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ODOUR CAUSING COMPOUNDS IN TREATED PIG MANURE: LIQUID AND GAS PHASES

by

YU, JINGCHENG 

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the FACULTY OF GRADUATE STUDIES AND RESEARCH, for acceptance, a thesis entitled ODOUR CAUSING COMPOUNDS IN TREATED PIG MANURE: LIQUID AND GAS PHASES submitted by YU, JINGCHENG in partial fulfilment of the requirements for the degree of MASTER OF SCIENCE.

John Feddes

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Daniel W. Smith

Date May 30, 1989

ABSTRACT

Odours emanating from pig confinement operations continue to create problems between pig producers and adjacent land users. Aeration of pig manure is very effective in controlling odours. However, the most common type of treatment in pig operations is anaerobic in nature and results in the production of odorous compounds. Technology for odour control during anaerobic treatment is available in the form of additives and oligolysis.

Commercially-available manure additives for odour control, Bio-gest and Nature-aid, have been marketed for more than twenty years. They are claimed to be effective in the control of pig manure odour. Little research has been carried out to establish the effectiveness of these products. An electro-chemical treatment, called "oligolysis", is also used to reduce odours. However, the effectiveness of this treatment has not been clearly demonstrated.

Three treatments of treated pig manure evaluated oligolysis, manure additives (Bio-gest and Nature-aid) and a control, for 13 odorous compounds in the liquid phase and 2 odorous compounds in the gas phase. These thirteen organic compounds were selected from the literature and on the basis of the capability of a single detector of a gas chromatograph.

Manure was stored in bio-reactors over an 8-week period (4 treatments X 3 replicates) for liquid pig manure studies and another 8-week period (4 treatment X 1 replicate) for gas phase studies. Manure was collected from pigs weighing within the 50 to 95 kg range. All compounds were analysed using gas chromotography, with the exception of ammonia, which was measured using a specific ammonia ion electrode and pH meter in liquid phase, and a Non-Dispersive Infrared Analyser in the gas phase.

A statistical analysis indicated that organic acids in the liquid phase were highest in the Bio-gest and Nature-aid treatments. Ammonia concentrations were lowest in the manure additive treatments (6.1 ppt and 5.7 ppt, respectively). The control and oligolysis treatments yielded similar concentrations of odorous compounds with the exception of lower propionic acid in the oligolysis treatment (3.0 ppt).

The oligolysis treatment eliminated hydrogen sulfide in the gas phase, whereas the mean concentration of ammonia was the highest (0.09%). The control treatment produced the

highest hydrogen sulfide (0.35%), but the lowest ammonia (0.06%) in the gas phase. Oligolysis treatment reduced the odour nuisance of the treated pig manure in both liquid and gas phases. The mean concentration of hydrogen sulfide in the Bio-gest treatment was found to be similar to that of the control treatment (0.3%). Hydrogen sulfide was reduced in the Nature-aid treatment (0.19%).

Settleable solids were not determined in the experiment. Total gas production rates (L/pig.day) and liquid manure temperatures are not significantly different among the treatments. The mean gas production rate and mean temperature are 14.3 L/pig.day and 21.2 °C, respectively.

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1. INTRODUCTION

'Why do pig farms have an offensive odour?' The question arises when one travels near a pig farm. Several decades ago, extensive livestock production was not a serious source of air pollution. However, the increasing demand for livestock products has resulted in more intensive housing systems. One of the major sources of air pollution from the pig production unit is odour. The unwanted release of these odours is not due to lack of research effort into their control. They do, however, indicate a lack of practical procedures that effectively control odour emission from high density operations (Barth, 1972). An increased sensitivity to pig operation odours by neighboring land users is also raising a need to control the odours.

Alberta Agriculture receives many complaints about offensive odours being emitted from pig farms. Lawsuit cases arise frequently over odours from the adjacent farms. A lawsuit in Charlo, New Brunswick, is just one example (Ghaly and Bulley, 1988). The smell from a newly-constructed pig barn offended neighbors to the extent that civil action was brought against the owner over their loss of enjoyment due to the nuisance odours created by his farm operation, even though he was in compliance with each government regulation concerning the operation.

Odours are released from manure storage, ventilation air, and during disposal and treatment. Scientists have been making efforts to reduce odours at their sources. Over one hundred odorous compounds have been identified from solid manure, liquid manure, gases produced from the manure, and the dust in the barns (Appendix A). When the odorous compounds mix, the complex interactions among them produce other offensive odours.

Environmentalists find that measurement of the odours is difficult even though several methods and instruments have been developed. Presently, odour measurement can not be done reliably without human sensory judgement. Odour indicators are either a single or a composite of several individual odorous compounds mixed to resemble a particular odour. This method provides a simple approach for both odour measurement and odour control.

Odour control investigations, in the past, have involved physical treatments, chemical treatments, biochemical treatments, and electro-chemical treatments. A common strategy for

anaerobic treatment is to keep the conditions unfavorable for the odour producing bacterial growth, since odour causing compounds are products of bacterial activity. Physical treatment is focused on the control of the physical conditions of the manure in order to stop the release of the odours, such as lagoon cover and moisture control. Chemical treatments use chemicals to maintain unfavorable conditions for the release of the odours, such as the addition of ozone and chlorine. Biochemical treatments typically employ aeration and anaerobic fermentation to control odours.

A variety of additives are commercially available, which contain either bacteria, enzymes, or both. Their effectiveness has been evaluated by several researchers; however, the results are still not conclusive.

Electro-chemical methods have been applied to the control of the livestock odours. Two electrodes provide an electrical potential in the liquid manure. Results have indicated that this control method has both technical and economical feasibility.

The purpose of this study is to evaluate the effectiveness of different pig manure treatments upon specific odorous compounds.

2. LITERATURE REVIEW

2.1 Sources of Odour

The offensive smell produced by manure decomposition is a product of complex interactions of many individual odorous components mixed in the air (Muehling, 1969; Ghaly and Bulley, 1988). This decomposition begins when manure is voided (Ghaly and Bulley, 1988). Fresh-manure odour is less objectionable than odour from decomposing manure (Miner, 1982; Ghaly and Bulley, 1988; Barth et al., 1982). Fresh manure evolves large quantities of ammonia, but this ammonia is not accompanied by other objectionable decomposition products (Miner, 1982).

Ghaly and Bulley (1988) reported that odour originates from animal housing ventilation, manure storage, manure spreading or some forms of waste treatment. However, the majority of odour problems are related to the storage and spreading of manures (Carney and Dodd, 1988).

2.1.1 Ventilated Air

Odours produced in pig barns are the products of anaerobic digestion process using manure as the substrate. The exhausted air from the pig barns releases the odours to the atmosphere. Ghaly and Bulley (1988) stated that the concentration of odours in the exhaust air is proportional to the ventilation rate. High ventilation rates dilute the gases and, therefore, the odour has a less objectionable strength. Animal housing requires minimum ventilation during winter, thus increasing odour problems. Muehling (1969) found that dilution methods did not reduce or cure the overall odour problem.

Odours exhausted from farm buildings were often associated with dust particles (Miner, 1982; Barth et al., 1982). Hammond et al. (1979) identified 19 volatile organic compounds in the dust from swine buildings which were the suspected sources of odour.

2.1.2 Storage

Manure is stored in a solid, semi-solid or liquid form. With solid wastes, where the manure is typically stored in piles or heaps, odour problems are less pronounced than with slurries because decomposition is slower in solid manure than in liquid manure (Williams, 1984(b)). Since heat is not dissipated by convection in solid manure as in slurries, the manure may heat up enough to inhibit microbial growth (Hobson and Robertson, 1977).

Lagoons are frequently used for pig manure treatment and storage (Miner, 1982). Anaerobic degradation of manure produces malodorous gases. Hammond et al. (1979) found that odours at points remote from a lagoon were mediated by particles. Further work at Iowa State University has postulated that these particles are generated by the bursting of bubbles at the lagoon surface (Miner, 1982).

2.1.3 Manure Application

Landspreading is widely practiced for manure utilization and disposal. Odorous gases are released that were confined in the slurry during storage. Thickness of the spread material also affects odour production. Thinly spread manure tends to dry faster and odour production is reduced as microbial activity becomes limited (Ghaly and Bulley, 1988).

2.2 Biochemical Decomposition of Pig Manure

Animal wastes are decomposed either aerobically or anaerobically depending on the availability of free oxygen. Aerobic bacteria require free oxygen for their growth and reproduction. Anaerobic bacteria obtain their required oxygen from the food which they consume. Their growth is inhibited by free oxygen (Barth and Polkowski, 1974). Figure 2.1 and Figure 2.2 present the pathways of aerobic and anaerobic manure decomposition, respectively.

If aerobic conditions were maintained, an "earthy" odour would persist, which is not usually a nuisance problem (Ghaly and Bulley, 1988; Klarenbeek, 1985; Muehling, 1969). Anaerobic bacteria form odorous compounds such as hydrogen sulfide (H_2S), ammonia

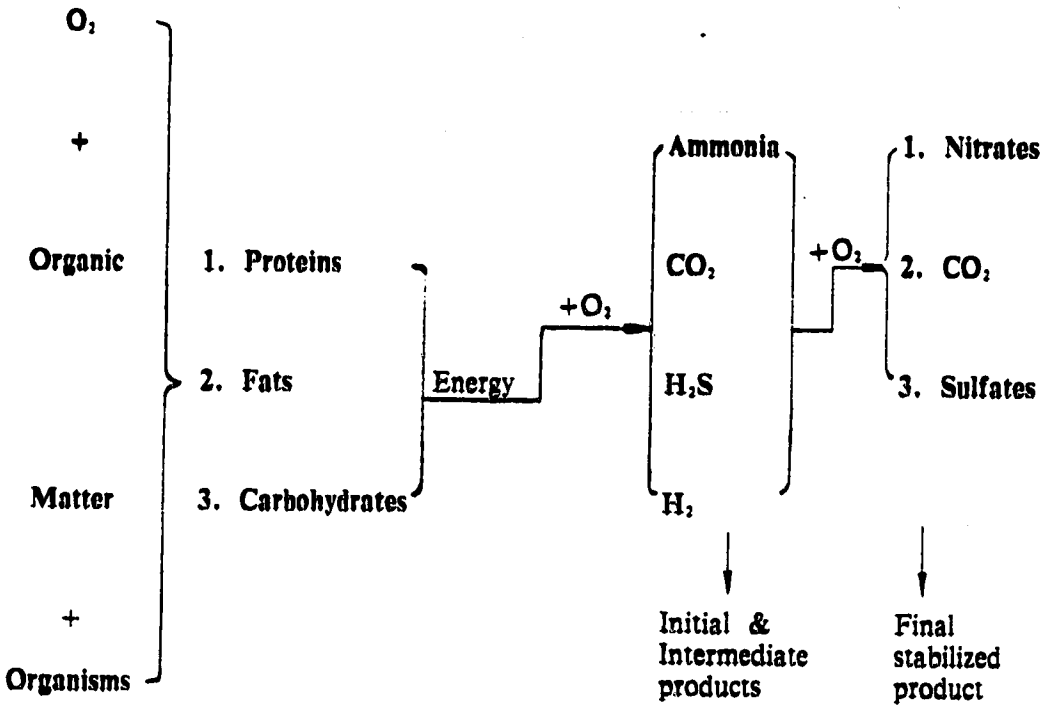


Figure 2.1 Aerobic Decomposition of Manure Organics
(Adapted from Barth and Polkowski, 1974)

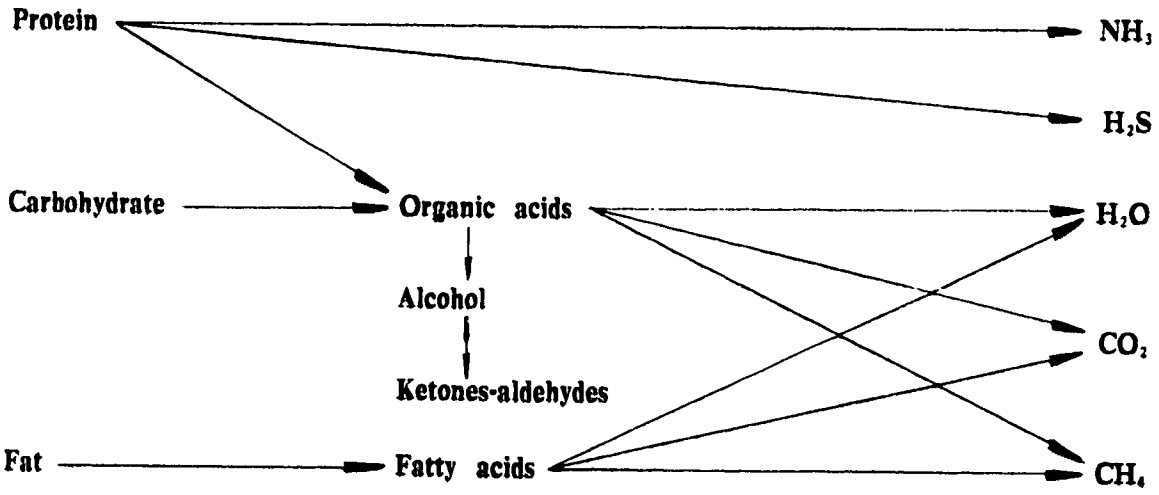


Figure 2.2 Anaerobic Decomposition of Manure Organics
(Adapted from Barber and McQuitty, 1974)

(NH_3) and volatile organic compounds (Dale, 1967). In the absence of O_2, the following reactions could also be carried out (Barth and Polkowski, 1974):

$$NH_3 + \text{alcohols} \longrightarrow \text{amines} \quad (2.2)$$

$$H_2S + \text{alcohols} \longrightarrow \text{mercaptans} \quad (2.3)$$

which results in the generation of odorous compounds.

Bacteria responsible for the decomposition of manure are commonly grouped into two classes according to the end products produced: acid forming and methane-producing (Merkel et al., 1969). In the first stage, complex molecules, such as cellulose, lipids and proteins are degraded into volatile acids, carbon dioxide (CO_2) and hydrogen by "acid formers". During the second stage, the "methane formers", or methanogens, convert the end products of the first stage to methane (CH_4) and CO_2. The stages take place concurrently and the stable operation of one stage might be related to that of another. Thus, for stable digestion of wastes, a balance has to be established between the activities of the two groups. Without sufficient methane-producing bacterial activity, sufficient quantites of organic acids would be produced to stop all methane production. Finally, all digestion would cease, and a sour tank of manure would result (Merkel et al., 1969).

2.3 Odorous Compounds and Their Description

2.3.1 Odorous Compounds

Ghaly and Bulley (1988), and Miner (1982) reported that 60 different volatile compounds were identified in gases emitted from animal waste. Presently, researchers have identified more than 100 specific volatile components in solid manure, liquid manure, gases emitted from manure, and dust in the swine house. These components are end products and intermediates of various biological reactions. Appendix A includes a list of 107 organic compounds contained in solid, liquid manure, gases emitted from manure and dust particles.

