Biogeosciences

Understanding emissions of ammonia from buildings and the application of fertilizers: an example from Poland

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Abstract. A Europe-wide dynamic ammonia (NH_3) emissions model has been applied for one of the large agricultural countries in Europe, and its sensitivity on the distribution of emissions among different agricultural functions was analyzed by comparing with observed ammonia concentrations and by implementing all scenarios in a chemical transport model (CTM). The results suggest that the dynamic emission model is most sensitive to emissions from animal manure, in particular how animal manure and its application on fields is connected to national regulations. To incorporate the national regulations, we obtained activity information on agricultural operations at the sub-national level for Poland, information about infrastructure on storages and current regulations on manure practice from Polish authorities. The information was implemented in the existing emission model and was connected directly with calculations from the Weather Research and Forecasting model (WRF). The model was used to calculate four emission scenarios with high spatial (5 km × 5 km) and temporal resolution (3 h) for the entire year 2010. In the four scenarios, we have compared a constant emission approach (FLAT), scenario (1) against (2) a dynamic approach based on the Europe-wide default settings (Skjøth et al., 2011, scenario DEFAULT); (3) a dynamic approach that takes into account Polish practice and less regulation compared to Denmark (POLREGUL); (4) a scenario that focuses on emissions from agricultural buildings (NOFERT). The ammonia emission was implemented into the chemical transport model FRAME (Fine Resolution Atmospheric Multi-pollutant Exchange) and modelled ammonia concentrations were compared with measurements. The results for an agricultural area suggest that the default

setting in the dynamic model is an improvement compared to a non-dynamical emission profile. The results also show that further improvements can be obtained at a national scale by replacing the default information on manure practice with information that is connected with local practice and national regulations. Implementing a dynamical approach for simulation of ammonia emission is a reliable but challenging objective for CTM models that continue to use fixed emission profiles.

1 Introduction

Ammonia is mainly emitted to the atmosphere from agricultural operations (Bouwman et al., 1997), but also from natural sources (e.g. Andersen et al., 1999; Hansen et al., 2013; Sutton et al., 1997). Agriculture's share in total ammonia emission in the European Union was 94 % in 2010 (European Environment Agency 2014, www.eea.europa.eu) and is largely from animal excreta and fertilizers. The contribution of natural emission is negligible compared to agricultural for most of the European area (Simpson et al., 1999; Friedrich, 2007). Ammonia is the main alkaline gas in the atmosphere (Hertel et al., 2012) and is responsible for neutralizing acids (sulphuric and nitric acid) formed through the oxidation of sulphur dioxide (SO_2) and nitrogen oxides (NO_x; Seinfeld and Pandis, 2006). This leads to the creation of ammonium (NH_4^+) salts, which are incorporated in atmospheric aerosols (Banzhaf et al., 2013; Reis et al., 2009). The emission of NH_3 makes a major contribution to the formations of particulate matter, PM_{10} and $PM_{2.5}$ (de Meij et al., 2009; Werner

et al., 2014), accounting for up to 50 % of the total mass of $PM_{2.5}$ (Anderson et al., 2003). As such, ammonia-containing aerosols are a very important component in regional and global aerosols processes (Xu and Penner, 2012). There is a direct climate penalty on ammonia emission (Skjøth and Geels, 2013), mainly because the volatilization potential of ammonia nearly doubles for every 5 °C increase in temperature (Sutton et al., 2013). In the fifth report of IPCC, ammonia emission is highlighted as an important component with a considerable feedback effect on climate and air quality that remains to be understood (IPCC, September 2013). Therefore, there is a need to improve the descriptions of ammonia emission models and advance the level of input data to these models (Flechard et al., 2013; Guevara et al., 2013; Wichink Kruit et al., 2012) and correspondingly use them with chemistry transport models. Ideally, this improved approach should directly use results from climate or numeric weather prediction models (Sutton et al., 2013) because the fluxes of ammonia with the surface are directly and non-linearly related to meteorology (Baklanov et al., 2014).

Ammonia affects the acidification of European soils that arises from the deposition of N from the atmosphere (Sutton et al., 2009; Theobald et al., 2009). The two governing processes for nitrogen deposition are wet deposition of ammonium-containing aerosols and dry deposition of ammonia (Bash et al., 2013; Hertel et al., 2012). Ammonia also contributes to the eutrophication of terrestrial ecosystems and surface waters and the development of a lower tolerance to stress in woodland and forests (Sutton et al., 1998, 2009). This eutrophication leads to loss of plant diversity in a wide range of habitats (Emmett, 2007; Jones et al., 2011; Stevens et al., 2004). Nitrogen deposition exceeds the critical loads in most European countries, such as France (van Grinsven et al., 2012), the Netherlands (Jones et al., 2011), Belgium (Jones et al., 2011), Germany (Nagel and Gregor, 2001) and Poland (Hettelingh et al., 2009; Kryza et al., 2013a). The regions with the highest nitrogen deposition are the areas with intense agricultural production, high ammonia emission and corresponding high deposition of ammonia containing compounds (Hertel et al., 2012; Wichink Kruit et al., 2012). The calculation of maps of critical load exceedance require chemical transport models (CTMs) to generate estimates of nitrogen deposition (Flechard et al., 2013). These exceedance maps generally require high spatial and temporal resolution in the atmospheric models (Geels et al., 2012; Mues et al., 2014) and it has been shown that this requires detailed information on emission from different agricultural operations (e.g. Skjøth et al., 2011). These operations also rely on national legislations on manure management (e.g. Gyldenkærne et al., 2005), regional husbandry methods (e.g. Skjøth et al., 2011), as well as prevailing crops and use of mineral fertilizer (Gyldenkærne et al., 2005; Misselbrook et al., 2006). This information can be obtained from agricultural databases in countries like Denmark (e.g. Gyldenkærne et al., 2005), the Netherlands (van Pul et al., 2008) and the

Table 1. The functions describing the temporal variation in NH_3 emissions from various activities*.

Function	Description	Required meteorological parameters
Fct1	Animal houses with forced ventilation	W_i, T_i
Fct2	Open animal houses	W_i, T_i
Fct3	Manure storage	W_i, T_i
Fct8	Spring application of manure on bare soil	$W_{corr} T_{corr}$
Fct9	Application of manure on crops	$W_{corr} T_{corr}$
Fct10	Summer application of manure	$W_{corr} T_{corr}$
Fct11	Autumn application of manure	$W_{corr} T_{corr}$
Fct12	Spring application of fertilizers	$W_{corr} T_{corr}$
Fct13	Summer application of fertilizers	$W_{corr} T_{corr}$
Fct14	Emission related to grassing cattle	$W_{corr} T_{corr}$
Fct15	Emission related to ammonia treated straw	$W_{corr} T_{corr}$

* Functions Fct4-Fct7 have not been simulated in this study (Fct4- Winter crops, Fct5-Spring crops, Fct6-Later spring crops, Fct7- Grass).

UK (Hellsten et al., 2008), but has so far not been available in countries with substantial ammonia emissions such as France, Italy and Poland. Simplified approaches to agricultural production methods (activity data) have therefore been applied in existing models that aim to make European-scale calculations (Skjøth et al., 2011), which will decrease the quality of the results. It has therefore been highlighted that there is a need to obtain national and detailed activity data and integrate this information into models (Flechard et al., 2013).

