AGRICULTURE'S CONTRIBUTION TO NITROGEN DEPOSITION IN ROCKY MOUNTAIN NATIONAL PARK

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ABSTRACT

Nitrogen deposition in Rocky Mountain National Park has been increasing steadily and is impacting both terrestrial and aquatic ecosystems. Ammonia volatilization from fertilizer is estimated to contribute 20% of the N deposited in the park. The objectives of our research are 1) to determine N isotope ratios for ammonia sources, and to use this tool to evaluate the accuracy of the source predictions, and 2) to evaluate Best Management Practices for ammonia volatilization reduction on-farm and then to extend our results, in order to influence producer decision-making.

INTRODUCTION

Nitrogen emissions come from many sources including transportation, agriculture, power plants, and industry (Fenn et al., 2003b). Total atmospheric emissions of nitrous oxide (NOx) and ammonia (NH_3) increased from 23 Tg N yr^{-1} in 1860 to 93 and 189 Tg N yr^{-1} in the early 1990s and 2050 (prediction), respectively (Galloway et al., 2004). Rapid increases in population, urbanization, distance driven, and concentrated livestock production all contribute to increased N deposition in the West (Fenn et al., 2003b).

Atmospheric N deposition ranges from 2 to 7 kg ha^{-1} yr^{-1} (2 to 6 lb $acre^{-1}$ yr^{-1}) in the Rocky Mountains of Colorado and Wyoming (Burns, 2004). Over time, steady increases in N deposition have been documented in many areas of the western U.S. (Baumgardner et al., 2002). Williams and Tonnessen (2000) calculated an increase in N deposition of 0.32 kg N ha^{-1} yr^{-1} on Niwot Ridge east of the Continental Divide. Of the N deposited, about 45% is in the form of NH_3 gas, and up to 87% of that is attributed to fertilizer use and livestock production (Fenn et al., 2003b). Since NH_3 is an unregulated pollutant, there has been increasing concern and political activity encouraging its regulation in recent years.

Ammonia is a very important alkaline constituent in the atmosphere. It reacts readily with acidic substances such as sulfuric acid, nitric acid, nitrous acid, or hydrochloric acid to form ammonium salts that occur predominantly in the fine particle (size <2.5 μm) fraction (Finlayson-Pitts and Pitts, 1999). Different estimates have been reported for the residence time of NH_3 gas ranging from 2.8 h to 4 days (Erisman et al., 1988; Dawson, 1984). Ammonium sulfate and ammonium nitrate, the most commonly found ammonium salts, have low deposition velocities and prolonged atmospheric residence times. Assuming an atmospheric residence time of 6 days and a wind velocity of 5 m s^{-1}, the transport distance of $(NH_4)_2SO_4$ and NH_4NO_3 may be as large as 2500 km or 1550 miles (Irwin and Williams, 1988). Some scientists have estimated the lifespan of ammonium aerosols (salts) at up to 15 days, allowing them to travel even longer distances (Aneja et al., 1998).

Ammonia and subsequently derived ammonium (NH_4^+) are removed from the atmosphere by dry and wet deposition. Dry deposition occurs primarily by diffusion (NH_3) and Brownian motion (fine particle NH_4^+). In contrast, wet deposition occurs with precipitation. Ammonium salts such as $(NH_4)_2SO_4$ are hydroscopic and act as cloud condensation nuclei, facilitating rainout of these ammonium salts to the ground surface. Background N deposition is considered to be 0.2 kg ha^{-1} yr^{-1} (Galloway et al., 1982), but the average wet deposition in the Loch Vale Watershed of Rocky Mountain National Park averaged 2.6 kg N ha^{-1} yr^{-1} (1.0 kg as NH_4-N) from 1984-1991 (Baron et al., 1994). Dry deposition is often estimated to be 50% of wet deposition, thus making total deposition 3.9 kg N ha^{-1} yr^{-1} (3.6 lb $acre^{-1}$ yr^{-1}) (Williams and Tonnessen, 2000). The eastern flank of the Colorado Front Range has been attributed with the highest N deposition in the Rocky Mountains (Baron et al., 2000).

