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Modeling agricultural air quality: Current status, major challenges, and outlook

Yang Zhang[a,*], Shiang-Yuh Wu[b,c], Srinath Krishnan[a], Kai Wang[a], Ashley Queen[a], Viney P. Aneja[a], S. Pal Arya[a]

[a]*Department of Marine, Earth and Atmospheric Sciences, North Carolina State University, Raleigh, NC 27695-8208, USA*
[b]*Department of Environmental Quality, Richmond, VA 23240, USA*
[c]*Clarke County, Nevada Department of Air Quality and Environmental Quality, Las Vegas, NV 89155, USA*

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Abstract

Agricultural air quality is an important emerging area of atmospheric sciences that represents significant challenges in many aspects of research including measurements, modeling, regulations, emission control, and operation managements. This work presents a review of current status, major challenges, and future research needs and opportunities of several important aspects of agricultural air quality modeling including chemical species, concentration and deposition measurements for model verification, emission inventories, major physical and chemical processes, model application and evaluation, and policy implications.

Keywords: Agriculture; Air quality; Ammonia; Reduced nitrogen; 3-D modeling

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1. Introduction

Air quality research in the past half century focuses largely on criteria pollutants such as nitrogen oxides (NO_x), sulfur dioxide (SO_2), ozone (O_3), and particulate matter with an aerodynamic diameter equal or less than 2.5 μm ($PM_{2.5}$). Limited attention has been given to non-criteria air pollutants such as reduced nitrogen- and sulfur-containing compounds from agricultural sources (e.g., ammonia (NH_3), hydrogen sulfide (H_2S), nitrous oxide (N_2O)) that may play important roles in the formation of tropospheric O_3, SO_2, acids, and $PM_{2.5}$, and the eutrophication of the ecosystems. Agriculture provides a major source of those nitrogen- and sulfur-containing compounds (e.g., livestock, fertilizer, soils, and biomass burning). For example, 90% of the atmospheric NH_3 emission results from animal production and emissions from slurries and manures in the US (Davison and Cape, 2003) and many European countries (Van Der Hoek, 1998; Hutchings et al., 2001; Sotiropoulou et al., 2004). Growing evidence has shown that the increased size and geographical concentration of animal-feeding operations (AFOs) and agricultural crop production are increasing the emissions of odor (e.g., organic acids) and trace gases (e.g., carbon dioxide (CO_2), methane (CH_4), NO_x, NH_3,

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[*] Corresponding author. Tel.: +1 919 515 9688; fax: +1 919 515 7802.
E-mail address: yang_zhang@ncsu.edu (Y. Zhang).

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and H_2S) to the atmosphere (e.g., NRC, 2003; Aneja et al., 2006). Increases in the emissions of those agriculturally emitted compounds in the US and abroad and their adverse impacts on the quality of the air, water, soil, the biodiversity, and the entire agro-ecosystem have raised growing public and regulatory concerns. For example, atmospheric nitrogen deposition has been considered to be one of the top three causes for global biodiversity loss in this century following land use and climate change (Sala et al., 2000); and it will post serious threat to biodiversity (Phoenix et al., 2006) and ecosystem (Sanderson et al., 2006). In addition, NH_3 likely plays an increased role in $PM_{2.5}$ formation as the emissions of sulfur oxides (SO_x) and NO_x are reduced in the coming years and the promulgation of a more stringent 24-h average National Ambient Air Quality Standard (NAAQS) of $35\,\mu g\,m^{-3}$ by the US EPA for $PM_{2.5}$. Recognizing the growing needs in this research area, a number of governmental agencies such as the US Department of Agriculture (USDA), the National Science Foundation (NSF), the US Environmental Protection Agency (EPA), the North Carolina Division of Air Quality (NCDAQ) and several universities and research organizations such as the North Carolina State University (NCSU), Duke University, Purdue University, the Air and Waste management Association (A&WMA), and the Ecological Society of America co-sponsored the first workshop on agricultural air quality (WAAQ) in the US during June 3–8, 2006 to synthesize existing measurements and modeling results and identify emerging research needs for agricultural air quality (AAQ) (http://www.esa.org/AirWorkshop). As indicated at the WAAQ by the keynote speaker, Dr. Ralph Cicerone, the president of the US National Academy of Sciences, the research on agricultural air quality in the US is much behind compared with countries in Europe such as the Netherlands, Denmark, the UK, Scotland, and Spain.

Air quality models (AQMs) accounting for emissions, transport, transformation, and removal of air pollutants provide a powerful tool to simulate the fate, distributions, and impact of agriculturally emitted air pollutants. National Research Council has clearly identified a need for three-dimensional (3-D) transport/transformation models in providing scientific basis for the development of relevant mitigation strategies (NRC, 2003). In this paper, current status and major challenges associated with AAQ modeling are reviewed. The deficiencies and uncertainties in current AQMs, model inputs, and measurements will be indicated along with recommendations regarding potential model improvements and data needs. Finally, the important implications of results from 3-D AQMs in developing relevant regulations and control strategies for agricultural air quality as well as future research opportunities for studying agriculture-related pollutants and their impacts on air quality, human health, and regional climate will be discussed.

2. Current status

The development of feasible regulations of air emissions from AFOs requires a scientific basis that is currently lacking due largely to inadequate funding from governmental agencies, little attention from scientific communities for AAQ research, and the fact that many producers do not want to report emissions from their operations because of the potential for increased scrutiny. The National Air Emissions Monitoring Study (NAEMS) has recently been established to measure emissions from all major types of AFOs including broiler systems, dairy farms, and swine/poultry houses and related manure storage facilities. Knowledge gaps and critical needs for agricultural air quality research have been recently identified by National Research Council (NRC, 2003) and the USDA Agricultural Air Quality Task Force (http://www.airquality.nrcs.usda.gov/AAQTF/). Significant uncertainties lie in nearly all aspects of research including the sparseness of monitoring stations and observational data of emissions, concentrations, and deposition fluxes, the lack of accurate emission inventories and reliable measurement methodologies, poorly-quantified health-effect associated with the AFOs-emitted species, and the needs for process-based emissions models and 3-D transport/transformation models to support regulation and policy-making.

2.1. Species of concern

Many species can be emitted from confined animal feeding operations and burning of crop residue (Aneja et al., 2006). Table 1 lists some major agriculturally-relevant reduced nitrogen and sulfur species that should be considered in AAQ modeling along with their reaction constants and lifetimes against oxidation reactions by the hydroxyl radical (OH). NH_3 is a major basic gas in the atmosphere and plays an important role in neutralizing acids.

Table 1
Important species to be considered in AAQ modeling, and their rate constants and lifetimes against OH reaction[a]

