

Title: Mitigation of ammonia from swine barns through UV treatment of exhaust air **NPB #08-117**

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Industry Summary:

The use of deep UV light was investigated for the purpose of reducing ammonia from barn exhaust. The objectives of the study included (1) determining the amount of 254 and/or 185 nm light required to remove standard fractions of ammonia from model barn air, (2) examining the feasibility of providing this dosage in a realistic treatment time consistent with air turnover in barn exhaust conditions, (3) determining the chemical fate of the ammonia, (4) understand the significance of reasonable variables, such as humidity and presence of VOCs.

The research was conducted by using a gas flow system that ran quartz-tube coil through a laboratory scale lamp setup that could irradiate the gas flowing through the tube with either 254 nm or a combination of mainly 254 light along with some 185 nm light. (They are generated in tandem by use of certain relatively inexpensive lamps.) At the exit port of the quartz coil, several analytical methods were used. A direct ammonia analyzer was used, as were mass spectrometry and infrared spectroscopy. Of these, the latter was the most sensitive, and also provided the most information on the fate of the ammonia.

Irradiation with 254 nm light has previously been shown to mitigate certain VOCs, but it was found that it has little or no effect on the concentration of ammonia in air. By adding the 185 nm light, an entirely new oxidation mechanism is introduced, in which the air itself becomes the "fuel". Initial experiments in this study used "dry air" mixtures, meaning that the air consisted largely of nitrogen and oxygen, with water excluded. To this was added ammonia in concentrations that ranged from about 10 ppm, up to 500 ppm, where normal barn exhaust contains ammonia at concentrations of 10 - 100 ppm. Irradiation of this flowing ammonia-containing air with the combination 254/185 nm light was shown to be effective in removing NH_3 below detection limits with sufficiently high dosage. The major mechanism by which this occurs is the photolysis of molecular oxygen, which produces atomic oxygen and consumes the ammonia. However, atomic oxygen in air also produces ozone and nitrogen oxide (N_2O). Both of these gases remained in the exhaust.

As additional gases were added to the laboratory mixture (both hydrogen sulfide [H_2S] and water), levels of the ozone and N_2O were mitigated. A larger scale experiment would be required to find out whether these could be

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brought down to acceptable levels either "naturally" through their consumption by the various pollutants in the air, or through a simple scrubbing of the exhaust (e.g., through activated carbon or similar materials). It was found that water at reasonable relative humidities for barn exhaust would have a significant impact on the mitigation of ammonia, i.e., requiring a higher dosage. However, no major impact by VOCs is anticipated.

As anticipated, the chemical fate of the ammonia is its oxidation. Depending on the initial concentration, either ammonium nitrate or nitric acid was observed as the major nitrogen-bearing product. No evidence for intermediate nitrogen oxides (NO_x) compounds was obtained, implying that they are oxidized rapidly and efficiently up to the final product of nitrate.

Because of technical limitations of the setup, it was not possible to immediately determine whether the required dosage corresponded well to realistic dosages that could be easily done in barn exhaust systems. The flow/irradiation times used in the experiments (of up to a few minutes) were longer than would normally be reasonable for gas flow through barn exhausts; however the intensity of light was also lower than ought to be feasible. This, and the question of ozone and N_2O remain the most important obstacles in bringing such a solution to industrial use. The fundamental science of converting ammonia to its natural oxidation product by means of photochemistry is sound.

Scientific 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, NH_3 concentrations, humidity, and presence of H_2S . Ammonia, initially at relevant barn exhaust concentrations in air, is completely, or at least substantially, reduced by irradiation with 185 nm light. The irradiation chamber consisted of 13 low pressure Hg lamps irradiating a 7.6 m quartz coil (1 mm wall thickness) after passing through approximately 25 mm ambient air. Each lamp provides an output of 8 W 254 nm irradiation and 0.02 W 185 nm irradiation. Both the ambient air and quartz walls reduce the intensity of 185 nm light significantly, so a more realistic "immersion" lamp setup, as would be used in the actual application of the technology would be considerably more efficient. Additionally, more efficient 185 nm lamps are certainly available. Nonetheless, this setup, ammonia could be reduced to undetectable levels (< 1 ppm) in dry air from initial concentrations of 50 ppm, using a hydraulic residence time of 3.9 minutes. Approximately 50% reduction would be obtained with a hydraulic residence time of 1 minute. 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 N_2O (derived from N_2 in the air), NH_4NO_3 , and HNO_3 . It is presumed that atomic oxygen is the primary photochemical product that begins the oxidative cascade. The data show that removal of NH_3 is plausible, but highlights concerns over ozone and N_2O emission. Addition of water at near 100% relative humidity does curtail ammonia removal, but also reduces ozone and N_2O formation by 80-90%. Addition of 15 ppm H_2S reduced N_2O by approximately 15% but did not have a significant effect on ozone or ammonia.

