UV Treatment of Ammonia for Livestock and Poultry Barn Exhaust Applications

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ABSTRACT

The feasibility of using deep UV treatment for abatement of ammonia in livestock and poultry barn exhaust was examined in series of laboratory scale experiments. These experiments simulated moving exhaust air with controlled UV wavelength and dose, NH₃ concentrations, humidity, and presence of H₂S. Ammonia, initially at relevant barn exhaust concentrations in air, is completely, or at least substantially, reduced by irradiation with 185 nm light. Reactions were monitored using chemiluminescence detection, GC-MS, and high resolution FTIR, of which the latter was found to be the most informative and flexible. Detected nitrogen-containing products included N₂O, NH₄NO₃, and HNO₃. It is presumed that atomic oxygen is the primary photochemical product that begins the oxidative cascade. The data show that removal of NH₃ is plausible, but highlights concerns over ozone and N₂O emission.
Introduction

Agricultural ammonia (NH₃) emissions from commercial farms have significantly increased in recent years – animal waste and fertilizers are major sources of ammonia.¹,² The 2002 EPA inventory estimated that agricultural sources contribute approximately 80% of the total ammonia emissions in the U.S.³ Livestock farms were estimated to contribute 10% of NH₃ emissions (ca. 430,000 tons/year). Ammonia, hydrogen sulfide (H₂S), and other odorous compounds volatilized from commercial animal confinements negatively affect the local and regional air quality, create unpleasant conditions for neighbors and people traveling on passing highways. Heightened ammonia levels raise the pH of soil and water and create untenable conditions for fish and plants through eutrophication.¹ Unsurprisingly, ammonia emissions are subject to considerable concern and regulation.

Ammonia is classified as a hazardous substance under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and the Emergency Planning and Community Right-To-Know Act (EPCRA). Production of more than 250 ton/y of any individual pollutant requires that the source obtain a permit. Livestock production facilities exceeding a certain threshold of animals may be required to report NH₃ emissions greater than 100 lbs/day (45.5 kg/day), as required under the CERCLA and the EPCRA.⁴ JK: Please review the previous sentence for accuracy. It was my understanding (after reading several EPA documents which are referenced here) that regulation was only applicable to facilities that exceeded a certain threshold? The US Environmental Protection Agency initiated the Air Compliance Agreement with US livestock industry through the National Air Emissions Monitoring Study (NAEMS) in which emissions from animal feeding operations (AFOs) were monitored over a two-year period that began in 2007.⁵ *** The data collected is being used to develop methodologies to monitor emissions from AFOs, to determine emission limits, and help determine compliance of current regulations. Federal rules and regulations on NH₃ emissions, particularly related to AFOs, are currently being assessed. I’m lost. Why do we have to cite non-relevant NAEMS studies; the only point we're making is that there is regulation? Especially ones that do not appear to be refereed?

Or


I did not have access to the above references, so I did not add them. JK: could you send copies of these to us if you feel that they are relevant?

Ammonia is also considered a secondary precursor to fine particulate matter (PM$_{2.5}$), as it suffers a number of chemical reactions in ambient air that lead to the formation of small particles.$^{2,6}$ The EPA’s final rules do not require that NH$_3$ be regulated as a PM$_{2.5}$ precursor, but a State may choose to regulate ammonia emissions in nonattainment areas if it is proven to be a significant contributor to that area’s fine particulate matter concentrations.$^{7}$ The EPA has elected this case-by-case policy as a result of substantial uncertainties in ammonia emission inventories and the “complex” nature of its involvement in PM$_{2.5}$ formation. Revised this paragraph.

Ammonia emissions from AFOs have been measured in a number of previous studies in the US and Europe.$^{2,8,9}$ While the final estimates of NH$_3$ emissions and emission factor JK: What is an emission factor? Doesn't sound quite right. are being developed, it is clear that larger AFOs will be subject to the mandatory reporting of NH$_3$ emissions (at emissions above 45.5 kg/day). As such, the AFOs are in need of reliable mitigation technologies for NH$_3$ mitigation.

Livestock buildings have been reported to emit [NH$_3$] ranging from 0.2 to 9.2 g/h-AU.$^{2,8-11}$ It should be self-evident that NH$_3$, once produced, does not easily disappear. By ordinary chemical means, the best that can be achieved is to convert it to something less noxious, such as nitrate. Biological fixation to N$_2$ and reduction of its production are probably the only means by which to obtain no or truly benign
byproducts. Clearly, the simplest way to reduce NH$_3$ emissions is to reduce the number of animals, but this seems politically difficult to accept and is generally not discussed.$^{12}$

Other control strategies involve modifications of diet, animal housing, manure storage, and aerobic/anaerobic treatment.$^{13-17}$ Reduced protein feed can be used to optimize animal diets with regard to their amino acids requirements, which minimizes excretion of nitrogenous compounds in waste that are later converted to NH$_3$ by up to 39%.$^{12}$ Changes to building structure or the use of tie-stalls have reduced NH$_3$ volatilization anywhere from 27 to 80%.$^1$ However, tie-stalls bring about concern for animal welfare.$^1,^{12}$ Changes in manure storage and treatment can be very effective, but often are not economical.$^1$

Ultraviolet (UV) irradiation treatment has been very effective and economically practical for reducing odorous emissions in the food processing and recycling industries.$^{18}$ Exhaust is blown through a filter to trap aerosols and particulate matter, then passed through a UV chamber where irradiation with 254 nm light occurs. Using this method, odorous emissions have been reduced by up to 96%.$^{18}$ Therefore, it is practical to consider the use of UV light treatment as an option for the abatement of ammonia and other odorous compounds from commercial swine barns.

In the current work, the chemical fate of ammonia is determined after exposure to UV light (185 nm and 254 nm) in air. For this application, 185 nm light is essential for generation of the reactive species that degrade NH$_3$, as 254 nm light is not significantly absorbed by either ammonia or the major components of air. The concentration of remaining ammonia as well as the identity and quantity of new gases is established. The effects of added water and H$_2$S on ammonia removal and the growth/decay of nitrous oxide (N$_2$O) are studied. The results reported here provide a foundation for the determination of the suitability of UV treatment for ammonia mitigation from commercial swine barn emissions.