Compound	Chemical name	Rate constant, k, ($T = 298\,\mathrm{K}$) $\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$	Lifetime	References
NH_3	Ammonia	1.6×10^{-13}	72.3 days	DeMore et al. (1997) Atkinson et al. (1997a, b)
CH_3NH_2	Methylamine	2.2×10^{-11}	12.6 h	Atkinson (1989)
		1.7×10^{-11}	16.3 h	Carl and Crowley (1998)
$(CH_3)_2NH$	Dimethylamine	6.5×10^{-11}	4.3 h	Atkinson (1989) Carl and Crowley (1998)
$(CH_3)_3N$	Trimethylamine	6.1×10^{-11}	4.6 h	Atkinson (1989)
		3.6×10^{-11}	7.7 h	Carl and Crowley (1998)
$C_2H_5NH_2$	Ethylamine	2.8×10^{-11}	9.9 h	Finlayson-Pitts and Pitts (2000)
		2.4×10^{-11}	11.6 h	Carl and Crowley (1998)
HCN	Hydrogen cyanide	3.4×10^{-14}	340.4 days	Atkinson (1989)
CH_3CN	Methyl cyanide	8.8×10^{-15}	2.2 yrs	Wine et al. (2002)
	(Acetonitrile)	2.6×10^{-14}	1.2 yrs	Hynes and Wine (1991)
$(CH_3)_3CNH_2$	*t*-Butylamine	1.2×10^{-11}	23.2 h	Koch et al. (1996)
$CH_3NHC(O)CH_3$	*N*-methylacetamide	5.2×10^{-12}	53.4 h	Koch et al. (1997)
$CH_3NHC(O)C_2H_5$	*N*-methylpropionamide	7.6×10^{-12}	36.6 h	Koch et al. (1997)
$(CH_3)_2NC(O)CH_3$	*N*,*N*-dimethyl acetamide	1.4×10^{-11}	19.8 h	Koch et al. (1997)
N_2O	Nitrous oxide	7.2×10^{-11}	54 days	Atkinson et al. (1997a)
CH_4	Methane	6.3×10^{-15}	5.3 yrs	Atkinson et al. (1997a) Seinfeld and Pandis (1998)
CH_3SSCH_3	Dimethyl disulfide	2.3×10^{-10}	1.2 h	Atkinson et al. (1997a)
CH_3SH	Methanethiol	3.3×10^{-11}	8.4 h	Atkinson et al. (1997a) Seinfeld and Pandis (1998)
H_2S	Hydrogen sulfur	4.8×10^{-12}	57.9 h	Atkinson et al. (1997a) Seinfeld and Pandis (1998)
CH_3SCH_3	Dimethyl sulfide	5.0×10^{-12}	55.6 h	Seinfeld and Pandis (1998)
		6.5×10^{-12}	42.7 h	Atkinson et al. (1997a)
CS_2	Carbon disulfide	4.7×10^{-12}	59.1 h	Atkinson et al. (1997a)
COS	Carbonyl sulfide	1.9×10^{-15}	19.2 yrs	Seinfeld and Pandis (1998)
		2.0×10^{-15}	16.9 yrs	Atkinson et al. (1997a)

[a] A mixing ratio of 1.0×10^6 molecules cm^{-3} is assumed for OH in the calculation of lifetime for all species except N_2O, whose major sink is the oxidation by O(^{1}D). A mixing ratio of 3.0×10^3 molecules cm^{-3} is assumed for O(^{1}D) in the calculation of the lifetime of N_2O.

The overall lifetime for NH_3 is short (~0.9 day, Adams et al., 1999) because of its fast dry deposition rate to the surface. Its lifetime against the oxidation of OH, however, is relatively long (2–3 months). The typical mixing ratios range from 0.1 to 10 ppb (0.07–7 $\mu g\,m^{-3}$) (Seinfeld and Pandis, 1998). Table 2 lists observed NH_3 concentrations on various surfaces, with the highest NH_3 mixing ratio of 34.8 $\mu g\,m^{-3}$ occurring at an agricultural site near hog farm operation facilities in eastern NC. NH_3 oxidation contributes to about 6% of the total global NO_x emissions (Seinfeld and Pandis, 1998). Ammonium ion (NH_4^+) can be formed once NH_3 is scavenged by and dissolved into cloud/rain/fog droplets. NH_4^+ salts are a major component of $PM_{2.5}$ which has important health and climatic effects. They have a longer lifetime than NH_3 (e.g., 5 days for $(NH_4)_2SO_4$, IPCC, 2001) and can thus be transported in a long distance. Other reduced nitrogen species include cyanide compounds (e.g., hydrogen cyanide (HCN)), aliphatic and aromatic amines (e.g., methylamine (CH_3NH_2)). While the lifetime against OH for HCN is about a year, those for amines are 4–53 h. Cyanide is used in pesticides and rodenticides, silver and metal polishes, photographic and electroplating solutions, metallurgical processes and fumigating products. It is very toxic to humans; long-term inhalation exposure may cause central nervous system effects and may even cause death. CH_4 and N_2O are greenhouse gases that are included in the emission inventories of the Intergovernmental Panel on Climate Change

Table 2
Examples of NH_3 measurements on various surfaces

Concentrations ($\mu g\,m^{-3}$)	Compensation points	V_d ($mm\,s^{-1}$)	F_d ($ng\,m^{-2}\,s^{-1}$)[a]	Surfaces	Periods/Conditions	Methods	References
2.5–4	Not reported	36	192.52	Coniferous forest in the Netherlands	April, 1988 to March 1990	Denuder and micrometeorological gradient method using a 36 m high tower	Duyzer et al. (1992)
1.5–5.04	3–4 $\mu g\,m^{-3}$	16	−0.083 to 0.036[b]	Mineral-fertilized wheat crop at a location about 50 km north of London	Spring 1991 to Spring 1992, at a height of 1 m, with T of 5.3–20.4 °C	Annular denuder system	Yamulki et al. (1996)
0–6	Not reported	Not reported	−50 to 40	Arable cropland	May, 1992, above a canopy (0.6–0.7 m tall) approaching anthesis	Continuous wet annular denuder	Sutton et al. (1998)
0.45	0.2 $\mu g\,m^{-3}$	5.2–26.3	−8.1 to −3.5	Moorland vegetation in southern Scotland	February–August 1995, the height of V_d and F_d measurements is 1 m	Continuous wet annular denuder	Fowler et al. (1998)
5.2	Not reported	56–63	0 to −370	Dense deciduous and coniferous forest with a mean tree height of 20 m	November 1992–1994	Continuous-flow denuder	Wyers and Erisman (1998)
2.7 ± 1.7 (Baltimore) 1.0 ± 0.8 (Solomons) October 1998–September 1999 5.55 (mean) 0.12 (minimal) 34.8 (maximum)	Not reported	Not reported	−12.09 to 40.76[b]	Water surface in the Chesapeake Bay in Baltimore and Solomons, MD	Rural and urban environments from March–December, 1997, and January–December, 1998	Filter packs and a honeycomb denuder/ filter system	Larsen et al. (2001)

Table 2 (*continued*)

Concentrations ($\mu g\, m^{-3}$)	Compensation points	V_d ($mm\, s^{-1}$)	F_d ($ng\, m^{-2}\, s^{-1}$)[a]	Surfaces	Periods/Conditions	Methods	References
January 1999–December 2000							
5.6±5.13	Not reported	Not reported	Not reported	An agricultural site (Clinton) in eastern NC; 2.6 m above a short grass surface	October 1998–September 1999; January 1999–December 2000	Annular denuder system	Robarge et al. (2002); Walker et al. (2006a)
Daytime: 4.69±4.75 (summer), 5.69±4.71 (spring), 7.6±6.54 (fall), 1.73±2 (winter); Nighttime:2.76±2.43 (summer), 3.41±2.62 (spring), 7.25±6.14 (fall), 1.37±1.50 (winter)	Not reported	39.4±27.9 (summer daytime) 24.1±19.2 (winter daytime) 7.6±16.9 (summer nighttime) 0.7±1.7 (fall nighttime)	−110±140 (summer) −110±150 (spring), −140±190 (fall) −20±30 (winter)	Natural surfaces near animal farms and waste storage and treatment lagoons, in Raleigh, NC, US	Fall 2001, winter, spring, and summer 2002 at two heights (2 and 6 m)	Thermo Environmental Instruments Inc. (TEI) Model 17 C, Chemiluminescence Ambient Ammonia Analyzers, micrometeorological gradient method	Phillips et al. (2004)
0.58–5.32	Not reported	Not reported	12–185[b] (estimated based on the Carnegie Mellon University (CMU) NH_3 inventory V. 2.0)	Three sites in the Coastal Plain region of NC	January–December 2000 at Clinton May–December 2000 (Lenior) January–December 2000, Morehead City	Annular denuder system	Walker et al. (2004)
Not reported	<1.0 nmol NH_3 mol^{-1} air			Canopies of pine, spruce, and aspen			Langford and Fehsenfeld (1992)
Not reported	>25 nmol NH_3 mol^{-1} air			Senescing wheat plants			Morgan and Parton, (1989)
Not reported	0.44–4.1 nmol NH_3 mol^{-1} air			Brassica napus plants	25 °C, with N supply level of 0.05, 0.1, and 0.165 mol N $plant^{-1}$ during growth stages		Schjøerring et al. (1998)

[a] Negative values represent deposition.

