>et al.</i> (1998)
Grassland	Schagerbrug, The Netherlands	intensively managed, manure was spread							0-6000 <sup>pl</sup>	Mosquera <i>et al.</i> (2001)
Grass: Lolium perenne L. (ryegrass)	Wageningen the Netherlands	Intensively managed grassland, whole year	0.5-4.0 $\mu\text{g NH}_3 \text{ m}^{-3}$	0.5-4.0	6	10			Average for temp. < 12°C: 1156, average for temp. > 12°C: 588 <sup>pl</sup>	Van Hove <i>et al.</i> (2002)

Vegetation	Location	Conditions	Comp. point (various units)	Comp. point ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Conc. air ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Temp. (C)	$\text{NH}_4^+$ conc. Apoplast (mM)	pH apoplast	$\Gamma$ (dimless)	References
Grassland	Püspökladány, Hungary	natural grassland, only fertilized once with 100 kg N/ha (normally not done)							Spring: 7240 (100-18000) Summer 200 (100-400) Autumn 5186 (100-12000) Winter 1733 (100-5000) <sup>a)</sup> $\Gamma$ found from model results (optimal fit)	Horváth <i>et al.</i> (2005)
Grass: Lolium perenne (rye grass)	Wageningen, The Netherlands	non fertilized grassland, 5 months	0.5-29.7 $\mu\text{g NH}_3 \text{ m}^{-3}$ average 7 $\mu\text{g NH}_3 \text{ m}^{-3}$	0.5-29.7 7 (average)		7-29			2200 $\pm$ 1600	Wichink Kruit <i>et al.</i> (2007) Wichink Kruit (2010)
Grass: Lolium perenne L. (ryegrass)	Bush, UK	Intensively managed grassland, before fertilization from apoplast concentrations	-	-	-	-			before fert: 20 just after fert: 2000 then > 100 for 10 days <sup>a)</sup>	Loubet <i>et al.</i> (2002)
Grass: Lolium perenne L. (ryegrass)	Zegveld, The Netherlands	Intensively managed grassland, fertilization about 300 kg N ha <sup>-1</sup> year <sup>-1</sup>	19 $\mu\text{g NH}_3 \text{ m}^{-3}$	19		20			4751 <sup>b)</sup>	Plantaz (1998)
Grass-clover	Oensingen, Switzerland	micrometeorological method, 16 months intensively managed							620 <sup>a)</sup>	Flécharde <i>et al.</i> , 2010

Vegetation	Location	Conditions	Comp. point (various units)	Comp. point ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Conc. air ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Temp. (C)	NH <sub>4</sub> <sup>+</sup> conc. Apoplast (mM)	pH apoplast	$\Gamma$ (dim.less)	References
Grass-clover	Kerzermos, Switzerland	intensively managed	0.5-2.5 $\mu\text{g NH}_3 \text{ m}^{-3}$	0.5-2.5	3-4		Extreme values: a) 0.015 b) 0.030	Extreme values a) 6.1 b) 6.8	20-200 <sup>a)</sup>	Herrmann <i>et al.</i> (2001)
Grass: <i>Lolium perenne</i> L. and <i>Phleum pratense</i>	Braunschweig, Germany	Intensively managed grassland, 250 kg N ha <sup>-1</sup> yr <sup>-1</sup> , from apoplast concentrations in the field, height above soil 0.1 m	0.2 $\mu\text{g NH}_3 \text{ m}^{-3}$	0.2		15			92 <sup>b)</sup>	Herrmann <i>et al.</i> (2009)
Grass: <i>Lolium perenne</i> L. and <i>Phleum pratense</i>	Braunschweig, Germany	Intensively managed grassland, 250 kg N ha <sup>-1</sup> yr <sup>-1</sup> , from apoplast concentrations in the field, height above soil 0.3 m	0.2 $\mu\text{g NH}_3 \text{ m}^{-3}$	0.2		15			92 <sup>b)</sup>	Herrmann <i>et al.</i> (2009)
Grass: <i>Lolium perenne</i> L. and <i>Phleum pratense</i>	Braunschweig, Germany	Intensively managed grassland, 250 kg N ha <sup>-1</sup> yr <sup>-1</sup> , from apoplast concentrations in the field, height above soil				15			459 <sup>b)</sup>	Herrmann <i>et al.</i> (2009)
Grass: <i>Lolium perenne</i> L. and <i>Phleum pratense</i>	Braunschweig, Germany	Intensively managed grassland, 250 kg N ha <sup>-1</sup> yr <sup>-1</sup> , from apoplast concentrations in the field				15			Before cutting 100-200 <sup>b)</sup>	Herrmann <i>et al.</i> (2009)

