AMMONIA EMISSIONS:
WHAT TO KNOW BEFORE YOU REGULATE

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Introduction: Ammonia-Not your ordinary air pollutant

Currently, there is limited regulation of ammonia (NH_3) emissions as a matter of federal policy. The Clean Air Act (CAA) provides the federal authority for any regulation of these emissions. Although there are some reporting requirements for NH_3 under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and Emergency Planning and Community Right-To-Know (EPCRA), these statutes do not provide authority to regulate emissions of NH_3. The intent of this white paper is to provide awareness of ammonia as a necessary lifecycle compound that has points of risk to air quality that would be complex to effectively regulate.

There is ever increasing pressure to change NH_3 policy primarily due to concerns about nutrient enrichment of large water bodies, such as the Chesapeake Bay. Recently, the EPA has been petitioned to list NH_3 as a criteria pollutant and this request is somewhat supported by the report from the EPA's Integrated Nitrogen Panel to the Science Advisory Board. There is also the more immediate concern of EPA's treatment of NH_3 as a precursor to fine particulate matter ($PM_{2.5}$). Regulation of NH_3 as a precursor to $PM_{2.5}$ will make it a regulated pollutant under the CAA.

Consideration of NH_3 as an air pollutant will require the EPA to acknowledge and address the role of NH_3 in the full nitrogen (N) cycle and specifically address emission reduction measures that do not merely transfer NH_3 from one environmental medium to another. EPA's statutory authority and its organizational structure may limit its ability to adequately and appropriately address a compound like NH_3. The Agricultural Air Quality Task Force (AAQTF) recognizes the concerns about excess N in the environment; however, it also recognizes the critical role of reactive N in supporting plant and animal life. It will be most challenging to determine "excess reactive N" as a pollutant of concern rather than "reactive nitrogen."

It will be difficult to regulate only the "excess" portion of reactive N, particularly since "excess" cannot be defined as a constant. Roughly 60- 85% of NH_3 emissions in the United States are estimated to come from agricultural sources, a sector that varies considerably from the traditional industrial sources addressed by the environmental statutes. In fact, in most of these statutes, there is recognition that agricultural sources are different; and some regulatory exemptions are provided. Congress did not anticipate the application of the CAA to agricultural sources or it would have included some exemptions as well. Nevertheless, regulation of NH_3 emissions under the CAA will make it extremely difficult for EPA to consider the positive value and need for fertilizer NH_3, which could have huge implications for the viability of the domestic and global food supply.

Most of the public's concerns about NH_3 emissions have arisen due to the proliferation of large Concentrated Animal Feeding Operations (CAFOs) and their environmental and health impacts. A CAA regulatory approach to NH_3 may also encompass emissions from crop production – a source that is currently exempt from federal regulation. Some NH_3 emissions from the crop canopy, and exchange within the crop canopy (i.e. crop leaf NH_3 absorption), of many field crops is a natural and seasonal process; ranges in some environments have been documented in the scientific literature.

To date, pollutants regulated under the CAA are considered "bad" for public health and for the environment; and the statute is designed to limit the impacts of these pollutants by reducing or eliminating their emissions. As EPA moves to regulate greenhouse gases, it is encountering difficulty in applying the existing statute in its consideration of carbon dioxide as a pollutant, which is a necessary component of the life cycle of plants and animals. Regulation of NH_3 emissions within the constraints of the existing CAA will prove no less daunting and may lead to costly and illogical outcomes with little actual benefit to the environment or human health.

Ammonia's role in agriculture

Nitrogen is an essential nutrient for all life on earth. It is one of the most widely distributed elements in nature, however, the soil only accounts for a minute fraction of lithospheric (earth crust and upper-most solid mantle) N. Of this soil N, only a small fraction is in a form directly available to plants. Therefore, N is the nutrient most often limiting plant growth in terrestrial ecosystems. The most readily available forms of nitrogen for plant growth are nitrate (NO_3^-) and ammonium (NH_4^+). These forms of plant available N ultimately derive from atmospheric N_2 gas, which constitutes 78% of the earth's atmosphere. Nitrogen from the atmosphere is made available for plant growth via biological fixation by soil microorganisms, atmospheric electrical discharges, and manufacture of synthetic N fertilizers. Other inputs of N into the soil system include incorporation of crop resides and animal manures. These organic N sources along with other organic N present in soils can be mineralized by soil microorganisms into NH_4^+ and then converted to NO_3^-.

