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ÉCLAIRE

**Effects of Climate Change on Air Pollution Impacts and Response
 Strategies for European Ecosystems**

Seventh Framework Programme

Theme: Environment

**D4.1. Improved pollution- and climate-sensitive exchange
 parameterisations for the main inorganic Nr compounds**

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1. Executive Summary

- To make surface exchange parameterisations for the main atmospheric reactive nitrogen (Nr) pollutants responsive to climate and to pollution levels, physical and chemical processes must be described less empirically, more mechanistically, ideally derived from first principles. This is especially true for non-stomatal deposition of Nr.
- The ideal way to achieve this is to consider chemical reactions and interactions explicitly, which govern uptake rates not only on canopy surfaces but also in the air column, in coupled fashion to turbulent transport above and within the canopy.
- The multi-layer Ecosystem Surface eXchange (ESX) model, developed in ECLAIRE (see Deliverable 4.4), represents a major step forward for addressing surface exchange of Nr (and also O₃, VOC) and responses to changes in pollution and climate. The development of ESX is an on-going process, and a community effort, which relies on other, complementary sub-models providing parameters (emission potentials, resistances, etc) at the different ecosystem levels.
- For NH₃, we present a concept for deriving European fields of soil and vegetation emission potentials (Γ values), at the annual scale, suitable for bi-directional models such as (but not limited to) ESX. The proposed scheme provides Γ values across land uses as well as their temporal variations, in response to season (phenology) and fertilisation. Meta-modelling is used to provide simplified, regression-based functional relationships of Γ values from multiple runs of ecosystem and NH₃ volatilization models.
- For a more mechanistic representation of the non-stomatal sink for water-soluble and/or Nr-aerosol interacting compounds (NH₃, HNO₃, HONO, HCl, SO₂), we adapted and improved an existing model (DEWS) of chemical interactions on wet leaf surfaces, with a view to eventually coupling DEWS to ESX.
- For the specific case of near-surface NH₄NO₃ evaporation in warm conditions and its impact on overall inorganic Nr dry deposition rates, an empirical, measurement-based correction scheme for NH₄NO₃ deposition velocity was developed, which has been incorporated into the EMEP model.

2. Objectives:

The general objective of D4.1 was to improve the surface exchange parameterisations for the main atmospheric reactive nitrogen (Nr) pollutants (gases: NH_3 , HNO_3 , NO_2 , and aerosols: NO_3^- and NH_4^+), and to provide algorithms suitable for inclusion in chemical transport models (CTM). Through a better understanding of the underlying physical and chemical mechanisms, the improved exchange schemes should better simulate changes in atmospheric deposition and emission patterns in response to changes in climate and in atmospheric composition.

Particular emphases were to be given to i) NH_3 exchange through an integrating analysis of NH_3 flux measurements in the ECLAIRE flux network, which should lead to parameterisations suitable for translation into the EMEP model; and ii) the effect of NH_4NO_3 aerosol volatilisation near warm surfaces on overall NH_4^+ , NO_3^- , NH_3 and HNO_3 deposition rates.

Our strategy, adopted early on (March 2012) within WP4, to address the afore-mentioned objectives regarding Nr (but also O_3) exchange modelling (improved, climate- and pollution-sensitive, multi-pollutant parameterisations for CTM applications), consisted of the development of a new multi-layer surface/atmosphere modelling framework, ESX (ECLAIRE Ecosystem Surface eXchange), rather than simply re-parameterising existing big-leaf (bulk) models. ESX should treat within- and above-canopy turbulence, diffusion and chemistry explicitly and dynamically (including gas and aerosol phases, as well as the aqueous and particle phases for leaf/canopy surface pollutant pools) (see M36 ECLAIRE-WP4 Periodic Activity Report).

While ESX is the focus of deliverable D4.4, many conceptual developments in ESX were motivated by the objectives of D4.1. The activities reported below occurred in parallel to the development of ESX, and some outputs should ultimately feed into ESX as part of EMEP. However, the concepts and models developed in this deliverable are generic and may prove suitable for other surface exchange schemes and CTMs.

3. Activities:

3.1 Definition of a concept for a generalised NH_3 exchange scheme for CTMs

Ammonia emissions and deposition are currently treated separately in most CTMs, including EMEP; emissions from agricultural point sources (animal housing, manure storage areas) and from diffuse sources (field-applied manures and fertilisers) are gridded and distributed temporally from national or European-scale inventories, and are thus independent of weather, soil and other controlling factors; while NH_3 exchange with ecosystems is treated as dry deposition only (canopy resistance model).

The activities in this section focused on building a strategy for improving the representation of ecosystem/atmosphere NH_3 exchange in CTMs, at the regional scale. This needs to address both i) weather- and soil-dependent peak emissions from fertiliser field applications, and ii) bi-directional NH_3 exchange in background conditions, both in semi-natural ecosystems and in agro-ecosystems outside fertilisation events, explicitly for all land uses of all grid squares of the modelling domain. (Note that we did not seek to address NH_3 emissions from fixed/point sources, such as animal housing and manure storage and treatment areas).

For both peak emissions and bi-directional NH_3 exchange in background conditions, the Γ concept is central to an improved modelling of fluxes (Sutton et al., 2013). Γ is the ratio of NH_4^+ to H^+ ions in the different substrates of the ecosystem (in leaf apoplast, soil solution, leaf surface water films, leaf litter) and it controls the NH_3 emission (or uptake) potential as a function of temperature only. In two- or multiple-layer canopy exchange modelling, values of Γ are required at the different levels, whether as part of canopy compensation point models (Nemitz et al., 2001), or as part of canopy turbulent chemical processing models such as ESX (see deliverable D4.4). The Γ values do not depend on the model structure, however they are very variable across biomes and land uses, and also over time, whether in response to phenology or season, or to nitrogen fertilization. Γ -based modelling approaches are needed to predict the impact of climate change on NH_3 emissions and deposition (Sutton et al., 2013).

Figure 1 shows a summary of the concept developed in ECLAIRE WP3-4 for deriving Γ values, and their spatial and temporal variations at the annual and regional scales, that are required as inputs to bi-directional exchange models as part of CTMs. This makes use of both review-based empirical parameterizations (Massad et al., 2010) and of meta-modelling approaches for simplifying mechanistic models.

Γ values are needed in semi-natural vegetation as well as in agricultural systems, but without the impacts of soil management (ploughing, seeding, N fertilization) and harvest, the temporal variations in Γ (in soils and plants) of unmanaged systems are likely much smaller. Thus in a first approach, the literature review-based regression approach by Massad et al. (2010), and the corresponding parameterization scheme MNS-2010, are proposed as robust solutions for unfertilized ecosystems, with stomatal Γ increasing exponentially with atmospheric N deposition above $10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (for details, concept and verification, see Deliverable 3.2).

In agricultural systems, meta-modelling approaches are proposed in Fig. 1, as an alternative to fully mechanistic ecosystem modelling, to deliver either empirical relationships of Γ as a function of the main controlling variables (for example, soil moisture, soil pH, temperature for soils treated with manures), or alternatively but less flexibly, European-scale maps and time series of Γ values, derived from multiple runs of process-based models. Meta-modelling is useful in a CTM context because mechanistic models describing e.g. NH_3 volatilisation dynamically and at high temporal resolution, such as the VOLT'AIR model (Genermont and Cellier, 1997), require detailed input data on soil (structure, pH, cation exchange capacity, organic matter content, etc), fertiliser types and application techniques, etc, which may not be available at the regional scale. Further, such process-based models are likely too CPU intensive for online coupling with CTM.

The outputs of meta-modelling are thus typically empirical relationships derived from multiple regressions, which account for the effects of the main controlling factors without the burden of explicit and computationally expensive detailed process calculations. Here the CERES-EGC crop model was run at the European scale and its plant biomass and N-content outputs were used to derive stomatal Γ_s values for the main crops. Soil-related output variables from the same CERES-EGC runs were used to derive background soil Γ_g levels. Meta-modelling of this kind could also be envisaged in future for unmanaged ecosystem (e.g. forest) models that explicitly treat N turnover in plant and soil.

For fertilizer-related NH_3 emission peaks a meta-model of soil Γ was developed from the volatilization model VOLT' AIR. Note that the VOLT' AIR Γ meta-modelling approach was derived, but quite distinct, from the VOLT' AIR *emission* meta-modelling of Deliverable 3.1, the purpose of which was to provide offline NH_3 emission time series for CTMs. The advantage of a Γ meta-model for fertilised soils is that there will be a coupled online interaction of $\Gamma_{\text{fertilizer}}$ with the multi-layer (e.g. ESX) model at the process level.

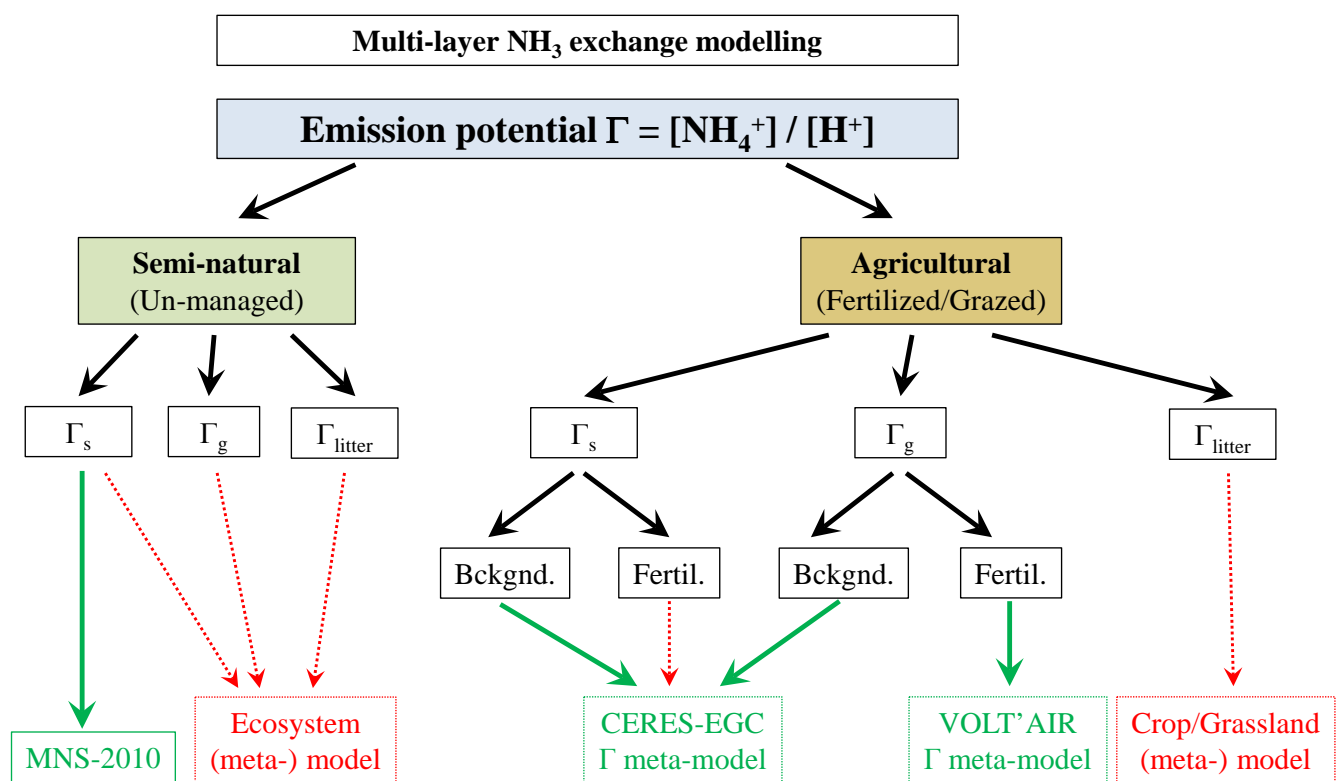


Figure 1. Summary of the approach proposed for deriving Europe-wide fields of ecosystem Γ values (NH_3 emission potentials in stomata/apoplast Γ_s , ground/soil including fertiliser Γ_g , and in litter Γ_{litter}), required as inputs to bi-directional exchange models. MNS-2010 refers to the parameterization scheme by Massad et al. (2010). Green solid arrows denote solutions explored within ECLAIRE WP3-4; red dotted arrows indicate potential solutions to investigate in future.