Vegetation	Location	Conditions	Comp. point (various units)	Comp. point ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Conc. air ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Temp. (C)	$\text{NH}_4^+$ conc. Apoplast (mM)	pH apoplast	$\Gamma$ (dim.less)	References
Grass: <i>Lolium perenne</i> L. and <i>Phleum pratense</i>	Braunschweig, Germany	Intensively managed grassland, 250 kg N ha <sup>-1</sup> yr <sup>-1</sup> , from apoplast concentrations in the field				15			After cutting 30-200 <sup>al</sup>	Herrmann <i>et al.</i> (2009)
Grass: <i>Lolium perenne</i> L. and <i>Phleum pratense</i>	Braunschweig, Germany	Intensively managed grassland, 250 kg N ha <sup>-1</sup> yr <sup>-1</sup> , from apoplast concentrations in the field				15			After fertilization 250-1600 <sup>al</sup>	Herrmann <i>et al.</i> (2009)
Grass: <i>Lolium perenne</i> L. dominated field	Braunschweig, Germany	Grassland, received 250-350 kg N ha <sup>-1</sup> yr <sup>-1</sup>							Uncut: 140; shortly aft fert. with 100 kg N ha <sup>-1</sup> ; 1500; after a few days 350	Mattsson <i>et al.</i> (2009a)
Grass: <i>Lolium perenne</i> L. (ryegrass)	Braunschweig, Germany	Grassland, received 250-350 kg N ha <sup>-1</sup> yr <sup>-1</sup>	3.3±0.75 nmol mol <sup>-1</sup>						326 <sup>al</sup>	Mattsson <i>et al.</i> (2009b)
Grassland dominated by <i>Lolium perenne</i> L. (ryegrass)	Braunschweig, Germany and in laboratory	Grassland received 300 N ha <sup>-1</sup> yr <sup>-1</sup>							No $\Gamma$ from whole field, only from: Tall green leaves 50-2600 Wet litter 400000	David <i>et al.</i> (2009)

Vegetation	Location	Conditions	Comp. point (various units)	Comp. point ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Conc. air ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Temp. (C)	NH <sub>4</sub> <sup>+</sup> conc. Apoplast (mM)	pH apoplast	$\Gamma$ (dim.less)	References
Grass: <i>Phleum pretense</i>	Braunschweig, Germany	Grassland, received 250-350 kg N ha <sup>-1</sup> yr <sup>-1</sup> , from apoplast concentrations	0.3±0.03 nmol mol <sup>-1</sup>			25			30 <sup>b)</sup>	Mattsson <i>et al.</i> (2009b)
Grass: <i>Festuca pretensis</i>	Braunschweig, Germany	Grassland, received 250-350 kg N ha <sup>-1</sup> yr <sup>-1</sup> , from apoplast concentrations	6.45±0.45 nmol mol <sup>-1</sup>			25			637 <sup>b)</sup>	Mattsson <i>et al.</i> (2009b)
Grass: <i>Lolium multiflorum</i>	Braunschweig, Germany	Grassland, received 250-350 kg N ha <sup>-1</sup> yr <sup>-1</sup> , from apoplast concentrations	1.5±0.75 nmol mol <sup>-1</sup>			25			148 <sup>b)</sup>	Mattsson <i>et al.</i> (2009b)
Grass: <i>Poa pratensis</i>	Braunschweig, Germany	Grassland, received 250-350 kg N ha <sup>-1</sup> yr <sup>-1</sup> , from apoplast concentrations	1.05±0.15 nmol mol <sup>-1</sup>			25			104 <sup>b)</sup>	Mattsson <i>et al.</i> (2009b)
Grass: <i>Dactylis glomerata</i>	Braunschweig, Germany	Grassland, received 250-350 kg N ha <sup>-1</sup> yr <sup>-1</sup> , from apoplast concentrations	5.25±0.9 nmol mol <sup>-1</sup>			25			518 <sup>b)</sup>	Mattsson <i>et al.</i> (2009b)
Grass: <i>Holcus lanatus</i>	Braunschweig, Germany	Grassland, received 250-350 kg N ha <sup>-1</sup> yr <sup>-1</sup> , from apoplast concentrations	0.3±0.03 nmol mol <sup>-1</sup>			25			30 <sup>b)</sup>	Mattsson <i>et al.</i> (2009b)
Grass: <i>Bromus mollis</i>	Braunschweig, Germany	Grassland, received 250-350 kg N ha <sup>-1</sup> yr <sup>-1</sup> , from apoplast concentrations	0.2±0.01 nmol mol <sup>-1</sup>			25			20 <sup>b)</sup>	Mattsson <i>et al.</i> (2009b)
<i>Phaseolus vulgaris</i> L. var. 'Hawkesbury Wonder' (common bean)	Laboratory	20-40 days old, 6 plants	2.5±0.13 nbar	1.7±0.09		26			217 <sup>b)</sup>	Farquhar <i>et al.</i> (1980)
Maize ( <i>Zea mays</i> L., Pioneer hybrid 3379)	Nebraska, USA	Average growing season	7.1±1.0 $\mu\text{g NH}_3\text{-N m}^{-3}$ daytime (canopy) comp. point is lower at dusk	9.5	-	-			-	Harper and Sharpe (1995)