Modern day agriculture has been shaped by the ability to chemically fix N from the atmosphere to yield NH_3. The NH_3 produced can be directly used as a fertilizer (anhydrous NH_3) or used to produce a variety of other N fertilizers (see Appendix). The use of commercial fertilizers, along with other modern agricultural technologies such as irrigation, pesticides, and new crop varieties, resulted in the doubling of global cereal grain production in the last 40 years. Therefore, the impact of fertilizer NH_3 on crop yields has been an integral part of sustaining a growing global population.

While essential for crop growth, NH_3 can also be lost from the system via volatilization. However, unlike many of the regulated pollutants which are governed strictly by chemical or mechanical processes, NH_3 emissions are generally governed by chemical and biological processes that cannot be easily predicted or controlled. In soil solution the equilibrium of NH_3 and NH_4^+ is dependent on pH with a lower pH generally favoring NH_4^+. This relationship is very important as NH_4^+ is relatively stable in soils and can be held on the soil cation exchange sites or fixed in certain clays, while NH_3 is volatile and may be lost from the system as a gas. There is a large annual and seasonal variation in soil ammonium NH_4^+ concentrations and NH_3 losses due to geographic region, cropping system, management practices and even field variability, which makes NH_3 volatilization particularly difficult to estimate with any certainty.

Geographic region is an important consideration because of the effects of climatic conditions and soil characteristics. Warmer, humid climates will be more favorable for mineralization of soil organic N to NH_4^+. The N in urea and urea-containing fertilizers and manures will likewise be converted (hydrolyzed) to NH_4^+ more rapidly in warm, moist soil conditions with neutral pH. A portion may be converted to NH_3 and lost to the atmosphere if not incorporated beneath the soil surface by rainfall or irrigation. Drier soils and cooler climates will have a slower rate of N mineralization as well as slower conversion (i.e. hydrolysis) of urea to NH_4^+, thus potentially reducing losses. Soils with a high clay content, particularly soils with high vermiculite and illite clays, have a greater capacity to sorb or fix NH_4^+, making it less plant available as well as less available to losses as NH_3. Soils with acidic pHs (<6) generally have less risk of NH_3 emissions after application of urea-containing N sources than those with a pH>7.5 Even within the same field, NH_4^+ availability and NH_3 volatilization can vary due to variation of soil properties such as clay content, pH, moisture, temperature, microbial activity and the pools of N available (i.e. fertilizer, manure, soil organic N). In the absence of N additions, ammonia volatilization risks are quite low.

The cropping system also influences N use and NH_3 losses. Certain crops such as alfalfa, clover, soybeans, and peas can fix atmospheric N to meet or provide a substantial amount of the N needed for good yields. Other crops typically need input of nitrogen to achieve good yields. A reduction in the use of commercial fertilizers and manures for crop production reduces the potential for NH_3 losses; however, there is a risk involved with this approach as the N demand of the crop to meet production goals must still be met. Otherwise, decreased production could inadvertently increase the overall environmental footprint of agricultural production and result in significant declines in yields at a time when global food supply must be doubled to meet a growing population. In addition, soil organic matter and soil organic N may be depleted by continued crop harvest removal without replacement; seriously threatening system productivity and sustainability. Crops themselves can be a net source of NH_3 to the atmosphere. Plants can both absorb and release NH_3 to the atmosphere, depending on factors such as growth stage, diurnal respiration cycles, and crop N content.

One of the largest impacts on N utilization and NH_3 losses from agriculture is land management practice. The choice of N source, rate, timing, method of N application, and the management of crop residues affect NH_3 losses. Among these management choices, appropriate soil incorporation of the N source can significantly reduce the risks of ammonia volatilization losses. It is important to remember that not every unit of N will react the same way and produce a consistent amount of NH_3. Emissions will vary daily, seasonally and spatially depending on multiple factors that cannot be easily controlled such as weather, soil conditions, and microbial activity. There is a need to develop an inventory of actual measured ammonia emissions from long-term cropping system (including grasslands), zero-N unfertilized land (in last 10 to 20 years) and selected “natural” systems. This will be important to establishing some baseline natural emissions estimates.

