

***Ozonation of Swine Manure Wastes to Control Odors
And Reduce the Concentrations of Pathogens
And Toxic Fermentation Metabolites***

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Abstract

The use of ozone for the remediation of nuisance odorous chemicals in liquid swine manure slurry was investigated. Gaseous ozone was bubbled directly into stored swine manure slurry in a continuously stirred batch reactor. One-liter samples of swine slurry were ozonated to achieve ozone dosages of 1.0, 2.0 and 3.0 g ozone/liter of waste. Olfactometric determinations demonstrated a significant reduction in odors in ozonated samples as compared to raw and oxygenated samples. Volatile fatty acids, nitrate, phosphate and ammonia concentrations were unchanged by ozonation. The biochemical oxygen demand (BOD) and the chemical oxygen demand (COD) were essentially unaffected by ozonation. The concentrations of odorous phenolic microbial metabolites (e.g., phenol, p-cresol and p-ethylphenol) and odorous indolic microbial metabolites (e.g., 3-methylindole and indole) were reduced to non-detectable levels by ozonation. Hydrogen sulfide concentrations were reduced slightly by the process, with a concurrent increase in the sulfate concentration. *E. coli* counts were reduced by a factor of three log units and total coliforms showed a one log decrease in concentration after treatment with ozone at 1.0 g/L.

The results of this study demonstrate clearly that at the pH values studied (ca. 7), ozonation is effective for the elimination of the malodors associated with stored swine slurry and for killing potentially pathogenic bacteria, without increasing the concentrations of major pollutants of current concern, (i.e., nitrate and phosphate) and without oxidizing ammonia, which is a major plant nutrient.

Introduction

The odor produced by livestock manure during prolonged uncovered storage and upon land application has become a growing nuisance with the increasing sprawl of urban housing onto agricultural land (Stallings, 1976). The nuisance potential is related to the offensive nature of the manure that has been stored for several months and the intensity of these odors. In Michigan, odors emanating from livestock waste are the number one complaint against livestock farms. Increasingly stringent federal and state regulations concerning public health, in addition to increasing litigations, demand that the livestock industry take action to reduce this problem.

Ozone (O_3) is recognized as an effective process for treating industrial effluents, drinking water and sewage (Block, 1982; Metcalf & Eddy, 1990). This process is used extensively in Europe and in more than 200 water and sewage treatment plants in North America (Debevec, 1990; Fressonnet-Chambarlhac et al., 1983; Glaze, 1987; Rice and Dimitriou, 1997). The ozonation of manure represents an opportunity to reduce both the offensive nature and the intensity of these odors. This represents an advantage (over other technologies) for applying manure to crop land that usually receives manure. The ozonation of the manure slurry can result in an increase in the amount of land that can benefit from the manure nutrients and reduce the potential for creating odor nuisances in the communities surrounding the livestock operations. Increasing the pool of available land for manure application reduces the tendency to over-apply manure nutrients to crop land, thereby, reducing the potential to leach nutrients and deteriorate the quality of the underlying groundwater. Additionally, since manure storage is the most capital-intensive component of manure management systems, eliminating the need for storage covers to control odors represents an initial fixed cost reduction and a decrease in the labor and management costs.

Ozone is a powerful oxidizing agent, generally produced from dry gas (i.e., air or oxygen) with an electric discharge generator or using ultraviolet radiation. This unstable gas is only slightly more soluble than oxygen in water, with a saturation value of 600 mg/L at one atmosphere and 20°C. In water, ozone decomposes to form free radicals by a process that is still not well understood. Ozone will readily attack C-C double bonds, C-N bonds, aromatic groupings and heterocyclic compounds. Many aldehydes, ethers, alcohols and hydrocarbons also are oxidized by ozone (Reynolds et al., 1989). Many chemicals which are not oxidized directly by ozone could be oxidized by the OH radicals or the superoxides which form as a result of the decomposition of ozone. Ozone (or the secondary oxidants formed during the decomposition of ozone) will adversely affect the components of cytoplasmic membranes, enzymatic systems, and even nucleic acids. High concentrations of ozone will lyse bacterial cells. (Block, 1982).