The aim of this paper is to obtain activity information on agricultural operations at the subnational level for Poland, one of the largest agricultural countries in Europe, and implement these data in an existing ammonia emission model (Skjøth et al., 2004, 2011). We will connect the model directly with the meteorological calculations from the Weather Research and Forecasting model (WRF, Skamarock and Klemp, 2008) according to the suggestion of Sutton et al. (2013).

With this we will compare a constant emission approach (FLAT), scenario (1) against (2) a dynamic approach based on the Europe-wide default settings (Skjøth et al., 2011, scenario DEFAULT); (3) a dynamic approach that takes into account Polish practice and less regulation compared to Denmark (POLREGUL); (4) a scenario that focuses on emissions from agricultural buildings (NOFERT). We will test all four scenarios for a full year with a simplified CTM in order to minimize the computational penalty and discuss the results from our four scenarios against related results that have been obtained for Denmark (Skjøth et al., 2011), Germany (Skjøth et al., 2011) and France (Hamaoui-Laguel et al., 2014).

2 Methodology

2.1 Emission model

NH_3 emissions have been calculated with a dynamic model originally developed for Denmark. The fundamentals of the model are provided by Gyldenkærne et al. (2005) and Skjøth

et al. (2004, 2011). The general idea behind the emission model is to use the gridded annual total NH$_3$ emissions (data described in the next section) and to use available activity data to make a disaggregation of the gridded annual totals into specific agricultural sectors with a similar emission pattern. The emission from each sector then uses a parameterization that depends on both the volatilization as a function of meteorology and the temporal pattern of the activity. This creates a set of additive continuous emission functions, denoted as Fct$_i$, typically with a time resolution of 1 or 3 h. The methodology allows for either normalization to full agreement with national annual official emissions (Skjøth et al., 2011) or freely fluctuating emissions due to meteorology, where the freely fluctuating emissions can be either larger or smaller compared to official estimates (Skjøth and Geels, 2013). The emission parameterization consists of 16 additive continuous functions (Table 1), describing emissions from animal houses and storage (three functions), application of manure and mineral fertilizer (seven functions), emission from crops (four functions), grazing animals, ammonia treatment of straw and road traffic. The individual functions are distributed into two groups: Gaussian functions for short term emission sources and annual functions. Both groups respond to the environmental variables wind speed and temperature. The Gaussian functions are linked to a crop growth model developed by Olesen and Plauborg (1995). The crop growth model uses accumulated temperature sums to determine the timing of the maximum value of the individual Gauss functions. The applied functions were originally derived for Danish conditions and presented in Skjøth et al. (2004) but Skjøth et al. (2011) suggest that a majority of the functions may be directly applicable for a large part of Europe. Default values were therefore implemented by Skjøth et al. (2011) for many European countries. Several of the underlying studies for producing parameterizations, such as the applied growth model (Olesen and Plauborg, 1995) and the farm surveys by Seedorf et al. (1998a, b), are based on Europe-wide studies and are considered appropriate for large geographical regions (Skjøth et al., 2011), while the parameterizations for manure application may need adaptation to national regulation, which is known to change over time (Skjøth et al., 2008).

The functions for emission from livestock housing and manure storage are defined in Eq. (1), and the temporal profile of emission depends on air temperature and wind speed in a given grid cell:

$$\mathrm{Fct}_i = \frac{E_i(x,y)}{\mathrm{Epot}_i(x,y)} \times (T_i(x,y))^{0.89} \times (W_i(x,y))^{0.26} \quad i = [1;3]. \quad (1)$$

$E_i(x,y) \, [\mathrm{kg \, ha^{-1} \, year^{-1}}]$

$\mathrm{Epot}_i(x,y) \, [\mathrm{unitless}]$

$T_i(x,y) \, [^\circ\mathrm{C}]$

$W_i(x,y) \, [\mathrm{m \, s^{-1}}].$

Index i refers to functions 1–3 and x and y refer to the coordinates in the east-west direction and south-north direction. Fct$_1$ refers to animal houses with forced ventilation, Fct$_2$ refers to open animal houses, and Fct$_3$ to manure store. $E_i(x,y)$ is the emission input into the model and $\mathrm{Epot}_i(x,y)$ is the emission potential scaling factor for a given grid cell. The emission potential is used to scale the annual emission up/down in accordance with the officially reported value. Input emission data for Sect. 2.2. $T_i(x,y)$ is the temperature in either animal houses or at the surface of the manure storage, and W is either the ventilation inside the building or the 10 m wind speed above the storages. Ventilation is parameterised by using a large European data set from Seedorf et al. (1998a, b). The derivation is fully described in Gyldenkærne et al. (2005) and uses outside temperatures and management practice in open and closed barns. The emission potential is approximated by the 2 m air temperature, provided by the WRF model and a simple parameterization for temperatures and ventilation in livestock housing systems (Gyldenkærne et al., 2005). The WRF model configuration and evaluation is provided in the following sections.

Functions Fct$_4$–Fct$_{15}$ are related to plant growth and include emissions from plants and emissions due to applications of fertilizer and manure (Table 1). Functions 4 to 15 depend on both air temperature and wind speed. The temporal variations for these activities have therefore been parameterized by the Gauss functions (Eq. 2).

$$\mathrm{Fct}_i = \left(W_{\mathrm{corr}} \times T_{\mathrm{corr}} \frac{E_i(x,y)}{\mathrm{Epot}_i(x,y)} \right)$$
$$\times \frac{e^{\left(\frac{(t-\mu_i(x,y))^2}{-2\sigma_i^2(x,y)} \right)}}{\sigma_i \sqrt{2\pi}} \quad i = [4;15]. \quad (2)$$

Here, μ_i is the mean value for the parameterized distribution. This means that μ_i (given in days or hours) corresponds to the time of the year when the Gaussian function obtains its maximum value. This is the optimal time for the farmer to apply manure according to crop growth. Therefore, the value of μ_i depends on the results from the crop growth model which vary from cell to cell over the entire model grid. σ_i is the spread of the Gauss function, which here parameterizes the amount of time that all farmers carry out this specific activity in each grid cell. A large σ_i means that the emission from the corresponding activity takes place during most of the year, while a small σ_i means that emission takes place during a

few weeks. Here t is the actual time of year. The temperature correction T_{corr} and the emission potential $Epot_i(x, y;$ calculated in the preprocessing) is given in Eqs. (3) and (4).

$$T_{corr} = e^{(0.0223 \times t(x,y))} \quad \text{for } i = 8, 9, 10, 11, 12, 13 \quad (3)$$

$$T_{corr} = 1 \quad \text{otherwise}$$

$$Epot_i(x, y) \neq 1 \quad \text{for } i = 8, 9, 10, 11, 12, 13 \quad (4)$$

$$Epot_i(x, y) = 1 \quad \text{otherwise}$$

The emission from plants is only included in the inventories for a few countries (e.g. Gyldenkærne et al., 2005) and can in principle be calculated on-line in a chemical weather forecast model (e.g. Sutton et al., 2013) by using a mechanism that describes the bi-directional flux (Massad et al., 2010). Emissions from plants were therefore not included here.

