Controlling Gas and Odour Emissions from Swine Facilities using Zinc Oxide Nanoparticles

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ABSTRACT Zinc oxide (ZnO) nanoparticles were evaluated in this study as a possible measure to mitigate the level of gases in swine buildings. Two deployment techniques were used: direct mixing of ZnO nanoparticles into the slurry and gas filtration with nanoparticles as filtering media. The objective of this work was to determine the impact of the treatment on reducing ammonia, hydrogen sulphide and odour emissions from swine manure.

Experiments were carried out in two identical and fully instrumented experimental chambers at the Prairie Swine Centre barn facility in Saskatoon, Saskatchewan. For mixing method, the manure slurry in one chamber was treated with ZnO nanoparticles (Treatment) while the other one was configured as a normal swine room (Control) with no treatment applied. For filtration method, a ventilation air recirculation system was installed in both rooms; one had a blank filter (Control) and the other chamber had a fluidized bed filter with ZnO nanoparticles (Treatment). Three replicate trials were conducted for each treatment approach. Results showed that the addition of ZnO nanoparticles into the manure achieved more than 95% reduction in H$_2$S level; no significant effect on NH$_3$ concentration was observed. Effectiveness of ZnO nanoparticles was persistent in maintaining low H$_2$S level up to 15 days after treatment application. On the other hand, the ventilation air recirculation system with ZnO filter achieved significant reduction in both H$_2$S and NH$_3$ concentrations at the animal- and human-occupied zones.

Keywords: nanoparticles, gas emission, manure, swine, zinc oxide
Introduction

Emissions of hydrogen sulphide (H$_2$S), ammonia (NH$_3$) and odour from hog production operations are largely produced from fresh or stored manure (Hartung and Phillips, 1994). These emissions have been a long-term concern to humans, animals and the environment despite several abatement strategies that have been investigated and adopted at the farm scale. Taking advantage of recent advances in nanotechnology, Asis (2008) has evaluated the use of nanoparticles in controlling H$_2$S, NH$_3$ and odour emissions from swine manure in a fully controlled small-scale test set-up and results revealed that mixing and filtration methods using zinc oxide (ZnO) nanoparticles showed the greatest potential for controlling these environmental emissions. However, there is a gap of translating these results to actual swine production conditions. Nanoparticles and manure gases can react and behave differently under different conditions, thus further investigation of the effectiveness of ZnO nanoparticles in an environment that closely represent actual barn conditions was needed. Additionally, room scale experiments under conditions close to normal production setting would provide the opportunity to test the effectiveness of this treatment technology in actual livestock operations.

Prior to room-scale experiments, semi-pilot scale tests in an open system environment were conducted to evaluate operational factors such as nanoparticle-to-slurry ratio for mixing method, and filter design, face velocity and nanoparticle loading amount for filtration method. Results showed that the mixing treatment required a particle-to-slurry ratio of 3 g of ZnO per litre of slurry to control H$_2$S and NH$_3$ levels. For the air filtration treatment, a fluidized bed filter design with 0.28 g/cm$^2$ loading rate and rated at 0.5 m/s face velocity was found to be the most effective combination in controlling gas levels. Using these parameters, room-scale experiments were then carried out in specially-designed chambers at the Prairie Swine Centre Inc. (PSCI) barn facility.

MATERIALS AND METHODS

Room Specifications

The effectiveness of each treatment approach was evaluated in two identical environmental chambers at PSCI barn facility in Saskatoon, Saskatchewan. The chambers were configured to represent normal swine production rooms. Each has inside dimensions of 4.2 m (L) x 3.6 m (W) x 2.7 m (H) with partial slatted concrete flooring within the pen area (Figure 1). Underneath the slatted floor was a 900-litre manure collection tub with dimensions of approximately 2 m (L) x 1.25 m (W) x 0.3 m (H). Each chamber was operated on a negative pressure ventilation system with one side wall fan (H18, Del-Air Systems Inc., Humboldt, SK, Canada). Fresh air entering into each chamber was preconditioned using either a 5-ton air conditioning unit (Raka-060 CAZ, Setra Systems, Boxborough, MA, USA) or a 10-kilowatt electric heater (Chromalox, Dimplex North America Ltd., Cambridge, ON, Canada), and an air filtration unit (Circul-Aire USA-H204-B, Dectron International, Roswell, GA, USA) with a 0.6-metre diameter centrifugal fan (Delhi BIDI-20, Delhi Industries Inc., Delhi, ON, Canada). Sensors and other monitoring instruments were deployed in each chamber, and were calibrated and checked to ensure proper operation during the course of the experiment.