Ozonation potentially can reduce odor levels in stored livestock manure by (1) killing the odor-producing microorganisms; thus controlling the rate of production of odorous metabolites, and (2) oxidizing the odorous metabolites produced by anaerobic fermentation; thus decreasing their concentration. From the standpoint of public health and surface run-off contamination resulting when livestock manure is applied to the land, ozonation would offer an additional advantage in killing pathogenic microorganisms.

The objective of this study was to determine the effect of ozonation on the odor of stored swine waste slurry.

Experimental Methods

SWINE WASTE SLURRY

The swine waste slurry used in this study was collected from the Swine Teaching and Research Farm, Department of Animal Science, Michigan State University, East Lansing, MI. The sample was collected from near the bottom of the storage pit, (e.g., the anaerobic region of the slurry), because most of the chemical components which contribute to the offensive odor of stored livestock waste are found in this section. The combined urine and feces produced by starter pigs, in addition to water used to flush beneath the slotted flooring of their housing, contributed to the swine waste slurry. Large solids were removed from the collected swine waste slurry by passage through a sieve (2 mm). The slurry was ozonated within approximately one hour after being collected from the storage pit. This was done to minimize any chemical or biological changes in microbial activity as a result of the removal of the slurry sample from the anaerobic conditions. Surplus waste slurry was stored at 4°C for a maximum of three days.

OZONATION PROCEDURE

The ozonation apparatus used was a one-liter glass batch reactor which was operated in a continuously stirred batch mode. Ozone was generated from dried oxygen using a U.S. Ozonair Model No. CT-1200 ozone generator (Ozonair, South San Francisco, CA). The oxygen was dried using a molecular sieve trap (S/P Brand #G5301-21, Rancho Cordova, CA). The generator produced an ozone concentration of 1.3% by volume in the oxygen stream. A slurry sample size of one liter was used for all ozonation experiments. The ozone was bubbled directly into the waste slurry at a flow rate of 1.1 L/min. To reduce foaming, 1.0 mL of an anti-foaming agent (Anti-foam 289, Sigma Chemical Co., Milwaukee, WI) was added to the waste slurry prior to ozonation. Excess gaseous ozone was destroyed by passage of the effluent gas through gas washing bottles containing 2% potassium iodide (Mallinckrodt Specialty Chemicals, Paris, KY) solution, prior to releasing the effluent gas to the environment.

The concentration of ozone entering and exiting the reactor was determined by iodometric titration (Standard Methods, 1975) to measure the total ozone that reacted with the sample slurry. To adapt this method to the higher ozone concentrations used in this study, a 0.1 N sodium thiosulfate (Mallinckrodt Specialty Chemicals, Paris KY) solution was used for the initial titration, followed by a 0.005 N sodium thiosulfate solution for near the titration endpoint. By determining the concentration of ozone entering the reactor, and the ozone concentration exiting the reactor, the amount of ozone that had reacted with the slurry could be estimated.

The effluent gas traps were changed at ten minute intervals to determine the change in ozone demand during the ozonation process. A control reaction was conducted by passing high purity oxygen through 1-liter of swine waste slurry for an exposure time

equivalent to that of the 3.0 g/L ozone dosage. No attempt was made to control the pH of the manure slurries. The initial pH of the raw manure was 6.5.

OLFACTOMETRY

The odor intensities of both the raw and oxygenated slurry samples were compared to that of the ozonated slurry. These controls allowed a comparison of possible odor changes due to aeration. An olfactory sensory panel compared odor intensity from raw, oxygenated and samples ozonated at rates of 1.0, 2.0 and 3.0 g/L using a 1-butanol olfactometer (ASTM E544-75). 1-Butanol was diluted in air to the concentrations shown in Table I. Dilution air was provided from a gas cylinder. Six participants smelled the raw, oxygenated and ozonated slurries, presented in random order, and compared their odor intensities with the odor emanating from each sensory port and selected the port (1 of 8) that compared most closely in odor with the slurries. The mean concentrations then were used for odor intensity comparisons between the raw, oxygenated and ozonated slurries. The sensory panel also ranked the slurries in order of highest to lowest odor intensity. In addition, the panel was asked to choose the sample with the higher odor intensity for a series of paired sample comparisons. A rank order was established for the slurries on the basis of this paired comparison.