2.3.2 Odorous Compounds Description

Organic Acid

Acetic and propionic acids have a sweaty and putrid odour, which are different from the odour from carboxylic acids such as butyric or isovaleric acids (Yasuhara and Fuwa, 1977(a); 1979(c)). Butyric and isovaleric acids have very strong malodours (Yasuhara and Fuwa, 1977(a)). But the odour from phenylacetic acid is more offensive in comparison with butyric and isovaleric acids (Yasuhara and Fuwa, 1977(a); 1979(c)). This odour is the same as that from acidic pig manure (Yasuhara and Fuwa, 1977(a)). C_4-C_6 carboxylic acids are also malodorous (Yasuhara and Fuwa, 1979(c)). Hammond et al. (1979(c)) reported that butyric acid was one of the major odour contributors in filtered air from swine houses.

Alcohol and Carbonyl

Alcohols and carbonyls are judged unimportant in determining the nature of the air borne odours in the swine house (Merkel et al., 1969). Yasuhara and Fuwa (1977(b)) concluded that aldehydes did not play any role in the generated odour from swine manure. However, the results obtained by Hartung et al. (1970) indicated that, in high concentrations, the lower aldehydes generated odours that caused difficulties in breathing. Aldehydes also are suspected of being involved in the generation of sulfur compounds which are malodorous. Schaefer (1980) in the Netherlands constructed a model system consisting of an aqueous solution of aldehydes, H_2S, methylmercaptan and ammonia at pH 5 in a concentration ten times as high as that found in chicken manure. Several dozen sulfur compounds formed after several days. The greater part of these compounds showed the same gas chromatography (GC) properties as those present in chicken manure. One of these compounds was 2,6-dimethylthi-3-ine-carbonaldehyde which was detected in the ventilating air of laying hen houses. He observed a significant correlation between the odour concentration of the ventilation air and the relative concentration of this sulfur compound. Schaefer (1980) recommended the development of an instrumented method to measure the odour level of laying hen houses with the aid of this compound. Yasuhara and Fuwa (1977(b)) discovered o-aminoacetophenone for the first time and found that this compound fused with odours of

other odoriferous substances becoming a new malodour. Yashuhara and Fuwa (1977(b)) also found that trithiapentane, terathiahexane, 2-pentadecanone, 2-hexadecanone and 3,3-dimethyl-2-thiapentane were odoriferous. Alcohols are involved in the generation of the odorous compounds. They react with NH_3 and H_2S and produce amines and mercaptans as illustrated previously (eq. 2.2 and 2.3). Hammond et al. (1979) reported diacetyl and hexanal as the odour contributors in filtered air from a swine house.

Phenol

Phenols are found to have a rather pleasant and sweetish odour. Although they do not contribute any offensiveness to the odour of swine manure, they most certainly contribute to the total odour (Yasuhara and Fuwa, 1977(a)). Previous research conducted in the Netherlands showed p-cresol concentrations to have the highest correlation with odour concentration. The p-cresol measurement was being used in the Netherlands for estimating the odour-reducing capacity of biological air scrubbers that were used in the odour control of the ventilation air from piggeries (Schaefer, 1980).

Heterocycle

Indole and skatole are associated with fecal odours that were identified in solid, liquid and gas from anaerobically decomposed swine manure (Appendix A). However, the indole and skatole odours are different from that of swine manure, although they were thought to contribute to the total odour of swine manure. Ethylindole also is found to be odoriferous (Yasuhara and Fuwa, 1977(b)). Hammand et al. (1979) concluded that tri- and tetra-methylpyrazine were the major odour contributors in the filtered air from a swine house.

Amine

Swine odours are assessed as complex mixtures of amines, whose odours resemble that of ammonia and sulphur-containing compounds, which might be characterized as H_2S or decomposing sewage odour (Merkel et al., 1969). Also, quinazoline is an odorifeous

compound (Yasuhara and Fuwa, 1977(b)).

Sulfur Compounds

Schaefer (1980) reported that sulfur compounds played an important role in the odour from hen manure even though their concentrations were very low. Benzothiazole is an odoriferous sulfur compound (Yasuhara and Fuwa, 1977(a)). A sulfur compound known as 2,6-methylthi-3-ine-cabonaldehyde has significant correlation with the odour concentration of the ventilating air in the laying hen houses, as described previously.

Interactions

Compounds present at slightly below threshold concentrations appear to give intense odours (Hill and Barth, 1976(b); Sweeten, 1975). Frijters (1978 as cited by Miner, 1982) indicated that the intensity of odour mixtures was less than the sum of the independent odours. Yasuhara and Fuwa (1977(a)) found that odour did not always result from major components. However, when odours are combined, five reactions are possible, namely, addition, independence, reduction, synergism, and averaging (Barth and Hill, 1976).

The most intense odours in filtered swine house air are attributable to tri- and tetra-methylpyrazine, p-cresol, butyric acid, diacetyl, and hexanal (Hammond et al., 1974 as cited by Miner, 1982).

Yasuhara and Fuwa (1979(c)) and Hammond et al. (1974 as cited by Miner, 1982) agreed that odour is formed by mixing phenols and carboxylic acids. Miner (1982) also reported that acids and phenols caused offensive odours in swine house air. Carbonyls present in liquid manure also cause objectionable odours. Offensive odour is strengthened by mixing carboxylic acids and phenols which add an adhesive nature to the total odour (Yasuhara and Fuwa, 1979(c)). Merkel et al. (1969) and Hartung et al. (1970) drew similar conclusions that amines, H_2S, and organic sulfur compounds were probably the most noticeable contributors to the odours in swine houses. Hammond et al. (1974 as cited by Miner, 1982) reported that the most intensive odours in filtered swine house air were attributable to tri- and

tetra-methylpyrazine, p-cresol, butyric acid, diacetyl and hexanal.

2.3.3 Factors Affecting Odour Production and Emission

Vapour Pressure

Volatile compounds are released to the atmosphere or retained in the manure depending upon their vapour pressures and solubilities (Ghaly and Bulley, 1988). For a material to be present in the atmosphere, it has to escape from the liquid phase. Thus vapor pressure is important. The compounds with higher vapor pressures are more prevalent in ambient air within a swine unit. Within a specific homologous series, vapor pressures generally decrease with increasing molecular weights (Merkel et al., 1969). Thus, the smaller members of any series should be the more evident in the ambient air, with respect to atmospheric composition.

Solubility and pH

The solubility of a compound in water is another important factor in evaluating its significance as an atmospheric contaminant. Insoluble gases, such as methane, escape immediately after being produced, whereas more soluble compounds, such as NH_3, are retained in solution and become available for use in other metabolic processes (Merkel et al., 1969). Solubility of many compounds, and hence the odour, is markedly influenced by the solution's pH (Barth and Polkowski, 1972; Merkel et al., 1969). Merkel et al. (1969) gave a particularly good example stating that under conditions of high pH, almost no odour was detected while, under acidic conditions, the H^+ and HS^- ions combined, escaped and produced the typical sulfide odour. High pH will limit the emission of volatile acids and H_2S. Low pH would diminish release of NH_3 and amines (Barth et al., 1982). Ghaly and Bulley (1988) made similar discoveries about the relationship between the release of gases and pH value.

Temperature and Water Content of Stored Manure

Odour production is dependent on the temperature and water content of the stored manure. Odour producing bacteria require water and favorable growing temperatures (Barth and Hill, 1976). The objectionable nature of manure odours also increases with increased

temperature, water content and time in storage (Barth et al., 1982). As the temperature of the manure increased, an increase in the rate of gas formation occurs. Dilution water tends to enhance the microbial activities of the manure and as a result more gases are produced.

Water losses through evaporation also increase with an increase in temperature which results in objectionable compounds such as the release of amines, as they distill from the water vapour (Barth and Polkowski, 1974). Miner (1982) reported that the concentrations of butyric acid and pyrazines in swine house air were correlated with high temperatures and low relative humidities.

Storage Time

In storage, an initial period exists during which the dissolved oxygen in the material is consumed by the aerobic bacteria, then the anaerobic bacteria take over and malodorous compounds begin forming. As storage time increases, the concentration of organic acids, ammonia and sulfides also increase (Ghaly and Bulley, 1988).

Pig Housing System

Klarenbeek (1985) conducted an experiment to assess the odour emissions from different types of pig housing. The results showed an increase in odour emission with an increase in slatted floor area. Odorous gases can escape more easily from a storage pit underneath a floor as the slatted area increases. His results also indicate that a decrease in odour emission is obtained through removal of the manure by means of hydraulic flushing.

2.4 Odour Control Strategies

Since undesirable odours are a result of anaerobic bacterial activity, reducing odour production requires that conditions be made unfavorable for the odour producing bacterial growth, or for the emission of odorous components. The total elimination of odour may be neither feasible nor necessary (Evans and Thacker, 1985; Barth et al., 1982). Approaches such as reducing the moisture content, manure temperature, controlling pH, applying bacterial agents, and providing an aerobic environment to the manure were studied by several researchers (Barth and Hill, 1976; Barth et al., 1982).

2.4.1 Physical Treatment

The growth of bacteria requires favourable moisture levels and temperatures in the decomposition of swine manure as described previously. Drying has been used effectively for odour control (Barth and Hill, 1976). Gunn and Kolstee (1974) satisfactorily covered a 60' X 150' swine manure lagoon with plastic film which prevented offensive odours from becoming a nuisance.

Lindvall et al. (1974) in Sweden reported that incorporation of manure into soil resulted in a substantial reduction in odour. The manure is buried 150 to 200 mm below the soil surface by means of an injector.

2.4.2 Chemical Treatment

pH Adjustment

Day (1966(c) as cited by Muehling, 1969) tried pH adjustment using hydrated lime to control odour from liquid swine manure. Dissociation of H_2S is a strong function of pH; above 9.5, the partial pressure of H_2S becomes insignificant (Miner, 1982). Adjustment of pH along with certain bactericidal treatments has proven to have temporary effects on odour production (Barth and Hill, 1976). High pH limits the emission of volatile acids such as H_2S. Low pH diminishes the release of NH_3 and amines. This treatment can reduce emissions of one or more odorants, but may encourage the release of other odorants. Barth et al. (1982) called it a 'self defeating' practice.

Addition of Oxidizing Agent

Ozone

Ozone (O_3) is one of the most powerful oxidizing agents (Barth and Hill, 1976). Van Der Bosch and Buchanan (1975) studied its use for liquid pig manure odour suppression. The results have showed that odour production is controlled with O_3 treatment. Greater bacteriological control is obtained when the concentration of solids in the liquid manure is reduced. Liquid manure when treated with O_3 results in an increase in pH which diminishes

the release of H_2S. This treatment does not have a significant effect on the volatile fatty acid, total solids or total volatile solids content of the liquid manure (Van Der Bosch and Buchanan, 1975). Barth and Hill (1976) reported that O_3 was effective in reducing the strength of the odorant methylamine (CH_3NH_2). The concentration of CH_3NH_2 is reduced from 25 to 2 parts per million (ppm) by increasing the O_3 application to four time the stoichiometric and increased contact time.

Chlorine

Muehling (1969) claimed that chlorine treatment was most effective for odour control. Chlorine prohibited all bacterial activities causing septic conditions and combined with NH_3 as to form chloramine, which prevented its release. This treatment also substantially reduced the production of H_2S, CO_2 and CH_4.

Potassium Permangante ($KMnO_4$)

Potassium permangante is also an oxidizing agent. Faith (1964) evaluated this odour control method with several manure handling and storage techniques. He concluded that the best application of this material was as a surface treatment on beef cattle feedlots. However, this conclusion was rejected by Miner (1982).

Paraformaldehyde

The addition of paraformaldehyde to manure was studied by Seltzer et al. (1969 as cited by Miner, 1982). The function of paraformadehyde is to convert NH_3 into non-volatile hexamethylenetetramine which reduces the emission of NH_3. He found that paraformaldehyde (flakes) effectively killed a number of microorganisms.

Other Chemical Treatments

Day (1965 as cited by Muehling, 1969) reported that odours could be eliminated by bubbling air through distilled water and several chemicals including oxidizing and reducing agents, and basic and acidic solutions. Odours from lagoon sludge could be dispelled by adding activated charcoal, used motor oil, and oxidizing agents such as sodium hypochlorite (Chlorox) and hydogen peroxide H_2O_2. Vanilla flavouring was suggested for control of lagoon odours, but pure extract and imitation flavouring are not found to be effective (Philips and

Le Roux, 1984). Pine oil is also used as a chemical masking agents for abating the odours (Philips and Le Roux, 1984).

2.4.3 Biochemical Treatment

Aeration

Aerobic biological treatment effectively eliminates offensive odours from slurry by supplying oxygen to the natural bacteria in slurry, which then biologically oxidize the odorous compounds to innocuous end-products (Williams, 1984(b); Barth and Hill, 1976). For example, in continuously oxidised manure, p-cresol is completely degraded and the volatile fatty acids are oxidised to a level of approximately 200 ppm (Demuynck et al., 1985). Oxygen is normally supplied by mechanically aerating the slurry. The results obtained by Williams (1984(b)) have shown that diluted slurries (less than 1.5% TS) were inherently more stable than the more concentrated ones (3 to 4.5% TS) and that, generally, a small increase in treatment time gives a larger increase in stability. Diluted slurries are stablilised for 360 days after 3-day, high-rate batch aeration, while the most concentrated slurries (4.5% TS) are fully stabilised for 30 days after 9 day treatment. However, aeration is only effective over a short term. The well aerated manure is found to smell again after two to three weeks of spreading (Demuynck et al., 1985).

Oxidation ditches (Dale, 1967) and aerated lagoons (Miner, 1982) are typical examples of aeration treatment. Lagoons and other manure storage facilities have been improved by the application of a range of air incorporation equipment (Dale, 1967). However, aeration treatment is not economically feasible and has numerous maintenance problems (Chang et al., 1988).

Anaerobic Digestion

Welsh et al. (1976) evaluated the effectiveness of anaerobic digestion (temperature less than 35°C) on swine manure odour control. Their results indicated that anaerobic digestion was fairly effective in reducing odours. Demuynck et al. (1985) agreed with this conclusion, but some negative quality remained in the odour (Welsh et al., 1976). A digestion

temperature of 35°C is more effective for reducing odour than the process at 25°C. In certain cases, increased solid retention times and agitation rates are found to improve the odour-reducing capability of anaerobic digestion. The latter affects may be due to the increase of microbial acitivity. Anaerobically digested manure remains more stable than aerobic treated manure over a long period of time (Demuynck et al., 1985).

Biofilter

Biofilters have been used, particularly in Germany (Phillips and Le Roux, 1984). Odorous airflow is passed through a layer of filter material (compost, filamentous peat, etc.), followed by biodegradation of the captured odour components. The odour components are transferred from the gas phase to the liquid and solid phase through the particles in the filter material. On these particles, a microbial degradation of the odour components takes place. Van Der Hoek and Oosthoek (1985) carried out similar research. In their system, the odorous air went through packing material, as the odorous compounds are decomposed by bacterial action (aerobic bacteria). Packing materials used include soil, worm-worked waste, and peat fibres mixed with feather or pine cuttings.

Licht and Miner (1978) built a cross-current, wet packed-bed air (or particle) scrubber with the similar concept to Van Geelen and Van Der Hoek (1977 as cited by Miner, 1982) in Holland. The scrubber yielded a removal efficiency of 50% and 90%, respectively for particles greater than 1 micron and greater than 5 micron in diameter. An average value of 21% was observed for NH_3 removal, with a range of 7.7% to 38%. For odour removal, there was a high correlation between removal of particles and detected quality difference in odour intensity. Schirz in Germany (1977 as cited by Licht and Miner, 1978) obtained similar results.