**Experimental**

**Materials.** All gas blends were certified within ± 2% accuracy. Air contained 21.5% O$_2$, ≤ 10 ppm CO, ≤ 1000 ppm CO$_2$, and ≤ 24 ppm H$_2$O. Hydrogen sulfide and N$_2$O stock gases were blended with N$_2$
at 15 ppm and 5 ppm, respectively. Ammonia stock gases were 50 ppm in air, 500 ppm in air, and 500 ppm in N₂. Water was purified to a resistivity above 18 MΩ/cm.

**Irradiations.** Photolyses were carried out using a photochemical reactor containing thirteen 185/254 nm low pressure mercury lamps with quartz walls with an output power of approximately 0.02 watts and 8 watts for 185 nm and 254 nm light, respectively.¹⁹ The 185 nm light was attenuated by passage through approximately 25 mm of ambient air before hitting the walls of the quartz reaction coil. Temperatures inside the reactor were kept very near ambient with a fan built into the reactor floor. All analyses were performed downstream from the reactor at room temperature (ca. 293 K) and atmospheric pressure. Gas flow rates were controlled using mass flow controllers. Figure 1 shows the gas delivery/reaction system using quarter-inch (approx 6 mm) O.D. tubing and fittings made of a perfluoroalkoxy (PFA) material. The quartz reaction coil was constructed from a 7.6 m length of 185 nm-transparent quartz tubing with an 8 mm I.D. and 10 mm O.D., which allows for 65% transmission of 185 nm light at 1 mm wall thickness. The total interior volume of the coil exposed to irradiation was 394 mL. The setup is illustrated in Scheme 1.
Scheme 1. Gas delivery and UV treatment system. The water addition segment and the gas sampling bulb were installed when appropriate. \textsuperscript{a}MFC = mass flow controller. \textsuperscript{b}Representation of the reaction coil which is placed inside the Rayonet photochemical reactor. \textsuperscript{c}Contained 200 mL of water. \textsuperscript{d}Used to collect samples for GC-MS analysis. \textsuperscript{e}FTIR or NH\textsubscript{3} chemiluminescence analyzer.

Analysis. Reactions were analyzed by high resolution FTIR, chemiluminescence, or GC-MS. For IR measurements, 16 scans were taken over roughly 30 s while the gas was continuously passed through a 500 mL FTIR gas cell with a path length equal to 7.2 m (15 cm, 48 reflections). The spectrometer was equipped with a DTGS detector and a 12 mm slit width allowing for 1 cm\textsuperscript{-1} resolution. The scanner was constantly purged with N\textsubscript{2} to reduce the background signal from air. The following frequencies were used to monitor and determine concentrations: 967 cm\textsuperscript{-1} for NH\textsubscript{3},\textsuperscript{20} 1,040 cm\textsuperscript{-1} for O\textsubscript{3},\textsuperscript{21} and 2,236 cm\textsuperscript{-1} for N\textsubscript{2}O.\textsuperscript{20} NH\textsubscript{3} (50 ppm) and N\textsubscript{2}O (5 ppm) standards were diluted with air or N\textsubscript{2} respectively and the new concentrations were measured to obtain calibration curves (Figures S1 and S2).

FTIR results for NH\textsubscript{3} at higher flow rates and low concentrations were compared to measurements taken with a digitalized chemiluminescence ammonia analyzer, which could measure a maximum NH\textsubscript{3} concentration of 100 ppm with a minimum flow rate of 600 mL/min.

Analyses by GC-MS were performed using a 25 m CP Volamine column with 0.25 \textmu m I.D. and 5 \textmu m film thickness and a TOF mass spectrometer. The GC temperature program was 40 °C (2 min) ramped at a rate of 20 °C/min to 200 °C (2 min). Accurate mass was collected using 2,4,6-Tris(trifluoromethyl)-1,3,5-triazine as a reference. Quantitative GC-MS calibrations for gas concentrations were not obtained since ammonia quantification was unreliable due to adsorption to the sampling flask walls.

Results

Adsorption of NH\textsubscript{3} to walls. FTIR and chemiluminescence-based measurements of ammonia in dry air demonstrated that there was an initial period of time required to obtain a steady, constant signal from NH\textsubscript{3} under otherwise constant conditions. This was attributed to NH\textsubscript{3} adsorption to surfaces of the
system and depended on both the initial concentration of ammonia ([NH₃]₀). The time required to reach a steady state in the adsorption/desorption equilibrium was particularly long with the IR system – far longer than the hydraulic residence time (HRT) of the gas in the system – typically 30 min for 500 ppm NH₃ and 210 min for 50 ppm NH₃. Nearly 4 h was required to achieve a constant absorption signal for 50 ppm [NH₃]₀ at a flow rate of either 100 or 600 mL/min, which suggested a flow rate independence in the range of concentrations being used. A representative IR response curve for constant [NH₃]₀ with no irradiation is illustrated in the supporting information (Figure S3).

Once a steady state had been established in dark conditions, the lights were turned on and changes were monitored. At a flow rate of 600 mL/min (irradiation HRT 0.67 min), 50 ppm NH₃ was reduced to 25.5 ppm within 15 min, as detected by the chemiluminescence NH₃ analyzer, whereas FTIR showed a 45% reduction of NH₃ after 30 min. (Although the irradiation HRT remains constant at 0.67 min, the total HRT for the path of the gas to the IR detector is longer by approximately 1.5 min, due to the 500 mL gas capacity of the cell. There it is to be expected that the response times of the two measurements would differ somewhat. However, the ultimate reduction percentages obtained by FTIR (45%) and chemiluminescence techniques (51%) are well within 10% of each other. This control clearly established that the variation in the length of time required to reach a steady state during the photolysis is likely an artifact of the difference in surface area to which ammonia adsorbs. In all cases, the observed time required to reach a steady state for [NH₃] as detected by IR is limited by gas adsorption/desorption from the walls and does not directly measure the reaction kinetics or the actual HRT in the reactor coil. The latter are undoubtedly faster than the effective response time of the instrument. However, percent conversion and products could be determined and results acquired using the same analysis system can be compared.

