AN EVALUATION OF LIQUID DAIRY
MANURE TREATMENTS BY BIOLOGICAL,
CHEMICAL AND ORGANOLEPTIC
TECHNIQUES

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ABSTRACT

AN EVALUATION OF LIQUID DAIRY MANURE
TREATMENTS BY BIOLOGICAL, CHEMICAL
AND ORGANOLEPTIC TECHNIQUES

By

Charles C. Stallings

Various compounds have been added to manure to
prevent the formation or release of malodors. Under dif-
ferent conditions inconsistent results have been recorded.
The source (species) of manure appears to play a dominant
role in efficacy of the compound added. This study was
designed to test various compounds now in use plus some
others using fresh and decomposed liquid dairy manure.

In Experiment I fresh liquid dairy manure (13
percent dry matter) was treated with paraformaldehyde
(7000; 10,000; 30,000 PPM), acrolein (1 and 100 PPM),
H_3PO_4 (657; 1000; 10,000 PPM), $NaClO_4$ (250; 500; 2000 PPM),
H_2O_2 (75; 150; 300 PPM) or $KMnO_4$ (250; 500; 1000 PPM).
Paraformaldehyde at 7000 and 30,000 PPM markedly reduced
microbial counts below control values for 22 days. H_3PO_4
at 10,000 PPM and $NaClO_4$ at 2000 PPM slightly reduced
microbial counts at day one and eight, but by day 15 values

were similar to control. H_3PO_4 at 657 PPM slightly reduced counts at eight and 15 days.

The pH of paraformaldehyde and H_3PO_4 treated manure tended to be below those of control manure. The pH was inversely related to treatment concentration. The group mean for $NaClO_4$ treated manure was lower than pH from control manure but pH was not inversely related to treatment concentration. These changes in pH should not be extreme enough to cause problems when added to the soil.

Two days after addition of paraformaldehyde to manure concentration of ammonia in the air space over fresh manure was lower than control (p < .05). This trend continued for the duration of the experiment (21 days) indicating decreased decomposition and odor production. At day seven 2000 PPM $NaClO_4$ treated manure had greater concentrations than the two lower treatment concentrations (p < .005).

Fresh manure treated with paraformaldehyde at 7000 and 10,000 PPM reduced odor offensiveness to below "faint offensiveness" compared to control at approximately "definite offensiveness." Similarly odor strength was reduced. $KMnO_4$ at 1000 PPM reduced offensiveness to just above "faint offensiveness" compared to control at above "definite offensiveness."

In Experiment II decomposed liquid dairy manure (one percent dry matter) was treated with lime (5000 and

10,000 PPM), paraformaldehyde (1000; 5000; 10,000 PPM), H_2O_2 (100 and 500 PPM) or $KMnO_4$ (500 and 1000 PPM). Lime and $KMnO_4$ increased pH above control manure. Paraformaldehyde tended to decrease pH.

Offensiveness ratings at day one were reduced by 500 PPM H_2O_2 and 500 and 1000 PPM $KMnO_4$ to below "faint offensiveness" compared to control at approximately "strong offensiveness."

The same additives were evaluated in Experiment III and Experiment II. Dry matter of the partially decomposed liquid dairy manure used in Experiment III averaged 5.6 percent. Microbial numbers were not reduced at day one, but by day eight paraformaldehyde reduced counts. Microbial numbers were inversely related to treatment concentration.

As in Experiment II, pH's of lime and $KMnO_4$ treated manures were greater than control. Paraformaldehyde treated manure tended to be lower than control. These pH changes would probably not cause problems in the soil.

Lime treated manure had higher total ammonia (NH_3 and NH_4^+) concentrations than control manure ($p < .05$) at day four. At day 11 paraformaldehyde treated manure had total ammonia concentrations lower than control ($p < .005$). Total ammonia concentration was inversely related to treatment concentration.

Offensiveness ratings were inconsistent, but $KMnO_4$ tended to reduce odor offensiveness below that of control

at all three periods evaluated, although not below the "faintly offensive" rating.

Experiment IV, using decomposed liquid dairy manure (4.7 percent dry matter), evaluated paraformaldehyde (5000 vs. 10,000 PPM), H_2O_2 (100 vs. 500 PPM) and $KMnO_4$ (500 vs. 1000 PPM) to determine which treatment concentration to test further. Paraformaldehyde (5000 PPM), H_2O_2 (500 PPM) and $KMnO_4$ (500 PPM) were chosen and used to compare treatments against themselves. Paraformaldehyde did not decrease offensiveness in decomposed manure and possibly increased it. H_2O_2 decreased offensiveness consistently at 0.5 and 1.5 hours after addition possibly up to 30 to 32 hours. These results were complicated by foaming. $KMnO_4$ reduced offensiveness possibly within six to eight hours until eight days at which time the experiment was terminated. Data seem to indicate results will depend to some degree on treatments compared at one time.

In Experiment V decomposed liquid manure (five percent dry matter) was treated with Odor Mask (1430 PPM), Pit-Zyme (360 PPM) or Sep-Zyme (360 PPM). Odor Mask was found to increase offensiveness at this concentration. Pit-Zyme decreased offensiveness at day eight. Sep-Zyme "O" did not change offensiveness rating. Further study needs to be made with these compounds.

Results of this study indicate certain treatments evaluated were effective in changing odor produced from

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fresh as well as decomposed dairy waste. Most of these
changes could be attributed to either antimicrobial or
oxidative properties of the additive that prevented forma-
tion of malodors or destroyed malodors already produced.

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Finally, my thanks to my wife, Martha Ann, for assistance in preparing this manuscript and making it all worthwhile.

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I. INTRODUCTION

Liquid manure systems have become more common due
to the increase of intensive dairy production in many areas
of the country. One reason is that liquid manure can be
handled mechanically with a minimum input of labor. A
disadvantage of this system is the greater volume of waste
to be handled and disposed of, due to the necessity of
adding water to get manure into a liquid form. Another
drawback is increased odor problems associated with this
type of manure handling system.

Over 45 compounds have been identified in odorous
air over animal wastes. Most of these are reduced organic
compounds that are intermediate or end products of anaerobic
decomposition. Some of these gases are of a toxic nature
and are a concern to dairy farmers if present in sufficient
quantities. Both human and animal deaths have occurred in
isolated instances under enclosed conditions. Although
these toxic gases present problems at certain times, odors
probably receive the greatest amount of attention and com-
plaints.

Odors can be released during manure storage as well
as when applying to the land. The latter is usually the

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biggest producer of odors. Most odor problems can be pre-
vented by proper manure management techniques, but with
the encroaching suburbs into agricultural areas, many
farmers find themselves with nonrural neighbors who object
to odors more than do usual rural residents. As a result
some situations necessitate the use of additives to con-
trol the release of odorous compounds into the atmosphere.
This study was undertaken to evaluate certain additives
presently in use as well as some that may have potential
use.

II. LITERATURE REVIEW

Characteristics of the Nose

The perception of an odor is a very complex process in that many intricate physiological mechanisms are involved. Because of this complexity the odor code has not been entirely elucidated, but many of the essential details are known.

For an odor to be detected it must enter the nasal cavity by the exterior nares and travel to the olfactory membranes that lie in the superior part of each nostril. Amoore et al. (1964) describe these organs as being two patches of yellowish tissue, each about 2.4 sq. cm. Embedded in these olfactory membranes are two types of nerve fiber which are involved in detection.

The major type of fiber is composed of bipolar nerve cells derived originally from the central nervous system, and there may be as many as 100 million of these cells in the olfactory epithelium (Guyton, 1971). These receptor cells have hairs or cilia that project into the mucus that coats the inner surface of the nasal cavity, and it is theorized that these hairs react to odorous molecules. These hairs in turn act to stimulate the olfactory cells,

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which cause an impulse to travel to the brain where it is
integrated and interpreted in terms of the quality and
quantity of the odor.

The lesser type of nerve fiber found in the
olfactory membrane is the trigeminal nerve, which is sensi-
tive to certain kinds of molecules. Montcrieff (1946)
describes this type of sensitivity by a dog that has had
the olfactory nerve severed but is still sensitive to
ammonia and other irritants. This chemical sensitivity
seems to be distinct from smell, and the receptors are the
free nerve endings of the trigeminal nerve.

The olfactory cleft is yellow in color compared
with the reddish tint of the interior surface of the nasal
cavities. Moncrieff (1946) states that the pigment appears
to be connected to the mechanism of the olfactory apparatus.
Moulton (1970) reports that in most mammals the olfactory
epithelium contains retinol, beta-carotene and at least
four noncarotenoid pigments considered to be chromopro-
teins. The yellowish-brown color is probably from the
noncarotenoid pigments. Theories implicating pigments in
the primary olfactory transduction process have many
difficulties, but the dense concentration of olfactory
pigments in some species imply some functional role.

Properties of Odorants

All odorous substances logically have certain
common basic properties since specific physiological

reactions must occur for an odor to be perceived. Backman (1917) concluded that both aqueous and lipoid solubility are necessary for an odorous molecule to be detected. Montcrieff (1946) postulates that odorous molecules must be volatile and thus have a vapor pressure. This volatility allows the molecules of the odorant to come into contact with the olfactory hairs which will initiate an olfactory response. Therefore a substance with a low vapor pressure will have fewer molecules in the air compared with a substance with a high vapor pressure.

Miner (1974) compiled a list of certain basic properties that have been observed in relation to odors:

1. Only volatile substances are odorous.

2. Air movement into the nasal cavity is necessary to feed the receptors.

3. When air movement stops, odor sensation vanishes.

4. Water, though having the characteristics of other odorants, has no odor (as detected by humans).

5. Gases such as oxygen and nitrogen have no odor.

6. Exposure to an odor produces a high initial response and a declining response with continued contact (adaptation).

7. A strong odorant completely exhausts the capacity to perceive the odor after 2 or 3 minutes of exposure (fatigue).

8. A change in odor sometimes occurs on dilution of the odorant.

9. Some animals have a better developed sense of smell than humans.

10. Isomers (having the same chemical composition) have widely differing smells.

11. Some compounds with widely differing chemical characteristics have similar smells.

12. Some odorants are perceived at a concentration of one millionth that of others.

The necessity of odorous molecules being both water and lipid soluble is explained by Amoore et al. (1964). Water solubility enables the molecules to reach the nerve endings which are covered by a watery film (mucus), and lipid solubility allows them to penetrate the nerve endings through the lipid layer that forms part of the surface membrane.

A scientifically valid odor theory must meet several criteria. Schultz (1964) explained that a valid odor theory must explain odor thresholds, suprathreshold intensity, adaptation to odors, differences in quality of odors, differences in odor relationship to chemical characteristics and still must follow the biochemical and physiological information known about the olfactory sense organ. This rigorous set of demands has hindered development of a completely valid odor theory.

In an attempt to unify differing aspects of olfaction Montcrieff (1966) described the mechanism as occurring in six stages:

1. The molecules of a volatile substance are lost to the atmosphere.

2. Some of the molecules, inspired with air into the nasal cavity, are directed to the olfactory receptors.

3. The odorous molecules are adsorbed on appropriate sites on the olfactory nerve cells.

4. The adsorption is accompanied by an energy change.

5. An electrical impulse, generated by the energy change, travels from the olfactory receptor to the brain.

6. The brain processes the information and transmits the sensation of smell.

Theories of Odor Perception

The first theories dealing with odor perception were formulated in the late 1800s and early 1900s. Montcrieff (1946) explained that most early theories were concerned with vibrations, and many theorized that actual contact of the odorous molecules with the olfactory region was unnecessary.

Most of the theories to date differ in the mechanism by which the odorant transmits the message to the olfactory nerve. Mechanisms that appear most feasible are molecular vibration, chemical reaction and physical adsorption.

Dyson (1938) introduced the vibrational theory which postulates that odorous substances possess intramolecular vibrations. Theoretically, these vibration frequencies fit specific receptor sites in the nose producing the initial stimulus for odor perception. Wright (1964) explains that the volatility, solubility, adsorbility, etc. may affect the odor quantity (strength), but the

quality of the odor will depend on the intra-molecular vibrations.

The chemical theory was proposed and evaluated by several researchers, but now has been largely discounted. The theory assumes the odorant molecules are changed via a chemical reaction after being adsorbed on the receptor sites, and this elicits an olfactory response.

Amoore (1963) proposed the stereochemical theory of odor perception. This theory involves a fit between the odor molecule and a receptor site. These sites are considered to be ultramicroscopic slots in the nerve-fiber membrane that have a distinctive shape and size. Amoore et al. (1967) have revised this original theory to allow for a two-dimensional instead of a three-dimensional fit. This is consistent with the theory that the cross-sectional area is the important steric characteristic of the odorant. Odor perception is stimulated by the energy change mediated by the adsorption of the odorant molecule on the olfactory nerve receptor site.

The penetration theory (Davies and Taylor, 1954) proposes that a puncture occurs in the lipoid membrane of the olfactory nerve when an odorous molecule is adsorbed. This leads to an unbalance of Na^+ and K^+ ions which is considered to be the stimulus for the olfactory perception process.

Barth (1970) summarized the major theories of olfaction and noted that all of them have two points in common:

1. Adsorption of the odorant molecule on the olfactory nerve is necessary for initiation of the process, and

2. The cross-sectional properties of the molecule are a controlling factor.

Odor Evaluation

An accurate qualitative and/or quantitative evaluation of an odor is difficult if not impossible. As a result many methods of evaluation have been developed most of which use a human odor panel.

Foster (1964) explains that even the most highly trained nose is variable. Therefore objective measurements necessitate the utilization of more than one nose. In other words any one person can produce an atypical response, but this can be moderated by using several noses. The likelihood that an atypical response will cause a misinterpretation is reduced in direct proportion to the number of persons on the odor panel.

A major problem with an odor panel is the possibility of olfactory fatigue. Barth (1970) observes that the initial response to an odor is strong, with a decreasing response with continued contact. Finally, after prolonged contact, the ability to perceive the odor is

exhausted. With a strong odorant this can occur in two to three minutes.

Montcrieff (1946) pointed out that odor fatigue is selective so that fatigue from one odor will not decrease the ability to perceive other odors. Baker (1964) observed that when background odors of similar type were present there was an inhibition of ability to evaluate the odor under study. However, when dissimilar background odors were present, enhancement of the ability to evaluate the odor under study was noted. He concluded that under no conditions should background odors be present in odor evaluation processes when exactness was desired.

Baker (1964) also tested the ability of odor panels to perceive odors at different environmental temperatures. Evaluation of odor was compared at environmental temperatures of 21°, 40° and 60°C. At 21° (room temperature) the panelists considered the odor to be dead compared to the 40° comparisons which they preferred. The 60° evaluations produced fleeting initial responses that were lost on second inhalation.

Mitchell et al. (1964) reported that the perception of odor is age and sex dependent. They observed that there is a progressive increase in olfactory perception thresholds from 8 to 25 years of age. After 25 the threshold remains relatively constant until around the age of 50 then declines. Women were observed to have a more sensitive

sense of smell than men, but it was not known if this was because of their sex or because fewer of them smoked.

Odor can be evaluated in terms of either strength (quantity) or quality. The most common method used to measure strength is by dilution to extinction (Miner, 1974). The odorant is diluted with an odor-free medium (usually air or water) until the odorant is just barely detectable. This is called the threshold value.

Odor strength is presented as either the threshold odor number (TON) or the odor intensity index (OII). The greatest dilution of the odorant with odor-free medium until the threshold is reached has been termed TON. The number of times an odorant must be diluted by half with an odor-free medium until the threshold is reached is called the OII. The odor intensity index is the more popular of the two methods.

Miner and Smith (1975) describe an instrument for field use which can relatively easily measure odor intensity. This instrument, called a scentometer, is a device that can mix air passed through activated carbon absorption beds (odor free air) with air from the environment (odorous air). This air mixture is then taken into the nostrils by the nasal outlets, and depending upon the size of the inlet port when the odor is first detected a dilution value can be determined.

Odor quality is more difficult to measure than odor strength. Burnett and Dondero (1968) attempted to measure odor quality by comparing treated liquid poultry manure to an untreated standard using an odor panel. They used a scale of similarity with 8 being "extreme similarity" down to 0 as "no similarity." Therefore a quantifiable number relates the treated manure to the standard untreated manure.

Ludington et al. (1969) used an odor panel to rate jars of manure from 0 as "not offensive" up to 10 as "very offensive." Jars were painted black so as not to bias the odor panel by seeing the manure. Cole et al. (1976) attempted to evaluate strength of odor as well as quality. Using an odor panel, quality was measured as above but strength was evaluated using a scale with 0 being "no odor" and 10 being "very strong." They concluded that the panelists could not distinguish between strength and offensiveness. In other words, a strong odor was usually an offensive odor.

In addition to the organoleptic methods of evaluating odors, several instruments have been used. The gas-liquid chromatograph (GLC) can separate and quantify the odorant compounds involved, but no measure of quality is obtained. The GLC has been found less sensitive than the nose in detecting odor (Kendall and Neilson, 1964). They concluded that panelists could detect odors in concentrations 10 to 100 times more dilute than the GLC.

Miner (1974) mentioned mass spectroscopy, thin-layer chromatography and even mechanical noses as being used in evaluation of odor, but none could equal the human nose in determining the quality and intensity of complex odorants.

Another approach is to capture an individual component of the odor by absorbing it in a solvent. Concentrations can then be measured by colorimetric or other techniques. Miner (1974) reviews methods for the capture and measurement of ammonia, hydrogen sulfide and mercaptans. The one or two components thus measured, do not necessarily give a good indication of the level of odor as importance of other components are ignored. Only a limited number of the gases have been routinely measured as parameters of odor intensity.

Compounds Involved in Odor Production from Animal Wastes

Miner (1974) has reported that about 45 compounds have been found in odorous air near animal wastes. He considers the amines, mercaptans, organic acids and heterocylic nitrogen compounds as being of greatest odor significance in air exposed to the products of anaerobic decomposition of livestock and poultry manures. His list of odorous compounds appears as Table 1. Most of the listed compounds are reduced intermediate or end products

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TABLE 1

Compounds Identified in the Air from the Anerobic
Decomposition of Livestock and Poultry Manure

Alcohols	Carbonyls	Esters
Methanol	Acetaldehyde	Ethyl formate
Ethanol	Propionaldehyde	Methyl acetate
2-Propanol	iso-Butyraldehyde	iso-Propyl acetate
n-Propanol	Hexanal	iso-Butyl acetate
n-Butanol	Acetone	iso-Propyl propionate
iso-Butanol	3-Pentanone	Propyl acetate
iso-Pentanol	Formaldehyde	n-Butyl acetate
	Heptaldehyde	
	Valeraldehyde	
	Octaldehyde	
	Decaldehyde	

Acids	Sulfides	Fixed Gases
Butyric	Dimethyl sulfide	Carbon dioxide
Acetic	Diethyl sulfide	Methane
Propionic		Ammonia
iso-Butyric		Hydrogen sulfide
iso-Valeric		

Amines	Nitrogen heterocycles	Mercaptans
Methylamine	Indole	Methylmercaptan
	Skatole	

Disulfides

Source: J. R. Miner (1974).

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of anaerobic decomposition sufficiently volatile to escape from the liquid phase.

Different gases have varying concentrations at which they can be perceived. Threshold limit values for various gases are shown in Table 2.

To evaluate the "total" quality of an odor it is almost impossible to add together the "subtotal" qualities of the individual gases. Baker (1964) reported that a mixture of two or more gases could be completely different from each individually. For example, sub-threshold concentrations of certain compounds when mixed together may or may not yield an odor. This interaction between gases can be either additive (the resulting odor is the sum of the individual components), synergistic (the resulting odor is greater than predicted by direct addition) or antagonistic (the resulting odor is less than expected by direct addition). He concluded that all three interactions will occur and synergism and antagonism were the rule and not the exception.