3.1.1. VOLT' AIR meta-modelling of soil Γ_g after fertilisation

The process-based VOLT' AIR NH_3 volatilization model was used in a meta-modelling approach to provide the Γ_g parameters, which describe the initial (maximum) soil emission potential following fertilisation ($\Gamma_{g,\text{max}}$) and the e-folding time (τ) of the exponential decay curve that is characteristic of NH_3 emission flux dynamics during the first few days after spreading, following the function proposed by Massad et al. (2010):

$$\Gamma_g = \Gamma_{g,\text{max}} e^{-t/\tau} \quad (1)$$

with t the time elapsed after spreading (days). Massad et al. (2010) proposed a τ default value of 2.88 days, but in reality the emission dynamics and the e-folding time will be heavily dependent upon weather (rainfall, temperature, etc), soil moisture and on the nature of fertilizer. Similarly, $\Gamma_{g,\max}$ depends on fertilizer type, weather and also on the application technique and whether fertilizer is incorporated into the soil. The VOLT' AIR model accounts for all these effects mechanistically and was therefore applied in a wide variety of conditions to derive empirical relationships for both $\Gamma_{g,\max}$ and τ , for three fertilizer types: slurry, farmyard manure (FYM) and urea ammonium nitrate (UAN). The full methodology, and the parameters of the multiple regressions to derive both $\Gamma_{g,\max}$ and τ , are described in detail in **Appendix 1** in this document.

The results of the multiple VOLT' AIR simulations indicate that the e-folding times are shortest for FYM and slurry, and despite a wide spread of values tend to be shorter than the default 2.88 days of MNS-2010 (Fig. 2). By contrast, τ values are much longer for UAN, and over these results show that using a single value for τ is over-simplistic.

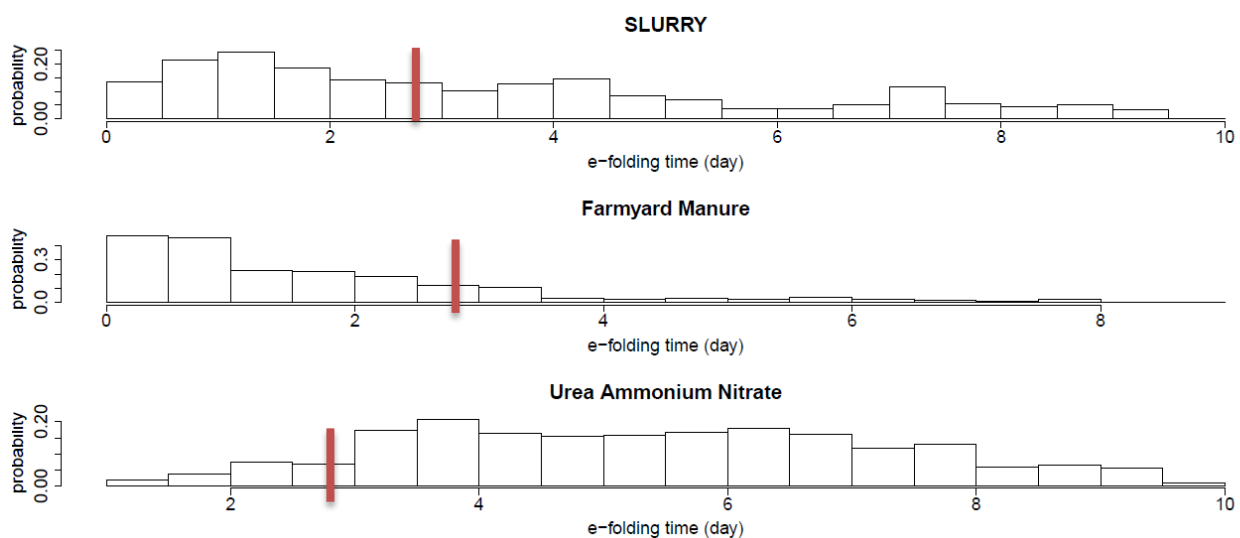


Figure 2. Probability distribution of the e-folding decay time τ (in days) for Γ_g for the three types of fertiliser modelled. For comparison, the e-folding time proposed by MNS-2010 of 2.88 day is given with a red bar on each graph.

The meta-model of $\Gamma_{g,\max}$ (Fig. 3) gives median values twice as large for slurry than for FYM and much smaller values for UAN on average but with a much larger variability for the latter. This reflects the dependence of NH_3 volatilisation from UAN to soil pH. Volatilisation from slurry and manure are less dependent on soil pH in these simulations as the pH of the fertilizer drives the emissions in VOLT' AIR. The very small values obtained for UAN actually shows that the exponential decay function may be misleading for urea-like fertilisers, whose temporal dynamics tend to be more Gaussian.

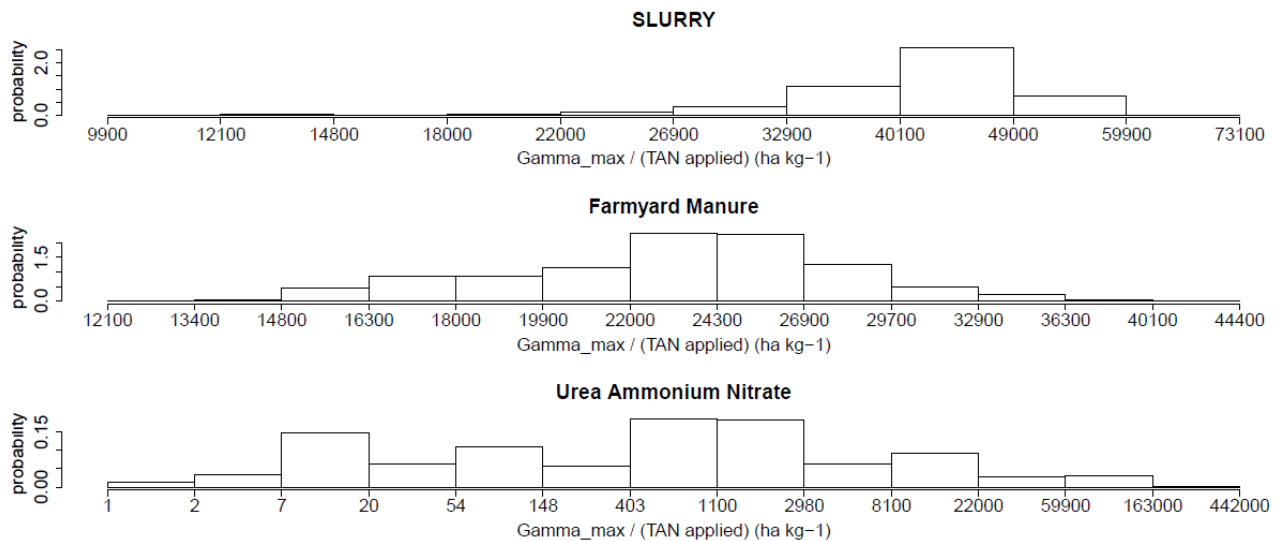


Figure 3. Histograms of $\Gamma_{g,max}$ (normalized by the applied TAN dose) obtained by meta-modelling of 1044 simulations of sites \times period for slurry, FYM and UAN.

The performance of the meta-model (assessed versus the full VOLT'AIR runs) is best for UAN, then slurry, with the simulation of FYM a little more challenging (see Table 5 and Fig. A2 in Appendix). The Γ_g functions derived in this meta-model may be integrated easily into the ESX or EMEP modelling frameworks for testing at the European scale. We should stress here that these results are based on a limited set of simulations of VOLT'AIR where only a few applications techniques were simulated. Extension of these results to techniques such as slurry incorporation, and to variable slurry and manure types, including changing substrate pH and density, is the focus of ongoing work, which will feed into an updated meta-model (see also WP3 periodic report).

3.1.2. CERES-EGC meta-modelling of stomatal Γ_s and background soil Γ_g

Values of Γ_g and Γ_s were obtained from simulation runs of the CERES-EGC crop model for the whole of Europe on a daily time step and with a $0.25^\circ \times 0.25^\circ$ grid resolution for three periods: a historical period (1950-2010) and two future periods with two different scenarios RCP4.5 (2010-2100) and RCP8.5 (2010 – 2100). The methodology and meta-model equations are described in detail in ECLAIRE Deliverable 3.2. As an example of the work, Fig. 4 shows the gridded outputs of annual mean Γ_g for 2005; the spatial variability of gamma soil values is tightly correlated to that of soil pH, with high values in alkaline soils and low values in acidic soils.

The European maps of background soil and stomatal Γ values, calculated for crops from CERES-EGC for the present day and for future conditions (RCP scenarios), are available for use as gridded inputs to EMEP/ESX and other CTMs. A meta-model based on these outputs (developed in similar fashion to the VOLT'AIR work – see above) is available for background soil Γ_g (Fig.4, see also Deliverable 3.2). Future work includes the development of a stomatal Γ_s meta-model, such that CTMs can call upon meta-model (regression-based) functions rather than spatial fields of Γ_s values calculated offline.

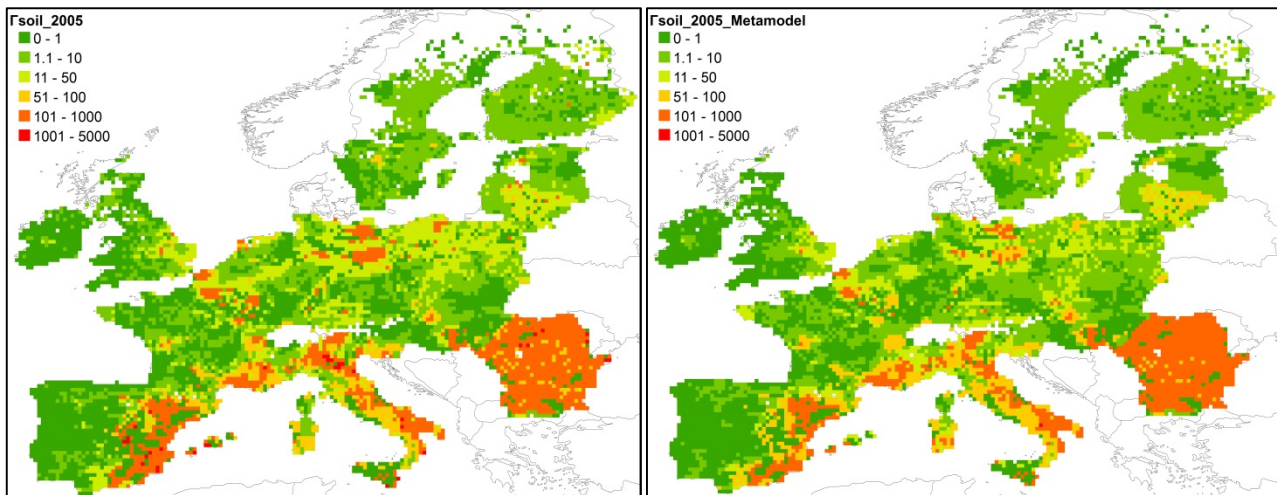


Figure 4: Spatial distribution of yearly average Γ_g values in European crops for 2005. Left panel: CERES-EGC full runs; right panel: meta-model. Note that the larger values in Romania and Bulgaria are due to a high default soil pH set to 7.