[b] Reported fluxes are converted from $\mu g\, N\, m^{-2}\, s^{-1}$ or $\mu g\, N\, m^{-2}\, d^{-1}$ or $kg\, N\, km^{-2}\, yr^{-1}$ to $ng\, NH_3\, m^{-2}\, s^{-1}$.

(IPCC) (IPCC, 2001) because of their climatic impact. CH_4 and N_2O account for 14% and 4.2%, respectively, of the total global warming temperature change (Jacobson, 2002). Their overall lifetimes are ~10 and 120 yrs, respectively. Exposure to their typical levels has no harmful health effects, although CH_4 is a precursor for ozone (O_3). Major reduced sulfur compounds include H_2S, dimethyl disulfide (CH_3SSCH_3), methanethiol (CH_3SH), carbon disulfide (CS_2), and carbonyl sulfide (COS). The lifetime of COS is 17–19 yrs, whereas those of other species are 1–59 h. H_2S is a colorless, toxic, flammable gas with a foul odor of rotten eggs and flatulence. Exposure to elevated concentrations of H_2S (e.g., >0.067 ppm or 0.1 mg m^3) may cause a number of health effects including loss of sense of smell, eye irritation, fatigue, olfactory and respiratory paralysis, pulmonary edema, threat to life, immediate collapse, and death. The oxidation of those reduced compounds produces SO_2, which is a precursor for acid deposition and is associated with impaired lung function and other respiratory diseases. In addition to species listed in Table 1, volatile organic compounds (VOCs) can be emitted from agricultural sources. For example, over 70 VOCs have been identified from dairy farms in northern Sweden (Sunesson et al., 2001), with the highest concentrations of 10–100 $\mu g\,m^{-3}$ for *p*-cresol, 2-butanone, ethylacetate, α-pinene, and Δ^3-carene. Multiple organic compounds have also been identified in the manure samples and in the air from dairy farms in the US (Miller and Varel, 2001; Rabaud et al., 2003; Filipy et al., 2006). The major VOCs in the air include acids, alcohols, aldehydes, esters, ketones, halogenates, butylamine, acetic acid, DMSO, ethyl ether, methyl isobutyrate, amines, aromatic compounds, and terpenes. Those in the liquid phase include L-lactate, alcohols, volatile fatty acids (VFA), phenols, indoles, aromatics, and benzoates. VOCs are important precursors for tropospheric O_3. Many VOCs can cause serious health problems such as cancer and other health and environmental effects.

Current 3-D urban-to-regional AQMs are designed to simulate the sources, transport, chemical transformation, and removal of major criteria air pollutants such as SO_2, NO_x, O_3, and PM and its composition (e.g., sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+)), and the important gaseous precursors of O_3 and PM such as VOCs. Those AQMs do not treat N_2O, H_2S, and most other reduced sulfur and nitrogen compounds. NH_3 is typically considered, but large uncertainties remain in emission inventories, chemistry, deposition, and dynamic treatments. The important processes of NH_3/NH_4^+ simulated in those AQMs include advection, diffusion, aerosol thermodynamics and dynamics (e.g., thermodynamic equilibrium reactions, gas/particle partitioning, nucleation, condensation/evaporation, and coagulation), dry deposition, the dissolution in cloud droplets and rain water, and subsequent scavenging and wet deposition (e.g., Zhang et al., 2004, 2006a).

2.2. Emissions

In the past decade, a number of studies have been focused on the measurements of emissions, concentrations, and deposition of agriculturally-generated NH_3 (e.g., Fowler et al., 1998; Aneja et al., 1998; Robarge et al., 2002; Phillips et al., 2004; Walker et al., 2002, 2004), N_2O (e.g., Walker et al., 2002), VOCs (e.g., Filipy et al., 2006), NH_4^+ (e.g., Aneja et al., 1998; Robarge et al., 2002; Walker et al., 2004), and $PM_{2.5}$ (Walker et al., 2006a). Major sources for NH_3 include livestock and fertilizer, accounting for 80–95% and 3–21% of total NH_3 emissions, respectively, in Europe (Van Der Hoek, 1998) and 55% and 7–9.5% of total NH_3 emissions, respectively, in the US (Battye et al., 1994), and 42.7% and 12% of total NH_3 emissions, respectively, on a global scale (Pacyna and Graedel, 1995). Other sources include soil, industry, on-road vehicles, waste disposal and recycling, humans, domestic and wild animals, forest fires, and slash burnings. N_2O is generated by biogenic (e.g., natural soils and oceans) and anthropogenic (e.g., fertilized fields, animal nitrogen excretion, fossil fuel combustion, traffic, and some industrial activities) sources. Agriculturally-emitted N_2O emissions account for 59% of total N_2O emissions globally (Duxbury et al., 1993). The principal agricultural sources include soil nitrogen, animal waste management systems, and nitrogen lost to the agricultural system. Major sources for CH_4 include natural wetlands, animals, rice cultivation, and biomass burning, accounting for 19.1–26%, 15.3–18.1%, 7.6–15.8%, 8.6–10.2% of global total CH_4 emissions (Pacyna and Graedel, 1995). The emission rates of VOCs from agricultural activities have seldom been measured; their percent contributions to total emissions of VOCs therefore remain uncharacterized.

Emission inventories of several agriculturally-emitted species such as NH_3 and N_2O have also

Table 3
Examples of emission inventories available for AAQ modeling

Species	Domains	Period	Grid resolutions	Methods	Source Categories	References
NH_3	UK	1993	Total non-gridded UK emissions and source-specific	Single constant emission factor for each source for UK	Agriculture	Pain et al. (1998)
NH_3	Greater Athens, Greece	1996	$4 \times 4\,km^2$	Single constant emission factor for each source except fertilizers whose emissions are only considered in spring.	Agriculture	Sotiropoulou et al. (2004)
NH_3	UK	1997	Total non-gridded; source-specific	Emission factors with seasonal variation and dependence on manure management practice	Agriculture	Misselbrook et al. (2000)
NH_3	Denmark	1996	Gridded at $5 \times 5\,km^2$	Emission factors with seasonal variation and dependence on manure management practice	Livestock, commercial fertilizers, crops, sewage sludge and NH_3-related straw	Hutchings et al. (2001)
NH_3	Ireland	1991, 2010	Total non-gridded emissions and source-specific	Single constant emission factors for each source accounting for the dependence on manure management practice	Agriculture	Hyde et al. (2003)
NH_3	Denmark	1999–2001	$16.67 \times 16.67\,km^2$	Dynamical emission parameterization with continuous gauss or temperature-dependent emission functions for specific agricultural activities under various climatic conditions and inter-year variations	Agriculture, road traffic	Skjøth et al. (2004)
NH_3	North Carolina and the San Joaquin Valley (SJV) of California	1997	County-level	Empirical source-specific emission factors with seasonal variations, but each manure management specific emission factor is uniform over the inventory domain	Animal housing, grazing, manure storage, and land spreading for livestock and fertilizer. Soils, vegetation, non-agricultural sources; mobile sources, industrial and combustion sources, sewage treatment plants; human breath & sweat, cigarette smoking, infant diapers, and pets	Battye et al. (2003)
NH_3	US	1999	County-level	Single constant emission factor for each source	Agriculture and non- agriculture	USEPA (2002)
NH_3	Contiguous US	Annual	County-level	The use of a process-based, temporally resolved emission model to calculate monthly and county-level emission factors based on climate conditions (temperature, wind speed, and precipitation) and farming practices; seasonal and geographic variation	Dairy cows	Pinder et al. (2004a, b)
NH_3	Contiguous US	1995	County-level	Monthly, county-level activity levels and emission factors that account for types of fertilizers	Commercial fertilizer application (excluding organic fertilizers such as manure)	Goebes et al. (2003)
NH_3	Eastern US	1990	County-level	Kalman filter inverse modeling to estimate monthly NH_3 emissions	All major sources	Gilliland et al. (2003)
N_2O	UK	1996	Total non-gridded UK emissions and source-specific emissions	Experimentally-determined emission factors; single constant emission factor for each source for UK	Farmed livestocks	Chadwick et al. (1999)
N_2O	UK	1990, 1995	Total non-gridded UK emissions and source-specific emissions	Using IPCC emission methodology and default source-specific emission factors	Agriculture	Brown et al. (2001)
N_2O	Japan, Europe	Non-year specific	Total global non-gridded emissions	Literature review	Nitrogen leaching	Sawamoto et al. (2005)