Most of Baker's results are based on mixtures of two compounds. Guadnagi et al. (1963) tested mixtures of up to ten odorants, and found the reactions are mostly additive rather than synergistic or antagonistic. Miner (1974) states that this would be anticipated in complex systems where the more common additive reaction outweighs the other unusual reactions. Apparently, extensive

TABLE 2

Threshold Limit Values* for Various Gases
Associated with Animal Waste Odors

Substance	Concentration 10^{-9} g/l
Acetaldehyde	360
Acetic Acid	25
Ammonia	35
n-Butyl acetate	710
Butyl mercaptan	35
Diethylamine	75
Dimethylamine	18
Ethylamine	18
Ethyl mercaptan	25
Isopropylamine	12
Methylamine	12
Methyl mercaptan	20
Triethylamine	100

*Threshold limit values refer to airborne concentrations under which nearly all workers may be repeatedly exposed without adverse effect.

Source: American Conference of Governmental Industrial Hygienists (1967).

interaction occurs to produce the odor perceived from the decomposition of animal waste. Thus, the odor which is smelled originates from many complex and different processes during the production of odorous gases plus their inter-action after escape from the liquid phase.

Ammonia and Amines

Merkel et al. (1969) detected ammonia and amines in the atmosphere of a swine building. White and Taiganides (1969) reported ammonia and amines in odors from dairy wastes using a GLC. Ulich and Ford (1975) used selective absorbents to show amines and possibly ammonia as important components of cattle feedlot odors.

Ammonia and amine formation result from decomposition of both animal and plant protein (Miner and Hazen, 1969). Urea, a constituent of urine, can be hydrolyzed to ammonia via urease (Sawyer, 1970). Also uric acid can be degraded to ammonia. The formation of ammonia and amines is shown in Figure 1a through 1d. The enzymes involved in these transformations are produced by microbes.

Ammonia is described as being pungent, sharp and somewhat irritating (Miner and Hazen, 1969). The amines have a similar odor, but very much more severe and longer lasting. Table 3 presents the odor thresholds of ammonia and some amines.

Amines are detectable at much lower concentrations than ammonia, and trimethylamine is the strongest amine

$$H_2N-\overset{\overset{O}{\parallel}}{C}-NH_2 \xrightarrow{\text{urease}} NH_3 + CO_2$$

urea   ammonia   carbon dioxide
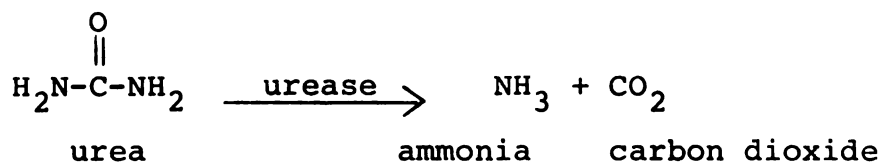
Fig. 1a.--Hydrolysis of Urea.

$$\overset{R}{\underset{COOH}{\overset{|}{H-\underset{|}{C}-NH_2}}} \xrightarrow{\text{deaminase}} NH_3 + \overset{R}{\underset{COOH}{\overset{|}{\underset{|}{C}=O}}}$$

amino acid   ammonia   α-keto acid
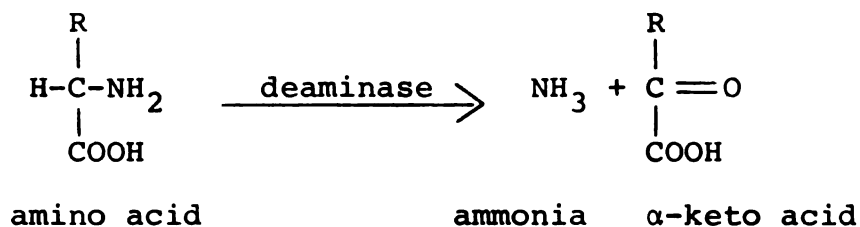
Fig. 1b.--Deamination of Amino Acids.

$$\overset{R}{\underset{COOH}{\overset{|}{H-\underset{|}{C}-NH_2}}} + \overset{R}{\underset{H}{\overset{|}{\underset{|}{C}=O}}} \xrightarrow{\text{transaminase}} \overset{R}{\underset{COOH}{\overset{|}{\underset{|}{C}=O}}} + \overset{R}{\underset{H}{\overset{|}{H-\underset{|}{C}-NH_2}}}$$

amino acid   ketone   α-keto acid   amine
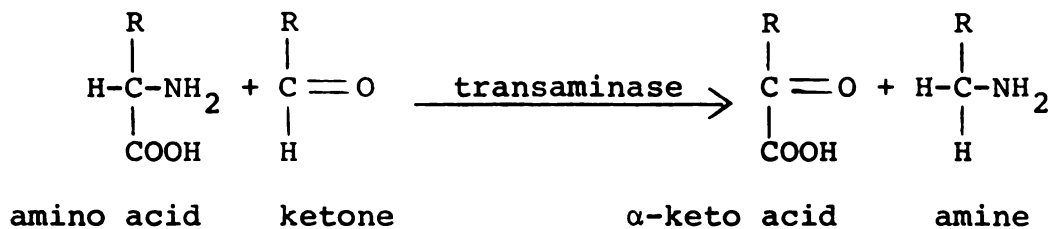
Fig. 1c.--Transamination of Amino Acids

$$R-CH_2-\overset{\overset{NH_2}{|}}{CH}-COOH \xrightarrow{\text{decarboxylase}} R-\overset{\overset{NH_2}{|}}{CH}-CH_3 + CO_2$$

amino acid   amine   carbon dioxide
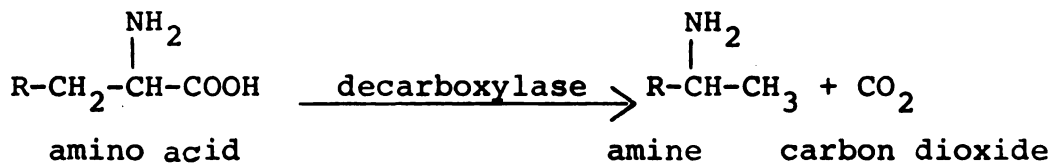
Fig. 1d.--Decarboxylation of Amino Acids.

Source of Fig. 1a and 1b: J. R. Bronk (1973).

Source of Fig. 1c and 1d: J. R. Miner and T. E. Hazen (1969).

TABLE 3

Odor Thresholds in Air

Compound	PPM (volume)
Ammonia	46.8
Methylamine	0.021
Dimethylamine	0.047
Trimethylamine	0.00021

Source: A. G. Stern (1968).

listed. Stephens (1971) considers all amines to have odors suggestive of feedlot areas.

Taiganides and White (1968) pointed out two significant properties of ammonia were being lighter than air and soluble in water. Thus ammonia moves in air throughout a building from the point of generation, and represents a significant loss of nitrogen from manure. Solubility in water allows liquid systems to keep much of the ammonia in the dissolved form.

Instances have been cited where ammonia levels caused discomfort to animals (Taiganides and White, 1968). In poultry houses, 20 PPM caused no sign of distress, but at 200 PPM, signs of discomfort were seen during the first few days, followed by loss of appetite and loss of weight. Birds exposed to 1000 PPM developed photophobia (fear of light) with very little mortality. Ammonia levels of 2000 PPM over a three to four week period caused keratocon-junctivitis (erosion of the cornea).

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A 30 kilogram gilt placed in an ammonia environment of about 280 PPM for 36 hours initially frothed at the mouth then had excessive secretions around the nose and mouth (Stombaugh et al., 1969). These excessive secretions persisted but frothing disappeared after a short time. A short, irregular respiratory pattern developed along with sneezing and head shaking. Convulsions occurred after 36 hours in this environment. After being taken from the environment the pig continued to have convulsions for three hours then appeared normal within a few hours.

Taiganides and White (1968) list ammonia as being an irritant of the throat and eyes. Coughing and frothing occur at high levels, and they consider 10 to 50 PPM acceptable for animals in confinement operations. With proper ventilation this can be achieved.

Miner and Hazen (1969) passed air from a swine building through a boric acid solution to capture ammonia and through acetic acid to collect the amines. They found ammonia concentrations to be below the threshold value previously given. They concluded either ammonia is not an important part of the odor or due to interaction with other odorous compounds a synergistic or additive reaction occurs allowing ammonia to be detected at concentrations below its threshold. The amines were not quantified, but methylamine, ethylamine and triethylamine were identified.

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Organic Acids

Deibel (1967) found butyric acid to be a component of decomposing poultry manure while fresh manure had none. Acetic, propionic, iso-butyric and iso-valeric acids were identified as components of chicken manure (Burnett, 1969). Bell (1971) found a correlation between the volatile fatty acid content and odor level in liquid poultry manure.

Volatile organic acids can be produced by the breakdown of protein and carbohydrates by microorganisms. Pathways for organic acid production from protein and carbohydrate are shown in Figure 2a and 2b.

$$
\begin{array}{ccc}
\text{H} & \text{H} & \text{H} \\
| & | & | \\
\text{R-C-COOH} \longrightarrow & \text{R-C-COOH} \longrightarrow & \text{R-C-COOH} \\
| & | & | \\
\text{NH}_2 & \text{OH} & \text{H} \\
\text{amino acid} & \text{hydroxy acid} & \text{volatile organic acid}
\end{array}
$$
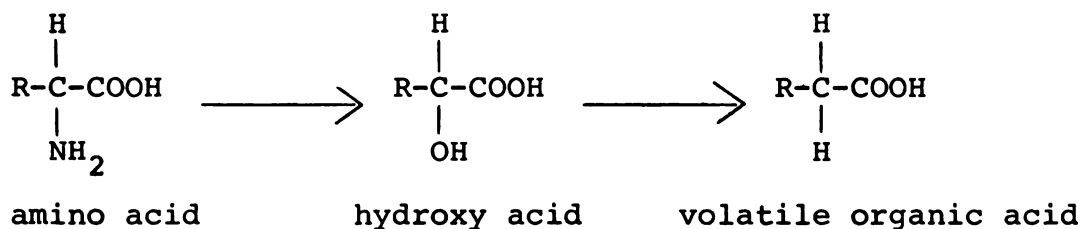
Fig. 2a.--Formation of Volatile Organic Acids from the Degradation of Amino Acids

$$
(C_6H_{12}O_6)n \longrightarrow C_6H_{12}O_6 \longrightarrow H_3C\overset{\overset{\text{O}}{\|}}{C}\text{-COOH} \longrightarrow R\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{H}}{|}}{C}}\text{-COOH}
$$

polysaccharide   monosaccharide   pyruvate   volatile organic acid
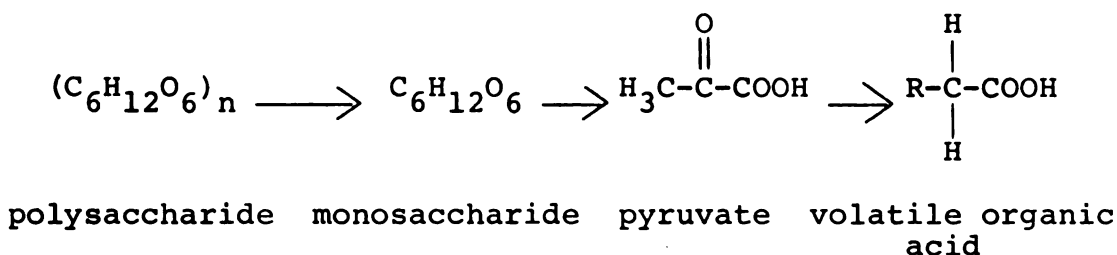
Fig. 2b.--Formation of Volatile Organic Acids from the Degradation of Carbohydrates.

Source of Fig. 2a and 2b: J. R. Bronk (1973).

Acetic acid is odorous at 1 PPM, and butyric acid at 0.001 PPM (Stephens, 1971). Miner (1974) states that butyric and valeric acids have very disagreeable odors while Gerrish (1974) describes acetic acid odor as similar to vinegar and propionic acid as similar to swiss cheese.

Miner (1974) describes a technique for the collection and measurement of volatile organic acids from the air. This is done by absorbing the VFA's in an alkaline solution, acidifying and distilling.

Hydrogen Sulfide, Disulfides, Sulfides and Mercaptans

Burnett and Dondero (1969) noted an increase in soluble sulfides with an increase in odor intensity in liquid poultry manure. Day et al. (1965) detected hydrogen sulfide in a swine unit. White et al. (1971) tentatively identified hydrogen sulfide, diethyl sulfide and dimethyl sulfide in air from liquid dairy waste using A GLC. A GLC and ionization mass spectrometer was used to confirm the presence of diethyl sulfide and dimethyl sulfide in dairy waste volatiles (Ifeadi et al., 1975). Ulich and Ford (1975) used selective absorption liquids to capture hydrogen sulfide, disulfides and mercaptans, and found all present in air above cattle manure. Fosnaugh and Stephens (1969) detected the mercaptans as being a component of feedlot odor.

White et al. (1971) state that decarboxylation of sulfur amino acids occurs with a release of amines and sulfur compounds. These sulfur compounds occur in several forms depending on the degree of breakdown. Under anaerobic conditions the sulfate ion is reduced to the sulfide ion which establishes an equilibrium with the hydrogen ion to form hydrogen sulfide. This is pH dependent.

Mercaptans (R-SH) have a structure similar to the alcohols (R-OH) except oxygen is replaced by sulfur. Mercaptans along with the other sulfur compounds are detectable at low levels in the atmosphere. Table 4 lists some of the common sulfur compounds, and concentrations

TABLE 4

Characteristics and Perceptible Concentrations
of Sulfur Compounds in Air

Substance	Odor Characteristic	Concentration causing faint odor 10^{-9} g/l
n-Butyl mercaptan	Strong, unpleasant	1.4
Carbon disulfide	Aromatic odor, slightly pungent	2.6
Ethyl mercaptan	Odor of decayed cabbage	0.19
Hydrogen sulfide	Odor of rotten eggs, nauseating	1.1
Methyl mercaptan	Odor of decayed cabbage or onions	1.1
Propyl mercaptan	Unpleasant odor	0.075

Source: J. P. Sheehy et al. (undated).

causing a faint odor in air. All of the compounds listed
have not been identified in the air from degradation of
animal wastes.

Of the sulfur compounds hydrogen sulfide occurs
most frequently in the atmosphere from animal waste decom-
position. Taiganides and White (1968) report that hydrogen
sulfide is heavier than air and thus will stay near the
floor in nonventilated and quiescent rooms. Also it is
soluble in water.

Animals exposed continuously to about 20 PPM
hydrogen sulfide have been described as being nervous,
having photophobia and anorexia (loss of appetite)
(Taiganides and White, 1968). At 50 to 200 PPM hydrogen
sulfide, vomiting, nausea and diarrhea may develop, and
at approximately 1000 PPM unconsciousness and death can
occur. Actual cases of hydrogen sulfide toxicosis in both
humans and animals have occurred in connection with storage
of manure.

Carbonyls

Carbonyls have been identified in a swine building
atmosphere using a GLC (Merkel et al., 1969; Hartung et al.,
1971). Bethea and Narayan (1972) found aldehydes as com-
ponents of odor evolving from beef cattle manure. Ifeadi
et al. (1975) identified carbonyls in dairy cattle waste.

Carbonyls get their name from the chemical carbonyl
group which is present in all aldehydes (R-$\overset{\text{H}}{\underset{}{\text{C}}}$=O) and

H
ketones (R-C-R). A scheme for their formation is in

Figure 3 as suggested by Miner (1974).

Hartung et al. (1971) say that carbonyls are

probably not the most noticeable offenders in air from

animal waste, but they can be penetrating and irritating

to the eyes and mucous membranes. The lower aldehydes,

such as formaldehyde, are suffocating at higher levels.

Hartung et al. (1971) found only one carbonyl

in the odor from liquid swine manure at a concentration

above the threshold value. They hypothesized that the

carbonyls that were present at concentrations below thresh-

old values would contribute to the overall odor through

additive interactions.

Indole and Skatole

Using a GLC Burnett (1969) identified indole and

skatole in the air over chicken manure. He found about

18 times more skatole than indole and concluded both were

a significant component of poultry waste odor. Bethea and

Narayan (1972) found both indole and skatole in the atmos-

phere from a steer confinement chamber.

Indole and skatole are both products of tryptophan

breakdown as indicated in Figure 4:

$$(C_6H_{12}O_6)_n \longrightarrow C_6H_{12}O_6 \longrightarrow H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-COOH$$

polysaccharide   monosaccharide   pyruvate

$$\xrightarrow[\text{conditions}]{\text{anaerobic}}$$

$$R-\overset{\overset{\displaystyle H}{|}}{C}=O$$

aldehydes

$$\xrightarrow[\text{conditions}]{\text{anaerobic}} \quad R-\overset{\overset{\displaystyle O}{\|}}{C}-R$$
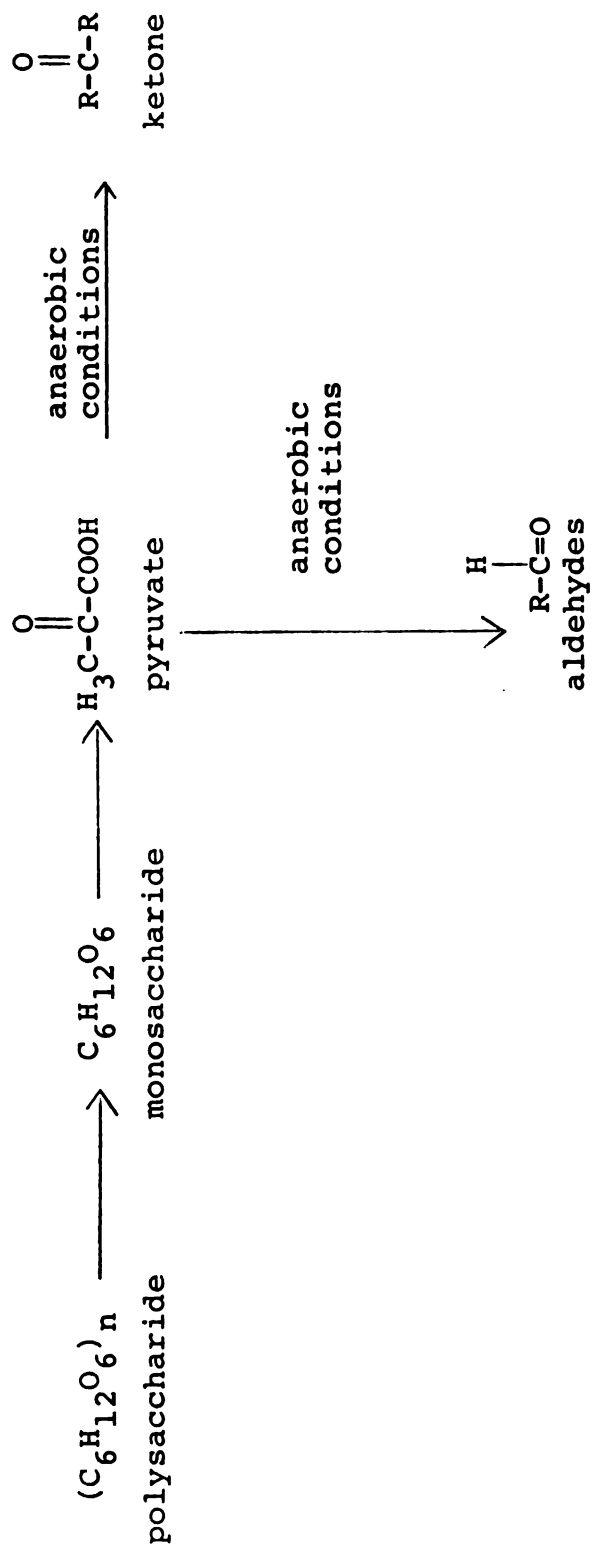
ketone

Fig. 3.--Formation of Aldehydes and Ketones by Anaerobic Decomposition.

tryptophan   skatole   indole
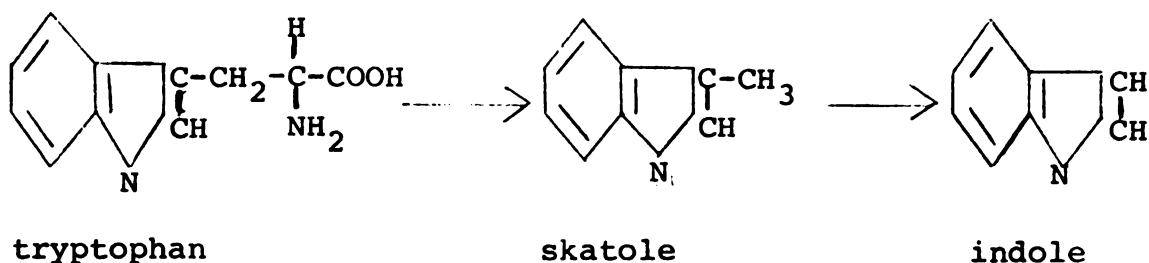
Fig. 4.--Breakdown of Tryptophan to Skatole and Indole.