Vegetation	Location	Conditions	Comp. point (various units)	Comp. point ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Conc. air ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Temp. (C)	$\text{NH}_4^+$ conc. Apoplast (mM)	pH apoplast	$\Gamma$ (dim.less)	References
Maize (Zea mays L., variety Pioneer 33J56)	Beltsville, MD, USA	Fully developed canopy (LAI ~ 4)	$6 \mu\text{g NH}_3 \text{ m}^{-3}$ (canopy)	6 (canopy)	-	-	-	-	-	Meyers <i>et al.</i> (2006)
Maize (Zea mays L., variety NES 1002)	Laboratory	1 plant	2.1 nbar	1.7		26			182 <sup>b)</sup>	Farquhar <i>et al.</i> (1979)
Maize (Zea mays L., variety NES 1002)	Laboratory	1 plant	5.9 nbar	4.1		25			575 <sup>b)</sup>	Farquhar <i>et al.</i> (1979)
Maize (Zea mays L., Pioneer varieties 31G66 and 31P41)	Lillington, North Carolina, USA	field, July/August, almost fully developed; 50 kg N/ha in April, 1.35 kg N/ha end of May							40.429 <sup>a)</sup> (mean 221)	Bash <i>et al.</i> (2010) Walker <i>et al.</i> (2012)
Rapeseed (Brassica napus)	Laboratory	Vegetative growth stage, 2N, 2 methods	$0.44 \pm 0.30 \text{ nmol mol}^{-1}$ $0.46 \pm 0.17 \text{ nmol mol}^{-1}$	0.32	-	25			43 and 45 <sup>b)</sup>	Husted and Schjoerring (1996), Mattson <i>et al.</i> (1998), Schjoerring <i>et al.</i> (1998a)
Rapeseed (Brassica napus)	Laboratory	Vegetative growth stage, 4N, 2 methods	$1.72 \pm 0.87 \text{ nmol mol}^{-1}$ $1.88 \pm 0.47 \text{ nmol mol}^{-1}$	1.26	-	25			170 and 186 <sup>b)</sup>	Husted and Schjoerring (1996) Mattson <i>et al.</i> (1998), Schjoerring <i>et al.</i> (1998a)
Rapeseed (Brassica napus)	Laboratory	Vegetative growth stage, 7N, 2 methods	$4.10 \pm 0.20 \text{ nmol mol}^{-1}$ $5.58 \pm 1.45 \text{ nmol mol}^{-1}$	2.99	-	25			405 and 551 <sup>b)</sup>	Husted and Schjoerring (1996) Mattson <i>et al.</i> (1998), Schjoerring <i>et al.</i> (1998a)
Rapeseed (Brassica napus)	Laboratory	Anthesis, 2N, 2 methods	$5.30 \pm 0.80 \text{ nmol mol}^{-1}$ $2.70 \pm 0.43 \text{ nmol mol}^{-1}$	3.87	-	25			523 and 267 <sup>b)</sup>	Husted and Schjoerring (1996)

Vegetation	Location	Conditions	Comp. point (various units)	Comp. point ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Conc. air ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Temp. (C)	NH <sub>4</sub> <sup>+</sup> conc. Apoplast (mM)	pH apoplast	$\Gamma$ (dim.less)	References
Rapeseed (Brassica napus)	Laboratory	Anthesis, 4N, 2 methods	3.32±0.90 nmol mol <sup>-1</sup> 3.07±0.31 nmol mol <sup>-1</sup>	2.42	-	25			328 and 303 <sup>b)</sup>	Husted and Schjoerring (1996)
Rapeseed (Brassica napus)	Laboratory	Anthesis, 7N, 1 method	4.17±1.17 nmol mol <sup>-1</sup>			25			41 <sup>b)</sup>	Husted and Schjoerring (1996)
Rapeseed (Brassica napus)	Laboratory	Senescence, 2N, 2 methods	< 0.90 nmol mol <sup>-1</sup> air	< 0.66	-	25			< 89 <sup>b)</sup>	Husted and Schjoerring (1996)
Rapeseed (Brassica napus)	Laboratory	Senescence, 4N, 2 methods	2.60±0.50 nmol mol <sup>-1</sup> air	1.90	-	25			257 <sup>b)</sup>	Husted and Schjoerring (1996)
Rapeseed (Brassica napus)	Laboratory	Senescence, 7N,12 methods	14.20±1.17 nmol mol <sup>-1</sup> air		-	25			-1402 <sup>b)</sup>	Husted and Schjoerring (1996)
Rapeseed (Brassica napus)	North Berwick, U.K., determination apoplast conc. in field	Leaves 0.5 m above soil, fertilizer: 285 kg N ha <sup>-1</sup> yr <sup>-1</sup>					0.41±0.03	5.66±0.05	187 <sup>c)</sup>	Husted <i>et al.</i> (2000)
Rapeseed (Brassica napus)	North Berwick, U.K., determination apoplast conc. in field	Leaves 0.75 m above soil, fertilizer: 285 kg N ha <sup>-1</sup> yr <sup>-1</sup>					0.26±0.03	6.15±0.04	367 <sup>c)</sup>	Husted <i>et al.</i> (2000)
Rapeseed (Brassica napus)	North Berwick, U.K., determination apoplast conc. in field	Leaves 1.25 m above soil, fertilizer: 285 kg N ha <sup>-1</sup> yr <sup>-1</sup>					0.38±0.06	6.05±0.04	426 <sup>c)</sup>	Husted <i>et al.</i> (2000)
Rapeseed (Brassica napus)	Laboratory apoplast	Late vegetative growth stage Leaf position, acropetal direction: 6-9	4.9 nmol mol <sup>-1</sup> (ionic strength = 0) 4.2 nmol mol <sup>-1</sup> (ionic strength = 25 mM)			25 C (assumed)	1.10±0.24	5.77±0.19	648 <sup>c)</sup>	Husted and Schjoerring (1995b)

