Whitepaper

PM2.5 – The Science of Gas to Particle Conversion And The Regulatory Impact to Agriculture

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Abstract
EPA first issued standards for particulate matter in 1971; and revised the standards in 1987 and 1997. In September 2006, the Agency revised the 1997 standards. The revised 2006 standards address two categories of particle pollution: *fine particles* ($PM_{2.5}$), which are 2.5 micrometers in aerodynamic diameter and smaller; and *inhalable coarse particles* (PM_{10}) which are smaller than 10 micrometers. EPA has decided to retain the existing 24-hour PM_{10} standard of 150 $\mu g/m^3$. In 2004, several areas in the United States were designated as not meeting the 1997 air quality standards for fine particulate matter ($PM_{2.5}$). In 2006, EPA strengthened the air quality standards for particle pollution. The Agency expects designations based on 2007-2009 air quality data to take effect in 2010.

For those areas designated non-attainment for $PM_{2.5}$ in 2004, State Implementation Plans (SIPs) are due in April of 2008. Some of these areas (South Coast AQMD, San Joaquin Valley APCD) have significant agricultural production activity, including both animal and cropland. Plans are being developed in these areas that address ammonia from agricultural operations, as a precursor or contributor to $PM_{2.5}$. Yet little is actually known about the actual ammonia emissions from agricultural operations (both animal and cropland), especially from a process standpoint. Furthermore, little is known on just how ammonia reacts in the atmosphere to form fine particulates, and to what degree.

Gas To Particle Conversion: Effects Of Intensively Managed Agriculture Upon The Atmospheric Environment Of The United States

The troposphere in the rural United States, especially Southeast (North Carolina), Southwest (Texas), West (California, Arizona), and Midwest poses additional challenges to our current understanding of the factors that contribute to fine particulate matter ($PM_{2.5}$) distributions. In contrast to heavily industrialized and urban regions, these environments are typically characterized by agricultural (animal and crop) operations. Emissions of ammonia (NH_3) are generally associated with intensive livestock agriculture and crop farming (Aneja et al., 2006).

Current estimates of NH_3 budgets in the troposphere show that about 90% of emissions in the U.S results from animal and crop production (Davison and Cape, 2003).

While air quality research in the past half century has focused largely on criteria pollutants such as nitrogen oxides (NOx), sulfur dioxide (SO_2), ozone (O_3), and fine particulate matter (aerodynamic diameter less than or equal to 2.5 microns), limited attention has been given to non-criteria pollutants such as reduced nitrogen and sulfur containing compounds from agricultural sources (both crop and animal). Examples include, ammonia., hydrogen sulfide, etc. Ammonia will likely play an increased role in PM2.5 formation (Baek et al., 2004a,b; 2006) as the emissions of sulfur oxides (SO_2) and NOx are reduced in the coming years and the promulgation of a more stringent 24- hour average national ambient air quality standard of 35 µg m^{-3} by the U.S EPA for $PM_{2.5}$.

The reactions between sulfuric acid (H_2SO_4), nitric acid (HNO_3), and hydrochloric acid (HCl), and water (H_2O) are the most important equilibrium reactions for gas/particle partitioning and the formation of ammonium (NH_4^+) salts in the atmosphere (Hu et al., 2007, Wu et al., 2007). Once formed, these 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 hydroxyl radicals (OH) and oxygen radical (O) to form sulfur dioxide. Aqueous phase chemistry of ammonia may also provide a mechanism for reduced nitrogen to repartition from larger particles to small particles thus forming new particles in ultra-fine mode.

For example, in the Southeast U.S. there is a complex mixture of atmospheric constituents, both rural and urban. Contributions from the metropolitan areas of Atlanta, Charlotte, Nashville, and Raleigh-Durham are influenced by the rural environments of the Southeast U.S. and by the heavily industrialized (Ohio River Valley) to the Northwest, as well as urbanized regions (Washington, DC to Boston) to the north, which export air masses rich in oxidized nitrogen and sulfur compounds. Consequently, the tropospheric chemical state in the rural Southeast is closely coupled with these polluted air masses together with the cycling of both locally reduced and oxidized nitrogen compounds; and emissions of natural and anthropogenic VOCs. In order to estimate the potential impact of such changing emission scenarios, it is critical to develop a detailed understanding of the physical and chemical factors and develop the capability to describe and model the influences of rural, agricultural emissions, and urban emissions as they combine to produce the air mass of the agricultural U.S.

The production, distribution, and sustenance of ozone and a major fraction of $PM_{2.5}$ in the troposphere are linked since they are derived from a common set of precursor emissions. The primary precursors for tropospheric ozone include oxides of nitrogen (NOx) and volatile organic compounds (VOCs). Fine particulate matter in the troposphere typically consist of several components and include sulfate, nitrate, ammonium, organic compounds, and water (Baek, 2002; Baek and Aneja, 2002). These components can reach the particulate phase via different physical and chemical processes so that the composition of airborne particles can differ significantly both spatially and temporally. Gas-to-particle conversions play an important role in determining both the total mass as well as the composition of airborne fine PM. These conversions depend intimately on the chemistry of the NOx-SOx-VOCs-NHx system. This system also results in production of ozone and acidic substances in the troposphere.