Burnett (1969) considers indole and skatole to be
important because of their strong, harsh odors that
tenaciously tend to cling to clothing for long periods.
Summer (1971) lists skatole as having an olfactory thresh-
old at 7.5×10^{-8} PPM.

Alcohols

Deibel (1967) found ethanol to be one of the
chief components of decomposing poultry manure odor.
Bethea and Narayan (1972) identified methanol, ethanol and
2-propanol in the atmosphere of a beef cattle confinement
chamber. Merkel et al. (1969) identified alcohols as being
present in a swine building atmosphere.

Alcohols are characterized by the hydroxy group
(R-OH), and are the result of the anaerobic fermentation
of carbohydrates as noted in Figure 5.

$$(C_6H_{12}O_6)_n \longrightarrow C_6H_{12}O_6 \longrightarrow H_3C-\overset{O}{\underset{||}{C}}-COOH \longrightarrow R-OH$$

polysaccharide   monosaccharide   pyruvate   alcohol
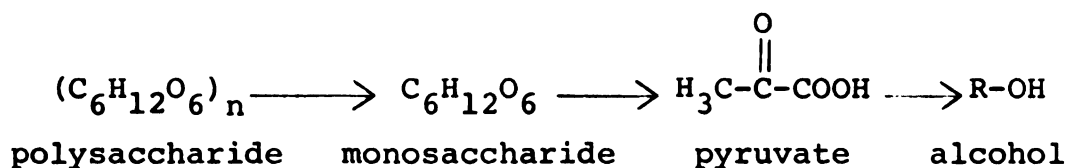
Fig. 5.--Formation of Alcohols by Anaerobic Decomposition.

Alcohols have olfactory thresholds that are high compared to many other components of anaerobic decomposition. Some of the more common ones are shown in Table 5. These values would lead us to believe that alcohols as a class are relatively unimportant as to odor intensity; however, their additive or synergistic effects are unknown.

TABLE 5

Olfactory Thresholds and Maximum Allowable
Concentrations for Some of the Alcohols

Pollutant	Threshold (PPM)	Max. Allowable Concentrations (PPM)
iso-Butanol	40	120
n-Butanol	11	100
Ethanol	50	1000
Methanol	5900	200

Source: W. Summer (1971).

Esters

Bethea and Narayan (1972) found the esters ethyl formate, methyl acetate, iso-propyl acetate, iso-propyl propionate and iso-butyl acetate as being components of odors from dairy cattle waste.

The formation of the esters involves the condensation of an alcohol and an organic acid. This reaction is shown in Figure 6.

$$R\text{-}OH \quad + \quad R\text{-}COOH \longrightarrow R\text{-}COOR'$$

alcohol   organic acid   ester
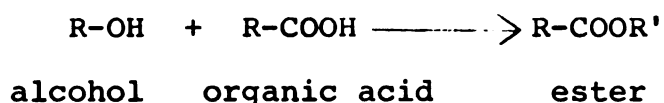
Fig. 6.--Formation of an Ester by Condensation of an
Alcohol and an Organic Acid.

The esters like the alcohols have relatively high
threshold values. Table 6 shows the odor threshold values
and maximum allowable concentrations for some esters.

TABLE 6

Olfactory Thresholds and Maximum Allowable
Concentrations for Some of the Esters

Pollutant	Threshold (PPM)	Max. Allowable Concentrations (PPM)
iso-Butyl acetate	4	200
n-Butyl acetate	7	150
Methyl acetate	200	200
iso-Propyl acetate	30	200
n-Propyl acetate	20	200

Source: W. Summer (1971).

Carbon Dioxide and Methane

Carbon dioxide and methane have been identified
in the atmosphere of a swine building (Day et al., 1965;
Skarp, 1975). Taiganides and White (1968) describe carbon
dioxide and methane as being colorless, odorless gases.
Carbon dioxide is heavier than air and highly soluble in
water, while methane is much lighter than air and only
slightly soluble in water.

Carbon dioxide is produced both in aerobic and anaerobic animal waste systems by microorganisms and usually in large amounts. Methane on the other hand will be produced only under anaerobic conditions under narrow ranges of temperature and pH. A pH below 6.5 inhibits methane producing bacteria (Miner, 1971).

Both gases are considered relatively unimportant in the total odor system since neither has an odor. Taiganides and White (1968) describe them both as asphyxiants having physiological effects only at high concentrations.

Taiganides and White (1968) point out that there is no scientific evidence that odors will affect the health of animals and humans even though these gases cause irritation. This was indicated by Winslow and Greenberg (1918) who kept young guinea-pigs under normal conditions and others of similar age in an atmosphere of foul smelling air that had been passed over human and dog feces. They found that during the first week the controls grew at a faster rate, but during the second week the two groups grew about equally. Therefore a foul odor per se apparently has no permanent ill-effect on growth.

Odor Production from Animal Wastes

Odor produced from decomposing animal waste varies with species of animal, ration consumed, amount of moisture

in the waste, temperature, pH and many other parameters plus some unknown factors.

Manure serves as a substrate for many microorganisms present in the environment. The subsequent breakdown of the complex manure components by these microorganisms produce odor. Microorganisms utilize the energy in manure and produce degradation products "further down" the metabolic chain.

Miner (1974) lists several ways of preventing formation of odorous breakdown products by maintaining an environment unsuitable for anaerobic microorganisms. They are: (a) provide an aerobic environment, (b) maintain the moisture content so low that growth is inhibited, (c) control the pH so that growth is inhibited, (d) adjust the temperatures outside the region of bacterial growth, (e) add a chemical which inhibits biological growth or (f) change the microbial population so the formation of specific odorous compounds is avoided.

Miner (1974) shows applications and limitations of each technique in Table 7.

Effect of Substrate on Odor Production

The type of manure produced will vary from animal to animal. The obvious example is the difference between ruminants and nonruminants. Miner (1971) explains the difference as being a basic difference in type of ration

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TABLE 7

Use of Restrictive Environments to Control
the Formation of Manure Odors by
Anaerobic Decomposition

Technique	Application	Limitation
Aerobic environment	Oxidation ditch Aerated lagoon	Power and equipment costs
Moisture control	Manure dryers Power ventilated poultry manure pits	Manure transport Control of water leaks
pH adjustment	Lime application	Ammonia release, cost, solids increase
Temperature	Freezing	Cost-handling
Chemical inhibition	Chlorination	Cost
Microbial population adjustment	Digestive aids	Technology

Source: J. R. Miner (1974).

consumed. Ruminant diets contain cellulose fibers while nonruminants contain little if any cellulose. Consequently ruminant feces usually contain greater amounts of cellulose fiber than nonruminants.

Composition of animal manure is dependent on digestibility, protein and fiber content of the ration, and the nature of feed additives in that ration (Loehr, 1968). These factors can directly affect the type of microorganisms that predominate in the manure. Rations high in cereals will produce feces with appreciable levels of starch. Miner (1971) states that fecal carbohydrates will stimulate both bacterial and fungal growth. The carbohydrates are broken down to organic acids, aldehydes, ketones and alcohols which can also stimulate growth of some types of microbiota. These products are all components of odor.

Ration composition has a major effect on the amount of waste produced as noted in Table 8 (Wells et al., 1972). The feed:waste ratio is much greater for the all concentrate ration, i.e., more of the concentrate feed is utilized and not excreted compared to the 12 percent roughage diet.

Loehr (1968) states that ruminants tend to produce relatively large amounts of fecal wastes compared to amounts of feed consumed. Simple stomached animals consume diets more highly digestible, therefore they usually produce less

["

microbial decomposition as nonruminant feces and thus, the
amount of odor produced may be less.

As feces composition varies from species to species
so will urine. Blosser (1964) observed that the urinary
wastes from herbivores tend to be more alkaline than urine
from carnivores or omnivores. Diets of herbivores contain
higher concentrations of potassium, calcium and magnesium
than diets of carnivores or omnivores and presence of these
elements increase pH of the urine. This may have a direct
affect on odor production since pH determines the degree
of volatility of odorous gases.

The production of odor from decomposing manure may
also be affected by compounds excreted in the waste such
as antibiotics, feed additives, plant phenolic residues,
etc. Morrison et al. (1969) suggested that antibiotics
excreted in the waste of beef cattle might have a direct
effect on decomposition characteristics. They concluded
that this effect could be by the antibiotic decreasing
the rate of breakdown by inhibiting the degradative micro-
organisms or antibiotic resistant microorganisms pro-
liferating and producing metabolites contributing to the
enhancement or abatement of feedlot odor.

As stated before, the waste characteristics will
vary depending on the type of ration consumed, but there
are certain basic characteristics that can be assumed for
each species. Dale and Day (1967) gave some of the average

physical properties of dairy cattle manure shown in

Table 9. This data was collected from seven high producing

dairy cows with an average weight of 1500 pounds.

TABLE 9

Some Properties of Dairy Cattle Manure

Average daily manure production	107.8	lbs.
Portion of manure as feces	68.8	percent
Portion of manure as urine	31.2	percent
Percent body weight	7.22	percent
Moisture content of feces	82.7	percent
Moisture content of urine	95.1	percent
Average moisture content of manure	87.5	percent

Source: A. C. Dale and D. L. Day (1967).

Miner and Smith (1975) compiled Table 10 comparing

the manure production of different species per 1000 live-

weight units.

On an equal weight basis the dairy cow produces

more feces and urine than any of the other domestic animals.

This is mainly due to the type and amount of feed since

dairy cows are fed for high levels of production. Poultry

excrete nitrogen as uric acid along with the feces, hence

no liquid urine is produced.

Dale (1971) observed that most of the odor control

research to that date had been done with either swine or

poultry wastes since odors from swine and poultry production

units were more objectionable. Since that time, concen-

trated confinement production units have become more

TABLE 10

Manure Production of Domesticated Livestock per 1000 Liveweight Units (lb. or kg.)

	Raw Manure (wt./day)	Feces: urine ratio
Dairy cow	82	2.2
Beef feeder	60	2.4
Swine feeder	65	1.2
Sheep feeder	40	1.0
Poultry layer	53	---
Poultry broiler	71	---
Horse	45	4.0

Source: American Society of Agricultural Engineers (1973).

common in the dairy industry with a resulting increase in odor problems.

Effect of Moisture on Odor Production

Ludington et al. (1969) reported that there was an apparent relationship between moisture content and level of offensiveness of manure. Sobel (1971) used chicken manure to show that as the percent moisture decreased from 90 to 10 a corresponding decrease in odor offensiveness occurred. Table 11 gives moisture content of wastes from four species.

Livestock manures usually contain 70 to 83 percent moisture and can be handled in this semisolid form. However because of high labor requirements and lack of satisfactory solids handling equipment, many operations add

TABLE 11

Moisture Content of the Manure and Feces of Selected Domesticated Animals

	Moisture (%) feces[a]	Moisture (%) manure[*][b]
Cow	83	85
Poultry	72	72
Swine	67	82
Sheep	74	77

*Fresh mixed manure and urine

[a]Source: E. E. Geldreich (1966).

[b]Source: S. A. Hart (1960).

moisture to manure and handle as a liquid. Using this system, wastes of over 90 percent water can be transported by pumps, spreader or irrigation equipment, but total volume is correspondingly increased (Loehr, 1974).

When moisture content is below 90 percent the manure usually must be scraped and handled as a semisolid or solid. Both liquid and semisolid forms of the manure will produce odors, but if 80 to 90 percent of the moisture is removed, no malodors will be produced (Loehr, 1974).

Sobel (1969) gives two possible methods for removal of water from manure. These are: (1) mechanical - a source of energy must be provided and (2) thermal - a natural source of energy can be used but climate is not always adequate. These methods will reduce the weight and volume of the manure. Sobel (1971) reported that the ideal

moisture content for storage of chicken manure was 10 to 15 percent. He further stated that the drying process is expensive and should only be used if there is an available market for the dried product.

Another method used to change the character of manure is to add a substance such as straw or sawdust to absorb some of the water (Sobel, 1969). This yields a product that can be handled as a solid, but there is still some odor problem.

Ifeadi et al. (1975), using an odor panel, compared odors of undiluted dairy manure (70 percent feces and 30 percent urine) and diluted dairy manure. This sensory evaluation indicated diluted dairy waste had a lower threshold level than undiluted manure. Therefore, the diluted waste needed a larger volume of air to render the volatiles odorless indicating the undiluted manure was not as offensive.

The removal of water from manure seems to be an effective way of preventing odor production by creating an aerobic environment. Cost and unsatisfactory climates for drying are two major problems encountered when using this technique as a means of odor control.

Effect of pH on Odor Production

The pH of manure influences the type of compounds transferred to the air since pH determines the degree of ionization. Ionized species have no vapor pressure and

will not contribute to odor since a vapor pressure is necessary for volatilization. Only compounds in the non-ionized form will be volatile.

The pH at which half of a compound is present in the nonionized form is called the pK_a. The pK_a for some of the compounds produced from decomposing manure is shown in Table 12.

TABLE 12

pH Values at Which Various Odorous Compounds
are 50 Percent Ionized at 25°C

Acidic Compounds	pH	Basic Compounds	pH
Acetic acid	4.75	Ammonia	9.25
Butyric acid	4.83	Dimethylamine	10.73
Hydrogen sulfide	7.04	Ethylamine	10.81
Propionic acid	4.87	Methylamine	10.66
		Trimethylamine	9.81

Source: R. C. Weast (1972).

Barth et al. (1972) showed the relationship between pH and the volatility of a compound. They observed that for the acidic compounds a pH less than the pK_a value would cause more than 50 percent of the compound to be in the volatile form while a pH of more than the pK_a of the basic compounds would have the same result. An example of this relationship is shown in Table 13.

As the pH increases the amount of sulfide found in the volatile form declines. At a pH of 10 or over, there

TABLE 13

Relationship of H_2S in Water at 25°C
as a Function of pH

pH	Fraction of sulfide present as H_2S
5.0	.99
6.0	.89
6.5	.71
7.0	.44
7.5	.20
8.0	.072
9.2	.0049

Source: American Public Health Association (1972).

would be essentially no H_2S produced, but at a pH of 5 or below almost all of the sulfide would be present as H_2S.

The pH of manure varies with buffering capacity, moisture content, type of substrate, etc. Miner (1971) describes the net result of organic degradation during the early phases as a conversion of many insoluble raw materials into soluble intermediates. This produces a sufficient concentration of organic acids to depress pH, and may allow changes in the dominant types of microorganisms.

According to Miner (1971) a pH from 6.5 to 8.5 favored growth of bacteria over that of fungi and yeasts. Acid conditions usually favored fungi, but some bacteria survived. Certain of the Lactobacilli produce lactic acid that will lower the pH to 5 or less, and thus prevent growth of certain other bacteria. This condition has been observed in manure from dairy cows fed silage.

Effect of Temperature on
Odor Production

All biological processes are temperature sensitive. Bacterial cell growth and enzyme activity have more activity at an optimum temperature and decrease as the temperature changes from that. Therefore in the winter, odor production is decreased due to slow degradative processes.

In addition to controlling the rate of degradation, temperature along with pH, dictates the fraction of total ammonia concentration that is in the NH_3 form. Miner (1974) developed Table 14 showing the percent of total ammonia as volatile NH_3 at different temperatures and pH.

TABLE 14

Fraction of Total Ammonia Concentration
Present as NH_3 as a Function of
Temperature and pH

| pH | Temperature (°C) | | |
	10	20	30
7	0.0018	0.0040	0.0081
8	0.018	0.038	0.075
9	0.22	0.30	0.45
10	0.65	0.80	0.89

Source: J. R. Miner (1974).

At all four stated pH values an increase in temperature increases the fraction of total ammonia present in the volatile form. At pH values less than 7.0 there is no

significant volatilization of ammonia and at 10 or above
the largest part of the ammonia is in the volatile form.

These observations show that pH and temperature
will have a direct effect on the type and amount of com-
pounds volatilized either by affecting rate of decomposition
or by determining the amount of the nonionized compound
present.

Aeration as a Means of Controlling Odors

One of the most common ways to prevent formation
of malodors from anaerobic decomposition is to aerate the
system. Aerobic bacteria require oxygen as a hydrogen
acceptor, while anaerobic bacteria can use carbon dioxide,
nitrates, sulfates or organic compounds. These plus other
products of anaerobic fermentation are involved in the odor
produced.

Jones et al. (1970) describe aerobic treatment of
livestock waste as being feasible for odor control and also
cite other advantages. These are: (1) partial decomposi-
tion of volatile (organic) solids into water and odorless
gases such as carbon dioxide, (2) destruction of most
pathogenic organisms, (3) reduction in the pollutional
characteristics of the wastes and (4) concentration of the
minerals which may be more readily applied to land.

Jones et al. (1970) mentioned two types of systems
for aerating animal wastes. One application was an oxi-
dation ditch of two main parts--a continuous open-channel

ditch with an aeration rotor that circulates the ditch contents thereby providing oxygen. A second type of aeration system was an aerobic lagoon either naturally or mechanically aerated. Naturally aerated lagoons depend upon algae to provide the oxygen necessary for aeration. Therefore a large surface area is necessary. Mechanically aerated lagoons utilize equipment that beats or blows air into the water so that they are not dependent on natural aeration.

Dale (1971) states that the oxidation ditch has little promise for treatment of dairy cow waste. Two problems encountered are excessive foaming and settling of undigested feed particles which restrict the flow of the oxidation ditch and the precipitated mass then becomes anaerobic. A mechanically aerated lagoon would be more applicable to dairy waste because foaming and precipitation are not problems (Dale et al., 1969).

The main purpose of an oxidation ditch is to degrade organic solids. Ogilvie and Dale (1971) suggested that this degradation could occur just as easily in the soil without a costly input of energy. They proposed short term aerobic treatment of dairy cow waste to remove the odorous components after storage under anaerobic conditions just before applying to the land. The odors are usually not a problem during storage, but are when the wastes are spread on fields. Therefore short term aeration (24 hours)

can be used to oxidize the reduced organic compounds before spreading. Thus in this type of anaerobic-aerobic system no breakdown of solids is desired because the main purpose would be odor control.

Chemical Addition as a Means of Controlling Odor

All operations cannot conveniently aerate their animal wastes, and therefore alternate methods are often needed. One practice is to alter or stop anaerobic microbial degradation by the addition of a chemical. Another principle is to chemically oxidize malodors to allow sufficient time for field spreading of the wastes. Still another principle alters the decomposition pathway to allow production of less objectionable odors. Additionally masking agents, counteractants and deodorants have been utilized in decreasing the offensiveness of manure odors.

Lime

Yushok and Bear (1948) added hydrated lime to poultry manure at 5 and 20 percent of total volume and found it effectively deodorized as well as reduced nitrogen loss. They argue that since most soil can benefit from liming, this method has no direct cost for odor control. Deibel (1967) found that the addition of lime to liquid poultry manure abated odor for seven to ten days after which time the smell of ammonia became very strong.

By maintaining the pH between 9 and 10 with lime,
Hammond et al. (1966) suppressed odors from liquid hog
manure. They used about 0.15 pound of hydrated lime per
100 pound hog per day which reduced production of hydrogen
sulfide, but did not prevent ammonia formation.