Vegetation	Location	Conditions	Comp. point (various units)	Comp. point ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Conc. air ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Temp. (C)	$\text{NH}_4^+$ conc. Apoplast (mM)	pH apoplast	$\Gamma$ (dim.less)	References
Rapeseed (Brassica napus)	Laboratory apoplast	Late vegetative growth stage Leaf position, acropetal direction: 8-10	4.3 nmol mol <sup>-1</sup> (ionic strength = 0) 3.7 nmol mol <sup>-1</sup> (ionic strength = 25 mM)				1.06±0.16	5.73±0.16	569 <sup>d)</sup>	Husted and Schjoerring (1995b)
Rapeseed (Brassica napus)	Laboratory apoplast	Late vegetative growth stage Leaf position, acropetal direction: 12-16	5.3 nmol mol <sup>-1</sup> (ionic strength = 0) 4.5 nmol mol <sup>-1</sup> (ionic strength = 25 mM)				1.03±0.14	5.83±0.08	696 <sup>c)</sup>	Husted and Schjoerring (1995b)
Rapeseed (Brassica napus)	Laboratory apoplast	Late vegetative growth stage Leaf position, acropetal direction: 15-21	5.9 nmol mol <sup>-1</sup> (ionic strength = 0) 5.1 nmol mol <sup>-1</sup> (ionic strength = 25 mM)				1.30±0.08	5.78±0.09	783 <sup>c)</sup>	Husted and Schjoerring (1995b)
Rapeseed (Brassica napus)	Laboratory chamber	Late vegetative growth stage	5.3± 3.6 nmol mol <sup>-1</sup> air			25				Husted and Schjoerring (1995b)
Rapeseed (Brassica napus)	Model, measurements	North Berwick, UK, from siliques (seed cases) only 1260	-		-	-			1260 <sup>a)</sup>	Nemitz <i>et al.</i> (2000b)
Rapeseed (Brassica napus)	Model, measurements	North Berwick, UK, from leaves only	-		-	-			390 <sup>a)</sup>	Nemitz <i>et al.</i> (2000b)
Rapeseed (Brassica napus)	From apoplast	Model input given	-		-	-			1200	Nemitz <i>et al.</i> (2001)
Rapeseed (Brassica napus)	Laboratory 2 methods	0 mM NO <sub>3</sub> <sup>-</sup> + 5 mM NH <sub>4</sub> <sup>+</sup> solution, dark	10.24±2.63 $\mu\text{g NH}_3 \text{ m}^{-3}$ 12.19±2.52 $\mu\text{g NH}_3$ $\text{m}^{-3}$			20			1830 and 2179 <sup>a)</sup>	Massad <i>et al.</i> (2009)
Rapeseed (Brassica napus)	Laboratory 2 methods	10 mM NO <sub>3</sub> <sup>-</sup> + 0 mM NH <sub>4</sub> <sup>+</sup> solution, dark	0.53±0.08 $\mu\text{g NH}_3 \text{ m}^{-3}$ 0.80±0.28 $\mu\text{g NH}_3 \text{ m}^{-3}$			20			95 and 143 <sup>b)</sup>	Massad <i>et al.</i> (2009)

Vegetation	Location	Conditions	Comp. point (various units)	Comp. point ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Conc. air ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Temp. (C)	$\text{NH}_4^+$ conc. Apoplast (mM)	pH apoplast	$\Gamma$ (dimless)	References
Rapeseed (Brassica napus)	Laboratory 2 methods	10 mM $\text{NO}_3^- + 2 \text{ mM NH}_4^+$ solution, dark	1.62±0.30 $\mu\text{g NH}_3 \text{ m}^{-3}$ 6.62±10.95 $\mu\text{g NH}_3 \text{ m}^{-3}$			20			290 and 1183 <sup>b)</sup>	Massad <i>et al.</i> (2009)
Rapeseed (Brassica napus)	Laboratory 2 methods	10 mM $\text{NO}_3^- + 5 \text{ mM NH}_4^+$ solution, dark	1.80±0.37 $\mu\text{g NH}_3 \text{ m}^{-3}$ 2.92±7.16 $\mu\text{g NH}_3 \text{ m}^{-3}$			20			322 and 522 <sup>b)</sup>	Massad <i>et al.</i> (2009)
Rapeseed (Brassica napus)	Laboratory 2 methods	0 mM $\text{NO}_3^- + 5 \text{ mM NH}_4^+$ solution, light	4.18±0.62 $\mu\text{g NH}_3 \text{ m}^{-3}$ 6.91±1.75 $\mu\text{g NH}_3 \text{ m}^{-3}$			20			747 and 1235 <sup>b)</sup>	Massad <i>et al.</i> (2009)
Rapeseed (Brassica napus)	Laboratory 2 methods	10 mM $\text{NO}_3^- + 0 \text{ mM NH}_4^+$ solution, light	0.48±0.10 $\mu\text{g NH}_3 \text{ m}^{-3}$ 0.63±0.10 $\mu\text{g NH}_3 \text{ m}^{-3}$			20			86 and 113 <sup>b)</sup>	Massad <i>et al.</i> (2009)
Rapeseed (Brassica napus)	Laboratory 2 methods	10 mM $\text{NO}_3^- + 2 \text{ mM NH}_4^+$ solution, light	1.74±0.22 $\mu\text{g NH}_3 \text{ m}^{-3}$ 2.57±1.30 $\mu\text{g NH}_3 \text{ m}^{-3}$			20			311 and 459 <sup>b)</sup>	Massad <i>et al.</i> (2009)
Rapeseed (Brassica napus)	Laboratory 2 methods	10 mM $\text{NO}_3^- + 5 \text{ mM NH}_4^+$ solution, light	1.50±0.16 $\mu\text{g NH}_3 \text{ m}^{-3}$ 2.14±2.11 $\mu\text{g NH}_3 \text{ m}^{-3}$			20			268 and 383 <sup>b)</sup>	Massad <i>et al.</i> (2009)
Soybean	Duplin county, North Carolina, USA	Measurements during a 2 month period	-	-	-	-			955 <sup>a)</sup>	Walker <i>et al.</i> (2006)
Wheat (spring wheat; Triticum aestivum L.)	Laboratory, Growth chamber	Early grain filling	14 $\mu\text{g NH}_3 \text{ m}^{-3}$	17 $\mu\text{g NH}_3 \text{ m}^{-3}$		25			2411 <sup>d)</sup>	Morgan and Parton (1989)
Wheat (spring wheat; Triticum aestivum L.)	Laboratory, growth chamber	Early grain filling	22 $\mu\text{g NH}_3 \text{ m}^{-3}$	26.7 $\mu\text{g NH}_3 \text{ m}^{-3}$		25			3786 <sup>e)</sup>	Morgan and Parton (1989)
Wheat	Sutton Bonington, C. England	$\Gamma$ value which simulates the measured $\text{NH}_3$ flux on a field during one day				-	0.1 (assumed)	6.8 (assumed)	631 <sup>e)</sup>	Sutton <i>et al.</i> (1995a)
Wheat	No information given	$\Gamma$ value which simulates the measured $\text{NH}_3$ flux on a field during one day					0.6 (assumed)	6.8 (assumed)	3786 <sup>e)</sup>	Sutton <i>et al.</i> (1995b)
Wheat	Rothamsted, UK	Emission is favored under warm and dry conditions	3-4 $\mu\text{g NH}_3 \text{ m}^{-3}$ (canopy)	3-4 (canopy)	1.50-5.04	-			-	Yamulki <i>et al.</i> (1996)

