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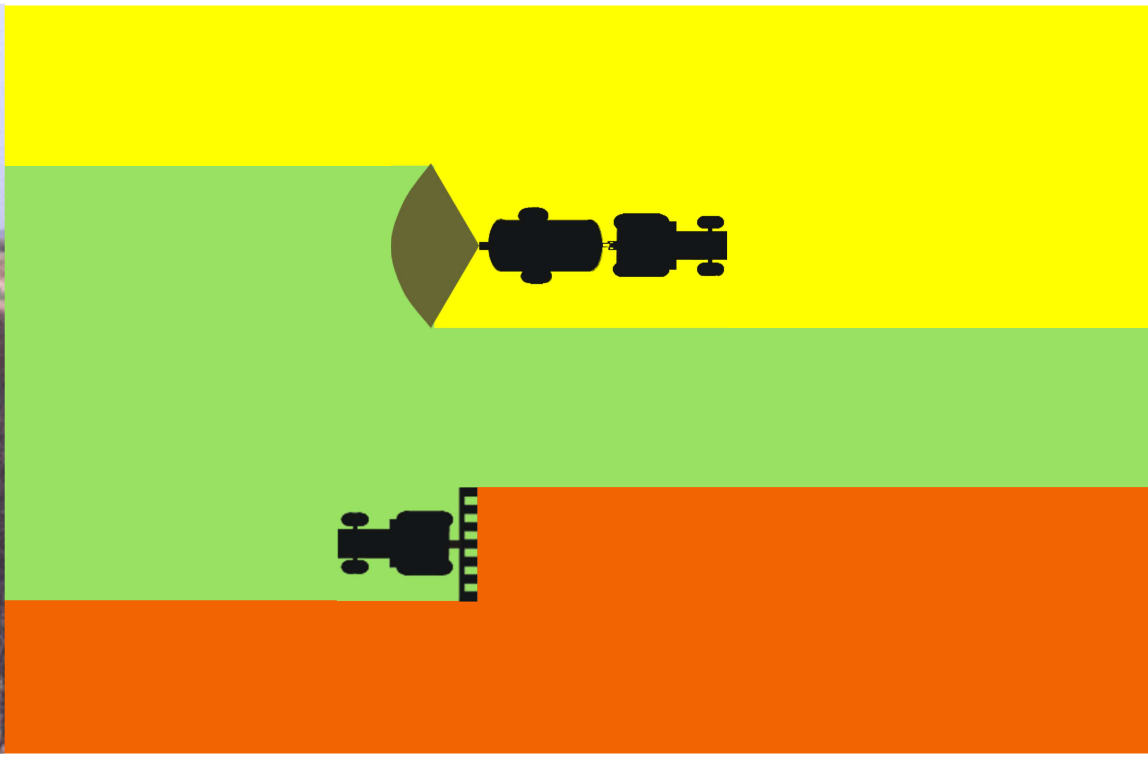

National Institute for Public Health
and the Environment
*Ministry of Health, Welfare and Sport*

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Plant Research International, part of Wageningen UR
Business Unit Agrosystems Research
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# Managementsamenvatting

Emissies van ammoniak bij toediening van dierlijke mest vormen ca. 40% van de totale ammoniakemissies in Nederland. Emissiefactoren zijn gebaseerd op de gemiddeld gemeten ammoniakemissie per toedieningsmethode onder de gemiddelde omstandigheden voor de mest, het weer, de bodem en het gewas. De variatie in de gemeten emissies is groot. Op dit moment kan deze variatie deels goed verklaard worden, maar een aanzienlijk deel ook niet. Vanuit het beleid en de praktijk wordt aangedrongen op verdere onderbouwing van de emissies, ook op regionaal- en bedrijfsniveau. Betere en gedetailleerdere informatie over welke factoren allemaal van invloed zijn op de emissie en welke factoren te beïnvloeden zijn, zou het beleid en de landbouwpraktijk handvatten bieden om de emissies beter te reguleren en te reduceren. Daarbij zouden meer dan de al bewezen invloedsfactoren gebruikt kunnen worden voor een verdere reductie van de emissie.

Op dit moment ontbreekt de informatie over het kwantitatief effect van een aantal mogelijke invloedsfactoren op de emissie en kunnen voor deze invloedsfactoren nog geen eventuele handvatten aangegeven worden.

De bronsterkte (mestgift en gehalte aan ammoniakale stikstof in de mest), de wijze van toediening van de mest, luchttemperatuur en windsnelheid zijn invloedsfactoren die aangetoond zijn via statistische analyse van de resultaten van beschikbare Nederlandse emissiemetingen. Het kwantitatieve effect van een aantal andere factoren die in theorie invloed zouden moeten hebben op de emissie kan met de gebruikte statistische modellen nog niet aangetoond worden, bijvoorbeeld omdat het effect in het complexe proces van ammoniakvervluchtiging soms wel en soms niet optreedt of omdat er te weinig waarnemingen beschikbaar zijn.

In de voorliggende studie zijn de mogelijkheden verkend voor verdere onderbouwing van invloedsfactoren op de emissie bij toediening van dierlijke mest door het gebruik van een procesmodel. In een procesmodel is de invloed van de verschillende factoren op het vervluchtigingsproces wiskundig beschreven. Mits het model de ammoniakemissie onder verschillende omstandigheden goed berekent kan het gebruikt worden voor de gewenste verdere onderbouwing van de emissies. Voor de verkenning werd gebruik gemaakt van het model Volt'air, dat voor Franse omstandigheden en onbeteelde grond ontwikkeld werd. Het model werd gebruikt voor vergelijking van het gesimuleerde en gemeten verloop van de ammoniakemissie voor typisch Nederlandse omstandigheden en bij een beperkt aantal Nederlandse veldexperimenten op bouwland.

Conclusies
- De berekende ammoniakemissie uit bovengronds toegediende mest met een typisch Nederlandse samenstelling op typisch Nederlandse grondsoorten kwam redelijk overeen met de waarden die daarvoor in Nederland gevonden worden.
- Simulaties bij verschillende bodemtypen en gemiddelde luchttemperaturen hadden het verwachte effect op de ammoniakemissie.
- Regen kort na de toediening reduceert de ammoniakemissie en dit effect werd in Volt'air gesimuleerd.
- Beperking van de ammoniakemissie door inwerken van de mest werd gesimuleerd; de simulaties gaven aan dat ammonium nog maar weinig bijdraagt aan de emissiesnelheid zodra deze in de grond zit.
- De eerste simulaties met verschillende mestsamenstellingen, grondsoorten en weersomstandigheden laten zien dat de afname in emissie direct na uitrijden van de mest niet goed overeenstemt met gegevens uit veldmetingen; de gesimuleerde emissiesnelheid is aanzienlijk hoger dan de gemeten snelheid.

Aanbevelingen
De eerste resultaten zijn positief, maar voor een goed gebruik en beter inzicht op de bruikbaarheid en functionaliteit voor Nederland zullen nog een aantal stappen gezet moeten worden:
- Uitbreiding met simulaties van meer experimenten om beter zicht te krijgen op het voorspelde effect van nog niet geteste invloedsfactoren zoals mestgift, ammoniumgehalte van de mest, en windsnelheid.
- Verbetering van de simulatie van de emissiesnelheid direct na uitrijden. Hiertoe zal naar verwachting basisonderzoek nodig zijn voor de modellering van het emissieproces aan het oppervlak grond en mest.

- Het effect van onderwerken van de mest wordt gesimuleerd door invoer van het percentage van het oppervlak waarop mest direct is blootgesteld aan de lucht. Deze parameter wordt vastgesteld op basis van visuele beoordeling. Dit is een erg ruwe wijze om een dergelijke belangrijke parameter in te schatten. Het wordt daarom aanbevolen om dit aspect beter te kwantificeren.
- Verdere ontwikkeling van het Volt'air model voor toepassingen bij mesttoediening op grasland.

# Abstract

The high variability of the total ammonia emission after manure application on agricultural land in the Netherlands can partly be linked to the application method, slurry characteristics and the meteorological conditions by statistical analysis of experimental results. Mechanistic models may improve the explanation of the high variability and better reveal the role of certain factors in the volatilization process provided that the simulated results agree well with field results. The performance of the French model Volt'air for simulation of $NH_3$ volatilization from field-applied manure was explored for the conditions of manure, soil, weather that occurred in a number of Dutch field experiments. First results showed that the simulated ammonia emission after surface spreading on bare soil agreed reasonably well with measured values in some field experiments. Simulated trends in effects of soil type, incorporation of the manure, air temperature, rain after application on the total emission were generally as expected from the field experiments, but very high initial $NH_3$ fluxes were simulated compared with measured values. Further development of the model and analysis of the effect of various factors on the emission is recommended to improve the fit of simulated and measured emissions.

# 1. Introduction

## 1.1 Background

The storage, handling and use of livestock manure and fertilizers on the farm and in agricultural fields are associated with the emission of ammonia ($NH_3$) and other gases. $NH_3$ emissions have a negative impact on the environment. To protect the environment, the European Union has adopted several directives, such as the National Emission Ceilings (NEC) directive (EC, 2001), prescribing national emission ceilings for $NH_3$.
For the national emission registration in the Netherlands the emission from the various sources are calculated and added up to lead to the total national emissions. The $NH_3$ emission from each source is described by an emission factor (EF). For manures, EF is defined as the amount of total ammoniacal nitrogen (TAN) lost by volatilization in % of the total TAN in the manure. The EF associated with the volatilization of ammonia after field application of manure is derived from field experiments with liquid manures in which different manure application techniques and methods were analysed under various field and weather conditions (Huijsmans & Schils, 2009). The actual $NH_3$ volatilization rate after liquid manure application is mainly determined by the application method, by the TAN applied (TAN content and manure application rate) and by meteorological conditions, such as wind speed and air temperature (Huijsmans *et al.*, 2001 & 2003). For the purpose of scaling up of the emission to the national level, the average EF's and the experimental conditions were considered representative for the conditions in practise in the Netherlands because all $NH_3$ emission experiments were carried out during the manure application periods, using manure as available.
However, for other purposes more detailed ammonia emissions for various circumstances may be required, for instance when further underpinning of the national EF would be required or for assessment of emissions at regional or farm scale. For this purpose a statistical model, based on a large number of field experiments is available for grassland (Huijsmans *et al.*, 2001) and for arable land (Huijsmans *et al.*, 2003). However, a number of factors that may effect the ammonia emission could not be identified as statistically significant with the straightforward statistical analysis of the available data at the time. It is commonly felt that a mechanistic model for the ammonia emission after field application of manure has the potential to further improve the understanding of the ammonia emission process and its determining factors. As such it can be used along with the statistical analysis of the field data. Moreover it can be used for the estimation of the ammonia emission for environmental conditions under which no measurements exist up till now and as a screening tool for emission reduction measures.
The present study comprises a brief review of the state of the art of mechanistic modelling and a first assessment of the performance of one of the mechanistic models for conditions of manure, soil and weather met in the Netherlands.