Ecological Impacts of Nitrogen Deposition

Slight increases in atmospheric N deposition can lead to measurable changes in ecosystem properties (Baron et al., 2000). Ecological ramifications, including increased forest and grassland productivity, eutrophication and acidification of freshwaters, hypoxia, and loss of biodiversity, have been documented in terrestrial, freshwater, and coastal ecosystems worldwide (Vitousek et al., 1997).

The alpine areas in the Rocky Mountains are particularly sensitive to small increases in N deposition due to extensive areas of exposed bedrock, steep slopes, limited extent of soils and vegetation, short growing seasons, and rapid hydrologic flushing during snowmelt (Williams et al., 1996; Fenn et al., 2003a). These factors result in a limited ability of these ecosystems to utilize or immobilize nutrients, thus impacting water quality down below.

Surface water NO_3-N levels have been increasing, in particular, east of the Continental Divide (Baron et al., 1994; Williams et al., 1996; Baron and Campbell, 1997; Baron et al., 2000; Fenn et al., 2003a), although there are studies reporting conflicting information (Clow et al., 2003). In some cases, plankton and diatom communities have been altered (Moraska Lafrancois et al., 2004; Wolfe et al., 2001). Lake concentrations range from <7 to 280 µg N/L (Lafrancois et al., 2003), and that variability has been attributed to differences in vegetation (Nydick et al., 2003). Unvegetated terrain (rocky and talus slopes) tend to be associated with high lake N concentrations, and areas with forest or wetland ecosystems with lower N concentrations.

Pine trees have demonstrated greater N:P ratios in their needles with increasing elevation (Williams et al., 1996); increasing elevation brings increased precipitation and increased wet deposition of N. In addition, trees on the east side have higher foliar % N, N:Ca, N:Mg, and N:P ratios along with reduced soil C:N and higher N mineralization potential (Rueth and Baron, 2002; Rueth et al., 2003).

A critical review of all the studies done in the Colorado Rockies pointed out conflicting results on ecological effects of N deposition and identified research priorities (Burns, 2004). Although Burns (2004) stated that the ecological effects of N deposition had not been clearly demonstrated due to the influence of other factors not being ruled out, he did conclude that ecosystem effects of N deposition are subtle but are likely to become more prominent with time.

Sources of Nitrogen Deposition

Agriculture has been estimated by the Colorado Department of Public Health and Environment (2006 reference) to contribute roughly 60% of the ammonia being emitted in eastern Colorado and deposited in Rocky Mountain National Park (about 40% from livestock and 20% from fertilizer). However, improved emissions inventories and source identification are needed (Williams and Tonnessen, 2000; Fenn et al., 2003b), and N isotope ratios provide one tool that could be used to verify whether the estimates of N deposition sources are correct.

The potential use of $\delta^{15}N$ signals to follow N transfers in ecosystems is based on the fractionation effects of the isotopes ^{15}N and ^{14}N. The ratio of the isotopes in atmospheric NH_3 will depend primarily on the N source, with agricultural practices producing significantly different $\delta^{15}N$ values than non-agricultural sources (Moore, 1977). The $\delta^{15}N$ in animal protein predominantly exhibits an enriched positive signal relative to feed, and this is attributed to the fractionation processes occurring during de-amination and transamination (Deniro and Epstein, 1981). Increasing trophic levels will increase the ^{15}N content in animal protein, with carnivores tending to have higher $\delta^{15}N$ values than herbivores. N isotopes can therefore, for instance, allow discrimination between feeding types (Ambrose and Deniro,1986).