Clearly, a detailed understanding of the cycling of atmospheric reduced and oxidized nitrogen compounds, their linkage with emissions of SO_2 and VOCs and subsequent oxidation products, as well as their spatial and temporal distributions, and their contribution to the chemical composition of aerosols is critical for developing and implementing abatement strategies for PM and acidic substances, and any future abatement strategies directed towards controlling critical load exceedances to sensitive ecosystems.

Draft Summary of Ammonia Air Emission Regulations in the US

Air emissions of ammonia from agricultural operations are currently not regulated under the Federal Clean Air Act (CAA). These emissions mainly stem from the application of inorganic nitrogen fertilizer and from livestock and poultry. Though ammonia is known to play some role in the formation of fine particulate matter, it is not classified by the EPA as a pre-cursor pollutant. Unlike most, if not all, of the current Hazardous Air Pollutants (HAPs) and their designated pre-cursors under the CAA, ammonia emissions from Animal Feeding Operations (AFOs) are biologically generated as a part of normal animal metabolism and excretion. In mammals, the mixing of urine and fecal material to produce ammonia occurs outside of the animal and in poultry this mixing to produce ammonia occurs internally prior to excretion by the bird.

Though ammonia is not designated as a pre-cursor pollutant under the CAA, several air districts in California have chosen to include ammonia controls as part of their State Implementation Plans (SIPs) in PM non-attainment zones. The South Coast Air District began limiting ammonia emissions from dairies in 2003 (Rule 1127). South Coast has also proposed poultry and non-dairy livestock ammonia emission controls in their 2007 plan that would be in addition to the controls required of AFOs under CA SB 700 (Florez). The San Joaquin Valley Air Pollution Control District (SJVAPCD) in January 2007 proposed ammonia emissions controls for biosolids, animal manure, and poultry litter. California usually sets the trend nationally for air emissions control strategies and the use of SIPs to address ammonia emissions may spread.

The regulation of ammonia emissions from AFOs has been popular at the state level as well. In many states, ammonia serves as a proxy for odor issues. Two states in particular have set ammonia emission control strategies for animal agriculture. California requires controls of all AFOs over a certain size regardless of species. In Idaho, dairies that are estimated to emit more than 100 tons of ammonia per year are required to implement best management practices to reduce ammonia emissions under a permit required by the Rules for Control of Ammonia from Dairy Farms.

The increased use of SIPS to reduce ammonia emission and the handling of ammonia emission issues by state legislatures is cause for concern. The continued use of the courts and enforcement actions through consent agreements is also alarming. Because ammonia generation in this context is due to natural animal physiology and metabolism, control methodologies become increasingly complex and must take into consideration the health and well being of the animals themselves. These sorts of natural, physiological constraints to controlling ammonia are not present in any other industry currently regulated under the CAA nor do they seem to have been taken into consideration by regulators and policy makers.

Recommendations

In 2008, state regulatory agencies will be forced to address fine particulate matter ($PM_{2.5}$) and its sources. With the presumption that ammonia plays a significant role in the formation of $PM_{2.5}$, agriculture may be significantly regulated. To ensure that agriculture is fairly and accurately treated, much must be done in the form of research, both on the particulate measurement and with model development. To accomplish these goals, the Emerging Issues Committee makes the following recommendations:

1. There needs to be greater scientific clarity on the role that ammonia plays in gas to particle ($PM_{2.5}$) conversion. Specifically, the USDA Agricultural Air Quality Task Force recommends that USDA conduct additional research on ammonia from agricultural sources, both cropland and animal and the role it plays in the formation of $PM_{2.5}$ in a timely manner, so as to assist states in the development of their $PM_{2.5}$ SIPs that may regulate agricultural production.

2. There is a substantial need to better understand the issue of dry deposition of gaseous ammonia and ammonium aerosols. The number of measurement studies on bidirectional exchange of ammonia are limited. The physiological basis for the uptake and deposition of ammonia/ammonium aerosol needs to be developed. The dry deposition models for estimating total deposition fluxes for use in air quality modeling framework are poorly parameterized in the U.S.

3. Development of a process-based model for ammonia emissions from agricultural sources is critical, particularly as to certain animal species. While much has been done to develop such a model for the dairy industry, no such model exists for the beef cattle, poultry or swine industry, nor does one exist for the application of ammonia-based fertilizers. In keeping with the National Research Council's recommendations in "Air Emissions from Animal Feeding Operations," USDA and other research dollars should be focused on developing process-based models as compared to emission factor research. Process-based models will be necessary in order to evaluate the efficacy of management changes and interventions in reducing ammonia emissions. It is the recommendation of the USDA Agricultural Air Quality Task Force that USDA establish process-based models for ammonia emissions for additional animal species that have not yet been addressed, and to conduct the necessary research for the development of the these models.