Animals (including humans) require N in the form of essential amino acids, which are the building blocks of protein. For the majority of domesticated animals (cattle, swine, poultry) dietary amino acids are provided via crops such as corn, soybeans, wheat, barley and forages (alfalfa, hay, silage), as well as by-products such as distillers grains. Feed N that is not utilized by the animals is excreted in the feces and urine. Nitrogen use efficiency in animals is fairly low. For example a lactating cow may excrete more than 70% of the N ingested in feed, with the majority in the urine. Most urinary N is in the form of urea, which upon excretion into the environment can be rapidly hydrolyzed to NH_4^+ by the urease enzyme found in feces and soil and subsequently converted to NH_3. Typical NH_3 emissions rates from animal housing range from 5 to 50% of N excreted, depending on animal species, housing system, manure handling practices, diet, and climatic variables. An additional amount of NH_3 can be lost during manure handling and storage as well as land application. The generation and emission of NH_3 from manure is influenced by multiple factors such as exposed manure surface area, airflow across manure surface, manure mixing, manure storage loading rate, ambient temperature, and manure age, temperature, moisture content, and pH. Accurately estimating these emissions is complicated, and as with land application of manures and fertilizers, may be difficult to monitor and control.

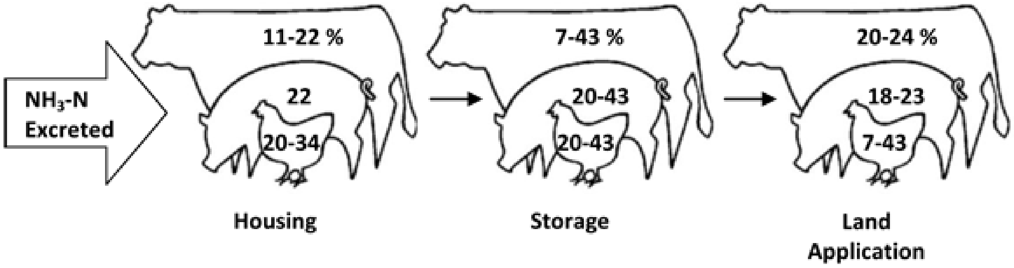

Figure 1. Percentage of ammonia (NH_3) emissions from animal housing, manure storage and land application for poultry, swine and cattle (EPA National Emissions Estimates, 2005).

Fate, transport, and transformation of atmospheric ammonia

Once NH_3 has been volatilized, it may be removed from the atmosphere by dry or wet deposition, leading to elevated risks of soil acidification and surface water eutrophication. While the scientific community has a fundamental understanding of the fate, transport and transformation of NH_3, quantifying those processes remains challenging. Ammonia gas has a short range dispersion due to its fast dry deposition, whereas particulate NH_4^+ may transport further. Ammonia dry deposition shows high variability due to variations in emission sources, land uses, management practices, and meteorological conditions. Current techniques for quantifying NH_3 transport and deposition include long-range transport models and techniques that couple direct measurements and theory. However, there is still large uncertainty associated with modeling the emission, transport and reactivity of NH_3 in the atmosphere making it difficult to assess the true impact of NH_3 emissions from agriculture on air quality.

Transformation of atmospheric NH_3 lies in its chemical reaction with acidic gas species to form particle-phase NH_4^+ salts, also known as secondary inorganic $PM_{2.5}$. Atmospheric NH_3 preferentially reacts with sulfuric acid (H_2SO_4) to form ammonium sulfate ($(NH_4)_2SO_4$). If more NH_3 is available, it then reacts with nitric acid (HNO_3) to form ammonium nitrate (NH_4NO_3). These chemical reactions are the most important equilibrium reactions for aerosol formation and are highly dependent on NH_3, NOx and SOx concentrations, humidity, and temperature. Although the fundamental knowledge about the formation of secondary NH_4^+ particulate is well established, understanding the behavior of such inorganic aerosols in agricultural environments (e.g., in the vicinities of animal facilities) is limited. For example, insignificant formation of NH_4^+ particulate was observed surrounding an egg farm due to lack of sufficient acidic gas concentrations. *Therefore, if regulation of* NH_3 *as a precursor to* $PM_{2.5}$ *formation is going to occur, additional understanding of the effect of agricultural* NH_3 *emissions on secondary* $PM_{2.5}$ *formation is needed.*