Day (1966) kept the pH of liquid hog manure between
9 and 11 using lime. Whenever the pH dropped to 9, more
lime was added. This treatment effectively eliminated
odors probably by inactivating anaerobic bacteria. The
amount of lime needed was 0.16 pound per 100 pound pig
per day.

Cole et al. (1974) found lime did not improve
swine manure slurry odor when the pH was maintained above
11. Also there was no noticeable reduction in sulfide
levels in the manure, but a strong ammonia odor developed
as a result of the increased pH.

There have been several conflicting reports as to
the effectiveness of lime in decreasing nitrogen loss and
the offensiveness of manure odor. One report indicated a
decrease in nitrogen loss while several other reports
stated an increase in the amount of ammonia volatilized to
the atmosphere with a resulting increase of ammonia odor.
This would seem to be inconsistent because ammonia repre-
sents a loss of nitrogen, and lime produces conditions
favorable for ammonia volatilization. Also an increased
ammonia odor would tend to add to the offensiveness in

many instances, although it may be more desirable than many of the other degradation products.

Sodium Hydroxide

Sodium hydroxide (NaOH) at 0.9 percent of total volume was found effective in preventing the development of malodors for 28 days from poultry dropping slurry (Benham, 1967). This treatment also reduced total aerobic bacteria and coliforms. Application of the equivalent of 6,000 gallons of liquid poultry manure containing 0.8 percent NaOH per acre of grassland had no deleterious effect on the vegetation.

NaOH would tend to act in much the same way as lime in raising the pH of the manure. If this were the case ammonia loss could be a problem when using NaOH as a means of controlling odors.

Chlorine

According to Loehr (1974) chlorine is an oxidizing agent capable of reacting with organic waste matter, reduced inorganics (H_2S and NH_3) and microorganisms. Many of the reactions compete with the use of chlorine for disinfecting purposes. The hypochlorite salts are one of the more common forms used in animal waste treatment, and are dissociated in solution to yield free ion (Na^+) and hypochlorous acid (HOCl).

Hammond et al. (1966) used calcium hypochlorite ($Ca(OCl)_2$) to treat liquid swine waste in a confinement unit. For effective odor control they found 0.1 pound of active chlorine per 100 pound hog per day was needed and concluded that odor reduction was a result of the anti-microbial action of chlorine.

Deibel (1967) added hypochlorite to liquid poultry waste, and caused the evolution of chlorine gas. This process is probably a result of the reaction of hypochlorite and uric acid. The chlorine treatment substantially reduced ammonia, hydrogen sulfide, methane and carbon dioxide production.

Swine pit contents of fecal matter and urine were treated with varying levels of sodium hypochlorite (NaOCl) and chlorine dioxide (ClO_2). Sulfide concentration in the manure dropped to very low levels within 15 minutes, but neither treatment had any significant effect on ammonia concentration. An odor panel evaluated the treatments and found 500 PPM of both compounds to be the most effective level to reduce odor (Cole et al., 1975).

Liquid dairy manure was similarly evaluated (Cole et al., 1975). Sulfide concentration in the manure was reduced only about half for NaOCl and ClO_2 at 250, 500 and 1000 PPM with no improvement in odor. This is in contrast to what the authors observed for swine manure where sulfide concentration was reduced by more than 90 percent

with a corresponding depression in odor strength. Their explanation is the odor panel judged the liquid dairy manure as being less strong and offensive than swine manure meaning there would probably not be as great a reduction in odor from dairy manure. Also total solids of the dairy manure was greater than the swine manure. Thus effectiveness of odor treatments may vary with solids content and relative odor offensiveness.

Results indicate that hypochlorite salts can be a feasible means of odor control for liquid swine and poultry waste. Effectiveness in liquid cattle waste is inconclusive because of limited data.

Paraformaldehyde and Formaldehyde

Paraformaldehyde was described by Seltzer et al. (1969) as being a mixture of polyoxymethylene glycols containing 90-99 percent polymerized formaldehyde, and is available in powder, granule and flake form.

Paraformaldehyde liberates formaldehyde gas as it depolymerizes. According to Seltzer et al. (1969) increased temperature will cause an increase in the rate of depolymerization. This formaldehyde is then free to react with ammonia to form the compound hexamethylenetetramine ($C_6H_{12}N_4$) which is a white, powdery, nontoxic, odorless substance.

Seltzer et al. (1969) used 0.5 up to 7 grams paraformaldehyde per 100 grams of fresh liquid poultry manure to determine the effect on obnoxious gas formation. The pH of the headspace over the manure was used to estimate ammonia production. Paraformaldehyde addition of 3 grams or above prevented ammonia production for 28 days, while addition of 0.5 and 1 gram prevented ammonia production for about one week. However after this week, levels were similar to control. Control manure developed a noticeable ammonia odor within 24 hours and reached a maximum pH of 11 within 48 hours indicating over 100 PPM ammonia. Bacterial counts made after 12 days indicated the addition of 1 gram paraformaldehyde lowered number of organisms per gram of manure from 10^9 to 10^8 when compared to control. Addition of 3 grams decreased counts to 10^3, while manure with 7 grams had no organisms. They concluded that the mode of action of paraformaldehyde on animal wastes was both chemical and antimicrobial.

After 28 days Seltzer et al. (1969) found increasing levels of nitrogen retained in poultry manure as level of paraformaldehyde increased. They also noted no indication that mortality or other symptoms of toxicity increased in poultry when litter was treated with paraformaldehyde. Flies when given a choice deposited eggs in control manure instead of manure treated with paraformaldehyde.

Paraformaldehyde added at one and three percent to poultry litter reduced bacterial counts to 10 percent of control, and mold counts to 1 percent of control (Veloso et al., 1974). The pH of the litter was slightly reduced for three weeks with the three percent treatment. No difference in the nitrogen retention was observed.

Sobsey et al. (1974) found the ability of formaldehyde to disinfect sewage improved as the pH was raised from 8 to 10.5. The biodegradability of formaldehyde gives this compound some advantage over other disinfectants. At low concentrations formaldehyde can serve as a substrate for bacteria, and therefore will not accumulate in the soil upon spreading.

Formaldehyde slightly reduced sulfide concentration in liquid dairy manure, but no decrease in odor was noted (Cole et al., 1975).

Ulich and Ford (1975) used an odor panel to evaluate the effectiveness of sprinkling paraformaldehyde flakes on the surface of beef cattle manure. The slight decrease in both odor offensiveness and strength was not sufficient to be economical.

Paraformaldehyde has been shown to be adequate in reducing ammonia release. In situations where ammonia concentrations in the air reach problem levels, such as in poultry houses, this technique can be applied. Results using formaldehyde or paraformaldehyde on cattle manure for

odor control is limited, but seems to be either ineffective or uneconomical.

Potassium Permanganate

Miner (1974) classified potassium permanganate ($KMnO_4$) as a powerful oxidizing agent that is most effective in acid solutions and least effective in neutral solutions. The reactivity of $KMnO_4$ will generally increase with increasing temperature and increasing concentration of oxidizable impurities.

A one percent $KMnO_4$ solution sprayed on a feedlot at the rate of 20 pounds of $KMnO_4$ per acre was more effective in controlling odors than some counteractants, masking agents and disinfectants tested at the same time (Faith, 1964).

Miner and Stroh (1975) applied $KMnO_4$ at the rate of 20 pounds per acre in a one percent solution to portions of a beef cattle feedlot. Ammonia evolution rates from selected portions were similar to that in untreated portions. To evaluate the effect on odor production a scentometer was used to determine the dilutions to threshold. No difference could be detected between the $KMnO_4$ and untreated areas.

Ulich and Ford (1975) found $KMnO_4$ to be effective in the suppression of odorous gases applied at the rate of 56 pounds per ton of beef manure. Upon further testing an odor panel determined 20 pounds per acre would be adequate.

$KMnO_4$ (100 to 500 PPM) adequately mixed with liquid swine manure caused a decrease in the sulfide concentration in the waste (Cole et al., 1975). When compared to other chemical oxidants $KMnO_4$ was least effective in reducing sulfide concentrations at one-half hour, but was most effective after a few days indicating a long term depression of odor. No change in ammonia concentration in the waste was observed. An odor panel rated the 500 PPM level as the best concentration for reducing odor strength.

At 250 to 1000 PPM $KMnO_4$ showed no substantial decrease in sulfide or ammonia concentrations in liquid dairy manure (Cole et al., 1975). An odor panel detected no odor reduction.

Ritter et al. (1975) mixed $KMnO_4$ with liquid dairy manure to reduce malodors. More than 90 percent of an odor panel found the treated manure to be "not offensive" or "mildly offensive" one hour after treatment. This was still true 24 hours after treatment. They conclude that $KMnO_4$ reduces odors from liquid dairy manure for at least 72 hours.

The results indicate $KMnO_4$ may be adequate in reducing offensiveness of liquid swine and dairy manure as well as beef feedlot manure, but some reports are contradictory. Further research under more controlled conditions is needed.

Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is an oxidizing agent commercially available as an aqueous solution ranging from three to 98 percent (Miner, 1974). Solutions greater than eight percent are corrosive and must be handled with care. In natural systems H_2O_2 can be broken down to water and molecular oxygen.

Hollenbach (1971) added a 50 percent H_2O_2 solution to a liquid dairy manure pit to a concentration of 100 PPM H_2O_2 using a circulating pump. When the pump was first started and before any H_2O_2 had been added, a sulfide odor was evident and air sulfide concentration increased. Upon addition of H_2O_2 no sulfide odor could be detected and only a slight odor remained after 18 hours of nonagitation. The hydrogen sulfide odor returned to previous level after reagitation.

In a similar trial Hollenback (1971) treated a liquid manure pit with a 50 percent H_2O_2 solution. Immediately after the first 100 PPM was added, a second 100 PPM dose was given. This additional H_2O_2 resulted in a further decrease in the odor from the manure. Sixteen hours later the sulfide level had returned to the level prior to treatment. Foaming difficulties were reported in the second trial.

O'Neill (1972) added varying levels of 10 to 15 percent H_2O_2 to liquid dairy manure. At 50 PPM H_2O_2

there was only limited success in odor control, but the sulfide odor was eliminated. At 125 PPM H_2O_2 only a silage-like odor was noticed. Originally sulfide was present in the liquid manure at levels greater than 5 PPM, but were reduced to zero by treatments of over 100 PPM H_2O_2. No foaming occurred.

Pig manure slurry was treated by O'Neil (1972) with 10 percent H_2O_2 to develop 115 and 275 PPM. Both levels reduced hydrogen sulfide levels to zero in the atmosphere over the slurry. The lower level was thought to be superior to the higher level probably due to improper mixing at the 275 PPM level.

Kibbel et al. (1972) added H_2O_2 at 100, 150, and 175 PPM to chicken manure slurry. This manure was spread on the land in strips according to treatment. Hydrogen sulfide was reduced to almost zero at all treatment levels of H_2O_2, and a resulting decrease in odor offensiveness occurred. The odors remained suppressed in the H_2O_2 treated plots compared with the control for the second and third day after application.

Ritter et al. (1975) added fresh bovine feces to liquid dairy pit manure over a six week period. After this period H_2O_2 was added. The minimum amount of H_2O_2 needed to eliminate the hydrogen sulfide was determined to be 12.5 PPM. This also increased dissolved oxygen content of the manure proportionally to the amount of H_2O_2 added.

Although the hydrogen sulfide was destroyed for a short period of time other malodors remained.

The effect of adding 30,000 PPM H_2O_2 to fresh bovine manure was investigated by Ulich and Ford (1975). Two tests using an odor panel gave contradictory results, but H_2O_2 reduced the release of sulfurous gases.

Cole et al. (1975) found that sulfide concentration in liquid swine manure was reduced to less than 1 PPM with doses of 300 and 500 PPM H_2O_2. Ammonia concentration was not changed. An odor panel found odor strength to be reduced at 300 and 500 PPM H_2O_2. Of the chemicals evaluated H_2O_2 was the most economical for prevention of odor problems.

Slight reduction in the sulfide content of liquid dairy manure with no reduction in the odor was noted with 250, 500, and 1000 PPM H_2O_2 (Cole et al., 1975). This is in contrast to what they observed in liquid swine manure. The solids content was higher in the liquid dairy manure perhaps indicating need of a larger dose of H_2O_2 to achieve results similar to the effectiveness in swine manure.

Most reports indicate H_2O_2 acts to decrease sulfide concentrations, but not all are certain if there is a corresponding decrease in odor offensiveness. Use of H_2O_2 may be satisfactory in some circumstances where foaming does not occur for at least partial odor control.

Masking Agents, Counteractants, Deodorants and Digestive Deodorants

These types of compounds are available commercially for the control of livestock odors (Miner, 1974). The masking agents have an acceptable odor designed to overcome the manure odor. Counteractants tend to cancel the odor of the waste. Deodorants destroy or eliminate the odorous components of the waste. The digestive deodorants are a combination of enzymes and bacteria used to change the degradation process so as to alter the production of odorous compounds.

The effectiveness of these four types of preparations was tested for odor control using liquid poultry manure by Burnett and Dondero (1968). An odor panel evaluation provided an index of comparison between treated and untreated manure. Masking agents and counteractants were the most effective in controlling odors with deodorants moderately effective. The digestive deodorants were least effective.

A dried bacterial and enzyme product was applied as a spray to the surface of a beef feedlot by Miner and Stroh (1975). The initial application was 10 pounds per acre. There tended to be a reduction in ammonia release from the surface. Scentometer evaluation five days after the initial treatment showed the treated area had a

measurably less intense odor than the control. Ten days after initial treatment no difference was detectable.

Jongebreur and van Geelen (1974) reported that a masking agent added to the air, gave effective control of manure odors from chicken and swine buildings. A counteractant was also effective in a poultry operation when added to the air. The authors doubted that inhabitants near livestock confinement areas would accept the smell of the treatments, especially that of the masking agent.

Concentrations of sulfide and ammonia along with odor strength were monitored for 56 days after swine and dairy pit manure were treated with commercial dried bacteria and enzyme preparations (Cole et al., 1975). No reduction in any of the three were found, and they concluded that these experiments do not substantiate the manufacturer's claims.

Ritter et al. (1975) evaluated the effect of a masking agent as well as several dried bacterial and enzyme preparations on odor offensiveness in liquid dairy pit manure. The digestive deodorants were added and evaluated after 48 hours. The masking agent was added one hour before evaluation. The odor panel indicated that only one of the digestive deodorants was effective in reducing odor offensiveness. The masking agent was found adequate for control of odor.

Masking agents and counteractants appear to be the most efficient of these compounds in controlling odor. Yet, masking agents can become so strong that they become offensive when present at sufficiently high concentrations (Taiganides and White, 1968). Also large quantities of masking agents are needed to overpower the odor from animal waste making their use expensive. The counter-actants are specific for certain odors yet very few of these counteracting pairs have been identified. Since odor from animal waste is made up of many components finding a counteractant to each appears almost impossible. The deodorants and digestive deodorants appear to have limited applicability for control of odors from livestock operations.

Other

Potassium nitrate (Ulich and Ford, 1975) and sodium nitrate (Cole et al., 1975) have been tested in odor prevention trials. Nitrate supplies a hydrogen acceptor so that the redox potential of the waste pit will not permit formation of odorous compounds. Potassium nitrate reduced strength and offensiveness of odor from bovine manure, however, it was an expensive method. Sodium nitrate reduced sulfide content of liquid swine and dairy manure but no decrease in odor strength was detected.

Deibel (1967) used direct ozone treatment in an attempt to oxidize odors in liquid poultry manure. No

reduction in odor was detected. Another technique involved adding ozone directly to the air inside a confinement building in an attempt to oxidize the malodors in the atmosphere (Haye, 1973). A reduction in odor was observed, but ozone can be harmful to animals and humans at low concentrations.

Orthodichlorobenzene was found by Cole et al. (1975) to be ineffective in reducing sulfide concentration in liquid swine and dairy manure. Also no reduction in odor was detected. On the other hand, Ulich and Ford (1975) observed that orthodichlorobenzene suppressed release of sulfurous gases in beef manure slurries and reduced odor. These authors concluded that it would be an economical method to control cattle feedlot odors during wet periods.

Sodium bentonite has been tested by Miner and Stroh (1975) for reducing odor from cattle feedlot surfaces. Sodium bentonite reduced ammonia release and odor intensity of the lot surface.

Activated carbon was added to both liquid swine and dairy manure to serve as an absorbent for malodors by Cole et al. (1975). Sulfide concentration was reduced in liquid swine slurry plus a slight decrease in odor strength. However in liquid dairy manure sulfide concentration was only slightly reduced with no reduction in odor.

Management as a Means of Controlling Odor

Under most conditions proper management can prevent the release of odors into the atmosphere so as not to be offensive to neighbors. Miner (1970) listed several principles that minimize odor. These are: (1) locate livestock operations away from residential areas, (2) keep feeding areas and animal pens dry, (3) design the system to prevent animals from becoming dirty and manure-covered and (4) prompt disposal of dead animals.

Gases produced during manure storage can present a problem. Location of storage tanks outside of livestock buildings reduces hazards to the animals from gas release upon mixing, but increases problems associated with movement of manure to the storage tank.

Spreading animal waste on land allows malodors to be released often resulting in complaints from neighbors. One way to prevent this is to inject the manure several inches under the soil surface (Dale, 1971). This method is applicable only when soil is in a workable condition, and cannot be used when soil is wet or when most crops are being grown.

When manure is applied directly on the surface of soil, as is usually the case, timing and site selection are two important criteria (Conner et al., 1971). Manure should not be spread so that the wind will take the odor to the neighbors, and if possible manure should be applied

at a distance so that the odor will dissipate before reaching anyone.

The control of odor from animal wastes has been approached from several directions. If foresight is used, most odor problems can be prevented by proper management techniques, but with the encroachment of suburbs into agricultural areas, many farmers find themselves with nonrural neighbors. Under these conditions proper manure management is essential. Since odors are usually only a problem during and after spreading addition of certain chemicals may offer short term odor control.

III. MATERIALS AND METHODS

Experiment I

Feces and urine were collected, pooled separately and each mixed before adding 63 percent fresh dairy cow feces, 27 percent urine and 10 percent water to 1.9 liter glass jars. Jars were used to simulate manure pits. Chemicals were added and thoroughly mixed to form the following concentrations in parts per million (PPM): paraformaldehyde (7000; 10,000; 30,000), acrolein (1 and 100), phosphoric acid (657; 1000; 10,000), sodium per-chlorate (250; 500; 2000), hydrogen peroxide (75; 150; 300) or potassium permanganate (250; 500; 1000). Paraformalde-hyde (Vineland Poultry Laboratories, Vineland, N.J.) and sodium perchlorate (source unknown) were added as a powder, potassium permanganate (Mallinckrodt Chemical Works, St. Louis, MO) as crystals, acrolein (Eastman Kodak Co., Rochester, N.Y.) and phosphoric acid (Mallinckrodt Chemical Works, St. Louis, MO) as a liquid and hydrogen peroxide (Mallinckrodt Chemical Works, St. Louis, MO) as a 30 per-cent solution. All treatment levels were done in dupli-cate.

The large number of jars required two trials.
Experiment la compared paraformaldehyde, acrolein and
phosphoric acid while Experiment lb compared sodium per-
chlorate, hydrogen peroxide and potassium permanganate.
All jars were stored at approximately 20°C.