Vegetation	Location	Conditions	Comp. point (various units)	Comp. point ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Conc. air ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )	Temp. (C)	NH <sub>4</sub> <sup>+</sup> conc. Apoplast (mM)	pH apoplast	$\Gamma$ (dim.less)	References
White clover (Trifolium repens L. cv. Seminole)	N <sub>2</sub> based treatment, Laboratory	From apoplastic concentrations	0.32-0.90 nmol mol <sup>-1</sup>						32.89 <sup>b)</sup>	Herrmann <i>et al.</i> (2002)
White clover (Trifolium repens L. cv. Seminole)	Low N NO <sub>3</sub> <sup>-</sup> solution, Laboratory	From apoplastic concentrations	0.20-0.47 nmol mol <sup>-1</sup>						20.46 <sup>b)</sup>	Herrmann <i>et al.</i> (2002)
White clover (Trifolium repens L. cv. Seminole)	High N NO <sub>3</sub> <sup>-</sup> solution, Laboratory	From apoplastic concentrations	0.32-0.54 nmol mol <sup>-1</sup>						32.53 <sup>b)</sup>	Herrmann <i>et al.</i> (2002)
White clover (Trifolium repens L. cv. Seminole)	N <sub>2</sub> based treatment, Laboratory	Cuvette and varying NH <sub>3</sub> concentrations	4 nmol mol <sup>-1</sup>						395 <sup>b)</sup>	Herrmann <i>et al.</i> (2002)
White clover (Trifolium repens L. cv. Seminole)	High N NO <sub>3</sub> <sup>-</sup> solution, Laboratory	Cuvette and varying NH <sub>3</sub> concentrations	4 nmol mol <sup>-1</sup>						395 <sup>b)</sup>	Herrmann <i>et al.</i> (2002)

**Notes:**

If no information is given, then the compensation point is the **stomatal** compensation point. If a canopy compensation point is known the word canopy is given in brackets. The word stomatal in brackets is only given if there is also given information on the canopy compensation point.

a) The  $\Gamma$  value is given by the authors.

b) The  $\Gamma$  value is calculated in this report from the compensation point and the temperature assuming that the ionic strength does not play a role.

c) The value is calculated in this report from the concentrations of NH<sub>4</sub><sup>+</sup> and the pH assuming that the ionic strength does not play a role.



## Appendix III.

### Literature data on crop residues and their N content

Extensive overviews of the amount of crop residues and their N content are given by Smit (1994) and Smit and Van der Werf (1992) (both reported by De Ruijter and Smit, 2007), Velthof and Kuikman (2000), Zwart *et al.* (2004) and Beinum and Westra (2004). Most of these data are also used in the overview of VLM (2008). Information from Feller *et al.* (2011) is supplemented by a table with information on dry matter content that can be accessed through internet (Anonymous, 2011). This information is considered as an update of earlier published values by Fink *et al.* (1999). A number of additional references with information on crop residues was added (Mitchell *et al.*, 2001; Neeteson and Carton, 2001; Riley, 2002), and all available data are linked to the crops as described by Statistics Netherlands (Table below). For each crop, single data were derived for calculation of national ammonia volatilization in the Netherlands (Table 2.2).

For potato, additional information was searched to distinguish seed potatoes, ware potatoes and starch potatoes. Most references in the table below give data apparently for ware potatoes. The amount of crop residues differs between ware potatoes and seed potatoes, as given by (Zwart *et al.*, 2004). For ware potatoes, the total N content in kg ha<sup>-1</sup> of Zwart *et al.* (2004) agrees with other sources, but their estimates for dry matter yield are higher, and for N content (in g kg<sup>-1</sup>) are lower than the other sources.

In Sweden, the amount of foliage at harvest was measured during five years and averaged 1860 kg ha<sup>-1</sup> dry matter with an N content of 21.4 g kg<sup>-1</sup> (Ekeberg and Riley, 1996).

From five field experiments in the Netherlands with late maturing potatoes, Vos (1997) derived regression equations that can be used to calculate the N content of the haulm at harvest. Assuming an N application of 250 kg ha<sup>-1</sup>, the average nitrogen standard for fertilization of potatoes in the Netherlands, haulm dry matter at harvest is 2050 kg ha<sup>-1</sup> dry matter, with 13.6 g N kg<sup>-1</sup> dry matter and a total content of 28 kg N ha<sup>-1</sup>.