3.2 Chemical modelling of leaf surface wetness/gas/aerosol interactions

The main atmospheric reactive nitrogen pollutants are water-soluble, and the presence or absence of liquid water on terrestrial surfaces is a key factor controlling N_r dry deposition rates. Canopy resistance-based deposition models typically assume that the non-stomatal resistance (R_w , R_{ns} , R_{ext}) is controlled by either relative humidity or by a surface wetness indicator (wet/dry) (Flechard et al., 2011). However, these parameterisations are often entirely empirical and offer little scope for exploring changes in deposition rates in response to changes in pollution and climate. A more mechanistically explicit treatment of the chemistry of water droplets or thin water films on vegetation surfaces, based on first principles (Henry's law, pH-dependent dissociation rates, condensed phase reaction rates, ion transfer through leaf cuticles, etc), is more appropriate for studying scenarios of change (warming, heat-waves, droughts, changing mixing ratios of ammonia vs acid gases).

The DEWS (Dynamic pollutant Exchange with Water films on vegetation Surfaces) model was adapted from the surface chemistry and exchange model by Flechard et al. (1999) with some substantial modifications. The original Visual Basic code was first ported to Fortran for compatibility and coupling with ESX. The Flechard et al. (1999) version used a forward (explicit) Euler numerical solution for the time integration of trace gas fluxes into or out of the water phase; this was changed to an analytical solution which could be derived after systematically formulating the model as a set of first-order ordinary differential equations. Also, where the previous version treated dissociation equilibrium and exchange + reaction dynamics in two separate steps, the new code treats dissociation, exchange and reaction simultaneously.

Although a full operational coupling of DEWS to ESX has not been achieved within the time frame of ECLAIRE, significant steps have been achieved in the harmonization of the Fortran codes. Some basic science issues have yet to be addressed, such as the physical basis for the treatment of the transfer resistance (R_d) at the air/water interface, and water-phase transport and kinetics. Related numerical issues also need to be resolved.

The modelling of soluble trace gas exchange between leaf surface water films and the atmosphere requires the knowledge of the canopy-scale amount of liquid water (VH_2O) present on leaf surfaces. This was first achieved through a bulk canopy Surface Wetness Energy Balance (SWEB) model after Magarey

et al. (2006). In a first approach, the SWEB model provides the bulk canopy VH_2O , which can be distributed through the N canopy layers based on a LAI profile. Future developments should target an explicit multi-layer version of SWEB.

However, while DEWS/SWEB addresses the chemical composition of visible (macroscopic) leaf wetness and the chemical reactions within, DEWS calculations cannot proceed once surface water has evaporated beyond a certain ionic strength. Even then, liquid water is often present on leaf surfaces beyond this point. Accumulated hygroscopic particles on leaf surfaces act as ‘dew condensation nuclei’, similar to cloud condensation nuclei in the atmosphere. An important part of the condensing water comes from stomatal transpiration and the elevated humidity within the leaf boundary layer. The condensing water forms highly concentrated solutions with specific chemical and physicochemical properties significantly different from dilute solutions.

We sought to address such conditions by invoking two aerosol chemistry models (PD-FiTE and AIOMFAC) in the context of the leaf surface. Calculations were first carried out using PD-FiTE (Partial Derivative Fitted Taylor Expansion), which is a Pitzer ion-interaction model and is able to calculate activity coefficients of aqueous electrolyte solutions up to very high concentrations. However, after consultation with the School of Earth, Atmospheric and Environmental Sciences of the University of Manchester (G. Mc Figgans and D. Topping), the AIOMFAC (Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients; Zuend et al., 2008) model was deemed to be more appropriate, and we investigated ways to couple AIOMFAC with DEWS, with AIOMFAC taking over from DEWS/SWEB in dry conditions for the calculations of leaf surface water storage and activity coefficients. Leaf surface relative humidity is a physical entity, with the water activity driving the partitioning of the chemicals between solids, liquids, and vapour. Adaptation issues that we encountered include the different geometry between airborne and deposited aerosols, the suitable parameterization of leaf surface humidity, and the different numbers of chemical species accounted for by DEWS and AIOMFAC.

3.3 An empirical parameterisation of fine nitrate deposition

Recent measurements have shown evidence that effective dry deposition rates of some aerosol chemical components are much larger than those of others. In particular, fine nitrate and fine ammonium often show effective dry deposition rates in excess of 10 and up to 200 mm s^{-1} , at the same time as the dry deposition rates of sulphate aerosol are small (0.1 to 5 mm s^{-1}). This has been attributed to the effect of volatile ammonium nitrate (NH_4NO_3) evaporating during the deposition process. This process represents an additional loss in addition to physical deposition and produces nitric acid (HNO_3) and ammonia (NH_3) which are taken up much more efficiently by semi-natural vegetation than NH_4NO_3 would have been, thereby increase the terrestrial sink for these aerosol compounds, reducing the transport distance and increasing nitrogen inputs into potentially sensitive ecosystems. This process is driven by the increased temperature near and within plant canopies, coupled to the reduced concentrations of NH_3 and HNO_3 in this region, both of which promote evaporation. These near and in-canopy gradients cannot be resolved by the vertical resolution of common chemistry and transport models and coupled chemistry climate models. The ESX model described in Deliverable D4.4 seeks to address such issues by explicitly simulating the interplay between chemistry / thermodynamics and bio-sphere/atmosphere exchange at the relevant scale.

An alternative approach is to develop an empirical parameterisation of the effective dry deposition velocity as a function of the relevant drivers, as a kind of subgrid parameterisation of the process. Thus, based on the available measurements, an empirical parameterisation of the dry deposition velocity (V_d) for NH_4NO_3 was developed as a function of friction velocity (u^*), leaf area index (LAI) and atmospheric stability (as characterised by the Obukhov length, L) (Figure 5). Whilst u^* is expected to be the

predominant controller of V_d , $1/L$ was found to be the best descriptor of the residual dependence. It can be shown that this stability parameter is proportional to the product of the temperature gradient (that drives evaporation during the deposition process) and the turbulence transport time scale (which provides time for the evaporation to occur).

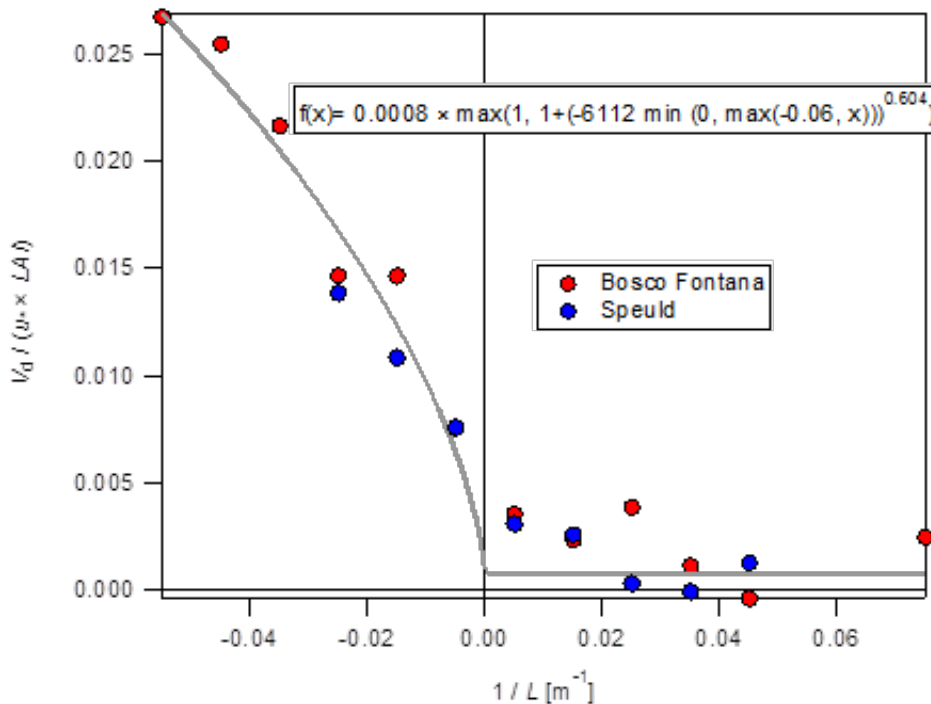


Figure 5. Parameterisation of the deposition velocity of fine aerosol nitrate from measurement data. The dependence of $V_d/(u_* \times LAI)$ on $1/L$ in unstable conditions reflects the on-going evaporation near and within plant canopies under conditions of strong vertical temperature gradient.

4. Results:

4.1 Verification of the VOLT'AIR Γ_g meta-model versus emission flux datasets

The values of the parameters $\Gamma_{g,max}$ and τ , describing the temporal dynamics of soil Γ_g after fertilisation (see Eq. 1), and simulated by the VOLT'AIR Γ_g meta-model (see Section 3.1.1 and Appendix 1), were tested versus actual field NH_3 flux measurements following cattle slurry spreading over grass and crops. Twelve spreading events in total, from the NitroEurope IP and ECLAIRE projects, were investigated (Fig. 6 and 7), in which measured fluxes were compared to fluxes modelled using the 2-layer MNS-2010 model, in two configurations: i) runs with $\Gamma_g =$ actual (measured) slurry Γ and default $\tau =$ constant 2.88 days (Massad et al., 2010); and ii) runs with Γ_g and τ as predicted by the VOLT'AIR Γ_g meta-model.

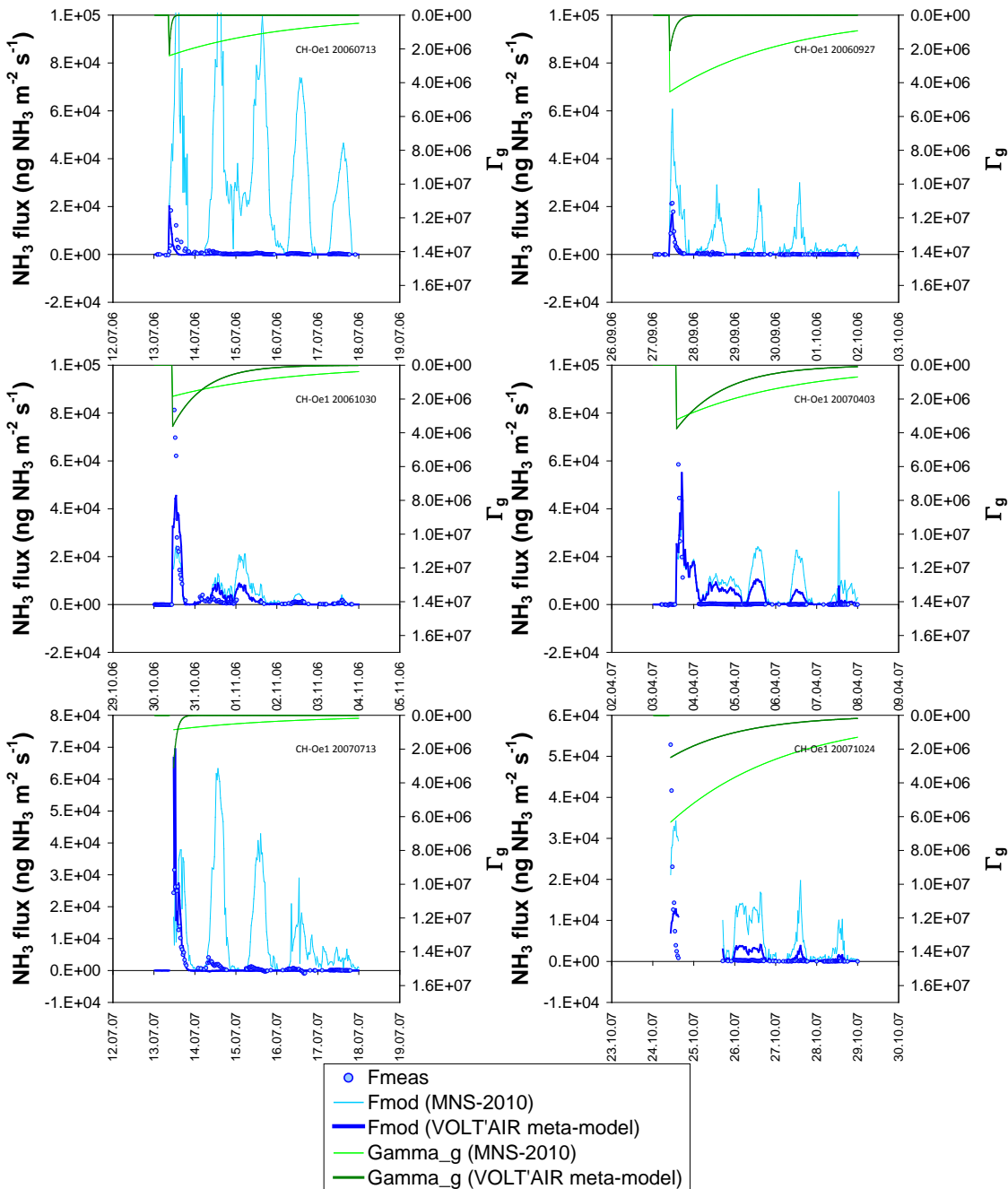


Figure 6. Comparison of measured and modelled NH_3 emission fluxes after cattle slurry spreading at the NitroEurope IP grassland site CH-Oe1 (Oensingen) in 2006-2007. The 2-layer MNS-2010 model was run using $\Gamma_{g,max}$ and τ parameters from either default values in MNS-2010, or from the VOLT'AIR Γ_g meta-model.