## 1.2 Mechanistic models to describe the ammonia volatilization process after field application

A concise description of the processes involved in the volatilization of ammonia after field-application of manure and the models employed to simulate these processes is given by Garcia *et al.* (2011). The physical processes involved in the volatilization of chemical compounds from animal manures applied on agricultural soils are numerous. Amongst them, heat and water transfers occurring at the soil surface are very important when considering the intense, short-term gaseous emissions such as observed after liquid manure application. The soil surface can be understood as the interface between the soil and the atmosphere. To account for soil surface as an interface, the soil layer under consideration must be as thin as possible. This thin layer is the "very place" where processes modifying the physical and chemical properties of the applied manure will affect the quantities emitted in gaseous form. To accurately account for the physical state and its evolution, models aiming at simulating gaseous emissions must be able to calculate the transfers from and to this surface layer at an appropriate time-step.

Within this framework, models specifically aiming at simulating gaseous emissions from agricultural soils focus on the physical, chemical and biological processes affecting a given compound. Time-steps used for the energy and water budgets usually vary from an hourly base (DNDC model by Li, 2000) to a daily one (CERES model by Gabrielle *et al.*, 1995 and STICS model by Brisson *et al.*, 2003). The discretization of the soil profile also varies from a single reservoir (DNDC) to several homogeneous layers (CERES and STICS). The surface layer is typically 10 to 20 cm thick. However, more detailed studies have shown that using a thinner surface layer improves the simulated emissions (Rolland *et al.*, 2008).

Transfer models, like Soil Vegetation Atmosphere Transfer (SVAT) models, have been developed to describe the current understanding of the physical and biophysical processes that occur between the atmosphere, vegetation and soil. They describe the physical processes that control energy and mass transfers in the soil-vegetation-atmosphere continuum (radiative, turbulent and water transfers) and provide estimates of the time course of soil and vegetation state variables with a fine time step compatible with the dynamics of atmospheric processes. In these SVAT models, the calculations of the energy budget, along with heat and water transfers, are much more refined than in models considering thick surface layers: the resolutions in terms of both the time-steps (typically in seconds) and the soil profiles (typically a few millimeters) are smaller.

Volatilization modeling is devoted to give answers to macroscopic agronomical challenges, but as volatilization is a surface process, volatilization models have to be able to consider the interactions between the micrometeorological conditions and the soil properties at fine enough spatial and temporal scales. Several mechanistic volatilization models have been built for ammonia volatilization after slurry application, a.o. by Van der Molen *et al.* (1990), Wu *et al.* (2003), Génermont and Cellier (1997; Volt'Air model), Sommer and Olesen (2000) and Beuning *et al.* (2008; AGRIN model). They were developed so as to find a middle road between the two types of models presented above, the agronomic ones and the SVAT ones. The main common purpose of these mechanistic volatilization models is to numerically determine the quantities and the dynamics of an applied chemical compound emitted in its gaseous form from the soil surface to the atmosphere. Following a more or less mechanistic approach, they all simulate the physical and chemical equilibriums of a given compound, as well as the energy budget of the soil surface, the transfers of heat, water, and solutes within the soil profile, in addition to the gaseous transfers between the soil and the lower atmosphere. They all are based on very classic soil heat and transfer models. Compared to SVAT models, a limited number of soil layers describe the soil near the surface (2 to 6) and their transfer models lie on simplifying assumptions: (i) vapour fluxes are ignored, (ii) heat and water fluxes are not coupled and (iii) soil hydraulic properties in the dry region are characterized by an extrapolation of analytic functions determined for the humid region. The processes controlling ammonia emission from field-applied livestock slurry were reviewed and their relative importance assessed by Sommer *et al.* (2003).

In the present study the Volt'air model as described by Génermont and Cellier (1997) was chosen for evaluation under conditions in the Netherlands because it is: 1) a mechanistic model which has been successfully used to explain measured differences in the ammonia volatilization in field experiments in France, 2) has well defined input of the characteristics of soil, manure, weather and application methods; 3) has been under continuous improvement since its inception (Garcia *et al.*, 2012) and 4) the software was made available by INRA (Institut National de la Recherche Agronomique) for evaluation of the performance for the conditions met in the Netherlands.

# 2. Description of the Volt'air model

## 2.1 Modelling of the ammonia volatilization process

The Volt'air model was described in detail by Genermont and Cellier (1997). The model is developed to simulate the volatilization of gases from bare agricultural soils, amongst others ammonia from surface applied or incorporated manure. The model deals with the chemical and physical equilibria between the various species of ammoniacal nitrogen (N) in the soil, the transfer of heat, water and ammoniacal N within the soil, and the transfer of ammonia, heat and evaporation between the topsoil and the lower atmosphere. These processes are simulated with short time intervals over several days, or several weeks following a slurry application in the field. The main components of the model, including the compartments and their inter-relationships are shown in Figure 1. The model is composed of six sub models. Three of them deal with ammoniacal N transfers and equilibria between ammoniacal N species:

1. physical and chemical equilibria in the soil,
2. aqueous and gaseous ammoniacal N transfers through the soil,
3. gaseous ammonia transfer from the soil to the atmosphere.

The other three simulate heat and water transfer in the soil:

4. water transfer in the soil,
5. heat transfer in the soil,
6. energy budget, water and heat exchange between the soil and the atmosphere.

The last three sub models are necessary because ammonia is transported with water in the soil, and the equilibria depend on the temperature and concentration in the soil water. Sub models (1), (2), (3) and (4) are the basis of the model: research applications may use a reduced model with only these four sub models when the required micrometeorological data such as soil surface temperature and evaporation have been directly measured. Sub models (5) and (6) make the model easier to operate because they allow calculation of several of these micrometeorological data, such as soil surface temperature and evaporation, from readily available meteorological data and surface descriptions.

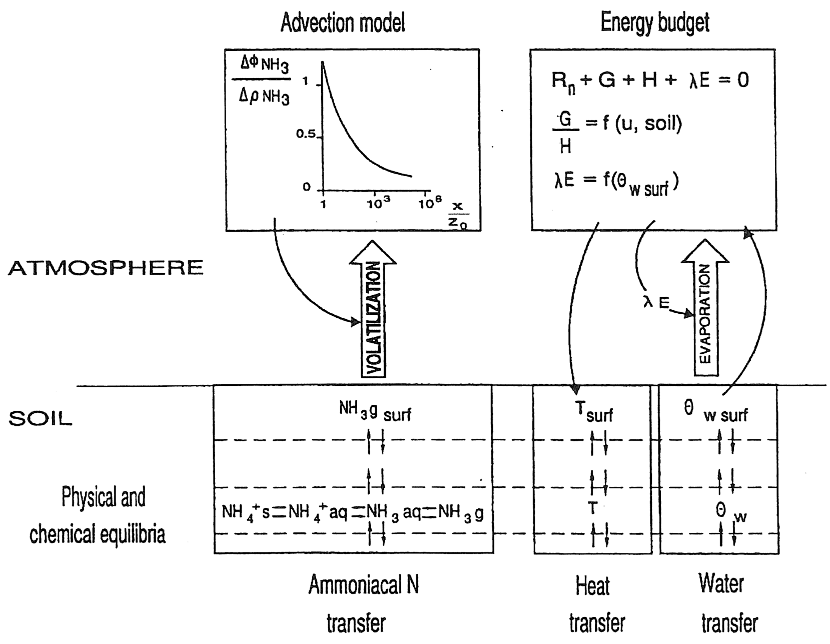



*Figure 1. Diagram of the Volt'air volatilization model (Genermont and Cellier,1997).*

The physical and chemical properties within each soil layer are considered to be uniform. The physical properties of the soil do not change with time after the slurry has been spread. The model assumes that urea is completely hydrolysed at slurry application, as urea is converted to ammoniacal N and carbonate within a few hours after excretion (Pakrou and Dillon, 1995). As ammonia volatilization is simulated over a relatively short time (up to 3 weeks), nitrogen transformations by organic matter mineralization, ammoniacal N uptake by plants, oxidation or nitrification are not accounted for. The mineralization of the organic N from the slurry is also considered to be negligible over the volatilization period. Time and space have been discretized so as to provide a good compromise between computing time and model precision. Basically, the upper 1 m of the soil is subdivided into several layers with depths: 2, 5, 10, 20, 50 and 100 cm. However, they can be changed to any depth progression. Garcia *et al.* (2012) improved the simulation of the volatilization process of manure at the soil surface by introducing a layer of manure on top of the soil, with known pH and concentrations of ammonia N species, with a total thickness depending on the slurry application rate and with water transport characteristics measured and described as for the soil layers. The time step must be large enough to allow the physical and chemical equilibria to be established, but short enough to describe the rapid changes in surface fluxes, surface temperature and water transfer in the soil. Génermont and Cellier (1997) used a time step of 15 minutes.

*Physical and chemical equilibria in each soil layer*

Several assumptions about chemical equilibria are made. It is assumed that the aqueous solutions behave like ideal solutions. Therefore theoretical values for ideal aqueous solutions are used to describe the equilibria for slurry, although it is a complex solution of various ionic species. Equilibria between the various forms of ammoniacal N are considered to develop instantaneous, as determined by temperature and pH of the solution. Two equilibria are modelled: the ionization of ammonia in water as $NH_4^+$ and the equilibrium between gaseous and aqueous $NH_3$. A third equilibrium develops in the soil as ammonium ions are absorbed by clay minerals and soil organic matter. However, binding is assumed not to occur within the time interval of several days to a few weeks.

*Water transfers between the soil layers*

Water fluxes between the centres of the soil layers are calculated using Darcy's law, generalized for the unsaturated zone. The fluxes are simulated using the initial water content and the hydraulic properties of the various soil layers, including the manure layer on top of the soil. The hydraulic properties of the soil layers are estimated using either the Clapp and Hornberger (1978) or the Van Genuchten–Mualem (Van Genuchten, 1980) functions. These functions relate the pressure head and the hydraulic conductivity to the soil water content. The parameters of these functions are estimated on the basis of the soil texture. Alternatively, the hydraulic properties may be directly supplied as user defined input of the parameters for the Van Genuchten functions.

*Heat transfers between the soil layers*

Heat fluxes between the centres of the soil layers are calculated using estimated parameters for the thermal conductivity and the volumetric heat capacity of the soil. Interactions between heat and water flow are not taken into account.

*Aqueous and gaseous ammoniacal N transfers between the soil layers*

The transfer of aqueous ammoniacal N in a porous medium is calculated using the classical convection-diffusion scheme and the transfer of ammonia gas is governed by diffusion only.

*Transfer of ammonia gas to the atmosphere*

Having the concentration of ammonia gas at the surface of the field, the transfer to the atmosphere is then calculated by the local advection analytical solution proposed by Itier and Perrier (1976). This scheme rests on the assumption that the volatilization flux is a function of the distance from the leading edge in the direction of the predominant wind.

