

A Special Issue of *JA&WMA* on Agricultural Air Quality: State of the Science

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The world's population has grown, from approximately 1.5 billion at the beginning of the 20th century to more than 6 billion today. This population increase has been accompanied by the rapid growth of intensive agriculture with its associated, significant impacts on the environment. Over the next 50 yr, the Earth's human population is predicted to increase from the current level to more than 9 billion, creating a parallel or disproportionate increase in demand for agricultural commodities—both crop and animal. Without scientific research to inform policy decisions, there will likely be greater environmental impacts associated with this future growth.^{1–3}

Though in transition, U.S. agriculture is still diverse, ranging from large, highly intensive and specialized commercial holdings to subsistence (i.e., family owned) farming, using mainly traditional practices. Consequently, impacts on the environment vary in scale and intensity and may be positive or negative. However, an increasing body of evidence shows that the increased size and geographical concentration of animal-feeding operations and agricultural crop production are increasing the emissions of odorous compounds (e.g., organic acids) and trace gases (e.g., carbon dioxide [CO₂], methane [CH₄], nitrous oxide [N₂O], nitrogen oxides [NO_x], ammonia [NH₃], and reduced sulfur compounds, such as hydrogen sulfide [H₂S]) to the atmosphere.^{2,4} For example, the livestock sector is estimated to be responsible for 18% of the greenhouse gas emissions, 65% of anthropogenic N₂O, and 64% of anthropogenic NH₃ nitrogen worldwide.⁵ Globally, the livestock sector is a leading player in the reduction of biodiversity; it is the major driver of deforestation, as well as one of the leading drivers of land degradation, pollution, climate change, overfishing, sedimentation of coastal areas, and facilitation of alien species. In addition to these global environmental impacts, in the United States, uncontrolled agricultural emissions will impact the ability of states to meet their legal obligations under the Clean Air Act. For example, NH₃ plays a significant role in PM_{2.5} formation, which will increase at the same time that the emissions of sulfur oxides (SO_x) and NO_x are decreasing and while the U.S. Environmental Protection Agency is

promulgating a more stringent 24-hr average National Ambient Air Quality Standard for PM_{2.5} of 35 μg m⁻³.⁴ Therefore, the potential health and environmental risks of intensified modern agriculture require that we develop emission abatement policies based on best available science; and by introducing regulations in the United States.³

In the United States, air quality research in the past half century, has focused largely on criteria pollutants such as NO_x, sulfur dioxide (SO₂), ozone (O₃), and particulate matter (PM_{2.5} and PM₁₀; i.e., aerodynamic diameters of less or equal to 2.5 μm and 10 μm, respectively). Limited attention has been given to non-criteria air pollutants such as reduced nitrogen-, sulfur-, and carbon-containing compounds. Compounds, such as NH₃, N₂O, H₂S, and volatile organic compounds (VOCs), play important roles in the formation of criteria pollutants such as tropospheric O₃, SO₂, and PM_{2.5}, as well as the eutrophication of ecosystems. These compounds interact in atmospheric reactions (e.g., gas-to-particle conversion),^{6–11} are transported by winds and return to the surface by wet and dry deposition processes.^{2,12} These compounds may have adverse effects on human health and the environment. Agriculture provides a major source of those reduced nitrogen-, sulfur-, and carbon-containing compounds through livestock production, fertilizer application, land use changes, and biomass burning.^{1,2,4}

There are no nationwide monitoring networks in the United States to quantify agricultural emissions of greenhouse gases (e.g., N₂O, CH₄, etc.), NO, reduced sulfur compounds, VOCs, and NH₃. In contrast, there is a large network in place to assess the changes in the chemical climate of the United States associated with fossil fuel energy production. The National Atmospheric Deposition Program/National Trends Network (NADP/NTN), which has been monitoring the wet deposition of sulfate (SO₄²⁻), nitrate (NO₃⁻), and ammonium (NH₄⁺) since 1978 and currently has some 250 sites across the United States (nadp.sws.uiuc.edu). Similarly, since 1987 the Clean Air Status and Trends Network (CASTNET) has been monitoring dry deposition of NO₃⁻, NH₄⁺ and HNO₃ (but not NH₃, NO, NO₂ or N₂O) at 70 sites primarily in the eastern United States

(www.epa.gov/castnet/). However, there are only a limited number of collocated sites where both dry and wet deposition of N species is measured.