Mitigation of ammonia emissions from animal production and land application of manures and commercial fertilizer

Although the majority of scientific literature addressing NH_3 emissions from animal production is focused on losses from manure storage systems, it is important to understand that NH_3 reduction strategies must be considered across the entire production spectrum. While some principles or strategies (e.g., dietary modification to reduce N excretion, reducing exposed manure surface area) for reducing NH_3 emissions are applicable to all animal species, certain practices (e.g., separation of urine and feces of swine manure, collection and frequent removal of manure with conveyor belts in laying-hen houses) are animal species specific.

Reduction of NH_3 emissions from animal production may be achieved either by selecting design and management schemes to reduce its generation (pre-generation), or by applying treatment and/or management strategies that mitigate emission to the atmosphere after it has been generated (post-generation). Table 1 lists practices for pre- and post-generation mitigation of NH_3 emissions. Some of these mitigation practices have found wide adoption while others are cost prohibitive.

Table 1. Practices for pre- and post-generation mitigation of NH_3 emissions in the USA.

Pre-generation	**Post-generation**
Dietary modification** (e.g., reduced crude protein)	Facility location to lessen impact emissions**
Frequent manure removal**	Barriers/shelter belts* (e.g., vegetative buffer)
Manure treatment* (e.g., additives, acidification, drying, separation)	Exhaust air treatment* (e.g., wet scrubber, biofilter)
Housing design (reduced manure surface)	
Covered manure storage*	
Sub-surface injection or rapid incorporation of manure into soil**	

** Practices with relatively wide adoption; * Practices with moderate adoption

Reduction of NH_3 emissions from land application of manures and commercial fertilizers can be achieved by altering management practices on farm. A primary method to conserve N and reduce NH_3 losses is to inject fertilizers and manure below the soil surface or incorporate fertilizers, manures and crop residues immediately after application or harvest. Also, urease inhibitors have been developed for use with some commercially available N fertilizers to delay conversion (usually up to 10 to 14 days) of urea to NH_4^+, providing additional management flexibility to allow irrigation, rainfall, or tillage to move the urea into the soil. For additional information on mitigating NH_3 emissions from commercial fertilizer see Appendix.

Before we regulate

One of the greatest challenges with regulation of NH_3 from agriculture is accurate measurement and estimation of NH_3 emissions. Ammonia emissions are fugitive, vary spatially and temporally, and are readily influenced by many factors (e.g., source, climate, management practices, etc.) making it difficult to determine at a farm level, a precise emission factor. Before emissions can be quantified, a decision will have to be made as to what constitutes a "farm". Agricultural NH_3 emissions can come from a variety of on-farm sources and the delineation of the farm boundary is an important decision. For example, a farm that only consists of field crops with fertilizer N application will have a limited source area, mainly the fertilized fields. On the other hand, a livestock farm will have the following NH_3 sources: animal housing, manure handling and storage, and fields receiving manure/fertilizer. In the case of a livestock farm, it is imperative that all NH_3 sources be considered, since altering the NH_3 in one sector can lead to changes in the loss of NH_3 in other sectors.

There is no easy and economical way to directly monitor emissions from commercial livestock and cropping farms, which will make emissions estimation and enforcement challenging. EPA's, and the livestock industry's, best ammonia emissions assessment effort thus far, the National Air Emissions Monitoring Study (NAEMS), to monitor emissions from livestock sources, met with limited success. Further, using monitored emissions data to develop emission factors for these sources is proving to be difficult.

Many of the on-farm mitigation strategies to reduce NH_3 emissions have been developed and tested in controlled environments. There has been limited validation of mitigation strategies for commercial farms. Therefore, the measurement of success of these mitigation strategies will always be a complicated issue. A mitigation strategy that works well in a controlled environment may not be as successful when implemented on farm. Due to the difficulty and expense of measuring NH_3 losses from production systems, there will have to be a different validation system set in place. Some of the validation processes proposed for carbon credits and trading may be the best (or only) approach for estimating the impacts of mitigation practices on NH_3 losses.