The emission flux model runs using Γ_g parameters derived from the VOLT'AIR meta-model performed consistently better than those using the default parameters, showing both i) initial flux levels generally

much closer to measurements, and ii) a generally much faster (exponential) decline in flux levels in the hours and days following spreading.

These results indicate that, for cattle slurry at least, a flux parameterisation based on an exponentially decreasing Γ_g , with initial maximum values and e-folding times predicted by the VOLT'AIR meta-model, could represent a viable option for a representation of field emission dynamics in a CTM application. The simple underlying equations (multiple regressions for the exponential parameters and the exponential decay function itself) can easily be implemented without excess computational cost, while still accounting for the soil and weather impacts on the emission process.

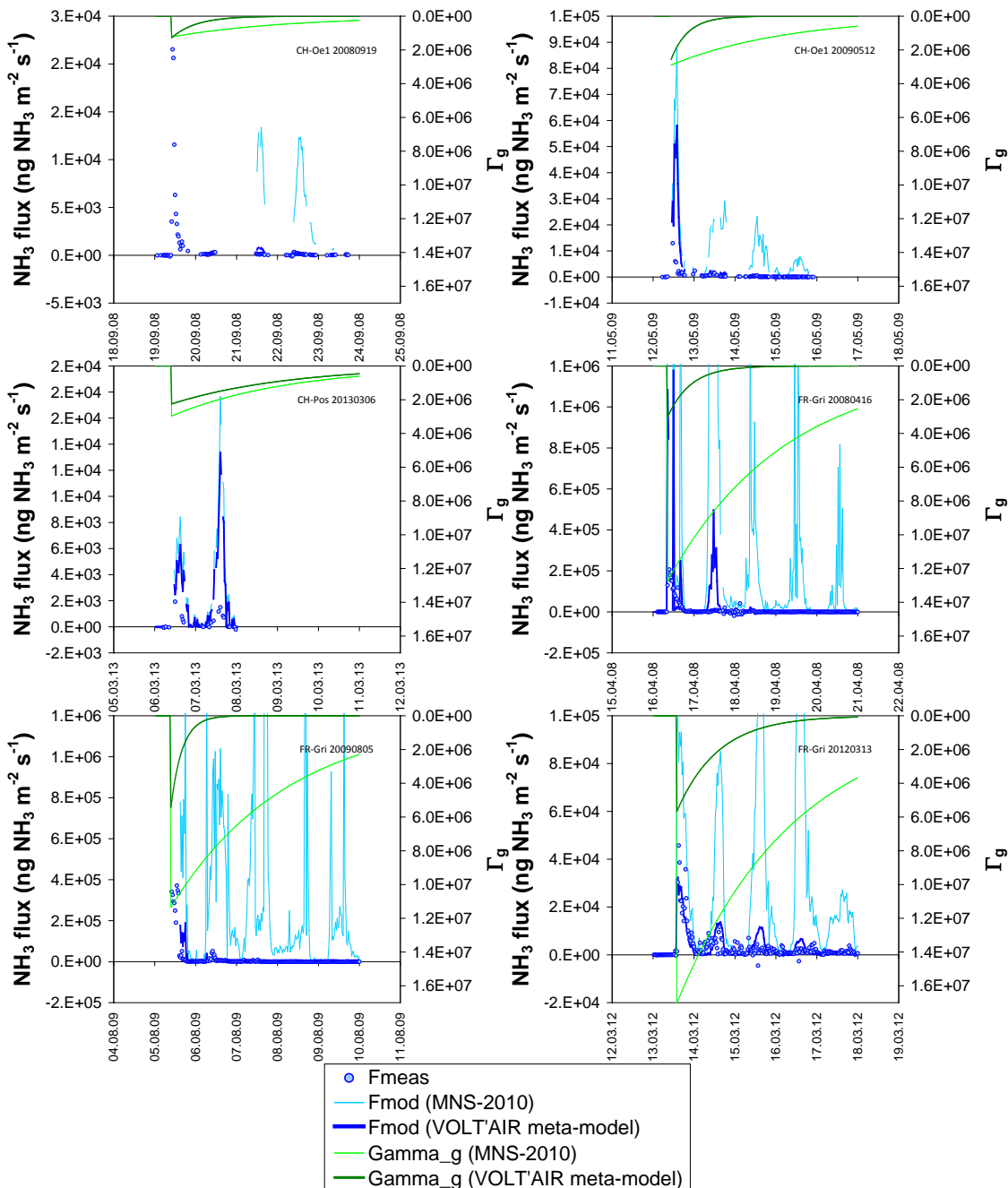


Figure 7. Comparison of measured and modelled NH_3 emission fluxes after cattle slurry spreading at the NitroEurope IP grassland site CH-Oe1 (Oensingen, 2008-2009) and at the ECLAIRE sites CH-Pos (Posieux, grassland, 2013) and FR-Gri (Grignon, arable, 2008-2012). The 2-layer MNS-2010 model was run using $\Gamma_{g,\text{max}}$ and τ parameters from either default values in MNS-2010, or from the VOLT'AIR Γ_g meta-model.

4.2 Testing of DEWS-AIOMFAC versus ECLAIRE and other datasets

DEWS was tested on grassland and forest flux datasets, including the data from the DE-Braunschweig experiment (EU-GRAMINAE project), from the NitroEurope IP CH-Oensingen site and from the IT-Bosco Fontana ECLAIRE intensive experiment. There are few datasets available for testing the model, that include all relevant inputs such as ambient concentrations of the main Nr species (NH_3 , HNO_3 , NH_4^+ , NO_3^-) but also other chemically interacting pollutants (eg SO_2 , HCl), as well as measured rainfall chemistry (pH, major ions including base cations), and indeed measured NH_3 (and other trace gas) fluxes for verification.

DEWS interaction with the AIOMFAC aerosol model occurs when leaf surface water either from dew or from rain evaporates, and there is a strong concentration of surface solutes into microscopic “wetness”, tending towards deliquescent particles. The reverse process, that of ambient water vapour absorption by salts growing into droplets, or minute “puddles” of increasing size, has been shown by Burkhardt and Hunsche (2013). By default, SWEB-type models would predict that all surface water evaporates ($\text{VH}_2\text{O} = 0 \text{ liter m}^{-2}$) in “dry” conditions because such models do not account for the water holding capacity of leaf surface particles. However, at each time step in DEWS, AIOMFAC estimates the amount of water bound to solutes present on the surface ($\text{VH}_2\text{O}_{\text{aerosol}}$) as a function of relative humidity (for $\text{RH} < 99\%$) and of the mole fractions of the major ionic species (Zuend et al., 2010). Whichever of the two values $\text{VH}_2\text{O}_{\text{SWEB}}$ or $\text{VH}_2\text{O}_{\text{aerosol}}$ is largest, is used for the chemistry calculations. The aerosol model also computes the activity coefficients of the major solutes and the partial pressures of relevant gases (NH_3 , HNO_3 , HCl).

Figure 8 shows the transition from macro- to micro-scopic wetness as predicted within DEWS by SWEB and AIOMFAC for the example of the GRAMINAE Braunschweig grassland (Burkhardt et al., 2009); $\text{VH}_2\text{O}_{\text{aerosol}}$ follows closely the variations in RH and is the relevant water quantity in dry conditions. Surface solution pH then typically drops to 4, while reaching less acidic levels around 6 following rainfall, and intermediary values (around 5) for dew (middle panel of Fig. 8). The lower panel of Fig. 8 shows the simulated NH_3 exchange fluxes, with F_d the non-stomatal canopy flux, F_s the stomatal flux, F_g the ground-level flux, F_t the sum of all three, and $F_{\text{NH}_3\text{meas}}$ from micrometeorological measurements. The agreement between DEWS and measurements is better in conditions when macro-wetness is present (first half of the 7-day period at Braunschweig), which is what the model was primarily designed for. For drier conditions the simulated F_d flux is very small and likely much underestimated, due to more complex (and likely mis-represented) chemical interactions between NH_3 (and other pollutant gases like HNO_3 and HCl) and deliquescent particles on the surface.

The challenge of modelling chemical exchange over macroscopically dry leaf surfaces was even more apparent at Bosco Fontana (Fig. 9). Surface relative humidity was mostly in the range 40%-80%, even at night, except for two days (06-07 July) following rainfall. The predicted $\text{SWEB_VH}_2\text{O}$ was therefore much lower on average, and $[\text{NH}_x]$ concentrations in surface wetness much higher (by a factor of 10 to 100), than in the Braunschweig example, resulting in large equilibrium surface NH_3 concentrations and limiting non-stomatal deposition (F_d mostly very small). However, the actual measured NH_3 dry deposition fluxes were large at Bosco Fontana, much larger than DEWS predictions, despite the prevalent dryness, and their magnitude cannot be explained by stomatal uptake alone (the model used in this case the actual stomatal conductances derived from measured latent heat fluxes). This points to a large non-stomatal NH_3 sink, possibly due to the large leaf surface aerosol loading in this polluted area of the Po Valley, which our current, simplified mechanistic representation in DEWS (based on NH_3 solubility in water) fails to explain. By contrast, NH_3 deposition during and after rain events on the afternoon and evening of 06 July (see close-up on Fig. 10) is fairly well reproduced by the model because the comparatively large amounts of free surface water provide a more appropriate context for the basic dissolution mechanisms simulated by DEWS.

