Technical note: Contribution of ammonia emitted from livestock to atmospheric fine particulate matter (PM$_{2.5}$) in the United States

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ABSTRACT

Ammonia emitted from animal feeding operations is an air pollutant contributing to the formation of fine particulate matter (PM$_{2.5}$), considered a major environmental risk to human health. In the United States, farm animals are the greatest contributor to gaseous ammonia emissions. Ammonia reacts with atmospheric nitric and sulfuric acids to form PM$_{2.5}$ (nitrate and sulfate), but the proportion of PM$_{2.5}$ attributable to ammonia emitted from animal farming operations has not been quantified. Thus, the objective of this analysis was to estimate the contribution of ammonia emitted from farm animals to PM$_{2.5}$ in the United States. The following approach was used: (1) the amount of ammonium in sulfate and nitrate PM$_{2.5}$ was calculated based on chemically speciated measurements published by the United States Environmental Protection Agency; and (2) the amount of ammonium in sulfate and nitrate PM$_{2.5}$ originating from livestock was assumed equal to the fraction of the total ammonia emissions attributable to livestock. Across different regions of the United States and under different weather conditions, PM$_{2.5}$ formed from ammonia emitted from livestock operations were estimated to contribute on average from 5 to 11% of the total PM$_{2.5}$ concentrations. In certain areas (North Central, for example) and in cool weather, farm animal contribution to atmospheric PM$_{2.5}$ concentration may be as much as 20%.

Key words: ammonia emission, fine particulate matter (PM$_{2.5}$), farm animal contribution

Technical Note

Ammonia emitted from animal feeding operations (AFO) is a major air and water pollutant contributing to surface water eutrophication, aerosol formation, soil acidification, and impaired visibility (USEPA, 2004a). Farm animals are considered the greatest contributor to anthropogenic ammonia emissions (in the United States, 50% of the total; NRC, 2003). The United States Environmental Protection Agency (USEPA) ruled on January 20, 2009, that all AFO with a minimum of 700 dairy cows or 1,000 cattle that did not sign the 2005 EPA Air Quality Compliance Agreement must notify emergency response officials if they emit ≥45 kg of ammonia or hydrogen sulfide in a 24-h period (USEPA, 2009). Animal feeding operations are exempt from reporting under the Comprehensive Environmental Response, Compensation, and Liability Act only for emissions from normal manure handling on farms; reporting is mandatory for other forms of release, such as from a burst anhydrous ammonia tank, breached lagoon or holding pond, or manure spills.

The importance of mitigating ammonia emissions from AFO in the United States is primarily related to the contribution of ammonia to formation of fine particulate matter (PM$_{2.5}$; particles with aerodynamic diameter ≤2.5 μm, sometimes referred to as “fine particles”; USEPA, 2004b), considered a major environmental risk to human health. Air pollution is estimated to cause approximately 2 million premature deaths worldwide per year (WHO, 2005). Of the pollutants monitored by the World Health Organization, particulate matter affects more people than any other air pollutant. Even low concentrations of air pollutants have been related to a range of adverse health effects (Oberdörster, 2001; Miller et al., 2007). Fine particulate matter is considered more dangerous than PM$_{10}$ because, when inhaled, PM$_{2.5}$ may reach the peripheral regions of the bronchioles and interfere with gas exchange inside the lungs (WHO, 2005). Several analyses have clearly indicated the potential for reducing atmospheric PM$_{2.5}$ concentrations through mitigation of ammonia emissions, including that from animal production systems (Goetz et al., 2008), and the consequent human health benefits (Ansari and Pandis, 1998; Pinder et al., 2007; Fann et al., 2009). In comparison, the effect of mitigating sulfur dioxide emissions appears to be much less effective (West et al., 1999).