**Flow rate comparison.** On a percentage basis, ammonia was removed to a greater degree when either the rate of flow was slowed or the initial concentration was lowered. For an [NH₃]₀ of 500 ppm, with a flow rate of 100 mL/min (4 min irradiation HRT), FTIR showed that over 80% of the ammonia was removed, i.e., the measured concentration at output was under 100 ppm. If the [NH₃]₀ was 50 ppm
in dry air and the flow rate remained the same, then no ammonia could be detected at the output after achieving steady state. Products, of course, varied in quantity between these two runs, but their identities remained the same. Unless otherwise noted, all further experiments were carried out at 100 mL/min flow rate, giving the 4 min HRT with out setup.

To verify that 185 nm light is necessary for ammonia abatement, NH$_3$ in air was photolyzed with standard low-pressure mercury bulbs (254 nm with 185 nm filtered out). Only a 3% reduction of NH$_3$ was observed, monitoring the absorption at 967 cm$^{-1}$ in the FTIR spectrum. These results are compiled in Table 1.

**Table 1.** Percent of ammonia removed under varied flow rates, NH$_3$ starting concentration, and excitation wavelengths.$^a$

<table>
<thead>
<tr>
<th>$[\text{NH}_3]_0$ (ppm)</th>
<th>Wavelength (nm)</th>
<th>Flow rate (mL/min)</th>
<th>HRT (min)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>185 + 254</td>
<td>600</td>
<td>0.66</td>
<td>45</td>
</tr>
<tr>
<td>500</td>
<td>185 + 254</td>
<td>600</td>
<td>0.66</td>
<td>10</td>
</tr>
<tr>
<td>50</td>
<td>185 + 254</td>
<td>300</td>
<td>1.31</td>
<td>76</td>
</tr>
<tr>
<td>500</td>
<td>185 + 254</td>
<td>300</td>
<td>1.31</td>
<td>25</td>
</tr>
<tr>
<td>50</td>
<td>185 + 254</td>
<td>100</td>
<td>3.94</td>
<td>100$^b$</td>
</tr>
<tr>
<td>500</td>
<td>185 + 254</td>
<td>100</td>
<td>3.94</td>
<td>83</td>
</tr>
<tr>
<td>500</td>
<td>254</td>
<td>100</td>
<td>3.94</td>
<td>3</td>
</tr>
</tbody>
</table>

$^a$ Irradiation chamber volume was 394 mL. Thirteen lamps, supplying 8 W 254 nm and 0.02 W 185 nm each, were used. $^b$Minimum detection limit (MDL) of ca. 1 ppm.

**Analysis of UV photolysis of NH$_3$ in dry air by GC-MS.** Samples from the photolysis of 50 ppm NH$_3$ in air were not easily analyzed by GC-MS due to limits in sensitivity. Subsequent studies using this method were done using $[\text{NH}_3]_0 = 500$ ppm in air for this reason. In addition, a higher $[\text{NH}_3]_0$ led to a larger accumulation of photodegradation products, allowing for both FTIR and GC-MS to be used for structural identification. Product identities by GC-MS are shown in Table 2. Entries 1-3 and 5 were
observed in the unphotolyzed sample, as expected. After irradiation, N₂O (entry 4) was the major product, although it overlapped with the NH₃ peak in the chromatogram. The abundance of N₂O was large enough to obtain an accurate mass (m/z = 44.0018 observed vs. 44.0011 calculated), confirming the identity. Molecular ion peaks for NO, NO₂, HONO, HNO₃, and H₄N₂ were not observed, even when a single ion search was done. Ozone, shown to be a major component by IR, was not detected by the GC-MS method.

**Table 2.** Identification of components by GC-MS present after 185/254 nm photolysis of 500 ppm NH₃ after 30 min of flow at 100 mL/min.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Retention Time (min)</th>
<th>Observed Mass (M⁺, m/z)</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.32</td>
<td>28.4045, 32.4056, 39.9686</td>
<td>Air (N₂, O₂, Ar)</td>
</tr>
<tr>
<td>2</td>
<td>1.43</td>
<td>43.9944</td>
<td>CO₂</td>
</tr>
<tr>
<td>3</td>
<td>1.53ᵃ</td>
<td>17.0284</td>
<td>NH₃</td>
</tr>
<tr>
<td>4</td>
<td>1.53ᵃ</td>
<td>44.0018</td>
<td>N₂O</td>
</tr>
<tr>
<td>5</td>
<td>1.88</td>
<td>18.3038</td>
<td>H₂O</td>
</tr>
</tbody>
</table>

ᵃPeaks overlap in GC trace, but were resolved by single ion chromatograms.

**High resolution FTIR analysis of NH₃ photolysis in dry air.** FTIR spectral changes were monitored over the course of the photolysis of 200 ppm NH₃ in air (Figure 1). The appearance of several new peaks accompanied the loss of NH₃ absorptions. Most of the new spectral features could be assigned to two major components. Absorptions around 2130, 1057, 1044, and 1030 cm⁻¹ were assigned to O₃.²¹ Bands at 3494, 2580, 2236, 2178, 1299, and 1258 cm⁻¹ were attributed to N₂O.²⁰ No major changes occurred in the 1500 to 2000 cm⁻¹ range that indicated the presence of NOₓ compounds (NO, NO₂/N₂O₄). The broad bands at 3228, 3067, 2882, 1428, and 1367 cm⁻¹ slowly grew in and were assigned to the presence of NH₄NO₃, which, of course, precipitates out under these conditions.²²,²³
After ending the photolysis and purging the system with dry N₂, a spectrum of the purged cell was acquired. The FTIR spectrum revealed that the latter features remain after purging and exposed weaker absorptions at 1051, 1045, and 832 cm⁻¹ (Figure 2). The frequencies reported here are all within expected ranges for various polymorphs of crystalline NH₄NO₃ films and aerosols.²²,²³

**Figure 1.** FTIR spectra of (a) 500 ppm [NH₃]₀ in air purged in the dark and (b) after 185 nm irradiation 200 ppm [NH₃]₀ in air at 100 mL/min (HRT = 3.9 min). The sample shown in (b) was diluted to 200 ppm [NH₃]₀ by addition of dry air that contained more CO₂ than the original 500 ppm [NH₃]₀ in air stock gas. The data in (b) were offset by 1.0 absorbance unit.
Figure 2. Spectrum obtained from static residue remaining in the IR gas cell under N₂ after the photolysis of 200 ppm NH₃ in air.