Nitrogen in excreted waste (i.e., animal or sewage waste) is mainly in the form of urea which is hydrolyzed to ammonia and converted to nitrate. Hydrolysis of urea produces a temporary rise in pH, a condition which favors the formation of ammonia which is easily lost by volatilization into the atmosphere. Ammonia lost from animal and human waste is strongly depleted in ^{15}N ($\delta^{15}N$ values in the range -10 to -15‰) (Freyer, 1978; Heaton, 1986). Nitrate and ammonium in fertilizers are usually derived by industrial fixation of atmospheric nitrogen by quantitative processes resulting in little overall isotopic fractionation, and these products therefore have $\delta^{15}N$ values close to zero.

Some authors have calculated critical levels of N deposition ranging from 1.5 kg N ha^{-1} yr^{-1} (Baron, 2006) to 4 kg N ha^{-1} yr^{-1} (Williams and Tonnessen, 2000). Current N deposition rates range from 2-7 kg N ha^{-1} yr^{-1} (Burns, 2004); therefore, many scientists have emphasized the need to reduce source emissions in order to protect mountain ecosystems (Fenn et al., 1998; Fenn et al., 2003b).

MATERIALS AND METHODS

Ammonia Source Tracking

A series of intensive field experiments is underway to investigate the $\delta^{15}N$ values from sources likely to contribute ammonia to the Rocky Mountains [i.e., dairies, feedlots, biosolids, native soils, forest fires, synthetic fertilizers, traffic sources, industry, wildlife, and human emissions (perspiration, breath)]. These sources will be measured temporally and spatially to gain information about variability in concentration and $\delta^{15}N$ values due to fractionation and dilution. All $\delta^{15}N$ (NH_3/NH_4^+) analysis will be conducted using a Carlo Erba NA 1500 elemental analyzer coupled to a VG Isochrom isotope ratio mass spectrometer in continuous flow mode (Holmes et al., 1998; Skinner et al., 2006a, 2006b).

Best Management Practice (BMP) Evaluation

Following a thorough literature review, we are in the process of demonstrating the most promising BMPs on feedlots and dairies in 2007 and 2008. The BMPs are being evaluated for their implementation costs and effectiveness in reducing ammonia emissions. To evaluate the effectiveness of the BMPs on farm, a few select BMPs are tested at each of 6 feedlots and 6 dairies to determine the ammonia reduction potential of the BMP. In order to do this, real-time ammonia concentration measurements are being taken pre and post BMP installation. Surface ammonia measurements are made using a unique composite surface emission collector developed at Colorado State University. The device works by collecting surface emissions from 16 tubes each encased by an inverted funnel staked 4 inches above the ground surface. The tubing leads to a sampling device which mixes the air sample at which time a real-time ammonia analyzer (Nitrolux-S, Pranalytic, CA) takes a sub-sample of the mixed air and provides a reading every minute. In addition, meteorological data is collected, as well as a variety of analytical data depending on the BMP being tested. A cost analysis will be conducted to determine the implementation cost per head and the cost efficiency (cost per unit reduction in ammonia concentration) of each BMP.

DISCUSSION

Regulation

Federal and state agencies are working together to develop cost-effective means for reducing N deposition. To do this, there is a critical need for better understanding of N emission source areas and source types that contribute to N deposition in the Front Range of Colorado (Campbell et al., 2007). Currently, wet deposition of inorganic N in Rocky Mountain National Park consists of approximately 55% NO_3 and 45% NH_4^+ (based on data from the National Atmospheric Deposition Program, 2007). It is believed that most of the NH_4^+ collected originates as NH_3 emissions from agricultural activities, primarily livestock and fertilizer. However, very little effort has been made to validate the sources that contribute NH_3 to the park.