Additives

The use of chemical and biological additives to achieve odour control without major alterations of existing facilities was studied by Miner (1982) and Chang et al. (1988). Odour-control additives are either added to manure-storage tanks or to the animal feed. Additives containing bacteria or enzymes alter the decomposition pathway of the animal

waste, helping to eliminate the odours. Some additives contain either enzymes or bacteria, while other deodorants are the combinations of enzymes, anaerobic and facultative bacteria (Ghaly and Bulley, 1988).

Research at the University of Illinois examined 24 commercial products that claimed to reduce odour problems existing in some swine buildings with below-floor manure pits. A sniff panel found that some commercial products had been slightly more effective than others, but none of them had significantly reduced odour levels or improved odour acceptability (The Furrow, 1979). Warburton et al. (1981) evaluated twenty-two commercial products marketed for the control of odours from anaerobic swine-manure pits. The results are generally disappointing. Masking agents, oxidizing agents, and bacterial and enzyme compounds were considered to be ineffective for odour control. Chang et al. (1988) conducted an experiment on a commercial manure additive. They reported that the additive tested did not significantly reduce the magnitude of the odour or decrease total solids content.

Miner and Stroh (1975) evaluated nine commercially available products for feedlot odour control. Ammonia release rate and odour intensity were used to compare odour control success. The nine products were:

1. *potassium permanganate ($KMnO_4$)*
2. *sodium bentonite*
3. *The Nose Knows*: manufactured by Hyde Park Chemical Company of Plainview, New York, NY.
4. *AGCO*: a natural plant extract for reduction of odours attributable to biological decomposition, manufactured by CLEW, Inc., of Hondo, TX.
5. *Odour Control Plus*: a dried bacterial and enzyme product compounded by Bower Industries, Inc. of Orange, CA.
6. *Zeolite C*: Succor Creek clinoptilolite
7. *Zeolite E*: erionite, zeolites mined by General Mining Division of the Anaconda Company
8. *LSS10 (Micro-aid)*: steroid saponin-based product, provided by Distributors Processing, Inc, of Porterville, CA.

9. ***Sanzyme***: a balanced combination of enzymes and surfactants, provided by Enzyme Industries of the U.S.A., Inc., of Lima, OH.

Miner and Stroh (1975) observed that ***sodium bentonite***, ***Odour Control Plus***, and the two ***zeolites*** consistently reduced the rate of NH_3 release when compared to untreated control areas. Odour intensity measurements confirmed the effectiveness of ***sodium bentonite***. ***Odour Control Plus*** had temporary effect on odour intensity reduction.

Feed additives used for manure odour modification have been studied. Although ration ingredients influenced the odour of fresh feces and urine, no usable feed additives have gained widespread application (Miner, 1982). Ghaly and Bulley (1988) reported that ***bentonite*** was effective when force-fed, but ineffective when mixed with rations. Yeast, sage brush, dry lacto, and wet lacto are found ineffective as feed additive odour-controlling agents. However, Goodall et al. (1988) evaluated a feed additive called Micro Aid (the same name and manufacturer as Miner and Stroh (1975) used in their experiment), which reduced NH_3 production. Micro Aid is added to poultry feed at a rate of 62 ppm. Ammonia reduction was 21.7% in vitro, and 24.8% in aerial NH_3 concentration.

2.4.4 Electro-chemical Treatment: Oligolysis

Muller (1985) in Germany used an electrolytic process, called "oligolysis", to treat liquid cattle and pig manure. A copper anode is placed just below the surface of the liquid, along with a counter-electrode located at the bottom of the pit. Copper ions are introduced from the copper anode into the liquid manure. The results indicate that the odour after 10 days are not unpleasant. Chiumenti et al. (1987) carried out similar research with vertically-installed copper and coal electrodes. Results showed that oligolitically-treated liquid manure had almost the same effectiveness as aeration treatment. Furthermore, an economical analysis indicated that the total annual cost of oligolysis treatment was roughly half that of aeration treatment.

2.5 Odorant Detection Techniques

2.5.1 Wet Chemistry

Wet chemical odour measurement lacks sensitivity and specificity. Odorants associated with animal production exist at low levels and hence concentrating procedures are often required (Barth et al., 1982).

Barth and Polkowski (1972) used distillation followed by titration (using sodium hydroxide (NaOH)) for determinating the total volatile organic acid (VOA). The direct distillation method was used for NH_3 measurement while a titrimetric method was used for H_2S measurement.

2.5.2 Gas Chromatography

Gas chromatography is presently the most dependable procedure for identifying odorous manure compounds. When instrument sensitivity is inadequate, concentrating procedures can be used (Barth et al., 1982). A range of detection techniques such as flame ionization, electron capture, flame photometric and electrolytic conductivity improved the selectivity and sensitivity of this technology. Schaefer (1980) analyzed sulfur compounds using GC with a flame photometer detector (FPD), which was very sensitive to sulfur compounds and insensitive to other organic compounds. Yasuhara (1977(a), 1979(c)) performed a series of pig manure odorous-compound identification tests from which he concluded that GC or GC-MS (Mass Spectrometry) was useful for identifying odorous components, even though they are ineffective for characterization of odour quality and intensity.

2.5.3 Detector Tubes

The gas detector tubes are fitted onto the bellows pump and air pumped into the tubes, the level at which the colour of the tubes changed upon saturation was noted (Ghaly and Bulley, 1988).

Some typical odorous compound detection techniques are listed in Table 2.1, which are summarized from Scheafer's literature (1980).

TABLE 2.1 Odorous Compounds Detection Techniques.

Odourous Compounds	Detection Technique	Condition
Organic acids	GC	measure manure extract
Ammonia	Wet Chemistry	distillation (pH=7.8) & titration (potassium biiodate)
Aldehydes	Wet Chemistry & GC	C^2-C^5 react with semicarbazide, GC measures quantity
Sulfur coumpound	GC	FP or TC detector
Phenols	GC	measure manure extract
Indoles	GC	measure manure extract

(Adapted from Scheafer, 1980)

2.6 Odour Measurement

Odour detection and measurement have relied traditionally upon human sensory judgement with the help of wet chemistry and gas chromatography (Carney and Dodd, 1988; Barth et al., 1982). Precision instruments have been used to replace the "nose" but with only limited success because of repeatibility (Ghaly and Bulley, 1988). The measurement of odour includes quality measurement and quantity measurement (intensity). Odour quality is "what you smell", or what something smells like. Odour intensity is the relative strength of the smell, which depended on the concentration of the odorants (Sweeten, 1975). Four basic approaches are used to measure odours (Sweeten, 1975). They are:

1. identification of odorous gases (chromatograph)
2. measurement of odorant concentration (wet chemistry & correlation)
3. measurement of odour intensity by vapour or liquid dilution (scentometer, etc.)
4. ranking of odour intensities by arbitrary offensiveness scales (panel).

Four independent factors are required for the complete characterization of an odour: intensity, character, hedonics and detectability (Tchobanoglous, 1979). Numerous methods are available for odour detection and measurement, but all have limitations (Sweeten et al.,

1982). Sensory odour measurement, which uses human odour panelists, has become well-established and widely accepted (Sweeten et al., 1982 and Tchobanoglous, 1979).

2.6.1 Quantity Measurement

This procedure consists of diluting odorous air with quantities of odour-free air. The number of dilutions required to reduce an odour to its minimum detectable threshold odour concentration (MDTOC) is noted by 50% of a group of panelists (Sweeten et al., 1982; Tchobanoglous, 1979; Barth, 1972). For example, if four volumes of diluted air are added to one unit volume of sampled air to reduce the odourant to its MDTOC, the odour concentration will be reported as five dilutions to MDTOC. This is accomplished by either static or dynamic methods entailing batch vs. continuous flow mixing (Sweeten, 1975). However, the sensory determination of this minimum threshold concentration is subject to a number of errors. They are described as follows (Tchobanoglous, 1979):

1. **Adaptation and Cross Adaptation**: When exposed continuously to a background concentration of an odour, the subject is unable to detect the presence of that odour at low concentrations. When removed from the background odour concentration, the subject's olfactory system will recover quickly. Ultimately, a subject with an adapted olfactory system will be unable to detect the presence of an odour to which one's system has adapted.
2. **Sample Modification**: Both the concentration and composition of odorous gases and vapours can be modified in sample containers and in odour-detection devices.
3. **Subjectivity**: When the subject has knowledge of the presence of an odour, random error can be introduced in sensory measurements. Often, knowledge of the odour may be inferred from other sensory signals such as sound, sight, or touch.
4. **Synergism**: When more than one odorant is present in a sample, a subject has been observed to exhibit increased sensitivity to a given odour because of the presence of another odour.

For a more reliable sensory measurement, Chang et al. (1988) suggested some basic principles to be followed while conducting odour panels:

1. Containers should be free of odour
2. Sample size should be large enough to be representative
3. Constant time interval between sample collection and evaluation
4. The panelists should not be able to see the product being evaluated
5. Sample identification system should not influence the panelists
6. Randomized sample order
7. The general conditions of the sniffing stations (light, temperature, etc.) must be kept constant.

2.6.2 Measurement Apparatus

The syringe dilution method (ASTM Method No. D-1391-57, 1971) consists of collecting a field sample which is tested later by a panel under controlled conditions. This procedure is very useful in measuring the odour intensity of high strength emissions (Barth, 1972).

Licht and Miner (1978) developed another sensory method, in which cotton cloth swatches are used to collect odours in a swine facility, then panelists provide sensory measurement of the odour intensity.

The butanol reference method (Sweeten et al., 1982) utilizes n-butyl alcohol (1-Butanol, C_4H_7OH) as a reference odorant to the odour being measured. This is an indirect measurement of odour intensity. The odour intensity of the test odour is reported as an equivalent to X ppm of 1-Butanol in air. McFarland et al. (1982) designed a 1-butanol scale dynamic olfactometer for ambient odour measurement. Panelists compare the intensity of ambient odours with intensity of discrete levels of 1-butanol provided by the olfactometer.

Two commercially-available vapour dilution devices are the Scentometer or Osmometer (Barth, 1972; Ghaly and Bully, 1988) and the Dynamic Olfactometer (Sweeten, 1975). Both operate on the same principle in which odorous gas streams are combined with

non-odorous gas streams at known ratios. The dilutions are increased and evaluated by a panel until its MDTOC is determined (Barth, 1972). Scentometer employs activated charcoal filters to purify the air which is used to dilute the odorous air. The operator holds the instrument to his nose and inhales purified air for a short time in order to remove any previous influences of the odorous air. Then, by removing his prepositioned fingers from one of four different sized holes, he tests the odour intensity of the ambient air at four different dilution ratios: 2, 7, 31 and 170. These levels of odour strength are consistent with that of a trained 'sniffer' who can differentiate between only five intensities of odour. An expert may recognize six (Moncrieff, cited by Barth, 1972).

The flowrate of the scentometer and the olfactometer can affect the outcome of the measurement (Klarenbeek, 1985). If the olfactometer flowrate is less than that sniffed, additional air from the interior of the experimental room dilutes the sample from the olfactometer. Dilution should take place in the olfactometer rather than diluting the output from the olfactometer.

A common problem associated with dilution devices is that they are designed normally for molecularly dispersed odorants and do not consider the ease with which particulates could be parcipitated by passage through valves and orifices, as many environmental odours are mediated through particulates, therefore, dilution devices have to be used with caution (Miner, 1982).

2.6.3 Aromagram

While gas chromatography is extremely useful in identification of odorants, it can not characterize the quality of the odour. To this end, the procedure can be coupled with olfactory evaluation. Schaefer (1980) developed the concept of 'aromagram', which is a combination of GC and panel results. Manure odours are separated on a GC column. Part of the separated compounds is led via a splitter to a flame ionisation detector (FID) and part outside the GC, where the smell is evaluated by a panel.

There are five techniques commonly used for sensory odour analysis: ranking, rating, magnitude estimation, dilution, and forced choice (Chang et al., 1988). Ranking requires that pairs or triplets be evaluated and placed in some assigned order. Rating requires the panelists to rate samples on a scale of 0 to 10 (or other scales, e.g. 0 to 5, Williams, 1984(a)) for both odour strength and odour offensiveness. The normal designation is that 0=no odour and 10=very strong and offensive. Magnitude estimation is similar to rating except that the panelists are given reference points (e.g. high and/or low odours) for use throughout the odour analysis to help establishing the magnitude of the scale. Dilution technique is used for estimating odour thresholds.

The results of odour measurement by liquid or vapour dilution are sometimes expressed as a threshold odour number (TON) (Barth and Hill, 1976) or "odour units". But since values of TON can be in the order of 10^5 or higher, they are usually written in terms of an odour intensity index (OII) (Sweeten, 1975). The OII is expressed as:

$$OII = \log_3 TON \tag{2.4}$$

2.6.4 Quality Measurement

Odour intensity is easier to measure than odour quality (Barth, 1972; Ghaly and Bulley, 1988). One of the difficulties in developing a universal theory is the inadequate explanation of why compounds with similar structures may have different odours and why compounds with very different structures may have similar odours (Tchobanoglous, 1979; Barth et al., 1982).

2.7 Odour Characterization and Indicator

Williams (1984(a)) conducted an experiment for determining the indicators for pig slurry odour offensiveness. The offensiveness rating is judged by a panel on a scale from 0 to 5. A highly significant ($p<0.001$) correlation occured between the logarithm of the supernatant BOD_5 (five-day biochemical oxygen demand) concentration and the odour offensiveness of piggery slurry. Thacker and Evans (1985) improved the models derived by

Williams (1984(a)) with supernatant BOD_5 and a similar model with total organic acids (TOA) concentration. The correlation coefficients are 0.96 and 0.93, respectively. Correlation coefficients of 0.86 and 0.88 are reported in Williams' models (1984(a)). The models are:

$$\text{Odour offensiveness} = 1.453\text{LOG}(BOD_5) + 2.320 \quad \text{(Thacker and Evans, 1985)} \qquad (2.5)$$

$$0.411\text{LOG}(BOD_5) + 3.16 \quad \text{(Williams, 1984(a))} \qquad (2.6)$$

$$\text{Odour offensiveness} = 2.378\text{LOG(TOA)} + 2.327 \quad \text{(Thacker and Evans, 1985)} \qquad (2.7)$$

$$4.47\text{LOG}(2.11(\text{TOA}) + 1.86) - 2.38 \quad \text{(Williams, 1984(a))} \qquad (2.8)$$

Evans and Thacker (1985) concluded that the supernatant BOD_5 provided a reliable indicator since it included a measure of most slurry odorants.