Figure 3. Extended 185/254 nm photolysis of 20 ppm [NH₃]₀ in dry air at 100 mL/min (Photolysis HRT = 3.9 min).

The observed steady state product distributions depended on [NH₃]₀, although the final O₃ concentration was not especially sensitive to [NH₃]₀. The absorbance shown in Figure 3 is typical and did not vary more than about ± 10% across all the irradiations using dry air.

N₂O. Nitrous oxide was also observed at appreciable concentrations as a product of photolysis. Figure 4 illustrates the interesting result that N₂O formation was enhanced with increasing [NH₃]₀. With [NH₃]₀ < 100 ppm, N₂O formation exhibited an initial growth period followed by a decay to a lower steady state concentration. It is not clear whether this non-monotonic growth is "real" or entirely attributable to absorption/desorption artifacts. With [NH₃]₀ > 100 ppm, the N₂O reached a steady state at the maximum observed concentration.
Figure 4. Photolysis (185/254 nm) of NH₃ in dry air. Solid lines represent the loss of NH₃. Dotted lines show the generation of N₂O.

**HNO₃ and NH₄NO₃.** After ammonia was no longer observed in the IR when low starting concentrations were used, a peak displaying a very distinctive Q-branch appeared at 1325 cm⁻¹ in addition to broad bands at 1710 and 895 cm⁻¹ indicated the presence of HNO₃ (Figure 3). At these low initial NH₃ concentrations, ammonium nitrate was not generally a significant feature in the IR spectrum until the lights were turned off and NH₃ was reintroduced to the system. At higher [NH₃]₀, where ammonia survived into the analysis chamber, the abundance of HNO₃ was low to undetectable, in favor of NH₄NO₃. (It is expected that the minimum detection limit of nitric acid would be comparable to that of ammonia, but without nitric acid standards, it was not rigorously determined.)

**High resolution FTIR analysis of NH₃ photolysis in the presence of H₂S.** Hydrogen sulfide is also commonly found in livestock farm emissions. H₂S is a concern because of its unpleasant characteristic “rotten egg” odor and potential human health hazards.¹ Reports on typical H₂S emissions vary greatly from 0 to 3,400 ppb.¹ JK to add refs. For purposes of reaching potential applications, it is desirable to determine whether NH₃ mitigation through UV treatment is affected by the presence of H₂S. The effect of H₂S on O₃ and N₂O (also objectionable gases to emit) was also a point of interest.
Experiments in which H$_2$S and N$_2$ were introduced into the gas mixture (Scheme 1, Gas B and Gas C) were conducted. These were conducted in such a way that the O$_2$ concentration was constant throughout the series, although it was lower than normal air, at about 8.6% instead of 21.5%; the sum of flow of a pure N$_2$ source and the H$_2$S source (in N$_2$) was kept constant. The [NH$_3$]$_0$ was kept constant at 20 ppm.

Figure 5 shows that the 185 nm photolysis of 20 ppm NH$_3$ in the presence of 9 ppm H$_2$S in this hypoxic "air" gave qualitatively similar product distributions to those observed during irradiations of low concentration ammonia in ordinary air. The FTIR spectrum taken early in the photolysis (Figure 5a) shows that N$_2$O was the dominant product. However, after the observed NH$_3$ concentration fell below a detectable limit (ca. 1 ppm) for an extended period, the spectral features of HNO$_3$ grew in and the N$_2$O absorptions were reduced (Figure 5b). This is a natural consequence of there being no NH$_3$ for nitric acid to protonate. However, once the lights have been turned off, and the presence of ammonia was restored, features attributable to ammonium nitrate became apparent (Figure 5c).

Figure 5. Comparison of FTIR spectra taken of the 185/254 nm photolysis of 20 ppm [NH$_3$]$_0$ flowing at 100 mL/min in hypoxic air (8.6% O$_2$) with 9 ppm H$_2$S after (a) 15 min and (b) 210 min of irradiation, and (c) extended photolysis, followed by 30 min continued flow in the dark.
Varying the concentration of H2S showed that hydrogen sulfide had little effect on the observed rate of loss of ammonia (Figure 6). However, the length of time required for NH3 to be undetectable by FTIR in the full set of H2S experiments was longer than the photolysis in dry air, which is almost certainly a result of the lower O2 concentrations in NH3/H2S gas mixtures used. This conclusion is buttressed by photolysis of NH3 in air diluted solely with N2 (0 ppm H2S in Figure 6) without any H2S added.

**Figure 6.** Photolysis (185/254 nm) of 20 ppm [NH3]0 in air in the presence of varied H2S concentrations in N2 balance flowed at 100 mL/min (HRT = 3.94 min). Solid lines represent the loss of NH3. Dotted lines represent generation of N2O.