2.2 Emissions input data and scenarios

The spatial pattern of NH_3 agricultural emission for Poland for the year 2010 was prepared using the methodology proposed by Dragosits et al. (1998), which is implemented in several atmospheric model systems over the UK (e.g. Oxley et al., 2013). Data on the animal number and fertilizer consumption, provided by the Polish National Statistical Office, were combined with the national emission estimates (KO-BIZE 2013) and spatially allocated using gridded data from the Corine Land Cover map (European Commission, 2005). Data on animal numbers were available at commune level and fertilizer consumption at province level. Detailed information about the calculation methodology used for Poland is described in Kryza et al. (2011). The annual NH_3 emissions were gridded to a spatial resolution of $5 \, \text{km} \times 5 \, \text{km}$ to be in accordance with the mesh in the meteorological model (Fig. 1).

The annual gridded NH_3 emissions were then used to construct four scenarios, termed FLAT (1), DEFAULT (2), POLREGUL (3) and NOFERT (4) (Table 2). Applying the scenarios DEFAULT and FLAT shows the advantage of implementation of the dynamic emission model (DEFAULT) instead of using a constant emission profile (FLAT). This step is especially important for the area of Poland, as the dynamic approach at high spatial and temporal resolution has not been used before and because Poland is a large country where the spatial variations in the climate cause changes in crop growth throughout the country, thereby affecting agricultural activity. Then, by replacing the default setup in the dynamic model with Polish practice and regulations (POLREGUL) we wanted to provide some outlines for the users of this or similar models concerning the expected range of changes in ammonia emission. This is considered particularly important due to the expanding use of this open-source model. These differences in emissions are caused by variations in agricultural practice in different countries, which are caused by both climate (thus affecting agricultural activity) and national regulations. A detailed description of the POL-
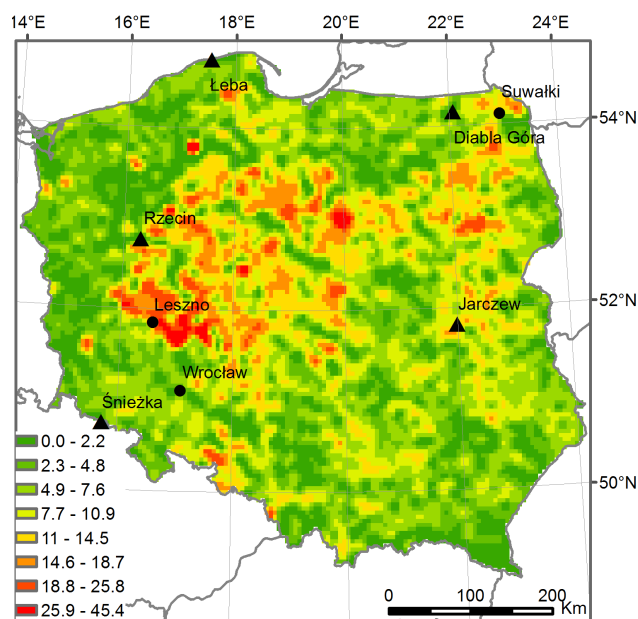
Figure 1. Total annual emission of NH_3 in 2010 [$\text{kg ha}^{-1} \text{yr}^{-1}$]. NH_3 measurement sites indicated by triangles. Additional locations discussed in the paper indicated by dots (Wrocław, Leszno, Suwałki).

REGUL approach is provided below. In the fourth scenario (NOFERT) we wanted to show the sensitivity of the dynamic model in respect to the application of manure and fertilizers, mainly in respect of spring ammonia emission peak, thereby demonstrating that the implementation of the method should carefully assess national regulations on manure application for optimal performance of the model.

For the POLREGUL scenario the information on Polish infrastructure and management methods was obtained from the IIASA (International Institute for Applied Systems Analysis) review for the Danish and Polish area (Klimont and Brink, 2004). Firstly, both countries have a ban on the application of manure and mineral fertilizer before 1 March. Secondly, the manure storage capacity in Poland is about 3 months, compared to 7–9 months in Denmark. This means that farmers in Poland need to apply manure during spring, summer and autumn. In Poland the solid and slurry fractions of the manure is applied differently due to national regulations. Solid manure goes into annual crops as only slurry is allowed on grasslands. Between 10 and 20 % of the slurry fraction is applied to grassland, which covers about 25 % of the entire agricultural area. Poland does not have a detailed nitrogen quota system at the field level like Denmark does, and the Polish regulations do not contain definitions of manure-N efficiency. The Danish regulations force farmers to apply most of the mineral fertilizer and husbandry manure into growing crops, and there is a strict limit on how much manure and mineral fertilizer is allowed to be added to each field in Denmark (Skjøth et al., 2008). A consequence is that

Table 2. The emission scenarios used in this study.

Scenario*	Description
FLAT (1)	No temporal variations.
DEFAULT (2)	A default emission distribution that matches the Europe-wide default settings in the ammonia emission model, based on the original Danish model (Skjøth et al., 2011).
POLREGUL (3)	A scenario that takes into account Polish practice and current and less regulation compared to Denmark (Klimont and Brink, 2004).
NOFERT (4)	An emission scenario that excludes the application of manure and mineral fertilizer.

* Scenarios DEFAULT, POLREGUL and NOFERT were prepared with the ammonia emission model (Skjøth et al., 2011) described in Sect. 2.1.

a limited amount of mineral fertilizer is used in Denmark and that the majority (90 %) is applied to growing crops (April–May) and the remaining part to grassland (summer). This is not the case in Poland, where there is a larger consumption of mineral fertilizer. Assuming that all fields in Poland receive sufficient fertilizer (manure and mineral) without an upper limit forced by regulation, a consequence is that as much manure as possible will be used early in the season and that the majority of the mineral fertilizer will be used on grasslands during summer (especially June, July and August) as there is a ban on applying mineral fertilizer to meadows and pasture after 15 August. Therefore, the simple assumption is that all fields will have equal amounts of manure and mineral fertilizers during spring and summer (Table 3, Poland scenario). Finally, the regulations in Poland allow farmers to apply manure to fields throughout October, which is not allowed in Denmark. A consequence is that the timing of this autumn application, when the farms empty their storages, has its peak 2–4 weeks later than in Denmark. We have therefore chosen ordinal day number 290 (counted from the beginning of January each year, in our study 2010) as the default peak time for this activity in Poland.

2.3 Meteorological input data – WRF model configuration and model performance

The Advanced Research WRF model was used with three one-way nested domains (Skamarock and Klemp, 2008). The outer domain (131×131 gridpoints) covers Europe with a horizontal resolution of $45\,\mathrm{km} \times 45\,\mathrm{km}$. The intermediate domain covers the area of central Europe with a resolution of $15\,\mathrm{km} \times 15\,\mathrm{km}$ (94×94 grid points). The innermost domain (194×194 gridpoints) covers the area of Poland at $5\,\mathrm{km} \times 5\,\mathrm{km}$ resolution. Meteorological data from the innermost domain are used in this study. Vertically, the domains are composed of 35 terrain-following hydrostatic-pressure coordinates, with the top fixed at 10 hPa. The simulation was driven by the NCEP final analysis available every 6 h with

$1.0° \times 1.0°$ spatial resolution. Analysis nudging was applied for the first two domains.