TABLE I. 1-BUTANOL CONCENTRATIONS AT EACH ODOR PORT

Odor Port Number	1-butanol concentration at each port (x 1000 ppm)
1	0.03
2	0.06
3	0.12
4	0.25
5	0.48
6	0.97
7	1.80
8	3.40

INORGANIC CHEMICAL ANALYSES

Phosphate and nitrate determinations were made using a Dionex Model No. 2000i/SP Ion Chromatograph (Dionex Corp., Sunnyvale, CA). An Ionpac AG4A pre-column and an Ionpac AS4A column were used for chromatographic separations. The slurries were prepared for chromatographic analysis by dilution in water (1:50) followed by filtration through a glass fiber filter (Gelman Sciences, Ann Arbor, MI), and subsequent filtration through 0.45 mm and 0.22 mm filters (Millipore Products Div., Bedford, MA). Centricon-3 concentrators (Amicon, Inc., Beverly, MA) were used to remove proteins. Chromatographic procedures were followed as described in the Dionex manual: Injection volume 0.5 mL, eluent used; 1.7 mM NaHCO₃, 1.8 mM Na₂CO₃, eluent flow rate; 2 mL/min., regenerant used; 25 mN H₂SO₄, regenerant flow rate; 5 mL/min.).

Ammonia concentrations were measured with an ammonia electrode (Model No. 476130, Corning Medical and Scientific, Medfield, MA) and a pH meter (Orion Model No. SA720, Orion Research Inc., Boston, MA). Determinations were made using the method of known ammonium ion addition, as described in the Corning manual.

COD determinations were made using prepackaged Hach vials (Hach Co., Loveland, CO) with a 0-1,500 mg/L COD range. The slurry was diluted (1:50) with water and 2 mL added to each of the vials. Two mL of distilled water was added to the vial and used as a blank. A spectrophotometer (Spectronic 21D, Milton Roy Co., Rochester, NY) was used for determining percent transmittance at a wavelength of 620 nm. COD values were made using a reference chart provided by the Hach Co. (Jirka and Carter, 1975).

BOD determinations were made using procedures outlined in *Chemistry For Environmental Engineers* (Sawyer and McCarty, 1978).

Hydrogen sulfide concentrations were determined using a purge and trap method. Slurry (200 mL) was acidified with 10 mL of 3.6 N H_2SO_4 , to lower the pH below 7.0. The predominant form of sulfide below pH 7.0 is H_2S . The H_2S then was purged from the slurry by sparging nitrogen gas (250 mL/min) through the continuously stirred reactor for 30 minutes. Nitrogen gas was used to remove the gas H_2S from the gas phase insuring the concentration gradient favored further gas expulsion from the liquid slurry. The nitrogen gas then was passed through 200 mL of a 0.14 N NaOH solution to trap the sulfide (S^{2-}). Determination of sulfide in the trap was in accordance with EPA Method 9030 (EPA, 1986), using 0.025 N iodine and 0.0062 N sodium thiosulfate solutions. Sulfide determinations were done in triplicate on 50 mL aliquots of the trap solution. To ensure consistent results, the trap solution required constant stirring during sampling.