been developed for model simulation and evaluation (e.g., Pain et al., 1998; Brink et al., 2001; Hutchings et al., 2001; Hyde et al., 2003; Goebes et al., 2003; Pinder et al., 2004 a, b). Table 3 lists some emission inventories developed in recent years. Many of them are developed with single constant emission factor (e.g., Battye et al., 1994; USEPA, 2002) or emission factors accounting for seasonal variation and dependence on manure management practice (e.g., Misselbrook et al., 2000; Hutchings et al., 2001; Hyde et al., 2003; Battye et al., 2003). The most advanced approaches involve the use of a process-based, temporally-resolved emission model based on climate conditions and farming practices (e.g., Pinder et al., 2004a, b), Kalman filter inverse modeling to estimate monthly NH_3 emissions (e.g., Gilliland et al., 2003), or dynamical emission parameterization with continuous gauss or temperature-dependent emission functions for specific agricultural activities (Skjøth et al., 2004).

Compared with emissions of criteria pollutants, NH_3 emission inventories are highly uncertain, because of inaccuracies in the activity data used, the use of uniform emission factors, inadequate temporal and spatial resolutions, inconsistent and/or incomplete source categories, and differences in the methods used. For example, the NH_3 emission inventories accounting for seasonal variabilities may differ by 25% from those that do not account for seasonal variability (Zhang et al., 2006b). The NH_3 emission inventories accounting for climate conditions and farming practices (e.g., the Carnegie Mellon University (CMU) national NH_3 emission inventories, Pinder et al., 2004a, b) may differ from other NH_3 inventories by 23–48% (Hu et al., 2007). NH_3 emission inventories have been identified as one of the major uncertainties in simulating $PM_{2.5}$ in AQMs. Their accurate characterization remains a major challenge in AAQ modeling.

2.3. Atmospheric transport

Major atmospheric transport processes such as advection, horizontal/vertical diffusion, and turbulent mixing for NH_3 are treated similarly to other gaseous species in AQMs. Typical schemes, algorithms, and parameterizations used in major 3-D AQMs are summarized in Russell and Dennis (2000), Seaman (2000) and Arya (2003). The typical Eulerian AQMs allow point source emissions to be mixed uniformly and instantly into the entire volume of a grid that generally has a scale of 20–30 km or greater; this treatment, however, does not represent the diffusion-limited nature of the plume that takes several hours to grow to typical size of the grid cell used in a regional AQM. The plume-in-grid (PiG) module enables a subgrid treatment that adequately describes the real-world pollutant plume. PiG treatments are only included in a few AQMs such as the US EPA Community Multiscal Air Quality modeling system (CMAQ) and the Comprehensive Air Quality Model with extensions (CAMx) (ENVIRON, 2004; Binkowski and Roselle, 2003). Karamchandani et al. (2006) compared simulations with and without PiG for the northeastern and southeastern US, and found that the PiG treatment leads to significant differences in surface concentrations of HNO_3, SO_4^{2-}, and NO_3^- on a regional scale.

During the massive release of NH_3 and H_2S at animal production facilities, plumes may remain a subgrid scale feature and require PiG treatments. While the existing PiG module may be applied to simulate the short-range dispersion of NH_3, it may not be applicable for buoyant plume rise of NH_3 and H_2S, as it is developed for plume rise from power plant stacks that are much higher than animal-rearing facilities. The appropriateness of current buoyant plume rise scheme used in AQMs under different meteorological conditions (e.g., stable, neutral, unstable) must be reexamined for AAQ modeling. Another distinct feature of NH_x transport is that it is characterized by the short-range dispersion of NH_3 and long-range transport of NH_4^+. Very few models can accurately simulate both. In addition, the NH_3 emissions from manure and fertilizer are a function of the atmospheric turbulence and temperature; this dependence is not typically included in 3-D AQMs. Representing those processes in 3-D AQMs poses significant challenges for AAQ modeling. In addition, simulated NH_x transport is affected by inaccuracies in simulated meteorological variables such as temperature and wind field.

2.4. Chemistry, thermodynamics, and dynamics

While the atmospheric chemistry of reduced nitrogen and sulfur compounds has been extensively studied during the past three decades, no existing chemical mechanism has been developed for its incorporation into 3-D AQMs. Table 4 lists some atmospheric reactions that may be necessary to accurately simulate their chemical transformation

Table 4
Potentially important reactions involving reduced nitrogen and sulfur species

No.	Reactions	References
Reduced nitrogen compounds		
R1	$NH_3(g) + OH(g) \rightarrow NH_2 + H_2O$	DeMore et al. (1997), Atkinson et al. (1997a, b), Seinfeld and Pandis (1998)
R2	$NH_2(g) + O_2(g) \rightarrow NH_2O_2\ (g)$ $\rightarrow NO(g) + H_2O(g)$ $\rightarrow OH(g) + HNO(g)$	Finlayson-Pitts and Pitts (2000)
R3	$NH_2(g) + NO(g) \rightarrow N_2H(g) + OH(g)$ $\rightarrow N_2(g) + H_2O(g)$	Finlayson-Pitts and Pitts (2000)
R4	$NH_2(g) + NO_2(g) \rightarrow N_2O(g) + H_2O(g)$ $\rightarrow NH_2O(g) + NO(g)$	Finlayson-Pitts and Pitts (2000)
R5	$NH_2(g) + O_3(g) \rightarrow$ Products	Finlayson-Pitts and Pitts (2000)
R6	$2NH_3(g) + 4O_3(g) \rightarrow 2HNO_3(g) + 2O_2(g) + 2H_2O(g)$ (lower NH_3 and HNO_3) $\rightarrow NH_4NO_3(s) + 4O_2(g) + H_2O(g)$ (higher NH_3 and HNO_3)	Renard et al. (2004) and references therein
R7	$NH_3(g) + SO_2(g) \leftrightarrow NH_3SO_2(g)$	Becke-Goehring (1960), Meyer et al. (1980)
R8	$2NH_3(g) + SO_2(g) \leftrightarrow (NH_3)_2SO_2(g)$	Landreth et al. (1974)
R9	$2NH_3(g) + SO_2(g) + H_2O(g) \leftrightarrow (NH_4)_2SO_3(s)$	Landreth et al. (1974)
R10	$NH_3(g) + SO_3(g) \rightarrow {}^{+}H_3N{-}SO_3H^{-}(g) \rightarrow H_2N{-}SO_3H(s)$ (low RH conditions) $\rightarrow (NH_4)_2SO_4(s)$ (high RH conditions)	Canagaratna et al. (1996), Lovejoy (1997)
R11	$2NH_3(g) + CH_3C(=O)ONO_2 + H_2O \rightarrow NH_4CH_3CO_2(s) + NH_4NO_2(s) + 0.5O_2$	Finlayson-Pitts and Pitts (1986)
R12	$CH_3NH_2 + OH \rightarrow$ Products	Atkinson (1989), Carl and Crowley (1998)
R13	$(CH_3)_2NH + OH \rightarrow$ Products	Atkinson (1989), Carl and Crowley (1998)
R14	$(CH_3)_3N + OH \rightarrow$ Products	Atkinson (1989), Carl and Crowley (1998)
R15	$C_2H_5NH_2 + OH \rightarrow$ Products	Carl and Crowley (1998), Finlayson-Pitts and Pitts (2000)
R16	$HCN + OH \rightarrow CN + H_2O$	Atkinson (1989)
R17	$CH_3CN + OH \rightarrow CH_2CN + H_2O$	Hynes and Wine (1991), Seinfeld and Pandis (1998)
R18	$(CH_3)_3CNH_2 + OH \rightarrow$ Products	Koch et al. (1996)
R19	$CH_3NHC(O)CH_3 + OH \rightarrow$ Products	Koch et al. (1997)
R20	$CH_3NHC(O)C_2H_5 + OH \rightarrow$ Products	Koch et al. (1997)
R21	$(CH_3)_2NC(O)CH_3 + OH \rightarrow$ Products	Koch et al. (1997)
R22	$(CH_3)_2NH + O_3 \rightarrow CH_3N = CH_2 + CH_3NO_2 + CH_3NHCO + HCHO + CO_2$	Tuazon et al. (1984), Finlayson-Pitts and Pitts (2000)
R23	$2(CH_3)_2NH + HCHO \rightarrow (CH_3)_2NCH_2N(CH_3)_2 + H_2O$	Tuazon et al. (1984), Finlayson-Pitts and Pitts (2000)
R24	$(CH_3)_2NCH_2N(CH_3)_2 + O_3 \rightarrow (CH_3)_2NCHO$	Tuazon et al. (1984), Finlayson-Pitts and Pitts (2000)
R25	$(CH_3)_3N + O_3 \rightarrow CH_3NO_2 + HCHO + CO_2$	Tuazon et al. (1984), Finlayson-Pitts and Pitts (2000)
R26	$NH_3(g) + HNO_3(g) \leftrightarrow NH_4NO_3(s)$	Seinfeld and Pandis (1998), Jacobson (2005)
R27	$NH_3(g) + HNO_3(g) \leftrightarrow NH_4^+(l) + NO_3^-(l)$	Seinfeld and Pandis (1998), Jacobson (2005)
R28	$NH_3(g) + HCl(g) \leftrightarrow NH_4Cl(s)$	Seinfeld and Pandis (1998), Jacobson (2005)
R29	$NH_3(g) + HCl(g) \leftrightarrow NH_4^+(l) + Cl^-(l)$	Seinfeld and Pandis (1998), Jacobson (2005)
R30	$NH_3(g) \leftrightarrow NH_3\ (l)$	Clegg and Brimblecombe (1989)
R31	$NH_3(l) + H_2O \leftrightarrow NH_4^+(l) + OH^-$	Clegg and Brimblecombe (1989)
R32	$NH_3(l) + H^+ \leftrightarrow NH_4^+(l)$ (for low pH conditions)	Emerson et al. (1960)