The results suggest that H2S does have a moderate effect on N2O formation or consumption in the presence of ammonia, where steady state N2O concentrations are lower at higher levels of H2S. There does appear to be a saturation point for this effect, though, as indicated by the results for 6 ppm and 9 ppm H2S. Nitrous oxide concentrations were reduced by more than half in the presence of these higher concentrations of H2S. Figure 7 also shows that, in the absence of ammonia altogether, the formation of N2O was suppressed even more greatly by 9 ppm H2S. The maximum is earlier, and about 7 times lower, and the steady state concentration of N2O is nearly zero. Table 3 provides a summary of the effects of H2S and H2O (discussed in the next section) addition.
Table 3. Qualitative summary of the effects of gas composition changes observed by FTIR.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Additive to NH$_3$</th>
<th>N$_2$O Effect</th>
<th>O$_3$\textsuperscript{b}</th>
<th>NH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$S, 3 ppm</td>
<td>Slightly reduced (\textit{ca. 15%c})</td>
<td>Not significant</td>
<td>Not significant</td>
</tr>
<tr>
<td>H$_2$S, $\geq$ 6 ppm</td>
<td>Appreciably reduced (\textit{ca. 50%c})</td>
<td>Not significant</td>
<td>Not significant</td>
</tr>
<tr>
<td>H$_2$O\textsuperscript{d}</td>
<td>Significantly reduced (\textit{ca. 80%c})</td>
<td>Significantly lower (\textit{ca. 80 to 90%})</td>
<td>Incomplete removal\textsuperscript{e}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Initial NH$_3$ concentration was 20 ppm for all reactions. \textsuperscript{b}Ozone measured by absorbance. \textsuperscript{c}Approximate percent reduction. \textsuperscript{d}Nearly identical results for 36\% relative humidity (8400 ppm, 0.84\%) and 58\% relative humidity (13,600 ppm, 1.36\%). \textsuperscript{e}Ammonia displacement from walls was likely to contribute to this observation. See text for details.

**High resolution FTIR analysis of NH$_3$ photolysis in humid air.** It is well known that NH$_3$ emission levels vary greatly by season.\textsuperscript{1} Changes in temperature and humidity likely contribute to this.\textsuperscript{1} Therefore, attempts were made to investigate the effect(s) of moisture. Higher concentrations of H$_2$O greatly affected the apparent abatement of ammonia. In the presence of water (Figure 6), a steady state of [NH$_3$] was not achieved after 5 h of monitoring. This was probably a consequence of more complex adsorption/desorption equilibria, as well as partial solvation of ammonia by water, and the attendant acid/base chemistry, but the current data do not give a complete explanation.

An attempt was made to find out with experiments of manageable length whether ammonia remained at the end of a reasonable time period of photolysis. This was done by filling the IR detector with N$_2$ and disconnecting it from the system. Photolysis was conducted in the ordinary fashion for either 5 min or 135 min before reconnecting to the IR cell. By this method, if NH$_3$ remained after exposure to UV
light, it would be forced to "grow in" rather than "grow out", and a greater confidence that such a positive NH₃ signal would be obtained.

Ammonia was detected when the gas mixture (of either 36% or 58% rel. humidity) was photolyzed for 5 or 135 minutes before connecting to the N₂-filled FTIR gas cell. However, a steady state was not obtained, but rather an initial rise in NH₃ absorption, followed by a slow, steady drop occurred. This result implies that the survival of ammonia is "real", but that the final, steady state value is again dependent on complex equilibria involving water and NH₃, including interactions within the detection cell.

The effect of water on other gases was easier to quantify. As shown in Figure 8, the steady state [N₂O] is significantly lower with water in the air. Nitrous oxide was found to reach a steady state of 3-4 ppm in the presence of water and 6-7 ppm in the absence of water. Ozone levels were also dramatically affected. The maximum IR absorbance obtained for ozone when water vapors were present were only 10-20% of those obtained for dry samples.

![Figure 8](image)

**Figure 8.** Effect of humidity on the 185/254 nm photolysis of 20 ppm [NH₃]₀ in air at 100 mL/min. aAt higher concentrations of moisture, the NH₃ calibration was often skewed. In this case, the data were normalized to 20 ppm NH₃.
Discussion

Considerable effort has long gone into understanding atmospheric chemistry and photochemistry. The application we consider here is simply a very special case of that broader effort. As a result, in this discussion, we are able to take advantage of considerable known data about reactions and rate constants that may be relevant to the abatement of ammonia via photochemical means. The interpretation is necessarily somewhat speculative, but considering known chemistry and rate constants can support or rule out certain possible pathways that could not be directly observed in this study.

The primary photochemical events. Under dry air conditions used this research, N₂ was the most abundant component at a concentration of approximately 780,000 ppm, followed by O₂ with a concentration of almost 215,000 ppm. Carbon dioxide and water were present at levels of ≤ 1000 ppm and ≤ 24 ppm, respectively. Added ammonia ranged from 10 - 500 ppm, depending on the dilution and gas standard used. Under these conditions, the vast majority of 185 nm photons are absorbed by O₂, rather than any of the other components of the mixture, and it is thus the photochemistry of molecular oxygen that begins the reactive cascade. (The absorption cross sections for the two gases are given in the supporting information.)

Upon 185 nm excitation, cleavage of O₂ occurs yielding two ground state oxygen atoms, O(^3P) (eq 1). Combination O(^3P) with ubiquitous O₂ to generates (eq 2). In a process commonly referred to as the Chapman cycle, however, O₃ also serves as a source of oxygen atoms: photolysis of ozone with either 185 or the more abundant 254 nm light produces O₂ and atomic oxygen in its first excited state, O(^1D) (eq 3). The quantum yield for the photochemical dissociation of ozone is near unity.

\[
O_2 + h\nu \rightarrow O(^3P) + O(^3P) \quad (1)
\]

\[
O(^3P) + O_2 + M \rightarrow O_3 + M \quad k = 6.0 \times 10^{-34} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1} \quad (2)
\]

\[
O_3 + h\nu \rightarrow O_2 + O(^1D) \quad (3)
\]

*Rate constant at the low pressure limit.*
Using an estimate of $2.5 \times 10^{19}$ molecules cm$^{-3}$ at 300 K, the pseudo-second order rate constant for reaction in eq 2 is $1.5 \times 10^{14}$ cm$^3$ molecules$^{-1}$ s$^{-1}$. Evaluating the rate constant for direction reaction between O($^3P$) and NH$_3$ (eq 12) at 300 K gives $4.6 \times 10^{-17}$ cm$^3$ molecules$^{-1}$ s$^{-1}$. Thus, also given the overwhelmingly large pool of O$_2$ relative to NH$_3$, it is safe to conclude that only a vanishingly small fraction of O($^3P$) reacts directly with NH$_3$. Instead, most of it participates in the ordinary Chapman cycle, combining with molecular oxygen to produce ozone. Ozone can then absorb light at *either 185 or the much more abundant 254 nm wavelength* to produce O$_2$ and the first excited state of atomic oxygen, O($^1D$). (This conclusion does not necessarily imply, however, that the small fraction of O($^3P$) that does react with ammonia is not significant to ammonia consumption.)