Total organic acids are major contributors to the supernatant BOD_5 and hence closely correlate with it. Technically, TOA provide a more useful indicator because of the much shorter analysis time (Evans and Thacker, 1985). Chemical Oxygen Demand (COD) should not be used as an odour indicator, as supernatant COD contains a non-biodegradable fraction. The COD test does not measure the oxygen demand of NH_3, which can be an important odorant, but it does measure CH_4 which has no odour (Barth and Polkowski, 1972). The selection of indicators depends on time and the availability of equipment, etc. (Williams, 1984(a)). Williams (1984(a)) suggested that VFA, TOA, indoles and phenols indicated acceptable and unacceptable limits of offensiveness during aerobic treatment and correlated linearly with offensiveness during post-treatment storage, when expressed logarithmically. Also hydrogen sulfide is a misleading indicator during aerobic treatment, but is a useful indicator during post-treatment storage. Barth and Polkowski (1974) correlated OII with Volatile Organic Acids (VOA), NH_3 and H_2S. Odour intensity index correlated best with VOA concentration, next best with H_2S and poorest with NH_3. The best two odorants OII were expressed by VOA and NH_3. Inclusion of H_2S did little to improve the fit of the regression function. Barth and Polkowski's (1972) models are listed as follows:

$$OII = 3.04VOA^{0.20} \qquad R=0.92 \qquad (2.9)$$

$$OII = 0.64NH_3^{0.66} \qquad R=0.71 \qquad (2.10)$$

$$OII = 11.5H_2S^{0.09} \qquad R=0.80 \qquad (2.11)$$

$$OII = 2.70(VOA^{0.21}H_2S^{-0.01}) \qquad R=0.92 \qquad (2.12)$$

$$OII = 10.88(VOA^{0.31}NH_3^{-0.30}) \qquad R=0.94 \qquad (2.13)$$

$$OII = 10.2(VOA^{0.17}NH_3^{-0.31}H_2S^{-0.06}) \qquad R=0.96 \qquad (2.14)$$

3. OBJECTIVES

Odour nuisance in liquid manure storage systems continues to be a major concern on intensive animal confinement operations. Increased environmental sensitivity by neighbours adjacent to livestock operations demonstrates that effective odour control techniques must be developed and understood. Several options in anaerobic manure treatment are available to reduce odours; however, their effectiveness has not been clearly demonstrated through statistically-designed experiments. Two additives, Bio-gest and Nature-aid, have been marketed for more than twenty years. A scientific analysis of their effectiveness has not been reported in the literature. Another type of treatment involves an electrical current passed across two iron bars placed in manure. This treatment, referred to as oligolysis, indicates that this process was effective in reducing odours. The overall aim of this project was to evaluate three odour-control treatments (Bio-gest, Nature-aid and oligolysis) and a control for the amount and type of biological by-products generated within the liquid phase for each treatment over a period of time.

More specifically, four primary objectives can be identified as follows:

1. To treat pig manure in simulated storage pits with two commercially-available additives (Bio-gest and Nature-aid) and with an electrical current,

2. To measure the concentration of selected malodorous compounds in the liquid pig manure from these treatments by gas chromatography and other techniques,

3. To measure gas production rates and concentrations of selected compounds in the gas phase from the treated pig manure, and

4. To measure settleability of solids in each treatment.

4. SELECTION OF ODOUR CAUSING COMPOUNDS

As mentioned previously, more than 100 odour-causing compounds have been identified by researchers. These compounds are responsible for the total odours generated from pig manure. However, to measure all of these compounds concurrently is not feasible due to both technical and economical constraints. Therefore, odour causing-compounds must be selected in such a way that a manageable number of compounds will represent odour most closely.

Organic acids are prevalent contributors to pig manure odours (Yasuhara and Fuwa, 1979(c)). Sixteen organic acids have been identified in the liquid pig manure. Some of them include acetic, propionic, butyric, isobutyric, valeric, isovaleric and caproic acid. Acetic and propionic acids have a sweaty and putrid odour. Butyric or isovaleric acids have very strong malodours. Valeric acid also has disagreeable odour (Webster's Ninth Collegiate Dictionary, 1988). Isobutyric acid is another odorous component (Yasuhara and Fuwa, 1979(c)). The experiment carried out by Yasuhara and Fuwa (1979(c)) indicated that, when removing the acidic fraction from the extracted solution, the nuisance of the odours was reduced greatly.

Vapour pressures decrease with increasing molecular weights. The smaller members of a specific series are more evident in the ambient air. Therefore, eight organic acids with smaller molecular weights were selected for this pig manure odour evaluation study. They are acetic, propionic, butyric, isobutyric, valeric, isovaleric, caproic and heptanoic acids.

As described in a previous section, phenol has an odour that is rather pleasant; however, phenol does contribute to the total odour. Concentrations of p-cresol have the highest correlation with odour concentration. Yasuhara and Fuwa (1979(c)) and Hammond et al. (1974) have agreed that odours were formed by mixing phenols and carboxylic acids. Therefore, phenol and p-cresol were selected as two of the odorous compounds. Indole and skatole also were considered since thay have fecal odours especially in fresh manure. Ammonia is a well-known odour-causing compound. Ammonia in the liquid pig manure was studied, along with the above selected compounds.

Technical and economical constraints must be considered when selecting a number of odour-causing compounds to be included in the study. For example, sulfur compounds are contributors to pig manure odours; however, they can not be analysed with the same detector as used for the other twelve compounds. All of the selected compounds above, with the exception of ammonia, can be analysed concurrently on a GC with the same detector using FID. In the gas phase, only H_2S, NH_3, CH_4, CO_2 and N_2 concentrations were measured. The instrumentation for these gas measurement was made available by the Department of Microbiology, University of Alberta, with the exception of NH_3 which was measured by a Model 880 Non-Dispersive Infrared Analyzer in the Department of Agricultural Engineering, University of Alberta.

After the selection, these thirteen selected odour-causing compounds were obtained commercially and placed in a closed container with their lids sealed. The odour from this container when uncovered was perceived to be similar to that of anaerobically treated pig manure, which was encouraging.

5. EXPERIMENT

The manure odour treatment evaluation experiment was conducted using the Sinclair Swine Research Centre facilities on Edmonton Research Station (University of Alberta, Edmonton, Alberta). The research commenced on May 26, 1988, and ended on November 4 of the same year. Prior to the main experiment, the bio-reactors were filled with manure over a six-week period, then emptied to 100 mm from the bottom. These contents provided seed to the material introduced during the experiment. The entire experiment consisted of two sections, i.e., Part A and Part B. Part A (8 weeks, 4 treatments X 3 replicates) of the experiment covered the study of the odorous compounds retained in the liquid phase of the pig manure. Gas phase study was carried out in Part B (8 weeks, 4 treatments X 1 replicate).

5.1 Experimental Apparatus

Manure was added to 12 bio-reactors (closed plastic barrels with a volume of 2.26 m^3), their total cross-sectional areas being similar to that of a slatted-floor over a storage pit storing manure from 18 pigs (growers, 50 to 95 kg). The bio-reactors were set up as shown in Figure 5.1. Inlet tube height was adjustable, so that the end of the tube could be located 30 to 40 mm below liquid level before adding manure to avoid loosing gas. A thermistor (Fenwall Electronics, Framingham, MA) submerged in the liquid manure measured liquid manure temperature (Figure 5.1). Gases generated from the pig manure in the bio-reactor were collected in reinforced plastic bags. All gas bags were pressure tested by inflating the plastic bag until it was expanded completely, applying soap water solution on top of the plastic bag, and applying a load (approximately 2.5 kg) onto the expanded bag and checking for bubbles.

During the experiment, the gases in the bags always were released before the bags were expanded fully. Bio-reactor connections were sealed with silicone sealant and periodically each connection was checked throughout the experiment with a soapy water solution.

A solid floor with meshed dunging area was fabricated over three totally slatted-floored pens to accomodate 18 pigs (Figure 5.2). The solid floors were covered with rubber sheets. Animal manure was trapped beneath the meshed dunging area in a sealed

container.

5.2 Experimental Design

The mean weight of the pigs was approximately 50 kg at the beginning and 95 kg towards the end of the experiment. Their feed ration is shown in Appendix B. Manure consisting of feces, water spillage and urine was collected from 18 pigs every second day and added to the bio-reactor. The experiment consisted of three treatments plus a control. In Part A of the experiment, each treatment had three replicates. In Part B of the experiment, single replicate was used for each treatment.

Treatment A **(Control)**: a conventional anaerobic fermentation process of pig manure that simulated a typical storage pit.

Treatment B **(Oligolysis)**: an electrolytic process in which electrical potential differences occurred between two iron bars in liquid manure. Three bio-reactors were electrically connected in series. Electrical power (12VDC) was provided by a battery charger.

Treatment C **(Bio-gest)**: a commercially-available additive was added to the manure at an equivalent rate of 1 kg of dry material per 30 m^3 of manure (33 ppm). Bio-gest is a light brown-coloured dry powder. No information is available on the formulation of Bio-gest.

Treatment D **(Nature-aid)**: a commercially-available additive added to the manure at a rate of 1kg/250 m^3 (4 ppm). Nature-aid is in liquid form with a dark brown colour. No information is available on the formulation of Nature-aid.

5.3 Experimental Procedures - Part A (Liquid Phase)

5.3.1 Manure Collection and Distribution

1. Pig manure was collected from the dunging collection basins in each pen every second day;

2. The manure was mixed manually and separated into four equal fractions, one for each treatment;

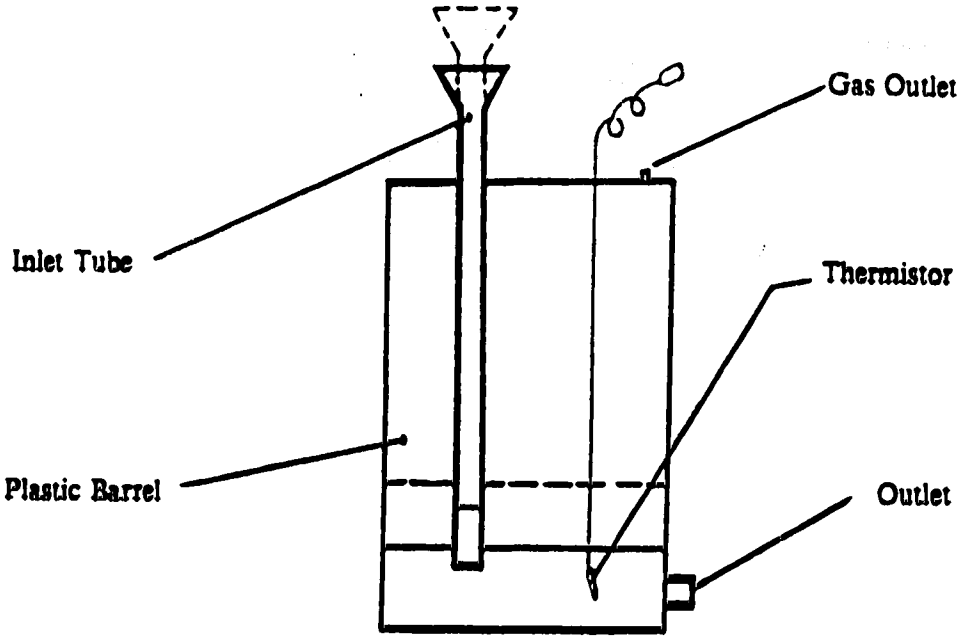


Figure 5.1 Bio-reactor (Plastic barrel) used in the experiment

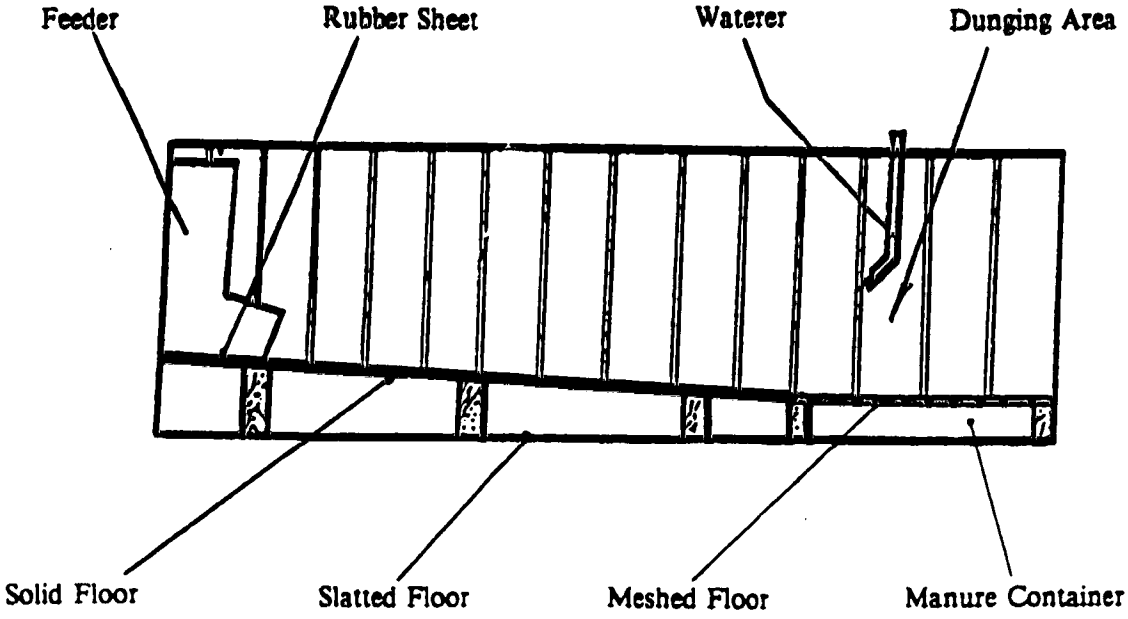


Figure 5.2 Solid floor and dunging area

3. Additives for treatment C and treatment D were measured, added and mixed. In accordance with the manufacturer's suggestion, additive C (Bio-gest) was mixed with water at an equivalent ratio of 48.9 mg dry powder per litre of water (26.6°C to 37.8 °C) and left for four hours before adding to the manure.

4. All inlet tubes were adjusted 30 to 40 mm below the liquid manure level to simulate surface application and yet prevent gases from escaping. The appropriate volume of manure was added to three bio-reactors in each treatment.

5. All containers were washed after each collection to prevent cross-contamination between treatments.

5.3.2 Sampling

Liquid manure samples were obtained bi-weekly using a vacuum pump and liquid trap (a glass cylinder, Figure 5.3). A course wire filtre was mounted at the end of the sampler to screen scum and hair from the treated manure. All sample bottles were placed on ice in a cooler to prevent further degradation of the liquid samples in the bottles. The samples were transported to the Alberta Environmental Center, Vegreville, Alberta.

5.3.3 Extraction of Odour-Causing Compounds

A total of thirteen odorous compounds were analyzed in the liquid phase, using gas chromatography. They were acetic, propionic, isobutyric, butyric, isovaleric, valeric, caproic, heptanoic acids and phenol, p-cresol, indole, skatole and ammonia. Other odour-causing compounds could not be analyzed.

The analysis was carried out in the Microbiology Branch at the Alberta Environmental Centre. Approximately 40 mL of liquid manure was centrifuged (3000g) for 10 minutes. Exactly 25 mL of supernatant was removed and placed in a 250 mL round bottom flask containing 20g NaCl. Following acidification of the mixture to pH 2 using 50% H_2SO_4, 30 mL diethyl ether was added. The contents of the flask were heated and refluxed for 1 hour (condenser temperature was 4 to 8°C). The contents were partitioned in a 100 mL volumetric

flask, the upper phase removed to a 50 mL of dioxane solution and made up with diethyl ether.

Samples of slurry were pH adjusted and extracted three times with diethyl ether to remove all components. The last extraction did not contain any compounds of interest as determined by gas chromatography. The extracted slurry was spiked with all purified compounds, re-extracted and assayed for odour components by gas chromatography. These results were compared to direct gas chromatography of the mixture of compounds to determine extraction efficiency.

