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Effect of grid resolution and spatial representation of NH₃ emissions from fertilizer application on predictions of NH₃ and PM₂.₅ concentrations in the United States Corn Belt

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Abstract

Ammonia (NH₃) emissions from fertilizer application is a highly uncertain input to chemical transport models (CTMs). Reducing such uncertainty is important for improving predictions of ambient NH₃ and PM₂.₅ concentrations, for regulatory and policy purposes and for exploring linkages of air pollution to human health and ecosystem services. Here, we implement a spatially and temporally resolved inventory of NH₃ emissions from fertilizers, based on high-resolution crop maps, crop nitrogen demand and a process model, as input to the Comprehensive Air Quality Model with Extensions (CAMx). We also examine sensitivity to grid resolution, by developing inputs at 12 km × 12 km and 4 km × 4 km, for the Corn Belt region in the Midwest United States, where NH₃ emissions from chemical fertilizer application contributes to approximately 50% of anthropogenic emissions. Resulting predictions of ambient NH₃ and PM₂.₅ concentrations were compared to predictions developed using the baseline 2011 National Emissions Inventory, and evaluated for closure with ground observations for May 2011. While CAMx consistently underpredicted NH₃ concentrations for all scenarios, the new emissions inventory reduced bias in ambient NH₃ concentration by 33% at 4 km × 4 km, and modestly improved predictions of PM₂.₅, at 12 km × 12 km (correlation coefficients r = 0.57 for PM₂.₅, 0.88 for PM-NH₄, 0.71 for PM-SO₄, 0.52 for PM-NO₃). Our findings indicate that in spite of controlling for total magnitude of emissions and for meteorology, representation of NH₃ emissions and choice of grid resolution within CAMx impacts the total magnitude and spatial patterns of predicted ambient NH₃ and PM₂.₅ concentrations. This further underlines the need for improvements in NH₃ emission inventories. For future research, our results also point to the need for better understanding of the effect of model spatial resolution with regard to both meteorology and chemistry in CTMs, as grid size becomes finer.

1. Introduction

Ammonia (NH₃) is the most abundant alkaline trace gas in the atmosphere, and precursor to PM₁₀ and PM₂.₅ (particulate matter (PM) with diameters ≤ 10 μm and 2.5 μm, respectively) (Bassett and Seinfeld 1983, Baek et al. 2004). PM₁₀ and PM₂.₅ are regulated for impacts on human health and welfare (e.g., visibility) by the current...
Clean Air Act Amendments in the United States of America (US) (US EPA 2016). Additionally, they influence the Earth’s radiative budget by having a net cooling effect (Pinder et al 2012, Smith and Bond 2014). Deposition of NH₃ and other reactive nitrogen species exacerbates environmental impacts such as soil acidification, surface water eutrophication and reduced ecosystem productivity (Krupa 2003, Erisman et al 2013). In view of its important role in the atmosphere, the US EPA Science Advisory Board has recommended NH₃ be considered as a harmful PM₂.₅ precursor (US EPA 2011).

In the US, dominant anthropogenic contributors of NH₃ emissions include livestock operations including manure management and land application (55%) and chemical fertilizers (26%) (US EPA 2015). However, relative source contributions vary based on regional agricultural practices. In the Corn Belt region in the Midwest US (hereafter Midwest), chemical nitrogen fertilizers are the dominant source of NH₃ emissions (55%, year 2011) (US EPA 2015). This region spanning the States of Illinois, Indiana, Iowa, Missouri, Nebraska and Kansas is dominated by corn and soybean cultivation (Green et al 2018) that accounts for nearly 60% of the US fertilizer sales (AAPFCO and The Fertilizer Institute 2014). In view of decreasing emissions of major PM₂.₅ precursors of sulfur and nitrogen oxides, emission controls for NH₃ from agriculture have been proposed as potentially cost-effective for further reduction of PM₂.₅ concentrations (Pinder et al 2007, US EPA 2011). However, sensitivity to NH₃ emission reductions vary seasonally and by region (Holt et al 2015, Bauer et al 2016).

State-of-the-art chemical transport models (CTMs) can improve our current understanding of linkages between NH₃ emissions from agriculture and air quality (Dennis et al 2013). Predictive capabilities of CTMs to model PM₂.₅ formation depend on accurate representations of spatial and temporal distributions of precursor emissions. As compared to other PM₂.₅ precursors, there are large uncertainties in NH₃ emissions (>50%) at the global scale and even higher uncertainties at regional and local scales (US EPA 2011, Sutton et al 2013). While field measurements of NH₃ emissions provide insight into inherent spatial and temporal trends, such studies in the US have largely focused on livestock waste (Aneja et al 2008, Zhang et al 2008). Measurements over fertilized cropland are limited to a few locations (e.g., (Walker et al 2013, Nelson et al 2017)) due to the resource-intensive and technical challenges of NH₃ flux measurements (Norman et al 2009). Hence modeling approaches have been adopted to characterize NH₃ emissions at the regional scale as inputs to CTMs (Goebes et al 2003). Regarding NH₃ emission inputs, current CTM predictions are limited by errors in grid-scale representation (Bray et al 2017) and timing of agricultural NH₃ emissions (Appel et al 2011), and lack or limited representations of bidirectional NH₃ exchange within CTMs (Cooter et al 2012, Battye et al 2016, Schiferl et al 2016). In particular, studies have recognized the need to better characterize NH₃ emissions from chemical fertilizers at high spatial (~32 km × 32 km) and temporal (hourly) resolutions (Appel et al 2011, Paulot et al 2014) to capture the episodic nature of this emission source and influence of local climatic and soil parameters. Yet, there is no conclusive evidence if increase in spatial and temporal resolution of NH₃ emissions improves CTM predictions, given the multitude of inputs that need to be developed at similar resolutions (Queen and Zhang 2008, Schaap et al 2015).

In the National Emissions Inventory (NEI) up to year 2011, NH₃ emissions from chemical fertilizers in the US are estimated using the emission-factor approach (Goebes et al 2003, US EPA 2014a). These county-scale, annual emissions are allocated to spatial and temporal resolutions required by CTMs using emission processing models (Paulot et al 2015) such as the Sparse Matrix Operator Kernel Emissions (SMOKE) (CMAS 2016). In the case of NH₃ emissions from chemical fertilizers, spatial allocation from coarser to finer CTM grid resolution is achieved using land cover maps as the spatial surrogate (Goebes et al 2003). Recent work has additionally accounted for crop nitrogen application rates, as demonstrated by the Improved Spatial Surrogate (ISS) approach (Balasubramanian et al 2015a) and the Magnitude and Seasonality of Agricultural Emissions model (Paulot et al 2014). Temporal allocation of annual emissions is based on seasonal nitrogen management data and crop planting and harvesting schedules that are averaged to hourly scale (Goebes et al 2003) or using semi-empirical models that estimate emissions as functions of hourly temperature and wind speed (Gyldenkerne et al 2005, Paulot et al 2014). Such approaches introduce errors in NH₃ emissions due to approximations in fertilizer usage at the county scale and use of European emissions factors that require evaluation for climatic and field management conditions in the US (Balasubramanian et al 2015a), homogenization across CTM grid cells (Walker et al 2012) and lack of accounting of local meteorological influences (Hendriks et al 2016). Subsequently, implementations of the NEI emissions within CTMs have been linked to underpredictions in modeled NH₃ and PM₂.₅ concentrations in comparison with observations (Rodriguez et al 2011, Schiferl et al 2016). Inverse modeling approaches to optimize NH₃ emissions have identified large underestimates in total NH₃ emissions for California and the Midwest, and errors in seasonality for emissions from chemical fertilizers in the Midwest (Paulot et al 2014), especially during spring (Heald et al 2012, Banzhaf et al 2013).