Figure 1-A shows the layout of the chamber used in mixing tests. Similar set-up was followed in filtration tests with the addition of the ventilation air recirculation system as shown in Figure 1-B. The recirculation system was composed of an axial fan (Godro Multifan, Vostermans BV, IL, USA), a 36-centimetre diameter galvanized sheet vertical duct where the filter housing was installed, and a 30-centimetre diameter horizontal duct with 8 equally-spaced 3.8-centimetre diameter holes. Contaminated air from the manure pit headspace was drawn in by the fan, passed through the test filter, and redistributed back to the chamber air space through the 8 small outlets in the recirculation duct. The air recirculation requirement, i.e., 0.5 m/s face velocity of the test filter and 105 litres per
second (Lps) output from the fan, was achieved by controlling the fan speed using a manual speed controller (Phason Model MSC-4, Winnipeg, Canada).

**Figure 1.** Layout of one of the environmental chambers used in mixing (A) experiments. Filtration tests were done on the same chamber with the added ventilation air recirculation system (B).

**Experimental Approach** Tests on the effectiveness of mixing and filtration techniques were carried out separately. Each test was conducted in three replicate trials; each trial lasted for 30 days. At the start of each trial, eight female grower pigs with average starting weights of about 28 kg to 30 kg were brought into each chamber. The first 15 days of the trial served as manure accumulation period to generate sufficient amount of manure in the tubs prior to gas sampling on Days 15, 20, 25 and 30.

Immediately after the first sampling (Day 15), treatments were applied. In mixing tests, ZnO nanoparticles at a rate of 3 g/L were mixed with the manure in the treated chamber while the manure in the control room was not treated with nanoparticles. In filtration tests, air filter with 0.28 g of ZnO nanoparticles per square centimeter of filter cross-sectional area was installed in the treated room; the control room also had a recirculation system but with a filter pad only (not loaded with nanoparticles). Thus, gas sampling done on Days 20, 25 and 30 of each trial corresponded to Days 5, 10 and 15 after treatment application.

Both chambers in each test were managed as identical as possible throughout the 30-day trial period. Air temperature was initially set at 21 °C and then gradually decreased to 18 °C at Week 4 following standard temperature guidelines for grower pigs. Indoor air quality (temperature, RH and ventilation rate) in each chamber was regularly monitored to ensure that both rooms had the same
environmental conditions. In addition, standard grow/finish diets were provided to pigs and were always weighed before putting into the feeders.

**Sampling procedure and data collection** During each test, hydrogen sulphide, ammonia and odour concentrations in treated and control chambers were monitored at three distinct locations within the chamber air space (Figure 2): at the pit (approximately 5 cm above manure surface), at pig’s height (about 0.5 m from pen floor), and at human level (about 1.6 m from floor). During sampling, manure slurry was agitated simultaneously and continuously for 5 minutes using a steel rake and a recirculating vacuum pump. Air samples were withdrawn from the three sampling locations at 2, 5 and 10 minutes from the start of agitation and collected in 10-litre Tedlar bags using a gas sampling apparatus, typically of a “sampling lung” set-up. Prior to gas collection, the Tedlar bags and sampling lines were purged with zero gas (Praxair, Saskatoon). Pigs were moved to an adjacent room during sampling and were returned to the room after sufficient ventilation was achieved.