The model uses the same configuration of physics as presented by Kryza et al. (2013b), including the Goddard microphysics scheme (Tao et al., 1989), Yonsei University planetary boundary layer scheme (Hong et al., 2006), MM5 similarity surface layer and RRTMG and RRTM schemes for short- and long-wave radiation (Iacono et al., 2008; Mlawer et al., 1997). The Kain-Fritsch cumulus scheme is applied for the first two domains (Kain, 2004). For the innermost domain, cumulus convection is explicitly resolved.

Because the WRF-derived spatial information on air temperature and wind speed is a key input for the emission model, the modelled meteorological data were extensively evaluated by comparison with the measurements. The measurements were available every 6 h from 69 meteorological stations located in Poland. The model error was calculated for each station and summarized using the domain-wide error: mean error (ME), mean absolute error (MAE) and index of agreement (IOA, unitless). The definitions of the aforementioned error measures are listed in the Supplement (Table S1). Air temperature at 2 m (T2) and wind speed at 10 m a.g.l. (W10), which are used by the dynamic model of ammonia emission, show good agreement with the measurements (Table 4). The air temperature is slightly underestimated, but the IOA is very close to 1.0. The wind speed is slightly overestimated, with the ME > 0.

2.4 The FRAME model

The standard version of the FRAME model provides information on the annual mean oxidized sulphur and oxidized and reduced nitrogen atmospheric air concentrations and deposition. A detailed description of the FRAME model is given in Singles et al. (1998), Fournier et al. (2004), Dore et al. (2006) and Vieno et al. (2010). Details on the model configuration for Poland can be found in Kryza et al. (2010, 2012) and Werner et al. (2014). FRAME is a Lagrangian model which describes the main atmospheric processes in a

Table 3. Relative distribution of the total NH_3 emission from the agricultural activities in Poland as defined by Fct_1–Fct_{15}. Poland default – distribution based on Europe-wide default settings, Poland scenario – distribution based on Polish practice and regulations.

Name	Fct1	Fct2	Fct3	Fct8	Fct9	Fct10	Fct11	Fct11a	Fct12	Fct13	Fct14	Fct15
Poland default	0.20	0.09	0.07	0.09	0.09	0.00	0.05	0.05	0.28	0.03	0.05	0.01
Poland scenario	0.20	0.09	0.07	0.07	0.05	0.02	0.07	0.07	0.10	0.20	0.05	0.01

Table 4. Domain-wide error statistics for 2 m temperature (T2) and 10 m wind speed (W10) over Poland for 2010.

	ME	MAE	IOA
T2	-0.68 K	1.79 K	0.99
W10	0.16 m s^{-1}	1.29 m s^{-1}	0.84

column of air moving along straight-line trajectories following specified wind directions. The model consists of 33 vertical layers of varying thickness, ranging from 1 m at the surface to 100 m at the top of the domain. As such the FRAME model is designed for studies where processes on local scale and landscape scale will be governing (e.g. ammonia emissions) and have a simplified treatment of long-distance transport and associated chemistry. Trajectories are advected with different starting angles at a 1° resolution using directionally dependent wind speed and frequency roses.

Vertical diffusion of gaseous and particulate species is described with K-theory eddy diffusivity, and solved with the finite volume method. The FRAME model chemistry scheme is similar to the one in the Lagrangian model used by the EMEP (European Monitoring and Evaluation Programme, Barrett and Seland, 1995). The prognostic chemical variables calculated in FRAME are: NH_3, NO, NO_2, HNO_3, PAN, $SO_2H_2SO_4$, as well as NH_4^+, NO_3^- and SO_4^- aerosol. NH_4NO_3 aerosol is formed by the equilibrium reaction between HNO_3 and NH_3. A second category of large nitrate aerosol is presented and simulates the deposition of nitric acid on to soil dust or marine aerosol. The formation of H_2SO_4 by gas phase oxidation of SO_2 is represented by a predefined oxidation rate. H_2SO_4 then reacts with NH_3 to form ammonium sulphate aerosol. The aqueous reactions considered in the model include the oxidation of S(IV) by O_3, H_2O_2 and the metal catalysed reaction with O_2.

Dry deposition of SO_2, NO_2 and NH_3 is calculated individually for five different land cover categories (arable, forest, moor-land, grassland and urban) using a canopy resistance model (Singles et al., 1998). Wet deposition is calculated with scavenging coefficients and a constant drizzle approach, using precipitation rates calculated from a map of average annual precipitation. An increased washout rate is assumed over hill areas due to the seeder-feeder effect. It is assumed that the washout rate for the orographic component of rainfall due to the seeder-feeder effect is twice that used for the non-orographic components (Dore et al., 1992).

Concentrations at the boundary of the model domain are calculated with the FRAME-Europe model, which is a model similar to FRAME but which runs for the whole of Europe on the EMEP grid at 50 km × 50 km resolution. For this study the model was adapted to run and provide results at monthly resolution. Monthly wind roses were developed from the WRF data using a method similar to that described by Dore et al. (2006). Information on rainfall for FRAME was calculated by using observed data from 210 rainfall sites in Poland. Geographically weighted regression kriging, with elevation used as an independent explanatory variable (Szymanowski et al., 2013), was used here to produce a 5 km × 5 km gridded data set that matches the meteorological grid from the WRF model.

FRAME was run four times for each month. Simulations for 1 month differ in the emission scenario, which are described in Table 2 (Sect. 2.2).

2.5 Measurements of ammonia (NH_3) and ammonium (NH_4^+) air concentrations & backward trajectories from the WRF model

Verifying observations are obtained from stations within the EMEP network (Aas et al., 2012). Four EMEP stations that measure daily air concentrations of gaseous ammonia and aerosol ammonium ($NH_3+NH_4^+$) and NH_4^+ are available for Poland: PL02 Jarczew, PL03 Śnieżka, PL04 Łeba, PL05 Diabla Góra (Fig. 1). Three of these EMEP stations are located in specific geographical areas, e.g. sea coast in the north (Łeba), the highest peak in the Sudety Mountains (Śnieżka), and a large forestland in NE Poland (Diabla Góra). These areas contain limited or even no agricultural activity. Only Jarczew station, located in central-eastern Poland, is located in an agriculture area, and therefore best suited for validation of the model results. One additional site from the NitroEurope network provided measured monthly ammonia concentration. This site, Rzecin, is located in a wetland area, which is surrounded by forests with full coverage of woodland within the nearest 1 km. Land cover outside this woodland is mainly agricultural, and with the highest ammonia emissions in Poland.

Error statistics ME, MAE and R for modelled and measured NH_3 concentrations were presented for each site individually, and mean statistics based on five stations were calculated for the entire year and for the periods with (March–October) and without application of manure (January, Febru-
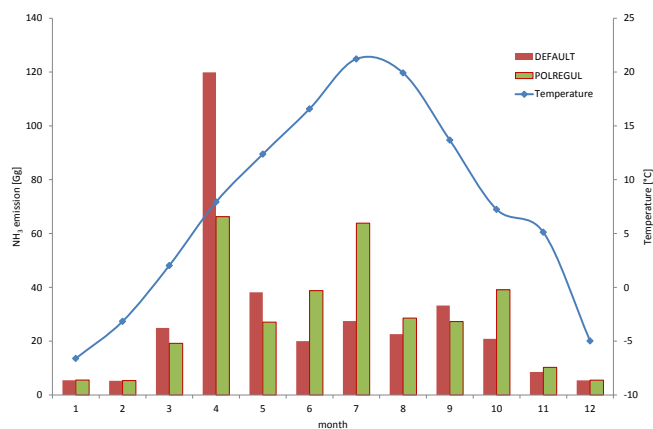
Figure 2. Monthly emission of NH$_3$ for DEFAULT and POL-REGUL run and average temperature in 2010.