MICROBIOLOGICAL ANALYSES

Volatile fatty acids (VFA) analyses were performed with a gas chromatograph (GC) (Model # 5840A, Hewlett-Packard, Avondale, PA) using a flame ionization detector (FID), equipped with an auto sampler and glass column (4 mm x 91 cm) packed with 60/80 Carbopack C/O 3% Carbowax 20M/0.1% H_3PO_4 (Supelco, Inc., Bellefonte, PA). VFA extraction was performed with a water 1% formic acid solution. Operating conditions for the GC were: injection temperature of 125°C, column temperature of 250°C, and FID temperature of 250° C. The carrier gas flow rate (helium) was 40 mL/min and the signal attenuation was 4. Volatile phenolic and indolic metabolite analyses were performed by GC using a stainless steel column (3.2 x 1.60 cm) packed with Supelcoport 10% SP-2100 100/120 Supelco, Inc. The analytes were extracted from slurry samples with diethyl ether. Operating conditions for the GC were: injection temperature of 200°C and FID temperature of 250° C. The column temperature was programmed at 125°C for 3 minutes, with a 10° C/min. increase to 170°C for 7.5 minutes. The carrier gas (nitrogen) flow rate was 40 mL/min.

E. COLI AND TOTAL BACTERIAL COUNTS

Aliquots of ozonated slurry were used to inoculate *E. coli* broth for coliform enumeration. *E. coli* and most probable number (MPN) of bacterial counts were performed using fermentation tubes and Bacto EC Medium (DIFCO laboratories, Detroit, MI). The procedure for determining *E. coli* and MPN of bacteria was taken from *Standard Methods*, 1980.

Results And Discussion***OLFACTOMETRY***

The olfactometry results for each individual and the group mean are given in Table II. The median response for the oxygenated control and raw swine slurry indicate no difference in odor intensity. The odor intensities for the three ozone dosages were found to be less than those for the raw manure and oxygenated samples. Because of the high variability in the responses, no statistically significant differences in the odor intensity measured among any of the ozonated samples were observed. All but one of the panelists believed the odor intensity of the raw waste to be significantly greater than that of the treated waste.

TABLE II. OLFACTOMETER RESULTS

Observer	Swine slurry odor equivalent for 1-butanol concentrations (x 1000 ppm)				
	Raw Slurry	Oxygenated Slurry	1.0 g/L Ozone Exposure	2.0 g/L Ozone Exposure	3.0 g/L Ozone Exposure
T	1.80	3.40	0.48	0.25	0.48
U	3.40	3.40	1.80	1.80	3.40
W	1.80	0.97	0.48	0.25	0.25
X	3.40	3.4	3.40	3.40	0.97
Y	1.80	0.97	0.48	0.48	0.36
Z	3.40	3.40	0.48	1.80	0.97
Mean	2.60	2.60	1.20	1.30	1.10

When the sensory panel members were asked to make forced choices between pairs of samples (Table III), the raw manure slurry was chosen as having a more intense odor than the oxygenated slurry and each of the ozonated slurries. The oxygenated slurry was chosen as having a more intense odor than any of the ozonated samples. The sample dosed at 1.0 g/L ozone was always chosen as being more intense compared to the 3.0 g/L ozone exposure. All but one panel member chose the 1.0 g/L ozone exposure as being more intense than the slurry exposed to 2.0 g/L ozone. Odor intensity was not significantly different between the 2.0 g/L and 3.0 g/L ozone dosages.

One-half of the observers chose the 2.0 g/L exposure and one-half chose the 3.0 g/L dosage as being more intense. Using Wilcoxon's single rank test (Neter et al., 1982), the differences between the 1 and 2 g/L dose and the 2 and 3 g/L doses were found not to be statistically significant. When the panel members were asked to rank all 5 samples in order from most intense to least intense, the raw manure sample always was ranked as having the most intense odor. There was no general agreement of order beyond this.