**Relevant reactions of O($^1D$).** Reactions involving O($^1D$) are very important in atmospheric chemistry, and this almost certainly holds true here. While much of the O($^1D$) is collisionally quenched to O($^3P$) (eq 4), it also suffers very rapid reactions with water, N$_2$O, and NH$_3$ (eqs 5, 6, and 11). Although under "dry" conditions ($\leq 24$ ppm in the stock gas supplied here), the great majority of O($^1D$) is quenched to O($^3P$), the Chapman cycle ensures that that it is continuously produced, so the reactions with low concentration components (e.g., H$_2$O, N$_2$O, NH$_3$, H$_2$S, and VOCs) remains important to their chemistry.

The reaction of O($^1D$) with H$_2$O produces 2 HO with a second order rate constant of $2.2 \times 10^{-10}$ cm$^3$ molecules$^{-1}$ s$^{-1}$. The stock "dry" air may contain enough H$_2$O ($\leq 24$ ppm) for this to be significant in competition with direct reaction with NH$_3$, at least at lower $[\text{NH}_3]_0$ and in the absence of significant humidity. HO, however, is also a critical oxidative species.

\[
\begin{align*}
\text{O}^1D + M & \rightarrow \text{O}^3P + M & k = \sim 3 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
\text{O}^1D + \text{H}_2\text{O} & \rightarrow \text{HO} + \text{HO} & k = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
\text{O}^1D + \text{N}_2\text{O} & \rightarrow \text{NO} + \text{NO} & k = 6.7 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
 & \rightarrow \text{N}_2 + \text{O}_2 & k = 4.9 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}
\end{align*}
\]
**N₂O formation and removal.** Peak N₂O concentrations reported here range up to almost 20 ppm, but were lower with the addition of water or H₂S. The detailed mechanism of the formation of N₂O through the photolysis of air is still under debate.²⁸⁻³¹ It has been proposed that N₂O is formed through either an association reaction between N₂ and O(¹D) (eq 7) or through the reaction of an undissociated electronically excited state of O₃ with N₂ (eq 8). While the pseudo-second order rate constant estimated for eq 7 is small, the huge concentration of N₂ may make up for this compared to other molecules that are 3 to 5 orders of magnitude less prevalent. The unknown rate constant for interaction of excited (pre-dissociated) ozone with N₂ means we cannot speculate much further.

\[
\text{O}(¹\text{D}) + \text{N}_2 \xrightarrow{M} \text{N}_2\text{O} \quad k = 7.8 \times 10^{-17} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \quad (7)
\]

\[
\text{O}_3^* + \text{N}_2 \rightarrow \text{N}_2\text{O} + \text{O}_2 \quad k = ? \quad (8)
\]

N₂O reacts with O(¹D) and can follow two possible pathways. The major reaction (eq 6a) yields 2 NO (60%), while the minor pathway regenerates O₂ and N₂ (eq 6b).²⁵,²⁸ Our results also demonstrated a significant increase in N₂O concentration with NH₃ present. Possible pathways to yield nitrous oxide from ammonia are discussed below in the next section. Lastly, while N₂O is also destroyed under 185/254 nm irradiation, much as O₃ is, a control photolysis of 5 ppm N₂O in N₂ exhibited no net loss, which indicates a reformation reaction analogous to the Chapman cycle is operative.²⁶

**Ammonia degradation.** Several pathways for the oxidative removal of NH₃ are feasible. Given a survey of the available literature, the first step almost certainly involves generation of the amino radical, NH₂. Four pathways are envisioned, some more important than others. Direct photolysis of ammonia (eq 9) appears negligible, given the high concentration of O₂. A second possibility, as shown in eq 10, is the reaction of NH₃ with hydroxyl radical (eq 5).²⁵,³² Although the rate constant is slower for other processes, the concentration of hydroxyl radical is not known, relative to other active oxygen species. (At high water concentrations, this route may be more significant, *vide infra.*) The reaction between
NH$_3$ and O($^1$D) (eq 11) is a probable route under dry conditions, particularly for high [NH$_3$]. As noted previously, the direct reaction between O($^3$P) and NH$_3$ seems very unlikely to be important.$^{34,35}$

\[
\begin{align*}
\text{NH}_3 + \text{hv} &\rightarrow \text{NH}_2 + \text{H} & (9) \\
\text{NH}_3 + \text{HO} &\rightarrow \text{NH}_2 + \text{H}_2\text{O} & k = 1.6 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} & (10) \\
\text{NH}_3 + \text{O}($^1$D) &\rightarrow \text{NH}_2 + \text{HO} & k = 2.5 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} & (11) \\
\text{NH}_3 + \text{O}($^3$P) &\rightarrow \text{NH}_2 + \text{HO} & k(T) = (1.8 \times 10^{-18})T^{2.1}\exp(-2620/T) \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} & (12)
\end{align*}
\]

On the other hand, if the reaction between NH$_3$ and HO (eq 10) is a major process, the addition of water to the photolysis would, intuitively, be expected to enhance the degradation of NH$_3$. This was not observed. While it is tempting to suggest that this implies that reaction with O($^1$D) is the major initiating pathway, the water addition experiments (vide infra) also make it clear that this is not the exclusive channel, either.

**Reactions of downstream nitrogen-containing intermediates.** The only nitrogen-containing downstream compounds detected were HNO$_3$ and NH$_4$NO$_3$ (in addition to N$_2$O). No hydrazine, which could be formed by dimerization of NH$_2$, was observed. The FTIR spectrum of hydrazine is strikingly similar to that of NH$_3$, but some frequencies are shifted by more than 2 cm$^{-1}$ and would have been detected. It is more likely that the amino radical will be oxidized, eventually yielding NO. (We assume NO would rapidly be oxidized further and not accumulate.) Again, the detailed pathways remain a matter of some debate in the literature, and the current experiments do not shed further light on those matters.$^{24-26,32,36}$ Nonetheless, a quick walk-through is merited for this discussion.