![Sampling points in the chamber: pit, animal and human levels.](image)

Gas samples in Tedlar bags were analyzed for H₂S and NH₃ concentrations. A hydrogen sulphide monitor with electrochemical sensor (Draeger PAC III, Draeger Canada Ltd., Ontario, Canada; accuracy: ± 5 % of reading) was used for monitoring H₂S concentration while an ammonia analyzer (Model Chillgard RT, MSA Canada, Edmonton, AB; accuracy of ± 2 ppm) was used to determine the NH₃ levels. In addition, odour samples in 10-litre Tedlar bags were sent to commercial olfactometry laboratories (University of Manitoba, Winnipeg and University of Saskatchewan, Saskatoon for mixing and filtration tests, respectively) and were analyzed following the British standard of odour measurement (EN13725, 2003) within 30 hours after sample collection.

**RESULTS AND DISCUSSION**

Each data bar in the succeeding figures represented the gas concentrations from samples collected at 2 minutes after the start of agitation. The H₂S, NH₃ and odour concentrations plotted as Day 0 values were measured prior to the application of ZnO nanoparticles (in the treated chamber) and served as baseline for subsequent sampling events.
**Hydrogen sulphide concentration** In mixing tests, the addition of ZnO nanoparticles into the manure at a rate of 3 g/L achieved more than 95% reduction in H$_2$S level (Figure 3-A). Initial H$_2$S concentrations (Day 0) at the pit, animal and human levels in the treated chamber were 596, 57 and 39 ppm, respectively, and were reduced to almost undetectable levels on Day 5 to Day 15 after ZnO nanoparticles has been applied. The untreated slurry from the control chamber, however, showed mostly increasing trends regardless of sampling location and monitoring days.

![Graph A](image1)

**Figure 3.** Mean (±SE) concentration of hydrogen sulphide in gas samples collected from treated and control chambers at different sampling locations and monitoring periods during room-scale tests of mixing (A) and filtration (B) methods, n=3.
In filtration tests, H$_2$S concentrations over the manure pit in the chamber with ZnO filter followed similar trend as that in the chamber with filter pad only (Control) as shown in Figure 3-B. However, at the animal- and human-occupied zones, significant H$_2$S reduction (P<0.05) was observed in the treated chamber unlike in the control chamber which showed no significant change (P>0.05) even with the installation of the ventilation air recirculation system with filter pad only. Over the 15-day continuous operation of the air filtration system with ZnO nanoparticles in the treated chamber, about 46% and 65% reduction in H$_2$S concentrations were achieved at the animal and human levels, respectively, relative to their initial concentrations of 94 ppm and 58 ppm, respectively.

The apparent decrease in H$_2$S level achieved with ZnO nanoparticles applied through mixing and filtration methods can be attributed to the known capacity of ZnO for adsorption of H$_2$S. Zinc oxide has been used as adsorbent for H$_2$S in drilling fluids (Sayyadnejad et al., 2008), sewage treatment (Bagreev et al., 2001), and gaseous air stream (Wang et al., 2008) during which the process produced water and an insoluble zinc sulphide as shown in the reaction below (Eq. 1):

$$\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O}$$ (1)

In addition, the reduction in H$_2$S in mixing tests could also be due to the antibacterial effect of ZnO nanoparticles. Several studies have shown that the deposition of ZnO nanoparticles on the surface of bacteria (Brayner et al. 2006) and the production of reactive oxygen species (ROS) from ZnO under normal lighting conditions (Fang et al., 2006) can inhibit the growth of bacteria responsible for the production of hydrogen sulphide in swine manure.

**Ammonia concentration** Figure 4 shows the effect of mixing and filtration treatments on ammonia concentration. In mixing tests, the concentration of ammonia at the different sampling locations (pit, animal and human levels) in the treated chamber on Days 5, 10 and 15 after treatment application were not significantly different (P>0.05) from their respective Day 0 values even though the application of ZnO nanoparticles in the treated chamber resulted to slight decrease in NH$_3$ (Figure 4-A). On Day 0, mean NH$_3$ concentrations at the pit, animal and human zones in the treated chamber were 25, 15 and 13 ppm, respectively, and decreased to 19, 11 and 10 ppm on Day 10 after treatment application. Ammonia levels in the control chamber were also unchanged during the 15 days of gas monitoring.