Determination of Total Aerobic
and Anaerobic Microorganisms

A sample was taken from one jar of each duplicate
at the highest and lowest level of treatment at 1, 8, 15
and 22 days after addition of chemicals. Jar contents
were mixed with a sterile metal spatula and a sample was
placed in a sterile glass baby food jar for transportation
to the laboratory. This sample was placed in a known
volume of sterile distilled water to make an approximate
1:10 dilution which was mixed in a sterile blender (Waring
Commercial Blender) for two minutes. One ml of the sample
was placed in nine ml of sterile distilled water in dup-
licate. A serial ten-fold dilution was done to eight
tubes using sterile one ml pipettes. Sterile Pasteur
pipettes were used to transfer one drop, calibrated at 1/35
ml, from each dilution in duplicate into plates of brain-
heart infusion agar. The plate tops were left slightly
open to allow the drops to dry. Each dilution was then
inverted and incubated at 37°C for 24 hours in an aerobic
(Blue M Incubator) or an anaerobic incubator (National
Appliance Co. Incubator). Each sample had 2 series of

plates in an anaerobic and 2 series in an aerobic environ-
ment. The lowest dilution that forms distinguishable
isolated colonies (usually 10 to 50 colonies) was counted.
The total count was calculated by the following equation:

$$\frac{\text{total counts}}{\text{per gram}} = \frac{\text{number of}}{\text{colonies}} \times \frac{1}{\text{dilution of drop}} \times \frac{\text{dilution}}{\text{factor}} \times 35$$

Values given were an average of duplicates.

Determination of pH

At 2, 7, 14 and 21 days after addition of chemicals,
pH was determined in each jar after complete mixing in
Experiment Ia. Experiment Ib was not evaluated at day 14,
but was at 2, 7 and 21 days after addition of chemicals.
This was done by placing the probe from a pH meter
(Sargent-Welch model L S) directly into the manure.

Determination of Total Solids

All jars were sampled after treatments were added
and total solids were measured after evaporation of water
at 100°C in a forced draft oven for 24 hours.

Determination of Ammonia in Air

Atmospheric ammonia (NH_3) was collected and quanti-
fied by methods described by Jacobs (1960) and Miner (1974)
at 2, 7 and 21 days after addition of chemicals. Standard
ammonium chloride solutions containing ammonia

concentrations of 12.2 to 366.0 micro grams were used to construct a standard curve from which unknown concentrations were calculated.

Odor Panel Evaluation

A panel of five people evaluated each jar 4 and 5 days after addition of treatments for quantity (strength) and quality (offensiveness) of the odor. Each panelist was given Table 15 for reference and asked to rate each numbered jar as to strength and offensiveness. No time limit was set. Manure was agitated before evaluation.

TABLE 15

Odor Evaluation

Strength (quantity)		Offensiveness (quality)	
0	No Odor	0	Not Offensive
1		1	
2	Very Faint	2	Very Faint Offensiveness
3		3	
4	Faint	4	Faint Offensiveness
5		5	
6	Definite	6	Definite Offensiveness
7		7	
8	Strong	8	Strong Offensiveness
9		9	
10	Very Strong	10	Very Strong Offensiveness

Experiment II

Pit contents were removed from the Michigan State University dairy farm liquid manure pit and after complete mixing, placed in 1.9 liter glass jars. The contents

consisted of dairy cow urine and fecal matter plus water
used to wash the milking parlor and milking apparatus.
Some of the water added to the pit contained detergents.

Jars were randomly assigned to a treatment con-
sisting of varying parts per million of either lime (5000
and 10,000), paraformaldehyde (1000; 5000; 10,000),
hydrogen peroxide (100 and 500) or potassium permanganate
(500 and 1000). Treatments were added directly to the
liquid manure and thoroughly mixed. Lime (United States
Gypsum, Chicago, IL) was added as a powder. All other
treatments were added as in Experiment I and all levels
were done in duplicate.

Determination of pH and
Total Solids

The pH and total solids were determined as in
Experiment I. The pH was done at -1, 1, 4, and 7 days
after addition of treatments.

Determination of Total Ammonia
in the Manure

A ten ml sample was taken from one jar of each
treatment level and diluted to 100 ml with distilled water
at day 2 and 10 after addition of chemicals. This was
agitated by a magnetic stirrer to keep all particles in
suspension. An ammonia probe ("Orion" Specific Ion
Electrode) connected to a Beckman digital pH meter model
4500 was placed into the diluted sample and ten drops of

10 M NaOH was added to convert NH_4^+ to NH_3 to which the
electrode is sensitive. Standard solutions of ammonium
chloride containing 14 and 140 mg per liter ammonia were
used for construction of a standard curve. Ammonia con-
centrations of the unknown samples were calculated from
the standard curve, and results were expressed as total
ammonia (NH_3 and NH_4^+).

Nitrate Determination

Each treatment level was tested for the presence
of nitrates. A drop from each level was added to the well
of a spot plate. To this a drop of diphenylamine was
added and a blueish ppt. indicated the presence of nitrates.
A standard nitrate solution (0.1 mg/ml) was used as a
reference, and color intensity estimated visually.

Odor Panel Evaluation

An odor panel of three people evaluated each jar
1, 3 and 8 days after addition of treatments. The pro-
cedure was the same as is described in Experiment I.

Experiment III

Liquid pit manure was obtained as in Experiment II
and placed in an open 55 gallon barrel. To this was added
fresh fecal matter and urine from lactating dairy cows.
This mixture remained at ambient temperature for one
month, then mixed and portions were added to 1.9 liter
glass jars.

Jars were randomly assigned to a treatment consisting of lime (5000 and 10,000 PPM), paraformaldehyde (1000; 5000; 10,000 PPM), hydrogen peroxide (100 and 500 PPM) or potassium permanganate (500 and 1000 PPM). Compounds were added as in Experiment I and II, but treatment levels were in triplicate.

Determination of Total Aerobic Microorganisms

After 1 and 8 days, a sample was taken from one jar of a triplicate at the highest and lowest level of treatment. The procedure for total aerobic microorganisms was the same as in Experiment I.

Determination of pH and Total Solids

Total solids and pH were determined as in Experiment I. The pH was determined at -1, 1, 4 and 9 days after addition of treatments.

Determination of Total Ammonia in the Manure

At days -2, 4 and 11, ammonia (NH_3 and NH_4^+) was determined as in Experiment II.

Odor Panel Evaluation

An odor panel of five people evaluated each jar 1, 2 and 8 days after treatments were added. The procedure was as in Experiment I.

Experiment IV

Several gallons of manure from the liquid manure pit at the Michigan State University dairy farm was placed in an open 20 gallon plastic container and fecal matter and urine from lactating dairy cows added. This mixture remained at room temperature for one month at which time contents were mixed and added to 1.9 liter glass jars.

Jars were randomly assigned to a treatment consisting of varying PPM of either paraformaldehyde (5000 and 10,000), potassium permanganate (500 and 1000) or hydrogen peroxide (100 and 500). Treatments were added as in Experiment I.

Determination of Total Solids

Total solids were determined from various selected jars as in Experiment I.

Odor Panel Evaluation

An odor panel of at least six people was used to compare treatments and treatment levels to a control. Each panelist was allowed to evaluate three jars of which one was a control and told to detect which one was least offensive and which was most offensive. Combinations of treated manure in each comparison (besides control) were paraformaldehyde 5000 vs. 10,000 PPM; potassium permanganate 500 vs. 1000 PPM; hydrogen peroxide 100 vs. 500 PPM; paraformaldehyde 5000 PPM vs. potassium permanganate 500

PPM; paraformaldehyde 5000 PPM vs. hydrogen peroxide 500 PPM; potassium permanganate 500 PPM vs. hydrogen peroxide 500 PPM. Comparisons were at three time periods: 9 to 15 hours, 36 to 40 hours and 8 days. Hydrogen peroxide at 100 vs. 500 PPM and hydrogen peroxide at 100 PPM vs. potassium permanganate at 500 PPM, were compared together against a control at 0.5 to 1.5 hours, 7 hours and 9 days.

Experiment V

Manure used in this experiment was taken from the same source as Experiment IV before addition to 1.9 liter glass jars. Treatments were added and thoroughly mixed to form the following concentrations in PPM: Sep-Zyme "O" (360), Pit-Zyme (360) and Odor Mask (1430). Sep-Zyme "O" (Sep-Ko Chemicals, Minneapolis, MN) and Pit-Zyme (source unknown) were added as a powder while Odor Mask (The Kalo Co., Quincy, IL) was added as a liquid.

Determination of Total Solids

Total solids were determined from various selected jars as in Experiment I.

Odor Panel Evaluation

An odor panel of at least eight people was used to evaluate treatments as in Experiment IV. Combinations of treated manure in each comparison (besides control) were Odor Mask vs. Pit-Zyme, Pit-Zyme vs. Sep-Zyme "O" and

Odor Mask vs. Sep-Zyme "O". Comparisons were at three
time periods: 9 to 15 hours, 33 to 39 hours and 8 days.

Statistical Analysis

Data from Experiment I, II and III were analyzed
with the Bonferroni t-Test (Miller, 1966) by comparing
means within each time period. Rankings from Experiment IV
and V were analyzed by the Wilcoxon Matched-Pairs Signed-
Ranks Test (Siegel, 1956).

IV. RESULTS

Experiment I

Manure (feces and urine) used in this experiment was taken directly from lactating dairy cows and put into jars along with water. This manure will be referred to as fresh manure because no decomposition occurred before addition of chemicals. This manure averaged about 13 percent dry matter, a value somewhat above that of most "liquid manures."

Microbial Counts

Paraformaldehyde, acrolein and phosphoric acid (H_3PO_4) added to fresh dairy manure produced responses in numbers of aerobic and anaerobic microorganisms shown in Table 16. Paraformaldehyde at 7,000 and 30,000 PPM markedly reduced total aerobic and anaerobic counts throughout the 22 day trial when compared with control. Acrolein at one and 100 PPM may have slightly reduced both aerobic and anaerobic counts. Aerobic and anaerobic counts were reduced at day one through 15 by 10,000 PPM H_3PO_4, but by day 21 values were similar to control.

Microbial numbers after addition of sodium perchlorate $(NaClO_4)$, hydrogen peroxide (H_2O_2) and potassium

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TABLE 16

Aerobic and Anaerobic Microbial Numbers[1] at Four
Intervals After Three Chemicals were Added
to Fresh Liquid Dairy Manure
(Experiment Ia)

Chemicals and Levels	Day			
	1	8	15	22
Aerobic Counts				
Paraformaldehyde (PPM)				
7,000	47×10^4	4×10^4	2.5×10^4	1.2×10^4
30,000	31×10^4	0.69×10^4	0.25×10^4	0.16×10^4
Acrolein (PPM)				
1	6×10^7	22×10^7 .	59×10^7	5.1×10^7
100	3.5×10^7	5.1×10^7	28×10^7	8.3×10^7
Phosphoric Acid (PPM)				
657	6.9×10^7	32×10^7	13×10^7	22×10^7
10,000	0.03×10^7	35×10^7	31×10^7	33×10^7
Control	7.8×10^7	140×10^7	73×10^7	35×10^7
Anaerobic Counts				
Paraformaldehyde (PPM)				
7,000	410×10^4	4×10^4	0.7×10^4	0.49×10^4
30,000	100×10^4	0.5×10^4	0.17×10^4	0.16×10^4
Acrolein (PPM)				
1	9×10^7	10×10^7	96×10^7	6.3×10^7
100	7.2×10^7	9.3×10^7	0.98×10^7	12×10^7
Phosphoric Acid (PPM)				
657	8.3×10^7	6.3×10^7	13×10^7	19×10^7
10,000	0.3×10^7	55×10^7	50×10^7	91×10^7
Control	5.2×10^7	290×10^7	22×10^7	9.7×10^7

[1]Each value an average of duplicates taken from the same jar
expressed as microorganisms per gram of treated manure.

permanganate ($KMnO_4$) to fresh dairy manure are presented
in Table 17. $NaClO_4$ at 2000 PPM reduced total aerobic
and anaerobic counts for eight days, but by day 16 counts
were similar to control. $NaClO_4$ at 250 PPM, H_2O_2 at 75 and
300 PPM and $KMnO_4$ at 250 and 1000 PPM did not alter counts
from control values.

The relationship between aerobic and anaerobic
microorganisms was such that none of the treatments resulted
in a change in one without a concurrent and similar change
in the other.

Table 16 and 17 have different control values
because they were done at two different time periods, and
no statistical evaluation could be made because there was
only one jar per value.

pH

Table 18 presents the relationship of paraformalde-
hyde, acrolein and H_3PO_4 treatment to pH with time. At
day two the pH group mean for paraformaldehyde was less
than control ($p < .005$), with no difference between concen-
trations although there was a tendency for pH to decrease
with increasing concentration of paraformaldehyde. The
pH group mean for paraformaldehyde was still less than
control ($p < .05$) at day seven, but at day 14 and 21 no
differences were detected.

The pH of acrolein treated manure was not different
than control at any day tested. At day two the pH group

TABLE 17

Aerobic and Anaerobic Microbial Numbers[1] at Four
Intervals After Three Chemicals were Added
to Fresh Liquid Dairy Manure
(Experiment Ib)

Chemicals and Levels	Day			
	1	8	15	22

Aerobic Counts

Chemicals and Levels	1	8	15	22
Sodium Perchlorate (PPM)				
250	30×10^7	63×10^7	110×10^7	91×10^7
2000	1.7×10^7	2.5×10^7	94×10^7	140×10^7
Hydrogen Peroxide (PPM)				
75	40×10^7	53×10^7	110×10^7	110×10^7
300	44×10^7	64×10^7	91×10^7	41×10^7
Potassium Permanganate (PPM)				
250	48×10^7	66×10^7	99×10^7	82×10^7
1000	50×10^7	61×10^7	93×10^7	100×10^7
Control	39×10^7	67×10^7	110×10^7	59×10^7

Anaerobic Counts

Chemicals and Levels	1	8	15	22
Sodium Perchlorate (PPM)				
250	28×10^7	79×10^7	160×10^7	120×10^7
2000	1.3×10^7	0.94×10^7	170×10^7	120×10^7
Hydrogen Peroxide (PPM)				
75	28×10^7	74×10^7	180×10^7	69×10^7
300	32×10^7	90×10^7	150×10^7	78×10^7
Potassium Permanganate (PPM)				
250	24×10^7	76×10^7	91×10^7	92×10^7
1000	31×10^7	66×10^7	120×10^7	80×10^7
Control	28×10^7	100×10^7	100×10^7	73×10^7

[1]Each value an average of duplicates taken from the same jar expressed as microorganisms per gram of treated manure.

TABLE 18

pH[1] at Four Intervals After Addition of Three Chemicals to Fresh Liquid Dairy Manure (Experiment Ia)

Chemicals and Levels	Day			
	2	7	14	21
Paraformaldehyde (PPM)				
7,000	6.35	6.20	6.35	6.40
10,000	6.25	6.00	6.10	6.10
30,000	6.00	5.95	5.95	6.20
mean	6.20^a	6.05^b	6.13	6.23
Acrolein (PPM)				
1	7.30	6.30	6.10	6.00
100	7.40	6.30	5.80	6.05
mean	7.35	6.30	5.93	6.03
Phosphoric Acid (PPM)				
657	6.90	6.40	5.80	6.20
1,000	6.60	6.45$_{ac}$	5.90	6.15$_{bd}$
10,000	5.85^c	5.85^{ac}	5.75	5.80
mean	6.45^a	6.23	5.82	6.05
Control	7.20	6.35	5.85	6.15
SEM[2]	.08	.07	.12	.07

[1]Each value an average of two jars.

[2]SEM = standard error of each mean of two jars on a given day.

[a]Significantly different (p < .005) than control within the same column.

[b]p < .05.

[c]Significantly different (p < .005) than means from lower treatment concentrations within the same treatment group within the same column.

[d]p < .01.

mean of H_3PO_4 treated manure was less than control (p <
.005) with pH of the 10,000 PPM treatment being less than
that of the lower two concentrations (p < .005). At day
seven the group mean was not different than control, but
pH of the 10,000 PPM treatment was less than control and
the two lower treatment concentrations (p < .005). At
day 14 no differences were detected between H_3PO_4 and
control, but by day 21 pH of the 10,000 PPM concentration
was less than control (p < .01) and the two lower treat-
ment concentrations (p < .05). These results demonstrate
pH decreased as H_3PO_4 concentration increased.

The pH of fresh dairy manure treated with $NaClO_4$,
H_2O_2 or $KMnO_4$ with time is presented in Table 19. At day
two no significant differences in treatments could be
detected although $NaClO_4$ tended to increase pH with
increasing concentrations. At day seven pH of manure
treated with $NaClO_4$ at 2000 PPM was greater than that
treated with the two lower concentrations (p < .005), but
none were different than control. The pH group mean for
manure treated with $NaClO_4$ at day 21 was less than control
pH (p < .025), and pH for the 2000 PPM $NaClO_4$ was higher
than that for the two lower treatment concentrations
(p < .05). Neither H_2O_2 nor $KMnO_4$ influenced pH.

Ammonia

Concentration of ammonia (NH_3) in the air over
manure as affected by treatment and time is presented in

TABLE 19

pH[1] at Three Intervals After Addition of
Three Chemicals to Fresh Liquid
Dairy Manure
(Experiment Ib)

Chemicals and Levels	Day		
	2	7	21
Sodium Perchlorate (PPM)			
250	6.35	6.35	6.10
500	6.40	6.45	6.10
2000	6.55	6.75[b]	6.30[c]
mean	6.43	6.52	6.17[a]
Hydrogen Peroxide (PPM)			
75	6.40	6.45	6.30
150	6.50	6.50	6.20
300	6.50	6.55	6.20
mean	6.47	6.50	6.23
Potassium Permanganate (PPM)			
250	6.55	6.55	6.30
500	6.60	6.55	6.25
1000	6.60	6.50	6.25
mean	6.58	6.53	6.27
Control	6.65	6.55	6.40
SEM[2]	.08	.06	.05

[1]Each value an average of two jars.

[2]SEM = standard error of each mean of two jars on a
given day.

[a]Significantly different (p < .025) than control
within the same column.

[b]Significantly different (p < .005) than means from
lower treatment concentrations within the same treatment
group within the same column.

[c]p < .05.

Table 20. Group mean ammonia concentration for parafor-

maldehyde at day two was lower than control (p < .05).

Due to the large variation from jar to jar, as indicated

by the large standard errors, no other statistically

significant differences in ammonia concentrations were

found, but values for paraformaldehyde treatments at all

times were less than for control, acrolein or H_3PO_4

treatments.

Concentration of ammonia in the air over manure

after addition of $NaClO_4$, H_2O_2 or $KMnO_4$ is presented in

Table 21. Ammonia concentration at day seven for the high

level $NaClO_4$ was higher than for the two lower concen-

trations (p < .005), but none were different than control.

No other differences were detected. H_2O_2 and $KMnO_4$

exerted no apparent changes on ammonia in air over the

manure.

When comparing data from Table 20 and Table 21

there was no consistent time trend for ammonia release

from fresh manure. Values in Table 20 decrease with time

while those in Table 21 increase. Manure used in these

two parts of the experiment was collected at different

times, and may have been different in some respects,

although conditions were kept fairly much the same.

Odor Panel Evaluation

Table 22 shows the relationship of addition of

paraformaldehyde, acrolein and H_3PO_4 to offensiveness

TABLE 20

Ammonia[1] in the Air Space over Fresh Liquid
Dairy Manure as Affected by Treatment
and Time (Experiment Ia)

Chemicals and Levels	Day			
	2	7	14	21
Paraformaldehyde (PPM)				
7,000	217	203	140	58
10,000	133	126	135	107
30,000	156	222	207	183
mean	169[a]	184	161	116
Acrolein (PPM)				
1	191	227	174	209
100	347	229	252	246
mean	269	228	213	228
Phosphoric Acid (PPM)				
657	282	228	217	277
1,000	212	278	195	309
10,000	239	185	204	265
mean	244	230	205	284
Control	366	271	269	202
SEM[2]	50	33	55	42

[1]Each value an average of two jars expressed as
micrograms of ammonia per liter of air.

[2]SEM = standard error of each mean of two jars on a
given day.

[a]Significantly different (p < .05) than control
within the same column.

