Atmospheric Environment xxx (2012) 1–12

Contents lists available at SciVerse ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Improving ammonia emissions in air quality modelling for France

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HIGHLIGHTS

► NH_3 emissions from mineral fertilizer spreading in France are simulated using a 1D mechanistic model.
► Emissions display high spatiotemporal variations depending especially on soil pH and rates and dates of fertilization.
► The comparison of modelled PM10 with observations shows that the spatiotemporal correlation is slightly improved.

ARTICLE INFO

Article history:
Received 4 January 2012
Received in revised form
31 July 2012
Accepted 1 August 2012

Keywords:
Modelling
Agriculture
Ammonia
Emissions
Air quality
PM10
Ammonium nitrate

ABSTRACT

We have implemented a new module to improve the representation of ammonia emissions from agricultural activities in France with the objective to evaluate the impact of such emissions on the formation of particulate matter modelled with the air quality model CHIMERE. A novel method has been set up for the part of ammonia emissions originating from mineral fertilizer spreading. They are calculated using the one dimensional 1D mechanistic model "VOLT'AIR" which has been coupled with data on agricultural practices, meteorology and soil properties obtained at high spatial resolution (cantonal level). These emissions display high spatiotemporal variations depending on soil pH, rates and dates of fertilization and meteorological variables, especially soil temperature. The emissions from other agricultural sources (animal housing, manure storage and organic manure spreading) are calculated using the national spatialised inventory (INS) recently developed in France. The comparison of the total ammonia emissions estimated with the new approach VOLT'AIR_INS with the standard emissions provided by EMEP (*European Monitoring and Evaluation Programme*) used currently in the CHIMERE model shows significant differences in the spatiotemporal distributions. The implementation of new ammonia emissions in the CHIMERE model has a limited impact on ammonium nitrate aerosol concentrations which only increase at most by 10% on the average for the considered spring period but this impact can be more significant for specific pollution episodes. The comparison of modelled PM10 (particulate matter with aerodynamic diameter smaller than 10 μm) and ammonium nitrate aerosol with observations shows that the use of the new ammonia emission method slightly improves the spatiotemporal correlation in certain regions and reduces the negative bias on average by 1 μg m^{-3}. The formation of ammonium nitrate aerosol depends not only on ammonia concentrations but also on nitric acid availability, which is often a limiting factor in rural regions in France, and on meteorological conditions. The presented approach of ammonia emission calculation seems suitable for use in chemistry–transport models.

1. Introduction

Ammonia constitutes the major basic gas in the atmosphere and plays an important role in atmospheric chemistry as a precursor of fine inorganic secondary aerosol (Sharma et al., 2007). It reacts with sulphuric and nitric acids to form ammonium sulphate ($(NH_4)_2SO_4$) and ammonium nitrate (NH_4NO_3) aerosol. Under favourable meteorological conditions, ammonium nitrate can contribute to PM2.5 and thus to PM10 concentration peaks (particulate matter with aerodynamic diameter smaller than 2.5 μm and smaller than 10 μm respectively) (Walker et al., 2004; Deutsch et al., 2008), which have been linked to a range of adverse health effects (Barrett et al., 2008; Pope et al., 2009). In Europe, ammonium nitrate can

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http://dx.doi.org/10.1016/j.atmosenv.2012.08.002

represent more than 30% (annual mean) of PM10 and PM2.5 (Putaud et al., 2004).

The formation of NH_4NO_3 depends on temperature and relative humidity which govern the equilibrium between ammonia and nitric acid gases and particulate ammonium nitrate therefore the partitioning between particle and gas phases (Stelson and Seinfeld, 1982; Cadle et al., 1982).

During the period March–April 2007, episodes with high PM pollution levels occurred in Western Europe. In France, these episodes concerned the northern regions. For these episodes (for example March 15 and April 16), daily PM10 mean concentrations measured with TEOM-FDMS (Tapered Element Oscillating Microbalance-Filter Dynamic Measurement System) exceeded 50 μg m^{-3} several times. The analysis of the aerosol composition showed high concentrations of ammonium nitrate over several regions.

The underestimation of PM10 modelled by the chemical transport model (CTM) CHIMERE (Schmidt et al., 2001; Bessagnet et al., 2004, 2008) within the operational platform for air quality monitoring and forecasting PREV'AIR (Honoré et al., 2008; Rouil et al., 2009) has been partly attributed to an underestimation of ammonium nitrate aerosol for which modelling is still associated with large uncertainties. The availability of ammonia is one of the most uncertain factors controlling the model performance in the calculation of secondary nitrate aerosol (Hass et al., 2003; Schaap et al., 2003, 2004). For this purpose, it seems important to improve the quality of our ammonia emissions (magnitude, temporal variability and spatial distribution).