Approximately 90% of the atmospheric NH₃ emission results from animal and crop agriculture in the United States¹³ and in many European countries.^{14–16}

Animal production results in emissions of hundreds of identified VOCs.^{17–22} The compounds identified are diverse and included many acids, alcohols, aldehydes, amides, amines, aromatics, esters, ethers, halogenated hydrocarbons, hydrocarbons, ketones, nitriles, other nitrogen-containing compounds, phenols, sulfur-containing compounds, steroids, and other compounds. Some of these compounds not only are responsible for unpleasant odors but also affect the comfort, health, and production efficiency of animals as well as the comfort and health of human workers.

H₂S, another major compound of concern from animal agriculture, is a colorless, potentially lethal gas released from swine manure decomposition.²³ It is produced as manure decomposes anaerobically, resulting from the mineralization of organic sulfur compounds as well as the reduction of oxidized inorganic sulfur compounds such as sulfate by sulfur-reducing bacteria.²⁴ The U.S. Center for Disease Control warns that brief exposures to high concentrations (>500 parts per million [ppm]) can cause unconsciousness or death.²⁵ Campagna et al.²⁶ have reported a correlation between elevated ambient H₂S concentrations and hospital visits for respiratory diseases. Donham et al.²⁷ reported that H₂S appeared to be the main toxic substance associated with death and illness for people with acute exposure to gases emanating from liquid manure. With a low odor threshold ranging from 0.0005 to 0.3 ppm,²⁵ it is also one of the primary gases released from swine facilities that is associated with odor complaints because of its characteristic “rotten egg” smell. Although H₂S is the major sulfur compound emitted from confined animal feeding operations,²⁸ there is a need to quantify other sulfur compound emissions such as: methyl mercaptan, CH₃SH; dimethyl sulfide, DMS or (CH₃)₂S; dimethyl disulfide, DMDS or (CH₃)₂S₂; carbonyl sulfide, COS; and carbon disulfide, CS₂.

N₂O is a greenhouse gas with an atmospheric lifetime of approximately 120 yr. N₂O is approximately 310 times more effective in trapping heat in the atmosphere than CO₂ over a 100-yr period.²⁹ It is produced naturally in soils through the microbial processes of denitrification and nitrification. These natural emissions of N₂O are increased by a variety of agricultural practices and activities, including the use of synthetic and organic fertilizers, growth of nitrogen-fixing crops, cultivation of organic soils, and the application of livestock manure to croplands and pasture. Each of these practices directly adds additional reactive nitrogen to soils, which can then be converted to N₂O. Indirect additions of nitrogen to soils can also result in N₂O emissions. Indirect additions include those processes by which nitrogen in applied fertilizer or manure volatilizes into NH₃ and NO_x and is redeposited onto the soil in the form of particulate NH₄⁺, nitric acid, and NO_x. Surface run-off and leaching of applied nitrogen into groundwater and surface waters can also result in indirect additions of nitrogen to the soil.

N₂O is also produced through the nitrification and denitrification of the organic nitrogen in livestock manure and urine. Agricultural sources (both crop and animal production) in the United States account for approximately 72% of N₂O emissions.³⁰

Air quality models 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. The National Research Council has clearly identified a need for three-dimensional transport/transformation models to provide a scientific basis for relevant mitigation strategies.

Recognizing the growing needs in this research area, a number of governmental agencies such as the U.S. Department of Agriculture, the National Science Foundation, the U.S. Environmental Protection Agency, the North Carolina Division of Air Quality and several universities and research organizations such as the North Carolina State University, Duke University, Purdue University, the Air & Waste Management Association, and the Ecological Society of America cosponsored the first Workshop on Agricultural Air Quality (WAAQ) in the United States during June 3–8, 2006, to synthesize and assess existing measurements and modeling results and identify emerging research needs for agricultural air quality (www.esa.org/AirWorkshop). As indicated at the WAAQ workshop, Dr. Ralph Cicerone, the keynote speaker and president of the U.S. National Academy of Sciences (NAS), described how research on agricultural air quality in the United States is much behind countries in Europe, such as the Netherlands, Denmark, the United Kingdom, Scotland, and Germany.

This special issue of the *Journal of the Air & Waste Management Association* contains 13 peer-reviewed scientific papers from the Workshop on Agricultural Air Quality: State of the Science. Other peer-reviewed papers have appeared in companion issues of *Atmospheric Environment*, *Journal of Environmental Quality*, and *Journal of Atmospheric Chemistry* during 2008.