Livestock operations contribute to PM$_{2.5}$ and particles with an aerodynamic diameter ≤10 μm (PM$_{10}$) emissions directly as dust, or indirectly as sulfate and nitrate formed from ammonia reacting with atmospheric nitric and sulfuric acids. The direct contribution of
The indirect (i.e., through ammonia) contribution of farm animals to PM$_{2.5}$, however, can be significant. Ruminants are inefficient utilizers of dietary N, and dairy cows, for example, can excrete 75 to 80% of dietary N in urine and feces (Hristov et al., 2004; Hultanen and Hristov, 2009). Urinary N, primarily in the form of urea (Bristow et al., 1992) following hydrolysis, is the main contributor to ammonia emission from livestock facilities (Bussink and Onema, 1998; Thomsen, 2000; Lee and Hristov, 2010). Depending on barn design and environmental factors, 30 to 50% of the N excreted in urine and feces by dairy cows can be lost as ammonia (Hristov et al., 2009, 2011). Losses in feedlot cattle are even greater. Flesch et al. (2007) reported that up to 65% of dietary N was lost as ammonia in a Texas feedlot. These significant ammonia emissions are contributing to atmospheric PM$_{2.5}$ formation. To our knowledge, however, the fraction of PM$_{2.5}$ attributable to ammonia emitted from animal farming operations has not been quantified. Therefore, the objective of the current analysis was to estimate the contribution of ammonia emitted from AFO to PM$_{2.5}$ in the United States.

Chemically speciated PM$_{2.5}$ measurements reported in the National Air Quality Status and Trends Report (USEPA, 2008) were used to estimate the contribution of ammonia emitted from livestock operations to atmospheric PM$_{2.5}$ concentrations. The USEPA (2008) report covers 6 geographic regions of the United States and 6 years (2002 to 2007). Only data for 2007 were used in this analysis. The USEPA report specifies seasonal trends in the atmospheric concentration of sulfate, nitrate, elemental carbon, organic carbon, and crustal matter (all considered PM$_{2.5}$) for the Northwest, Northeast, North Central, Southeast, Midwest regions, and Southern California. Organic carbon, sulfate, and nitrate, are considered the main contributors to PM$_{2.5}$, with a much lesser contribution of elemental carbon and crustal elements. Of these, only sulfate and nitrate, as ammonium salts, can be formed from ammonia emitted from farm animal facilities. Sulfuric and nitric acids can react with ammonia to form particulate (PM$_{2.5}$) ammonium nitrate, ammonium bisulfate, and ammonia sulfate (Figure 1). Atmospheric particle chemistry is complex; for a more detailed description of these processes, the reader is referred to USEPA (2004b).

Several assumptions were made for this analysis. First, we assumed that sulfate and nitrate PM$_{2.5}$ exist primarily as ammonium sulfate and bisulfate and ammonium nitrate, respectively. This assumption is based on existing literature (USEPA, 2004b). A study from Europe (Bencs et al., 2008), for example, concluded that, based on the neutralization and cation:anion atmospheric ratios, the major ionic components of PM$_{2.5}$ appeared mostly as ammonium sulfate and ammonium nitrate salts. Wang et al. (2005) reported similar prevalence of ammonium sulfate and ammonium nitrate in PM$_{2.5}$ in China. These authors indicated complete neutralization of SO$_4^{2-}$ by NH$_4^+$ and suggested that ammonium sulfate, rather than ammonium bisulfate, was the major species formed by SO$_4^{2-}$ and NH$_4^+$; ammonium nitrate was the major species formed from NH$_4^+$ and nitric acid. Therefore, it is reasonable to assume that most of the PM$_{2.5}$ sulfate and nitrate reported by USEPA (2008) are ammonium sulfate and nitrate.

A second assumption was that sulfuric acid contribution to PM$_{2.5}$ is minimal. This assumption was also based on existing literature (USEPA, 2004b; Wexler and Johnston, 2008), indicating that under most environmental conditions free sulfuric acid concentrations are usually low in the atmosphere. The implication of this assumption is that sulfate PM$_{2.5}$ in the USEPA (2008) report is assumed to consist of ammonium sulfate and bisulfate.

A third assumption was that the contribution of ammonia emitted from livestock operation to PM$_{2.5}$ is the same as the contribution to total ammonia emissions in the United States; that is, 50% (NRC, 2003). Not all anthropogenic ammonia emissions will react with atmospheric species to form PM$_{2.5}$. Other processes, such as settling on surfaces, uptake by plants and soils, and removal by rainfall represent a substantial disappearance of ammonia (Viets, 1974; Asman and van Jaarsveld, 1992). However, we can safely assume that the contribution of livestock ammonia to these loss processes is similar to the livestock contribution in the total national ammonia emissions.