*Energy budget, water and heat exchange between the soil and the atmosphere*

Heat and water vapour exchanges at the soil surface and surface temperature are calculated using the energy budget equation for a bare soil surface (Eq. 1):

$$Rn - G = H + LE \qquad \text{Eq. 1}$$

where Rn is the net radiation of the surface, G the soil heat flux, H the sensible heat flux and LE the latent heat flux or evaporation, all the fluxes being expressed in W/m². The fluxes are calculated with parameterizations that use standard meteorological data and easily available soil parameters.

## 2.2 Input parameters

The input parameters of the Volt'air model are supplied in 7 input files:
- 2 files with principally meteorological data that vary during the simulation period and are supplied for each time step in the simulation and
- 5 files with data that are constant during the simulation, i.e. characteristics of the soil, the manure, the location, general information and physical and chemical coefficients.

*Essential variable data on meteorological conditions*

The principal meteorological data per time step is provided in a file (.CSV) with 6 columns (A – F):
A: time (decimal day number since 1 January 0:00, three decimals),
B: mean air temperature (°C),
C: mean vapour pressure at saturation according to Tetens (kPa),
D: mean global radiation (W/m²),
E: mean wind speed (m/s),
F: sum of rainfall (mm).

The data start at a time before or at the starting time of the simulation and ends at the end of the simulation or later. The time values in these files should match exactly with the times of the start of simulation, the application of manure, the (optional) incorporation of the manure and the start time given in the other input files.

*Optional variable data*

While the data in the meteo file are essential to run the model, optional parameters may be supplied for when measurements are available. If not available these parameters are assumed to be fixed, default values or estimated from the essential meteo input. A value 'NR' is provided in the data file whenever measured data are not available. The optional variable data per time step is supplied in a file with 13 columns (A - K):
A: time (decimal day number since 1 January 0:00, three decimals),
B: mean wind direction (degree; North = 0 or 360),
C: field length (in direction of the wind) (m),
D: (measured) mean net incoming radiation (W/m²),
E: (measured) heat flux by conduction into the soil (W/m²),
F: (measured) mean sensible heat flux to the atmosphere (W/m²),
G: (measured) energy use for soil evaporation (W/m²),
H: (measured) temperature of the soil surface (°C),
I: (measured) reflected global radiation (W/m²),
J: (measured or modelled) upwind ammonia concentration in the air (µg/m³),
K: (measured or modelled) upwind ammonia volatilization flux (µg/m²s).

*Soil parameters*

The hydraulic characteristics of the soil may be derived from the texture of the soil using the estimates of the parameters of the pedo-transfer functions of Clapp and Hornberger (1978) or Van Genuchten-Mualem (Van Genuchten, 1980) available in the Volt'air model. These parameter estimates may be considered as best estimates for the common soil types in France. Alternatively, the parameters for the Van Genuchten-Mualem pedo-transfer functions (VG parameters) of the soil may be supplied directly, when better estimates of the parameters are available for the soil under study. All soil information is given in an input file with 17 columns (A – Q) and one line for each soil layer. The selected estimation method is given in the general input file. The directly supplied VG parameters are those in the columns M till Q:

A: (largest) depth of the soil layer (m); progressive depth layers suggested: 0.02, 0.05, 0.1, 0.25, 0.5 and 1.0 m,
B: clay content (g/kg dry soil),
C: silt content (g/kg dry soil),
D: sand content (g/kg dry soil),
E: initial gravimetric water content (g/kg dry soil),
F: soil pH,
G: organic carbon content (g/kg dry soil); (is about 0.5 x the organic matter content),
H: initial $NH_4^+$ content (mg/kg dry soil); (TAN),
I: initial $NO_3^-$ content (mg/kg dry soil),
J: cation exchange capacity measured according to Metson (cmol/kg); (CEC),
K: cation exchange capacity (cmol/kg); cobaltihexamine extraction (CEC),
L: bulk density (kg/m$^3$), field measurement,
M: volumetric soil water content at saturation (m$^3$/m$^3$),
N: residual volumetric soil water content (m$^3$/m$^3$),
O: constant alpha (m$^1$),
P: constant n,
Q: saturated hydraulic conductivity (m/s).

*Data on manure and application method*

The input data for the manure characteristics and optional tillage operations to incorporate the manure in the soil are given in a text file with one line per input value (Table 1). The number of lines depends on the options selected.

*Location coordinates of the field*

Input data on the location of the field are given in a file with two columns. Probably the degree of longitude and the degree of latitude of points on the circumference of the field can be given in this file, but in the present study no data (value NR) were used.

*General data*

The required general data pertain to the time step and period of simulation, options that determine the method of calculation by Volt'air and other general information. The general data are given in a text file with one line per data value. The following data are provided:

- start time of calculation (decimal day number),
- end time of calculation (decimal day number),
- time step (h),
- emission situation (P = in open field).

*Table 1. Volt'air input data on manure and application method.*

| Input data | Comments |
|---|---|
| Type of application | 0 = no application; 1 = manure |
| Number of tillage operations (after application) | Range 0 - 5 |
| *Optional lines for each tillage operation:* | |
| Time of tillage (decimal day) | |
| Type of tillage (not implemented, fixed value of 1) | |
| Depth of cultivation (m) | |
| Fraction of the manure incorporated in the soil | Visual assessment: 0 = none; 1 = all |
| Number of irrigations | |
| *Optional lines for each irrigation:* | |
| Time of irrigation (decimal calendar day) | |
| Water quantity applied (mm) | |
| Type of manure | 10 = slurry |
| Time of application (decimal calendar day) | |
| Amount of slurry applied ($m^3$ fresh slurry per ha) | When not available: slurry density ≈ 1000 kg/$m^3$ |
| Application method | 0 = broadcasted; 1 = in bands |
| *Optional line when application = in bands:* | |
| Fraction of the soil covered by slurry | When 'NR', default = 0.33 |
| Type of modelling of the slurry layer | 0 = applied within upper soil layer<br>1 = 1 layer of slurry on top of the soil<br>2 = 2 layers of slurry on top of the soil |
| Dry matter content of the slurry (g/kg fresh matter) | Not directly used in the model |
| Total nitrogen content (g/kg fresh matter) | |
| Total ammoniacal nitrogen content (g/kg fresh matter) | |
| Total Nitrate nitrogen (g/kg fresh matter) | If available, otherwise NR |
| Slurry pH | Required |
| Slurry CEC (cmol/kg dry matter) | If available, otherwise NR |
| Slurry density (kg/$m^3$) | When unavailable: slurry density ≈ 1000 |
| Bulk density of the slurry dry matter (kg/$m^3$) | When unavailable: slurry dm density ≈ 300 |
| Critical application rate for uniform application ($m^3$/ha) | When unavailable: 60 |
| *Optional line for Clapp-Hornberger soil water modelling:* | As selected in input file 'General data' |
| Correction factor for water infiltration in upper soil layer | (range 0 – 1) |
| *Optional lines for Van Genugten-Mualem soil water modelling and # 1 or 2 modelling of the slurry layer on top of the soil:* | As supplied in input file 'General data'<br>Default values (Garcia *et al.*, 2012): |
| VG parameter for the slurry: theta sat ($m^3/m^3$) | 0.996 |
| VG parameter for the slurry: theta res ($m^3/m^3$) | 0.373 |
| VG parameter for the slurry: alpha ($m^{-1}$) | 3.6 |
| VG parameter for the slurry: n (-) | 1.361 |
| VG parameter for the slurry: Ksat (m/s) | 8.34E-08 |

- choice of calculation of field length (OUI = calculation using the GPS coordinates supplied in location coordinates file and wind direction supplied in the optional meteo data file; NON = calculation using the field length as supplied in the optional variable data file).
- type of radiation used in energy budget calculations (G = global radiation, N = nett radiation, X = when energy budget calculation are not activated).

- Number of soil layers (1 - 10), as defined in soil parameter file.
- Estimation method for hydraulic characteristics of the soil (CH = Clapp&Hornberger; VG = Van Genuchten-Mualem).
- In case of CH:
  soil type (1 - 11), according to soil texture triangle of Clapp & Hornberger
- In case of VG:
  Estimation method for VG parameters (0 = automatic calculation by Volt'air using soil texture information; 1 = VG parameters defined by user)
- Longitude (degree)
- Reflected fraction of the incoming radiation (albedo) (0...1)
- Roughness length z0 (m), measured or estimated (for flat, bare soil: z0 = 0.01 m)
- Measurement height of air temperature (m)
- Measurement height of air humidity (m)
- Measurement height of wind speed (m)

*Physical-chemical data*

For the calculation of physical-chemical equilibria and transfers by diffusion, data are provided in a text file. The input for calculation of ammonia emission is:
- Diffusion coefficient of $NH_3$ in air ($m^2/s$)
- Diffusion coefficient of $NH_3$ in water ($m^2/s$ * 1010)
- One line with three data for each soluted type of N:
  Diffusion coefficient in water ($m^2/s$), molaire conductivity ($S/m^2$), ion charge.

## 2.3 Output

The output file concerning ammonia emission contains the results of the calculations of the fate of ammoniacal N after application of slurry. The following is listed for each time step:
Time (decimal day), $NH_3$ volatilization flux ($\mu g/m^2s$), cumulative losses of total and ammoniacal N (kg/ha), contents of ammoniacal N, nitrate N and urea N for each soil layer and for the total soil profile.

Other output files include those with output of the terms of the energy budget, the soil moisture situation and the pH of the soil, which can be used to check the correctness of the simulation of processes in and on the soil that determine the ammonia volatilization.

# 3. Using Volt'air for manure application on arable land in the Netherlands

The first series of runs with Volt'air were performed to get familiar with the input and output. Remarks and uncertainties on the use of the model are not reported here, but were listed to be communicated at a later stage with the builders of the model. The second series of runs was made to get a first impression of the ammonia emissions calculated by Volt'air for French conditions, application conditions for the Netherlands and the response for different soil types and temperatures (Section 3.1). A third series of runs was performed to compare the measured emissions in ten field experiments, carried out in the Netherlands, with the emissions simulated by Volt'air, using input parameters that describe the experimental conditions of manure, soil and weather as close to reality as possible (Section 3.2). Finally the effects of field length and the application of the available 2 layer slurry model on the simulated ammonia volatilization was assessed by running a limited number of simulations (Sections 3.3 and 3.4).

## 3.1 Simulations for typical manures, soils and temperatures in the Netherlands

The Volt'air model was supplied as used by Garcia *et al.* (2012), with a French volatilization dataset as an example. This dataset was previously used and thoroughly described by Génermont and Cellier (1997) and Garcia (2010). The dataset was generated in a study with dairy cattle slurry applied on March16th 1994 (Day Of Year (DOY) 75) at the INRA experimental station of Le Rheu, west of Rennes (France). A rate of 133 $m^3$/ha was applied on a 1.7 ha field in an approximately 8 hour time-span. The slurry had a low dry matter content (47 g/kg fresh matter), a low total ammoniacal nitrogen (TAN) content (0.86 g/kg fresh matter) and a pH of 7.12. The slurry was spread on a silt loam soil (USDA soil classification). The ammonia volatilization fluxes were measured over 15 days (until DOY 90) using micrometeorological methods. The mean air temperature in this period was about 10 °C and the wind speed 3 m/s. The components of the energy budget, along with surface state, air temperature, wind speed and precipitation rate were also directly measured, except for the latent heat flux which was estimated as the residual term of the energy budget. Measurements of the incident and reflected global radiation provided the albedos of the bare soil surface and of the slurry-covered surface.
The parameter estimates for the van Genuchten-Mualem water retention and hydraulic conductivity models (($\theta sat$, θr, α, n and Ksat), that are provided by the Volt'air model when soil texture input is chosen, are based on the pedo-transfer functions for French types of soils as provided by Bruand *et al.* (2002).