Process-based models present an alternative approach to developing emission inventories for agriculture. Such models advantageously predict spatial and temporal variations in NH₃ emissions, based on local variability in climate and soil conditions, and regional crop management practices (Brilli et al 2017).
Emissions estimated using process models have been incorporated into CTMs through different approaches. As an example, the Volt’Air model that simulates influences of meteorology and slurry application on transfer of nitrogen in the soil and exchange between soil and atmosphere to estimate NH₃ emissions (Génermont and Cellier 1997), has been implemented to improve sub-grid variability of emissions within the CHIMERE CTM (Hamaoui-Laguel et al 2012). The Environmental Policy Integrated Climate (EPIC) model has been adopted to simulate ammonium content in applied fertilizer, and coupled with the Community Multiscale Air Quality (CMAQ) CTM to subsequently capture bidirectional NH₃ exchange between soil and atmosphere inline at each time step (Cooter et al 2012, Bash et al 2013). More recently, the DeNitriﬁcation DeComposition (DNDC) model that simulates daily NH₃ emissions after fertilizer usage (Li et al 1992, Li 2000) was coupled with NEI to characterize daily NH₃ emissions for the Midwest (Balasubramanian et al 2015a). While it is highly desirable to integrate representations of field-scale processes within CTMs, extensive effort is required to develop parametrizations that adequately capture emission potentials of different trace gas ﬂuxes from soils (Flechard et al 2013).

In this study, we undertook an evaluation of the Comprehensive Air Quality Model with Extensions (CAMx) (Ramboll ENVIRON 2016), for two different approaches for spatially allocating NH₃ emissions from chemical fertilizer application and at two model spatial resolutions. CAMx is a state of the art CTM that has been widely implemented for air quality modeling studies focussing on multiple regions worldwide, as a part of academic and regulatory assessments (Ramboll ENVIRON 2016, Emery et al 2017). For spatial and temporal allocation of NH₃ emissions, we used the ISS spatial allocation method, to develop an NH₃ inventory at two spatial resolutions (4 km × 4 km and 12 km × 12 km), combined with the process DNDC model for temporal resolution at the daily scale (Balasubramanian et al 2015a). In an earlier study, we showed that DNDC successfully captured the temporal occurrence of NH₃ ﬂux peaks following chemical fertilizer application, by comparison to NH₃ ﬂux measurements in a typically fertilized corn ﬁeld in Central Illinois (Balasubramanian et al 2017). An US EPA regulatory modeling guidance document has recommended implementation of CTMs at spatial resolutions ﬁner than 4 km × 4 km for regions with strong emission gradients (US EPA 2014b). This is of importance to the Midwest that has dominant contributions of NH₃ emissions from chemical fertilizers. Region-speciﬁc CTM studies linking agricultural NH₃ emissions to air quality have been conducted over the Eastern US using CMAQ (Appel et al 2011, Zhang et al 2008, 2013) and CAMx (Zhang et al 2013), California using CMAQ (Bray et al 2017, Lonsdale et al 2017), and Colorado using CMAQ (Battye et al 2016) and CAMx (Rodriguez et al 2011, Thompson et al 2015). However, fewer studies have been conducted for the Midwest, with focus on modeling wintertime PM formation using CMAQ (Spak et al 2012, Kim et al 2014) and CAMx (Spak et al 2012). While CAMx has been identiﬁed as an appropriate CTM for PM2.5 prediction (Baker and Scheff 2007), it has not been as widely implemented as CMAQ for linking agricultural NH₃ emissions to air quality (Rodriguez et al 2011, Thompson et al 2015), thereby providing additional motivation to study CAMx performance for this application.

Based on these research motivations, we present a ﬁrst investigation of sensitivity of CAMx predictions to the method used for representation of NH₃ emissions and to the spatial resolution of gridded emission inputs. This study aims to bridge a gap in our understanding of CTM performance in a region of strong NH₃ emissions gradient that are predominantly a result of chemical fertilizer application in the US Corn Belt, by examining the sensitivity of CAMs to NH₃ emission representations. Such understanding is of scientific as well as of policy interest, as model predictions are often used to guide policy decisions.

2. Methods

2.1. Study region and time period

The Midwest represents a region of dominant chemical fertilizer sales in the US (>60% (AAPFCO and The Fertilizer Institute 2014)), high observed concentrations of ambient NH₃ (>1.8 μg m⁻³) (Puchalski et al 2015); and high wet deposition ﬂuxes of NH₃ (>3 kg-N ha⁻¹ yr⁻¹) (Lehmann et al 2007, Li et al 2016). A nested 4 km × 4 km domain was deﬁned over the Midwest surrounding the State of Illinois, within a parent (surrounding) domain over the contiguous US with 12 km × 12 km grid resolution (ﬁgure 1). May 2011 was chosen for evaluation because it represents the period of active planting and fertilizer usage dates for corn (USDA 2010). As a result, this period includes peak NH₃ ﬂuxes from chemical fertilizers, as veriﬁed by ﬁeld measurements at a site located in central Illinois (Nelson et al 2017). Year 2011 was chosen because it was the year with the most recent and updated NEI data (US EPA 2015), when this study was initiated.

2.2. Meteorology

The mesoscale, non-hydrostatic Weather Research and Forecasting—Advanced Research model, thereafter WRF, version 3.5.1 was used to develop 3D gridded meteorological ﬁelds (UCAR 2016). WRF was run for the
same geographical domains shown in figure 1, at the same 4 km × 4 km and 12 km × 12 km spatial resolutions. 30 vertical Eta Levels were used (from surface to 50 hPa), interpolated by WRF’s default algorithm for the entire model. Two-way nesting was employed to allow feedback of model parameters from the parent domain to the nested domain, and vice versa. Initial and boundary conditions for WRF simulations were driven by the 12 km North American Model (NAM) data, from the National Operational Model Archive and Distribution System, with 6-hour temporal resolution (NOAA 2016). Terrain input data were obtained from the WRF official website (UCAR 2016). The objective analysis program, OBSGRID was used for observational nudging, using National Centers for Environmental Prediction (NCEP) observational data (NCEP 2008, 2015). Following sensitivity analysis including 17 runs with different physical parameterizations (Fu 2016), the parameterization shown in table S1 is available online at stacks.iop.org/ERC/2/025001/mmedia was chosen as best performing in May 2011, for the Midwest US domain. WRF predictions from each sensitivity run was compared with measured data from the 19 stations of the Water and Atmospheric Resources Monitoring (WARM) network of the Illinois State Water Survey (ISWS 2016). Summary statistics for temperature, relative humidity, wind speed, wind direction and pressure are presented in table S2, for May 2011. WRF vertical outputs were kept constant as inputs to SMOKE and CAMx, and processed through the MCIPv4.2 (Otte and Pleim 2010) and wrf2camx (Ramboll ENVIRON 2017) programs, respectively.