Agriculture is the main source of atmospheric ammonia. Generally, inventories describe animal husbandry and fertilizer application as the first and second most significant sources respectively (Battye et al., 1994; ECETOC, 1994; Bouwman et al., 1997). In France, agricultural activities contribute 97% to anthropogenic ammonia emissions according to existing inventories (CITEPA, 2010) with about 40% due to land fertilization.

Ammonia emissions from manure and synthetic fertilizer spreading depend on a range of environmental conditions such as soil and air temperature (He et al., 1999), humidity, soil properties such as pH (He et al., 1999), texture and on agricultural practices such as fertilizer application rate and type (Hutchings et al., 2009a, 2009b). Therefore, they can show large spatial and temporal gradients, particularly, because the major part of fertilizers is applied in spring and fall, linked with the crop growing cycles.

Generally, to estimate ammonia emissions, the annual emission is calculated using data on livestock and fertilizer deliveries and average emission factors (Hutchings et al., 2009a, 2009b). The CHIMERE air quality model uses such a type of annual emission inventory together with temporal distribution profiles to obtain temporally resolved emissions. The annual emissions are provided by EMEP (*European Monitoring and Evaluation Programme*) using inputs originating from national submissions. As an alternative approach, ammonia emission modelling takes into account the main factors influencing ammonia volatilization.

Several studies have been performed to improve ammonia inventories for the purpose of supporting atmospheric models for secondary particulate formation particularly in the United States. Robarge et al. (2002) have constructed a multivariate regression model for predicting NH_3 concentrations depending on air temperature, wind direction and wind speed using measurements from North Carolina. Anderson et al. (2003) suggest designing experiments to improve emission factors and their resolution, by developing mass balance models and refining of the livestock activity level data. Other studies suggest that information about the timing of fertilizer application allows monthly resolution of emissions from this source category (Anderson et al., 2003; Diaz Goebes et al., 2003). In addition, in a recent study carried out in Europe (Skjøth et al., 2011), the temporal distribution of ammonia emissions was calculated using a dynamical model based on parameterisations for 13 activities emitting ammonia taking into account climatic conditions (air temperature and wind speed). However, until now, no explicit ammonia volatilization model has been coupled to a 3-D deterministic air quality model.

The objective of this study is to improve the estimate of ammonia in a chemistry–transport model. We have used a coupled approach to calculate the ammonia emissions. The process model VOLT'AIR (Génermont and Cellier, 1997; Garcia et al., 2011) was used to simulate ammonia emissions from fertilizer spreading. The emissions from animal houses and from storage and spreading of manure are taken into account using the national spatialised inventory (INS, ministry of Ecology). These new emission data are then used in CHIMERE to evaluate their impact on particulate matter levels in the atmosphere. In this work, the improvements of ammonia emissions are attempted for France as a first test case.

This paper is structured as follows: in Section 2, we describe the detailed methodology of (i) the VOLT'AIR model, (ii) the national spatialised inventory, (iii) the CHIMERE model, (iv) the data processing and (v) the general concept. Section 3 deals with the results of ammonia emission calculations for a selected spring period and their comparison with the standard method used in CHIMERE. The impact of these emissions on ammonium nitrate aerosol and PM10 modelled with CHIMERE is discussed in section 4. Then, in section 5, we evaluate the modelled concentrations of this aerosol by comparison with observations using statistical indicators. We finish with the conclusions and perspectives for this work.

2. Models and methods

2.1. VOLT'AIR model

VOLT'AIR is a mechanistic 1D vertical model describing the influence of agro-pedo-climatic conditions on ammonia volatilization. It allows the calculation of ammonia fluxes over agricultural land on an hourly basis from slurry (Génermont and Cellier, 1997; Garcia et al., 2011) and mineral fertilizers (ammonium nitrates, nitrogen solutions and urea) (Le Cadre, 2004; Le Cadre et al., 2004, 2009) applied to bare soil. The model treats the physical and chemical equilibria between the various species of ammoniacal-N ($NH_4^+ + NH_3$), heat, water and ammoniacal-N transfers in the soil, and the transfer of ammonia between the surface and the lower atmosphere. Water and ammoniacal-N transfers within the soil are calculated after the fertilizer application, possible irrigation and incorporation of the fertilizer in the soil. The ammoniacal nitrogen is available in the soil after the process of dissolution in the case of granular fertilizers (i.e. Ammonium Nitrate) and after urea hydrolysis in the case of urea and UAN (nitrogen solutions containing urea and ammonium nitrate) application. The distribution of ammoniacal-N between the three phases in the soil (adsorbed, dissolved and gaseous phases) and the equilibrium between ammonia and ammonium are calculated. By solving the energy balance equation, the soil surface temperature and evaporation are calculated. The input of water by rain, irrigation or fertilization, and the loss of water by evaporation are calculated for the surface layer of the soil. The volatilization is calculated using an advection model with the partial pressure of ammonia at the soil surface and soil roughness and friction velocity as input.

2.2. National spatialized inventory (INS)

The ammonia emissions from livestock husbandry occur throughout the steps of manure management: in the animal