The conditions for manure application in the Rennes experiment in France, for which the model has been tested, and the mean conditions in the Netherlands seemed to be rather different in terms of the application rate and the TAN content of the manure. Also, the hydraulic characteristics of the mostly clayey and sandy soils in the Netherlands may differ from those in France, where many soils are loamy in nature. Finally, the air temperature after application is known to be an important factor for the emission found in the Netherlands. Therefore, it was decided to first assess the effects of changing the input parameters for slurry, soil and air temperature in the example dataset from the experiment in France on the simulated emission of the ammonia by the Volt'air model . The emission in the experiments in the Netherlands is always measured during a period of about 96 hours after manure application because after this period the ammonia flux to the atmosphere has usually decreased to a very low, neglectable level. To study the behaviour of the emission simulated by Volt'air after the 96 hours period, the simulation period in Volt'air was set to 10 days for these first simulations.

*Slurry parameters*

The manure parameters supplied with the model (Table 1) were indicated as the French experimental case, although they were not necessarily representative for France. As Volt'air was extensively tested with these slurry parameters it was assumed that the Volt'air calculations were close to reality for this slurry parameter set. For the Netherlands,

the mean slurry parameters of the ammonia emission experiments on arable land of Huijsmans *et al.* (2003) were used. These slurry parameters may be assumed to be representative for the Netherlands, being the mean of many field experiments (Table 2).
For the series of simulations for some typical application conditions of the Netherlands, only broadcast spreading was selected as application method, as was done in the French experiment. The one slurry-layer system and the VG parameters for slurry, as reported by Garcia *et al.* (2012), were selected for modelling the slurry layer.

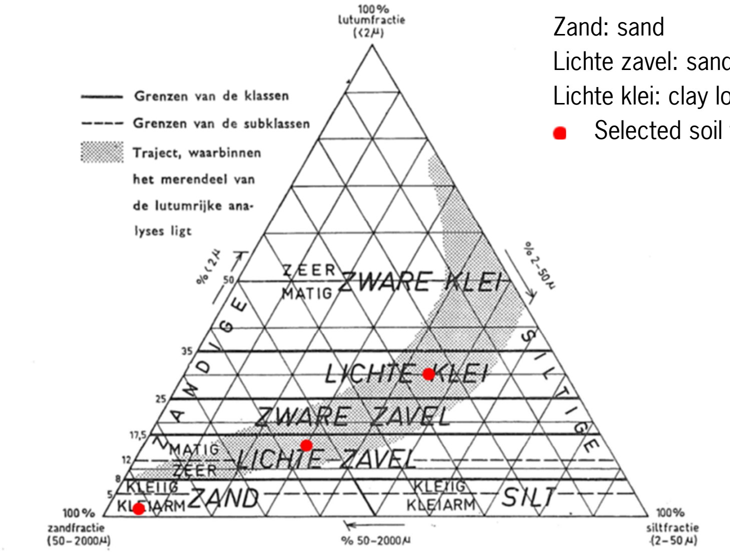
*Table 2. Input parameters used for slurry.*

| Manure parameter | French cattle slurry example | Dutch pig slurry | Remark |
|---|---|---|---|
| Type of application | 1 | 1 | organic N fertilizer |
| Number of tillage operations (after application) | 0 | 0 | |
| Number of irrigations | 0 | 0 | |
| N application; Type of fertilizer | 10 | 10 | slurry surface applied |
| Time of application (decimal calendar day) | 75.375 | 75.375 | |
| Amount of slurry applied ($m^3$ fresh slurry per ha) | 133 | 22 | |
| Application method | 0 | 0 | not in bands |
| Type of modelling of the slurry layer | 1 | 1 | 1 layer |
| Dry matter content of the slurry (g/kg fresh matter) | 47 | 80 | |
| Total nitrogen content (g/kg fresh matter) | 3 | 8 | |
| Total ammoniacal nitrogen content (g/kg fresh matter) | 0.86 | 4.4 | |
| Total Nitrate nitrogen (g/kg fresh matter) | NR | NR | n.a. |
| Slurry pH | 7.12 | 7.12 | |
| Slurry CEC (cmol/kg dry matter) | NR | NR | n.a. |
| Slurry density ($kg/m^3$) | 1000 | 1000 | |
| Bulk density of the slurry dry matter ($kg/m^3$) | 300 | 300 | |
| Critical application rate for uniform application ($m^3$/ha) | 10 | 10 | |
| theta sat ($m^3/m^3$) | 0.996 | 0.996 | VG parameters for |
| theta res ($m^3/m^3$) | 0.373 | 0.373 | slurry |
| alpha ($m^{-1}$) | 3.6 | 3.6 | |
| n (-) | 1.361 | 1.361 | |
| Ksat (m/s) | 8.34E-08 | 8.34E-08 | |

*Soil parameters*

In all simulations, the 6 layer soil profile used by Garcia *et al.* (2012) was selected. Three soil textures were selected that may be considered representative for the range of soils in the Netherlands (Figure 2): a sandy, a sandy loam and a clay loam soil.
Within the soil profile a differentiation in soil bulk density and initial water content was made for the topsoil (0 - 25 cm depth) and the subsoil (> 25 cm depth). The Van Genuchten equations were used to describe the hydraulic characteristics of these soils by selecting the VG estimation method in the general data input file. As French and Dutch soils with comparable clay content may have very different hydraulic properties due to for instance differences in clay type (swelling and shrinking) and silt content, two approaches to estimate the VG parameters were used.
The French approach was using the parameter estimations of Bruand *et al.* (2002) that were build-in in the Volt'air model. These parameters were selected by choosing estimation method 0 in the general data input file. The approach for the Netherlands was using the parameter estimations of Wösten *et al.* (2001), adapted for typical physical conditions of bare-soil (compared with grassland) as met during slurry application on arable land in the Netherlands. These parameters were selected by choosing estimation method 1 in the general data input file. It was

assumed that the soil was at field capacity (soil water matric potential of -10 kPa) during the start of the simulations. The soil data actually used in Volt'air for the various simulation runs is presented in Table 3.




Zand: sand
Lichte zavel: sandy loam
Lichte klei: clay loam
● Selected soil textures

*Figure 2. Selected soil textures representing the range of soil textures in the Netherlands.*

*Table 3. Soil types, soil composition, estimations of VG parameters and other parameters used in the simulations.*

<table>
<tr><th></th><th colspan="2">Sand</th><th colspan="2">Sandy loam</th><th colspan="2">Clay loam</th></tr>
<tr><td>Clay content (< 2 μm; g/kg)</td><td colspan="2">20</td><td colspan="2">150</td><td colspan="2">300</td></tr>
<tr><td>Silt content (2 - 50 μm; g/kg)</td><td colspan="2">50</td><td colspan="2">300</td><td colspan="2">450</td></tr>
<tr><td>Sand content (50 - 2000 μm; g/kg)</td><td colspan="2">930</td><td colspan="2">550</td><td colspan="2">250</td></tr>
<tr><td>$CaCO_3$ content (g/kg)</td><td colspan="2">20</td><td colspan="2">50</td><td colspan="2">50</td></tr>
<tr><td>pH</td><td colspan="2">6.0</td><td colspan="2">7.0</td><td colspan="2">7.0</td></tr>
<tr><td>Organic matter (g/kg)</td><td colspan="2">20</td><td colspan="2">20</td><td colspan="2">20</td></tr>
<tr><td>Organic carbon (g/kg)</td><td colspan="2">10</td><td colspan="2">10</td><td colspan="2">10</td></tr>
<tr><td>CEC</td><td colspan="2">70</td><td colspan="2">120</td><td colspan="2">180</td></tr>
<tr><td></td><td>topsoil</td><td>subsoil</td><td>topsoil</td><td>subsoil</td><td>topsoil</td><td>subsoil</td></tr>
<tr><td>Soil type indication by Wösten et al. (2001)</td><td>B1</td><td>O1</td><td>B8</td><td>O9</td><td>B10</td><td>O11</td></tr>
</table>

*Air temperature*

The air temperature after the application of slurry is provided per time step in the input file with essential meteorological data. The mean air temperature in the 10-days example input-file for meteorological data, based on the study in Rennes in 1994, was about 10 °C. To test the effect of air temperature, including the day-night variations, on the simulated ammonia emissions, all air-temperatures in the example input-file were raised by 5 and 10 degrees, to realize mean air temperatures of 15 °C and 20 °C, respectively. The typical mean air temperature after slurry application on arable land is 14 °C in the Netherlands (Huijsmans *et al.*, 2003).

*Results*

The total ammonia emission, simulated in Volt'air for the French and Dutch slurries, for the three soil textures considered representative for the Netherlands with the hydraulic properties estimated with the French and Dutch approach respectively and for mean air temperatures of 10, 15 and 20 °C are presented in Tables 4 and 5.

*Table 4. Cumulative (total) ammonia volatilization (% of TAN applied) 10 days after application for typically Dutch slurry, as compared to the French example slurry, on the three reference soils using French and Dutch parameterization of the Van Genuchten functions for the hydraulic properties of the soil, and for a mean air temperature after slurry application of 15 °C.*

| Slurry type | Soil parameterization | Sand | Sandy loam | Clay loam |
|---|---|---|---|---|
| French example cattle slurry. Application rate 133 $m^3$/ha; TAN content 0.86 g/kg; TAN application rate 114 kg/ha | VG, France (Bruand *et al.*, 2002) | 71 | 74 | 72 |
| | VG, Netherlands (adapted from Wösten *et al.* (2001) | 76 | 62 | 63 |
| Typically Dutch pig slurry Application rate 22 $m^3$/ha; TAN content 4,4 g/kg; TAN application rate 96 kg/ha | VG, France (Bruand *et al.*, 2002) | 82 | 92 | 89 |
| | VG, Netherlands (adapted from Wösten *et al.* (2001) | 83 | 80 | 80 |

The simulated total ammonia emission for typically Dutch slurry appeared to be higher than for the French slurry example (Table 4), which was more diluted, but applied at a much higher rate (Table 2). The TAN application rate was about the same.
Soil texture had little effect on the total ammonia emission when using the combination of French soil parameterization and French slurry and the combination of Dutch soil parameterization and Dutch slurry. Compared with the French soil parameterization, the Dutch parameterization tended to result in somewhat increased emissions for sand and in reduced emissions for sandy loam and clay loam. The relatively small and complex effects of soil type, physical soil condition and soil parameterization would agree well with the fact that soil type had no statistically significant effect on the ammonia emssion measured in field experiments in the Netherlands on arable land (Huijsmans *et al.*, 2003).