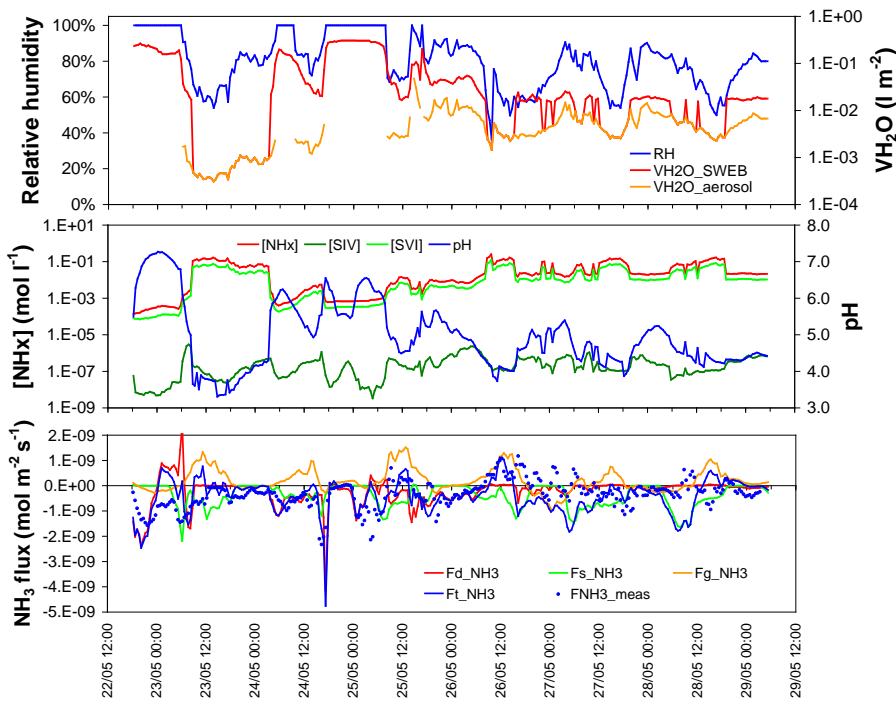


Figure 8. Example run of DEWS applied to cut grassland in moderately wet spring conditions during the GRAMINAE Braunschweig experiment. See text for details.

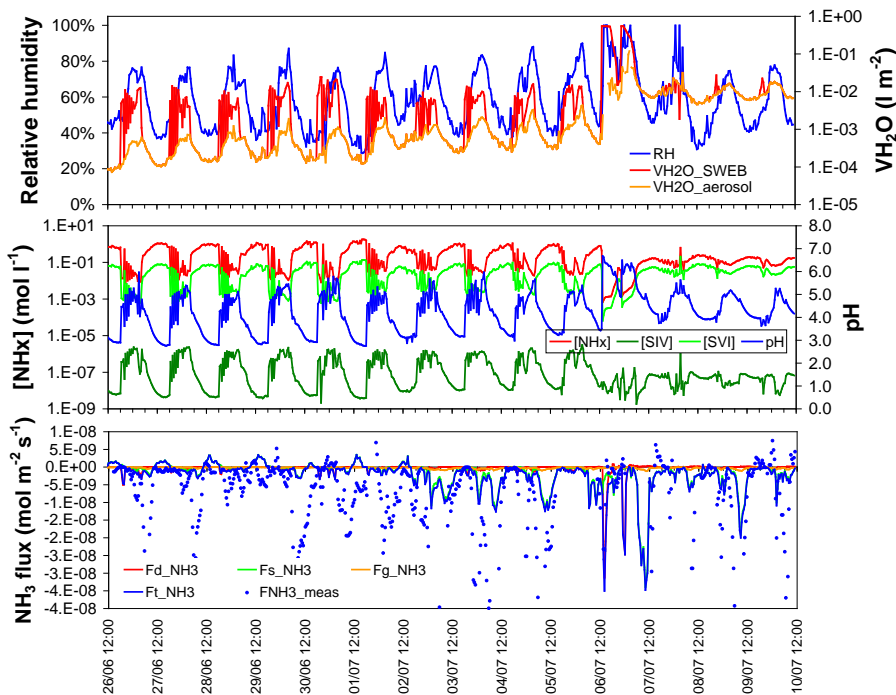


Figure 9. Example run of DEWS applied to mediterranean forest in dry summer conditions during the ECLAIRE Bosco Fontana experiment. See text for details.

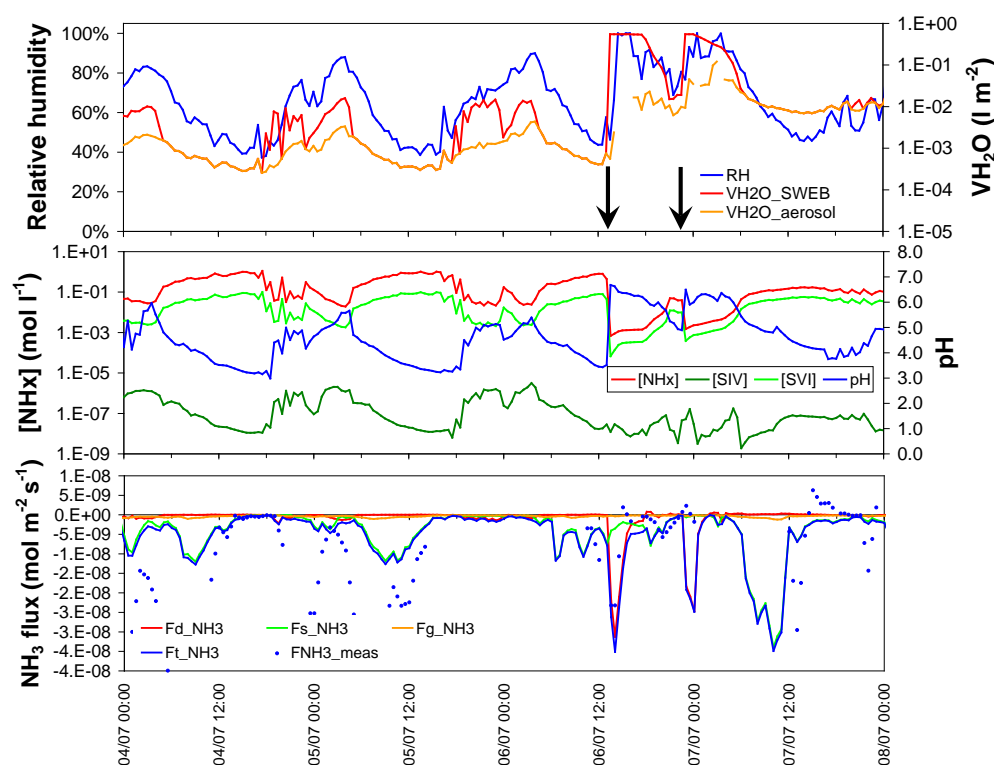


Figure 10. Focus on a 4-day period during the Bosco Fontana experiment, showing the impact of two rain events (black arrows, afternoon and evening of 06/July) on simulated non-stomatal NH_3 deposition (F_d).

The contribution of the AIOMFAC model to leaf surface solution chemical modelling is further illustrated in Fig. 11 by the comparison of the equilibrium surface potentials (partial pressures) for NH_3 , HNO_3 and HCl simulated by DEWS vs AIOMFAC. In DEWS these equilibrium partial pressures are computed by simple application of Henry's law for the partitioning between gas and water phases, accounting for pH effects and using a simplistic parameterisation for activity effects. By contrast, in AIOMFAC there is a much more advanced, state-of-the-art treatment of gaseous-liquid-solid interactions and equilibria, where the excess Gibbs energy is computed explicitly from long-range (ionic strength), medium range (cation-anion, ion-dipole) and short range (dipole-dipole, dispersion) interactions (Zuend et al, 2008, 2010). During the first part of the Bosco Fontana experiment, there is a reasonable agreement between DEWS and AIOMFAC for HNO_3 and HCl , with typical X_d values in the range $1\text{E-}9$ to $1\text{E-}8$ mol m^{-3} (in air) in daytime, but there is a considerable discrepancy (by a factor of 10-100) for NH_3 . After the rain events of 06/Jul, values for HNO_3 and HCl increase sharply in AIOMFAC, while those for NH_3 decrease, but not in DEWS, reflecting the impact of rainfall composition on surface chemistry. A full coupling of DEWS and AIOMFAC could, in future, shed further light on the complex interactions between gas-liquid-solid equilibria on the leaf surface and deposition of NH_3 and acid gas pollutants.

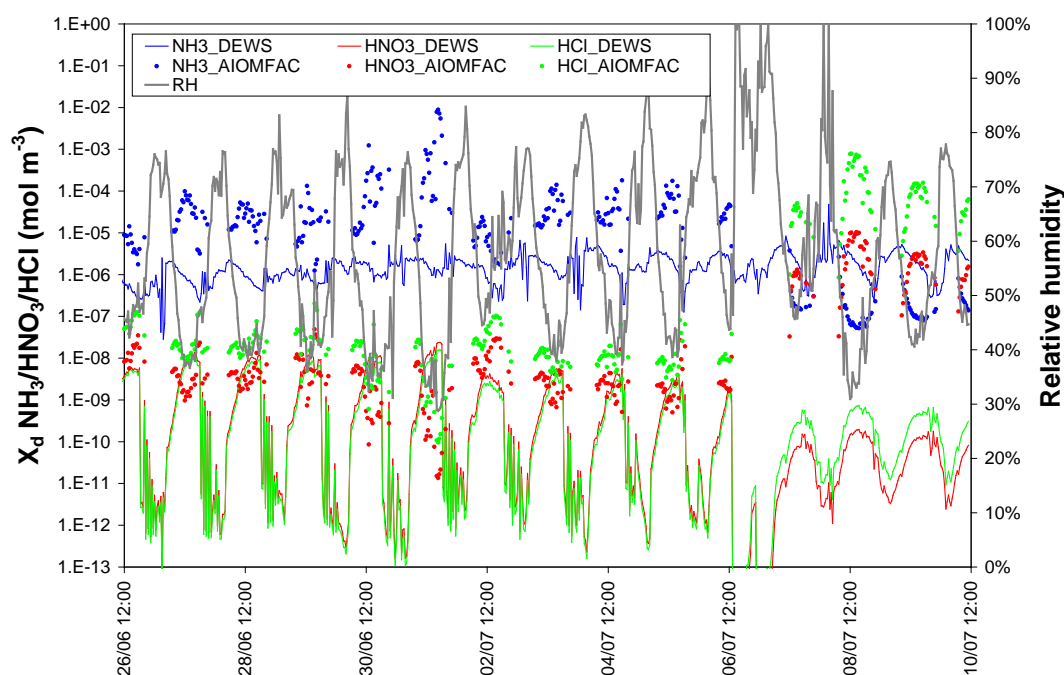


Figure 11. Time series of the equilibrium gaseous NH_3 , HNO_3 and HCl concentrations (X_d) above leaf surface solutions, as predicted by the DEWS and AIOMFAC thermodynamic modules, during the Bosco Fontana experiment.

4.3 Evaluation of the correction scheme for near-surface $\text{NH}_4\text{NO}_3/\text{NH}_3/\text{HNO}_3$ volatilisation

This parameterisation has been implemented in the EMEP MSC-W chemistry and transport model and compared with a reference run, in which $V_d/(u^* \times \text{LAI})$ was set to a constant value of 0.008 independent of L . We analysed the performance of the two parameterisations against measurement data, although an assessment of the performance of the correction scheme is not straight-forward. The parameterisation has been developed from the limited amount of nitrate flux data available and there are no independent flux datasets available for verification. Thus, the parameterisation is expected to reproduce the flux at the measurement sites, as long as the model resolution is sufficient and the model adequately predicts the driving parameters.

An alternative approach is to assess the performance of the updated model against concentration measurements at sites for which no flux data were available. While independent, the skill of the model in reproducing the concentration measurements does not only depend on the parameterisation of the surface sink but also on the ability of the model to reproduce emissions of the precursor gases (NH_3 and NO_x), atmospheric chemistry (e.g. HNO_3 production from NO_x) and atmospheric transport patterns.

Figure 12 shows an example of how well the two model variants (with and without evaporation) reproduces fine nitrate concentrations measured at two field sites during summer 2012, which includes data from one of the supersites of the PEGASOS/ECLAIRE Po Valley campaign at Bosco Fontana, Italy. At this site, there is evidence that the revised model parameterisation provides a somewhat better model performance overall, especially during the first 10 days of the campaign. However, individual days can also be found on which model performance deteriorates (e.g. 25 June and 7 July), while on some other days both versions of the model do not capture the measured concentration. The discrepancy on those days is too large to be caused by the deposition routine and is more likely to be linked to problems in predicting emissions or transport. Overall, evaporation lowers concentrations by 37% at this site during this measurement period.