Figure 3. Time series of the seasonal variation in emissions (POL-REGUL run) for various agricultural emission categories in Jarczew. Description in the legend concerns emission from functions (Fct) described in Table 1.
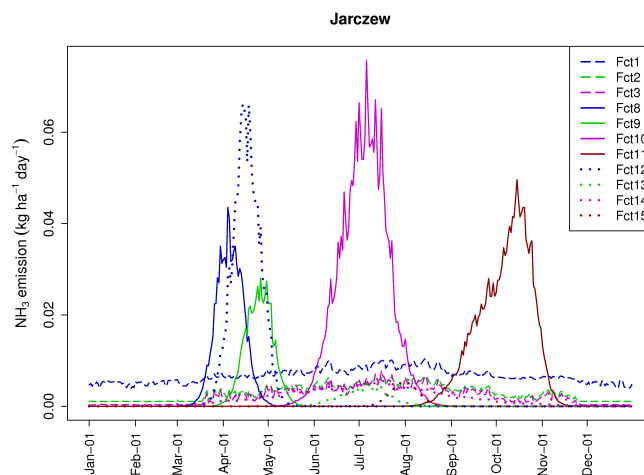
ary, November, December). The definitions of the error measures are listed in the supplementary material (Table 1).

Additionally, for Jarczew, the 3-hourly emissions from the dynamic model were aggregated into daily values and plotted with average daily concentrations from the station. The daily observations and aggregated model calculations were then sorted in two groups: (1) a group with high concentrations of NH$_3$ that were not simulated by the emissions model, and (2) the remaining days. Group 1 was then investigated in detail with air mass trajectories calculated with WRF data RIP version 4.5 (Stoelinga, 2009), which is a Fortran programme used for visualizing output from gridded meteorological data sets, was implemented to get 36 h backward trajectories for the Jarczew station.

Six trajectories were run for each day with an episode from group 1 once every 6 h. The trajectories were run for the receiving heights of 250 and 750 m, as it was suggested by Hernández-Ceballos et al. (2014) that trajectories between 300 and 700 m do not show large differences in transport path within the first 12–24 h. Each episode was then analyzed with respect to potential atmospheric transport from neighbourhood regions with high ammonia emissions.

3 Results

The results are organized as follows: first the annual ammonia emission and results from the POLREGUL option of the dynamic model for Poland are described. In the second subsection FRAME model concentrations from four runs (FLAT, DEFAULT, POLREGUL, NOFERT) are presented and compared with measurements. Finally, the relationship between the dynamically modelled emissions and measured concentrations for one selected station was presented.

3.1 NH$_3$ emission in Poland in 2010

Total ammonia emission (sum for the total country area) in Poland in 2010 was 270 Gg. The highest annual emissions are in the central part of the country, and locally exceed 35 kg ha^{-1} yr^{-1} (maximum 45 kg ha^{-1} yr^{-1}, Fig. 2). These are areas with agricultural activity contributing to the majority of NH$_3$ emissions in Poland. The NH$_3$ emissions are in the range of 1 to 10 kg ha^{-1} yr^{-1} over 70 % area of the country. The lowest emissions are in the west, north-west and south-east, where agricultural activity is less intense and large areas are covered with forests.

From analysis of the monthly total (Fig. 2), it can be seen that April is the month with the highest emissions for both the DEFAULT and POLREGUL model run. In the case of the DEFAULT run about 40 % of the annual emission is related to this month and minor emission peaks appear in March, July and September. For the POLREGUL scenario the April peak is lower by about 40 % in comparison to DEFAULT, and increased emission also appears in July and October (Fig. 2). Generally, there was higher emission in the period with an average monthly temperature above 5.0 °C.

The seasonal variation of emission (POLREGUL run) for different agricultural categories for the grid representing Jarczew station is shown in Fig. 3. In April, which is also the month with the highest ammonia emission for the total area of Poland, three functions have their highest values. At this time the peaks are observed for the application of manure on bare soils and the application of fertilizers and manure on crops. Application of manure (Fct10) is responsible for the peak of emission in summer and autumn. Emission related to livestock is dominated in Poland by Fct1 because of large-scale farming of pigs (37 cattle and 99 pigs per 100 ha of agricultural land, Central Statistical Office of Poland 2010,
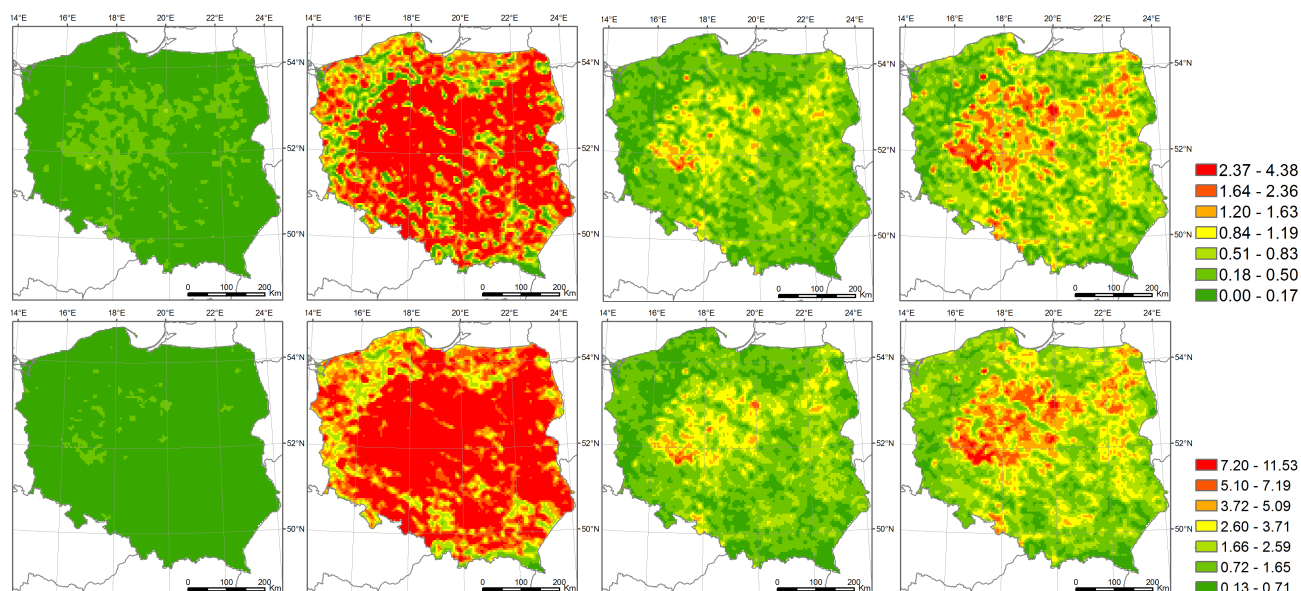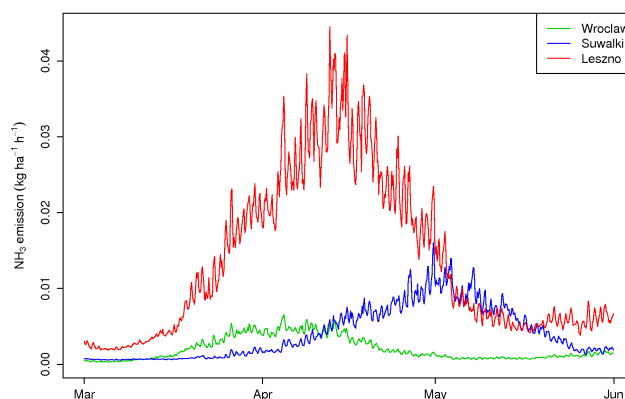
Figure 4. Top: spatial distribution of NH$_3$ emissions over Poland for February, April, June and September 2010 [kg ha^{-1} month^{-1}]. Bottom: monthly mean ammonia concentrations calculated with the FRAME model (POLREGUL) for February, April, June and September 2010 [µg m^{-3}].