2.3. Emissions
For NH3 emissions from chemical fertilizer application, we used the typical NEI-SMOKE approach (US EPA 2014a) as baseline to compare with the ISS-DNDC approach described in (Balasubramanian et al 2015a), for the domains shown in figure 1. In the ISS-DNDC method, spatial allocation to the CAMx grid resolution was based on 30 m × 30 m Cropland Data Layer maps for year 2011 (NASS 2014). NH3 emissions were spatially allocated using grid-scale areal extent of different crops and weighted with crop-specific nitrogen loading data. Temporal allocation from annual to the daily scale was achieved by implementing the process-based DNDC model. A comprehensive evaluation of DNDC indicated that the model satisfactorily replicated temporal trends in NH3 emissions post fertilizer usage, at the site scale (Balasubramanian et al 2017). Use of DNDC enabled the identification and inclusion of springtime NH3 emission peaks during planting season (May), as compared to seasonally averaged temporal factors in the typical NEI-SMOKE approach (Balasubramanian et al 2015a). ISS-DNDC emissions for the Midwest are available for the entire year of 2011 (Balasubramanian et al 2015b).

A comprehensive accounting of all PM2.5 precursor emissions is required for accurately modeling ambient NH3 and PM2.5 concentrations. Thus, we obtained emissions for sectors apart from the chemical fertilizer application from the NEI2011v6.2 modeling platform (US EPA 2017a). The NEI2011v6.2 platform reports criteria air pollutants and precursor pollutants for 60 emission sectors, that are grouped as point sources, nonpoint sources including agriculture, nonroad and onroad mobile sources, biogenic and fugitive dust sources,
and fires. The agricultural sector is further divided into NH$_3$ emissions from livestock manure management (classified by animal type and manure management system), and chemical fertilizer application (classified by fertilizer type). In this study, we use the ISS-DNDC approach to spatially and temporally allocate NH$_3$ emissions from chemical fertilizer application as mentioned previously, and use the spatial surrogates and temporal factors from the NEI2011v6.2 modeling platform for the other emission sectors (US EPA 2017a).

Four scenarios of emission inputs to CAMx were developed (table 1) to investigate how NH$_3$ spatial allocation influences CAMx predictions of NH$_3$ and PM$_{2.5}$ concentrations. Baseline emissions were first established using NEI 2011 for all emission sectors and allocated using spatial surrogates and temporal factors available within the NEIv6.2 modeling platform. Then NH$_3$ emissions from fertilizer application were modified based on the ISS-DNDC approach, by modifying spatial surrogate ratios and temporal factors provided in the NEIv6.2 modeling platform, using the ISS method, and daily fraction of annual NH$_3$ emissions estimated using DNDC, respectively (supplementary material, text S1). These modifications were applied to all States within the Midwest that were considered within the 4 km × 4 km domain shown in figure 1. In order to study sensitivity to spatial resolution, both baseline and hybrid ISS-DNDC emissions were processed for the Midwest at two spatial resolutions: (1) as a nested 4 km × 4 km grid within a parent 12 km × 12 km grid, and (2) on a uniform 12 km × 12 km grid.

### Emission scenarios used as inputs to CAMx in this study.

| Emissions       | Description                                                                 | Spatial domain defined in CAMx                                                                 | Spatial domain for evaluation |
|-----------------|-----------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|-------------------------------|
| Baseline-4 km   | NEI 2011 emissions processed using NEIv6.2 modeling platform and SMOKEv3.7 | Nested 4 km × 4 km Midwest + parent 12 km × 12 km contiguous US                               | 4 km × 4 km over Midwest      |
| Baseline-12 km  |                                                                              | 12 km × 12 km contiguous US                                                                   | 12 km × 12 km over Midwest    |
| ISS-DNDC-4 km   | Baseline emissions with modifications for NH$_3$ emissions from chemical fertilizers using ISS-DNDC approach | Nested 4 km × 4 km Midwest + parent 12 km × 12 km contiguous US                               | 4 km × 4 km over Midwest      |
| ISS-DNDC-12 km  |                                                                              | 12 km × 12 km contiguous US                                                                   | 12 km × 12 km over Midwest    |

2.4. CAMx configuration and inputs

CAMx v6.4 was implemented with parameterizations recommended by Zhang et al (2013) (table S3). Horizontal and vertical grid structures matched those of the meteorological inputs. Vertical diffusion is modelled with the default K- theory diffusion option. Horizontal advection is modeled with the Piecewise Parabolic Method (PPM) approach (Ramboll ENVIRON 2016). Gas phase chemistry mechanism CB6r4 is used. CB6r4 developed with a focus on ozone photochemistry, it also results in production of PM precursors such as sulfuric and nitric acids and semi-volatile organic compounds (Yarwood et al 2010). For aerosols, the 2-mode (coarse-fine) CAMx PM size distribution is used, in which all secondary particles are modelled as fine only. Aqueous sulfate and nitrate formation in cloud water is modeled with the RADM algorithm (Chang et al 1987). The thermodynamic partitioning of inorganic aerosol species (sulfate, nitrate, ammonium, and natural minerals) is based on the routine ISORROPIA v.1.6. (Nenes et al 1998). In CAMx, ISORROPIA is also called in every time step for cloudy grid cells to ensure that rapidly evolving (through aqueous chemistry) sulfate, nitrate and neutralizing cations, are in balance with the local environment. Secondary organic aerosol (SOA) is modeled with the routine SOAP (Secondary Organic Aerosol Partitioning) (Strader et al 1999). Aerosol and gas dry deposition is modeled according to resistance model Zhang et al (2001) for aerosols and Zhang et al (2003) for gases. Wet deposition is estimated by the scavenging model for gases and aerosols (Seinfeld and Pandis 2012). Wet deposition is invoked only if precipitation is reaching the surface, assuming cloud and precipitation exist in steady state during the hourly model time step. The model assumes that all gases are dissolved in cloud water in equilibrium with ambient air concentrations according to Henry’s Law solubility, aqueous dissociation, cloud water temperature and acidity; and all particles are taken up into cloud water. It is also assumed that all particle species within a particular size range (fine or coarse) are internally mixed and hydrophilic. Cloud water gas scavenging may be reversible but particle scavenging is irreversible (Ramboll ENVIRON 2016). CAMx was initialized during May 2011 with a three-day spin up starting May 1. While a longer spin up of about 2 weeks is ideal, a 3-day spin up period was reported to increase PM$_{2.5}$ concentrations by ∼0.1 μg m$^{-3}$ in Samaali et al (2009). Initial and boundary conditions for CAMx were generated using outputs from the Model for Ozone and Related Chemical Tracers (MOZART) model (NCAR 2017) and photolysis rates were generated using ozone column data.
Predicted hourly ambient NH₃, total PM₂.₅ and speciated PM₂.₅ (PM-NH₄, PM-sulfate (PM-SO₄) and PM-nitrate (PM-NO₃)) concentrations were extracted for further evaluation. The CAMx modeling framework adopted in this study, with linkages between various models, pre-processor programs and model inputs are shown in figure 2.