![Figure 1](https://example.com/figure1.png)
Therefore, to estimate the contribution of ammonia emitted from livestock operations to PM$_{2.5}$, the following approach was used.

**Ammonium in Nitrate and Sulfate PM$_{2.5}$ from USEPA**

First, the amount of ammonium in sulfate and nitrate PM$_{2.5}$ from the USEPA National Air Quality Status and Trends Report (USEPA, 2008) was determined. Crustal elements and organic carbon are not dependent on ammonia emissions; therefore, they were not included in the calculation.

**Nitrate.** Scenario A (ammonia contribution to the particulate nitrate mass was estimated on a molar basis):

Amount ($A_{\text{NH}_4\text{NO}_3}$) of atmospheric ammonium nitrate attributable to ammonia = NH$_4$ (mol) ÷ NH$_4$NO$_3$ (mol) = 18 ÷ 80 = 0.225 × nitrate concentration in air (μg/m$^3$).  \[1\]

Example 1 (Northeast, cool weather; USEPA, 2008):

$A_{1\text{NH}_4\text{NO}_3} = 1.610$ μg/m$^3$ (PM$_{2.5}$ nitrate mass) × 0.225 = 0.362 μg/m$^3$.

Scenario B (based on the assumption that particulate nitrate will not form if ammonia is not available; i.e., all nitrate PM$_{2.5}$ mass is attributable to ammonia):

Amount ($A_{\text{NH}_4\text{NO}_3}$) of atmospheric ammonium nitrate attributable to ammonia = 1 × nitrate concentration in air (μg/m$^3$).  \[2\]

Example 2 (Northeast, cool weather; USEPA, 2008):

$A_{2\text{NH}_4\text{NO}_3} = 1.610$ μg/m$^3$ (PM$_{2.5}$ nitrate mass) × 1 = 1.610 μg/m$^3$.

**Sulfate.** Scenario A (all ammonia is converted to ammonium sulfate):

Amount ($A_{(\text{NH}_4\text{HSO}_4)}$) of atmospheric sulfate attributable to ammonia = 2 × NH$_4$ (mol) ÷ (NH$_4$)$_2$SO$_4$ (mol) = 36 ÷ 132 = 0.272 × sulfate concentration in air (μg/m$^3$).  \[3\]

Example 3 (Northeast, cool weather; USEPA, 2008):

$A_{3(\text{NH}_4\text{HSO}_4)} = 4.39$ μg/m$^3$ (PM$_{2.5}$ sulfate mass) × 0.272 = 1.194 μg/m$^3$.

Scenario B (all ammonia is converted to ammonium bisulfate):

Amount ($A_{(\text{NH}_4\text{HSO}_4)}$) of atmospheric sulfate attributable to ammonia = NH$_4$ (mol) ÷ (NH$_4$)$_2$SO$_4$ (mol) = 18 ÷ 115 = 0.156 × sulfate concentration in air (μg/m$^3$).  \[4\]

Example 4 (Northeast, cool weather; USEPA, 2008):

$A_{4(\text{NH}_4\text{HSO}_4)} = 4.39$ μg/m$^3$ (PM$_{2.5}$ sulfate mass) × 0.156 = 0.685 μg/m$^3$.

Scenario C (sulfuric acid exists in the particulate phase and does not react with ammonia); in this case, the contribution of ammonia emitted from livestock operations to sulfate PM$_{2.5}$ was zero.

**Ammonium in Sulfate and Nitrate PM$_{2.5}$ from Livestock**

Second, the amount of ammonium in sulfate and nitrate PM$_{2.5}$ originating from livestock was assumed to be equal to the fraction of the total ammonia emissions attributable to livestock (50%, NRC, 2003 or 51%, Roy Huntley, EPA, Washington, DC, personal communication, 2009).