TABLE 21

Ammonia[1] in the Air Space over Fresh Liquid
Dairy Manure as Affected by Treatment
and Time (Experiment Ib)

Chemicals and Levels	Day		
	2	7	21
Sodium Perchlorate (PPM)			
250	169	238	388
500	187	224	402
2000	256	473[a]	346
mean	204	312	379
Hydrogen Peroxide (PPM)			
75	193	240	381
150	220	203	434
300	155	177	387
mean	189	207	401
Potassium Permanganate (PPM)			
250	222	256	435
500	238	265	453
1000	223	257	413
mean	228	259	434
Control	246	282	505
SEM[2]	31	35	51

[1]Each value an average of two jars expressed as micrograms of ammonia per liter of air.

[2]SEM = standard error of each mean of two jars on a given day.

[a]Significantly different (p < .005) than means from lower treatment concentrations within the same treatment group within the same column.

TABLE 22

Offensiveness and Strength Ratings[1] Four and
Five Days After Addition of Three
Chemicals to Fresh Liquid
Dairy Manure
(Experiment Ia)

	Offensiveness[2]	Strength[3]
Paraformaldehyde (PPM)		
7,000	3.9	4.6
10,000	3.3	3.5
30,000	4.5	4.9
Acrolein (PPM)		
1	6.4	6.4
100	6.0	6.8
Phosphoric Acid (PPM)		
657	5.9	5.8
1,000	5.0	4.7
10,000	5.0	5.7
Control	5.7	5.2

[1]Each value an average of two jars evaluated by five odor panelists each.

[2]0 = not offensive, 2 = very faint offensiveness, 4 = faint offensiveness, 6 = definite offensiveness, 8 = strong offensiveness, 10 = very strong offensiveness.

[3]0 = no odor, 2 = very faint odor, 4 = faint odor, 6 = definite odor, 8 = strong odor, 10 = very strong odor.

(quality) and strength (quantity) of fresh dairy manure at four and five days. Paraformaldehyde at 7000, 10,000 and 30,000 PPM decreased offensiveness ratings to 3.9, 3.3 and 3.5 respectively compared to control of 5.7. Strength ratings were 4.6, 3.5 and 4.9 respectively compared to control of 5.2. The lower the number the less the offensiveness or strength of the odor. Acrolein or H_3PO_4 did not reduce offensiveness or strength ratings.

Comparative ratings when $NaClO_4$, H_2O_2 and $KMnO_4$ were added and evaluated at four and five days, are in Table 23. $NaClO_4$, H_2O_2 and $KMnO_4$ at 250 and 500 PPM did not reduce offensiveness or strength ratings. $KMnO_4$ at 1000 PPM had an offensiveness rating of 4.4 and strength rating of 4.3 compared to control values of 6.5 and 6.1 respectively.

The correlation coefficients between offensiveness and strength for values in Table 22 (n = 90) and Table 23 (n = 100) were +.66 and +.71 respectively, thus establishing a fairly close relationship between odor quality and quantity. Therefore a strong odor would usually be considered an offensive odor.

Experiment II

Manure in this experiment was obtained from the liquid manure pit at the Michigan State University dairy farm which was from the milking parlor and equipment area, and will be termed decomposed manure. This manure averaged

TABLE 23

Offensiveness and Strength Ratings[1] Four
and Five Days After Addition of Three
Chemicals to Fresh Liquid Dairy
Manure (Experiment Ib)

	Offensiveness[2]	Strength[3]
Sodium Perchlorate (PPM)		
250	5.3	5.6
500	5.4	5.4
2000	5.6	5.4
Hydrogen Peroxide (PPM)		
75	6.4	6.7
150	6.0	5.7
300	6.2	6.0
Potassium Permanganate (PPM)		
250	6.3	5.8
500	5.9	5.6
1000	4.4	4.3
Control	6.5	6.1

[1]Each value an average of two jars evaluated by five odor panelists each.

[2]0 = not offensive, 2 = very faint offensiveness, 4 = faint offensiveness, 6 = definite offensiveness, 8 = strong offensiveness, 10 = very strong offensiveness.

[3]0 = no odor, 2 = very faint odor, 4 = faint odor, 6 = definite odor, 8 = strong odor, 10 = very strong odor.

about one percent dry matter indicating a large amount of wash water and little feces. This type of manure (decomposed) was evaluated to see if there were differences when compared to fresh manure.

pH

The pH's of this decomposed liquid dairy manure before and after addition of lime, paraformaldehyde, H_2O_2 and $KMnO_4$ are in Table 24. Lime increased mean pH to about 12 compared to control values of 7.1 to 7.3 ($p < .005$). At days one, four and seven, addition of 10,000 PPM elicited a larger pH than 5000 PPM (12.35 to 12.55 > 11.6 to 12.1, $p < .005$).

Paraformaldehyde at day one did not change pH from that of control, but at day four and seven pH was lower than that of control ($p < .005$). The pH at day four and seven for 10,000 PPM paraformaldehyde was less than that for the two lower concentrations ($p < .025$) indicating pH decreased with increasing paraformaldehyde concentrations.

H_2O_2 did not alter pH from that of control. $KMnO_4$ at day one, four and seven increased pH above that of control ($p < .005$). The pH at day four and seven for 1000 PPM $KMnO_4$ was greater than that for 500 PPM ($p < .05$ and .025 respectively), thus demonstrating pH increase with increasing $KMnO_4$ concentration.

TABLE 24

pH[1] Before and After Addition of Four
Chemicals to Decomposed Liquid
Dairy Manure (Experiment II)

Chemicals and Levels	Day			
	-1	1	4	7
Lime (PPM)				
5,000	6.85	11.60_b	12.10_b	11.75_b
10,000	6.80	12.35^b	12.55^b	12.55^b
mean	6.82	11.98^a	12.33^a	12.15^a
Paraformaldehyde (PPM)				
1,000	6.85	7.00	6.90	6.70_d
5,000	7.00	7.20	6.70	6.40^d
10,000	6.90	7.00	6.50^c	6.25^c
mean	6.92	7.07	6.70^a	6.45^a
Hydrogen Peroxide (PPM)				
100	6.90	7.05	7.25	7.20
500	6.80	7.00	7.10	7.10
mean	6.85	7.03	7.18	7.15
Potassium Permanganate (PPM)				
500	6.95	7.50	7.65_d	7.55_c
1,000	7.20	7.60	7.95^d	7.90^c
mean	7.08	7.55^a	7.80^a	7.73^a
Control	6.95	7.15	7.30	7.30
SEM[2]	.07	.06	.06	.06

[1]Each value an average of two jars.

[2]SEM = standard error of each mean of two jars on a
given day.

[a]Significantly different ($p < .005$) than control
within the same column.

[b]Significantly different ($p < .005$) than means from
lower treatment concentrations within the same treatment
group within the same column.

[c]$p < .025$.

[d]$p < .05$.

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Ammonia and Ammonium Ion

Data in Table 25 represents a preliminary trial testing the relationship between total ammonia in liquid manure to treatment. No statistical analysis was done because values represent only one jar per treatment level. No definitive conclusions could be made, but these data suggest some treatments reduced total ammonia. Therefore, this was pursued further in Experiment III.

Nitrate

Each treatment level was checked for presence of nitrates, but none were detected. Since this manure was low in dry matter (1 percent) and relatively clear the color reaction could have been detected.

Odor Panel Evaluation

Efficacy of lime, paraformaldehyde, H_2O_2 and $KMnO_4$ on changing odor offensiveness of decomposed liquid manure is present in Table 26. Lime did not reduce odor offensiveness much below five (faint to definite offensiveness) at the days evaluated. Paraformaldehyde at 5000 PPM reduced offensive rating at day one to 3.8 (faintly offensive), and at day three all concentrations may have caused a slight reduction. At day eight only the 1000 PPM paraformaldehyde reduced offensiveness (3.5).

At day one 500 PPM H_2O_2 and 500 and 1000 PPM $KMnO_4$ reduced offensiveness ratings to 3.0, 3.0 and 3.8

TABLE 25

Total Ammonia[1] in Manure After Addition of
Four Chemicals to Decomposed Liquid
Dairy Manure (Experiment II)

Chemicals and Levels	Day	
	2	10
Lime (PPM)		
5,000	203	192
10,000	199	164
Paraformaldehyde (PPM)		
1,000	255	218
5,000	213	129
10,000	210	85
Hydrogen Peroxide (PPM)		
100	253	228
500	245	190
Potassium Permanganate (PPM)		
500	246	185
1,000	249	168
Control	246	231

[1]Each value an average of duplicate samples taken
from the same jar expressed as milligrams of ammonia per
liter of manure.

TABLE 26

Offensiveness Ratings[1] at Three Intervals
After Addition of Four Chemicals to
Decomposed Liquid Dairy Manure
(Experiment II)

Chemicals and Levels	Day		
	1	3	8
Lime (PPM)			
5,000	5.8	7.3	6.5
10,000	6.5	6.7	4.8
Paraformaldehyde (PPM)			
1,000	5.3	5.0	3.5
5,000	3.8	5.0	6.0
10,000	4.5	5.0	7.5
Hydrogen Peroxide (PPM)			
100	5.5	7.0	5.0
500	3.0	6.8	7.3
Potassium Permanganate (PPM)			
500	3.0	5.7	5.8
1,000	3.8	4.8	5.8
Control	7.7	6.3	6.8

[1]Each value an average of two jars evaluated by
three odor panelists each using the scale: 0 = not offensive,
2 = very faint offensiveness, 4 = faint offensiveness,
6 = definite offensiveness, 8 = strong offensiveness,
10 = very strong offensiveness.

respectively compared to control values of 7.7. This reduction was to the "faintly offensive" range. By day three values were similar to control.

Experiment III

Fresh feces and urine was added to manure taken from the liquid manure pit at the Michigan State University dairy farm producing a product containing about 5.6 percent dry matter. This remained at ambient temperature for a month to allow partial decomposition before being used in this experiment, and will be referred to as decomposed manure. This manure was considered to be more like that found under field conditions since a larger amount of solids was in the manure than in Experiment II.

Microbial Counts

Aerobic microbial numbers after addition of lime, paraformaldehyde, H_2O_2 and $KMnO_4$ to partially decomposed liquid dairy manure is presented in Table 27. At day one all values were similar to control. However, by day eight paraformaldehyde reduced aerobic counts, and extent of reduction was greater as paraformaldehyde concentration increased. Lime, H_2O_2 and $KMnO_4$ additions did not reduce number of microorganisms, and possibly lime and $KMnO_4$ increased numbers.

TABLE 27

Aerobic Microbial Numbers[1] at One and Eight
Days After Addition of Four Chemicals
to Decomposed Liquid Dairy Manure
(Experiment III)

Chemicals and Levels	Day	
	1	8
Lime (PPM)		
5,000	89×10^5	330×10^5
10,000	140×10^5	530×10^5
Paraformaldehyde (PPM)		
1,000	110×10^5	40×10^5
5,000	100×10^5	5.1×10^5
10,000	86×10^5	0.4×10^5
Hydrogen Peroxide (PPM)		
100	98×10^5	180×10^5
500	75×10^5	250×10^5
Potassium Permanganate (PPM)		
500	84×10^5	320×10^5
1,000	86×10^5	420×10^5
Control	74×10^5	180×10^5

[1]Each value an average of duplicates taken from the
same jar expressed as microorganisms per gram of treated
manure.

pH

Some alteration in pH was noted when these chemicals were added to this type of manure (Table 28). Mean pH for lime addition was greater than for control ($p < .005$). Lime at 10,000 PPM increased pH above that of 500 PPM ($p < .005$) at day one, four and nine. Mean pH for paraformaldehyde addition was not significantly less than control until day nine ($p < .005$). At this time pH of the 10,000 PPM paraformaldehyde treatment was less than the lower two concentrations ($p < .005$), and the 5000 PPM was less than the lowest concentration ($p < .025$).

H_2O_2 did not change pH. $KMnO_4$ increased pH above control at day four ($p < .05$) and nine ($p < .025$). At 1000 PPM $KMnO_4$ pH tended to be higher than 500 PPM, but only at day nine was it significant ($p < .005$).

Ammonia and Ammonium Ion

Changes in total ammonia (NH_3 and NH_4^+) in liquid manure as influenced by treatment are shown in Table 29. Concentration of total ammonia after lime addition was higher than that of control ($p < .05$) only on day four. Paraformaldehyde reduced total ammonia at day 11 ($p < .005$), and the 10,000 PPM treatment was lower than the two lower ones ($p < .005$). Values indicate an inverse relationship of total ammonia to concentration of paraformaldehyde added. H_2O_2 and $KMnO_4$ did not change values relative to control.

TABLE 28

pH^1 Before and After Addition of Four
Chemicals to Decomposed Liquid Dairy
Manure (Experiment III)

Chemicals and Levels	Day -1	Day 1	Day 4	Day 9
Lime (PPM)				
5,000	5.67	7.27	7.77	8.20[d]
10,000	5.67	8.57[d]	8.67[d]	8.90[d]
mean	5.67	7.92[a]	8.22[a]	8.55[a]
Paraformaldehyde (PPM)				
1,000	5.60	5.57	5.97	5.87
5,000	5.70	5.57	5.87	5.63[e]
10,000	5.70	5.60	5.73	5.43[d]
mean	5.67	5.58	5.86	5.64[a]
Hydrogen Peroxide (PPM)				
100	5.70	5.57	6.07	6.07
500	5.67	5.60	5.93	6.20
mean	5.69	5.59	6.00	6.14
Potassium Permanganate (PPM)				
500	5.67	5.73	6.17	6.33[d]
1,000	5.70	5.87	6.43	6.60[d]
mean	5.69	5.80	6.30[c]	6.47[b]
Control	5.67	5.60	5.93	6.27
SEM^2	.03	.08	.10	.05

[1]Each value an average of three jars.

[2]SEM = standard error of each mean of three jars
on a given day.

[a]Significantly different (p < .005) than control
within the same column.

[b]p < .025.　　　　　[c]p < .05.

[d]Significantly different (p < .005) than means
from lower treatment concentrations within the same treat-
ment group within the same column.

[e]p < .025.

TABLE 29

Total Ammonia[1] in Manure Before and After
Addition of Four Chemicals to
Decomposed Liquid Dairy
Manure (Experiment III)

Chemicals and Levels	Day		
	-2	4	11
Lime (PPM)			
5,000	323	411	418
10,000	329	389	390
mean	326	400[b]	404
Paraformaldehyde (PPM)			
1,000	347	347	356
5,000	329	334	281
10,000	332	299	152[c]
mean	336	327	263[a]
Hydrogen Peroxide (PPM)			
100	342	358	386
500	331	348	390
mean	337	353	388
Potassium Permanganate (PPM)			
500	361	394	394
1,000	340	380	391
mean	351	387	393
Control	332	352	401
SEM[2]	7	13	20

[1]Each value an average of three jars done in duplicate expressed as milligrams of ammonia per liter of manure.

[2]SEM = standard error of each mean of three jars on a given day.

[a]Significantly different ($p < .005$) than control within the same column.

[b]$p < .05$.

[c]Significantly different ($p < .005$) than means from lower treatment concentrations within the same treatment group within the same column.

When the change of the ammonia concentration with time for the paraformaldehyde treatment was compared to the change with time in the control, they were different ($p < .005$).

Odor Panel Evaluation

Offensiveness ratings after treatment addition is present in Table 30. At day two 5000 PPM lime reduced offensiveness rating (3.7 vs. 5.5). Paraformaldehyde and H_2O_2 did not reduce odor offensiveness at the times evaluated. $KMnO_4$ tended to reduce odor offensiveness below that of control at all three days, although not below the "faintly offensive" rating.

Experiment IV

Manure used in this experiment was prepared by addition of fresh fecal matter and urine to liquid manure taken from the pit at the Michigan State University dairy farm. This material remained at room temperature for about a month before use in this experiment, and will be referred to as decomposed manure. Dry matter content was about 4.7 percent. This experiment was undertaken because results from odor evaluation in the first three experiments were hard to interpret.

Odor Panel Evaluation

Rankings of offensiveness for two concentrations of paraformaldehyde or control manures at three time

TABLE 30

Offensiveness Ratings[1] at Three Intervals
After Addition of Four Chemicals to
Stored Liquid Dairy Manure
(Experiment III)

Chemicals and Levels	Day		
	1	2	8
Lime (PPM)			
5,000	5.1	3.7	6.7
10,000	5.9	6.0	7.4
Paraformaldehyde (PPM)			
1,000	5.9	5.7	5.1
5,000	5.7	5.2	5.0
10,000	6.0	5.1	5.3
Hydrogen Peroxide (PPM)			
100	5.9	5.7	6.3
500	5.5	5.9	6.8
Potassium Permanganate (PPM)			
500	5.9	4.3	6.5
1,000	4.6	4.3	5.0
Control	5.3	5.5	6.9

[1]Each value an average of two jars evaluated by
five odor panelists using the scale: 0 = not offensive,
2 = very faint offensiveness, 4 = faint offensiveness,
6 = definite offensiveness, 8 = strong offensiveness,
10 = very strong offensiveness.

intervals are in Table 31. No significant differences in
rankings could be detected between the two treatment con-
centrations or between the treatments and control. There-
fore, paraformaldehyde did not reduce odor offensiveness
when added to this type of manure.

H_2O_2 at 100 and 500 PPM was ranked in reference to
control (Table 32). At nine and 15 hours after addition of
500 PPM H_2O_2 the odor was judged to be less offensive than
that for 100 PPM (p = .01) or control (p = .05). At 36 to
40 hours and eight days, no differences were detected.

Odor rankings of manure with 500 and 1000 PPM $KMnO_4$
added and control are in Table 33. At all three time
periods there was no significant ranking difference between
500 and 1000 PPM $KMnO_4$. Manure treated with 500 PPM $KMnO_4$
reduced offensiveness when compared to control (p = .01)
at all time periods. Manure treated with $KMnO_4$ at 1000 PPM
was judged to be less offensive than control at nine to 15
hours (p = .05), 36 to 40 hours (p = .01) and eight days
(p = .02).

Table 34 presents rankings for 5000 PPM parafor-
maldehyde, 500 PPM $KMnO_4$ and control manures. At nine
to 15 hours no difference in odor offensiveness was
detected between $KMnO_4$ and control, but paraformaldehyde
was more offensive (p = .01). By 36 to 40 hours no ranking
differences between paraformaldehyde and control was
detected, but $KMnO_4$ was less offensive than paraformaldehyde

TABLE 31

Odor Panel Rankings[1] at Three Time Periods Comparing Two Concentrations
of Paraformaldehyde (PF) and Control (Experiment IV)

Panelist	9-15 Hours			36-40 Hours			8 Days		
	PF 5,000 PPM[a]	PF 10,000 PPM[a]	Control[a]	PF 5,000 PPM[b]	PF 10,000 PPM[b]	Control[b]	PF 5,000 PPM[c]	PF 10,000 PPM[c]	Control[c]
A	2	1	3	3	1	2	3	2	1
B	2	1	3	2	1	3	2	1	3
C	1	2	3	1	2	3	2	3	1
D	1	3	2	2	1	3	3	2	1
E	3	1	2	2	1	3	2	3	1
F	2	1	3	3	2	1	2	1	3
G	1	2	3	1	2	3	1	3	2
H	3	2	1	2	1	3	1	2	3
I	1	2	3	2	3	1	1	2	3
J	2	1	3	1	3	2	1	2	3
K	2	3	1	-	-	-	-	-	-
L	2	3	1	-	-	-	-	-	-
M	2	1	3	-	-	-	-	-	-

[1]Each value a ranking given by each panelist using the scale: 1 = least offensive, 2 = moderately offensive, 3 = most offensive.

a,b,cTreatments having different superscripts within each time period differ significantly ($p \leq .05$).