TABLE III. PAIRED COMPARISON RESULTS

Choice having the stronger odor							
Ob- ser- ver	Raw vs Oxygen- ated	Oxygenated vs 1.0 g/L ozone dose	Oxygenated vs 2.0 g/L ozone dose	Oxygenated vs 3.0 g/L ozone dose	1.0 g/L vs 2.0 g/L ozone dose	1.0 g/L vs 3.0 g/L ozone dose	2.0 g/L vs 3.0 g/L ozone dose
T	Raw	Oxygenated	Oxygenated	Oxygenated	1.0 g/L	1.0 g/L	3.0 g/L
U	Raw	Oxygenated	Oxygenated	Oxygenated	2.0 g/L	1.0 g/L	3.0 g/L
W	Raw	Oxygenated	Oxygenated	Oxygenated	1.0 g/L	1.0 g/L	2.0 g/L
X	Raw	Oxygenated	Oxygenated	Oxygenated	1.0 g/L	1.0 g/L	3.0 g/L
Y	Raw	Oxygenated	Oxygenated	Oxygenated	1.0 g/L	1.0 g/L	2.0 g/L
Z	Raw	Oxygenated	Oxygenated	Oxygenated	1.0 g/L	1.0 g/L	2.0 g/L

ODOROUS METABOLITES AND VOLATILE FATTY ACIDS (VFAs)

Some of the odor-causing metabolites found in anaerobic swine manure have been described (Yasuhara et al., 1984). Among the odorous metabolites that have been found at high concentrations in swine waste slurry are the volatile fatty acids (e.g., acetic, propionic, isobutyric, butyric and valeric), the phenolics (e.g., phenol, *p*-cresol and *p*-ethylphenol) and the indolics (e.g., indole and 3-methylindole). Previous studies have established that *p*-cresol is the predominant volatile phenolic metabolite excreted in the urine and feces of swine (Spoelstra, 1978; Yokoyama et al., 1982), and is a major contributor of the characteristic odor of swine feces and housing facilities (Hartung, 1984).

The major phenolic metabolite detected in swine waste slurry was *p*-cresol. Indolic metabolites corresponding to indole and 3-methylindole also were present. After the oxidizing treatment with ozone, all of the phenolic and indolic metabolites were substantially destroyed by even the lowest ozone treatment dose (1.0 g/L), as assessed by gas chromatography. Concomitantly, there was a marked reduction in the offensive odor of the treated swine waste slurry. The oxygenated swine waste slurry (e.g., control) sample showed no reduction in these odorous metabolites in comparison to the untreated slurry samples. This would indicate that the volatile phenolic and indolic metabolites were not stripped from the slurry into the gas phase, but were destroyed by oxidation from the application of ozone.

The individual concentrations of the volatile fatty acids appeared to be unchanged by either aeration (oxygenated control), or by ozonation.

Therefore, not only were the concentrations of the representative odorous metabolites reduced but there was a significant reduction in the odor intensity perceived by the odor panel. This suggests that ozonation of liquid swine slurries has the potential to reduce the odor releases that occur during agitation, loading, transport and application to the soil surface. While there are benefits to injection to preserve ammonia nitrogen, from an odor perspective, surface application can be a lower cost option. Irrigation, which becomes an additional option, reduces the risk of soil compaction and increases

the time rate of surface application. This then reduces the time required to deliver the manure to cropland and facilitates application of manure during relatively short time windows when manure application is appropriate from a soil and crop management perspective. Even in situations where rapid incorporation of manure with a tillage tool is used to maximize the rate of incorporation of ammonia into the soil rather than allowing it to volatilize into the atmosphere, the odor releases that occur during application can be reduced significantly. This increases the number of appropriate management options for the livestock and crop producer.

E. COLI AND TOTAL COLIFORMS

A three-log decrease in *E. coli* was observed after treatment with ozone at 2.0 g/L and a one-log decrease in total coliforms after treatment with ozone at 1.0 g/L. Additional ozone treatment did not appear to decrease further *E. coli* and total coliform numbers in the slurry.