*Table 5. Cumulative ammonia volatilization (% of TAN applied) for mean air temperatures of 10, 15 and 20 °C in the 10 days period after application for a typically Dutch slurry on the three reference soils, using Dutch parameterization of the Van Genuchten functions for the hydraulic properties.*

| Mean air temperature after applicaton (°C) | Sand | Sandy loam | Clay loam | Mean |
|---|---|---|---|---|
| 10 | 77 | 70 | 68 | 72 |
| 15 | 83 | 80 | 80 | 81 |
| 20 | 89 | 85 | 85 | 86 |

The mean air temperature after application had a moderate effect on the simulated ammonia volatilization (Table 5). Compared with the volatilization at 15 °C, the volatilization decreased by 11% when the air temperature dropped to 10 °C and increased by 6% when the air temperature increased to 20 °C. The same trends in volatilization were also observed in the analysis of Dutch field experiments (Huijsmans *et al.*, 2003), but the effects were larger than those simulated with Volt'air.

## 3.2 Measured and simulated emissions in ten volatilization events in the Netherlands

The ability of Volt'air to simulate the volatilization process under various conditions of manure, soil and weather was further tested by comparing the measured and simulated volatilization progress in ten field experiments in the Netherlands.

*Available experimental data*

The material and methods used for field experiments on bare soil and soil with a wheat stubble in the Netherlands are described in detail by Huijsmans *et al.* (2003). In summary, the research was focussed on measuring differences in ammonia volatilization between various application techniques, which were surface application, various methods for direct incorporation in the top layer of the soil and deep placement of the manure. The experiments included various soil types, soil water contents, stubble heights, manure characteristics and weather conditions. The emission following surface application of manure was measured as a reference in all experiments.
The ammonia volatilization was measured using the micrometeorological mass balance method. The plots of an experiment always received manure at about the same time in the morning. The manure was applied on circular plots with a radius varying from 20 to 24 m. Measurements of the ammonia volatilization started shortly after the manure had been applied, usually within 5 minutes. Weather conditions, i.e. wind speed, air-temperature, relative humidity and global radiation were recorded every 10 minutes by a weather station. The weather data have been averaged over the duration of each interval that the $NH_3$ volatilization was measured which was about 0.5, 1.5, 3, 6, 12, 24, 48, 72 and 96 hours after application.

*Selected volatilization events and input data*

A number of volatilization events were selected to compare the simulated progress of volatilization after slurry application with field measured values. The selection of events was such that the effects of rainfall after application and the effects of different application techniques (surface spreading, direct incorporation and deep placement) could be simulated and assessed. Other characteristics of the field, the slurries and weather conditions were more or less randomly chosen. Four events were selected with surface application, four events with direct incorporation of surface-applied manure into the soil by a tillage operation to a depth of 15 cm and two events with deep placement by injection of the manure into the soil at a depth of 25 cm (Table 6). A summary of the timing and the characteristics of the manure, characteristics of the field and characteristics of the weather of the volatilization events is presented in Table 7. For the simulation series described in this section, fixed values were taken for field length (20 m) and soil roughness length (0.01 m) to represent the conditions during the experiments. The model with one slurry layer on top of the soil was chosen to simulate the volatilization events, as recommended by Garcia *et al.* (2012). In all simulations it was assumed that the manure was spread evenly over the total field area by choosing 10 $m^3$/ha as the minimum dose to achieve this in the manure input file. As measured weather data, excluding precipitation data, were only readily available as means per time interval of the ammonia volatilization measurements, hourly data of nearby KNMI weather stations (station Deelen for De Steeg and station de Kooy for Slootdorp) were used to reveal the variation in the weather data during the simulation period. Measured weather data on the field and the data of the KNMI stations, synchronized for time zone and summer/winter time, appeared to be very similar (Appendix I).

*Table 6. Selected volatilization events (Huijsmans et al., 2003) for comparison of measured volatilization with Volt'air simulation.*

| Event | Location | Year | DOY | Application method | Measured emission) in % of TAN applied |
|---|---|---|---|---|---|
| 1 | De Steeg, Havikerwaard | 1990 | 252 | Broadcast | 47 |
| 2 | De Steeg, Havikerwaard | 1990 | 252 | Incorporation | 14 |
| 3 | De Steeg, Havikerwaard | 1990 | 252 | Deep placement | 1 |
| 4 | Slootdorp, Oostwaardhoeve, field B2-1 | 1992 | 90 | Broadcast | 81 |
| 5 | Slootdorp, Oostwaardhoeve, field B2-1 | 1992 | 90 | Incorporation | 30 |
| 6 | Slootdorp, Oostwaardhoeve, field B2-1 | 1992 | 90 | Deep placement | 1 |
| 7 | Slootdorp, Oostwaardhoeve, field A15-2 | 1998 | 264 | Broadcast | 58 |
| 8 | Slootdorp, Oostwaardhoeve, field A15-2 | 1998 | 264 | Incorporation | 21 |
| 9 | Slootdorp, Oostwaardhoeve, field A15-2 | 1998 | 272 | Broadcast | 61 |
| 10 | Slootdorp, Oostwaardhoeve, field A15-2 | 1998 | 272 | Incorporation | 34 |

*Table 7. Application time and characteristics of the soil, the slurry and the weather after application [1].*

| Event | Start | Soil | | | Slurry | | | | Weather in 96 hour after application | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | texture | om [2]) | surface | appl. rate | $NH_4$-N | dry matter | pH | mean wind speed | mean air temp. | mean RH | sum global radiation | sum rainfall |
| | (DOY) | | (%) | | ($m^3$/ha) | (g/kg fresh) | (g/kg fresh) | | (m/s) | (°C) | (%) | (J/$cm^2$) | (mm) |
| 1 | 252.375 | S.loam | 3 | wheat stubble | 21.4 | 6.1 | 86.2 | 7.4 | 2.7 | 13 | 90 | 2454 | 7 [3]) |
| 2 | 252.354 | S.loam | 3 | wheat stubble | 21.5 | 6.1 | 86.2 | 7.4 | 2.7 | 13 | 89 | 2467 | 7 [3]) |
| 3 | 252.354 | S.loam | 3 | wheat stubble | 26.5 | 6.1 | 86.2 | 7.4 | 2.7 | 13 | 89 | 2467 | 7 [3]) |
| 4 | 90.344 | Sand | 4 | bare | 29.5 | 4.4 | 107.0 | 7.6 | 4.7 | 9 | 83 | 2983 | 0 |
| 5 | 90.375 | Sand | 4 | bare | 28.0 | 4.4 | 107.0 | 7.6 | 4.7 | 9 | 82 | 2947 | 0 |
| 6 | 90.344 | Sand | 4 | bare | 26.3 | 4.4 | 107.0 | 7.6 | 4.7 | 9 | 83 | 2991 | 0 |
| 7 | 264.354 | S.loam | 5.5 | wheat stubble | 21.5 | 4.8 | 73.7 | 8.5 | 3.9 | 15 | 84 | 3474 | 0 |
| 8 | 264.309 | S.loam | 5.5 | wheat stubble | 22.0 | 4.8 | 73.7 | 8.5 | 3.9 | 14 | 86 | 3480 | 0 |
| 9 | 272.358 | S.loam | 4 | wheat stubble | 20.8 | 4.7 | 62.3 | 8.1 | 6.1 | 12 | 93 | 1744 | 0 |
| 10 | 272.323 | S.loam | 4 | wheat stubble | 19.8 | 4.7 | 62.3 | 8.1 | 6.0 | 12 | 93 | 1752 | 0 |

[1]) Field length was 20 m for all events; [2]) Organic matter; [3]) Shortly after slurry application.

*Results*

The first comparisons of measured and simulated volatilization progress after slurry application were performed for the events in which the slurry was surface-applied. Simulations started with a time step of 1 hour, which fitted with the hourly weather data. As the calculations at this time step became unstable (extreme variations in ammonia flux), a time step of 15 minutes was used for events 1 and 4. For the same reason a time step of 5 minutes appeared to be necessary for events 7 and 9. The time step of the input files for the weather data were adapted accordingly, assuming wind speed, temperature, relative air humidity, global radiation and precipitation to be uniform within the original hour intervals recorded by KNMI. All other events were simulated with a time step of 1 hour. The total simulation time was equal to the duration of the experiments, i.e. 96 hours. Results of measured and simulated ammonia volatilization for the events are presented in Table 8 and Figures 3 to 13.

*Table 8. Measured and simulated total ammonia emission (% of TAN applied) after 96 hours after application for 10 recorded events in the Netherlands.*

| Event | Short description | Ammonia emission (% of TAN applied) | |
|---|---|---|---|
| | | measured | simulated |
| 1 | Broadcast surface application, rain after application | 47 | 43 |
| 2 | Soil incorporation, rain after application | 14 | 21 |
| 3 | Deep placement by injection | 1 | 1 |
| 4 | Broadcast surface application | 81 | 80 |
| 5 | Soil incorporation | 30 | 30 |
| 6 | Deep placement by injection | 1 | 4 |
| 7 | Broadcast surface application | 58 | 85 |
| 8 | Soil incorporation | 21 | 35 |
| 9 | Broadcast surface application | 61 | 85 |
| 10 | Soil incorporation | 34 | 34 |

Volt'air simulates cumulative ammonia emissions of 80-85% of the TAN applied for broadcast surface application (Table 8). When rainfall occurs shortly after application as in event 1, Volt'air simulates considerably less ammonia emission which agrees well with the measured emission. The simulation appeared to yield much higher initial ammonia volatilization fluxes than those actually measured during the first hours after slurry application. Particularly for events 7 and 9 (Figure 9 and 11 respectively), the initial volatilization fluxes were extremely high compared with the measured fluxes, which led to also high total emissions, despite the low fluxes later in the volatilization process. The high pH of the manure may have caused these initial high simulated emissions for events 7 and 9, while this forecasted effect of high slurry pH was not measured in the field experiments.

Incorporation of the manure into the soil and deep placement are techniques that reduce the emission of ammonia compared with broadcast surface spreading. The effect of application method on the ammonia emission could be statistically acknowledged for the measured data (Huijsmans *et al.*, 2003) and the effects are also well simulated in Volt'air as can be concluded from comparing the results for events 1-3, 3-6, 7-8 and 9-10. While for deep placement of slurry by injection a coverage of the manure by soil of 100% may be safely assumed, the figure for slurry coverage after soil incorporation is based on a rough estimate as measured data for or visual assessments of the coverage of the manure were not available. In fact, the results of the simulations mean that the Volt'air calculations represent well the fact that the ammoniacal N in the soil contributes relatively little to the volatilization of ammonia, compared with the contribution of slurry left on top of the soil. Consequently, correct modelling of the volatilization at the interface of slurry and air is of great importance for the ability to predict volatilization, as was also reported by Sommer and Olesen (2000), Sommer *et al.* (2003) and Garcia *et al.* (2012).