In response to a high level of concern among citizens living near RMNP and the National Park Service, the Colorado Air Quality Control Commission formed a Rocky Mountain National Park sub-committee in 2005 to evaluate sources of N deposition and to develop potential solutions. The Colorado Department of Public Health and Environment completed an ammonia inventory to identify the primary sources of ammonia in the state of Colorado; they found that when non-regulatable sources of ammonia (such as wildlife, native soils, and human perspiration) were removed from the inventory, agricultural contributions amounted to approximately 60% of statewide ammonia emissions with 40% from animal agriculture and 20% from fertilizer use. The Colorado Air Quality Control Commission recently approved a Nitrogen Deposition Reduction Plan for the Park built on the voluntary use of BMPs to reduce ammonia emissions from agriculture. In 5 years, an evaluation will be made to decide whether a voluntary approach to N deposition reduction is working.

BMP Identification and Education

We are developing an online factsheet series including photos from the BMP demonstration sites and a decision tree to aide producers in selecting optimum BMPs for their operation.

Ammonia volatilization ranges from 3 to 50% of added N-fertilizer depending on soil texture, cation exchange capacity (CEC), pH, moisture, type of fertilizer added, and method and rate of application. Volatilization reduces fertilizer use efficiency and increases costs, so there are strong incentives in place to conserve NH_3/NH_4^+ in the soil for crop uptake. Nonetheless, it is critical that we encourage and verify the use of fertilizer Best Management Practices to reduce NH_3 emissions from fertilizer.

Jones et al. (2007) identified high risk conditions for volatilization of ammonia from fertilizer including high soil temperature (>70˚F), moist soil, high soil pH (>7.0), low CEC, and the presence of soil cover such as crop residue, perennial forage, or an ash layer. Loss of ammonia from soils increases with increasing temperature (Nelson, 1982), and, therefore, losses of ammonia from topdressed urea applications are reduced by applying in cooler weather (Bruulsema, 2005). Hydrolysis converts urea to ammonium, through reaction with water; therefore, volatilization increases with soil moisture until the soil reaches saturation (Al-Kanani et al., 1991). Soil pH influences ammonia volatilization, as ammonium is converted to ammonia under basic conditions (Krupa, 2003). There is a negative correlation between CEC and ammonia volatilization, due to NH_4^+ fixation (Fenn and Kissel, 1976). Organic soil cover can increase volatilization through increased urease activity and reduced penetration of urea into soil.

Urea is the most widely-used fertilizer in the world due to its low cost and high nitrogen content. The highest ammonia volatilization rates usually occur from urea application, which typically emits between 6 and 25% of its nitrogen as ammonia (McGinn and Janzen, 1998). Lightner et al. (1990) found that liquid urea solution could reduce ammonia emissions by 35% compared to granular application. Soluble inorganic salts such as calcium chloride or potassium nitrate may by applied with fertilizer to reduce ammonia volatilization (Sommer et al., 2004).

Sub-surface banding or incorporation are known to reduce ammonia volatilization from fertilizer (Touchton and Hargrove, 1982; Bacon et al., 1986; Sommer and Christensen, 1992; Sommer et al., 2004; Grant, 2005). Applying urea prior to a rainfall or irrigation event (>0.05 inches) also results in improved incorporation into the soil and hence reduces volatilization (Jones et al., 2007).

Urea hydrolysis is mediated by an enzyme known as urease. Products have been developed that inhibit hydrolysis, thus reducing ammonia volatilization, as well (Byrnes and Freney, 1995). The main drawback of urease inhibitors is that they prevent urea in fertilizer from becoming plant available, thus limiting the amount of nitrogen available to plants.

Controlled-release fertilizers are another option to reduce ammonia volatilization. In a study including controlled-release fertilizers in Colorado, Shoji et al. (2001) found that a single application of controlled release fertilizer at 112 kg N ha^{-1} produced potato yields equivalent to those obtained under N fertilization treatments by basal dressing, topdressing, and fertigation, all of which required more N. A variety of polymer coatings are available and can be used to match N release with crop needs (Jones et al., 2007), thus increasing efficiency and reducing loss.

The ammonia source inventory estimates that 20% of the ammonia deposition in Rocky Mountain National Park comes from fertilizer use. Using BMPs improves fertilizer efficiency, reduces costs, and could decrease the ecological impacts of N deposition in the Rockies.

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