2.5. Evaluation of CAMx predictions
Operational evaluation of CTM predictions is recommended using graphical techniques and statistical evaluation in comparison with ground-based observation data (US EPA 2014c). In this study, predicted hourly concentrations of ambient NH₃, total PM₂.₅, PM-NH₄, PM-SO₄ and PM-NO₃ were evaluated graphically for all four emissions scenarios, using the Visualization Environment for Rich Data Interpolation (VERDi v1.5) tool (CMAS 2014). Observations were mapped using ArcGIS v10.4.1 (ESRI 2016). A custom program was developed using MATLAB version R2017a (The MathWorks Inc. 2017) to pair CAMx predictions with observations in space and time, for statistical evaluation. NH₃ is the most challenging pollutant to evaluate due to scarcity of measured data, at time resolutions matching the hourly resolution of CAMx. Observations of ambient NH₃ concentrations were obtained from the Ammonia Monitoring Network (AMoN), which reports ground-level NH₃ concentrations measured using Radiello® passive samplers, integrated over two-week sampling periods (NADP 2015). Predicted NH₃ concentrations were aggregated to match the time frame of AMoN observations at each station, as recommended by Schiferl et al (2016). Predicted NH₃ concentrations were converted from units of parts per million by volume (ppmv) to μg m⁻³ using average surface temperature and pressure observed across the Midwest obtained from ISWS (2016). Error introduced by using this standard conversion factor was < 5%, when accounting for the range in observed maximum and minimum temperature and pressure values during May 2011, at the Midwest observation sites (ISWS 2016). Further model evaluation was considered by comparing predictions of total PM₂.₅, and PM-NH₄, PM-SO₄ and PM-NO₃ concentrations to ground-level, integrated, 24-hour observations obtained from the quality assured Air Quality System (AQS) Data Mart (US EPA 2014c). PM₂.₅ predictions were similarly averaged to the 24-hr time resolution of AQS observations. Observation stations located in the boundary grid cells of the Midwest domain were removed from analysis to minimize impact of boundary conditions.

Closure between CAMx predictions and observations was evaluated using statistical metrics including normalized mean bias (NMB), root mean square error (RMSE) and correlation coefficient (r) (table S4). CAMx performance was compared to findings from other studies and to benchmarks recommended by Emery et al (2017), who identified the ‘goal’ (i.e., best achievable CTM performance that the top one-third of studies have met) and ‘criteria’ (i.e., current CTM performance that two-third of studies have met) performance. Recommended benchmarks are available for total and speciated PM₂.₅ as follows: Total PM₂.₅, PM-NH₄,
PM-SO₄: (1) goal (NMB < ±10%, r > 0.7) and (2) criteria performance (NMB < ±30%, r > 0.4) and for PM-NO₃: (1) Goal (NMB < ±15%), and (2) criteria performance (NMB < ±65%) (Emery et al 2017).

3. Results

3.1. CAMx performance evaluation
Performance evaluation statistics for NH₃, PM₂.₅, PM-NH₄, PM-SO₄, and PM-NO₃ are presented in table 2. Modeled results at the hourly scale were averaged to match the time scales of the measurements which are 14 days for NH₃ as reported by AMoN, and 24 h for PM species as reported in AQS. We focus on comparing differences resulting from alternative spatial representation of NH₃ emissions from fertilizer application.
### Table 3. Comparison of normalized mean bias (NMB) metric reported for NH$_3$ concentrations in this study with other studies

| Metric       | This study                  | Findings from other studies |
|--------------|-----------------------------|-----------------------------|
|              | Range of predictions        | Grid resolution | CTM | Reported value |
| **Ambient NH$_3$** |                             |               |     |               |
| NMB          | −93% to −63%                | ISS-DNDC-4 km (−63%)       | 4 km × 4 km | CAMx | −80% to −24%  | (Zhang et al 2013) |
|              | 4 km × 4 km                 | CAMx               | −0.55 | (Thompson et al 2015) |
|              | 12 km × 12 km               | CMAQ               | −67% to −53% | (Thompson et al 2015) |
|              | 12 km × 12 km               | CMAQ               | −77% to −58% | (Bray et al 2017) |
| r            | −0.17 to 0.57               | ISS-DNDC-12 km (0.57)    | 4 km × 4 km | CAMx | 0.10 to 0.15  | (Rodriguez et al 2011) |
|              | 4 km × 4 km                 | CAMx               | −0.04 to 0.23 | (Zhang et al 2013) |
|              | 4 km × 4 km                 | CMAQ               | 0.15 to 0.48 | (Kelly et al 2014) |
|              | 4 km × 4 km                 | CAMx               | 0.75 | (Thompson et al 2015) |
|              | 12 km × 12 km               | CMAQ               | 0.52 to 0.97 | (Battye et al 2016) |
|              | 2° × 2.5°                   | GEOS-Chem           | 0.6 to 0.8 | (Spak et al 2012) |
|              | 12 km × 12 km               | CMAQ               | 0.28 to 0.34 | (Bray et al 2017) |
| **Ambient total PM$_{2.5}$** |                             |               |     |               |
| NMB          | −40% to −25%                | Baseline-12 km (−25%)    | 4 km × 4 km | CMAQ | −45 to −32%  | (Wu et al 2008) |
|              | 4 km × 4 km                 | CAMx               | −58% to −17% | (Zhang et al 2013) |
|              | 12 km × 12 km               | CAMx               | 0.30 to 0.57 | (Spak et al 2012) |
| r            | 0.46 to 0.57                | ISS-DNDC-12 km (0.57)    | 4 km × 4 km | CAMx | 0.22 to 0.70  | (Zhang et al 2013) |
|              | 12 km × 12 km               | CMAQ               | 0.50 to 0.67 | (Kim et al 2014) |
| **Ambient PM-NH$_4$** |                             |               |     |               |
| NMB          | −61% to 6%                  | ISS-DNDC-12 km (6%)     | 4 km × 4 km | CMAQ | −35% to −29%  | (Wu et al 2008) |
|              | 4 km × 4 km                 | CAMx               | −40% | (Rodriguez et al 2011) |
|              | 2° × 2.5°                   | GEOS-Chem           | −48% to 40% | (Walker et al 2012) |
|              | 4 km × 4 km                 | CAMx               | −40% to −33% | (Zhang et al 2013) |
|              | 4 km × 4 km                 | CMAQ               | −57% to −11% | (Kelly et al 2014) |
|              | 4 km × 4 km                 | CAMx               | −31% | (Thompson et al 2015) |
| r            | 0.19 to 0.88                | ISS-DNDC-12 km (0.88)    | 12 km × 12 km | CAMx | 0.18 | (Battye et al 2016) |
|              | 4 km × 4 km                 | CAMx               | 0.21 to 0.28 | (Rodriguez et al 2011) |
|              | 12 km × 12 km               | CAMx               | 0.36 to 0.65 | (Spak et al 2012) |
|              | 4 km × 4 km                 | CAMx               | 0.20 to 0.90 | (Zhang et al 2013) |
|              | 4 km × 4 km                 | CMAQ               | 0.02 to 0.83 | (Kelly et al 2014) |
### Table 3. (Continued.)