In ware potato, Van der Schoot *et al.* (2002) found 1800 kg ha<sup>-1</sup> haulm at harvest, with an N content of 7.1 g kg<sup>-1</sup>, 12.6 kg ha<sup>-1</sup>. (Van Geel *et al.*, 2004) measured an N content of 15 g kg<sup>-1</sup> in two varieties of starch potato a few weeks before harvest. At harvest, the haulms were fully senesced and not measured. At the end of the growing season of potatoes, the total N content of the foliage decreases (Van Geel *et al.*, 2004). This can partly be caused by relocation of N from haulm to tuber, but also by senescence and leaf drop. Leaves that are on the soil surface decay and are generally not measured in the experiments. Leaf litter can contribute to ammonia volatilization (Sutton *et al.*, 2000).

A thesis from Belgium (Elsen, 2009) gives 3800 kg ha<sup>-1</sup> dry matter with an N content of 50 kg ha<sup>-1</sup>, 13 g kg<sup>-1</sup>. Fertilization affects the N content: 11.2 g kg<sup>-1</sup> without fertilizer, 14.8 g kg<sup>-1</sup> at recommended fertilizer application and 17.1 at the highest N application.

For both ware and starch potatoes, the following averages will be used in the current study (ranges from literature between brackets):

- Haulm dry matter (in kg ha<sup>-1</sup>): 2100 (1000-3800)
- N content (in g kg<sup>-1</sup>): 15.5 (7-25)
- N content (in kg ha<sup>-1</sup>): 31.5 (13-50)

For seed potatoes, only Zwart *et al.* (2004) have published data on the amount of haulm at harvest: 3889 kg ha<sup>-1</sup> dry matter with an N content of 23 g kg<sup>-1</sup> and 89 kg ha<sup>-1</sup>. Other estimate is 2000 kg ha<sup>-1</sup> dry matter with an N content of 40 g kg<sup>-1</sup>, 80 kg ha<sup>-1</sup>. (pers.comm. A.J. Haverkort, WUR-PRI). In the present study, average values will be used of 2700 kg dry matter ha<sup>-1</sup> with an N content of 32 g kg<sup>-1</sup> and 85 kg ha<sup>-1</sup>.

	Feller <i>et al.</i> , 2011		De Ruijter & Smit, 2009		VLM, 2008		Velthof & Kulkman, 2000		Zwart <i>et al.</i> , 2004		Beinum & Westra, 2004		Mitchell <i>et al.</i> , 2001		Neeteson & Carton, 2001		Riley, 2002			
	Amount (kg/ha)	Dry Content (%)	N content (g/kg dry)	N content (kg/ha)	Amount (kg/ha)	Fresh (kg/ha)	Dry (kg/ha)	Amount (kg/ha)	N content (kg/ha)	Amount (g/kg dry)	N content (kg/ha)	Amount (kg/ha)	N content (g/kg dry)	Amount (kg/ha)	N content (kg/ha)	Amount (kg/ha)	N content (kg/ha)	Amount (kg/ha)	N content (kg/ha)	
wheat	3000	10	25	75	2300	19	44	45-90	23	2593	4	9	1000	20	85	1000	20	20.0	2000	50
barley					5000	9	45	20-45	28	3960	6	26	5000	45	9.0	3000	25			
grain maize					3135	5	16	18-20	19	2880	6	16	3200			3200	25			
green pea									70	6250	7	43								
capucijner pea									74	1667	25	41				2300	27			44
dry bean									74	1667	18	29				2100	17			
field beans									16	1667	13	21				3800	38			
rapeseed									42											
caraway									37	2760	6	17								
poppy seed									20	1471	15	22								
linseed/flax									15-23	123	5	1								
cigory										2593	4	9								
hemp									23											
potatoes					1000	20	20	20-85	26				1000	20	20.0	2000	50			
- seed potatoes										3889	23	89								
- ware potatoes										2240	9	20								
- starch potatoes																				
sugar beet					4000	30	120	120	174	4845	18	87	4000	120	30.0	6300	125			
fodder beet									92											
strawberry - open field					1100	15	16	16-80	23											
<b>leaf and stem vegetables</b>																				
endive	1500	10	23	33	1500	30	45	30-80	1300	35	46	1219	34	27.9						
asparagus					800	29	23		24											
florence fennel	3000	10	30	90	3100	35	110	110												
leek	4080	12	25	102	1700	35	60	5-80	62	2420	30	73	3525	112	31.8					
celery	600	12	23	14	0	0	0	90-152												
head lettuce	500	5	36	18	600	33	20	5-41	25	770	34	26								
lettuce - iceberg	1000	5	26	26	1700	41	70	15-90	25	1990	30	60	1073	45	41.9					
spinach	500	10	40	20	700	50	35	5-60	62	720	35	25	701	34	48.5					25-60