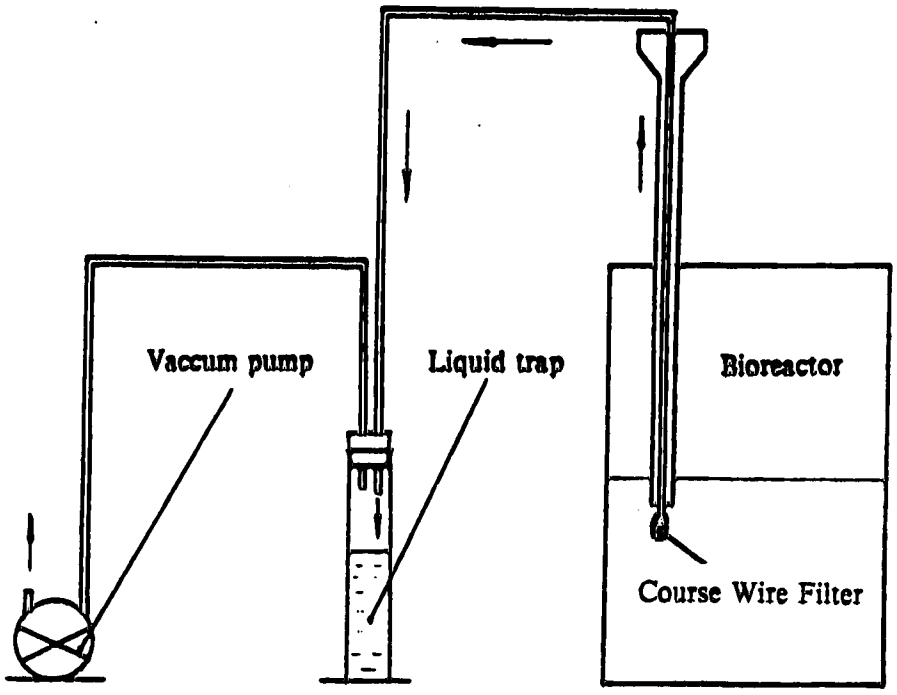


Figure 5.3 Liquid manure sampling apparatus

Extraction efficiency ranged from a low of 55% for acetic acid to a high value of 102% for p-cresol. All reported results in Appendix D have been adjusted to compensate for extraction differences.

5.3.4 Odorous Compounds Identification: Gas Chromatography

All analyses were performed on a Hewlett-Packard 5849A Gas Chromatograph (GC) complete with a 18835B capillary inlet system.

A. Instrument conditions were as follows:

1. Column: Nukol fused silica wide bore column, 0.53 mm ID, 30 m in length and 0.5 um film thickness (Supelco ltd.).
2. Injection system: Split mode using He carrier gas.
3. Detection: Flame ionization.
4. Quantification: Internal standard using 1,4 Dioxane.

B. Operating conditions were as follow:

1. Capillary system

Column flow rate:	7.2 mL/min
Column head pressure:	34.5 kPa
Split flow:	100 mL/min
Split ratio:	14.9
FID make-up:	85 mL/min
Hydrogen flow:	50 mL/min
Septum purge:	5 mL/min
Air flow:	240 mL/min

2. Separation conditions

Injector temperature: 125°C

FID temperature: 250°C

Oven: Isothermal at 125°C for two minutes then temperature programmed to increase 5°C/min to 220°C and held isothermal for 10 minutes.

5.3.5 Ammonia Determination in the Liquid Phase

Ammonia was determined using a specific ammonia ion electrode (Orion Research Inc., MA) and pH meter.

5.3.6 Settleable Solids

Settleable solids were measured with a settleable solids measuring cylinder. Liquid pig manure samples were poured into the cylinders and remained undisturbed for 24 hours, and then observed for settleability.

5.3.7 Total Nitrogen Measurement

Total nitrogen of the manure was determined by the Kjeldahl Method (Appendix C).

5.4 Experimental Procedures - Part B (Gas Phase)

Manure collection and distribution followed the same procedures as described in Section 5.3.1. The differece between Part A and Part B of the experiment was that, in Part B, each treatment had only one replicate, i.e., one bio-reactor for each treatment.

The gas phase herein refers to gases generated from the treated pig manure and collected in gas bags. Five gases were determined in the gas phase. They were H_2S, NH_3, CH_4, CO_2, and N_2. Gas production rates also were measured during Part B of the experiment.

5.4.1 Sampling

Gases stored in the collection bags were pumped into 1 L sampling bags for transportation to the Microbiology Department laboratory, University of Alberta.

5.4.2 Determination of the Main Components in the Gas Phase

The main components, H_2S, CH_4, CO_2 and N_2 in the gas phase were determined on the GC (Varian Aerograph Model 700) in the Microbiology Department laboratory, University of Alberta. An "HP 3390A Hewlett Packward Integrator" was connected to the GC. The operating conditions of the GC were as follows:

Column:	Poropack packed column, 3050 mm long, 5 mm in in diameter
Detector:	Thermal Conductivity (TC)
Carrier Gas:	Helium
Carrier Gas Pressure:	290 kPa
Flame Current:	150 mA
Attenuation:	4

5.4.3 Ammonia Determination in the Gas Phase

Ammonia was measured by a Model 880 Non-Dispersive Infrared Analyzer (Process Instruments Division, Beckman Industrial Corp., La Habra, CA). A dilution of one hundred was used since fullscale of the analyzer was 150 ppm. The analyzer operating conditions were as follows:

preheat: 24 hour

temperature: room temperature

flowrate: 12.6 L/s

5.4.4 Gas Production

The volumetric gas production was measured by a flowmeter (SHO-RATE Flowmeter, Brooks Instrument Division, Emerson Electric Co.) connected to a vacuum pump. The flowrate was adjusted to 125.8 L/s. Time was recorded by a stop watch.

6. RESULTS AND DISCUSSION

6.1 Liquid Phase

Figure 6.1 represents a typical GC response from odorous compounds identification in the liquid phase. The retention times in the GC of the 13 suspect malodorous compounds in the liquid manure are included in this figure. Raw data obtained from the liquid manure analysis are listed in Appendix D. Mean concentrations (expressed as parts per thousand, ppt) for the thirteen compounds in the liquid phase of the manure over the eight-week experiment for each treatment are tabulated in Table 6.1.

TABLE 6.1 Mean Concentrations (ppt) of Compounds in the Liquid Phase.

Compound	Treatment			
	Control	Oligolysis	Bio-gest	Nature-aid
Acetic acid	5.672	5.266	6.282	7.413
Propionic acid	3.186	2.957	3.450	3.918
Isobutyric acid	0.399	0.425	0.662	0.558
Butyric acid	2.921	2.804	3.538	3.951
Isovaleric acid	0.752	0.812	0.956	1.054
Valeric acid	0.577	0.524	0.654	0.703
Caproic acid	0.135	0.166	0.264	0.386
Heptanoic acid	0.020	0.026	0.034	0.066
Phenol	0.029	0.031	0.036	0.037
p-Cresol	0.095	0.077	0.099	0.140
Indole	0.004	0.000	0.000	0.006
Skatole	0.039	0.012	0.000	0.011
Ammonia	6.925	6.773	6.066	5.715

Indole and skatole were present in the fresh manure. However, very little was found in the treated liquid manure (Table 6.1). Indole and skatole are not considered in the discussion. Analysis of Variance and Mean Comparison were carried out on the experimental data. Appendix G and H give examples of analysis procedures of Analysis of Variance and Mean Comparison in the liquid phase. The results are summarized in Table 6.2 and Table 6.3. Concentrations of eleven compounds over an eight-week experiment are described graphically in Figures 6.2 to 6.12.

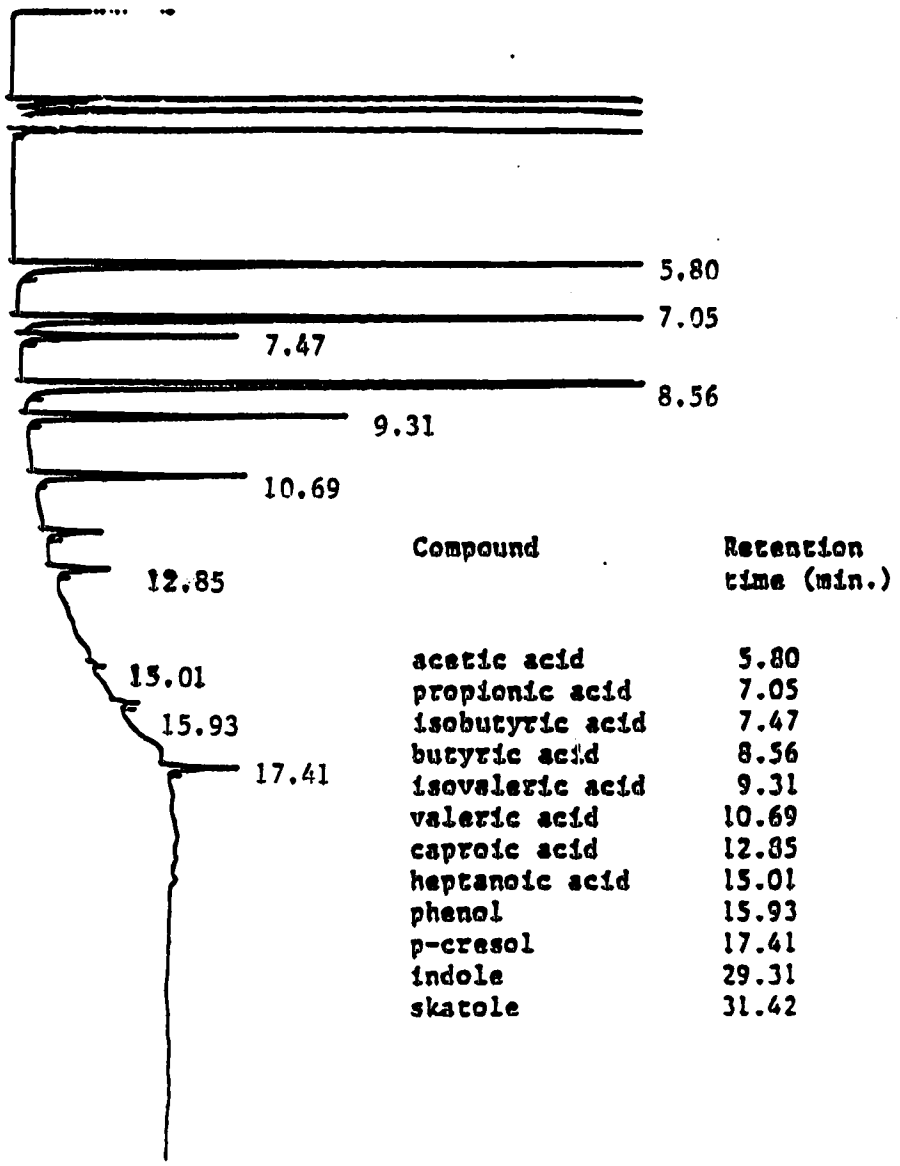


Figure 6.1 Typical GC response to the liquid phase.

TABLE 6.2 Analysis of Variance in Liquid Phase.

Compound	Treatment	Time X Treatment Interaction
Acetic acid	•••	=
Propionic acid	•••	•
Isobutyric acid	=	=
Butyric acid	•••	=
Isovaleric acid	•••	••
Valeric acid	•••	=
Caproic acid	•••	•
Heptanoic acid	•••	•
Phenol	•	=
p-Cresol	••	=
Indole	=	=
Skatole	=	=
Ammonia	•••	=

••• significant at 0.001 level of probability
•• significant at 0.01 level of probability
• significant at 0.05 level of probability
= not significant

TABLE 6.3 Student Newman Keuls (SNK) Test to Test Differences Among Means.

Compound	Treatment			
	Control	Oligolysis	Bio-gest	Nature-aid
Acetic acid	ab	b	a	c
Propionic acid	a	b	c	d
Isobutyric acid	a	a	a	a
Butyric acid	a	a	b	b
Isovaleric acid	a	a	b	b
Valeric acid	a	a	b	b
Caproic acid	a	a	b	b
Heptanoic acid	a	a	a	b
Phenol	a	a	a	a
p-Cresol	a	a	a	b
Ammonia	a	a	b	b

Note: Different letters along rows indicate difference ($P<0.05$).

Table 6.4 summarizes the results obtained from the Total Nitrogen (TN) measurement, temperature monitoring, and the color observations of the treated pig manure.

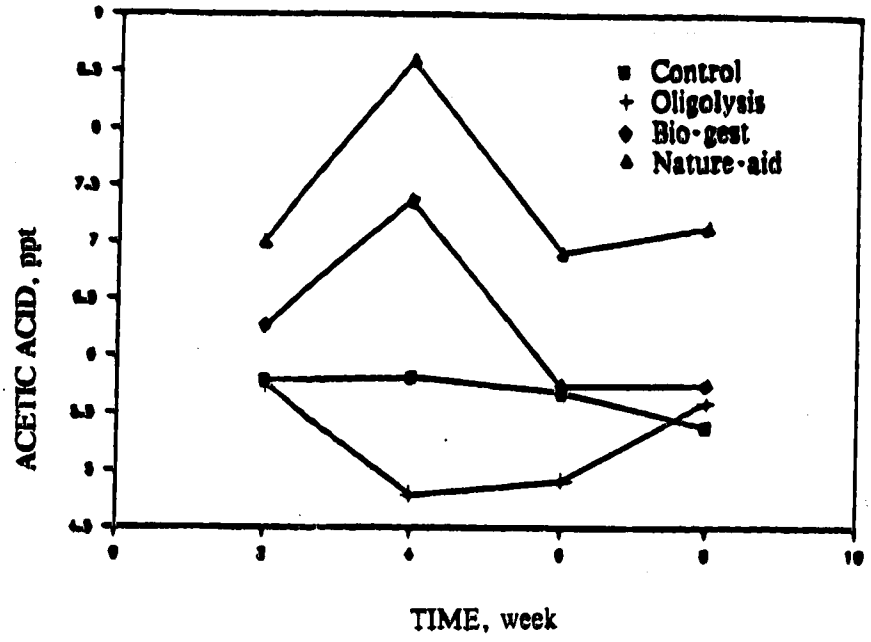


Figure 6.2 Acetic acid in four treatments over eight weeks.

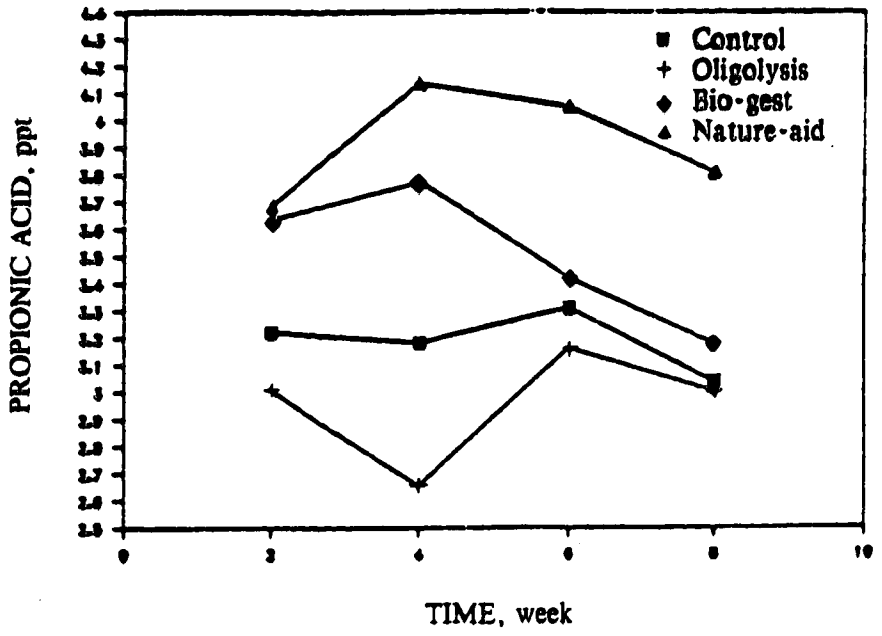


Figure 6.3 Propionic acid in four treatments over eight weeks.