| Metric        | This study | Findings from other studies |
|---------------|------------|-----------------------------|
|               | Range of predictions | Best scenario<sup>b</sup> | Grid resolution | CTM | Reported value |
|               |             |                             |                |
| Ambient PM-\(\text{SO}_4\) |             |                             |                |
| NMB           | \(-41\% \text{ to } 23\%\) | ISS-DNDC-12 km (23%) | 4 km \(\times\) 4 km | CMAQ | \(-0.17\) | (Wu et al 2008) |
|               |             |                             | 4 km \(\times\) 4 km | CAMx | \(-11\% \text{ to } 11\%\) | (Rodriguez et al 2011) |
|               |             |                             | 2° \(\times\) 2.5° | GEOS-Chem | \(-14\% \text{ to } 17\%\) | (Walker et al 2012) |
|               |             |                             | 4 km \(\times\) 4 km | CAMx | \(-39\% \text{ to } 1\%\) | (Zhang et al 2013) |
|               |             |                             | 4 km \(\times\) 4 km | CMAQ | \(-16\% \text{ to } 37\%\) | (Kelly et al 2014) |
|               |             |                             | 4 km \(\times\) 4 km | CAMx | 9% | (Thompson et al 2015) |
|               | 0.15 to 0.71 | ISS-DNDC-12 km (0.71) | 4 km \(\times\) 4 km | CAMx | 0.13 to 0.18 | (Rodriguez et al 2011) |
|               |             |                             | 12 km \(\times\) 12 km | CAMx | 0.38 to 0.55 | (Spak et al 2012) |
|               |             |                             | 4 km \(\times\) 4 km | CAMx | 0.10 to 0.80 | (Zhang et al 2013) |
|               |             |                             | 4 km \(\times\) 4 km | CMAQ | \(-0.26 \text{ to } 0.42\) | (Kelly et al 2014) |
|               |             |                             | 12 km \(\times\) 12 km | CMAQ | 0.36 to 0.68 | (Kim et al 2014) |
|               |             |                             | 4 km \(\times\) 4 km | CAMx | 0.78 | (Thompson et al 2015) |
| Ambient PM-\(\text{NO}_3\) |             |                             |                |
| NMB           | \(-84\% \text{ to } 38\%\) | Baseline-12 km (38%) | 4 km \(\times\) 4 km | CMAQ | \(-41\% \text{ to } -20\%\) | (Wu et al 2008) |
|               |             |                             | 4 km \(\times\) 4 km | CAMx | \(-90\% \text{ to } -50\%\) | (Rodriguez et al 2011) |
|               |             |                             | 2° \(\times\) 2.5° | GEOS-Chem | \(-65\% \text{ to } 80\%\) | (Walker et al 2012) |
|               |             |                             | 4 km \(\times\) 4 km | CAMx | \(-93\% \text{ to } -57\%\) | (Zhang et al 2013) |
|               |             |                             | 4 km \(\times\) 4 km | CMAQ | \(-40\% \text{ to } 2\%\) | (Kelly et al 2014) |
|               |             |                             | 4 km \(\times\) 4 km | CAMx | 57% | (Thompson et al 2015) |
|               | 0.10 to 0.64 | Baseline-12 km (0.64) | 4 km \(\times\) 4 km | CAMx | 0.10 to 0.15 | (Rodriguez et al 2011) |
|               |             |                             | 12 km \(\times\) 12 km | CAMx | 0.47 to 0.66 | (Spak et al 2012) |
|               |             |                             | 4 km \(\times\) 4 km | CAMx | 0.03 to 0.30 | (Zhang et al 2013) |
|               |             |                             | 4 km \(\times\) 4 km | CMAQ | 0.15 to 0.48 | (Kelly et al 2014) |
|               |             |                             | 12 km \(\times\) 12 km | CMAQ | 0.53 to 0.64 | (Kim et al 2014) |
|               |             |                             | 4 km \(\times\) 4 km | CAMx | 0.58 | (Thompson et al 2015) |

<sup>a</sup> Reported \(r\) metrics from other studies are presented in table S5.

<sup>b</sup> Values in parentheses indicate the calculated statistical metric for the best performing emission scenario in this study. NMB values are reported as %.
combined with DNDC predicted NH₃ emission peak timing and temporal evolution, and model grid resolution. Evaluation statistics from this study are compared with other studies in table 3.

### 3.1.1. NH₃ concentration predictions

Spatial distribution of monthly average predictions of ambient NH₃ concentrations obtained using the four emission scenarios for May 2011 are shown in figures 3(a) and (b) (baseline-4 km and ISS-DNDC-4 km scenarios, respectively) and figures 3(c) and (d) (baseline-12 km and ISS-DNDC-12 km scenarios, respectively). At AMoN stations, observed NH₃ concentrations ranged between 1.98 and 10.11 μg m⁻³ (figure 3(e)), while corresponding predicted concentrations ranged between 0.32 to 2.1 μg m⁻³. Ambient NH₃ concentrations are underpredicted by CAMx for all scenarios, with the smallest NMB = −63% for the ISS-DNDC-4 km scenario. Highest NH₃ concentrations were predicted in the ISS-DNDC-4 km scenario with concentrations >2 μg m⁻³. Highest predicted concentrations were observed in western (State of Iowa) and eastern (State of Indiana) parts of the domain and in smaller spatial extents in the south. Identified regions with high predictions are collocated with areas of elevated NH₃ emissions resulting from intensive fertilizer usage for corn planted grid cells (~55%
of cropland in Iowa, 50% of cropland in Indiana (NASS 2014), in comparison to emission maps presented in Balasubramanian et al (2015a). Predicted NH3 concentrations are lower for the 12 km × 12 km scenarios compared to the 4 km × 4 km scenarios; indicating spatial homogenization of NH3 emissions in the coarser grid due to averaging of sub-grid scale emission peaks. Thus, NH3 emissions and CAMx predicted concentration trends were further investigated, at three AMoN sites (Bondville and Alhambra, rural agricultural sites; and Indianapolis, urban site), where observations were available.