TABLE 32

Odor Panel Rankings[1] at Three Time Periods Comparing Two Concentrations
of H_2O_2 and Control (Experiment IV)

Panelist	9-15 Hours			36-40 Hours			8 Days		
	H_2O_2 100 PPM[a]	H_2O_2 500 PPM[b]	Control[a]	H_2O_2 100 PPM[c]	H_2O_2 500 PPM[c]	Control[c]	H_2O_2 100 PPM[d]	H_2O_2 500 PPM[d]	Control[d]
A	3	1	2	2	1	3	2	3	1
B	3	2	1	3	2	1	3	2	1
C	3	1	2	1	2	3	2	3	1
D	2	1	3	3	1	2	2	1	3
E	3	1	2	2	3	1	3	1	2
F	2	1	3	2	1	3	1	2	3
G	3	1	2	1	3	2	3	2	1
H	1	2	3	3	1	2	2	1	3
I	3	2	1	1	3	2	1	3	2
J	3	1	2	3	1	2	1	2	3
K	3	2	1	-	-	-	-	-	-
L	2	1	3	-	-	-	-	-	-
M	3	1	2	-	-	-	-	-	-

[1]Each value a rating given by each panelist using the scale: 1 = least offensive, 2 = moderately offensive, 3 = most offensive.

a,b,c,dTreatments having different superscripts within each time period differ significantly ($p \leq .05$).

TABLE 33

Odor Panel Rankings[1] at Three Time Periods Comparing Two Concentrations
of KMnO$_4$ and Control (Experiment IV)

Panelist	9-15 Hours			36-40 Hours			8 Days		
	KMnO$_4$ 500 PPM[a]	KMnO$_4$ 1000 PPM[a]	Control[b]	KMnO$_4$ 500 PPM[c]	KMnO$_4$ 1000 PPM[c]	Control[d]	KMnO$_4$ 500 PPM[e]	KMnO$_4$ 1000 PPM[e]	Control[f]
A	2	3	1	1	2	3	2	1	3
B	1	2	3	2	1	3	1	3	2
C	3	1	2	2	1	3	2	1	3
D	1	2	3	2	1	3	2	1	3
E	2	1	3	2	1	3	1	2	3
F	2	1	3	2	1	3	2	1	3
G	1	3	2	1	2	3	1	3	2
H	1	2	3	1	2	3	1	2	3
I	1	2	3	1	2	3	1	2	3
J	2	1	3	2	1	3	2	1	3
K	2	1	3	-	-	-	-	-	-
L	1	2	3	-	-	-	-	-	-
M	1	2	3	-	-	-	-	-	-

[1]Each value a rating given by each panelist using the scale: 1 = least offensive, 2 = moderately offensive, 3 = most offensive.

a,b,c,d,e,f Treatments having different superscripts within each time period differ significantly (p $\leq$ .05).

TABLE 34

Odor Panel Rankings[1] at Three Time Periods Comparing Paraformaldehyde (PF)
to KMnO$_4$ and Control (Experiment IV)

Panelist	9-15 Hours			36-40 Hours			8 Days		
	PF 5000 PPM[a]	KMnO$_4$ 500 PPM[b]	Control[b]	PF 5000 PPM[c]	KMnO$_4$ 500 PPM[d]	Control[d]	PF 5000 PPM[e]	KMnO$_4$ 500 PPM[f]	Control[e]
A	3	1	2	3	2	1	3	1	2
B	3	1	2	2	1	3	3	1	2
C	3	2	1	3	2	1	3	2	1
D	3	1	2	3	1	2	3	1	2
E	3	2	1	2	1	3	2	1	3
F	3	1	2	1	2	3	1	2	3
G	3	2	1	3	1	2	2	1	3
H	3	2	1	3	1	2	3	1	2
I	2	3	1	3	1	2	3	1	2
J	3	1	2	3	1	2	3	1	2

[1]Each value a rating given by each panelist using the scale: 1 = least offensive, 2 = moderately offensive, 3 = most offensive.

[a,b,c,d,e,f]Treatments having different superscripts within each time period differ significantly (p $\leq$ .05).

(p = .01). Also odor ranking for $KMnO_4$ treated manure did not differ from that of control. At day eight $KMnO_4$ was less offensive than paraformaldehyde (p = .01) and control (p = .02) indicating a long-term odor reduction due to $KMnO_4$ addition.

Odor rankings of manure with 5000 PPM paraformaldehyde, 500 PPM H_2O_2 and control show some differences (Table 35). H_2O_2 treatment and control were not different at nine to 15 hours, but paraformaldehyde was more offensive than H_2O_2 (p = .01) and control (p = .02). At 36 to 40 hours no difference in odor offensiveness between the two treatments and control could be detected, but paraformaldehyde was more offensive than H_2O_2 (p = .02). No differences in odor offensiveness were detected at day eight.

Table 36 presents odor comparisons of 500 PPM $KMnO_4$, 500 PPM H_2O_2 and control manures. At nine to 15 hours no differences were detected, but by 36 to 40 hours, control was more offensive than $KMnO_4$ (p = .01) or H_2O_2 (p = .05) treated manures. No difference was detected between the two treated manures. $KMnO_4$ treated manure was less offensive than H_2O_2 (p = .05) or control manures (p = .02) at day eight, with no difference between control and H_2O_2 treated manure.

Rankings of offensiveness of 100 and 500 PPM H_2O_2 and control manures are in Table 37. Both 100 and 500 PPM H_2O_2 treatments reduced offensiveness when compared to

TABLE 35

Odor Panel Rankings[1] at Three Time Periods Comparing Paraformaldehyde (PF) to H_2O_2 and Control (Experiment IV)

Panelist	9-15 Hours			36-40 Hours			8 Days		
	PF 5000 PPM[a]	H_2O_2 500 PPM[b]	Control[b]	PF 5000 PPM[c]	H_2O_2 500 PPM[d]	Control[cd]	PF 5000 PPM[e]	H_2O_2 500 PPM[e]	Control[e]
A	3	1	2	3	1	2	2	3	1
B	3	1	2	3	2	1	3	2	1
C	3	2	1	3	1	2	3	1	2
D	3	1	2	3	1	2	3	1	2
E	3	1	2	3	1	2	3	1	2
F	3	2	1	1	2	3	1	2	3
G	3	2	1	3	2	1	2	1	3
H	2	3	1	1	2	3	3	2	1
I	3	1	2	3	1	2	3	2	1
J	2	1	3	3	1	2	3	2	1

[1]Each value a rating given by each panelist using the scale: 1 = least offensive, 2 = moderately offensive, 3 = most offensive.

a,b,c,d,e Treatments having different superscripts within each time period differ significantly ($p \leq .05$).

TABLE 36

Odor Panel Rankings[1] at Three Time Periods Comparing $KMnO_4$ to H_2O_2 and Control (Experiment IV)

Panelist	9-15 Hours			36-40 Hours			8 Days		
	$KMnO_4$ 500 PPM[a]	H_2O_2 500 PPM[a]	Control[a]	$KMnO_4$ 500 PPM[b]	H_2O_2 500 PPM[b]	Control[c]	$KMnO_4$ 500 PPM[d]	H_2O_2 500 PPM[e]	Control[e]
A	2	3	1	1	2	3	1	3	2
B	1	2	3	2	1	3	1	2	3
C	3	2	1	1	2	3	2	1	3
D	1	2	3	1	2	3	1	2	3
E	1	2	3	1	2	3	1	2	3
F	1	2	3	1	3	2	1	3	2
G	2	1	3	1	2	3	2	3	1
H	2	3	1	2	1	3	2	3	1
I	1	2	3	2	1	3	2	1	3
J	2	1	3	1	3	2	1	3	2

[1]Each value a rating given by each panelist using the scale: 1 = least offensive, 2 = moderately offensive, 3 = most offensive.

a,b,c,d,e Treatments having different superscripts within each time period differ significantly (p ≤ .05).

TABLE 37

Odor Panel Rankings[1] at Four Time Periods Comparing Two
Concentrations of H_2O_2 and Control (Experiment IV)

Panelist	1/2-1 1/2 Hours			6-8 Hours		
	H_2O_2 100 PPM[a]	H_2O_2 500 PPM[a]	Control[b]	H_2O_2 100 PPM[cd]	H_2O_2 500 PPM[c]	Control[d]
A	2	1	3	3	1	2
B	2	1	3	2	1	3
C	2	1	3	1	2	3
D	2	1	3	2	1	3
E	1	2	3	3	1	2
F	1	2	3	3	1	2

Panelist	30-32 Hours			9 Days		
	H_2O_2 100 PPM[e]	H_2O_2 500 PPM[e]	Control[e]	H_2O_2 100 PPM[f]	H_2O_2 500 PPM[f]	Control[f]
A	3	1	2	2	3	1
B	1	3	2	3	1	2
C	3	2	1	3	1	2
D	2	1	3	2	1	3
E	2	1	3	1	2	3
F	1	3	2	2	1	3
G	1	3	2	2	1	3
H	-	-	-	3	1	2

[1]Each value a rating given by each panelist using the scale:
1 = least offensive, 2 = moderately offensive, 3 = most offensive.

[a,b,c,d,e,f]Treatments having different superscripts within
each time period differ significantly ($p \leq .05$).

control manure (p = .05) at 0.5 to 1.5 hours, and there was no difference in offensiveness between concentrations of H_2O_2. At six to eight hours the 500 PPM H_2O_2 treated manure was less offensive than control (p = .05), with no difference in offensiveness between 100 PPM H_2O_2 treated manure and the other two (500 PPM H_2O_2 and control). After this time no differences were detected.

Odor rankings of manure with addition of 500 PPM H_2O_2, 500 PPM $KMnO_4$ and control show consistent differences (Table 38). At 0.5 to 1.5 hours H_2O_2 treated manure was less offensive than $KMnO_4$ or control manures (p = .05). At six to eight hours both H_2O_2 and $KMnO_4$ treated manure was less offensive than control (p = .05), but H_2O_2 treated manure was less offensive than $KMnO_4$ (p = .05) and control manures (p = .02) at 30 to 32 hours. By nine days $KMnO_4$ treated manure was less offensive than H_2O_2 (p = .01) and control manures (p = .02).

Experiment V

Manure used in this experiment was the same as that in Experiment IV, except manure was allowed to remain at room temperature for about three months before use, and will be referred to as decomposed manure. Dry matter content was about five percent. This experiment was undertaken to compare some of the commercial products now on the market.

TABLE 38

Odor Panel Rankings[1] at Four Time Periods Comparing
H_2O_2 to $KMnO_4$ and Control (Experiment IV)

Panelist	1/2-1 1/2 Hours			6-8 Hours		
	H_2O_2 500 PPM[a]	$KMnO_4$ 500 PPM[b]	Control[b]	H_2O_2 500 PPM[c]	$KMnO_4$ 500 PPM[c]	Control[d]
A	1	2	3	2	1	3
B	1	2	3	2	1	3
C	1	3	2	2	1	3
D	1	3	2	2	1	3
E	1	3	2	1	2	3
F	1	2	3	1	2	3

Panelist	30-32 Hours			9 Days		
	H_2O_2 500 PPM[e]	$KMnO_4$ 500 PPM[f]	Control[f]	H_2O_2 500 PPM[g]	$KMnO_4$ 500 PPM[h]	Control[g]
A	1	2	3	2	1	3
B	1	3	2	2	1	3
C	1	3	2	3	1	2
D	1	3	2	2	1	3
E	1	3	2	2	1	3
F	2	1	3	2	1	3
G	1	3	2	3	2	1
H	-	-	-	2	1	3

[1]Each value a rating given by each panelist using the scale:
1 = least offensive, 2 = moderately offensive, 3 = most offensive.

[a,b,c,d,e,f,g,h]Treatments having different superscripts within each time period differ significantly ($p \leq .05$).

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Odor Panel Evaluation

Rankings of offensiveness of 1430 PPM Odor Mask, 360 PPM Pit-Zyme and control manures are in Table 39. No differences in offensiveness could be detected until eight days. At this time Odor Mask treated manure was more offensive than Pit-Zyme or control manure (p = .05).

Table 40 presents odor comparisons of 360 PPM Pit-Zyme, 360 PPM Sep-Zyme "O" and control manures. No differences in odor offensiveness could be detected until day eight. Pit-Zyme treated manure was less offensive than control manure (p = .05), but not different than Sep-Zyme "O".

Odor rankings of 1430 PPM Odor Mask, 360 PPM Sep-Zyme "O" and control manures showed no consistent differences (Table 41) at the times evaluated.

TABLE 39

TABLE 39

Odor Panel Rankings[1] at Three Time Periods Comparing Odor Mask
to Pit-Zyme and Control (Experiment V)

Panelist	9-15 Hours			33-39 Hours			8 Days		
	Odor Mask 1430 PPM[a]	Pit-Zyme 360 PPM[a]	Control[a]	Odor Mask 1430 PPM[b]	Pit-Zyme 360 PPM[b]	Control[b]	Odor Mask 1430 PPM[c]	Pit-Zyme 360 PPM[d]	Control[d]
A	1	2	3	1	3	2	1	2	3
B	3	1	2	1	3	2	3	2	1
C	2	1	3	2	3	1	3	2	1
D	3	2	1	3	1	2	3	1	2
E	1	3	2	3	1	2	3	1	2
F	3	1	2	3	2	1	3	2	1
G	1	2	3	3	2	1	3	1	2
H	2	1	3	3	1	2	3	2	1

[1] Each value a rating given by each panelist using the scale: 1 = least offensive, 2 = moderately offensive, 3 = most offensive.

a,b,c,d Treatments having different superscripts within each time period differ significantly (p ≤ .05).

TABLE 40

TABLE 40

Odor Panel Rankings[1] at Three Time Periods Comparing Pit-Zyme to Sep-Zyme "O" and Control (Experiment V)

Panelist	9-15 Hours			33-39 Hours			8 Days		
	Pit-Zyme 360 PPM[a]	Sep-Zyme "O" 360 PPM[a]	Control[a]	Pit-Zyme 360 PPM[b]	Sep-Zyme "O" 360 PPM[b]	Control[b]	Pit-Zyme 360 PPM[c]	Sep-Zyme "O" 360 PPM[c]	Control[d]
A	1	3	2	2	3	1	1	3	2
B	1	3	2	2	3	1	2	1	3
C	1	3	2	3	2	1	1	3	2
D	3	1	2	1	2	3	2	3	1
E	3	2	1	2	1	3	1	3	2
F	2	1	3	2	1	3	1	2	3
G	1	3	2	2	3	1	2	1	3
H	1	3	2	1	3	2	2	1	3

[1]Each value a rating given by each panelist using the scale: 1 = least offensive, 2 = moderately offensive, 3 = most offensive.

[a,b,c,d]Treatments having different superscripts within each time period differ significantly ($p \leq .05$).

TABLE 41

Odor Panel Rankings[1] at Three Time Periods Comparing Odor Mask
to Sep-Zyme "O" and Control (Experiment V)

Panelist	9-15 Hours			33-39 Hours			8 Days		
	Odor Mask 1430 PPM[a]	Sep-Zyme "O" 360 PPM[a]	Control[a]	Odor Mask 1430 PPM[b]	Sep-Zyme "O" 360 PPM[b]	Control[b]	Odor Mask 1430 PPM[c]	Sep-Zyme "O" 360 PPM[c]	Control[c]
A	3	2	1	1	2	3	1	3	2
B	3	2	1	1	3	2	3	2	1
C	2	1	3	2	1	3	3	1	2
D	3	1	2	2	1	3	2	1	3
E	1	2	3	3	1	2	3	1	2
F	3	1	2	3	1	2	3	2	1
G	1	3	2	2	3	1	3	1	2
H	2	3	1	2	1	3	2	1	3

[1]Each value a rating given by each panelist using the scale: 1 = least offensive, 2 = moderately offensive, 3 = most offensive.

[a,b,c]Treatments having different superscripts within each time period differ significantly ($p \leq .05$).

V. DISCUSSION

Results of these experiments indicate certain of
the treatments evaluated were effective in changing odor
produced from fresh as well as decomposed dairy waste.
Most of these changes could be attributed to either anti-
microbial or oxidative properties of the additive that pre-
vented formation of malodors or destroyed malodors already
produced.

Table 42 was included in an attempt to demonstrate
the diversity of the manure used in these experiments.
Manure varied in dry matter content and length of storage
before treatment.

Influence on Microbial Numbers by Additives

Experiment I was undertaken to evaluate treat-
ments on the prevention of odorous compound formation in
fresh dairy manure. Paraformaldehyde at 7000 and 30,000
PPM depressed total aerobic and anaerobic microbial numbers
for at least 22 days (Table 16). The amount of reduction
increased with time and paraformaldehyde concentration, with
numbers being lowest for 30,000 PPM at day 22. At this
time aerobic and anaerobic counts for 30,000 PPM parafor-
maldehyde were 0.16×10^4 and 0.16×10^4 respectively

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TABLE 42

Characteristics of Manure Used in
Experiments I through V

Experiment	Dry Matter (%)	Length of Storage Before Treatment Addition	Type of Manure
I	13.0	0	fresh
II	1.0	< 1 month	decomposed
III	5.6	1 month	decomposed
IV	4.7	< 1 month	decomposed
V	5.0	< 3 months	decomposed

Experiment I treatments: paraformaldehyde, acrolein, H_3PO_4, $NaClO_4$, H_2O_2 and $KMnO_4$.

Experiments II and III treatments: lime, paraformaldehyde, H_2O_2 and $KMnO_4$.

Experiment IV treatments: paraformaldehyde, H_2O_2 and $KMnO_4$.

Experiment V treatments: Pit-Zyme, Sep-Zyme "O" and Odor Mask.

compared with control (35 x 10^7 and 9.7 x 10^7 respectively).
This was a reduction of over 99 percent for both aerobic
and anaerobic counts. This antimicrobial action of para-
formaldehyde was also observed by Seltzer et al. (1969)
and Veloso et al. (1974). Formaldehyde is the active
bactericidal agent, and is formed by the depolymerization
of paraformaldehyde. This reaction occurs slowly under
most conditions, allowing for prolonged bactericidal action.

Paraformaldehyde addition to decomposed manure at
1000, 5000 and 10,000 PPM did not reduce aerobic counts at
day one, but at eight days counts were reduced to below
25 percent of control (Table 27). At day eight 10,000
PPM paraformaldehyde reduced aerobic counts to 0.5 x 10^5
compared with control (180 x 10^5). This was a 99 percent
reduction in numbers.

Acrolein was bactericidal at all concentrations
added. H_3PO_4 at the highest concentration produced a
slight reduction in aerobic and anaerobic counts until
after day 15 in fresh manure, but by day 22 values were
similar to control (Table 16).

$NaClO_4$ at the highest concentration produced a
reduction in aerobic and anaerobic counts until day eight
in fresh manure, but by day 15 values were similar to
control (Table 17).

Bactericidal action of acrolein, H_3PO_4 and $NaClO_4$
at the concentrations added was probably not sufficient

to prevent formation of odorous compounds in fresh manure.

Lime in decomposed manure, and H_2O_2 and $KMnO_4$ in fresh and decomposed manure produced no change in microbial counts. The oxidants, H_2O_2 and $KMnO_4$, would tend to produce conditions favorable to aerobes, but at concentrations used, this was not detected in these microbial counts. Ritter et al. (1975) found dissolved oxygen to increase in manure proportionally to the amount of H_2O_2 added, and thus would expect more aerobes to be present. It may have been our assay for aerobes and anaerobes was not precise enough to note differences.

Selective bactericidal action may have occurred with some treatments. For example lime raised pH to above 10 which is above the optimum for most bacteria (Miner, 1971), and only the least fastidious bacteria would be expected to survive and grow at this pH. H_2O_2 may selectively act as a bactericide to sulfate reducing bacteria that are responsible for formation of hydrogen sulfide (FMC Corporation). Therefore, even though total numbers of bacteria may not be reduced certain species may not grow or survive. Such a shift in microbial population could change odor characteristics.

Aerobic microbes were more numerous in fresh than in decomposed waste. This could be due to more sub-strate (dry matter) in the fresh manure indicating a

greater rate of decomposition, and therefore more microbes.

Many of the aerobic microbes were probably facultative anaerobes meaning they would also be present under anaerobic conditions. Thus the total number of microorganisms in Experiment I was probably not the sum of aerobic and anaerobic counts since there would tend to be some overlap between the two.