The 300 papers (both oral and poster) presented at the workshop were broad in scope and supported workshop objectives to:

- (1) Assess the state of science regarding agricultural air quality,
- (2) Build on our knowledge of research, policy, economic, and societal well-being associated with agricultural air quality,
- (3) Foster multidisciplinary communication, exchange of ideas, and partnerships, and
- (4) Recommend changes and improvements in measurement technologies and monitoring methodologies, modeling, and best management and production practices to mitigate air pollutant emissions from agricultural sources.

Topics addressed in this dedicated special issue include emissions of odor, NH₃, and CH₄; their transport, transformation (gas-to-particle conversion), deposition, and fate. Advances in potential environmentally superior technologies for animal agricultural waste treatment are reported. Applications are described that use solid-phase microextraction and multidimensional gas chromatography mass spectrometry-olfactometry to characterize odor. The role of NH₃ in PM_{2.5} formation is described. Isotopic

composition of rainwater in conjunction with back trajectory analysis is used to examine source-receptor relationships. Policy options and regulations for NH₃ abatement for both U.S. and Europe are examined.

The editor is grateful to all the authors and attendees, the conference organizers, and the International Executive Scientific Advisory Committee Members. The conference organizers and the guest editor hope that the papers in this dedicated issue provide the *Journal* readers with useful information that they can use not only today, but also for years to come.

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REFERENCES

1. Millennium Ecosystem Assessment, FAO, 2005; available at <http://www.millenniumassessment.org/en/Reports.aspx> (accessed 2008).
2. Aneja, V.P.; Schlesinger, W.H.; Niyogi, D.; Jennings, G.; Gilliam, W.; Knighton, R.E.; Duke, C.S.; Blunden, J.; Krishnan, S. Emerging National Research Needs for Agricultural Air Quality; *Eos. Trans. AGU* **2006**, *87*, 25-29.
3. Aneja, V.P.; Schlesinger, W.H.; Erisman, J.W. Farming Pollution; *Nature Geosci.* **2008**, *1*, 409-411.
4. Aneja, V.P.; Schlesinger, W.H.; Knighton, R.E.; Jennings, G.; Niyogi, D.; Gilliam, W.; Duke, C.S. *Workshop on Agricultural Air Quality: State of the Science*, North Carolina State University, Raleigh, NC, 2006; ISBN 0-9669770-4-1, p 1314.
5. FAO 2006. Livestock's Long Shadow. United Nations, Food and Agriculture Organization; available at http://www.virtualcentre.org/en/library/key_pub/longshad/A0701E00.pdf.
6. Ansari, A.S.; Pandis, S.N.; Response of Inorganic PM to Precursor Concentrations; *Environ. Sci. Technol.* **1998**, *32*, 2706-2714.
7. Adams, P.J.; Seinfeld, J.H.; Koch, D.M. Global Concentrations of Tropospheric Sulphate, Nitrate and Ammonium Aerosol Simulated in a General Circulation Model; *J. Geophys. Res.* **1999**, *104*, 791-813.
8. Baek, B.H.; Koziel, J.; Aneja, V.P. A Preliminary Review of Gas-to-Particle Conversion, Monitoring, and Modeling Efforts in the USA; *Int. J. Global Environ. Issues* **2006**, *6*, 204-230.
9. Baek, B.H.; Aneja, V.P.; Tong, Q. Chemical Coupling between Ammonia, Acid Gases, and Fine Particles; *Environ. Pollut.* **2004**, *129*, 89-98.