The hourly modelled emission fluxes and predicted NH3 concentrations at these sites are shown in figure 4 for all emission scenarios. As anticipated, rural sites exhibit higher emission fluxes (figures 4(a) and (b)) than urban sites (figure 4(c)) due to presence of agricultural activities. The impact of spatial homogenization at coarser grid scale is evident as the 4 km × 4 km emission scenarios exhibit higher NH3 emission flux in comparison to the 12 km × 12 km scenarios. In terms of timing, localized emission peaks captured in the ISS-DNDC scenarios (predicted in the third week of May due to fertilizer application during active planting dates for corn) are higher in magnitude compared to the baseline approach for both 4 km × 4 km and 12 km × 12 km scenarios that represent seasonally averaged emissions. However, trends in diurnal patterns in emissions are similar both baseline and ISS-DNDC, as they are driven by the same hourly temporal profile (Balasubramanian et al 2015a) obtained from the NEIv6.2 modeling platform. Since NH3 has a short lifetime (order of hours) (Adams et al 1999, Aneja 2001), trends in predicted NH3 concentrations were anticipated to follow spatial and diurnal patterns in NH3 emissions (Balasubramanian et al 2015a). However, the modeled spatial patterns are not identical across the domain. We hypothesize that NH3 emissions in CAMx were potentially transported and consumed faster within the model domain compared to the ambient environment, but this hypothesis requires further analysis. We also examined hourly variations in NH3 concentrations at the three chosen sites (figures 4(d)–(f)). The data show that: (1) while NH3 emissions (figures 4(a)–(c)) peak around noon, predicted NH3 concentrations (figures 4(d)–(f)) show maxima in late afternoon, and (2) peak modeled daily NH3 concentrations do not follow trends in daily NH3 emission peaks at site scale. Our findings are qualitatively similar to measurement and modeling results presented by Persinne et al (2009). Our findings indicate that while the ISS-DNDC approach can capture localized and episodic NH3 emissions in comparison to the baseline approach, errors due to uncertainties in emission estimates still result in errors in CAMx predictions of NH3 concentrations.

3.1.2. PM2.5 concentration predictions

Comparison of predicted (figures 5(a)–(d)) and observed total PM2.5 (figure 5(e)) concentrations in the Midwest, showed an underestimate for all emissions scenarios with lowest NMB for both baseline scenarios (−27% for baseline-4 km, −25% for the baseline-12 km), and comparable correlations, with the two ISS-DNDC scenarios producing slightly higher r (0.55 for ISS-DNDC-4 km, 0.57 for ISS-DNDC-12 km). The extent of PM2.5 under-predictions was much smaller, compared to NH3 underpredictions. Spatial distribution of predictions of total PM2.5 concentrations in the Midwest under four emission scenarios are shown in figures 5(a) and (b) (baseline-4 km and ISS-DNDC-4 km scenarios, respectively) and figures 5(c) and (d) (baseline-12 km scenarios).
and ISS-DNDC-12 km scenarios, respectively). Observed PM$_{2.5}$ concentrations, averaged for May, ranged between 5.1 and 17.2 $\mu$g m$^{-3}$ (figure 5(e)) in comparison to predicted averaged concentrations (6.67 to 8.35 $\mu$g m$^{-3}$), at the AQS stations. Based on recommended benchmarks (Emery et al, 2017), criteria CTM performance was met for predictions obtained using ISS-DNDC approaches at both 4 km $\times$ 4 km and 12 km $\times$ 12 km grid resolutions in regards to $r(>0.4)$ metrics. The baseline-4 km and baseline-12 km scenarios produced higher concentrations (>12 $\mu$g m$^{-3}$) in the north–east part of the domain and over Lake Michigan compared to the corresponding ISS-DNDC scenarios.

Comparison of predicted (figures 6(a)–(d)) and observed (figure 6(e)) PM-NH$_4$ concentrations showed underpredictions for the two 4 km scenarios and positive NMB for the ISS-DNDC-12 km scenario (NMB = 6%). Observed PM-NH$_4$ concentrations ranged from 0.2 to 1.6 $\mu$g m$^{-3}$ (figure 6(e)) in comparison to predicted concentrations (0.4 to 2.7 $\mu$g m$^{-3}$) at the AQS stations (figures 6(a)–(d)). The two 12 km scenarios gave the highest correlations (12 km baseline $r = 0.85$ and ISS-DNDC-12 km $r = 0.88$), providing evidence of grid resolution effect for the case of PM-NH$_4$. This finding could relate to the availability of NH$_3$ in the atmosphere as noted from figures 3 and 4. In case of the 4 km $\times$ 4 km emission scenarios, we postulate that

![Figure 5. Spatial trends in PM$_{2.5}$ predictions ($\mu$g m$^{-3}$) averaged over May 2011 for the (a) baseline-4 km, (b) ISS-DNDC-4 km scenarios (c) Baseline-12 km and (d) ISS-DNDC-12 km scenarios. (e) Observed PM$_{2.5}$ concentrations ($\mu$g m$^{-3}$) at AQS stations in the Midwest averaged over May 2011 (colors matched with graduated scale used for predictions).](image-url)
higher emission fluxes result in an increase of free ammonia over short periods of time, that is potentially advected or deposited before chemical transformation; thereby resulting in smaller magnitude of speciated PM$_{2.5}$ predictions. Spatial distribution of average predictions of PM-NH$_4$ concentrations under the four emissions scenarios are shown in figures 6(a) and (b) (baseline-4 km and ISS-DNDC-4 km scenarios, respectively) and figures 6(c) and (d) (baseline-12 km and ISS-DNDC-12 km scenarios, respectively). Average predicted PM-NH$_4$ concentrations ranged between 0.1 and 3.6 μgm$^{-3}$ across the Midwest. Baseline-4 km and baseline-12 km scenarios exhibited larger spatial variability and predicted higher concentrations (>2.2 μgm$^{-3}$) in the eastern part of the Midwest not seen in the corresponding ISS-DNDC scenarios. Similar grid related differences were observed for PM-SO$_4$, with the 4 km scenarios (figures 7(a) and (b)) similarly underpredicting (NMBs = −40% and −41%) and the 12 km scenarios (figures 7(c) and (d)) similarly overpredicting (NMBs = 25% and 23%). Observed PM-SO$_4$ concentrations at AQS stations in the Midwest ranged from 0.8 to 4.1 μgm$^{-3}$ (figure 7(e)) in comparison to corresponding predictions (1.4 to 3.1 μgm$^{-3}$). Correlations are poor in the 4 km × 4 km scenarios ($r = 0.15$), but much higher for the 12 km scenarios ($r = 0.70$ and 0.71 for baseline-12 km and ISS-DNDC-12 km, respectively). Spatial distributions of average predictions of PM-SO$_4$ concentrations under the four emissions scenarios are shown in figures 7(a) and (b) (baseline-4 km and ISS-DNDC-4 km scenarios, respectively) and figures 7(c) and (d) (baseline-12 km and ISS-DNDC-12 km scenarios, respectively). Average predicted PM-SO$_4$ concentrations ranged between 0.8 and 7.2 μgm$^{-3}$, across the Midwest, with all four scenarios exhibiting higher concentrations of PM-SO$_4$. 