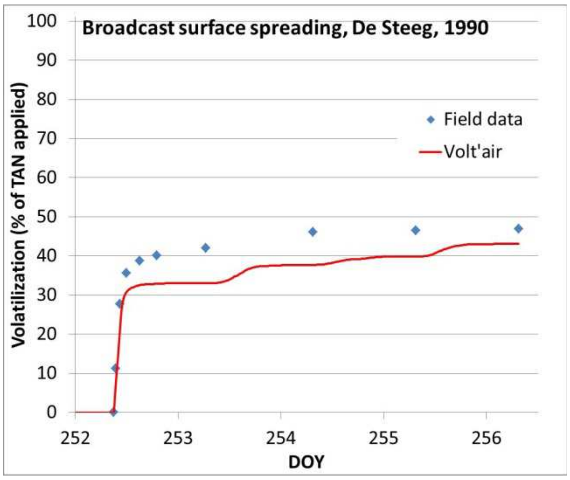



*Figure 3. Measured and simulated ammonia volatilization for event 1.*

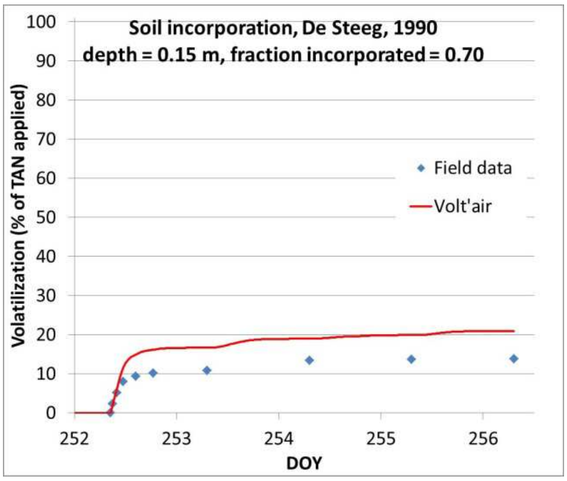



*Figure 4. Measured and simulated ammonia volatilization for event 2.*

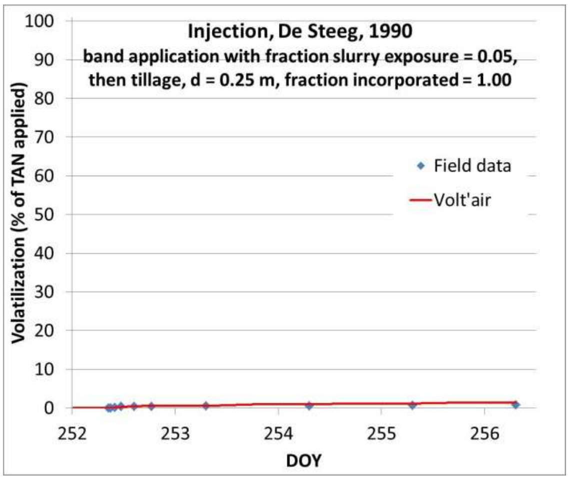



*Figure 5. Measured and simulated ammonia volatilization for event 3.*

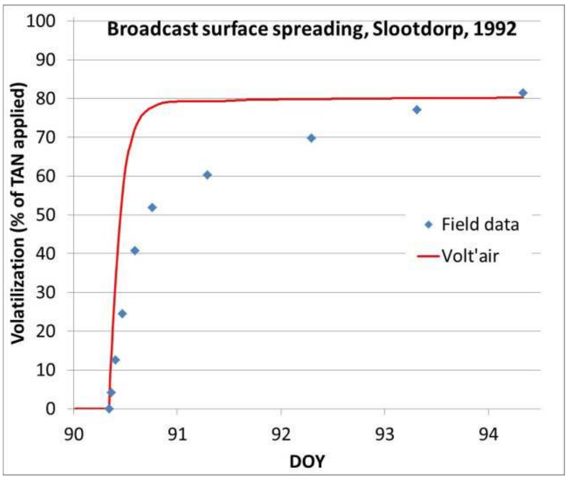



*Figure 6.* *Measured and simulated ammonia volatilization for event 4.*

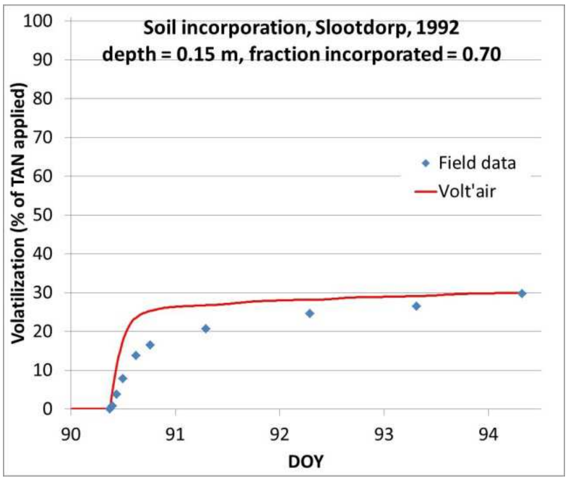



*Figure 7.* *Measured and simulated ammonia volatilization for event 5.*

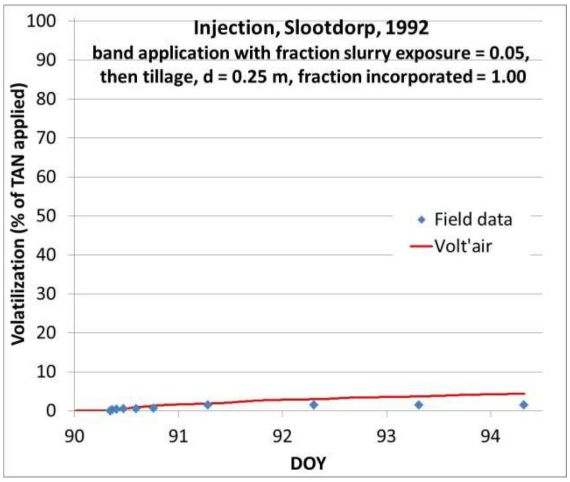



*Figure 8.* *Measured and simulated ammonia volatilization for event 6.*

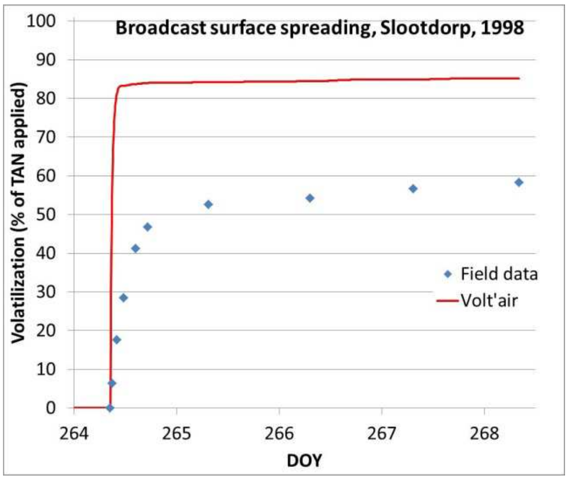



*Figure 9.* *Measured and simulated ammonia volatilization for event 7.*

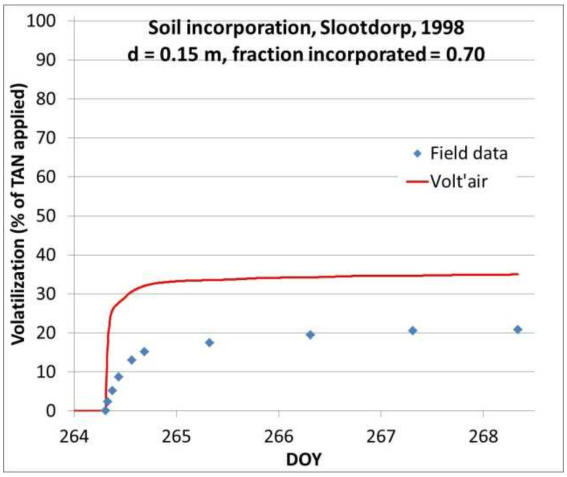



*Figure 10.* *Measured and simulated ammonia volatilization for event 8.*

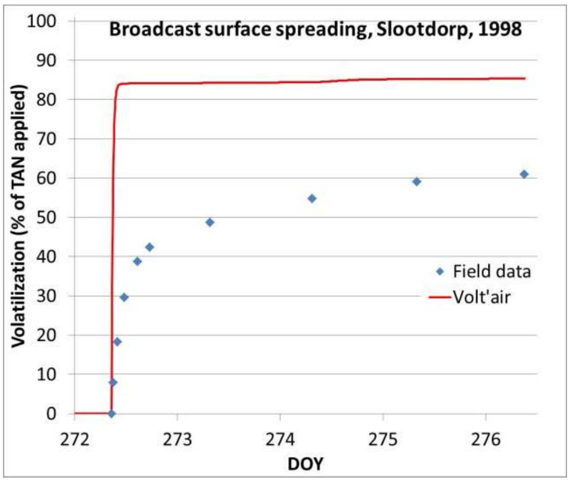



*Figure 11.* *Measured and simulated ammonia volatilization for event 9.*

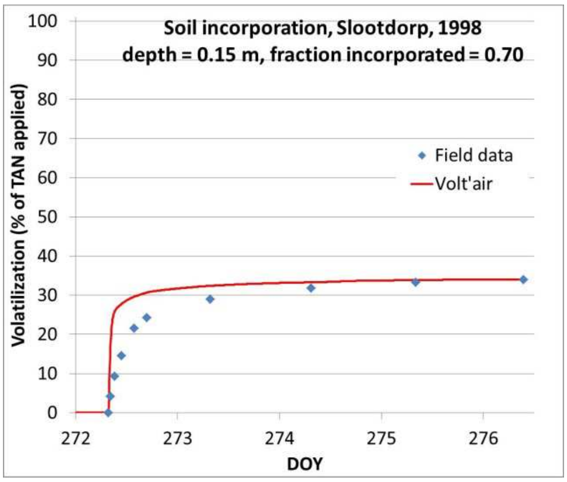



*Figure 12.* *Measured and simulated ammonia volatilization for event 10.*

## 3.3 Effect of field length on simulated volatilization

The effect of field length on the total emission of ammonia is of special interest because field measurements are mostly carried out on relatively small fields, while fields in practice are often much longer in the direction of the wind. Therefore some additional simulations were done for the events described in section 3.2 with a varying field length (Table 9). The results show that the field length had a very limited effect on the total ammonia emission for three of the events (4, 7 and 9) while the emission decreased with field length for events 1 and 2, where rainfall occurred after application. As reported by Genermont & Cellier (1997), the emission rate from smaller fields is initially higher than on larger fields, while the reverse is true at later stages of the emission (Figure 8 in their publication). Finally, at the end of the emission proces, the simulated total emission (in % of TAN applied) from small fields is about the same as the total emission from larger fields as may be the case in events 4, 7 and 9. However, when the emission process is stopped early, which may happen due to infiltration of the ammoniacal N to deeper soil layers bij rainfall after application (events 1 and 2), the simulated total emission may decrease with field length.