10. Baek, B.H.; Aneja, V.P. Measurement and Analysis of the Relationship between Ammonia, Acid Gases, and Fine Particles in Eastern North Carolina; *J. Air & Waste Manage. Assoc.* **2004**, *54*, 623-633.
11. Aneja, V.P.; Wang, B.; Tong, Q.; Kimball, H.; Steger, J. Characterization of Major Chemical Components of Fine Particulate Matter in North Carolina; *J. Air & Waste Manage. Assoc.* **2006**, *56*, 1099-1107.
12. Hicks, B.B.; Draxler, R.R.; Albritton, D.L.; Fehsenfeld, F.C.; Hales, J.M.; Meyers, T.P.; Vong, R.L.; Dodge, M.; Schwartz, S.E.; Tanner, R.L.; Davidson, C.I.; Lindberg, S.E.; Wesely, M.L. Atmospheric Processes Research and Processes Model Development. State of Science/Technology, Report No. 2. National Acid Precipitation Assessment Program, 1989.
13. Schlesinger, W.H.; Hartley, A. A Global Budget for Atmospheric NH₃; *Biogeochemistry* **2006**, *15*, 191-211.
14. Van der Hoek, K.W. Estimating Ammonia Emission Factors in Europe: Summary of the Work of the UNECE Ammonia Expert Panel; *Atmos. Environ.* **1998**, *32*, 315-316.
15. Sotiropoulou, R.E.P.; Tagaris, E.; Pilinis, C. An Estimation of the Spatial Distribution of Agricultural Ammonia Emissions in the Greater Athens Area; *Sci. Total. Environ.* **2004**, *318*, 159-169.
16. Erisman, J.W.; Bleeker, A.; Hensen, A.; Vermeulen, A. Agricultural Air Quality in Europe and the Future Perspectives; *Atmos Environ.* **2008**, *42*, 3209-3217.
17. Tamminga, S. Gaseous Pollutants by Farm Animal Enterprises. In *Farm Animals and the Environment*; Phillips, C., Piggins, D., Eds.; CAB International: Wallingford, U.K., 1992; pp 345-357.
18. Hartung, J.; Phillips, V.R. Control of Gaseous Emissions from Livestock Buildings and Manure Stores; *J. Agr. Eng. Res.* **1994**, *57*, 173-189.
19. Zahn, J.A.; Hatfield, J.L.; Do, Y.S.; DiSpirito, A.A.; Laird, D.A.; Pfeiffer, R.L.; Characterization of Volatile Organic Emissions and Wastes from a Swine Production Facility; *J. Environ. Qual.* **1997**, *26*, 1687-1696.
20. Zahn, J.A.; DiSpirito, A.A.; Do, Y.S.; Brooks, B.E.; Cooper, E.E.; Hatfield, J.L. Correlation of Human Olfactory Responses to Airborne Concentrations of Malodorous Volatile Organic Compounds Emitted from Swine Effluent; *J. Environ. Qual.* **2001**, *30*, 624-34.
21. Schiffman, S.S.; Bennett, J.L.; Rayme, R.J.H. Quantification of Odors and Odorants from Swine Operations in North Carolina; *Agr. Forest. Meteorol.* **2001**, *10*, 213-240.
22. Blunden, J.; Aneja, V.P.; Lonneman, W.A. Characterization of Non-Methane Volatile Organic Compounds at Swine Facilities in Eastern North Carolina; *Atmos. Environ.* **2005**, *39*, 6707-6718.
23. *Toxicological Review of Hydrogen Sulfide* (CAS No. 7783-06-4). EPA/635/R-03/005. U.S. Environmental Protection Agency: Washington, DC, 2003.
24. Non-Water Quality Impact Estimates for Animal Feeding Operations. In: *Proposed Rule Development Document for Concentrated Animal Feeding Operations (CAFOs)*. EPA 821-R-01-003 (Chapter 13); U.S. Environmental Protection Agency: Washington, DC, 2001; available at http://www.epa.gov/npdes/pubs/cafo_nonwaterquality.pdf (accessed 2008).
25. Agency for Toxic Substances and Disease Registry (ATSDR). *Profile for Hydrogen Sulfide (Draft for Public Comment)*. U.S. Department of Health and Human Services, Public Health Service: Atlanta, GA, 2004.
26. Campagna, D.; Kathman, S.J.; Pierson, R.; Inserra, S.G.; Phipper, B.L.; Middleton, D.C.; Zarus, G.M.; White, M.C. Ambient Hydrogen Sulfide, Total Reduced Sulfur, and Hospital Visits for Respiratory Diseases in Northeast Nebraska, 1998-2000; *J. Expo. Anal. Env. Epidemiol.* **2004**, *14*, 180-187.
27. Donham, K.J.; Knapp, L.W.; Monson, R.; Gustafson, K. Acute Toxic Exposure to Gases from Liquid Manure; *J. Occup. Med.* **1982**, *24*, 142-5.
28. Blunden, J.; Aneja, V.P. Characterizing Ammonia and Hydrogen Sulfide Emissions from a Swine Waste Treatment Lagoon in North Carolina; *Atmos. Environ.* **2008**, *42*, 3277-3290.
29. Warneck, P. *Chemistry of the Natural Atmosphere*, 2nd ed.; Academic Press: New York, 2000; pp 484-485, 511-528.
30. U.S. Emissions Inventory 2005: Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2003, 2005; U.S. Environmental Protection Agency: Washington, DC; available at <http://www.epa.gov/nitrous1/sources.html> (accessed 2008).

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