Introduction – The researchable question and its importance to producers

Agricultural ammonia (NH_3) emissions from commercial farms have significantly increased in recent years – animal waste and fertilizers are major sources of ammonia. The 2002 EPA inventory estimated that agricultural sources contribute approximately 80% of the total ammonia emissions in the U.S. Ammonia, hydrogen sulfide (H_2S), 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. Deliterious effects of ammonia on soil and water are well documented. 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. Unsurprisingly, 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).

Ultraviolet (UV) irradiation treatment has been very effective and economically practical for reducing odorous emissions in the food processing and recycling industries. 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. This basic notion was tested for the removal of ammonia through the work funded by this proposal, save that 185 nm light was required. As it is clear that the ammonia does not simply "disappear", determining the byproducts of the 185 nm irradiation and oxidation products of the ammonia was also investigated.

Objectives (taken from the research proposal)

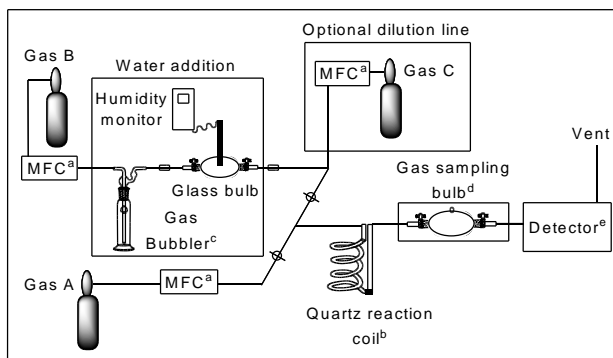
1. Determine the dose of 254 nm and/or 185 nm irradiation required for significant mitigation of ammonia mitigation from air samples containing ca. 100 ppm NH₃. Optimize with use of TiO₂ or other photocatalytic film as necessary. Suitable benchmarks include 50%, 90% and 99% reduction.
2. Examine the feasibility of providing this dosage in a treatment time that is consistent with air turnover rates and environmental conditions in swine barn exhaust.
3. Determine the chemical fate of the ammonia, as its degradation byproducts will certainly be released into the atmosphere.
4. Understand any significant effects of such reasonable variables as humidity and VOC concentrations.
5. (If time allows) Document the effect of realistic dust models on the degradation of ammonia.

Of these objectives, numbers 1, 3, and 4 were successfully achieved.

Materials & Methods

Materials. All gas blends were certified within $\pm 2\%$ accuracy. Dry air contained 21.5% O₂, ≤ 10 ppm CO, ≤ 1000 ppm CO₂, and ≤ 24 ppm H₂O. Hydrogen sulfide and N₂O stock gases were blended with N₂ 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 M Ω /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 schematically illustrated in Scheme 1.



Scheme 1. Schematic of the gas delivery and UV treatment system. The water addition segment and the gas sampling bulb were installed when appropriate. ^aMFC = mass flow controller. ^bRepresentation of the reaction coil which is placed inside the Rayonet photochemical reactor. ^cContained 200 mL of water. ^dUsed to collect samples for GC-MS analysis. ^eFTIR, MS, or NH₃ 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⁻¹ resolution. The scanner was constantly purged with N₂ to reduce the background signal from air. The following frequencies were used to monitor and determine concentrations: 967 cm⁻¹ for NH₃, 1,040 cm⁻¹ for O₃, and 2,236 cm⁻¹ for N₂O. NH₃ (50 ppm) and N₂O (5 ppm) standards were diluted with air or N₂ respectively and the new concentrations were measured to obtain calibration curves

FTIR results for NH₃ at higher flow rates and low concentrations were compared to measurements taken with a digitalized chemiluminescence ammonia analyzer, which could measure a maximum NH₃ 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 mm I.D. and 5 μm 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(trifluoro-methyl)-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, by objective

Determine the dose of 254 nm and/or 185 nm irradiation required for significant mitigation of ammonia mitigation from air samples containing ca. 100 ppm NH₃. Optimize with use of TiO₂ or other photocatalytic film as necessary. Suitable benchmarks include 50%, 90% and 99% reduction.