	Feller <i>et al.</i> , 2011		De Ruijter & Smit, 2009		VLM, 2008		Velthof & Kulkman, 2000		Zwart <i>et al.</i> , 2004		Beinum & Westra, 2004		Mitchell <i>et al.</i> , 2001		Neeteson & Carton, 2001		Riley, 2002	
	Amount (kg/ha)	Dry content (%)	N content (g/kg dry)	(kg/ha)	Amount (kg/ha)	N content (g/kg dry)	(kg/ha)	Amount (kg/ha)	N content (kg/ha)	Amount (kg/ha)	N content (g/kg dry)	(kg/ha)	Amount (kg/ha)	N content (kg/ha)	Amount (kg/ha)	N content (kg/ha)	Amount (kg/ha)	N content (kg/ha)
<b>root and tuber crops</b>																		
bunch carrot	1100	11	15	17	0	0												
washed carrot	3000	12	25	75	3300	23	75	3300	25-115							25-60		
celeriac	4000	10	25	100	3500	26	90		90-120									
red beet	3000	15	17	50	2200	19	42		45									
salsify	6000	40	10	60	1000	5	5		60-100			1039	5	4.8				
onion	3200	16	19	60	3100	13	40		10-100			2886	87	30.1				
winter carrot																		
<b>cabbage crops</b>																		
cauliflower	4050	9	38	153	3500	34	120	32640	80-175			89	5000	33	165	134	38.0	80-120
kale	3750	15	23	88	3100	27	85		85-130									
broccoli	5500	10	35	193	3700	42	155		90-230				3600	33	120			
chinese cabbage	3000	6	30	90	1500	43	65		30-110				1775	33	58			
red cabbage	4900	14	21	105	5000	35	175		14-200				4500	28	125	2776	99	35.7
green cabbage	5250	15	27	140	4500	31	140		90-190									
								55600- 8600-										
Brussels sprouts	11700	18	22	260	8600	16	135	87300	15100	90-335			7500	20	150	4680	126	26.9
white cabbage	5500	11	27	150	4300	27	115		30-250				5500	21	113	4341	87	20.0
								4300								3100	89	150-250
<b>leguminous crops</b>																		
pea	4800	15	27	128	6300	30	188		30-190							6300	188	29.8
green bean	3960	18	22	88	2900	33	95		30-95									
field beans																		
								13020- 4370-										
<b>fruit vegetables</b>																		
courgette	4000	8	38	150					115-175									
<b>other vegetables</b>																		
																		86



## **Appendix IV.**

### **Field period of crop residues**

Experts<sup>1</sup> were consulted on the time crop residues remain on the field after harvest. Only crop residues with an N content higher than 12.7 g kg<sup>-1</sup> were evaluated, as below this value no ammonia volatilization occurs (see Chapter 2). The expert information was converted into a fraction of the residues that contributes to ammonia volatilization, based on incorporation into the soil and the time at the soil surface (see also Table 2.2).

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<sup>1</sup> H. Pijenburg, DLV; H. van den Akker, DLV; E. Tomassen, DLV; L. Persoon, DLV; C. den Herder, DLV; P.H. Roelfsema, Suikerunie; P.G.I.M. Koopmans, Suikerunie; I.J.M. Brouwers, Suikerunie.

Crop	Field period of crop residues	Fraction
Grain maize	A green manure crop after harvest is required, and the majority of the crop residues is incorporated.	0.1
Potatoes	Haulms are killed by herbicides, with seed potatoes sometimes preceded by flailing. Before lifting the tubers, the dead foliage is chopped by flailing. Time between haulm destruction and harvest is 2 to 4 weeks. Most dead foliage is covered by soil during tuber harvest, but dead stems remain on the soil surface.  Seed potatoes are killed by the end of July, most ware potatoes and starch potatoes by September.	0.75
Sugar beet	Derived from type of defoliator, soil tillage and soil type (see information below table)	0.27
Strawberry - open field	Foliage is directly after harvest incorporated to prevent diseases	0
Endive	See under lettuce - iceberg	
Asparagus	Foliage turns yellow and needles drop. Dead stems are mown, cut and incorporated	1.0
Leek	Residues from cleaning leek are returned to a field and remain on top of the soil for about 2 weeks (max 3-4 weeks) to allow the residues to decay and dry. Then the residues are incorporated	0.5
Head lettuce	See lettuce – iceberg. Head lettuce is mainly grown in greenhouses	
Lettuce - iceberg	After harvest, residues are partly incorporated with a disc harrow. Between 25% and 50% of the residues remain on top of the soil for 1 or 2 weeks before the field is plowed.	0.25
Spinach	About 90% of the area is tilled with days.	0.1
Bunch carrot/ washed carrot	Foliage is partly mixed with soil during harvest, and is incorporated after 10-14 days.	0.15
Salsify	As under winter carrot	
Winter carrot	Leaves are partly mixed with soil during harvest. Estimates vary between 'incorporation after 10-14 days', '75% is incorporated at harvest' and 'on clay soil, the field is plowed as soon as possible after harvest, before rainfall'	0.15
Cauliflower	See under broccoli	
Broccoli	Broccoli and cauliflower: 30 percent of the crops are grown on sand, 70 percent on clay. On sand, residues are chopped and incorporated with a disk harrow. This reduces the amount of residues on top of the soil by 50%. About half of the crop area is followed by a next crop within the same season and the soil is ploughed shortly after harvest.  On clay soil in the province of Noord Holland, residues remain on the field for a longer time. When crops are followed by another crop within the same season, the soil is plowed and residues are incorporated shortly after the entire field is harvested. It can take a number of weeks before the entire field is harvested. At harvest, part of the foliage is detached when harvesters walk through the field, another part is cut. Estimates for these residues vary between 5-10% and 67% of the total amount of residues present. The part of the residues that remains on the living plant dies in winter time.	0.60
Red cabbage	See under broccoli	
Green cabbage	See under broccoli	
Brussels sprouts	Residues remain on top of the soil for a number of weeks to decay. Plowing before winter when fields are harvested early. Most fields are harvested in winter and residues remain on the field until spring.	1.0
White cabbage	See under broccoli	
Pea	Often followed by another crop. Then, residues remain on the soil for 7-10 days	0.25
Green bean	On sand often grown after pea, and residues remain on the soil after harvest. On clay often as main crop. Of the total area, 2/3 is grown as main crop, generally followed by a green manure crop. Soil is then tilled within 2 days after harvest, sometimes later when soil is dry and rain is required.	0.33

### Sugar beet – additional information

The type of defoliator determines the amount of foliage on top of the soil after harvest. Foliage can be spread sideward on land where the beets are harvested (conventional systems), or can be placed between the beet rows (integral systems). Integral systems are increasingly used (more than 50%), and with these systems most of the foliage is covered by soil after harvest of the beets (estimates vary between 70 and 90%).