*Table 9. Simulated ammonia emission (% of TAN applied) as effected by field length.*

| Event | Short description | Field length (m) | | |
|---|---|---|---|---|
| | | 10 | 20 | 100 |
| 1 | Broadcast surface application, rain after application | 46 | 43 | 38 |
| 4 | Broadcast surface application | 80 | 80 | 79 |
| 7 | Broadcast surface application | 86 | 85 | 85 |
| 9 | Broadcast surface application | 86 | 85 | 85 |
| 2 | Soil incorporation, rain after application | 21 | 21 | 18 |

## 3.4 Effect of a '2-layer' and a 'dry' slurry configuration

The importance of correct modeling of the slurry–air interface was reported by Garcia *et al.* (2011). He showed that the surface layer must be as thin as possible to accurately represent the surface as an interface with the atmosphere and, thus, correctly account for its physical conditions. Garcia (2010) assumed that the optimal thickness value of 1 mm would allow a quick response to meteorological forcing and a correct representation of the drying event. Therefore, he separated the slurry into two layers: an interface slurry layer of 1 mm thickness and the remaining depth of slurry beneath on an experimental basis. His results, using the Rennes dataset, indicate minor differences in simulated cumulative volatilization for the 1-layer and the 2-layer slurry system. As the 2-layer slurry option was available in the model, its effect on volatilization from less diluted Dutch slurry data was assessed. Simulation with the French experimental slurry and the 10 days meteorological Rennes dataset of the Rennes experiment for a sandy loam with Dutch parameterization of the hydraulic properties, showed a noticeable difference in cumulative ammonia emission between the 1-layer and 2-layer slurry configurations (Table 10, Figure 13). Compared with the 1-layer model, the 2-layer slurry model caused an increase of the initial ammonia flux, which was somewhat closer to measured values in the Rennes experiment, according to Garcia (2010). When tried with the Dutch dataset for manure, soil and weather of volatilization event 4, the 2-layer model caused a slight decrease of the simulated initial volatilization fluxes and a negligible change in the total cumulative emission (Table 10, Figure 14). Also in this case the simulated volatilization with the 2-layer model was slightly closer to the measured volatilization than with the 1 layer model.

*Table 10. Measured and simulated ammonia emission (% of TAN applied) as effected by the slurry model.*

| Event | Short description | Measured | Slurry model | |
|---|---|---|---|---|
| | | | 1-layer | 2-layer |
| - | Broadcast surface application, Rennes dataset for meteo and slurry, sandy loam with Dutch parameterization of hydraulic characteristics. | n.a. | 48 | 41 |
| 4 | Broadcast surface application (Dutch slurry) event 4 | 81 | 80 | 80 |

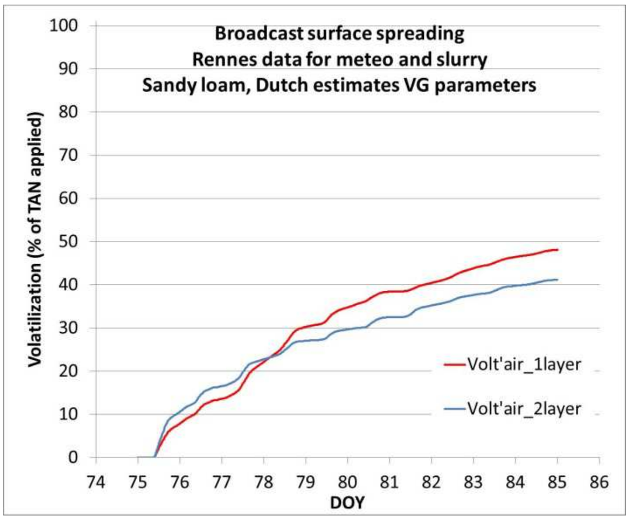



*Figure 13. Simulated ammonia volatilization for a cattle slurry (as used in Rennes experiment) with relatively low dry matter and TAN contents, with the 1-layer and 2-layer slurry configurations.*

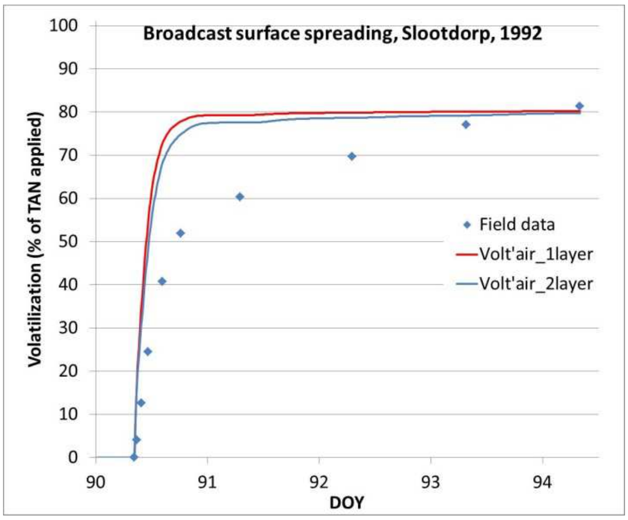



*Figure 14. Measured and simulated ammonia volatilization for a pig slurry (volatilization event 4) with relatively high dry matter and TAN contents, with the 1-layer and 2-layer slurry configurations.*

In recent experiments of Garcia *et al.* (2012) simulation of the initial volatilization fluxes was improved by using a "wet + dry" slurry configuration. In this configuration a wet slurry layer was modelled for the first few hours and, thereafter, this layer was replaced by a relatively dry slurry layer with different hydraulic parameters (Table 11). These simulations were performed with a dataset for cattle manure (dataset Li08, TAN content 2.9 g/ kg fresh, dose 35 $m^3$/ha) that has more resemblance with Dutch manure than the slurry in the Rennes dataset. The results obtained with dataset Li08 and a single slurry layer were comparable with the findings for Dutch pig manure in this report: an overestimation of the volatilization flux at the initial stage of volatilization when using the 1-layer slurry model (Figure 15). Simulations with the "wet + dry" slurry configuration improved the simulated volatilization in the sense that the simulated values for the volatilization were closer to the measured values, because replacing the wet slurry by the dry slurry caused a decrease of the volatilization flux. As Dutch pig manure is relatively 'dry' compared with the French experimental manures, the simulation for event 4 was also tried with the VG parameters for 'dry' manure. In contrast with the findings of Garcia *et al.* (2012) the volatilization fluxes simulated with the 'dry' slurry were somewhat higher than those simulated with the wet slurry (Figure 16).

*Table 11. Measured VG parameters for wet and dry slurry as reported by Garcia et al. (2012).*

| Parameter | Wet slurry | 'Dry slurry' |
|---|---|---|
| Saturated water content ($m^3/m^3$) | 0.996 | 0.403 |
| Residual water content ($m^3/m^3$) | 0.373 | 0.110 |
| Alpha ($m^{-1}$) | 3.600 | 0.672 |
| n | 1.36 | 1.12 |
| Saturated hydraulic conductivity (m/s) | 8.34 $10^{-8}$ | 8.34 $10^{-8}$ |
| Density of the dry matter (kg/$m^3$) | 150 | 150 |

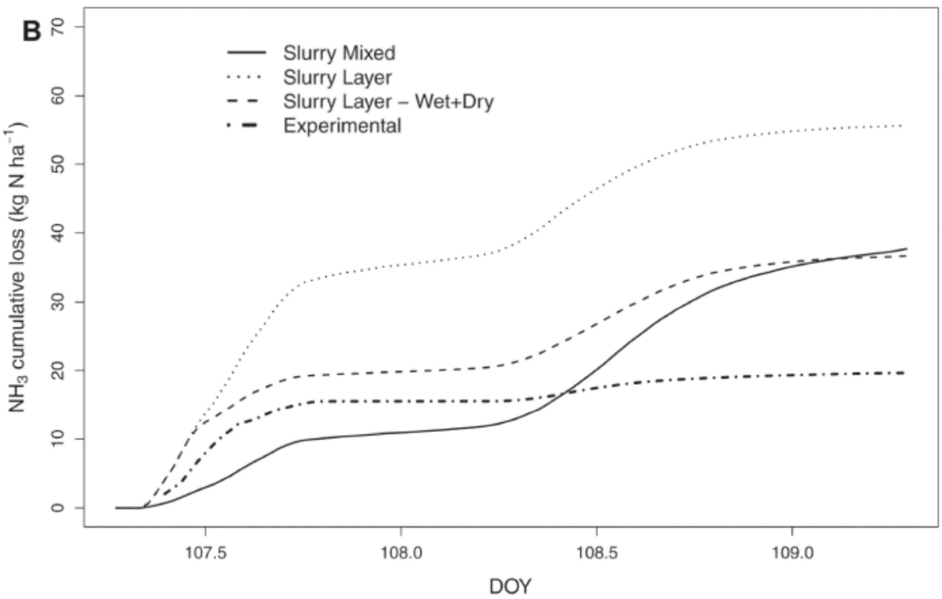



*Figure 15. Comparison of measured and simulated cumulative ammonia volatilization loss for the Li08 dataset using the slurry configurations 1) slurry mixed in top 2 cm of the soil, 2) layer of wet slurry on top of the soil and 3) an initial wet slurry layer, replaced by a relatively dry slurry layer on DOY 107.5 (first afternoon after application). Source: Garcia et al., 2012.*

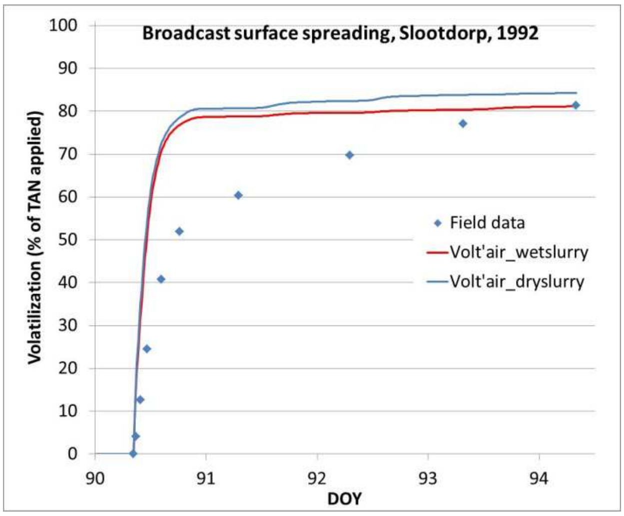



*Figure 16.* *Measured and simulated ammonia volatilization for a pig slurry (volatilization event 4), with wet and 'dry' slurry layer configurations.*

# 4. Discussion

The effects on the volatilization rate of characteristics of the soils, the slurries, the weather and the application methods that were measured in the Dutch field experiments on ammonia volatilization on arable land were statistically analyzed by Huijsmans *et al.* (2003). They analyzed the effects in linear mixed models by the method of residual maximum likelihood. Only terms that were statistically significant and that had a noticeable effect on the volatilization rate were included in the model. The best fitting statistical model for arable land included terms for the application method, the application rate and the TAN content of the slurry, the wind speed, the temperature and a term describing a fixed decay rate of the volatilization flux after application. This model could explain 83% of the variance of the measured volatilization rates. Within the range of experimentation, the other measured characteristics, being dry matter content of the manure, slurry pH (not reported), soil type, soil moisture content of the top layer, stubble height, relative humidity of the air, and incoming radiation did not contribute to further statistical explanation of the volatilization rate. The simulations with Volt'air in this report confirm the effects of application method and temperature; the simulated effects on the total ammonia volatilization agree reasonably well with the measured effects. The performance of Volt'air on simulating the effects of application rate, TAN content and wind speed were not systematically tested in this study. Therefore, no conclusions could be drawn whether the simulated effects of these parameters on the $NH_3$ volatilization agree with the experimental results.