Example (Northeast, cool weather; USEPA, 2008):

All examples (A1 to A4) = Nitrate or sulfate PM$_{2.5}$ mass attributable to ammonia (0.362, 1.610, 1.194, or 0.685 μg/m$^3$, $A_{1\text{NH}_4\text{NO}_3}$, $A_{2\text{NH}_4\text{NO}_3}$, $A_{3(\text{NH}_4\text{HSO}_4)}$, and $A_{4(\text{NH}_4\text{HSO}_4)}$, respectively) × 0.51 = 0.185, 0.821, 0.609, or 0.349 μg/m$^3$ (respectively).

**Proportion of Total PM$_{2.5}$ Attributable to Livestock**

The proportion of total PM$_{2.5}$ ($P_{\text{total}}$) attributable to livestock (through nitrate, sulfate, and bisulfate formation) was calculated as follows:

$$P_{\text{total}}(\%) = \text{sulfate, bisulfate, and nitrate PM}_{2.5}$$

originating from livestock ammonia emissions (μg/m$^3$) ÷ total PM$_{2.5}$ (μg/m$^3$) × 100.
Example for scenario A-nitrate and scenario A-sulfate (Northeast, cool weather; USEPA, 2008):

\[
P_{\text{total}} \text{ (from } A_1\text{NH}_4\text{NO}_3 \text{ and } A_3(\text{NH}_4\text{)}_2\text{SO}_4; \%) = \text{nitrate and sulfate PM}_{2.5} \text{ mass attributable to ammonia from livestock } (0.185 + 0.609) \div 10.06 \mu g/m^3 \text{ (total PM}_{2.5} \text{ for the region and cool weather)} \times 100 = 7.9\%.
\]

In this analysis, we assumed that ammonia contribution to PM_{2.5} was through formation of nitrate and sulfate (USEPA, 2004b). The various models developed in Eq. [1] through [4] represent possible chemical reactions involving ammonia conversion into PM_{2.5} and offer lower and upper estimates of the effect of ammonia emitted from livestock facilities on atmospheric PM_{2.5} concentrations. Two scenarios for ammonia contribution to nitrate PM_{2.5} were developed. In scenario B (Eq. [2]), it was assumed that atmospheric nitric acid remains in gaseous state if ammonia is not available; therefore, this model would represent the upper estimate of ammonia contribution to nitrate formation. Based on the Pinder et al. (2007) analysis, scenario B (Eq. [2]) is likely occurring more frequently than scenario A (Eq. [1]), and estimates for ammonia contribution to nitrate formation through Eq. [2] are likely more representative than those using Eq. [1]. The calculated contribution based on scenario A (Eq. [1]) represents the lower estimate for this species.

With sulfate, only the molar contribution of ammonia to sulfate or bisulfate formation was estimated because sulfuric acid can exist in liquid state and is considered PM_{2.5}. Because of its reactivity and abundance of ammonia, sulfuric acid is rapidly converted to sulfate and is usually not present as free acid in the atmosphere (USEPA, 2004b; Wexler and Johnston, 2008). Conditions when sulfuric acid exists in the particulate phase and directly contributes to PM_{2.5}, however, are possible (scenario C above). In these cases, the contribution of ammonia emitted from livestock to sulfate PM_{2.5} would be overestimated in this analysis. The upper and lower estimates for ammonia contribution to sulfate formation in this analysis were derived based on the 2 possible sulfate products formed from ammonia, ammonium sulfate and ammonium bisulfate. As noted by Wexler and Johnston (2008), the molar concentration ratios of ammonium and sulfate in urban environments are generally in the range of 1 to 2. This is in agreement with the assumption in Eq. [3] and [4], suggesting a mixture of ammonium bisulfate and ammonium sulfate; that is, partial or complete sulfate neutralization.