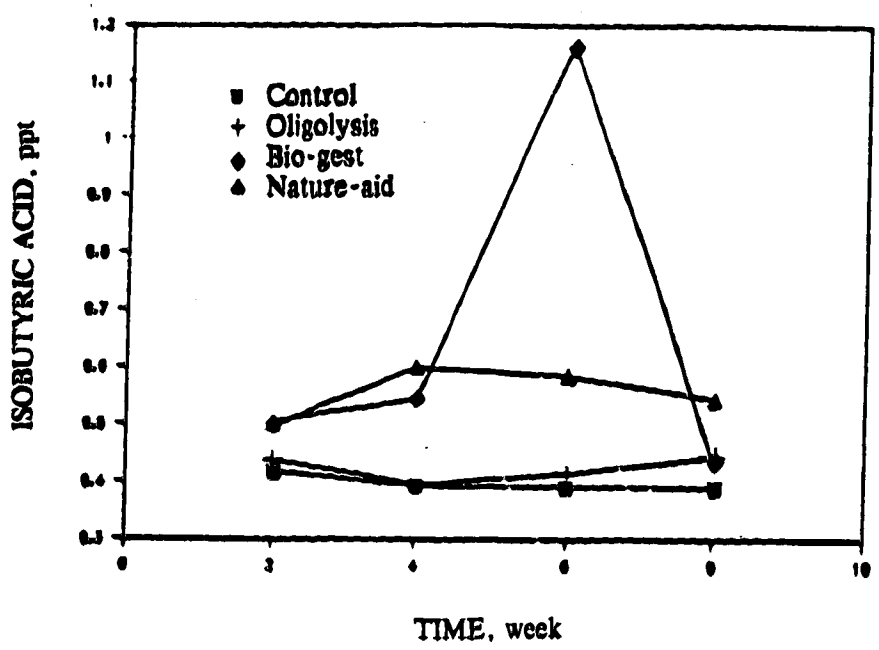


Figure 6.4 Isobutyric acid in four treatments over eight weeks.

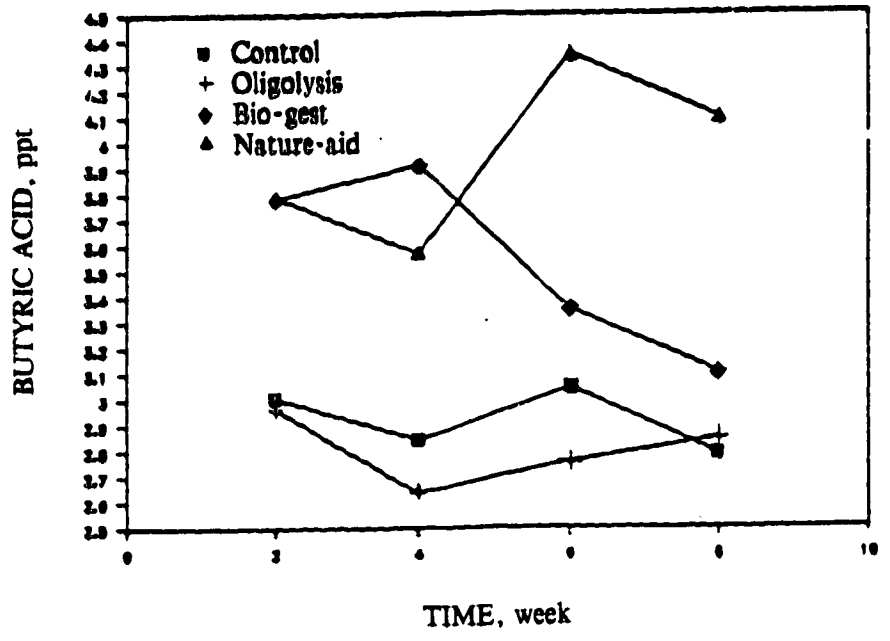


Figure 6.5 Butyric acid in four treatments over eight weeks.

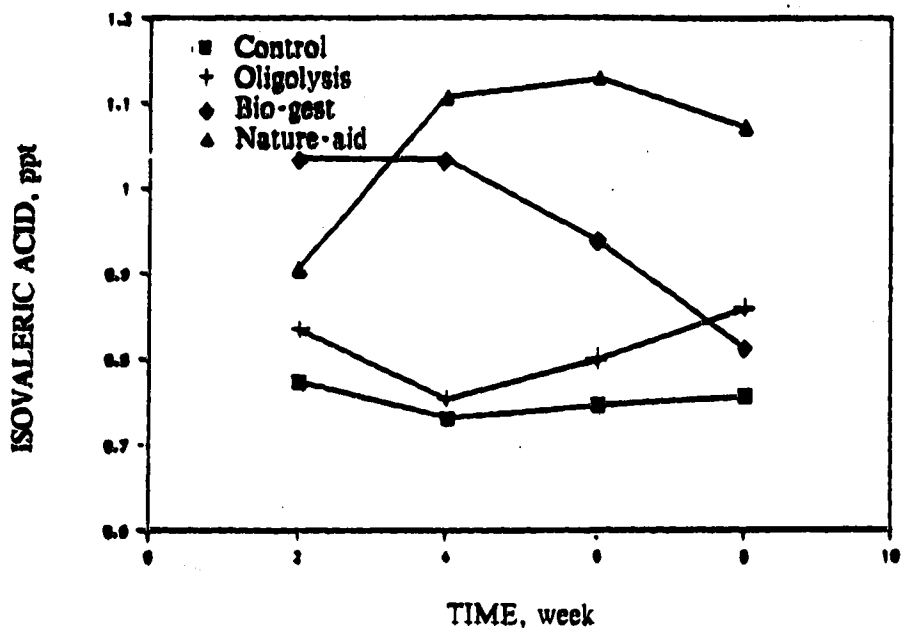


Figure 6.6 Isovaleric acid in four treatments over eight weeks.

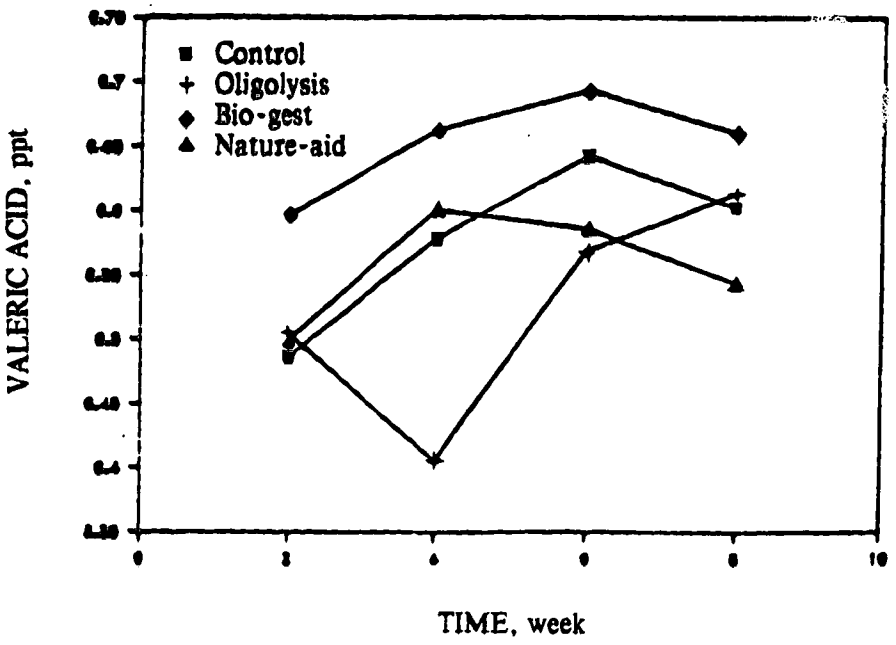


Figure 6.7 Valeric acid in four treatments over eight weeks.

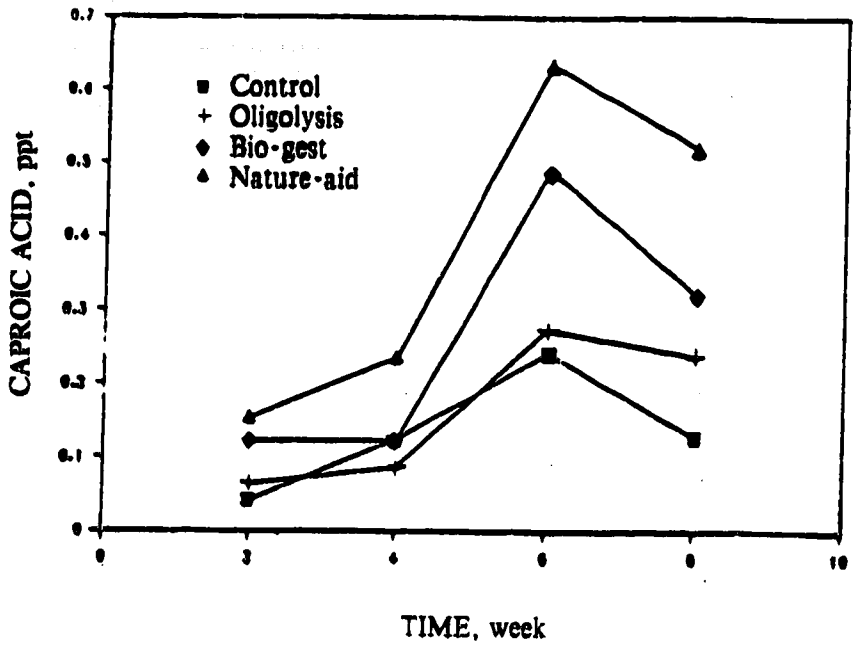


Figure 6.8 Caproic acid in four treatments over eight weeks.

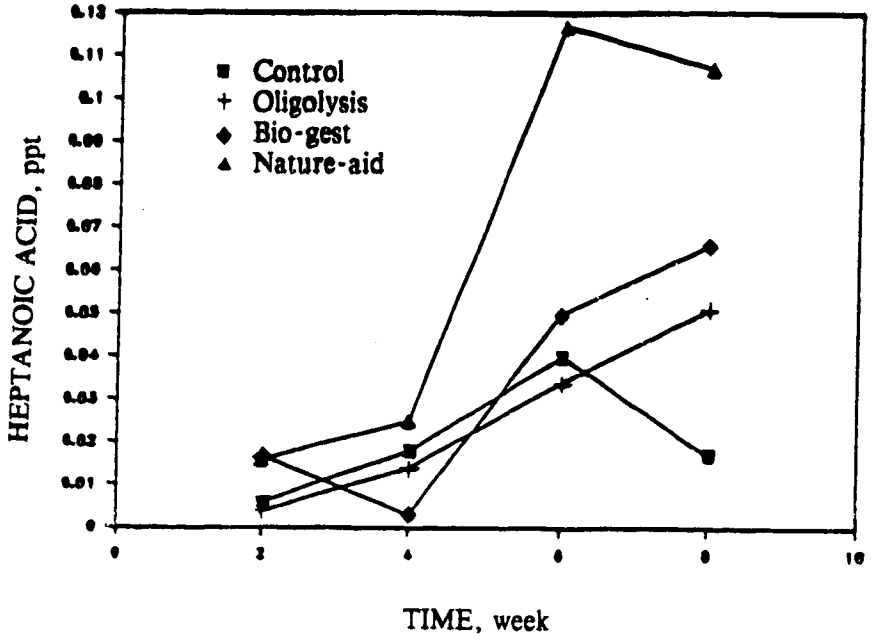


Figure 6.9 Heptanoic acid in four treatments over eight weeks.

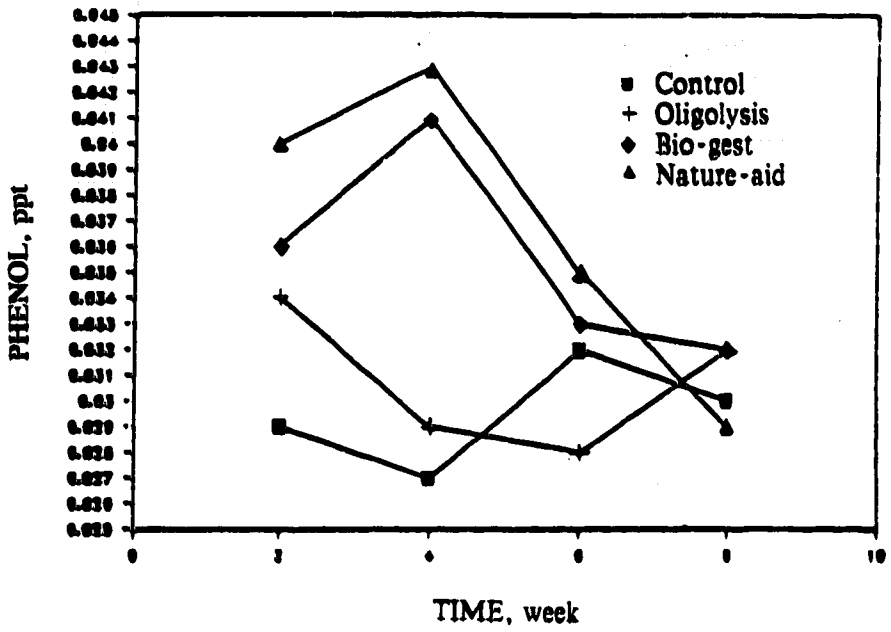


Figure 6.10 Phenol in four treatments over eight weeks.

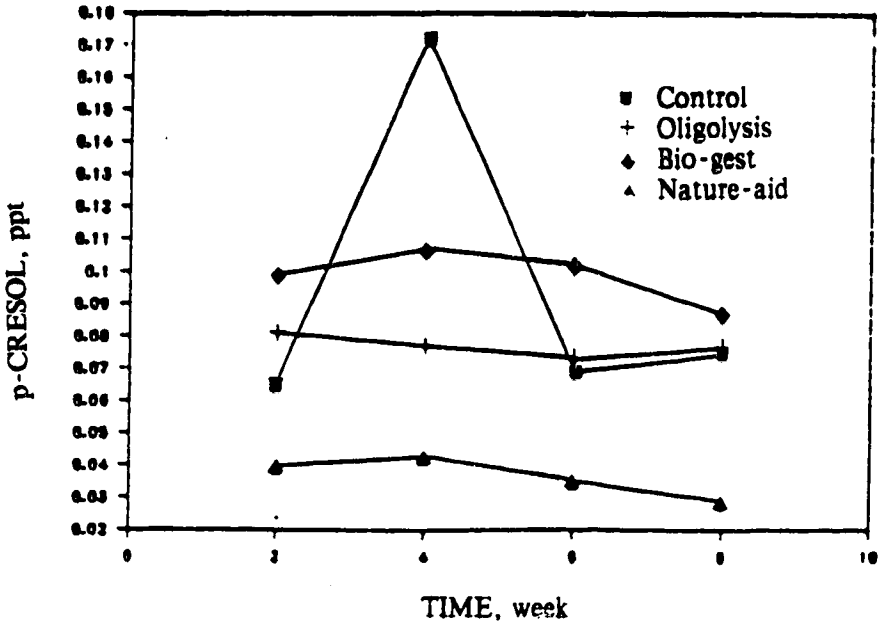


Figure 6.11 p-Cresol in four treatments over eight weeks.