Table 4 (*continued*)

No.	Reactions	References
R33	$(NH_4)_2SO_4(s) \leftrightarrow 2\ NH_4^+(l) + SO_4^{2-}$	Seinfeld and Pandis (1998), Jacobson (2005)
R34	$NH_4HSO_4(s) \leftrightarrow NH_4^+(l) + HSO_4^-$	Jacobson (2005)
R35	$(NH_4)_3H(SO_4)_2(s) \leftrightarrow 3\ NH_4^+(l) + HSO_4^- + SO_4^{2-}$	Jacobson (2005)
R36	$NH_4NO_3(s) \leftrightarrow NH_4^+(l) + NO_3^-(l)$	Seinfeld and Pandis (1998), Jacobson (2005)
R37	$NH_4Cl(s) \leftrightarrow NH_4^+(l) + Cl^-(l)$	Jacobson (2005)
R38	$NH_4HCO_3(s) \leftrightarrow NH_4^+ + HCO_3^-$	Jacobson (2005)
R39	$NH_3(l) + CO_2(l) + H_2O \leftrightarrow NH_4^+(l) + HCO^-(l)$	Renard et al. (2004) and references therein
R40	$NH_3(l) + NH_4^+(l) + HCO_3^-(l) \leftrightarrow 2\ NH_4^+(l) + CO_3^{2-}(l)$	Renard et al. (2004) and references therein
R41	$NH_3(l) + HCO_3^-(l) \leftrightarrow NH_2COO^-(l) + H_2O$	Renard et al. (2004) and references therein
Reduced sulfur compounds		
R42	$H_2S + OH \rightarrow SH + H_2O$	Seinfeld and Pandis (1998)
R43	$CH_3SCH_3 + OH \rightarrow CH_3SCH_2 + H_2O$ $CH_3SCH_3 + OH + M \leftrightarrow CH_3S(OH)CH_3 + M$	Atkinson et al. (1997a), Seinfeld and Pandis (1998)
R44	$CS_2 + OH + M \rightarrow HOS_2 + M$	Atkinson et al. (1997a), Seinfeld and Pandis (1998)
R45	$COS + OH \rightarrow CO_2 + HS$	Atkinson et al. (1997a), Seinfeld and Pandis (1998)
R46	$COS + O \rightarrow CO + SO$	Seinfeld and Pandis (1998)
R47	$CH_3SSCH_3 + OH \rightarrow CH_3S(OH)SCH_3$ $\rightarrow CH_3SOH + CH_3S$	Yin et al. (1990), Finlayson-Pitts and Pitts (2000)
R48	$CH_3SH + OH \rightarrow CH_3S(OH)H$ $\rightarrow CH_3S + H_2O$	Seinfeld and Pandis (1998), Finlayson-Pitts and Pitts (2000)

and evolution. While the oxidation reactions of NH_3, HCN, CH_3CN, and COS by OH in the gas-phase (R1, R16, R17, R45, and R46) are slow at typical ambient concentrations (e.g., $<$ a few ppbs of NH_3), other reactions may occur in the gas-, aqueous-, and particulate-phase with a non-negligible or sometimes rapid rate under conditions of excess NH_3 and H_2S that may be experienced over agricultural regions. For example, the reaction of NH_3 with O_3 (R6) may initially produce HNO_3(g) and proceed rapidly when the concentrations of NH_3(g) and HNO_3(g) are high to form crystalline NH_4NO_3(s) (Renard et al., 2004). The oxidation of SO_2 by NH_3 (R7–R9) to form SO_3 can be completed in less than 5 min under normal ambient conditions (Renard et al., 2004). SO_3 can be neutralized rapidly by NH_3 to form crystalline particle of sulfamic acid ($H_2N–SO_3H$) under low RHs and to form $(NH_4)_2SO_4$ under high RHs (R10). NH_3 may also react with peroxyacetyl nitrate (PAN), a major photochemical product, in an urban environment such as California with a massive release of NH_3 (R11) (Renard et al., 2004). Other alkyl amines such as CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, and $C_2H_5NH_2$ can also react with OH (R12–15 and R18–R21) and O_3 (R22, R24, R25) under typical, moderately-polluted conditions (Finlayson-Pitts and Pitts, 2000). NH_3 can directly react with HNO_3 and HCl in the gas phase to yield NH_4NO_3(s), NH_4Cl(s), or aqueous NH_4^+, NO_3^-, and Cl^-, which are in equilibrium with their gaseous precursors via reactions R26–29. NH_3 is a soluble species with a Henry's law coefficient of $62\,M\,atm^{-1}$ (Seinfeld and Pandis, 1998) (R30). Dissolved NH_3(l) can dissociate into NH_4^+ (R31–R32), which can react with other anions such as SO_4^{2-}, NO_3^-, Cl^-, and HCO_3^- to form solid ammonium sulfates, nitrates, chlorides, and carbonates via (R33–R38); those salts can also dissociate back to their ionic forms and potentially "outgas" NH_3 under certain ambient conditions (e.g., when ambient NH_3 concentration is very small, Wells et al., 1998). Reactions R26–R38 are the most important equilibrium reactions for gas/particle partitioning and the formation of NH_4^+ salts in the atmosphere. Once formed, those particles can be activated by cloud droplets to form cloud condensation nuclei (CCN), which will affect the earth radiation budget and climate through cloud formation, lifetime, and precipitation. Major reduced sulfur compounds can also be oxidized by atmospheric oxidants such as OH and O via R42–R48. Those reactions will ultimately produce sulfate via increased SO_2. Aqueous-phase chemistry of NH_3 may also provide a mechanism for reduced nitrogen to re-partition from larger particles to small particles, thus forming new particles in ultra-fine mode, which may provide a plausible explanation of observed formation of ultra-fine mode particles associated with orographic cloud during nighttime (Wells et al., 1998).