The decay of the volatilization rate with time after application probably depends on the infiltration speed of the free water fraction of the manure with most of the dissolved ammoniacal nitrogen, the drying speed of the manure surfaces exposed to the atmosphere and possibly the adsorption to soil particles or biochemical changes. Volt'air simulates these processes to a certain extent and good progress was made by Garcia *et al.* (2011, 2012) by introducing a separate slurry layer on top of the soil. However, the simulations with different manures, soils and weather conditions after application in this report show that the decay of the volatilization rate often does not correspond with results from field experiments. Notably, for Dutch pig manure Volt'air simulates a very high initial volatilization. It is recommended, therefore, to continue research focussed on understanding the initial processes after application in and under the slurry layer on top of the soil.

Covering of the slurry by soil appears to be a very effective method to reduce the ammonia volatilization. For use in Volt'air, the fraction of slurry covered by soil after certain tillage methods should be determined by visual assessment. This seems to be a very crude way of determining such an important parameter. It is recommended to try to develop new methods to measure the fraction of slurry covered by soil after incorporation. This could contribute to the further development of low-emission methods, even without extensive field testing, and could considerably improve the simulation of the $NH_3$ volatilization with Volt'air.

In this study, the minimum slurry application rate to achieve complete coverage of the field by slurry was assumed to be 10 $m^3$/ha, which meant that the application rates in the Dutch experiments with surface application (range 14 – 39 $m^3$/ha) were assumed to be sufficient for complete coverage of the field with slurry. It should be checked whether this is a realistic assumption as Garcia *et al.* (2012) estimate that the minimum dose required for complete coverage of the field by slurry is 60 $m^3$/ha.

From the simulation of the volatilization in event 1 it is suggested that Volt'air simulates the effect of rain shortly after application well. This effect was not analysed by Huijsmans *et al.* (2003) because rain as a separate factor was hard to statistically quantify, amongst others because precipitation occured in few experiments only. In the specific case of event 1, the time of rainfall and the amount of rainfall was reported. It is suggested that mechanistic modelling could potentially be used to quantify the effects of rainfall.

Simulated total ammonia emission from small fields and large fields was equal except for the case where the volatilization process was prematurely ended by rainfall (Table 9), due to flushing the ammoniacal ammonia to deeper soil layers. It is suggested that this simulation behaviour is a result of the fact that no other sinks of ammonia than transport to deeper soil layers is provided in Volt'air. As other ammoniacal nitrogen sinks may well exist, such as adsorbtion to the soil and 'immobilization' due to formation of a crust on top of the manure, it is suggested that there may be an effect of field size on the ammonia emission in reality. Another factor that will play a role in the effect of field size is the time needed to apply the manure on a whole field. When the application lasts a few hours or more, most of the ammonia in the manure applied at the start of the operation may already have been emitted before manure is applied at a later stage on another part of the field. In that case the expected volatilization reduction effect of a larger field size will be less, compared with theoretical instantaneous application on the whole field. This means that the time needed to apply the manure should also be taken into account. Similarly, Huijsmans and De Mol (1999) showed that  the variation of the time lag between surface application and subsequent incorporation of manure at field scale significant effect on the ammonia volatilization. At field scale the reduction of incorporation is significantly less than the potential reduction in case of instantaneous incorporation.

# 5. Conclusions and recommendations

In this study Volt'air was used for the simulation of a limited number of field experiments on the application of manure on arable land. It was found that the trends in effects of application method and temperature were reasonably well simulated, in agreement with experimental results. Volt'air is capable of simulating the effect of rain fall on the evaporation of ammonia. However, few experimental data exist for validation of the results.

A striking phenomena is that Volt'air calculates a very high initial volatilization compared with the experimental results. The reason for this is not clear but should be sought in the dynamics of the diffusion in the first slurry/soil layers, the depletion of ammoniacal nitrogen by infiltration of liquid into the soil, evaporation of water in the slurry or other factors.

Extended simulations using weather, soil and slurry conditions for which experimental results are available will be necessary to get a better insight in the performance of Volt'air for Dutch conditions. Of particular interest are comparisons of simulated and experimental results for varying application rates, TAN- and dry matter contents of the manure and wind speeds.

The evaluation and further development of the Volt'air model, preferably also for manure application on grassland, will contribute to a better understanding and estimation of the ammonia volatilization from manure applied on the field under various conditions. It is recommended to carry out further development of the Volt'air model in close cooperation between research institutions that are active in ammonia volatilization research within Europe.

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# Appendix I.
# Weather conditions during the field experiments

De Steeg, 1990, DOY 252, broadcast surface application of slurry, KNMI station Deelen.

| | | Cumulative time after slurry application (hr) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 0.5 | 1.5 | 3.0 | 5.9 | 9.9 | 21.5 | 46.4 | 70.5 | 94.2 |
| Precipitation (mm) | KNMI | 0 | 0 | 4.6 | 1.2 | 1.5 | 0 | 0 | 0 | 0 |
| Mean wind speed | field | 3.9 | 4.7 | 4.4 | 3.5 | 3.3 | 2.1 | 1.5 | 0.5 | 0.8 |
| (m/s) | KNMI | 3.0 | 3.6 | 2.7 | 2.4 | 1.8 | 0.4 | 1.3 | 0.7 | 0.7 |
| Mean air temperature | field | 13.8 | 14.4 | 14.2 | 14.1 | 13.5 | 9.5 | 12.2 | 12.6 | 12.4 |
| (°C) | KNMI | 13.5 | 14.3 | 14.0 | 13.7 | 12.5 | 8.2 | 12.9 | 12.7 | 12.7 |
| Mean relative humidity | field | 85 | 82 | 91 | 94 | 93 | 98 | 91 | 91 | 83 |
| (%) | KNMI | 97 | 96 | 93 | 96 | 94 | 99 | 91 | 89 | 82 |
| Cumulative global radiation | field | 16 | 69 | 155 | 312 | 439 | 445 | 1708 | 2454 | 3634 |
| ($J/cm^2$) | KNMI | 19 | 69 | 158 | 273 | 292 | 364 | 1686 | 2583 | 3784 |

Slootdorp, 1992, DOY 90, broadcast surface application of slurry, KNMI station De Kooy.

| | | Cumulative time after slurry application (hr) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 0.5 | 1.5 | 3.0 | 6.0 | 10.0 | 22.7 | 46.8 | 71.2 | 95.7 |
| Precipitation (mm) | KNMI | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Mean wind speed | field | 6.2 | 7.1 | 7.0 | 5.6 | 3.8 | 3.2 | 2.9 | 2.2 | 4.5 |
| (m/s) | KNMI | 5.7 | 5.9 | 5.3 | 4.4 | 3.9 | 3.3 | 3.8 | 2.5 | 3.7 |
| Mean air temperature | field | 9.0 | 9.3 | 10.7 | 12.9 | 11.7 | 6.6 | 7.4 | 8.4 | 6.8 |
| (°C) | KNMI | 8.2 | 8.4 | 8.8 | 9.6 | 6.7 | 5.5 | 5.7 | 6.7 | 5.7 |
| Mean relative humidity | field | 82 | 80 | 76 | 70 | 77 | 98 | 89 | 92 | 82 |
| (%) | KNMI | 81 | 80 | 80 | 79 | 92 | 92 | 90 | 89 | 82 |
| Cumulative global radiation | field | 25 | 88 | 223 | 641 | 764 | 770 | 1858 | 2983 | 3924 |
| ($J/cm^2$) | KNMI | 48 | 161 | 325 | 587 | 659 | 706 | 1852 | 2972 | 4067 |

Slootdorp, 1998, DOY 264, broadcast surface application of slurry, KNMI station De Kooy.

| | | Cumulative time after slurry application (hr) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 0.5 | 1.6 | 3.1 | 6.0 | 8.8 | 23.0 | 46.8 | 70.9 | 95.6 |
| Precipitation (mm) | KNMI | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Mean wind speed | field | 3.2 | 3.9 | 5.2 | 5.7 | 5.4 | 3.2 | 3.6 | 2.9 | 2.3 |
| (m/s) | KNMI | 3.8 | 4.6 | 5.3 | 5.0 | 5.0 | 3.9 | 4.0 | 2.8 | 2.7 |
| Mean air temperature | field | 13.2 | 14.4 | 16.0 | 17.4 | 17.8 | 11.3 | 11.6 | 14.1 | 15.7 |
| (°C) | KNMI | 14.1 | 15.4 | 16.2 | 17.3 | 15.8 | 12.1 | 12.4 | 15.3 | 16.4 |
| Mean relative humidity | field | 90 | 84 | 75 | 68 | 69 | 95 | 95 | 91 | 89 |
| (%) | KNMI | 89 | 83 | 76 | 78 | 76 | 95 | 95 | 91 | 87 |
| Cumulative global radiation | field | 7 | 62 | 255 | 841 | 1265 | 1387 | 2143 | 3474 | 4254 |
| ($J/cm^2$) | KNMI | 83 | 283 | 598 | 1035 | 1137 | 1193 | 2007 | 3312 | 4144 |

Slootdorp, 1998, DOY 272, broadcast surface application of slurry, KNMI station De Kooy.

| | | Cumulative time after slurry application (hr) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 0.5 | 1.4 | 3.0 | 6.1 | 9.0 | 23.1 | 46.9 | 71.3 | 96.5 |
| Precipitation (mm) | KNMI | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Mean wind speed | field | 7.2 | 7.4 | 8.5 | 7.0 | 6.9 | 4.4 | 5.9 | 4.6 | 2.8 |
| (m/s) | KNMI | 7.6 | 7.6 | 6.4 | 7.1 | 4.6 | 5.0 | 7.0 | 5.7 | 3.9 |
| Mean air temperature | field | 13.1 | 13.6 | 14.3 | 15.1 | 14.4 | 13.3 | 9.3 | 6.8 | 6.0 |
| (°C) | KNMI | 14.8 | 15.4 | 14.8 | 16.0 | 13.7 | 13.7 | 9.8 | 8.1 | 7.2 |
| Mean relative humidity | field | 100 | 99 | 94 | 92 | 97 | 98 | 92 | 76 | 88 |
| (%) | KNMI | 91 | 90 | 85 | 99 | 93 | 98 | 89 | 71 | 88 |
| Cumulative global radiation | field | 12 | 51 | 150 | 344 | 402 | 411 | 591 | 1744 | 1988 |
| ($J/cm^2$) | KNMI | 40 | 121 | 197 | 262 | 269 | 304 | 494 | 1628 | 1898 |