Figure 6. Spatial trends in PM-NH$_4$ predictions (μgm$^{-3}$) averaged over May 2011 for the (a) baseline-4 km, (b) ISS-DNDC-4 km scenarios (c) baseline-12 km and (d) ISS-DNDC-12 km scenarios. (e) Observed PM-NH$_4$ concentrations (μgm$^{-3}$) at AQS stations in the Midwest averaged over May 2011 (colors matched with graduated scale used for predictions).
(>4 μg m⁻³) in the eastern part of the domain. Among all speciated PM species, PM-SO₄ is relatively well-mixed in the atmosphere and exhibited larger spatial homogeneity, because of the preferential uptake of sulfuric acid as compared to nitric acid by free NH₃, and slow rates of formation and removal (Park et al 2006).

Comparison of PM-NO₃ predicted (figures 8(a)–(d)) and observed (figure 8(e)) values showed poor performance of the 4 km × 4 km scenarios with \( r = 0.12 \) and 0.1 for baseline-4 km and ISS-DNDC-4 km, respectively, with these two scenarios underpredicting (NMBs = −79% and −84%). Results for the 12 km × 12 km scenarios are confounding, with higher correlations (\( r = 0.64 \) and 0.52 for baseline-12 km and ISS-DNDC-12 km) but baseline-12 km overpredicted (NMB = 38%) while ISS-DNDC-12 km underpredicted (NMB = −54%) PM-NO₃. Spatial distribution of average predictions of PM-NO₃ concentrations range between 0.07 and 3.8 μg m⁻³ across the Midwest domain under the four emissions scenarios that are shown in figures 8(a) and (b) (baseline-4 km and ISS-DNDC-4 km scenarios, respectively) and figures 8(c) and (d) (baseline-12 km and ISS-DNDC-12 km scenarios, respectively). Observed PM-NO₃ concentrations at AQS stations ranged between 0.09 and 1.6 μg m⁻³, in comparison to the corresponding predicted concentrations (0.13 to 4 μg m⁻³). Compared to the ISS-DNDC scenarios, baseline-4 km and baseline-12 km scenarios predicted higher concentrations (>1.0 μg m⁻³) in the north-east part of the Midwest, where colder temperatures were observed in comparison with the rest of the Midwest (ISWS 2016). Further research is warranted to investigate these trends and establish how speciated PM formation is impacted by availability of NH₃ in the atmosphere and in consideration of meteorological parameters such as temperature and atmospheric stability.
4. Discussion

Evaluation of NH₃ predictions is limited by the lack of NH₃ observational data. Currently the AMoN network provides the best ground-based spatial coverage of NH₃ observations in the US, available since 2007, with coarse time resolution averaged over 14 days. While satellite monitoring and aerial measurements provide additional information, such information is not readily available because the effort currently requires complex data assimilation and processing, and is not directly comparable with ground level measurements because it is integrated over the atmospheric column (Clarisse et al 2009, Schiferl et al 2016, Warner et al 2016). In this study, due to the sparse coverage of AMoN stations, there were only 5 prediction-observation pairs available for statistical evaluation, over our focal region of the US Corn Belt that has high agricultural NH₃ emissions from fertilizers, in May 2011. Therefore, the reported evaluation is indicative of model performance rather than conclusive. However, our findings reassert the underpredictions reported in the literature, irrespective of use of ground-based observations (table 2), aerial or satellite data for the evaluation (Schiferl et al 2016, Warner et al 2016).
Summary of evaluation statistics from this and previous studies (table 3) show consistent underpredictions in NH₃ concentrations, by a factor of 2 or higher in studies implementing CAMx (Thompson et al 2015, Malm et al 2016), CMAQ (Battye et al 2016), European CALIOPE-EU (Pay et al 2012) and GEOS-Chem (Schiferl et al 2016). The largest underpredictions were identified near agricultural sites that were characterized by high ambient NH₃ concentrations (Kruith et al 2012, Butler et al 2015, Vogt et al 2013). The magnitude of our underpredictions are higher and similar to Bray et al (2017), where CMAQ underpredicted NH₃ concentrations by a factor of 4.5 in comparison with satellite observations. One explanation is the smaller source contributions of NH₃ from chemical fertilizers in cited studies, as compared to this study. In studies over Eastern US and Colorado, fertilizer usage accounted for 20% or less of anthropogenic NH₃ emissions, whereas in the Midwest region we examine, the contribution is as high as 55% (US EPA 2015). This indicates the need for regionally specific modeling of NH₃ emissions from fertilizer application; because even though this source contributes half or less of total NH₃ emissions, it can introduce large biases in ambient NH₃ and PM2.5. Identified underpredictions in NH₃ concentrations could result from potential errors in total NH₃ emissions developed using the emission-factor approach for the Midwest, a case supported by comparisons with satellite measurements (Clarisse et al 2009) and inverse modeling efforts (Paulot et al 2014). Such uncertainties include uncertainties in planting and fertilization dates and use of generalized regional fertilizer application practices, as farm scale practices are not available. There is a further need for development and evaluation of alternative methods to estimate total NH₃ emissions used as inputs to CTMs, supported by a denser monitoring network for both NH₃ fluxes and concentrations. While this study indicates an advancement in this direction, reported findings indicate a need to further explore the use of satellite data and process models to capture variations in NH₃ emissions based on complex crop, soil and weather interactions. Examples in this direction include US EPA’s use of EPIC (Williams et al 1983, 1984) in the compilation of the latest available NEI 2014 (US EPA 2017b), efforts to evaluate the DNDC model with field measurements (Balasubramanian et al 2017) and use of satellite data to identify NH₃ emission hotspots and quantify emission inventory uncertainties (van Damme et al 2018, Zhu et al 2015b).

Another source of differences in NH₃ concentration predictions between baseline and ISS-DNDC scenarios could result from the representation of NH₃ deposition within CAMx. CAMx currently does not model bidirectional exchange of NH₃, unlike other CTMs that account for canopy compensation points to predict ambient NH₃ concentrations (Flechard et al 2013). An example is integration of the EPIC model with bidirectional exchange in CMAQ that increased ambient NH₃ concentrations by 14% across the US (Bash et al 2013). However, this may vary across CTMs. A similar implementation in the GEOS-Chem model resulted in larger underestimates (factor 2–5) in predicted NH₃ concentrations (Zhu et al 2015a). Subsequently, Schiferl et al (2016) did not include the bidirectional scheme, and recommended an increase in model grid resolution. In comparison, introduction of bidirectional exchange in the LOTOS-EUROS model increased predictions of NH₃ concentrations by 30%–40% over agricultural areas due to increase in NH₃ lifetime and transport distance (Kruith et al 2012). Hence, implementation of a bidirectional exchange scheme within CAMx, at high spatial resolutions (≤ 12 km × 12 km), is pertinent, as it could reduce identified underpredictions by extending the time period of NH₃ volatilization and lifetime in the atmosphere. Still all studies suggest that the current magnitude of NH₃ emissions is underestimated and require further development.