Similar to H$_2$S, NH$_3$ levels above the manure pit in both chambers during the filtration experiments were not significantly different (P>0.05) over time (Figure 4-B). This was expected since the configuration of the ventilation air recirculation system installed in the control and treated chambers only treats gases after they have been released from the source (pit). Unlike the control chamber, the addition of air filtration system with ZnO nanoparticles in the treated chamber led to about 36% and 42% reduction in NH$_3$ concentration at the animal and human levels, respectively, relative to their initial concentrations of 15 ppm and 12 ppm, respectively.

In addition, it was observed that H$_2$S and NH$_3$ reductions at the human zone in the treated chamber were higher than those at the animal level. This could be due to the air movement in the chamber during sampling. Not all gases emitted from the manure at the pit were drawn in by the recirculation fan; a portion may go upward through the floor slats and most likely be captured at the animal level which was about 0.5 m above the pen floor. On the other hand, the recirculation duct expelled treated air that passed through the ZnO filter through outlets directed towards the human zone.
Figure 4. Mean (±SE) concentration of ammonia in gas samples collected from treated and control chambers at different sampling locations and monitoring periods during room-scale tests of mixing (A) and filtration (B) methods, n=3.

Unlike H\textsubscript{2}S which has a known chemisorption process with ZnO as governed by equation 1, limited information on the reaction kinetics between ZnO and NH\textsubscript{3} can be found in literature. The most likely reasons could be the possible competition between H\textsubscript{2}S and NH\textsubscript{3} molecules for the adsorption sites of ZnO (Chung et al., 2005) and the physical adsorption process occurring between ZnO and NH\textsubscript{3}, which is relatively weaker than chemisorption (Masel, 1996); these mechanisms support the only slight reduction in ammonia concentration achieved from both mixing and filtration methods with ZnO nanoparticles.
Odour levels Due to the limited availability of the olfactometry laboratory at the University of Manitoba, only one batch of samples from mixing tests was sent for odour analysis. These samples were collected at the pit, animal and human levels on the third sampling event (Day 15 after treatment application) of the third trial. Measured odour levels in the samples from the treated chamber was slightly lower than in the control chamber especially above the manure pit as shown in Figure 5-A. This trend could be attributed to the lower H₂S levels observed in the chamber treated with ZnO nanoparticles. Six out of ten compounds with the lowest odour detection thresholds (i.e., the strongest odourants) are sulphur-containing compounds (O'Neill and Phillips, 1992). On average, odour concentration in the treated and control chambers was 1960 OU/m³ and 2423 OU/m³, respectively.

Figure 5-B shows the odour concentrations at the different sampling locations in each chamber during the room-scale tests on the filtration method. Prior to the installation of the test filters (Day 0), odour levels in the control and treated chambers were almost the same with average values of 2551 OU/m³ and 2536 OU/m³, respectively. Similar to H₂S and NH₃, odour concentrations in the control chamber almost remained unaffected over 15 days of monitoring. In contrast, a decrease in odour concentrations at the animal- and human-occupied zones in the treated chamber was observed. Initially, mean odour concentrations at the animal and human levels in the treated chamber were 2888 OU/m³ and 2087 OU/m³, respectively, and were reduced to 2278 OU/m³ and 1689 OU/m³, respectively on Day 5 after ZnO filter application. The decrease in odour concentration especially in the human zone could be attributed to the lower gas levels in this area as a result of the operation of filter system with ZnO nanoparticles. Statistical analysis, however, revealed that the reduction was not significant (P>0.05).
CONCLUSIONS
Room-scale experiments revealed that the addition of ZnO nanoparticles into the slurry reduced gas levels, specifically H₂S, at the source (manure pit), resulting to almost undetectable H₂S levels at the animal- and human-occupied zones. On the other hand, partial filtration of the gases from the source using a ZnO filter installed in a recirculation duct set-up did not decrease the gas levels at the source but could likely reduce the gas concentrations at the animal and human levels to comply
with the STEL (15 ppm for H$_2$S). The partial filtration set-up can be made more effective with better capture of gases emitted from the source to pass through the filtration system.

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**REFERENCES**