INORGANIC CHEMICAL ANALYSIS

The results of the inorganic analyses of the treated slurries are shown in Table IV. The pH of the slurry was increased in the oxygenated control from 6.5 to 7.1. The ozonated samples exhibited similar pH changes to 7.1, 6.9 and 6.9 for the 1.0 g/L, 2.0 g/L and 3.0 g/L ozone dosages, respectively. Ammonia concentration appears to be unchanged by ozonation. This agrees with previous studies (Singer and Zilli, 1975), which found that, in pure solutions, the kinetics of the reaction of ozone with ammonia to form nitrate is slow at pH values less than 9.1. Phosphate ion also appears to be unchanged by ozonation. The hydrogen sulfide concentration was lower in the oxygenated control than in the raw slurry, presumably due to air stripping effects. The 3.0 g/L ozone dosage contained more than twice the hydrogen sulfide concentration as the control. Since the time of aeration for both tests was the same, this might indicate that the ozone oxidized some of the sulfur-containing organic compounds, such as mercaptans, releasing sulfides. However, the sulfide concentration still remained lower than that of the raw swine slurry.

The results of the COD analysis showed no significant change due to ozonation of the swine waste slurry. However the BOD increased between the oxygenated control and the 1.0 g/L ozone dose by approximately 14%. The BOD of the 2.0 g/L dosed sample then decreased to approximately that of the control, while the 3.0 g/L dosed sample had a 22% reduction in BOD, showing that ozone is capable of oxidizing BOD.

OZONE DEMAND

The effluent gaseous ozone concentration was measured periodically during a 6 hour ozonation experiment (See Figure 1). As the ozone leveled off after 3.0 grams of ozone had been added to the slurry, 3.0 g/L was chosen as the maximum dosage to be used in subsequent experiments. To determine possible trends with increased ozone dosages, separate batches of slurry were exposed to ozone dosages of 1.0 g/L, 2.0 g/L and 3.0 g/L. The ozone demands exerted by the slurry are shown in Table V. The

ozone demand curves for the three replicate experiments of 2.0 g ozone dosages are plotted in Figure 2. The 2.0 g/L ozone dosage, (labeled trial number 1), was performed on the same day as the 1.0 g/L and 3.0 g/L ozone dosages. The repeats of 2.0 g/L ozone dosage (trials no. 2 and 3) were both performed two weeks later. The swine slurry used in trials 2 and 3 appeared to be more viscous, and vigorous stirring was difficult. The ozone demand measured after 10 minutes for the 1.0 g/L, 2.0 g/L and 3.0 g/L dosages all were 90% to 98% of the influent ozone. The duplicate 2.0 g/L dosages had ozone demands of 81% and 85% at a 10 minute ozonation time. After ozonation for 40 minutes the ozone demand was similar in all three 2.0 g/L dosage experiments, likely due to breakdown of solids, allowing for more efficient stirring. As our ozonation system was not designed to maximize mass transfer of ozone into the slurry, with a more efficient contact system, this ozone dosage might be reduced.

TABLE IV. CHEMICAL ANALYSIS OF RAW, OXYGENATED AND OZONATED SWINE SLURRY

WASTE TREATMENT	pH	COD (mg/L)	BOD ₅ (mg/L)	Nitrate (mg/L)	Phosphate (mg/L)	Ammonia (mg/L)	Hydrogen Sulfide (mg/L)
Raw	6.48						21.4
Oxygenated	7.07	54,200	29,800	71.3	1,080	12,900	8.0
1.0 g/L DOSE	7.13	58,100	34,100	80.7	1,180	14,900	10.8
2.0 g/L DOSE	6.86	46,900	29,200	73.2	1,190	13,200	16.0
2.0 g/L DOSE*	6.90	76,500	26,200	79.9	1,620	13,200	10.7
2.0 g/L DOSE*	6.90	73,400	24,200	69.8	1,300	13,600	13.2
3.0 g/L DOSE	6.89	52,700	23,300	73.8	1,220	12,800	16.4

NOTE: *-indicates samples taken at a later date, higher COD is not reflective of an increase caused by ozonation, but a higher raw sample COD.