All gaseous reactions (i.e., R1–R25) are currently not treated in AQMs. Only a few heterogeneous or aqueous reactions have been included in aerosol thermodynamic modules used in AQMs. For example, R26, R28, R30, R31, and R33–R35 are treated in the aerosol thermodynamic module in CMAQ, ISORROPIA (Nenes et al., 1999), and R26–31 and R33–38 are included in an alternative module in the North Carolina State University (NCSU)'s version of CMAQ, EQUISOLV II (Jacobson, 2005). Those missing reactions represent major model deficiencies in representing of chemistry of reduced nitrogen and sulfur species. An appropriate chemical mechanism that includes important reactions in all phases must be developed and incorporated into AQMs. Ansari and Pandis (1999) and Zhang et al. (2000) provide comparative reviews of several thermodynamic modules that are currently used in major AQMs. They differ in terms of species and equilibrium reactions included, assumptions made, activities calculated, and numerical methods used to solve equations. The gas/particle partitioning of NH_3/NH_4^+ is studied using both 3-D AQMs and several aerosol thermodynamic modules to understand the formation of ammonium salts under various meteorological and chemical conditions (Blanchard and Hidy, 2003; Wang et al., 2006; Vayenas et al., 2005).

Reduced nitrogen and sulfur compounds and their particulate forms can undergo a number of dynamic processes including gas/particle mass transfer, nucleation, coagulation, and condensation/evaporation. Modules for each of those processes that are currently used in 3-D AQMs are reviewed in Zhang et al. (1999, 2004). Growing evidence has shown that NH_3 may play an important role in new particle formation through ternary nucleation involving sulfuric acid (H_2SO_4), water vapor (H_2O), and NH_3 (e.g., Coffman and Hegg, 1995; Weber et al., 1997). This process has recently be incorporated into CMAQ and compared with several binary nucleation parameterization (Zhang et al., 2005; Zhang and Jacobson, 2005), although it has not yet been included in most other AQMs.

Table 5 summarizes model treatments of gas-phase chemical mechanism, aqueous-phase chemistry, aerosol treatments, dry and wet deposition, PiG treatments and special treatments for NH_x included in several representative AQMs that have been applied for NH_x simulations including the a statistical, long-term model TREND, the High Resolution Limited Area Model (HIRLAM)/EMEP the meteorological synthesizing centre-west (MSC-W) unified Eulerian model, CMAQ, the modified US EPA Regional Acid Deposition Model (RADM), and CAMx.

2.5. Removal

NH_x can be removed by dry and wet deposition processes in the atmosphere, which can contribute to terrestrial acidification and eutrophication. Similar to other species, dry deposition of NH_3 is simulated in AQMs based on the classic resistance theory of Wesely (1989). Three resistances are considered in this theory: aerodynamic resistance (R_a), quasi-laminar resistance (R_b), and surface or canopy resistance (R_c), among which the canopy resistance is the most difficult one to simulate, because (1) it consists of several resistances that vary highly with the type of ground or water surfaces, R_{cg} or R_{cw}, (e.g., heathland, moorland, meadow, forest, sea water), plants (e.g., oak vs. spruce) and tissues on or inside leaf pores (e.g., cuticular resistance, R_{cut}, vs. stomatal resistance, R_s) as well as many other physical and chemical conditions such as light, temperature, and solubility of the gas; (2) it lacks canopy-scale measurements to verify the model results. Different from most gases that are consistently deposited, the NH_3 fluxes over fertilized agricultural lands and grazed grasslands are bi-directional, with both deposition and emission occurring in parallel (Sutton et al., 1994, 1998). Farquhar et al. (1980) introduced a so-called NH_3 compensation point (χ) to determine the direction of the fluxes. Emission occurs when the ambient concentration of NH_3 is below χ, otherwise deposition occurs. The value of χ depends on many physiological, climatic, and environmental factors

Table 5
Examples of model treatments for simulating agriculturally-emitted species

Models	TREND	The HIRLAM/EMEP MSC-W Unified Eulerian model, v2.0	CMAQ	CAMx	RADM
Gas-phase chemistry	None	140 reactions among 70 species based	RADM2[a], 158 reactions among 57 species CBM-IV[a], 93 reactions among 36 species SAPRC99, 214 reactions among 72 species	CBM-IV[2] SAPRC99[a]	RADM2[a], 158 reactions among 57 species
Aqueous-phase chemistry	None	Aqueous oxidation of SO_2 by O_3, H_2O_2, and O_2 catalyzed by Fe^{3+} and Mn^{2+}); no aqueous nitrate formation	Aqueous oxidation of SO_2 by O_3, H_2O_2, and O_2 catalyzed by Fe^{3+} and Mn^{2+}), CH_3OOH and $CH_3C(O)OOH$; no aqueous nitrate kinetic reactions	Same as CMAQ	Same as CMAQ
Aerosol treatments	A constant NH_3 to NH_4^+ conversion rate of $8 \times 10^{-5}\,s^{-1}$.	EQSAM thermodynamic module; nucleation, condensation/volatilization and coagulation for SO_4^{2-}, NO_3^-, NH_4^+, BC, OC, mineral dust and sea-salt; modal size representation (4 modes)	ISORROPIA thermodynamic module; Secondary aerosol formation/partitioning, nucleation, condensation/volatilization and coagulation for SO_4^{2-}, NO_3^-, NH_4^+, BC, OC, and sea-salt; modal size representation (3 modes)	ISORROPIA thermodynamic module; Secondary aerosol formation/partitioning, nucleation, condensation/volatilization and coagulation for SO_4^{2-}, NO_3^-, NH_4^+, BC, OC, and sea-salt; Sectional (10-section) or modal size representation (2 modes)	MARS-A thermodynamic module, no dynamic treatments, bulk phase treatment for SO_4^{2-}, NO_3^-, and NH_4^+.
Dry deposition	Resistance transfer approach of Wesely (1989) for NH_3 only with a constant surface resistance of $30\,s\,m^{-1}$. A constant surface resistance of $600\,s\,m^{-1}$ for NH_4^+	Resistance transfer approach of Wesely (1989) for gases and particles. The wet diameters are used to calculate V_d for particles in each mode.	Resistance transfer approach of Wesely (1989) for gases and particles. mode-averaged V_d for particles is calculated for the total particle number, surface, and volume of each mode, no V_d is computed for individual PM species such as NH_4^+, SO_4^+, and NO_3^-	Resistance transfer approach of Wesely (1989) for gases and that of Slinn and Slinn (1980) for particles.	Resistance transfer approach of Wesely (1989) for gases and particles; V_d of NH_4^+ and NO_3^- are assumed to be the same as SO_4^{2-}
Wet deposition	In-cloud and sub-cloud scavenging of NH_3 and NH_4^+, with the same scavenging coefficient for both NH_3 and NH_4^+.	In-cloud and sub-cloud scavenging of gases and particles; complete scavenging for accumulation and coarse mode particles; parameterization for Aitken nuclei mode particles; mode-dependent particle in-cloud scavenging ratio and sub-cloud collection efficiency	Henry's law equilibrium for gases; complete scavenging for accumulation and coarse mode particles; parameterization for Aitken nuclei mode particles	Henry's law equilibrium for gases; in-cloud and sub-cloud scavenging of gases and particles	Henry's law equilibrium for gases; complete scavenging for particles
Plume-in-grid treatment	No	No	Yes	Yes	No
Special treatments for NH_x	Overall highly-simplified treatments to allow for long-term simulations	Scaled stomatal resistance of NH_3 based on that of O_3. Parameterized non-stomatal deposition of NH_3 as a function of temperature, humidity, and molar SO_2/NH_3	An empirical equation is used to compute the cuticular resistance for NH_3.	Not reported	Modified NH_3 dry deposition calculation; add MARS-A to treat conversion of NH_3 to NH_4^+
Example applications	Asman and van Jaarsveld, 1992, Lekkerkerk, 1998	Jonson et al., 1998, Simpson et al., 2006	Sakurai et al., 2005; Wu et al., 2005, 2007; Hu et al., 2007	Pavlovic et al., 2006	Mathur and Dennis, 2003