Formation of PM_{2.5} greatly depends on region and weather conditions. The lowest sulfate concentrations were reported for the Northwest (1.4 to 1.7 μg/m^3) and the highest for the Southeast, Northeast, and Midwest (4.4 to 9.8 μg/m^3; USEPA, 2008). Sulfate concentrations are generally higher in the warm months of the year (May–September). Based on the USEPA (2008) report, the largest sources of sulfate are SO_{2} emissions from electrical utilities and industrial boilers. Marine vessels are a major contributor in Southern California. Concentrations of nitrate are considerably higher in the cool months (October–April) and are lower in the Northeast (1.6 μg/m^3) and the Southeast (0.3 μg/m^3) compared with the Northwest or Southern California (4.0 μg/m^3). The largest sources of nitrates are NO_{x} emissions from highway vehicles, electric utilities, and industrial boilers.

Figures 2, 3, and 4 represent the estimated indirect (i.e., through ammonia) contributions of livestock to PM_{2.5} for various regions in the United States in cool and warm weather conditions (total PM_{2.5} concentrations are based on USEPA, 2008). If ammonia contribution to nitrate formation is estimated on a molar basis (Eq. [1]) and all sulfate particles are as ammonium sulfate (Eq. [3]), the estimated contribution of ammonia emitted from livestock facilities to the total PM_{2.5} concentration ranges from 5.5 (Northwest) to 8.1% (North Central) for cool weather (Figure 2) and from 2.7 (Northwest) to 8.5% (Midwest) for warm weather (Figure 3). If bisulfate is formed (Eq. [4]), the contribution ranges from 3.6 (Southeast) to 6.4% (North Central) and from 1.6 (Northwest) to 5.0% (Midwest), respectively. If all ammonia is converted to nitrate (Eq. [2]) and ammonium sulfate (Eq. [3]; the worst-case scenario), livestock contribution to PM_{2.5} would be significantly greater: from 6.8 (Southeast) to 21.3% (North Central) in cool weather (Figure 4). If ammonia reacts to form nitrate according to Eq. [1] and bisulfate (according to Eq. [4]), livestock contribution to PM_{2.5} would range from 1.6 (Northwest, warm weather) to 19.5% (North Central, cool weather). The effect of using Eq. [1] or [2] on the estimates for the warmer months would be negligible because the nitrate contribution to atmospheric PM_{2.5} in warm weather is zero for most regions (except Southern California; USEPA, 2008). In the cooler months, the formation of ammonium nitrate is favorable, and hence the presence of ammonia can significantly increase PM_{2.5} concentrations. In warm weather, the proportion of PM_{2.5} concentration due to livestock is below 10% for most regions (11.4% for Southern California; nitrate, Eq. [2], sulfate, Eq. [3]).

Overall, this analysis suggests that farm animal contribution to atmospheric PM_{2.5} concentration may be significant in certain areas and climatic conditions (around 20% for the North Central region in cool weather) and reduction of ammonia emissions may
Figure 2. Concentrations of fine particulate matter (PM$_{2.5}$; nitrate, Eq. [1], sulfate, Eq. [3]) for regions in the United States in cool weather conditions (October–April). White bars represent PM$_{2.5}$ attributable to livestock (actual concentrations in μg/m$^3$ shown above the bars); shaded bars represent PM$_{2.5}$ not attributed to livestock.

Figure 3. Concentrations of fine particulate matter (PM$_{2.5}$; nitrate Eq. [1], sulfate Eq. [3]) for regions in the United States in warm weather conditions (May–September). White bars represent PM$_{2.5}$ attributable to livestock (actual concentrations in μg/m$^3$ shown above the bars); shaded bars represent PM$_{2.5}$ not attributed to livestock.
be an effective PM$_{2.5}$ mitigation practice (Pinder et al., 2007; Fann et al., 2009). Across different regions and weather conditions, PM$_{2.5}$ formed from ammonia emitted from livestock operations were estimated to contribute on average from 5 to 9% (using nitrate Eq. [1] or [2], respectively, if ammonium bisulfate is formed) and from 7 to 11% (nitrate Eq. [1] or [2], respectively, if ammonium sulfate is formed) of the total PM$_{2.5}$ concentrations. As direct PM$_{2.5}$ emissions (dust) from farm animals are negligible, the contributions estimated in this analysis would closely represent the total effect of livestock on PM$_{2.5}$ concentrations in the United States. Results of this analysis are consistent with month-long air quality simulations for the Eastern United States (Pinder et al., 2007; Tsimpidi et al., 2007).

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