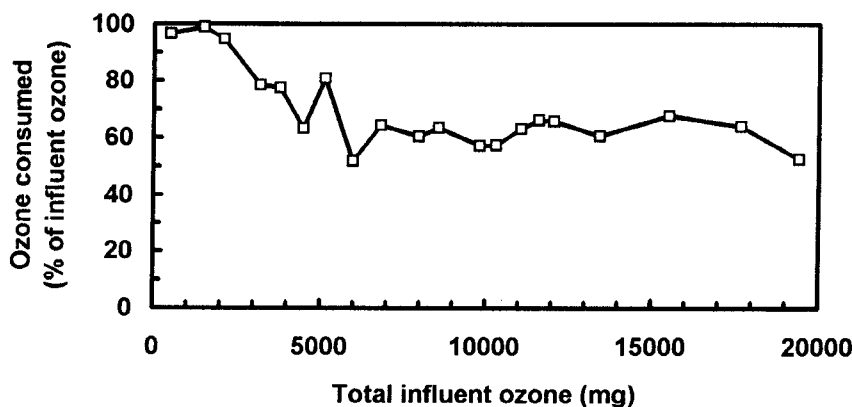


Figure 1. Long term ozonation of stored swine waste slurry.

TABLE V. OZONE DEMAND

Ozone dose (g/L)	Total ozone consumed (mg)	Ozone consumed (as a percent of influent ozone)
1.0	895	89.5
2.0 (test #1)	1480	74.1
2.0 (test #2)	1480	73.9
2.0 (test #3)	1510	75.7
3.0	2450	81.5

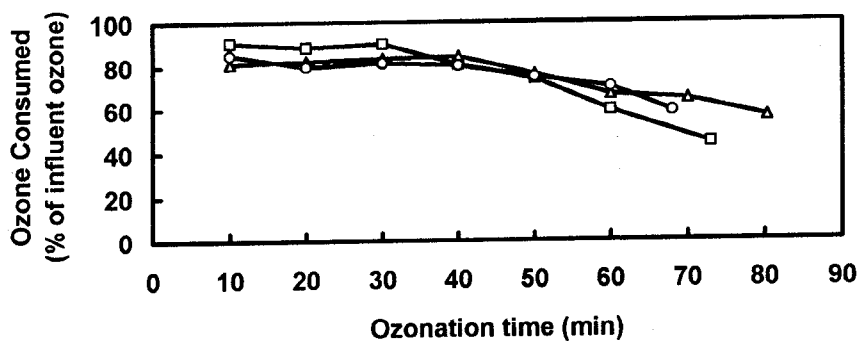


Figure 2. Amount of ozone consumed by the swine manure slurry, (□: trial 1, Δ: trial 2, ○: trial 3).

Conclusions

- Ozonation at a rate of 1 g/L or greater removes the phenolic bacterial metabolites phenol, p-cresol, and p-ethylphenol and the indolic bacterial metabolite 3-methylindole which contribute to odor from swine manure to non-detectable levels.
- On the basis of the median responses of the odor sensory panel intensity measurements, using paired comparisons, ozonation at a dose of 1 g/L or higher results in a perceptible reduction in odor intensity compared to raw manure and oxygenated manure. The odor-reducing effects of ozonation are additional to those caused by release of gases caused by oxygenation or agitation.

3. On the basis of the median responses of the odor sensory intensity measurements made by the panel using the 1-butanol olfactometer (ASTM E544-75), there were no perceptible changes in odor intensity among the 1, 2, or 3 g/L ozone doses.
4. Ozonation does not cause changes in levels of nitrogen; phosphorus; chemical oxygen demand; or volatile fatty acids, including acetic, propionic, butyric, isobutyric, isovaleric and n-valeric acids.
5. Oxygenation and ozonation increase the pH of the slurry from the acidic range for stored swine manure to near neutrality for oxygenated or ozonated swine manure.
6. *E. coli* levels were reduced by three log units and total coliform levels were reduced by one log unit due to ozonation.
7. Reduction of concentrations of odor-producing metabolites and perceived odor intensity occurred in the presence of relatively large concentrations of oxidizable organic matter. There appears to be preferential oxidation of odorous metabolites over other forms of organic matter.
8. The findings of this study indicate that ozonation is a viable process to reduce odor levels prior to land application of swine slurry. This can be accomplished without altering the nutrient content or increasing concentrations of the primary pollutant, nitrate ion.