http://stat.gov.pl/). Due to meteorological conditions (temperature), their contribution is doubled in the summer season in comparison to winter.

The spatial distribution of ammonia emission for selected months of each season (February, April, June and September) is presented in Fig. 4. The monthly averages for the total area of Poland are equal to 0.11, 2.56, 0.42, 0.70 kg ha^{-1} in February, April, June and September respectively. The maximum values are observed in April in the central part of the country, where they reach 10–12 kg ha^{-1}.

For the three selected locations (names of the locations are taken after the nearest towns, marked in Fig. 1) in Poland – Wrocław (south-west), Suwałki (north-east) and close to Leszno (middle-west) – hourly emissions for the selected period (from March to May) are shown in Fig. 5. Two of these locations represent the areas of the longest (Wrocław) and the shortest (Suwałki) growing season in Poland. The spring increase in emission appears first in Wroclaw (middle of March) and then almost 4 weeks later in Suwałki. Leszno is located in the area with the highest ammonia emissions in Poland. Due to diurnal variability in air temperature and wind speed there is a day–night variation in emission. The mean for the entire year diurnal variation is equal to 20 % (Wrocław) −25 % (Leszno), with the lowest values during winter (about 10 %) and highest in spring and summer (about 30 %).

Figure 5. The hourly variation in simulated NH$_3$ emissions for POLREGUL scenario. Data from March to May for three locations in Poland (Wrocław, Suwałki and Leszno).

3.2 NH$_3$ concentration calculated with the FRAME model

The spatial distribution of modelled NH$_3$ concentration from the POLREGUL scenario for February, April, June and September is illustrated in Fig. 4. The highest concentrations are in the agricultural areas in the central part of Poland, with maximum values equal to 1.32, 26.0, 16.5 and 9.2 µg m^{-3} for February, April, June and September respectively. High spatial correlation ($\geq$ 0.9) between the modelled ammonia emission and FRAME ammonia concentration (Fig. 4.) was calculated for each month.

Table 5. FRAME model results – error statistics for the individual sites (mean from 12 months).

Statistic	Run	Rzecin	Jarczew	Łeba	Śnieżka	Diabla Góra
ME (μg m^{-3})	FLAT	−0.34	0.31	0	0.13	−0.13
	DEFAULT	−0.32	1.44	0.26	0.56	−0.02
	POLREGUL	−0.36	1.3	0.24	0.51	−0.07
	NOFERT	−0.76	−0.5	−0.14	0.21	−0.47
MAE (μg m^{-3})	FLAT	0.63	0.62	0.24	0.16	0.25
	DEFAULT	0.68	1.75	0.48	0.56	0.74
	POLREGUL	0.39	1.66	0.33	0.51	0.68
	NOFERT	0.76	0.55	0.18	0.21	0.49
R (unitless)	FLAT	0.02	0.72	−0.18	0.14	0.06
	DEFAULT	0.48	0.55	0.06	0.38	−0.28
	POLREGUL	0.85	0.84	0.65	0.65	−0.55
	NOFERT	0.92	0.81	0.64	0.43	−0.8
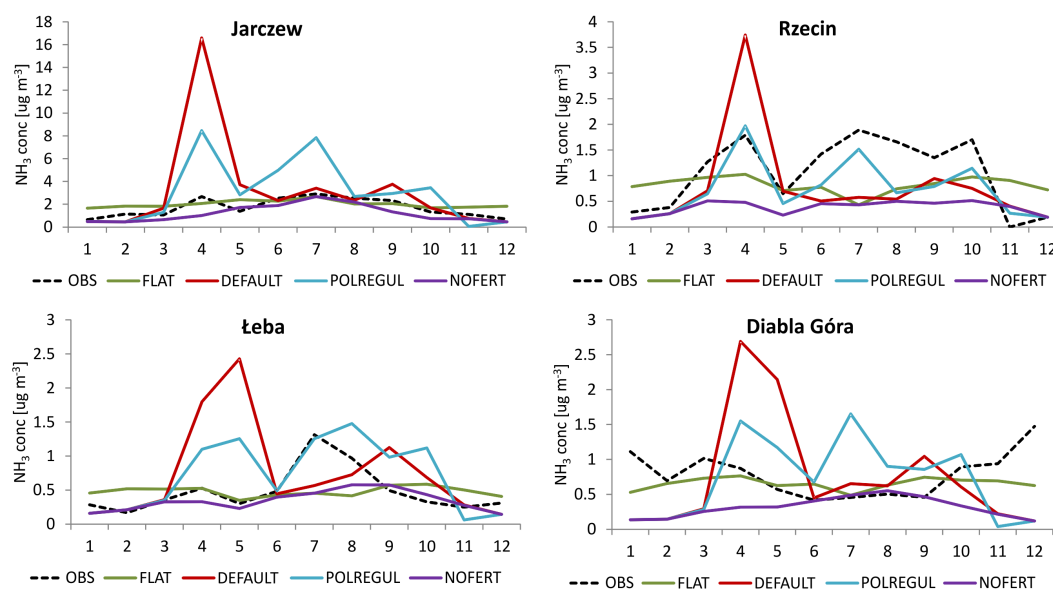
**Figure 6.** Time series of modelled and measured NH$_3$ concentrations for 2010.

Time series and error statistics of modelled (FLAT, DEFAULT, POLREGUL, NOFERT) and measured NH$_3$ concentrations are presented in Fig. 6 and Table 5. For most sites (Rzecin, Jarczew, Łeba and Śnieżka) R and MAE are best for the NOFERT and POLREGUL runs. The best performance was obtained for Jarczew and Rzecin. For each station the DEFAULT run calculates that the concentrations peak in April which is not present in the measurements or is much higher than observed (Jarczew, Rzecin). Application of Polish practice in the dynamic model has improved the results most significantly in comparison to the DEFAULT for Rzecin and Jarczew. Jarczew is the only station located directly in an agricultural area, whereas Rzecin is under the influence of an agricultural region with the highest ammonia emission in Poland. The poorest performance for each model run is for Diabla Góra, for which the measured time series has a different pattern in comparison to the other sites. High measured concentrations for this station are obtained in late autumn and the winter months.