[a] RADM2—the Regional Acid Deposition Model version 2; CBM-IV—the Carbon-Bond Mechanism, version IV; SAPRC99-the Statewide Air Pollution Research Center gas-phase mechanism.

such as types of surface, ambient temperature, RH, plant growth stages, and N supply level. It ranges from below 1 nmol NH_3 mol^{-1} air in canopies of pine, spruce, and aspen (Langford and Fehsenfeld, 1992) to over 25 nmol NH_3 mol^{-1} air in spring wheat plants (Morgan and Parton, 1989). Table 2 lists the measured χ on some surfaces. Several methods have also been developed to predict χ under given ambient conditions including the use of apoplastic pH and NH_4^+ concentration (Schjøerring et al., 1998).

While the default dry deposition module may be appropriate for low nitrogen systems such as unfertilized heathland, moorland, forest canopies, and sea/lake surfaces where the exchange is generally uni-directional, it cannot simulate the bi-directional exchange observed over fertilized agricultural croplands and grazed grasslands. A dry deposition scheme for bi-directional exchange is therefore needed to accurately represent the fluxes of NH_3 in AQMs. This bi-directional feature poses challenges to traditional dry deposition models which are based on either one-directional (no emissions, e.g., Wesely, 1989) or a simple bi-directional exchange via a stomata or canopy resistance to deposition (e.g., Farquhar et al., 1980; Sutton et al., 1993). More advanced resistance models accounting for capacitance of leaf surfaces have been developed to simulate the bi-directional NH_3 surface–atmosphere exchange (e.g., Sutton et al., 1998; Nemitz et al., 2001). In the model of Nemitz et al. (2001), the canopy-scale flux is determined by the difference between the ambient NH_3 concentration and the canopy NH_3 compensation point, which is determined by the competing processes of deposition to the leaf cuticle, bi-directional stomatal exchange (i.e., stomatal compensation point), and bi-directional exchange with soil (i.e., soil compensation point).

Another difficulty in simulating dry deposition of NH_3 lies in the fact that there is a general paucity of dry deposition velocity, V_d, and flux, F_d, measurements for model verification. Since the first measurements of V_d, and F_d of NH_3 and NH_4^+ by Dabney and Bouldin (1985) and Duyzer et al. (1987), a number of field studies have been conducted (e.g., Sutton et al., 1993, 1998; Aneja et al., 1998; Phillips et al., 2004; Walker et al., 2006b). A comprehensive review of measurements of dry deposition of reduced nitrogen conducted before 1993 is given in Sutton et al. (1994). Some recent measurements are listed in Table 2. Those studies report V_d values for NH_3 of 0.07–6.3 cm s^{-1} with maximum velocities typically occurring during unstable, daytime conditions. Weekly-average dry deposition data are routinely collected through the US EPA Clean Air Status and Trends Network (CASTNet), which measures V_d and F_d of HNO_3, SO_2, NH_4^+, SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Ca^+, and Mg^{2+} at various locations in the US. Krishnan et al. (2006) conducted a preliminary evaluation of dry deposition module in CMAQ at a 4-km resolution with limited observational data. They also found that the V_d and F_d are sensitive to parameters used in the calculation of R_{cut} and canopy wetness content. Some flux measurements have also been used to determine the corresponding compensation point (e.g., Fowler et al., 1998). Lack of detailed data on terrain characteristics and land use at a fine scale also introduces large uncertainties in stimulating dry deposition of NH_x.

Wet deposition of NH_x may be more important in areas with low NH_3 emissions and high precipitations. Both below- and in-cloud scavenging are commonly included in AQMs. The below-cloud scavenging coefficient is calculated as a function of precipitation at a fixed temperature in early work (e.g., Asman and Janssen, 1987; Galperin and Sofiev, 1998). The in-cloud scavenging coefficient of NH_x is calculated as a function of precipitation and the height of the mixing layer (e.g., Asman and Janssen, 1987). Wet scavenging schemes commonly used in AQMs are summarized in Guelle et al. (1998) and Russell and Dennis (2000). The wet deposition of NH_x has been estimated for several regions including Germany (e.g., Asman and van Jaarsveld, 1992), UK (Metcalfe et al., 1998), the eastern US (e.g., Mathur and Dennis, 2003), and the southeastern US (e.g., Queen et al., 2006). 3-D simulations are also conducted to study the sensitivity of predicted precipitation and wet deposition amounts of NH_x to cloud microphysics treatments (Queen et al., 2006).

2.6. *Model application and evaluation*

While the study of ammonium nitrate (NH_4NO_3) with 0–3-D models as one of the modeling species can be traced back to the early 1980s (e.g., Russell et al., 1983), modeling studies focusing on the fate and transport of agriculturally-emitted pollutants such as NH_3 and NH_4^+ are sparse on all scales, as compared with criteria air pollutants such as SO_x, NO_x, O_3, and $PM_{2.5}$. 1–3-D Lagrangian models have been used in most modeling studies on agriculturally-emitted pollutants at a grid resolution of 16 × 16–150 × 150 km^2 (e.g., Russell et al., 1983; Asman and Janssen, 1987; Metcalfe et al., 1998; Erisman et al., 1998; Skjøth et al., 2004). Asman and Janssen (1987) conducted the first modeling of atmospheric NH_x ($= NH_3 + NH_4^+$) transport in Europe, while Russell et al. (1983) reported one of the first modeling studies on the formation and transport of NH_4NO_3 in the US. Very few NH_x modeling studies are conducted using the Eulerian framework, which is generally more computationally expensive than Lagrangian models. These 3-D Eulerian modeling studies have been conducted on a global scale or a large continental scale at a relatively-coarse resolution from 150 × 150 km^2 to $5^\circ \times 3.5^\circ$ (e.g., Dentener and Crutzen, 1994; Galperin and Sofiev, 1998; Adams et al., 1999; Rodhe et al., 2002; Sanderson et al., 2006). Urban-to-regional simulations using 3-D Eulerian or Lagrangian chemistry and transport models at finer resolutions of 4 × 4–80 × 80 km^2 have also been performed but focused primarily on European countries (e.g., Galperin and Sofiev, 1998; Metcalfe et al., 1998; Skjøth et al., 2004) and are very limited in other regions (e.g., in the Kanto region of Japan (Sakurai et al., 2005); eastern US (Russell et al., 1993; Mathur and Dennis, 2003); western US (e.g., Russell et al., 1983), southeastern US (e.g., Wu et al., 2005, 2007), and the southern US (Pavlovic et al., 2006)). Table 6 shows several 3-D model applications for NH_x including transport, chemistry, and deposition of NH_x for current and future years, the effect of nitrogen deposition on world biodiversity, and the impacts of NH_3 emission control on deposition.

Model evaluation for NH_x simulations has been conducted with very limited observational data; it is conducted primarily at an operational level in terms of spatial distribution, temporal variation, and statistical trends (e.g., Mathur and Dennis, 2003; Wu et al., 2005, 2007). Some sensitivity simulations are conducted to investigate the roles of NH_3 emissions in forming $PM_{2.5}$ and to evaluate the accuracy of the NH_3 emission inventory used (e.g., Lekkerkerk, 1998; Hu et al., 2007). For example, Wu et al. (2007) conducted CMAQ simulations and evaluations using the observational datasets such as the Interagency Monitoring of Protected Visual Environments (IMPROVE), the EPA Speciation Trends Networks (STN), CASTNet, and the NC Department of Environment and Natural Resources (NCDENR). Higher levels of evaluation (e.g., diagnostic, sensitivity, and probalistic) are necessary to provide in-depth understanding of the model biases in simulating NH_x. Continuous measurements of mixing ratios, emission fluxes, and dry and wet deposition amounts of NH_x at a time resolution of 1 h over multiple sites are urgently needed to verify model performance.