Soil tillage generally is carried out shortly after harvest. On clay and loam soil, winter wheat is often sown after harvest of the sugar beet, and plowing and sowing is done as soon as possible to avoid bad soil structure in case of rain. It is estimated that about 75% of the area is plowed within 1 or 2 weeks, incorporating all crop residues. When only a cultivator is used to loosen tracks, about 25% of the foliage is covered with soil. Fields that are loosened with a cultivator are plowed later in the year, but before the winter. The combination of type of defoliator and soil tillage after harvest gives an estimate of 10% of all foliage that remains on top of clay soil for a number of weeks.

Sandy soils generally are plowed in spring. After sugar beet harvest, about half of the growers till the soil with a cultivator or disk harrow, on average about 1 week after harvest. During tillage with a disk harrow, the majority of the foliage is covered with soil. From the combination of type of defoliators and soil tillage after harvest, it is estimated that 50% of all foliage on sandy soils remains on top of the soil for several weeks.

From the division over soil types (Table III-1), average value for the Netherlands is  $42\% \times 50\% + 58\% \times 10\% = 27\%$  of the foliage that remains on top of the soil for several weeks.

*Table III-1. Sugar beet area per soil type in 2008 (source: Dutch sugar industry; [www.bietenstatistiek.nl](http://www.bietenstatistiek.nl); accessed 01-10-2011).*

Soil type	Origin	Share (%)
Clay (25% lutum or more)	Sea clay	16
	River clay	2
Loam (less than 25% lutum)	Sea	40
	River	1
Sand		26
Peat/dalgrond'		13
Löss		3



## **Appendix V.**

### **Land use class dependent parameters within DEPAC**

In the DEPAC module with which the ammonia exchange was calculated in this study, a number of plant parameters are needed. The table below specifies the values for the plant parameters (denoted as land use) in DEPAC. The values for land use class grass are the standard/common used values except for the low and high value of  $\gamma_{\text{stom\_fac}}$ . Parameters which are equal for all land use classes (except grass) are in general set to the standard/common value for the generic land use class arable. The meaning of the various plant parameters is not given here and can be found in Van Zanten *et al.* (2010).

Land use	sgs50	dsgs	egs50	degs	laimin	lai max	s_lai_len	e_lai_len	b	h	Gamma_fac low value	Gamma_fac mid value	Gamma_fac high value	T opt	T min	T max	gmax	vpdmax	Vpd min
grass	0	0.0	366	0.0	2.0	3.5	140	135	-	-	500	2000	4000	26	12	40	270	1.3	3.0
corn	140	0.0	270	0.0	0.0	5	50	15	14	2.5	200	1500	4000	25	5	45	300	0.9	2.8
summer wheat	70	0.0	245	0.0	0.0	5	40	20	14	1	500	2000	4000	25	0	35	300	0.9	2.8
winter wheat	1	0.0	230	0.0	0.0	5	40	20	14	1	500	2000	4000	25	0	35	300	0.9	2.8
potatoes	140	0.0	265	0.0	0.0	5.5	25	40	14	0.75	500	1000	2000	18	6	30	300	0.9	2.8
beets/carrots/cole	110	0.0	285	0.0	0.0	4.5	40	40	14	0.6	500	1000	2000	20	0	35	300	0.9	2.8

#### Parameters used in calculations of LAI

sgs50	= growing season at 50 degrees latitude (days)
dsgs	= shift in start growing season (days/degree latitude)
egs50	= end growing season at 50 degrees latitude (days)
degs	= shift in end growing season (days/degree latitude),
laimin	= leaf area index at start and end of growing season (m <sup>2</sup> leaf/m <sup>2</sup> ground surface)
laimax	= maximal leaf area index (m <sup>2</sup> leaf/m <sup>2</sup> ground surface)
s_lai_len	= length of starting phase of LAI (days)
e_lai_len	= length of end phase of LAI (days)

#### Parameters used in calculation of Rc\_stom (see vanZanten *et al.* (2010) for more information of the parameters)

F_min	= minimal correction factor for Fpar; set for all land use classes in this study at 0.01
Alpha	= vegetation-specific parameter in light correction factor; set for all land use classes in this study at 0.009
Topt, Tmin, Tmax	= temperatures used in Ftemp
g_max	= maximal conductance
vpd_max	= maximum value for vapour pressure deficit vpd
vpd_min	= minimum value for vapour pressure deficit vpd



**Parameters used in calculation of R<sub>inc</sub>**

- b = empirical constant
- h = vegetation height

**Parameters used in calculation of stomatal gamma**

- gamma<sub>stom\_c\_fac</sub> = factor in linear relation between gamma<sub>stom</sub> and NH<sub>3</sub>
- gamma<sub>soil\_c\_fac</sub> = idem for soil compensation point, currently only specified for land use class water.