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Key Words

Ozone; Ozonation; Swine Manure; Odor Control; Phenolic Compounds;

Résumé

L'utilisation de l'ozone pour lutter contre les substances à l'origine des mauvaises odeurs du purin de porcherie a été étudiée. De l'ozone en phase gazeuse a été injecté par bullage dans une cuve contenant le purin liquide, agité en permanence, selon un procédé par cuvée. Des échantillons de 1-L de purin ont été ozonés avec des taux de 1,0-2,0-3,0 g/L. Des mesures olfactométriques ont montré une réduction significative des odeurs en comparaison avec les échantillons bruts ou simplement traités à l'oxygène. Les teneurs en acides gras volatils, nitrates, phosphates et ammonium n'ont

pas été modifiées par l'ozonation. La demande biologique en oxygène (DBO) et la demande chimique en oxygène (DCO) n'ont pas été modifiées de façon significative. Les concentrations en métabolites phénoliques odorants des microorganismes (c'est à dire = c.a.d. phénol, p-crésol et p-éthylphénol) et les métabolites indol (c.a.d. indol et 3-méthylindol) ont été réduites en dessous de la limite de détection. Les concentrations en sulfure d'hydrogène ont légèrement diminué avec augmentation concomitante des sulfates. Le nombre d'*E. coli* a été réduit d'un facteur égal à trois logs, et les coliformes totaux ont diminué d'un log après un traitement en ozone égal à 1 g/L.

Les résultats de cette étude ont démontré clairement que, au pH étudié (pH = 7), l'ozonation est efficace pour l'élimination des substances malodorantes associées au stockage de purin de porcheries et pour tuer les bactéries potentiellement pathogènes sans augmenter la concentration des polluants associés (c.a.d. nitrate et phosphate) et sans provoquer l'oxydation de l'ammonium, qui est un aliment important des installations.

Zusammenfassung

Der Einsatz von Ozon zur Beseitigung störender Chemikaliengerüche in flüssigem Schweinegülleschlamm wurde untersucht. Ozon wurde gasförmig direkt in flüssig gelagerte Schweinegülle in einen kontinuierlich gerührten Batchreaktor eingeblasen. Proben von einem Liter dickflüssiger Schweingülle wurden mit 1,0, 2,0 und 3,0 g Ozon pro Liter behandelt. Olfactometrische Bestimmungen zeigten eine deutliche Verminderung des Geruchs in den ozonisierten Proben im Vergleich zu unbehandelten und nur mit Sauerstoff behandelten Proben. Flüchtige Fettsäuren, Nitrat-, Phosphat- und Ammoniumgehalte wurden durch die Ozonisierung ebenfalls nicht verändert. Der BOD und der COD wurden durch die Ozonisierung ebenfalls nicht verändert. Die Konzentrationen von stark riechenden, phenolartigen biologischen Metaboliten (z.B. Phenol, p-Kresol und p-Ethylphenol) und stark riechenden indolartigen, mikrobiologischen Metaboliten (z.B. 3-Methylindol und Indol) wurden durch die Ozonbehandlung auf nicht nachweisbare Konzentrationen verringert. H₂S-Konzentrationen wurden schwach verringert, bei gleichzeitigem Sulfatanstieg. *E. coli* wurden um drei Log-Stufen und die gesamten Coliforme eine Log-Stufe durch die Behandlung mit Ozon von 1 g/L vermindert.

Die Ergebnisse der Studie zeigen deutlich, daß bei den gegebenen pH-Werten (7) Ozon sehr wirksam zur Geruchsbekämpfung und Abtötung pathogener Keime in Schweinegülle eingesetzt werden kann, ohne dabei die Gehalte von anderen Belastungen zu erhöhen (z.B. Nitrat und Phosphat) und ohne Ammonium zu oxidieren, das ein wertvoller Pflanzennährstoff ist.