2.7. NH_3 emission control and policy implications

The health and environmental concerns of agriculturally-emitted air pollutants have led regulators and policy makers from the US and other countries to begin considering mitigation strategies for those pollutants. For example, regulations for NH_3 emission reductions from the livestock farming have been initiated and enforced in the Netherlands to meet stringent emission and deposition of NH_3 targets (Lekkerkerk, 1998). In the US, although there is currently no national ambient air quality standards (NAAQs) for those pollutants, a reporting requirement for the large released quantities of NH_3 and H_2S from AFOs has been enforced under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Emergency Planning and Community Right-to-Know Act (EPCRA), as part of the Clean Water Act (CAA). In addition, mitigation measures are being taken at a state level. For example, both Minnesota and Texas have state ambient air quality standards for H_2S; the NC Environmental Management Commission is one of the first agencies in the US to adopt rules for odor control from swine farms in 1999.

Reducing NH_3 emissions has been addressed by both the government and research community as an important policy issue in Europe, although no much attention has been given in the US. A number of studies have been performed to study the efficiency of various abatement options (e.g., Mccubbin et al., 2002), which requires the consideration of multi-discipliny aspects of the issue including environmental impacts, biophysical processes, and agricultural operations (e.g., soil, land use, crop, fertilizer, irrigation). Several models have been used for regulatory applications. For example, Cowell and Apsimon (1998) have developed the Model for the Assessment of Regional Ammonia Cost Curves for Abatement Strategies (MARACCAS) to assess the cost-effectiveness of potential abatement measures and to design the efficient abatement strategies. Mccubbin et al. (2002) applied the S–R

Table 6
Examples of model applications for simulating agriculturally-emitted species

Models[a]	Applications	Domains	Periods	Grid resolutions	References
TM3 global chemistry model	Nitrogen deposition and its effect of nitrogen deposition on world biodiversity	Global	2000–2050	5° × 3.75°	Rodhe et al. (2002); Phoenix et al. (2006)
3-D HadAM3 global climate model and the STOCHEM Lagrangian chemistry model	Present and future deposition of acidic nitrogen and sulfur species	Global	1990, 2090	5° × 5°	Sanderson et al. (2006)
3-D Eulerian chemistry and transport model MSC-E	Long-range transport and deposition of NH_x	Northern Hemisphere/ Europe	1991–1994	$150 \times 150\,km^2$ for N.H. $50 \times 50\,km^2$ for Europe	Galperin and Sofiev (1998)
OPS transport model and DEADM deposition model	Short- and long-distance transport and deposition of SO_x, NO_y, and NH_x	The Netherlands	1980–1994	$5 \times 5\,km^2$ from OPS $1 \times 1\,km^2$ for SO_x and NO_y, $5 \times 5\,km^2$ for NH_3 from DEADM	Erisman et al. (1998)
FRAME 1-D Lagrangian statistical trajectory model	NH_3 emissions, transport, and deposition	Great Britain	Not reported	$5 \times 5\,km^2$	Singles et al. (1998)
Statistical long-term atmospheric transport model TREND	Impact of NH_3 emission control on deposition	Europe	2000–2010	$60 \times 60\,km^2$	Lekkerkerk (1998)
3-D Lagrangian transport and chemistry model HARM	Wet deposition of NH_4^+	UK	2010	$20 \times 20\,km^2$	Metcalfe et al. (1998)
A 3-D Eulerian model MADE-50	Transport and deposition of nitrogen species	Europe	January–December 1992	$50 \times 50\,km^2$	Jonson et al. (1998)
The 3-D HIRLAM/EMEP MSC-W Unified Eulerian model, v2.0	Concentrations and depositions of reactive nitrogen species	Europe	2000; May, 2002 to July 2003	$50 \times 50\,km^2$	Simpson et al. (2006)
3-D ACDEP Lagrangian variable scale transport chemistry model	Concentration of NH_x	Denmark	1999–2001	$16.67 \times 16.67\,km^2$	Skjøth et al. (2004)
CMAQ	Spatial distribution and seasonal variation of NH_x	The Kanto region of Japan	January–December 2000 Summer, 2002	$15 \times 15\,km^2/5 \times 5\,km^2$ (nested)	Sakurai et al. (2005)
Caltech photochemical airshed model	Dry deposition flux of nitrogen-containing compounds	Los Angeles	August 1982	$5 \times 5\,km^2$	Russell et al. (1993)
3-D RADM	Seasonal and annual distribution of concentrations and deposition amounts of NH_x	The contiguous US	30 five-day episodes representative of the late 1980s-early 1990s	$36 \times 36\,km^2$	Mathur and Dennis (2003)
3-D CMAQ	Seasonal variation and process analysis for NH_x and related species	Southeast US (centered in NC)	August and December 2002	$4 \times 4\,km^2$	Wu et al. (2005, 2007); Hu et al. (2007)
3-D CAMx4.11	Transport and fate of NH_x	South US/Southeast Texas Houston-Galveston area	August 22–September 6, 2000	$36 \times 36\,km^2$ $12 \times 12\,km^2$ $4 \times 4\,km^2$	Pavlovic et al. (2006)

[a] HadAM3—the Hadley Centre climate model; MSC-E—the meteorological synthesizing centre-East; OPS–the Operationele Prioritaire Stoffen model; DEADM—the Dutch empirical acid Deposition Model; FRAME—fine resolution ammonia exchange; HARM—the Hull acid rain model; MADE-50—the multi-level acid deposition model for Europe with 50 km resolution; HIRLAM—the high resolution limited area model; ACDEP—the atmospheric chemistry and Deposition model; MSC-W—the meteorological synthesizing centre-west; CMAQ—the Community multiscale air quality modeling system; RADM—the regional acid deposition model; CAMx—the comprehensive air quality model with extensions.

matrix AQM and suggest that reducing livestock NH_3 emissions by 10% can lead to particulate-related health benefits of over \$4 billon yr^{-1}. The Regional Air pollution INformation and Simulation (RAINS) model includes seven options for NH_3 control strategies including lowing nitrogen feed, air purification, animal housing adaptations, covered storage of manure, low NH_3 application of manure, urea substitution, and stripping and absorption techniques in fertilizer industry (Klimont, 2001). It has been applied to study impact of NH_3 abatement on the emissions of CH_4 and N_2O for 1990 and 2010 (Brink et al., 2001).

3. Major challenges, future directions, and outlook

Large uncertainties in current agricultural air quality modeling lie in several aspects including (1) inaccurate emission inventories as a result of erroneous activity levels, the use of uniform emission factors, inaccurate temporal variations, poor spatial resolution, inconsistent source categories, and inconsistency in the methods used; (2) inaccurate meteorological predictions (e.g., temperature, wind speed, wind direction, and precipitation); (3) a lack of a detailed information on terrain characteristics and land use at a fine scale (e.g., surface roughness and vegetation); (4) missing, or inadequate model treatments of chemical and physical processes (e.g., gas- and aqueous-phase chemistry for NH_3, gas/particle partitioning, aerosol dynamics, and dry and wet deposition); (5) inability to simulate both the short-range dispersion and deposition of NH_3 near the ground and the long-range transport and fate of NH_4^+ at higher elevations downwind of sources; (6) high uncertainty in the dry deposition parameterization of NH_3; and (7) a paucity of observations of emissions, concentrations, and deposition suitable for model verification and evaluation. Reducing those uncertainties presents significant research challenges and directions in the coming years. Resolving them has profound impacts on air quality, human health, agro-eco environment, and biodiversity as well as important policy implications from local to global scales. It requires an integrated effort nationwide and worldwide from scientists, engineers, policy-makers, managers, and public.

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