For three model runs (FLAT, DEFAULT, NOFERT) correlation coefficients are lowest for the summer period in comparison to the entire year (Table 6), whereas the summer period has the highest correlation coefficients for the POLREGUL scenario. The POLREGUL scenario therefore improved the results significantly in comparison to DEFAULT for summer period – the correlation coefficient increased from 0.21 to 0.73 and MAE decreased from 0.83 to 0.68.

Table 6. FRAME error results – error statistics from all sites for summer (III-X) and winter (XI-II) period. Unit for ME and MAE is µg m^{-3}, R is unitless.

	FLAT			DEFAULT			POLREGUL			NOFERT		
	year	III-X	XI-II	year	III-X	XI-II	year	III-X	XI-II	year	III-X	XI-II
ME	0.07	−0.12	0.25	0.23	0.7	−0.25	0.16	0.65	−0.32	−0.31	−0.36	−0.25
MAE	0.23	0.21	0.25	0.54	0.83	0.25	0.5	0.68	0.32	0.31	0.36	0.25
R	0.26	0.04	0.48	0.48	0.21	0.75	0.01	0.73	−0.71	0.72	0.7	0.75
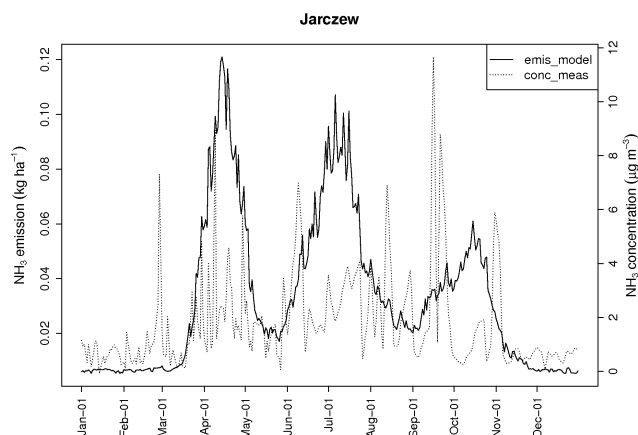
Figure 7. Modelled emission (POLREGUL) and measured concentration for the Jarczew station.

3.3 Comparison of daily emissions with measured concentrations and backward trajectories case study

Due to the high spatial correlation between ammonia emission and concentration (Fig. 4) we looked for the relationship between the dynamically modelled emissions and measured concentrations for the Jarczew station (Fig. 7). The main peaks in emissions (April, September) are reflected in the concentration data. There are also some peaks in concentrations (e.g. end of February, beginning of June and end of October) which are not resolved by the emission model. These could suggest the limitations of the emission model, or could be related to meteorology which has resulted in the transport of ammonia from neighbouring areas. Backward trajectories, for the mentioned high concentration episodes (end of February, beginning of June and end of October), were calculated with the RIP tool (Fig. 8) in order to check whether it is possible to connect these observed peaks in concentrations with atmospheric transport of ammonia. We have found that for these episodes the trajectories have a similar pattern - transport from the south or south-west sector. The air masses that reached Jarczew have during these episodes passed areas with high ammonia emissions in comparison to the local area surrounding the station.

4 Discussion and conclusions

The temporal and spatial variability of ammonia emission has been analysed over Poland with four scenarios: FLAT (no temporal variation), DEFAULT (matches the Europe-wide default settings in the ammonia emission model, Skjøth et al., 2011), POLREGUL (takes into account Polish infrastructure and less regulation compared to DEFAULT) and NOFERT (excludes application of manure and mineral fertilizer).

The emissions were then implemented in the FRAME model for a fast response on simulating the effect of the scenarios in relation to atmospheric chemistry. The results show that, in general, the model results for the agricultural areas were improved by applying a dynamical model by using Europe-wide (default) settings instead of using a fixed emission profile. If Polish practice and national regulation is incorporated into the emission model, the FRAME model performance is further improved.

The model results show large difference in emissions between months, as well as between day and night. This is due to increased volatilization of ammonia caused by increased temperatures (Eqs. 1 and 2) and emission from animal and mineral fertilizer that are applied over short time periods during spring, summer and autumn (Eq. 2). Taking into account the entire area of the country, the highest emission is obtained during spring (especially in April). The spring emission peak (and corresponding concentrations) is mainly related to the application of fertilizers and manure, which is clearly illustrated by comparing the POLREG and NOFERT simulations (Fig. 6). The sensitivity of the model to the application of manure is highlighted by the large difference between the DEFAULT and POLREGUL scenarios. In April the emission is 40 % lower in the POLREGUL scenario than in the default scenario. This is not surprising as previous results have shown that national regulation can change emissions from manure to increase by more than 100 % in spring and decrease to less than 10 % during summer (Skjøth et al., 2008). The scale and character of changes between the POLREGUL and DEFAULT simulations with the dynamic ammonia model will vary between countries and depend on local agricultural infrastructure and practice. The dynamic model predicts the spring peak in emission to start in southwest Poland and then progress to the rest of the country (Fig. 5). South-west Poland has the longest growing season
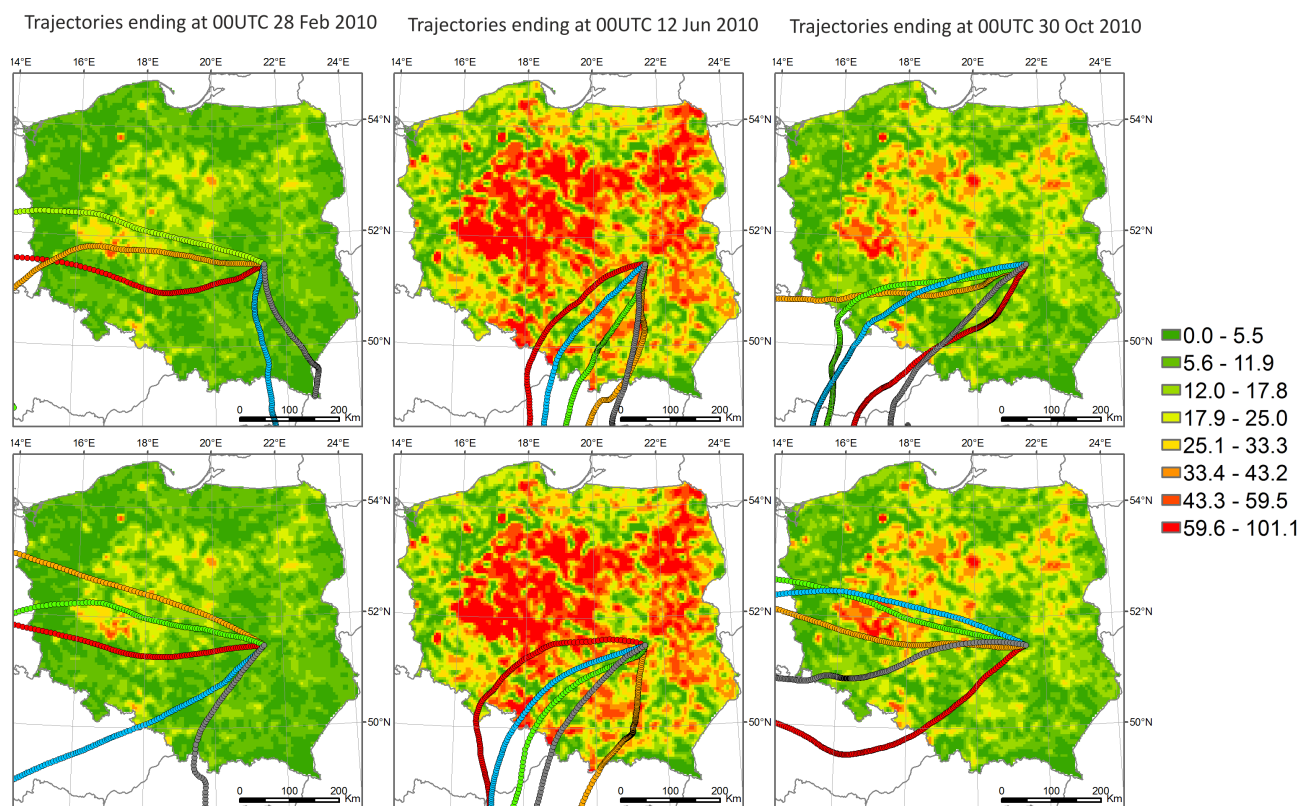
Figure 8. 36 h backward trajectories ending in Jarczew during episodes (25–27 February 2010; 09–11 June 2010; 10–29 October 2010) with high NH_3 measured concentrations. The first trajectory (gray) starts at 12.00 of the first day of each episode, and then starts every 6 h, and are presented in the following colours: blue, green, orange, red. Spatial distribution of modelled ammonia emission during the episodes (unit: $g\,ha^{-1}\,48\,h^{-1}$).