The initial step involves the reaction of NH$_2$ with either O$_2$, O$_3$, HO$_2$, or O($^3$P). Although the reaction with O$_2$ is intuitively satisfying because of the latter's high concentration, the rate constant is very low (eq 13), and this reaction is not considered important.$^{32}$ Under less pristine conditions, formation of NH$_2$O through reaction of NH$_3$ with HOO or O$_3$ (eqs 14 and 15).$^{26,36}$ (In dry air photolysis, O$_3$ would seem rather more abundant.) NH$_2$O would likely collide with O$_2$ very rapidly, forming HNO and the
peroxy radical (eq 16). Equation 15b shows an alternative outcome for the reaction of NH$_2$ with HO$_2$ producing HNO and H$_2$O, which is argued to be dominant product outcome.$^{32,36}$ The collision of NH$_2$ with O($^{3}$P) can lead to three possible product outcomes (eq 17a-c), but eq 17b is the major reaction pathway, again favoring the production of HNO.$^{26,36,37}$

\[
\begin{align*}
\text{NH}_2 + \text{O}_2 & \rightarrow \text{NH}_2\text{OO} & k = <6 \times 10^{-21} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
\text{NH}_2 + \text{O}_3 & \rightarrow \text{NH}_2\text{O} + \text{O}_2 & k = 1.9 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
\text{NH}_2 + \text{HO}_2 & \rightarrow \text{NH}_2\text{O} + \text{HO} & k = ? \\
& \rightarrow \text{HNO} + \text{H}_2\text{O} & k = 7 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
\text{NH}_2\text{O} + \text{O}_2 & \rightarrow \text{HNO} + \text{HO}_2 & k = 1 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
\text{NH}_2 + \text{O}^3\text{P} & \rightarrow \text{products} & k = (9 - 15) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
& 5-13\% \rightarrow \text{NH} + \text{OH} & (17a) \\
& 87\% \rightarrow \text{HNO} + \text{H} & (17b) \\
& \text{minor} \rightarrow \text{NO} + \text{H}_2 & (17c)
\end{align*}
\]

Regardless of the details, nitrosyl hydride (HNO) is almost certainly formed during the oxidation of ammonia.$^{37}$ Several steps are required to go from here to HNO$_3$ through the NO$_x$ compounds, and the major possibilities$^{25,32,36-38}$ are given in eqs 18-25. (Notably, O($^{3}$P) is thought to play a role here.$^{25}$) None of these compounds accumulated enough to be observed by IR at steady state concentrations until the formation of nitric acid.

\[
\begin{align*}
\text{HNO} + \text{HNO} & \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} & k = 4 \times 10^{-15} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
\text{HNO} + \text{hv} & \rightarrow \text{NO} + \text{H} & (19) \\
\text{HNO} + \text{O}^3\text{P} & \rightarrow \text{NO} + \text{HO} & k = 3.8 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
\text{NO} + \text{O}^3\text{P} & \rightarrow \text{NO}_2 & k = 3 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
\text{NO}_2 + \text{O}^3\text{P} & \rightarrow \text{NO}_3 & k = 2.2 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
\text{NO}_2 + \text{NH}_2 & \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} & k = 1.9 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
\text{NO}_2 + \text{NO}_3 & \rightarrow \text{N}_2\text{O}_5 & k = 1.4 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
\text{NO}_2 + \text{HO} & \rightarrow \text{HNO}_3 & k = 2.5 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
\end{align*}
\]
At low enough [NH₃], HNO₃ was the major form of nitrate observed. However, as [NH₃] was increased, NH₄NO₃ became the major product. When the atmosphere is saturated with ammonium nitrate, a fraction is transferred to the aerosol phase, which was observed as a thin film on the mirrors and windows of the IR cell that eventually formed during the photolysis of higher NH₃ concentrations (> 200 ppm).²⁵ A white residue could also be seen on parts of the quartz reaction coil near the outlet in these reactions.

\[ \text{NH}_3 + \text{HNO}_3 \rightleftharpoons \text{NH}_4\text{NO}_3 \]  

(26)

**Effects of water vapor.** Compared to "dry air", introduction of humidity may be the greatest perturbation, compared to addition of other components of livestock barn air such as VOCs.³⁹ Although water is often thought of as benign, it is present at high concentration and reacts with at least one of the key intermediates in this chemistry. Fully humid (100% relative humidity) air at 1 atm and 25 °C contains slightly over 3% water, i.e., > 30,000 ppm. Even very dry air (10% RH) would have > 3000 ppm water, two orders of magnitude greater than most realistic ammonia concentrations in barn air.

Although, even at these high concentrations, most of the O(¹D) is deactivated to O(³P), the fraction of O(¹D) that reacts chemically is diverted strongly toward water (to produce HO), going from "dry" to moist air, and thus away from reaction with NH₃ or N₂. The qualitative observations reported Table 3 are that addition of water during photolysis reduces steady state concentrations of N₂O and O₃, and that the steady state concentration of ammonia goes up. Although we do not report proper simulations with all the reactions discussed here, surely the increase of water from ~20 ppm to thousands of ppm will reduce the rate of formation of ozone and N₂O by providing this additional channel of O(¹D) consumption. Similarly, a reduction in the initiation of ammonia consumption by reaction shown in eq 11 is expected. Finally, a qualitative reduction in O₃ is expected if hydroxyl radical is produced, due to its reaction to form hydroperoxyl radical and molecular oxygen, eq 27. Indeed, a reduction of O₃ levels was observed.
However, the additional hydroxyl radical formed by O(\textsuperscript{1}D) reacting with water is apparently not enough to compensate for the lost direct reaction of O(\textsuperscript{1}D) with NH\textsubscript{3}. Although final steady state levels of ammonia were not obtained in all cases in the reported experiments, it is clear that the addition of water reduced the amount of NH\textsubscript{3} removal in a qualitative sense.