At a second, more rural measurements site, situated in Scotland, the model with the revised deposition routine clearly provides a closer fit to the measurements. Here the average decrease in concentrations is

22%. One difference between the two measurement sites is that Bosco Fontana is situated in the middle of an area with large agricultural NH_3 and industrial NO_x emissions, while at the Scottish site, high concentration events as observed during this example period are due to longer range transport.

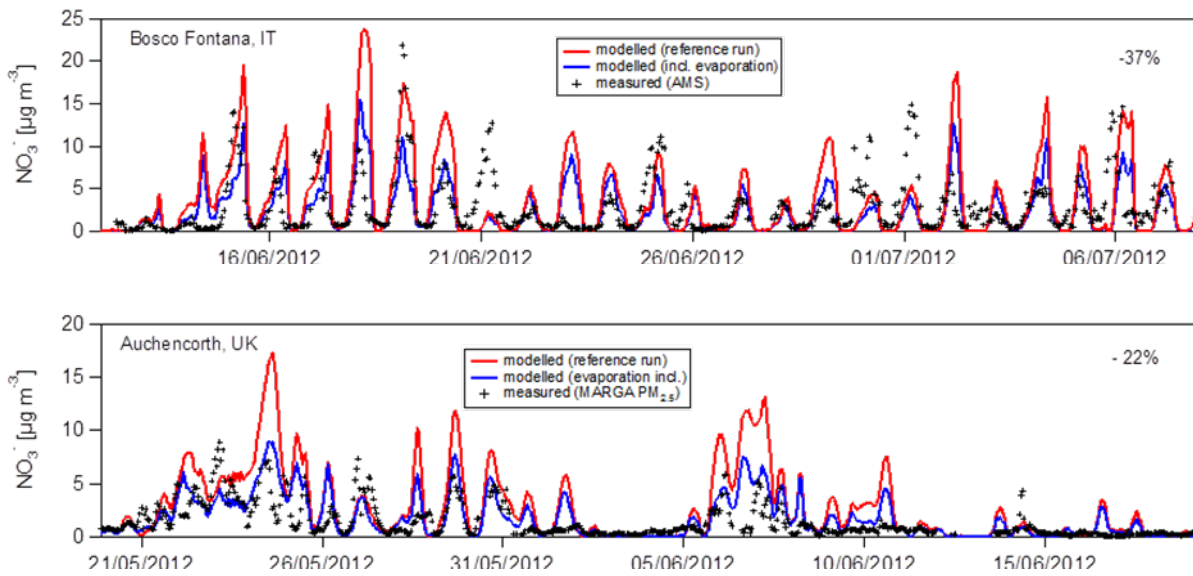


Figure 12. Comparison of the fine nitrate concentration at Bosco Fontana, Italy (PEGASOS/ECLAIRE Po Valley campaign) and a Auchencorth Moss, Scotland, UK, predicted with the EMEP4UK chemistry and transport model, using an aerosol dry deposition velocity for fine nitrate, which does not include (reference run) and does include the effect of evaporation during deposition.

5. Milestones achieved:

MS18 - Incorporation of results from flux monitoring data generated within ÉCLAIRE into modelling framework

Ammonia flux data in background conditions from Posieux, Bosco Fontana, Grignon and Speulderbos were processed using the Massad-Nemitz-Sutton 2010 bi-directional scheme (see deliverable D3.2).

Ammonia flux measurements from Bosco Fontana were used to evaluate the DEWS leaf surface wetness chemical model (see section 4.2).

Ammonia emission fluxes following manure spreading at Grignon and Posieux were processed using the VOLT' AIR model and meta-model (see section 4.1).

MS19 - Calibration of model parameterisation completed

The VOLT' AIR Γ_g meta-model, derived from multiple runs of VOLT' AIR (see Deliverable 3.1), was parameterized for three types of nitrogen fertilizer, and verified against field measurements for cattle slurry.

The Massad-Nemitz-Sutton (MNS-2010) bi-directional scheme for NH_3 exchange was re-parameterised on the basis of ECLAIRE and other datasets (see deliverable D3.2)

6. Deviations and reasons:

This deliverable was delayed until the final month of the project. The delay occurred because there was a change of strategy to tackle the objectives of WP4 in general and of this deliverable in particular. The original plan was to improve parameterisations for pollutant exchange in *existing models*, while we instead chose to address these objectives by *creating a new multi-layer surface exchange model (ESX)*. The basic idea was to reduce empiricism and increase the representation of mechanisms from first physical and chemical principles. Creating a new model takes much more time than to re-parameterize/re-calibrate and existing one, and there were inevitable set-backs and coding issues to deal with. Since this deliverable dealt with some component modules for ESX (for ex. DEWS), there were knock-on effects of delays in ESX.

7. Publications:

- Bertolini T., Flechard, C.R., Fattore, F., Nicolini, G., Stefani, P., Stefano, M., Valentini, R., Vaglio, L.G., Castaldi, S. (2015). Dry and bulk atmospheric nitrogen deposition to a West-African humid forest exposed to terrestrial and oceanic sources. *Agricultural and Forest Meteorology* (in press).
- Burkhardt J., Hunsche M. (2013): 'Breath figures' on leaf surfaces – formation and effects of microscopic leaf wetness. *Frontiers in Plant Science*, 4; doi: 10.3389/fpls.2013.00422. <http://www.frontiersin.org/Journal/10.3389/fpls.2013.00422/full>
- Burkhardt, J., Pariyar, S. (2015) How does the VPD response of isohydric and anisohydric plants depend on leaf surface particles? *Plant Biology* <http://dx.doi.org/10.1111/plb.12402>
- Cieslik, S., Tuovinen, J.-P., Baumgarten, M., Matyssek, R., Brito, P. and Wieser, G., 2013. Gaseous exchange between forests and the atmosphere. *Developments in Environmental Science* 13, 19-36.
- Ferrara R.M., Loubet B., Decuq C., Palumbo A.D., Di Tommasi P., Magliulo V., Masson S., Personne E., Cellier P., Rana G., 2014. Ammonia volatilisation following urea fertilisation in an irrigated sorghum crop in Italy. *Agricultural and Forest Meteorology*, 195-196, 179-191.
- Flechard, C.R., Massad, R.-S., Loubet, B., Personne, E., Simpson, D., Bash, J.O., Cooter, E.J., Nemitz, E. and Sutton, M.A. 2013. Advances in understanding, models and parameterisations of biosphere-atmosphere ammonia exchange, *Biogeosciences* 10, 5183–5225.
- Personne, E., Tardy, F., Générmont, S., Decuq, C., Gueudet, J.-C., Mascher, N., Durand, B., Masson, S., Lauransot, M., Fléhard, C., Burkhardt, J. and Loubet, B., 2015. Investigating sources and sinks for ammonia exchanges between the atmosphere and a wheat canopy following slurry application with trailing hose. *Agric. For. Meteorol.*, 207: 11-23.
- Simpson, D. and Tuovinen, J.-P., 2014. ECLAIRE Ecosystem Surface Exchange model (ESX). In: *Transboundary particulate matter, photo-oxidants, acidifying and eutrophying components. EMEP Status Report 1/2014*, Norwegian Meteorological Institute, pp. 147-154.
- Sutton, M.A.; Reis, S.; Riddick, S.N.; Dragosits, U.; Nemitz, E.; Theobald, M.R.; Tang, Y.S.; Braban, C.F.; Vieno, M.; Dore, A.J.; Mitchell, R.F.; Wanless, S.; Daunt, F.; Fowler, D.; Blackall, T.D.; Milford, C.; Flechard, C.R.; Loubet, B.; Massad, R.; Cellier, P.; Personne, E.; Coheur, P.F.; Clarisse, L.; Van Damme, M.; Ngadi, Y.; Clerbaux, C.; Skjoth, C.A.; Geels, C.; Hertel, O.; Wichink Kruit, R.J.; Pinder, R.W.; Bash, J.O.; Walker, J.T.; Simpson, D.; Horvath, L.; Misselbrook, T.H.; Bleeker, A.; Dentener, F.; de Vries, W. 2013. Towards a climate-dependent paradigm of ammonia emission and deposition. *Philosophical transactions of the Royal Society of London. Series B, Biological sciences* 368 (1621) 10.1098/rstb.2013.0166.

8. Meetings:

(other than annual ECLAIRE General Assemblies)

19-23 March 2012, CEH, Edinburgh. WP4 meeting, launch of ESX project

06-08 May 2013, Univ. Bonn. WP4-ESX meeting

28-29 August 2013, ECN, Amsterdam. DEWS meeting

26-28 May 2014, CEH Edinburgh. Joint C1-ESX meeting; also meeting with G. Mc Figgans / D. Topping of Univ. Manchester

26-29 August 2014, Chalmers Univ., Gothenburg. Coding meeting, ESX-DEWS coupling.

09-13 March 2015, Univ. Bonn. Coding meeting, DEWS-AIOMFAC coupling.

9. Appendix 1: Methodology for the development of the VOLT'AIR Γ_g meta-model

The process-based VOLT'AIR NH_3 volatilization model was used to provide meta-model Γ_g parameters that are comparable and compatible with the Massad, Nemitz and Sutton (2010) framework (MNS-2010), which is first described briefly.

9.1. The basic 2-layer MNS-2010 modelling framework

The MNS-2010 NH_3 exchange scheme is a two-layer resistance bi-directional model that includes a parameterisation of the soil and leaves emission potential. In this model the most sensitive parameters for NH_3 deposition are non-stomatal resistance to NH_3 deposition (R_w) and the stomatal resistance (R_s). Stomatal resistance modelling has been constantly improved in the past 30 years. Improvement of the non-stomatal resistance was the object of the deliverable D3.2.

The direction and magnitude of the NH_3 is mainly driven by the compensation point of the soil and the leaves. The compensation point is the concentration in equilibrium with the considered compartment of the ecosystem. This equilibrium results from a thermodynamical equilibrium between the gaseous and the aqueous phase of NH_3 , mainly driven by temperature, and a chemical equilibrium in the liquid phase, dependent on pH. It is convenient to consider the emission potential, Γ , which is temperature independent and is defined as the ratio of NH_4^+ to H^+ concentration in the water pools of the ground and in the stomates:

$$\Gamma_g = \frac{[\text{NH}_4^+]_{\text{soil}}}{[\text{H}^+]_{\text{soil}}} \quad \text{and} \quad \Gamma_s = \frac{[\text{NH}_4^+]_{\text{apo}}}{[\text{H}^+]_{\text{apo}}} \quad (1)$$

The MNS-2010 scheme provides parameterisations for short-term temporal changes in Γ_g and Γ_s following the field application of mineral and organic fertilisers to agro-ecosystems. Based on the literature review, both ground emission potentials are modelled as exponential decay functions of time with an e-folding time constant $\tau = 2.88$ days:

$$\Gamma_{g,s} = \Gamma_{g,s}^{\text{max}} e^{-t/\tau} \quad (2)$$

Where t is the time in days and $\Gamma_{g,s}^{\text{max}}$ is the maximum initial value of Γ at the time of fertilisation. It is a linear function of the applied N fertiliser dose for the stomatal Γ_s ($\Gamma_{s,\text{max}} = 12.3 * N_{\text{app}} + 20.3$). For Γ_g the maximum value depends on the application:

- For grazing, $\Gamma_{g,\text{max}} = 4000$, based on the literature review ;
- For organic fertilisation, $\Gamma_{g,\text{max}} = \frac{\text{TAN}_{\text{slurry}}}{10^{-\text{pH}_{\text{slurry}}}}$, where TAN is the total ammoniacal nitrogen content of the slurry.
- For mineral fertilisation, $\Gamma_{g,\text{max}} = \frac{N_{\text{applied}}}{\theta_s M_N l_s h_m 10^{-\text{pH}_{\text{soil}}}}$, where N_{applied} is the applied fertiliser amount (kg N ha^{-1}), M_N is the nitrogen molar mass (14 g mol^{-1}), θ_s is the soil percentage water content (fraction), l_s is the soil layer where fertiliser is applied (0.05 m), h_m is to convert hectares to m ($=10\,000 \text{ m}$) and pH is the pH of the soil solution after fertiliser application.