In comparing results of performance evaluation for PM₂.₅ and its components PM-NH₄, PM-SO₄ and PM-NO₃, the effect of model grid resolution is more pronounced, than the method used to allocate fertilizer NH₃ emissions. The method of emission allocation has an effect on spatial trends in predicted concentrations and is therefore important in studies where CTMs like CAMx are applied over local scales. Overall, estimated NMB and r metrics for total and speciated PM₂.₅ in this study are in the reported range from other CTM studies. PM-NH₄ exhibited improved performance compared to most CTM studies (table 3), especially for the ISS-DNDC-12 km scenario. Regarding previous CAMx performance results, in a comparative model performance study, CAMx exhibited improved performance in predicting PM₂.₅ in the southeast US (r = 0.31 to 0.7), as compared to CMAQ (r = 0.22 to 0.5) (Zhang et al 2013). Thompson et al (2015) demonstrated that CAMx satisfactorily reproduced annual predictions of PM-NH₄ (NMB = −31%, r = 0.71), PM-SO₄ (NMB = 9%, r = 0.78) and PM-NO₃ (NMB = 57%, r = 0.58) over the Rocky Mountain National Park in the US In evaluating CAMx, Rodriguez et al (2011) point to the effect of the extent of the spatial domain where they obtained improved correlation for PM₂.₅ (r = 0.40) for the entire US, in comparison with the Rocky Mountain National Park region (r = 0.15), indicating strong dependence of predictions on regional emission sources. These findings support recommendations by Emery et al (2017) to limit evaluation of CTM predictions of PM₂.₅ to domains not exceeding 1000 km × 1000 km, to capture regional source contributions, and over temporal scales of a month (but no more than three months), to account for seasonal differences. Similarly, impact of timing of NH₃ emissions on ambient speciated PM₂.₅ at the sub–daily scale deserves further study to resolve the identified poor correlation (r) indicated in table 3. While winter PM formation has not been addressed in this study, there is a need to better characterize variability in NH₃ emissions to reduce wintertime PM₂.₅.
overpredictions in the Midwest (Pitchford et al. 2009, Kim et al. 2014). By extension, observed low nighttime temperatures during May 2011 (4 °C to 15 °C, across the Midwest (ISWS 2016)) could result in enhancement of nighttime PM-NO₃. Identified poor closure metrics for PM-NO₃ could be attributed to larger underpredictions during nighttime in the Midwest and deserves further investigation.

While it was anticipated that higher-spatial resolution emissions and meteorology inputs will improve predictions of PM₂.₅, implementation of the 4 km × 4 km grid resolution did not improve model performance in comparison to the 12 km × 12 km grid resolution. Similarly, a study over North Carolina concluded that increasing spatial resolution did not improve PM predictions (Queen and Zhang 2008). Slight improvements in PM₂.₅ predictions using a 4 km × 4 km grid over Texas (NMB = −22%) were observed as compared to 12 km × 12 km (NMB = −33%) in a study by Misenis and Zhang (2010). While a multi-CTM evaluation in Europe identified significant improvement in PM₁₀ predictions at urban areas when reducing grid size from 50 km × 50 km to 14 km × 14 km, finer resolutions (<14 km × 14 km) did not show further improvements (Schaap et al. 2015). A comparison of PM₂.₅ predictions at 36 km × 36 km, 12 km × 12 km and 4 km × 4 km grid resolutions over Northeast US and western Europe indicated no statistically significant difference, except in winter for the finer 4 km × 4 km grid resolution, which was due to improved emissions representation from urban areas (Fountoukis et al. 2013). Similarly, no significant improvements were identified for health assessments as related to PM₂.₅ when implementing finer 4 km × 4 km grid spacing (Thompson et al. 2014). Studies support that for current CTM formulations, 12 km × 12 km is a suitable grid resolution for PM₂.₅ predictions (Appel et al. 2011, Schaap et al. 2015) and results from this study seem to support that conclusion. It appears that the 12 km × 12 km resolution represents an optimum trade-off between emissions representation within CTMs, and errors resulting from the higher-resolution emission inventory and meteorological inputs that can increase and propagate non-linearly within CTM algorithms (Valari and Menut 2008, Schaap et al. 2015). Implementation of the 12 km × 12 km grid resolution reduces computational time and resources required for generating predictions and output data management (Gan et al. 2016). However, finer spatial resolution is desirable for reactive nitrogen deposition studies that are an important consequence of air pollution, with 1 km × 1 km grid resolution identified as necessary for assessment of ecosystem damage (Dore et al. 2012), especially near agricultural sources (Butler et al. 2015). Therefore, the discussion about what is preferable spatial resolution given the current state of CTMs and what is desirable for health and ecosystem studies is far from closed.

Our findings come with two limitations. First, we consider a short modeling episode of one month (May 2011), which was an active planting month in the Corn Belt. Second, CAMx does not currently include bidirectional treatment of NH₃ fluxes. Given that exploring these limitations was out of scope for this study, we recommend two key directions for future research. First, a higher-resolution monitoring network for NH₃ and NH₄ fluxes and concentrations is required to spatially increase coverage over both rural and urban locations, and increase time resolution in NH₃ flux measurements from fertilized fields. Such measurements will help evaluate emissions estimated from process modeling and satellite-based approaches, and reduce uncertainties in total NH₃ emissions and also capture temporal occurrence of distinct emission peaks observed in the field (Walker et al. 2013, Nelson et al. 2017). Second, increased specificity and regularity of data collection related to fertilizer type and management practices will also be required to support such efforts (US EPA 2011). With continued research to improve emission representation at higher spatial resolutions and CTM formulations, the impact of grid resolution on ambient NH₃ and PM₂.₅ should be revisited.

5. Conclusion

In this paper we report findings from research aimed to understand the impact of NH₃ emissions from fertilizer application on CAMx predictions of ambient NH₃ and PM₂.₅ concentrations. Based on our findings, we conclude that future studies should carefully account for tradeoffs in model prediction accuracy when increasing grid resolution for emission inventory and meteorological inputs. While total NH₃ emissions play a key role in determining ambient air pollutant concentrations, we highlight that how NH₃ emissions are distributed in space and time within chemical transport models (CTMs) also significantly impacts total magnitude and spatial distribution of predictions of ambient NH₃ and PM₂.₅ concentrations, while keeping other inputs constant, including meteorological and model parameters, and emissions of other precursors and primary pollutants. Given that differences in spatial patterns of PM₂.₅ species concentrations have implications for identifying geographical areas of concern for human health, environmental justice, and ecosystem services, further research is required to study abundance of ambient NH₃ predicted by CTMs at high-spatial and temporal scales and the impact on PM₂.₅ formation. An approach, as we demonstrate, that uses process-based models to develop on- or off-line spatial and temporal factors can be further developed for preparing inputs to CTMs.
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