**Effects of H\textsubscript{2}S.** In the presence of H\textsubscript{2}S added to dry air, NH\textsubscript{3} was still successfully removed, at least reduced to levels undetectable by FTIR. Although hydrogen sulfide is a very reactive species (generally much more so than water), its effect on ammonia abatement is much smaller simply because so much less of it is added than with water (Figure 6). It is also worth noting again that the percentage of O\textsubscript{2} in the total atmosphere of these experiments was lower by 60\% than normal because the H\textsubscript{2}S standard was in N\textsubscript{2}, and all experiments regarding H\textsubscript{2}S were kept with this same quantity of O\textsubscript{2}. Of course, H\textsubscript{2}S itself is a gas that is a target for abatement in barn exhaust. H\textsubscript{2}S could be removed through similar oxidation pathways to NH\textsubscript{3} (eqs 28 – 30) except the reaction with O(\textsuperscript{3}P) and HO should be faster.\textsuperscript{26,33} In more general atmospheric chemistry, it is accepted that the major pathway for H-abstraction from H\textsubscript{2}S occurs through the reaction with HO (eq 28).\textsuperscript{24,26} The reaction rate of H\textsubscript{2}S with O(\textsuperscript{1}D) is not reported in most literature sources, so this pathway cannot be ruled out (eq 30).

\[
\begin{align*}
\text{H}_2\text{S} + \text{HO} & \rightarrow \text{HS} + \text{H}_2\text{O} & k = 4.8 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{s}^{-1} \\
\text{H}_2\text{S} + \text{O(}^3\text{P}) & \rightarrow \text{HS} + \text{HO} & k = 2.2 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{s}^{-1} \\
\text{H}_2\text{S} + \text{O(}^1\text{D}) & \rightarrow \text{HS} + \text{HO} & k = ? \\
\end{align*}
\] (28)

It is both notable and very important that N\textsubscript{2}O emissions are reduced by the presence of H\textsubscript{2}S (although, again, the O\textsubscript{2} concentration also changed). N\textsubscript{2}O is a known sink for NO\textsubscript{2}, as discussed
earlier. However, in the presence of HS, NO₂ is rapidly consumed at a greater rate than competitive pathways for its conversion to N₂O (eq 31). Since nitrous oxide is a known oxidant, it is also possible that nitrous oxide directly reacts with H₂S, but there is little literature available on this reaction.

$$\text{HS} + \text{NO}_2 \rightarrow \text{HSO} + \text{NO} \quad k = 5.8 \times 10^{-11} \text{ cm}^3 \text{molecules}^{-1} \text{s}^{-1} \quad (31)$$

Regardless of the details, however important they may be, it cannot escape mention that a significant potential limitation to the photochemical abatement of ammonia could result from regulation of N₂O and/or ozone emissions. The results reported here, however are tantalizing in their suggestion that the additional VOC (and, potentially, dust) pollutants would act as an internal "scrubber" for N₂O and ozone. Of course, such reactions would serve to oxidize the other pollutants as well. We are confident that various parameters, such as the 185/254 nm ratio, light intensity, flow rate, and potential diversion of the natural dust in real systems would allow for certain ranges of ozone or N₂O emissions to be achieved; we also believe such engineering-scale experiments will require pilot scale testing over the laboratory synthetic air experiments we report here. What do you think of this paragraph I added?

**Conclusions and implications**

Abatement of small molecule contaminants that exist in livestock barn exhaust but do not themselves absorb direct irradiation at 254 nm can be brought about by indirect photochemistry initiated by absorption of 185 nm light, mainly by atmospheric oxygen. Formation of atomic oxygen follows, and in the absence of other "contaminants", atomic oxygen reacts with the species in air to form ozone, N₂O, and (when water is present) hydroxyl radical, HO. Hydroxyl radical and reactions of atomic oxygen are, presumably, the major agents involved in the oxidation of NH₃, H₂S, and similar species. In laboratory conditions, the complete removal (> 99%) of 50-10 ppm ammonia was obtained in the absence of significant concentrations of water. With 58% relative humidity, the ammonia abatement was less significant with only ca. 25% removal for 20 ppm [NH₃]₀.
The hydraulic residence times of this very inefficient irradiation system, of the order of a few minutes, suggest that the much more efficient irradiations that could be obtained by direct exposure of exhaust airs with turbulent air flow to high-flux lamps might be brought down to more practical HRTs of the order of seconds with proper design and lamp intensity.

FTIR spectra revealed spectral features consistent with HNO₃, NH₄NO₃, N₂O, and ozone as the major downstream photolysis products. Under the current reaction conditions, NH₃ degradation likely begins with the reaction of O¹D to generate the NH₂ radical, putting the nitrogen into the manifold of reactive species that will oxidize further. Once NO is generated, the products observed in the FTIR spectrum, N₂O, NH₄NO₃, and HNO₃, are readily formed. Nitrous oxide is a greenhouse gas whose formation will be at least as important as ozone to consider in further development of this technology.⁴⁰

When H₂S was present in the reaction mixture, N₂O formation was reduced. It is possible (we believe likely) that in the presence of other components found in swine farm exhaust, such as other VOCs, the generation of nitrous oxide could be further reduced and the steady state concentration of ozone is likely to be lower, due to the consumption of atomic oxygen by the other oxidizable species. Elimination of water from barn air is thoroughly impractical, so the somewhat lower efficiency of ammonia abatement in humid air is a factor that will have to be dealt with in further studies. We speculate that the effect of VOCs, present in much smaller concentrations, on ammonia treatment will be much smaller than that of water, but experiments are required to verify this. Particulate matter in the barn air is also a concern due to its light scattering effects, but would also consume some of the undesirable ozone and possibly N₂O. Ammonium nitrate could be removed mechanically along with other particulate matter, as needed.

The current experiments surely demonstrate that the photolysis method of ammonia abatement is viable at the level of proof of principle, but more realistic models would be required to see how well the higher energy input and the shorter HRTs of barn exhaust manifolds could be implemented.
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