(Żmudzka, 2012) and is the area where farmers initiate their field activities in Poland. In this region, field work, including application of fertilizers or manure, can start earlier than in other regions of the country. This aspect of a "northward progressing ammonia plume" due to spring application is therefore very well captured by the model and has also been implemented in the GEOS-CHEM model (Paulot et al., 2014) and DEHM models (Skjøth et al., 2011).

Major NH_3 emission peaks modelled for the Jarczew agricultural station are also observed in NH_3 concentration measurements. However, some peaks in concentrations are not reflected in the emission data. As suggested by Asman et al. (1998) and Fowler (1998), atmospheric ammonia can be transported up to 100 km. According to Geels et al. (2012) the fraction of locally emitted NH_3 depositing locally is of the order of 15–30 % for a grid of $16\,km \times 16\,km$. In our study, the analysis of backward trajectories showed that increased concentrations can be related to transport of ammonia from neighbouring areas with high emission. A more thorough investigation on this scale requires more sophisticated modelling tools than FRAME.

FRAME is a relatively simple Lagrangian model and the results were found to be in good agreement with measurements for Poland (Kryza et al., 2011, 2012; Werner et al., 2014) and for the UK (Dore et al., 2015). This enables us to run several scenarios for the entire year without a large computational overhead. Similar principles to FRAME are present in local scale models like OML (Geels et al., 2012) and OPS (Van Jaarsveld, 2004; Velders et al., 2011). It is shown with these models that in relation to ammonia and on spatial scales of 0.5–16 km, it is sufficient to neglect chemical transformation and wet deposition even on a daily and weekly basis (Geels et al., 2012). OML and FRAME use similar principles for the near-source domain. In relation to ammonia and the fate due to chemical conversion and wet deposition, the FRAME methodology is more advanced than the OML method. Although the OML model does not include chemical conversion or wet deposition, the annual correlation coefficients are high (0.7–0.75) and the bias is low when compared with observations. This shows that the governing processes on ammonia concentrations on this scale are due to emissions and dispersion within the agricultural areas and only to a small degree chemical conversion and deposition (dry and wet). These results correspond well with the two latest reviews on this subject (Hertel et al., 2006, 2012).

The monthly correlation coefficients obtained with the FRAME model for the agricultural sites are comparable to the model results that are obtained with both DEHM (Skjøth et al., 2011) and the DAMOS system (Geels et al., 2012). Application of Polish practice into the ammonia dynamic model improves the FRAME results in comparison to the European default settings of the dynamic model. This suggests that similar improvements can be obtained for other European areas. For Polish conditions, with lack of detailed information about location of the agricultural fields and the location, amount and type of livestock, a higher mean absolute error for the dynamic simulations is observed in comparison to the constant emission approach. This also suggests that spatial allocation of emissions might have a greater influence on concentration results obtained from a dynamic than from a constant emission approach.

One of the sites (Diabla Góra) has an inverted time series in comparison to all other stations – the highest ammonia concentration appears in late autumn and in the winter months. Our calculations, which took into account only agricultural sources, were not able to catch peaks in this period. The Diabla Góra station is located in a large forested area called "Borecka Forest", surrounded by lakeland, with a small contribution of arable land in the region. Open water areas (Barrett, 1998; Sørensen et al., 2003) and natural land areas (Duyzer, 1994) have been shown to emit NH_3. Emission of NH_3 from ecosystems are found to take place when the atmospheric NH_3 concentration is lower than the stomatal NH_3 compensation point (Mattsson et al., 2009), as a result of decomposing leaf litter and due to cuticular desorption (David et al., 2009; Hansen et al., 2013). As suggested by Hansen et al. (2013), natural ammonia emission from deciduous forests should be considered as an emissions source which could be dynamically simulated with atmospheric transport models. Another factor that can cause an increase in ammonia concentrations within a plant canopy coupled with altered microclimate could be evaporation of ammonium-containing aerosol (Fowler et al., 2009; Nemitz et al., 2004). Ammonium-chloride, ammonium-nitrate and ammonium-bi-sulphate are all formed from reversible processes in the atmosphere. Natural emission could explain the high ammonia concentrations at the Diabla Góra station in autumn and late autumn (until beginning of December), when mean daily temperature is above zero and no snow cover present. Based on the emission and measurements data as well as model results it is difficult to explain the high ammonia concentrations in the mid-winter period. These could be more efficiently studied with chemistry transport models which are connected online with both meteorology like GATOR-MMTD (Jacobson et al., 1996), WRF-Chem (Grell et al., 2005), GEM-AQ (Kaminski et al., 2007), and a dynamic ammonia emission model.

The dynamical approach has consistently provided good results for agricultural regions during the winter months, which is due to the large response on ammonia emission from agricultural buildings caused by outside temperatures. An implementation of this type of emission model into CTM online coupled with meteorology will be a direct response to the suggestion by Sutton et al. (2013) and a direct coupling between ammonia emission, meteorology and chemistry and can address some of the challenges in the modelling of air pollution that have been highlighted (Baklanov et al., 2014).

For regional modelling of ammonia in Europe, the overall results suggest that it will be an advantage to move from a static to a dynamic approach. The Europe-wide default setting in the model given by Skjøth et al. (2011) can be expected to improve the results over large areas, but a better picture over Poland will be obtained if the values from Table 2 in Skjøth et al. (2011) are replaced with the values from our POLREGUL scenario. Further improvement on ammonia emissions is likely to be related to natural sources (Hansen et al., 2013; Riddick et al., 2014) as well as the dependence on emission from fertilizer on soil type as shown by the CHIMERE model (Hamaoui-Laguel et al., 2014). These initiatives are currently being addressed by the ECLAIRE project (http://www.eclaire-fp7.eu/), which focuses on climate driven emissions (BVOCs and ammonia) as suggested by the latest IPCC report (2013), that calls for more studies on the feedback mechanisms between climate and air quality.

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