The time response of Γ_s was evaluated and optimised based on comparison with ECLAIRE datasets in deliverable 3.2. In this work we have improved Γ_g following fertilisation (mineral and organic) using meta-modelling based on the Volt'air volatilisation model.

9.2. Approach for developing a meta-model of NH_3 emission potential following fertilisation

Soil emissions following fertilisers applications are the higher diffuse contributions of tropospheric NH_3 . It is therefore essential to improve the parameterisation of these emissions, of which Γ_g is the main driver.

There exist a number of process-based models that predict NH_3 volatilisation following fertiliser application in the field. However these models are two complex and computer demanding to be included directly in a CTM. A convenient way to overcome this difficulty is to use meta-modelling concepts. The concept is to fit an empirical function to the model output using a set of input variables and parameters that covers the maximum range of possibility, for the empirical function to be as representative as possible. This method was applied in the deliverable 3.1 to develop a “generalised NH_3 emission model” for three different fertiliser types (slurry, farm yard manure (FYM) and mineral fertiliser) based on simulation results for a large range of European climate and soil conditions with the the Volt’air process-based model (Genermont and Cellier, 1997). The generalised NH_3 emission meta-model provided the *cumulated volatilisation over 30 days* and the *duration of the emissions* defined as the time at which the cumulated emissions attained 95% of the total volatilisation.

In this work, we have developed a meta-model for Gamma based on equation (2):

- The *duration of the emissions* provided by the generalised NH_3 emission meta-model (deliverable 3.1) to determine the e-folding time τ .
- The $\Gamma_{g,\max}$ was determined from Volt’air outputs, based on the same set of simulations as those used for deliverable 3.1. A meta-model of $\Gamma_{g,\max}$ was proposed for mineral and organic fertilisation.

9.3. VOLT’AIR simulations used for the meta-model

The ammonia volatilisation meta-model developed based on Volt’air simulation is detailed at length in deliverable 3.1. In short, it is based on multiple simulations of the mechanistic ammonia volatilisation model Volt’air (Genermont and Cellier, 1997), on a European database. The European Soil Database (ESDB, Panagos, 2006; Panagos et al, 2012) was used after mapping from soil types (FAO 1985 classification) to soil textures (USDA classification using the FAO Harmonized World Soil Database (FAO/IIASA/ISRIC/ISS-CAS/JRC, 2008). The simulations were based on 522 polygons representative of soil conditions. The JRC European soil pH map (Böhner et al., 2008) was used to estimate soil pH at the centroid of each polygon. The hourly meteorological variables (air temperature, water vapour pressure, solar radiation, wind speed, rainfall and soil moisture index) were taken from the EMEP chemical transport model in 2008 in each of the 522 soil polygon centroids. Typical slurry and Farmyard (FYM) parameters for European situations were used and urea ammonium nitrate solution (UAN) was used as a typical mineral nitrogen fertiliser. Two application dates were chosen for representing spring and summer application periods giving a total of 1044 simulations. Each simulation consisted in a 1 month spin up simulation followed by a 1 month simulation following application.

Table 1: Summary of the application parameters used in the three Volt’air scenarios

	Slurry	FYM	UAN
Application rate	60 m ³ ha ⁻¹	60 t ha ⁻¹	100 kg N ha ⁻¹
Total ammoniacal Nitrogen content	0.862 g kg fresh matter → 52 kg NH ₄ -N ha ⁻¹	0.53 g kg fresh matter → 32 kg NH ₄ -N ha ⁻¹	25% of total N as NH ₄ -N + 50% of total N as Urea-N
pH	7.0	8.0	5.77
Dry mater content (%)	4.69	20.0	(aqueous solution)
Application method	Splash plate	Broadcast	Uniform application
Application dates	First day of April and September	First day of April and September	First day of April and September

9.4. The generalised NH_3 emission meta-model

The generalised NH_3 emission meta-model predict the cumulated emission after 30 days as percentage of the total ammoniacal nitrogen applied. The final form of the meta-model was chosen by comparing the statistical performance of three different meta-model formulations:

1. MLRL: The Multiple linear regression of the logarithm of the cumulated emission after 30 days $\ln(\%TAN)$;
2. MLRT: Multiple linear regression of the transformed cumulated emission after 30 days $\ln\left(\frac{1}{(100-\%TAN)-1}\right)$.
3. LR: Logistic residual model. This formulation fits a logistic curve to the temperature response of the cumulated emission after 30 days (%TAN) and then fits the residuals using multiple linear regression of the remaining soil and meteorological variables.

The MLRT approach was retained as it gave better performance than the MLRL model and a similar performance as the LR approach. The coefficient values for this formulation for the three fertiliser types are shown in Table 2.

Table 2: Coefficient values used in the NH₃ emission meta-models. The mean and cumulated meteorological data are averaged over the month following fertilisation

Coefficient	Slurry	FYM	UAN
Constant	6.03	4.91	-7.21
Mean Air Temperature (°C)	0.356	0.117	0.268
Mean Water Vapour Pressure (kPa)	-2.19	-1.11	-1.73
Mean Solar radiation (W m ⁻²)	-0.00735	-0.00515	-0.00331
Mean wind speed (m s ⁻¹)	0.103	0.100	0.234
Total rainfall (mm)	-0.00497	-0.00239	-0.00527
Latitude (°N)	-0.112	-0.0609	-0.0686
Clapp and Hornberger texture class	-0.0642	--	--
Soil pH (H ₂ O)	--	-0.0444	1.03
Sand (0-100%)	-0.00810	--	--
Clay (0-100%)	--	-0.00585	-0.0102
Soil organic C content (0-100%)	0.255	--	0.108

Another set of meta-models was parameterised for the time needed to volatilise 95% of the total 30 day emissions, using the same meta-model structure (Table 3) which included the %TAN volatilised from the first set of models as a parameter.

Table 3: Coefficient values used in the meta-models for the number of days to 95% of total emissions. The mean and cumulated meteorological data are averaged over the month following fertilisation.

Coefficient	Slurry	FYM	UAN
Constant	5.28	32.2	2.49
30 day meta-model emission (% TAN)	-0.0232	-0.237	0.00797
Mean Air Temperature (°C)	--	0.755	-0.159
Mean Water Vapour Pressure (kPa)	-2.45	-11.1	--
Mean Solar radiation (W m ⁻²)	0.00324	-0.0162	0.00922
Mean wind speed (m s ⁻¹)	0.359	0.661	0.0865
Total rainfall (mm)	-0.00700	-0.00980	-0.00404
Latitude (°N)	--	-0.214	0.0321
Soil pH (H ₂ O)	-0.277	-0.590	-0.363
Sand (0-100%)	0.0170	0.0133	--
Bulk density (g cm ⁻³)	-2.34	--	-1.47

9.5. Determination of the e-folding time τ of the ground emission potential based on the duration of emissions of the meta-model

The e-folding time τ of equation 2 was determined from meta-models for the number of days to 95% of total emissions assuming the NH_3 emission potential Γ_g and the volatilisation followed the same daily dynamics. Indeed, assuming the flux is following an exponential decay with time, the cumulated flux is deduced as:

$$F_{\text{NH}_3}(t) = F_{\text{NH}_3}^{\text{max}} e^{-t/\tau} \quad (3)$$

$$F_{\text{NH}_3}^{\text{cumulated}}(t) = \int_0^t F_{\text{NH}_3}^{\text{max}} e^{-t'/\tau} dt' \quad (4)$$

$$F_{\text{NH}_3}^{\text{cumulated}}(t) = F_{\text{NH}_3}^{\text{max}} \times \tau \times (1 - e^{-t/\tau}) \quad (5)$$

The number of days to 95% of total emissions $t_{95\%}$ is then deduced from (5) recognising that $F_{\text{NH}_3}^{\text{cumulated}}(t_{95\%}) = 0.95 \times F_{\text{NH}_3}^{\text{max}}$, hence leading to the following equality:

$$\frac{F_{\text{NH}_3}^{\text{cumulated}}(t_{95\%})}{F_{\text{NH}_3}^{\text{max}}} = 0.95 = (1 - e^{-t_{95\%}/\tau}) \quad (6)$$

Which after simple manipulations gives:

$$\tau = \frac{-t_{95\%}}{\ln(0.05)} \approx \frac{t_{95\%}}{3} \quad (7)$$

Hence the e-folding time is simply the number of days to 95% of total emissions $t_{95\%}$. Figure A1 shows that emissions following manure application are much shorter than the ones following slurry application. Urea ammonium nitrate application leads, even to much longer emission periods. It is clear from Figure A1 that the average period of 2.88 day used in MNS-2010 is too large for manure and slurry, and too short for mineral fertiliser. It also shows that using a single value for τ is over-simplistic.

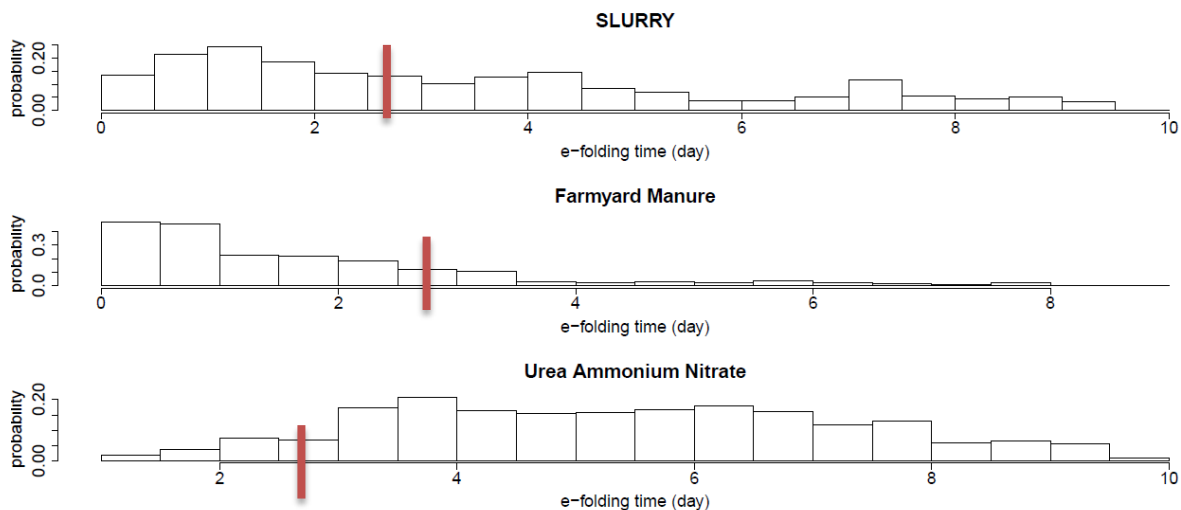


Figure A1. Probability distribution of the e-folding decay time τ (in days) for Γ_g for the three types of fertiliser modelled. By contrast the e-folding time derived in MNS-2010 of 2.88 day is given with a red bar on each graph.