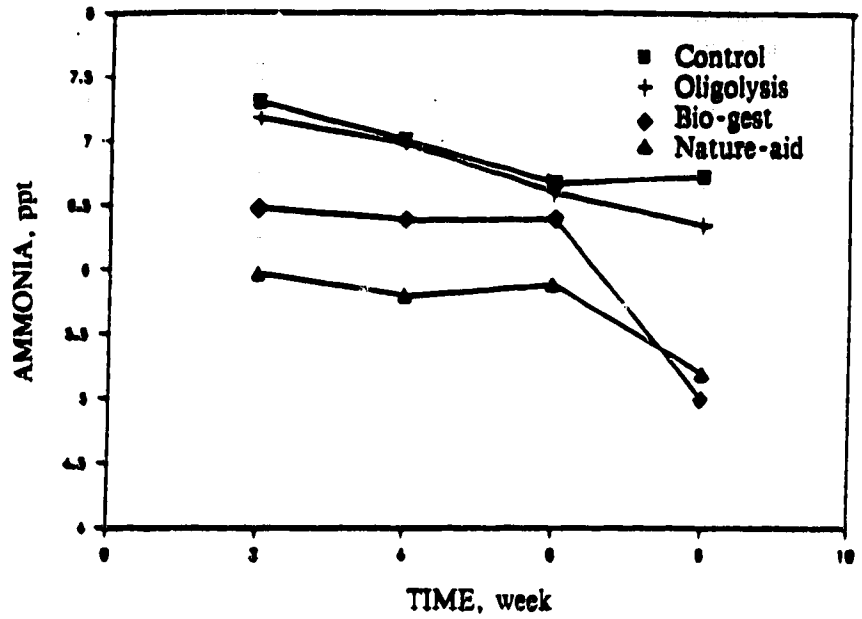


Figure 6.12 Ammonia in four treatments over eight weeks

TABLE 6.4 Other General Observations from the Liquid Phase.

Treatment	Item		
	Total Nitrogen (%)	Temperature (°C)	Color
Control	0.745	21.1	dark brown
Oligolysis	0.764	21.3	darker brown
Bio-gest	0.753	21.0	light brown
Nature-aid	0.745	21.3	dark brown

6.2 Gas Phase

A typical GC response obtained from the gas phase analysis is shown in Figure 6.13. The retention times of the compounds in the gas phase also are listed. Unknown compounds were found in Treatment A (with retention times of 17.25 and 19.07 min.), Treatment C (with a retention time of 19.63 min.) and Treatment D (with a retention time of 18.46 min.) with low concentrations. These compounds were not identified since no standard gases were available for their identification. Mean concentrations of the five compounds in the gas phase of the treated pig manure are tabulated in Table 6.5. Raw data from gas phase analysis are

listed in Appendix E.

TABLE 6.5 Mean Concentrations (%) of Compounds in the Gas Phase.

Compound	Treatment			
	Control	Oligolysis	Bio-gest	Nature-aid
N_2	11.70	11.51	17.48	28.14
CH_4	9.94	9.91	9.20	7.70
CO_2	78.13	78.42	73.10	64.14
H_2S	*0.35	ND	*0.30	**0.19
NH_3	0.06	0.09	0.07	0.08

* average from three measurements, the rest were obtained from four measurements.
** detected only once
ND Non-detectable

Analysis of Variance and Multi-Comparison of the means were carried out on the experimental data obtained from the gas phase. The procedures are shown in Appendix I and J. The results are summarized in Table 6.6 and Table 6.7.

TABLE 6.6 Analysis of Variance - Gas Phase.

Compound	Treatment	Time
N_2	=	=
CH_4	=	**
CO_2	=	=
H_2S	***	**
NH_3	*	***

*** significant at 0.001 level of probability
** significant at 0.01 level of probability
* significant at 0.05 level of probability
= not significant

TABLE 6.7 Summary of the SNK Test Result - the Gas Phase.

Compound	Treatment			
	Control	Oligolysis	Bio-gest	Nature-aid
N_2	a	a	a	a
CH_4	a	a	a	a
CO_2	a	a	a	a
H_2S	a	b	a	b
NH_3	a	ab	b	ab

Note: Different letters along rows indicate differences ($P<0.05$).

Gas production rate was described on both a per pig basis (L/pig.day) and a per litre of manure basis (L/L.day). The ranges of gas production rate obtained from each treatment are summarized in Table 6.8. The mean gas production rates are also included in Table 6.8. The mean volumetric gas production rates for each treatment are graphically presented in Figure 6.19. The variation of outside temperature is also included in the figure.

TABLE 6.8 Ranges of Gas Production Rate.

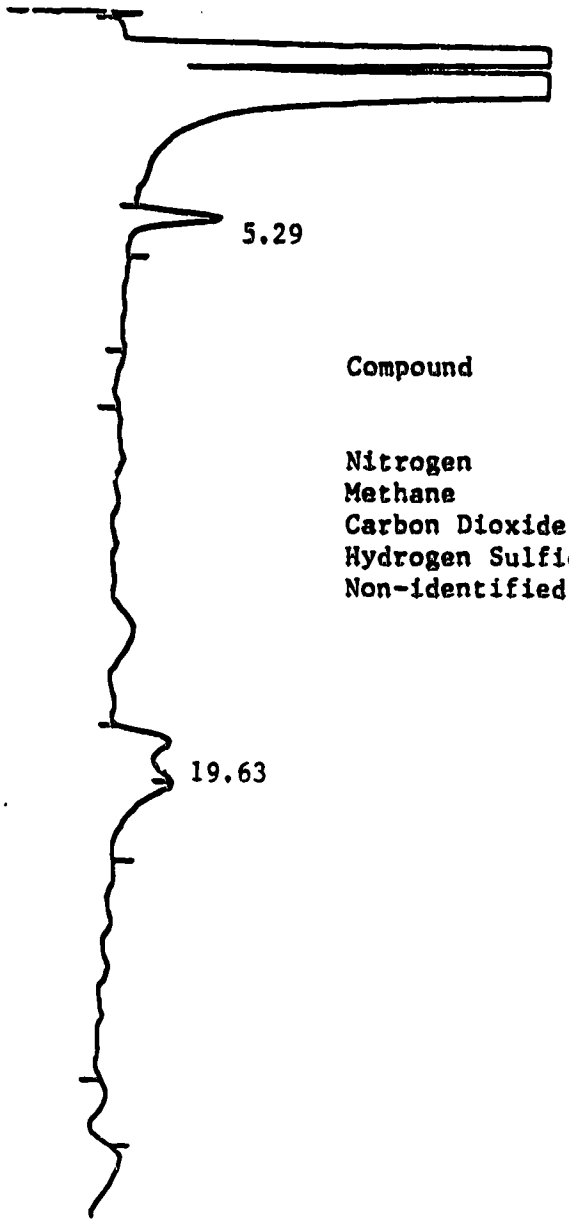
Treatment	Gas Production Rate					
	(L/pig.day)			(L/L.day)		
	min.	max.	mean	min.	max.	mean
Control	5.5	21.0	14.5	0.097	0.32	0.222
Oligolysis	5.2	18.9	13.1	0.093	0.29	0.202
Bio-gest	6.0	20.8	14.8	0.110	0.29	0.226
Nature-aid	5.3	20.4	14.9	0.094	0.32	0.230

Note: mean manure production for 75 kg pig is 3.2 L/day.

The statistical results in Table 6.2 indicate that the treatments were significantly different for concentrations of nine compounds in the liquid manure. Phenol and p-Cresol were significantly different at levels of $P<0.05$ and $P<0.01$, respectively. Interactions (treatment by time) are significant for the four compounds (propionic, isovaleric, caproic and heptanoic acids). Interactions were only significant among the organic acids. This implied that the concentrations of those four organic acids were not only treatment dependent but also treatment-time dependent. Replicates were not found to be significantly different.

The statistical results in Table 6.6 also indicate that the treatments were significantly different for the concentrations of H_2S and NH_3 in the gas phase, at significant levels of $P<0.001$ and $P<0.05$, respectively. Concentration over time was significant in three compounds, i.e., CH_4, H_2S and NH_3.

The author routinely smelled the gases generated from each treatment while conducting the gas production measurements. The odours were evaluated at the exhaust from the sampling pump. The odours from Treatments A, C and D were so offensive that odours could be sensed only at approximately 100 mm from the exhaust. In the oligolysis treatment,



Compound	Retention Time (min.)
Nitrogen	0.74
Methane	0.95
Carbon Dioxide	1.43
Hydrogen Sulfide	5.29
Non-identified Compound	19.63

Figure 6.13 Typical GC response to the gas phase.

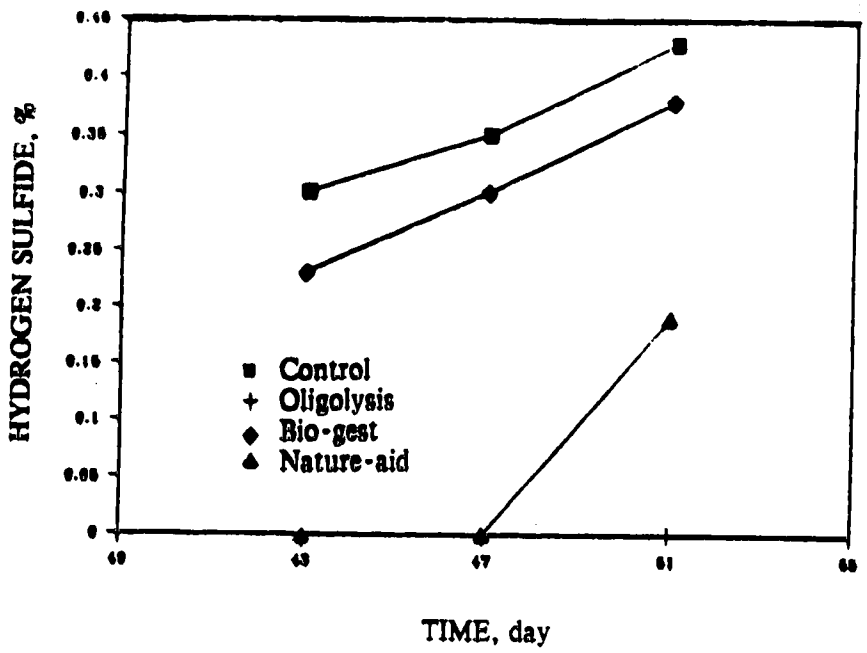


Figure 6.14 Hydrogen sulfide in the gas phase.

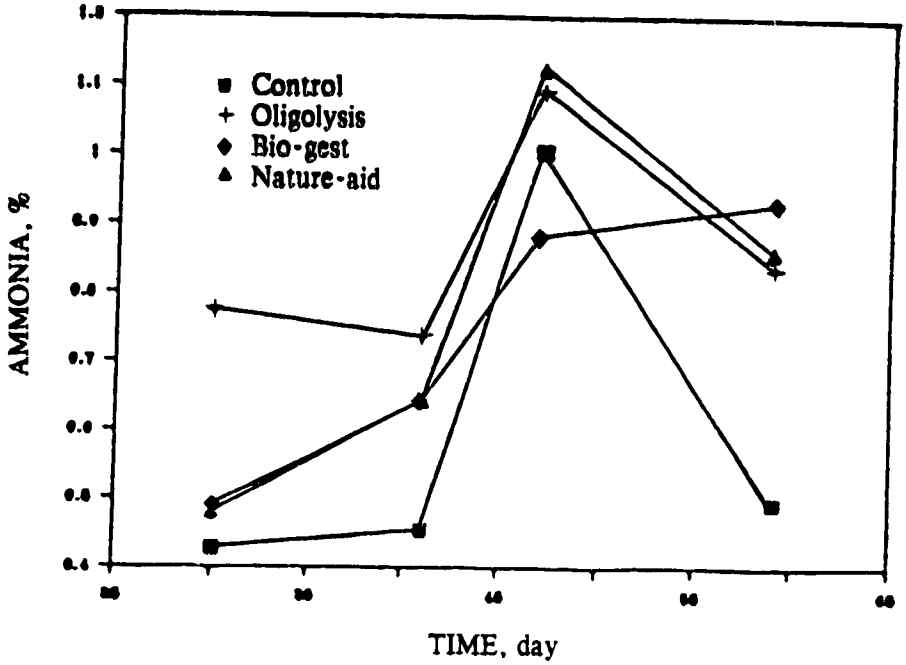


Figure 6.15 Ammonia in the gas phase.

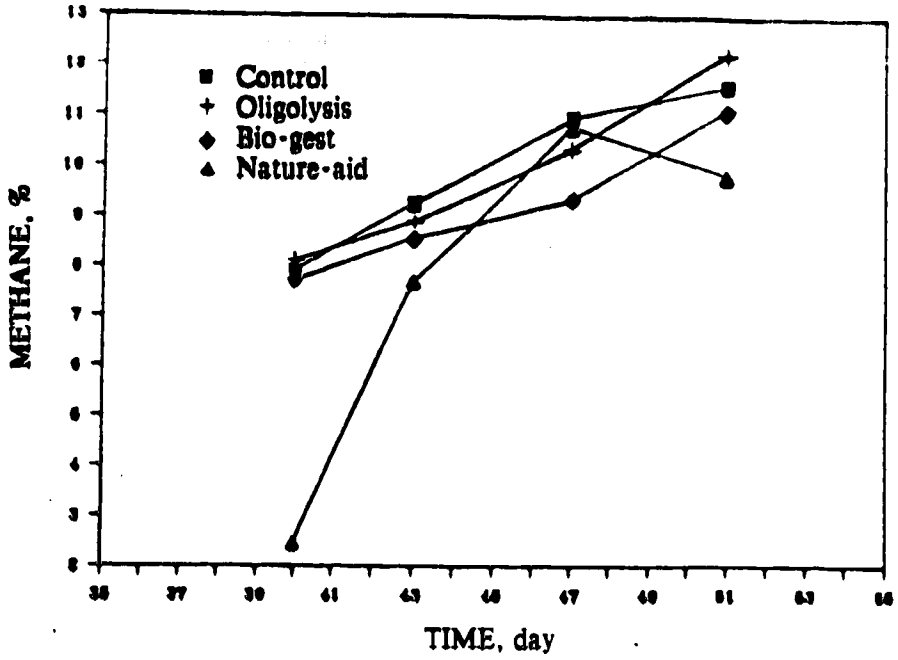


Figure 6.16 Methane in the gas phase.