Influence on pH by Additives

Paraformaldehyde decreased pH in fresh and decomposed manure which agrees with observations made by Veloso et al. (1974). This pH decrease probably results from decreased ammonia concentrations in the manure. Fluctuations of pH with time were reduced indicating a decreased rate of decomposition and decreased production of odorous compounds. This reduced decomposition was a direct result of the decreased number of microorganisms present in the manure.

The pH was reduced as concentration of H_3PO_4 in fresh manure increased (Table 18). An explanation for the reduced microbial numbers in H_3PO_4 treated manures for one and eight days caused by a simultaneous decrease in pH is not readily evident since at day 21 H_3PO_4 reduced pH, but microbial numbers were as great or greater than control.

$KMnO_4$ tended to have no effect on pH of fresh manure, but tended to increase it in decomposed manure.

This pH increase is a result of MnO_4^- reacting with hydrogen ions to produce water. The difference between fresh and decomposed manure can be explained by the fact that dry matter in fresh manure was 13 percent compared to 5.6 percent or below in decomposed manure. Thus concentration of added $KMnO_4$ per unit of dry matter was less for fresh manure. Also fresh manure would tend to counteract the expected pH increase from $KMnO_4$ by production of organic acids during anaerobic decomposition.

Lime increased pH values in decomposed manure at all concentrations used. This pH increasing property of lime was used by Hammond et al. (1966), Day (1966) and Cole et al. (1974) to reduce offensiveness of liquid swine manure. Lime probably does not decrease production of odorous compounds, but does change composition of gases volatilized. For example with pH 10 or above, very little hydrogen sulfide or organic acids would be volatized while ammonia and amine volatilization would increase (Miner, 1974).

Acrolein added to fresh manure or H_2O_2 to fresh and decomposed manure did not alter pH values from control.

In fresh manure pH tended to decrease with time while in decomposed manure it increased. This relationship was statistically significant when controls in Table 18 and 19 were compared to controls in Table 24 and 28. Fresh manure would be undergoing fermentation and produce organic

acids, thus decreasing pH. Decomposed manure would probably have completed fermentation of readily available carbohydrate and pH would be increasing due to ammonia production from protein degradation. Also microbes in decomposed manure may be converting organic acids to methane resulting in a pH increase.

Influence on Ammonia and Ammonium Ion by Additives

The pH of most treated or control manure was near or below neutral (pH 7) indicating most of the ammonia was in the NH_4^+ nonvolatile form. Ammonia (NH_3) concentrations in the air space over all manures in Experiment I were such that volatilization of ammonia had to occur, but would not have been expected at the observed pH values. More careful observation revealed the top layer of manure became basic (pH > 8) allowing release of ammonia (NH_3) while the center and bottom remained neutral or acidic. Therefore, there was stratification during storage of this manure. This is probably similar to what occurs in large storage tanks where NH_3 can escape from the upper portion while the lower portion remains acidic.

Ammonia concentrations in the air space over manure were measured with the idea that ammonia concentration would be related to other odorous gases. Miner and Stroh (1975) considered ammonia to be volatilized in quantities

sufficiently related to the more odorous compounds so that ammonia could be used as an odor indicator.

Ammonia concentration in the manure air space was significantly reduced by paraformaldehyde at day two and this trend continued for 21 days although this trend was not statistically significant because of excessive variation from jar to jar (Table 20). This reduction of ammonia was probably a result of bactericidal properties of formaldehyde reducing breakdown of urea and proteins. Also the nonvolatile compound hexamethylene tetramine could have been produced by reaction of formaldehyde and ammonia (Seltzer et al., 1969).

$NaClO_4$ caused no change in air space ammonia concentrations except at day seven when ammonia concentration was positively related to amounts of $NaClO_4$ added. The pH of the 2000 PPM $NaClO_4$ treatment was slightly elevated, but insufficiently high to account for the ammonia in the air since small fluctuations in pH did not result in concurrent changes in gaseous ammonia concentrations.

No differences in ammonia concentrations were detected over acrolein, H_3PO_4, H_2O_2 or $KMnO_4$ treated manures. Miner and Stroh (1975) found no difference in ammonia desorption in $KMnO_4$ treated manure.

Ammonia in the air space over all manures in Experiment I had extremely large variation from jar to jar

so that no definite conclusions can be made from these
results. Also treatments could change pH and thus ammonia
in the air over treated manure without decreasing offen-
siveness. These results indicate that ammonia by itself is
a fairly poor measurement of changes in odor offensiveness.

Ammonia volatilization represents a loss of
nitrogen from manure. Miner (1974) used data from
Hashimoto and Ludington (1971) and calculated that at a pH
of 8.0 and a temperature of 20° the nitrogen content of
liquid poultry manure would be lowered 3.3 percent per day
by ammonia volatilization. A pH of 9.0 would decrease
nitrogen at a rate of 23 percent per day. This system was
agitated keeping dissolved ammonia in contact with the air.
In a nonagitated system as used in this study a slower rate
of desorption would be expected. Also, stratification
would occur with much of the lighter material forming a
crust producing a barrier between dissolved ammonia and
air.

In Experiments II and III total ammonia present in
manure as NH_4^+ and NH_3 was measured to determine treatment
effects on formation and liberation. Only at the high pH
observed in lime treated manure would the major portion of
ammonia be in the NH_3 form.

In Experiment II total ammonia (NH_4^+ and NH_3)
concentrations decreased with time but in Experiment III
they increased. This might be explained on the basis

of differences in dry matter content and extent of decomposition during manure storage before tests were initiated. Manure in Experiment II had about one percent dry matter while Experiment III averaged 5.6 percent. Also manure in Experiment II had been decomposing for several weeks and decomposition was nearly complete, while that in Experiment III had decomposed for about four weeks before the tests were conducted. Thus more ammonia (NH_4^+ and NH_3) formation would be expected in Experiment III resulting in a net increase in ammonia while Experiment II would decrease due to volatilization and decreased breakdown of proteins. Ammonia as used here would be an indication of anaerobic decomposition (protein degradation).

Total ammonia found in the manure in Experiment III was almost twice the amount in Experiment II, and was approximately related to the amount of substrate present.

Addition of paraformaldehyde slightly decreased total ammonia in decomposed manure at day four, and significantly reduced it at day 11 (Table 29). This reduction was not likely due to atmospheric loss since decreased desorption of ammonia from paraformaldehyde treated manure was found in Experiment I. Ammonia may have been oxidized to nitrate (NO_3^-) with agitation of manure, but this was discounted when no nitrates were found. Therefore, the decreased ammonia concentration must have resulted from reduced degradation caused by the bactericidal action of

formaldehyde and/or the binding of formaldehyde to ammonia. The result would be increased nitrogen retention as was observed by Seltzer et al. (1969).

Lime acted to increase total ammonia present in the treated manure at day four, but at day 11 no difference from control could be noted (Table 29). This increase in ammonia may have resulted from a temporary increase in protein degradation during the first days after addition of lime, but this relationship is uncertain.

Influence on Odor Panel Evaluation by Treatments

Odor offensiveness of fresh manure treated with paraformaldehyde at 7000 and 10,000 PPM were reduced to below "faintly offensive" (Table 22). Strength was reduced, but not as much as offensiveness. Control manure was rated as "definite offensiveness" for quality and "definite odor" for quantity. The apparent smell of formaldehyde at 30,000 PPM paraformaldehyde caused both odor offensiveness and strength to be above that of the lower two concentrations. Odor control with 30,000 PPM paraformaldehyde must be considered inadequate. Personal evaluation indicated paraformaldehyde was a better treatment in reducing odor offensiveness in fresh manure than was acrolein or H_3PO_4.

This reduction in odor offensiveness with the lower two concentrations of paraformaldehyde can be attributed to the prevention of odorous compound formation

by the bactericidal action of the formaldehyde. Also the odor of formaldehyde may have masked the natural odor of manure causing it to be less offensive to the odor panel.

This reduction in offensiveness relates to the decreased ammonia concentration in the air above para-formaldehyde treated manure, probably a result of decreased degradation. In treatments where no reduction in degradation occurs there would probably be no decrease in the amount of ammonia in the air over manure even though there is a decrease in offensiveness. Therefore this method of using ammonia as an odor indicator probably would not be applicable in all cases.

Correlation coefficients between odor offensiveness and strength were r = +.66 and +.71 respectively (Table 22 and 23). This indicates the odor panel could not effectively separate the two, and this was observed by Cole et al. (1974). One reason for this might be the nose becomes less sensitive after smelling an odor for a relatively short period of time. Odor fatigue could also be responsible for the large amount of variation in scores assigned duplicate jars by the odor panel.

Because of the fairly high positive correlation between offensiveness and strength only offensiveness was evaluated in Experiments II and III. No consistent depression of odor offensiveness was perceived with para-formaldehyde in Experiment II, but there was a slight

depression in Experiment III. This indicates that para-
formaldehyde may not be effective in reducing offensiveness
of odorous compounds already produced, and agrees with Cole
et al. (1975).

$KMnO_4$ at 1000 PPM decreased odor offensiveness and
strength in fresh manure to the "faintly offensive" level
while control was rated above "definitely offensive"
(Table 23). Odor strength was reduced to just above a
"faint odor" compared to control of a "definite odor." In
decomposed manure $KMnO_4$ treatment may have decreased
offensiveness slightly, but this depression is not certain
from odor panel results. Personal evaluation of decomposed
manure (Table 26) indicated $KMnO_4$ decreased odor offensive-
ness within a few minutes after addition.

Odor changes after lime addition to fresh manure
was not evaluated, but Experiments II and III indicate
little effectiveness for lime in decreasing odor offensive-
ness in decomposed manure. Personal evaluation revealed a
strong smell of ammonia resulting from this treatment.
This odor to most panelists seemed just as offensive as
the natural odor. This is in contrast to what was observed
by Hammond et al. (1966) and Day (1966) using liquid swine
manure.

Acrolein, H_3PO_4, $NaClO_4$ and H_2O_2 did not prevent
odor formation in fresh manure. Acrolein, H_3PO_4 and $NaClO_4$
were added to decomposed manure and a personal evaluation

made. No decrease in odor offensiveness could be detected and these treatments were not further evaluated. H_2O_2 added to decomposed manure was evaluated with an odor panel in Experiments II and III, and little if any decrease in offensiveness was detected.

In the first three experiments no statistical differences could be detected with various treatments. The method of odor evaluation used in these first three experiments resulted in an excessive amount of olfactory fatigue and/or confusion of odor panelists. Therefore means, personal evaluations and literature information were used to determine which treatments would be tested in Experiment IV. Paraformaldehyde, $KMnO_4$ and H_2O_2 were chosen.

The method of evaluating offensiveness in Experiment IV was one of relative offensiveness of two treatments compared with control. Odor fatigue and panelist confusion were reduced by decreasing number of jars evaluated at any one time and in any one comparison.

Paraformaldehyde at 5000 and 10,000 PPM did not decrease offensiveness at the intervals evaluated (Table 31). H_2O_2 at 500 PPM decreased offensiveness compared to 100 PPM H_2O_2 and control at nine to 15 hours (Table 32). $KMnO_4$ at 500 and 1000 PPM reduced odor offensiveness for the duration of the experiment (eight days) (Table 33). Decomposed manure was used in these evaluations.

Based on these results the least concentration of additive that reduced odor was tested further. Paraformaldehyde did not reduce odor offensiveness, therefore the least concentration was used based on results of Experiment I.

Paraformaldehyde at 5000 PPM added to decomposed manure was more offensive than H_2O_2, $KMnO_4$ and control manures. Personal evaluation revealed a strong formaldehyde odor.

In a three-way comparison 500 PPM $KMnO_4$ treated manure was less offensive than paraformaldehyde, but not different from control until day eight (Table 34). This may be explained on the basis of a small difference between $KMnO_4$ and control manures when compared to paraformaldehyde manure. In another three-way comparison $KMnO_4$ treated manure was less offensive than control after 36 to 40 hours, but not different than H_2O_2 manure (Table 36). At day eight $KMnO_4$ treated manure was less offensive than both. Thus extent of odor offensiveness will depend to some degree on treatments compared.

In another three-way comparison, 500 PPM H_2O_2 treated manure was less offensive than paraformaldehyde manure, but no difference could be detected when compared to control (Table 35). When H_2O_2 treated manure was compared to $KMnO_4$ and control manures no difference could be detected until 36 to 40 hours when both treatments were less offensive than control, but no different between

themselves (Table 36). At day eight H_2O_2 manure was not different than control.

These results indicate paraformaldehyde was not effective in reducing odor offensiveness of decomposed manure but probably enhanced it. $KMnO_4$ reduced offensiveness possibly on a short-term as well as long-term basis. H_2O_2 may have reduced odor offensiveness, but this odor reduction is not certain.

Because the effect of H_2O_2 was equivocal at the times evaluated an evaluation at 0.5 to 1.5 hours was then made. At this time both 100 and 500 PPM H_2O_2 treated manure were less offensive than control manure, but by seven hours only 500 PPM treated manure was less offensive than control (Table 37). By 30 to 32 hours no odor reduction was detected.

Odor of manure treated with 500 PPM H_2O_2 was less offensive than $KMnO_4$ or control manures at 0.5 to 1.5 hours (Table 38). At seven hours both treatment manures had less offensive odor than control. At 30 to 32 hours H_2O_2 treated manure was again less offensive than $KMnO_4$ and control manure, but by day eight the $KMnO_4$ treated manure was less offensive.

In these trials $KMnO_4$ was added as crystals to the manure. The lag in odor reduction may be reduced by using dissolved aqueous $KMnO_4$. This agrees with the lag in

sulfide destruction after addition of $KMnO_4$ observed by Cole et al. (1975).

A problem encountered in the last part of Experiment IV was foaming caused by the highest concentration of H_2O_2. This may have reduced offensiveness by trapping odorous gases in the bubbles resulting in a decreased offensiveness. The 100 PPM H_2O_2 caused a slight foaming. Foaming as a result of addition of H_2O_2 was reported by Hollenbach (1971). He indicated this could be prevented by adding less concentrated solutions.

Results from these evaluations are not consistent in all cases but H_2O_2 tended to be most effective in reducing odor offensiveness on a short-term basis, possibly up to 30 to 32 hours. Crystalline $KMnO_4$ tended to consistently reduce offensiveness for longer time periods (eight days), and possibly for short periods.

Ritter et al. (1975) found H_2O_2 at 12.5 PPM decreased sulfide levels in liquid dairy manure but other odorous compounds remained. Ninety percent of those odor panelists rated manure with $KMnO_4$ at 480 PPM to be "not offensive" or "mildly offensive," and $KMnO_4$ was effective for at least 72 hours indicating a long-term reduction.

Cole et al. (1975) found H_2O_2 and $KMnO_4$ at 500 PPM to reduce odor strength in liquid swine manure, but these treatments added to liquid dairy manure showed little improvement. The reason given for this was dairy manure

was judged to be much less offensive (faint to definite offensiveness) than swine manure meaning a reduction in offensiveness must be down to the "very faintly offensive" range.

Both studies were done using an odor panel rating manure as to strength or offensiveness on a one to ten scale. Odor fatigue may have been a factor in producing these inconsistent results.

Compounds found to be most efficacious were paraformaldehyde added to fresh manure, H_2O_2 in decomposed manure and $KMnO_4$ to some degree in both.

For these compounds to be acceptable for use in controlling odors from animal wastes they must not present a problem when added to the soil. Neely (1966) stated at low concentrations formaldehyde can serve as a substrate for bacteria, and therefore will not accumulate in the soil upon spreading. The concentrations of formaldehyde found to be most effective in fresh manure was greater than that evaluated by Neely. Therefore more evaluations would need to be made before it could be assumed that this concentration of formaldehyde would degrade. H_2O_2 will decompose to water and oxygen both of which are innocuous (Miner, 1974). Cole et al. (1974) considered $KMnO_4$ to be safe since it is used in potable water treatment.

Addition of K^+ to the soil as $KMnO_4$ at 500 PPM (0.257 pounds/ton) would not cause problems with toxicity

because most dairy manure contains over 5 pounds of potassium per ton. Therefore $KMnO_4$ additions would increase potassium by only five percent. Effects of Mn addition to soils are speculative.

Some of the manure used in Experiment IV was found to contain fruit fly larva. Treatments containing paraformaldehyde completely eradicated those present, but no decrease could be seen in jars treated with $KMnO_4$ or H_2O_2. Seltzer et al. (1969) noticed flies, given the choice between paraformaldehyde treated manure and untreated, chose to deposit eggs in the untreated. This could be of some value in preventing fly breeding in animal wastes.

H_2O_2, $KMnO_4$ and paraformaldehyde currently cost about $ .50, $ .70 and $1.90 per pound commercially. At concentrations of 500, 500 and 5000 PPM respectively a cost of $2.09, $2.91 and $72.90 respectively would be required to treat 1000 gallons of liquid manure.

Miner (1974) estimated the average 1000 pound cow produced 88 pounds of manure (urine and feces) per day. This is about 16 tons of manure per year. To this about 3.2 tons of water per year (20 percent) will be added to keep manure in a liquid form giving a total of 19.2 tons of liquid manure per cow per year. H_2O_2, $KMnO_4$ and paraformaldehyde would cost $10.03, $13.97 and $350.02 respectively to treat waste from each 1000 pound cow per year.

These calculations are assuming all manure will be treated. In situations where only a small portion such as a tank load is in need of treatment, H_2O_2 may be adequate for short-term odor control when added directly to the spreader wagon. This was tried by Kibbel et al. (1972), and found to reduce offensiveness of manure from liquid manure tanks.

Experiment V was a preliminary trial evaluating the commercial products Odor Mask, Sep-Zyme "O" and Pit-Zyme. Results indicated 1430 PPM Odor Mask was more offensive than other treatments or control. Sep-Zyme "O", a dried enzyme, at 360 PPM did not decrease offensiveness. Pit-Zyme, a dried enzyme, at 360 PPM did decrease offensiveness at day eight probably a result of odor masking.

Insufficient trials using definitive odor evaluation techniques have been performed with this type of product. Therefore any recommendations concerning effectiveness would be strictly presumptuous.

VI. SUMMARY

1. H_3PO_4 and $NaClO_4$ were slightly bactericidal when added to fresh liquid dairy manure. Paraformaldehyde was bactericidal in fresh and decomposed dairy manure for at least 22 days.

2. Paraformaldehyde, H_3PO_4 and $NaClO_4$ tended to decrease pH. $KMnO_4$ in decomposed manure, but not fresh, raised pH as did lime.

3. The pH of fresh liquid manure tended to decrease with time while decomposed manure increased.

4. Ammonia (NH_3) in the air space over fresh manure as well as ammonia (NH_3 and NH_4^+) dissolved in manure was decreased by paraformaldehyde. Lime increased the amount of ammonia (NH_3 and NH_4^+) dissolved in decomposed manure, but this relationship was observed for only one day.

5. Odor panel results indicate paraformaldehyde at 7000 PPM may be adequate to prevent formation of odorous compounds and reduce offensiveness in fresh manure, but not in decomposed manure. H_2O_2 at 500 PPM reduced offensiveness on a short-term basis, but results were compounded by foaming.

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$KMnO_4$ at 500 PPM was partially effective in fresh and decomposed manure being most effective on a long-term basis (eight days).

6. H_2O_2, $KMnO_4$ and paraformaldehyde at above concentrations would cost $2.09, $2.91 and $72.90 respectively to treat 1000 gallons of liquid manure.

7. H_2O_2 added to a spreader wagon may be the most economical way to treat portions of manure when there is no need to treat all of it. Foaming problems may be overcome by adding as a dilute solution.

8. For situations where all the manure is in need of treatment, $KMnO_4$ may be the most effective although slightly more expensive than H_2O_2. Best results would probably be obtained by adding to the manure pit several days before spreading.

9. Paraformaldehyde was not an economical alternative, but in situations where ammonia or fly breeding is a problem it may be feasible when added to the top layer of manure.

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