9.6. Developing the meta-model of $\Gamma_{g,\text{max}}$

The initial maximum value $\Gamma_{g,\text{max}}$ was calculated at each site location and for each period (“summer” and “spring”), from ammonium concentration in the water pool and soil pH in the first soil layer of the Volt’air model outputs. Since $\Gamma_{g,\text{max}}$ is directly dependent on the amount of N applied, it is normalised by the amount of ammoniacal nitrogen applied TAN_{applied} (kg N ha^{-1}):

$$\frac{\Gamma_{g,max}^{Volt'air}(site,period)}{TAN_{applied}} = \frac{[NH_4^+]_{soil}(0-2\text{ cm},1\text{ h})}{TAN_{applied} \times 10^{-pH_{soil}}} \quad (8)$$

The $\Gamma_{g,max}^{meta-model}$ meta-model was then computed using a multiple linear regression of the logarithm of $\Gamma_{g,max}^{Volt'air}$:

$$\ln\left(\frac{\Gamma_{g,max}^{meta-model}(site,period)}{TAN_{applied}}\right) = [a_0 + \sum_{1:m} a_i x_i(site,period)] \quad (9)$$

where $a_0 \dots a_m$ are model coefficients and $x_1 \dots x_m$ are the soil and meteorological variables at the time of application (not averaged) which are by nature dependent on the sites and periods. The linear regression retrieves the $a_0 \dots a_m$ coefficients that minimize the mean square error of the logarithms using the linear model (lm) function in R:

$$MSE = \frac{1}{N} \sum_{all\ sites\ and\ periods} \left[\ln\left(\frac{\Gamma_{g,max}^{Volt'air}}{TAN_{applied}}\right) - \ln\left(\frac{\Gamma_{g,max}^{meta-model}}{TAN_{applied}}\right) \right]^2 \quad (10)$$

The best model was performance was chosen using a stepwise algorithm where each single parameter is successively added and dropped. The best model is the one that maximises the Akaike An Information Criterion ($AIC = -2\ln(L) - 2(N_p + 1)$), where L is the likelihood and N_p the number of parameters of the model.

Table 4 gives the parameters of the meta-model for each fertiliser type, while Figure A2 and Table 5 give the goodness of fit of the meta-model against Volt'air simulations. The statistical indicators show that for UAN and slurry the meta-modelling approach gives very reliable estimates of the model (model efficiency > 0.93, RRMSE < 0.05), while for Manure (FYM), the meta-model fails to correctly reproduce the Volt'air model (model efficiency = 0.59), although the RRMSE remains very small (, RRMSE = 0.011). The difficulty in finding the FYM meta-model comes from a non-linear response of the logarithm of the volatilisation to the air temperature in this case. The meta-model structure (Table 4) shows that ammonia volatilisation from UAN is highly correlated to the soil pH and rainfall at the time of application plays a great role in diminishing volatilisation in both UAN and Slurry. FYM is first correlated to air relative humidity.

Table 4. Coefficient values of the meta-model of $\ln\left(\frac{\Gamma_{g,max}^{meta-model}}{TAN_{applied}}\right)$. The meteorological data to use here are hourly averaged values at the time of application. Both estimates and standard errors are given. UAN: Urea Ammonium Nitrate. FYM: Farnyard Manure

Coefficient	Slurry		FYM		UAN	
	Estimate	Estimate	Estimate	Std. err.	Estimate	Std. err.
a_0	10.31132	0.01714	10.55287	0.02871	-7.17741	0.05285
Air temperature (°C)	0.01462	0.00071	-0.01375	0.00186	0.02298	0.00136
Water vapour pressure (kPa)	-0.11794	0.00953	-0.23481	0.02640	-0.07090	0.01824
Global radiation (W m ⁻²)	0.00032	0.00001			0.00004	0.00002
Wind speed (m s ⁻¹)	0.01511	0.00089	-0.01696	0.00243	-0.00879	0.00170
Rainfall (mm)	-0.61450	0.00962	-0.04482	0.02700	-0.17304	0.01841
SWC (0-2 cm) (g/kg dry soil)	-0.00019	0.00004	0.00056	0.00010	-0.00277	0.00007
Soil pH	-0.00716	0.00213			2.25562	0.00817
Clay content (%)	0.00177	0.00020	-0.00410	0.00049	-0.00104	0.00038
Silt content (%)	0.00129	0.00014	0.00086	0.00040	-0.00288	0.00027

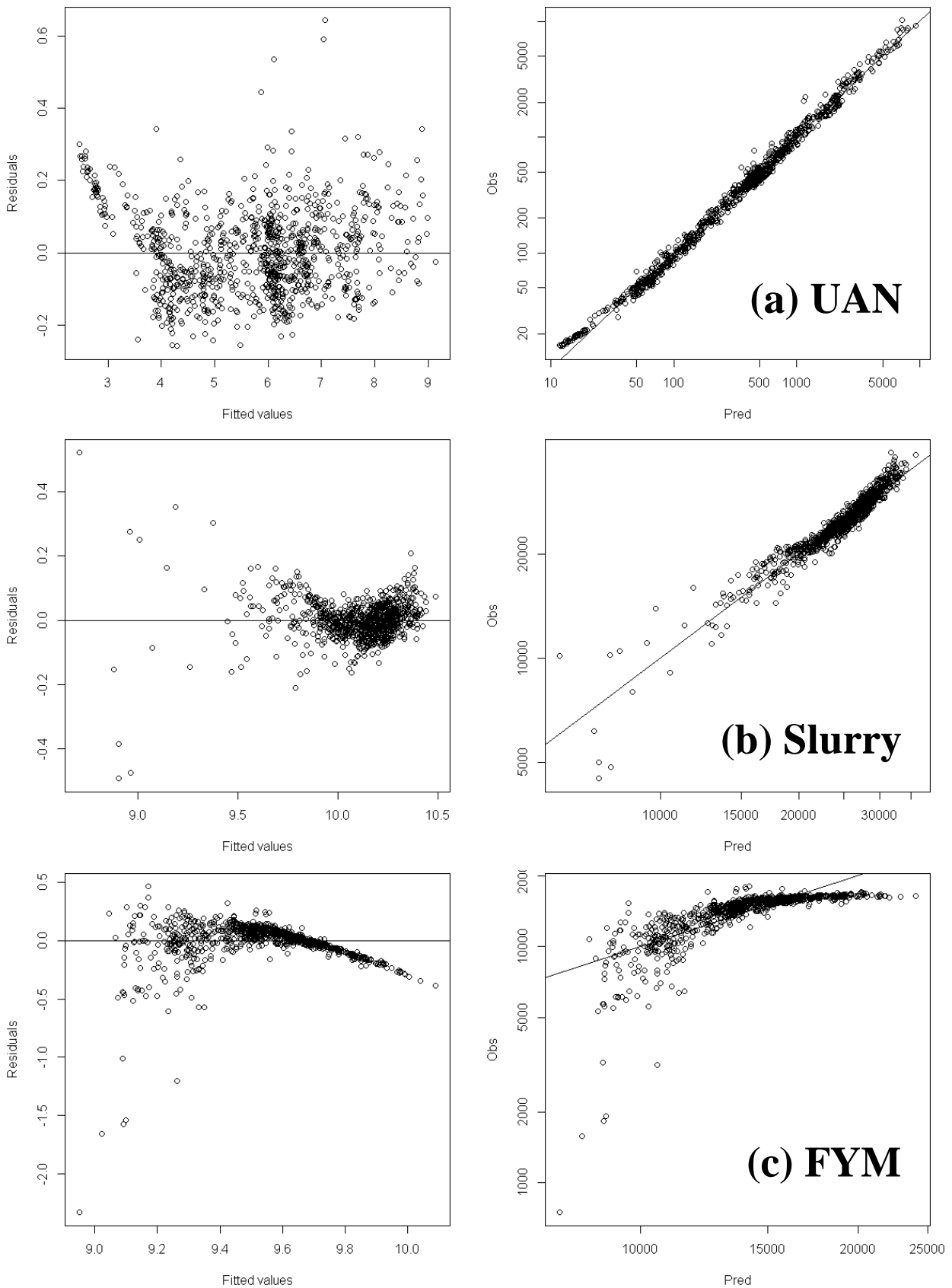


Figure A2. Residuals versus observed and predicted versus observed values of $\Gamma_{g,max} / N_{applied}$. Note that “observed” values actually refer to those simulated by the “full” VOLT’AIR (i.e., not measurements), while “predicted” are those given by the meta-model with the parameters as given in Table 4.

Table 5: Quality of fit of the meta-model of $\Gamma_{g,max}$ for Urea Ammonium, Nitrate (UAN), Slurry, and Farmyard Manure (FYM).

Coefficient	UAN	Slurry	FYM
RMSE	197	1260	1640
RRMSE	0.26	0.050	0.11
MAE	75	960	1200
RMAE	0.097	0.038	0.084
Bias	25.2	42.8	98.4
EF	0.98	0.93	0.59

RMSE = Root Mean Square Error, RRMSE = Relative Root Mean Square Error, MAE = Mean Average Error, RMAE = Relative Mean Average Error, EF = Efficiency

The meta-model of $\Gamma_{g,max}$ gives median values twice as large for slurry than for farmyard manure and much smaller values for UAN on average but with a much larger variability for that latter case (Fig. A3). This reflects the dependency of NH_3 volatilisation from UAN to soil pH. Volatilisation from slurry and manure are less dependent on soil pH in these simulations as the pH of the product drives the emissions in Volt'air. The very small values obtained for UAN actually shows that the exponential decay function may be too simplistic for urea-like fertilisers whose dynamics shows a rather Gaussian shape.

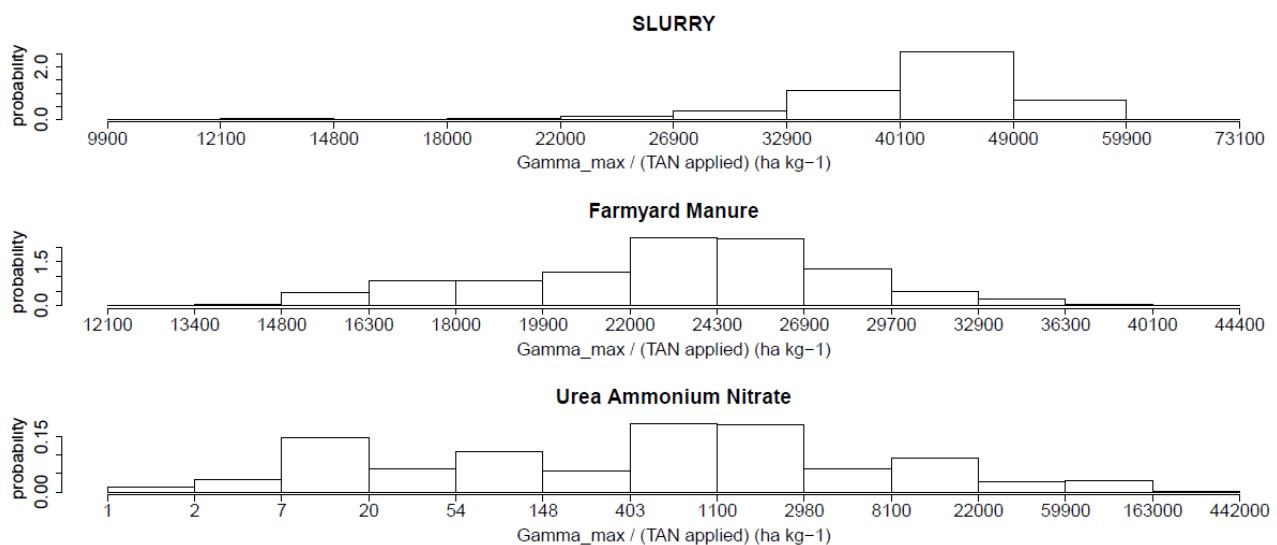


Figure A3. Histograms of $\Gamma_{g,max}$ (normalized by the applied TAN dose) obtained by meta-modelling at the 1044 sites \times period for slurry, Farmyard Manure and UAN.

We should stress here that these results are based on a limited set of simulations of VOLT'AIR where only a few applications techniques were simulated. Extension of these results to techniques such as slurry incorporation, and to variable slurry and manure types, including changing substrate pH and density, is an ongoing work, which will be fed into an updated meta-model (see WP 3 periodic report).

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