Proceeding to regulation without proven methodologies for measurement of agricultural sources of NH_3 and the ability to demonstrate scientifically the effectiveness of reduction practices, does not seem appropriate.

The validity of regulating NH_3 emissions in agricultural areas may be challenged since it has been shown in some areas that particulate formation in non-attainment areas is insensitive to reductions in NH_3 concentrations (short of eliminating all emissions). Is it valid to regulate NH_3 when in many cases it will likely not produce the desired $PM_{2.5}$ reduction outcome?

Two very important issues related to mitigating on-farm NH_3 losses are the potential negative impacts on yield/productivity and the cost of implementing mitigation practices. As previously stated, N is essential to both crop and animal production, and when not supplied in sufficient amounts, will decrease both crop yield and animal productivity, risk declining soil system health and sustainability, and generate a loss for producers and perhaps even increase the overall environmental footprint of agricultural activities. Certain management or mitigation practices may be too costly for many producers given the current market value of agricultural commodities. So any regulation aimed at reducing NH_3 emissions will need to consider the cost of these reduced emissions and how these costs will be recovered by our farmers and ranchers.

Final Thoughts

Perhaps like no other air pollutant that EPA regulates, NH_3 is a critical component of a natural biological cycle. Thus, an understanding of the fundamental science of the N cycle and the sources, fate and transport of the compounds in this cycle, and recognition of the gaps in that knowledge base, are essential prior to proceeding to regulation of crop and animal production under the prescriptive provisions of the Clean Air Act. Development of monitoring methodologies, measurement tools, and improved models for agricultural sources are needed. Identification and effectiveness of best management practices to reduce "excess" NH_3 are needed with practices validated at the field level prior to widespread use and implementation.

A collaborative dialogue with the agricultural community needs to occur prior to considering regulation. Current approaches of voluntary and incentive-based efforts are accomplishing significant improvements in soil health and reducing erosion and loss of nutrients, and agencies should recognize these improvements.

EPA can assist constructive dialog by avoiding regulatory silos and embracing holistic approaches in development of policies as it focuses on the agricultural sector. "One size fits all" style requirements should be avoided so that practices may continue to naturally evolve in consideration of all the needs expected of agriculture; air and water quality protection, adequate food production, safety and costs, and rural socio-economic viability. Conflicting and redundant regulatory and non-regulatory programs that address the same practice are not beneficial to communities or the environment, are a waste of valuable time and money, and are harmful to the development of collaborative sustainable relationships.

Farmers of the U.S. and the world must meet the food, fiber, and fuel needs of the predicted nine billion people by 2050. Increased yields from existing farmland are imperative if this challenge is to be met. Preserving, maintaining and improving soil health is essential to ensuring production levels. Any policies, regulations and incentive programs to address excess reactive N must factor agricultural sustainability into its approach as a top priority. Therefore, any regulation of ammonia under the Clean Air Act must address its impact on the sustainability of domestic and global food supply as part of the mandatory statutory requirement to evaluate public health and welfare effects and the vitality of rural communities.

Authors: Sally Shaver, April Leytem, Robert Burns, Hongwei Xin, Lingjuan Wang-Li, Lara Moody, Nicole Embertson, Eileen Fabian-Wheeler
United States Department of Agriculture, Agricultural Air Quality Task Force

Reference cited:
EPA National Emissions Estimates, 2005. www.epa.gov/ttnchie1/net/2005inventory.html

APPENDIX

Commercial N Fertilizer Sources Susceptible to Loss and Mitigation Practices

The early 20th century discovery of how to synthesize nitrogen (N) fertilizer was a transformational event in human history. The ability to capture relatively inert N_2 gas and convert it to the more reactive ammonia (NH_3) form ultimately led to dramatically increased agricultural productivity. It is estimated that about half of the world's population now depends on N fertilizer inputs for their food supply.