In retrospect, this objective was worded naively, in more of an engineering than chemical sense, as if the science were well established. Also, the sample geometry and other conditions (e.g., concentrations) will affect the dosages required.

This said, it was found that 254 nm irradiation – as reasonably expected – is ineffective at removing ammonia, while 185 nm irradiation of air creates sufficiently oxidizing conditions to accomplish this as stated. Using a mere quarter-watt of 185 nm, 50 ppm ammonia in dry air could be >99% removed (~400 mL irradiation volume, ~4 min hydraulic residence time [HRT]), whereas ~50% removal could be obtained with ~1 min HRT.

The use of TiO₂ was not investigated due to practical considerations that favor not needing its use.

Examine the feasibility of providing this dosage in a treatment time that is consistent with air turnover rates and environmental conditions in swine barn exhaust.

Insufficient data were obtained to determine this, given realistic barn air exhaust.

Determine the chemical fate of the ammonia, as its degradation byproducts will certainly be released into the atmosphere.

The ammonia is converted to nitric acid in the absence of remaining ammonia, and is captured as ammonium nitrate if additional ammonia remains.

Additionally, the formation of ozone and N₂O are important considerations.

Understand any significant effects of such reasonable variables as humidity and VOC concentrations.

Water that is present at high relative humidity is present at a much higher concentration than any other VOC possibly would be. It has an impact on ammonia mitigation that is larger than we anticipate for any other realistic additional "contaminant". Approximately 50% reduction of ammonia was observed under conditions that would have nearly completely eliminated ammonia in the absence of water.

The explanation of this is somewhat speculative due to the chemical complexity of the system, but the best assumption appears to be that water serves to intercept atomic oxygen in its most reactive state, i.e., O(¹D), in competition with the reaction by ammonia.

VOCs are likely to reduce formation of N₂O, and potentially ozone, based on initial experiments. We believe that VOCs at realistic concentrations will have only modest effect on ammonia mitigation, compared to dry air. This is supported by some data using hydrogen sulfide as a co-contaminant.

(If time allows) Document the effect of realistic dust models on the degradation of ammonia.

Time did not allow for this objective to be investigated.

Discussion: Significance of the results and benefits to pork producers

This study shows that 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. In particular, ammonia concentrations can be reduced. Ammonia is fully oxidized to nitrate; intermediate NO_x compounds are apparently quite short-lived. However, other compounds that need to be considered are ozone and nitrous oxide (N₂O), the other natural byproducts of oxygen photolysis.

Formation of atomic oxygen follows from 185 nm photolysis air, 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 direct reactions of atomic oxygen are, presumably, the major agents involved in the oxidation of NH_3 , H_2S , and various VOCs that might be present.

The hydraulic residence times required for near 100% ammonia abatement using this relatively inefficient irradiation system were of the order of a few minutes. However, direct exposure of exhaust airs with turbulent air flow to higher output lamps would be much more efficient, and we speculate that more practical HRTs of the order of a few seconds might be achieved with proper air flow design and lamp intensity.

When H_2S was present in the reaction mixture, N_2O formation was reduced. We believe that the other VOCs will also reduce the N_2O and ozone in the exhaust, 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. Particulate matter in the barn air is also a concern due to its light scattering effects, but its organic constituents would also consume some of the undesirable ozone and N_2O . Ammonium nitrate could be removed mechanically along with other particulate matter, as needed. Ambient dusts also will mean that turbulent flow in full-scale applications (along with direct lamp exposure to the air) is essential, in order that all air is reasonably exposed to light.

The experiments reported here, thus, serve as positive proof of principle. Subsequent work that would be required to bring photochemical ammonia and VOC abatement to practical application would include some further laboratory scale work that took into account more complex gas mixtures and a pilot/model scale design and testing.