Ammonia (NH_3) is the foundation for the nitrogen (N) fertilizer industry. It can be directly applied to soil as a plant nutrient or converted into a variety of common N fertilizers. Ammonia has the highest N content of any commercial fertilizer, making it a popular source of N. When NH_3 is applied directly to soil, it is a pressurized liquid that immediately becomes a vapor after leaving the tank. Ammonia fertilizer is always placed at least 10 to 20 cm (4 to 8 in.) below the soil surface to prevent its loss as a vapor back to the atmosphere. Various types of tractor-drawn knives and shanks are used to place the NH_3 in the correct location. Ammonia is sometimes dissolved in water to produce "aqua ammonia", a popular liquid N fertilizer in some regions. Aqua ammonia does not need to be injected as deeply as NH_3, which provides benefits during field application and has fewer safety considerations.

Urea is the most commonly used N fertilizer in the world. It is most commonly incorporated into the soil or applied to the soil surface. Due to the high solubility, it may be dissolved in water and applied to soil as a fluid, added with irrigation water, or sprayed onto plant foliage. After urea contacts soil or plants, a naturally occurring enzyme (urease) begins to quickly convert the urea back to NH_4^+ in a process called hydrolysis. During this process, the N in urea is susceptible to undesirable gaseous losses as NH_3. Urea hydrolysis, typically occurs within several days after application. The ammonium is subsequently converted in soil to nitrate through nitrifying bacteria. Understanding these transformations helps with management decisions to use urea most efficiently.

Although urea is the most widely used N fertilizer in the world, it has a disadvantage in that it is susceptible to ammonia loss after application. These losses are site-specific, and in severe cases can range between 10 - 40% of the applied N if the fertilizer remains on the soil surface for a prolonged period. Considerable efforts have been made to slow the conversion of urea to ammonia and reduce the magnitude of volatilization losses to the atmosphere. Incorporation into the soil and use of urease inhibitors are two management practices used to mitigate ammonia losses.

Urea ammonium nitrate (UAN) makes an excellent source of N nutrition for plants. However, since half of the total N is present as urea, extra management may be required to avoid volatile losses. When UAN remains on the surface of the soil for extended periods (a few days), soil enzymes will convert the urea to NH_4^+, a portion of which can be lost as ammonia gas. Therefore, UAN should not remain on the soil surface for more than a few days in order to avoid significant loss. UAN solutions are commonly injected into the soil beneath the surface, sprayed onto the soil surface, dribbled as a band onto the surface, added to irrigation water, or sprayed onto plant leaves as a source of foliar nutrition. Urease inhibitors can also be used with UAN solutions to reduce ammonia loss.

Ammonium sulfate is used primarily where there is a need for supplemental N and sulfur (S) to meet the nutritional requirement of growing plants. Since it contains only 21% N, there are other fertilizer sources that are more concentrated and economical to handle and transport. However, it provides an excellent source of S that has numerous essential functions in plants, including protein synthesis. After addition to soil, the ammonium sulfate rapidly dissolves into its ammonium and sulfate components. If it remains on the soil surface, the ammonium may be susceptible to gaseous loss in alkaline conditions. In these situations, incorporation of the material into the soil as soon as possible, or application before an irrigation event or a predicted rainfall is advisable.

Urease Inhibitor. Most enzymes, including urease, can be disrupted by specific chemical additives. Thousands of compounds have been screened to find a chemical that specifically inhibits urease, is safe to handle, compatible with urea fertilizer, and not overly persistent in the environment. Commercially available urease inhibitors are best suited for application with urea or solutions of UAN that will be applied directly on the soil surface or to grassland. Under these conditions, the inhibitor delays conversion to ammonia (up to 10 to 14 days) and provides additional management flexibility to allow irrigation, rainfall, or tillage to move the urea into the soil. Once below the soil surface, the potential for ammonia loss is greatly reduced. Urease inhibitors have also been shown effective at decreasing the toxicity of urea placed near germinating seeds.

Urease inhibitors are used to temporarily reduce the activity of the enzyme and slow the rate at which urea is hydrolyzed. There are many compounds that can inhibit urease, but only a few that are non-toxic, effective at low concentrations, chemically stable and able to be mixed with or coated onto urea-containing fertilizers. There are many organic compounds, especially structural analogues of urea, capable of inhibiting urease.

Appendix References

Nutrient Source Specifics – Ammonia; Urea; Urea Ammonium Nitrate; Ammonium Sulfate; Urease Inhibitors. IPNI. www.ipni.net/specifics
Nitrogen Notes – Managing Nitrogen; Managing Urea. IPNI. www.ipni.net/publications