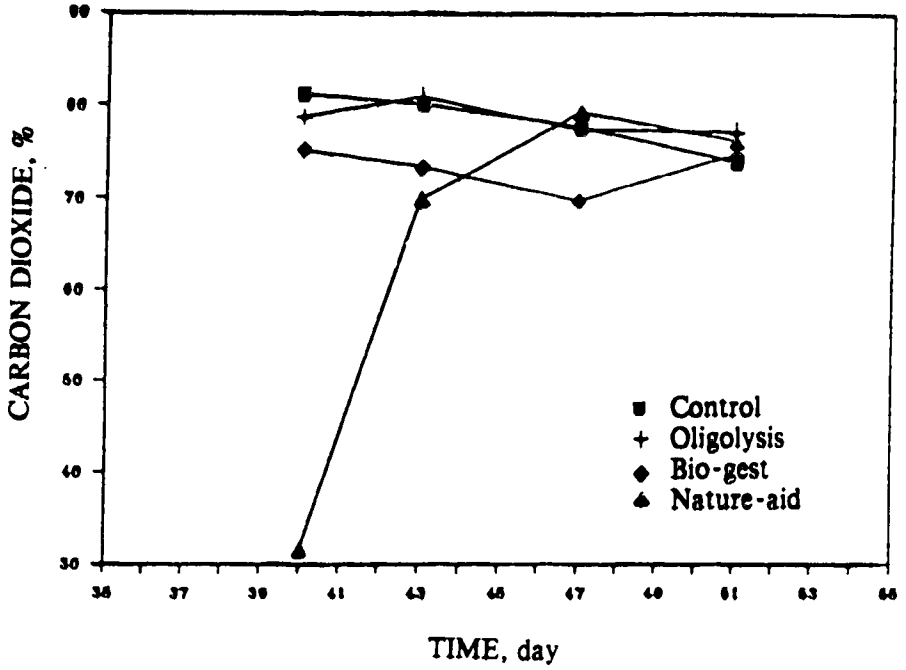


Figure 6.17 Carbon dioxide in the gas phase.

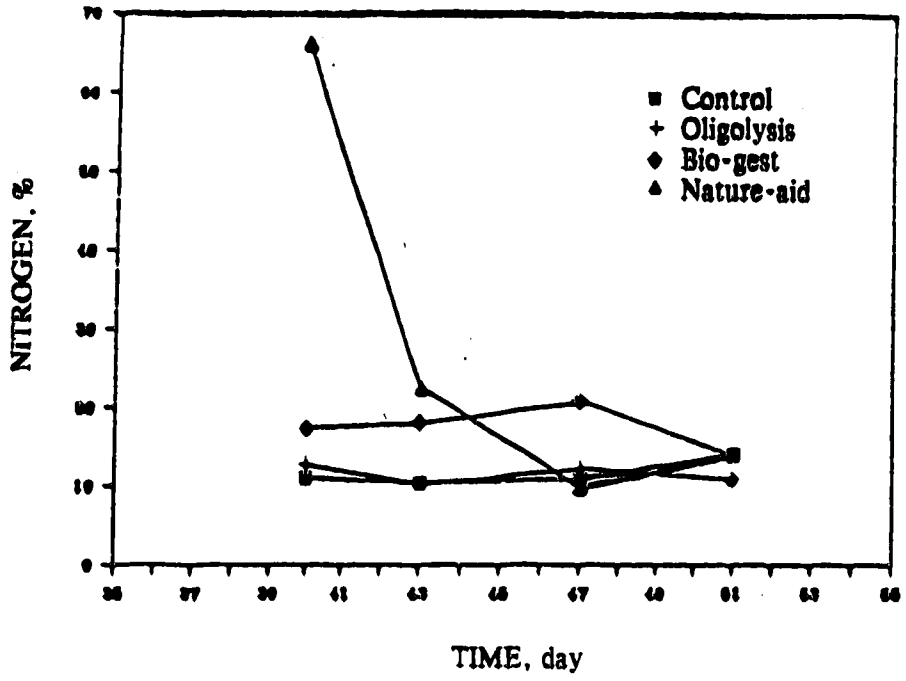


Figure 6.18 Nitrogen in the gas phase.

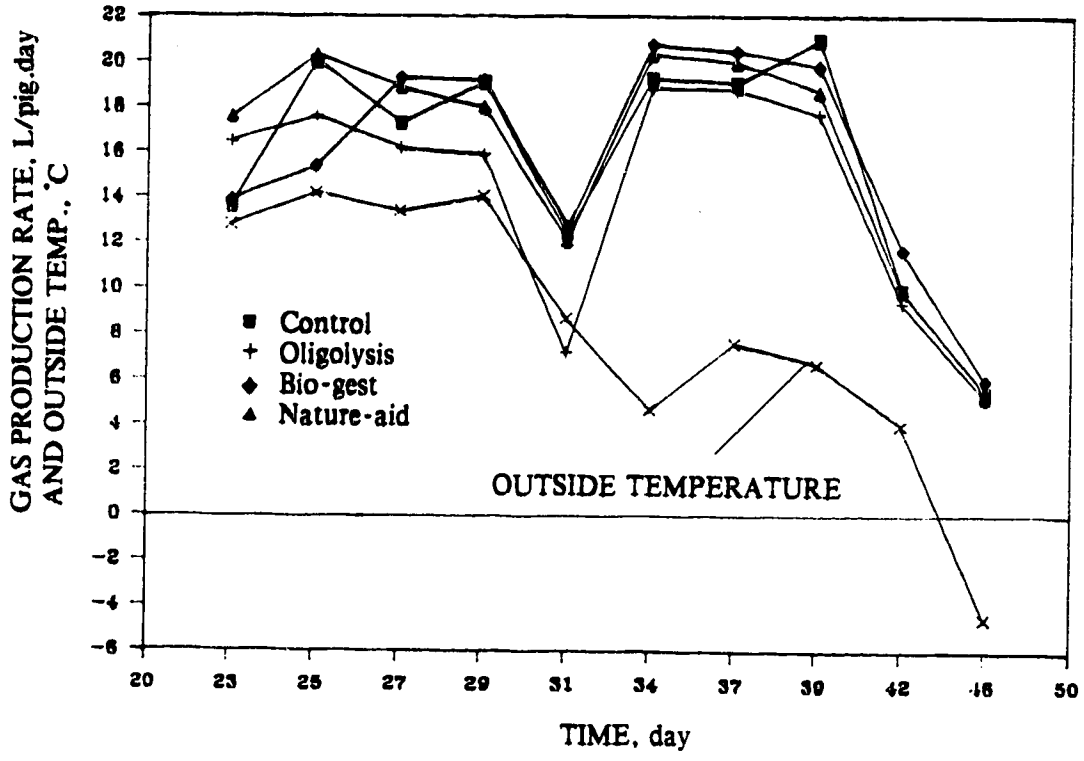


Figure 6.19 Gas production rates in the four treatments.

odours could be sensed within 40 mm of the exhaust. The gas offensiveness from the oligolysis treatment was considerably less than that of other three treatments. The liquid manure also was sniffed while taking liquid samples. The differences in smell of liquid manure from each treatment were not as apparent as in the gases but a less objectionable smell was again noted in the oligolysis treatment. This odour evaluation is merely that of the author and not that of a panel.

6.3 Treatment Effects

Treatment A: Control

Figures 6.2 to 6.12 and Table 6.1 show that the control treatment produced the lowest mean concentrations of isobutyric, isovaleric, caproic, heptanoic acids and phenol, but the highest concentration of ammonia, and had the second lowest mean concentration of acetic, propionic, butyric, valeric acids and p-cresol. The control treatment is assumed to be a typical batch anaerobic fermentation process, with which other treatments could be reliably compared.

Figures 6.15 to 6.19 and Table 6.5 show that the control treatment produced the highest mean concentrations of H_2S and CH_4, and the lowest mean concentration of NH_3 in the gas phase. Ammonia values obtained in the liquid phase of the control treatment (Figure 6.12) were opposite to those obtained in the gas phase (Figure 6.16), along with the mean concentrations (Table 6.1 and 6.5). The concentrations of ammonia retained in liquid and gas phases of the treated pig manure will be discussed in a latter section. In the control treatment, the mean concentrations of N_2 and CO_2 were the second lowest (11.70%) and the second highest (78.13%), respectively.

Treatment B: Oligolysis

Oligolysis treatment yielded the lowest mean concentrations of acetic, propionic, butyric, valeric acids and p-cresol, and had the second lowest mean concentrations of isobutyric, isovaleric, caproic, heptanoic acids and phenol in liquid manure. The SNK test results in Table 6.3 indicated that there were no differences between the Control and Oliglysis

treatments in relation to the mean concentrations of all compounds studied in the liquid phase.

The concentration of H_2S was so low in the oligolysis treatment that it could hardly be detected. The introduction of ferrous ions in the oligolysis treatment eliminated H_2S in the gas phase of the treated pig manure. Voermans (1985) reported that 'waste with high iron contents prevented the presence of H_2S in the biogas'. Furthermore, Chiumenti et al. (1988) stated that 'small quantities of metal ions dissolve by electrolysis and sterilize microorganisms'.

The smells of the treated pig manure in the oligolysis treatment, from both liquid phase and gas phase, were obviously less objectionable than other treatments. On the basis of the data collected, this was attributed to:

1. the elimitation of H_2S out of the gas phase, since H_2S is a very odoriferious compound.

2. lower levels of organic acids (acetic, propionic, butyric, valeric acids and p-cresol) in the liquid phase (Table 6.1).

Soluble sulfides may exist in anaerobic pig manure as dissolved hydrogen sulfide (H_2S), bisulfide ions (HS^-) and sulfide ions ($S^=$). These three forms are collectively termed total soluble sulfides (T.S.S.). The equilibrium existing between the three forms of soluble sulfides is very dependent on the pH of the pig manure. Desorption of dissolved hydrogen sulfide results in an accumulation of gaseous H_2S. above a sulfide-containing liquid pig manure (Barber and McQuitty, 1974). In the oligolysis treatment, dissociation of dissolved hydrogen sulfide may results in the precipitation of insoluble metal sufides, i.e. ferrous sulfide (FeS). Figure 6.21 is proposed for a graphic presentation of the oligolysis treatment. The black color of the treated pig manure from the oligolysis treatment also may indicate the formation of the FeS. According to the description by Barber and McQuitty (1974), oligolysis treatment is the promotion of anaerobic corrosion for the control of hydrogen sulfide in pig manure.

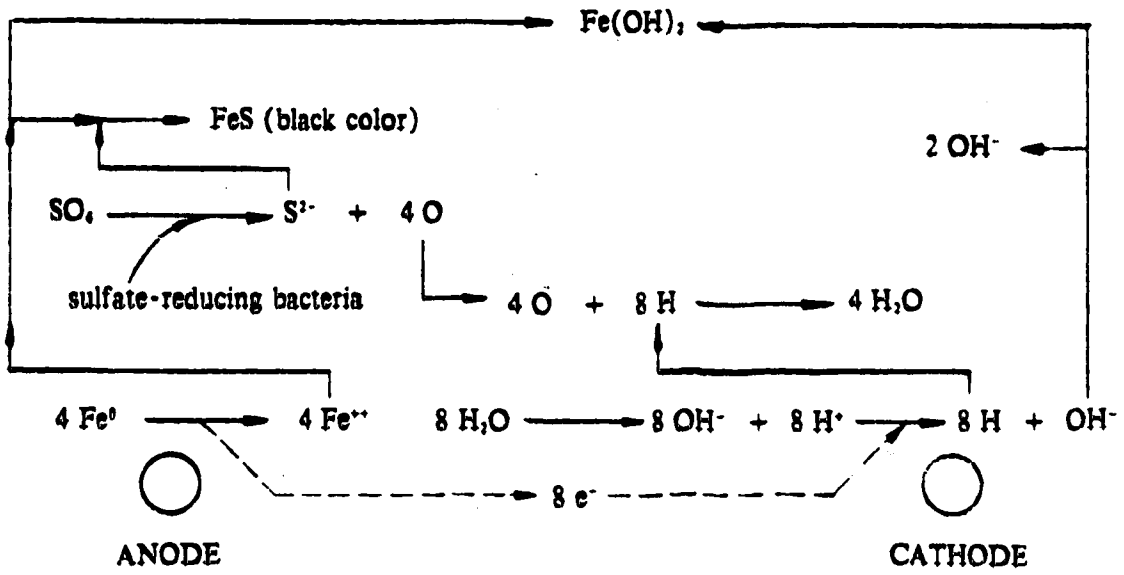


Figure 6.21 A Graphic Presentation of the Oligolysis Treatment (Adapted from Barber and McQuitty, 1974)

The mean concentrations of NH_3 were the highest in the oligolysis treatment. However, the smell was not as objectionable as it was in the control treatment, even though the control treatment yielded the lowest NH_3 concentration in the gas phase. Therefore, doubt exists as to whether or not NH_3 plays a predominant role in the odour intensity of treated pig manure. Williams (1984(a)) concluded that NH_3 was of no value as an odour indicator.

There were no differences between control treatment and oligolysis treatment in the mean concentrations of N_2, CO_2 and CH_4 in the gas phase (Table 6.5).

3. Treatment C: Bio-gest

In the liquid phase, all mean concentrations of compounds in this treatment were higher than those in both Treatments A and B, with the exception of ammonia. Isobutyric acid exhibited the highest mean concentration in this treatment. Compared to other treatments, the concentration of organic acids was increased in this treatment; however, the concentration of NH_3 in the liquid phase decreased.

The mean concentration of H_2S was the second highest in the Bio-gest treatment. There is no significant difference between Treatments A and C in relation to the mean concentrations of H_2S in the gas phase of the treated pig manure (Table 6.5).

4. Treatment D: Nature-aid

The mean concentrations of nine organic compounds (acetic, propionic, butyric, isovaleric, valeric, caproic, heptanoic acids, phenol and p-cresol) obtained from the liquid phase were highest in this treatment (Table 6.1). However, ammonia concentration in the liquid phase was the lowest among all four treatments.

The mean concentration of H_2S was found to be the second lowest in the Nature-aid treatment. Although H_2S was detected only once in treatment D (Nature-aid), the smell of the treated pig manure did not appear to be different from treatments A and C. Treatment D produced the lowest mean concentrations of CH_4 and CO_2, and the highest N_2 concentration.

Figures 6.17, 6.18 and 6.19 show that, before the second gas samples were taken, treatment D yielded very low CH_4 and CO_2 concentrations, but very high N_2. Two possibilities exist:

1. The degradation reactions were partially inhibited before the second sample was obtained due to the initial dose of Nature-aid. However, the results obtained in the liquid phase study (Part A of the experiment) did not indicate this.

2. The N_2 concentration (66.14%, Applendix E) in the first sample was approximately similar to those of ambient air (the concentration of N_2 in atmosphere is 78.084%, Pearson, 1988). Since only single replicate was used in Part B of the experiment, erroneous sample was the most possible reason for the abnormal data, i.e., a certain amount of ambient air was mixed with sample gases.

Each treatment exhibited its own characteristic trend in organic compound concentrations (Figures 6.2 to 6.12) in the liquid phase, perhaps with some exceptions. For example, in the oligolysis treatment, nine out of the eleven compounds exhibited concentration decreases from the second week to the fourth week, with the exception of caproic and heptanoic acids. The concentrations of eight compounds were increased from the fourth to the sixth week with the exception of phenol, p-cresol and ammonia. The concentrations of the eight compounds were increased from the sixth week to the eighth week, with the exception of propionic acid, caproic acid and ammonia.

Statistically, Treatments C and D produced higher concentrations of propionic, butyric, isovaleric, valeric and caproic acids than Treatments A and B. In Treatment D, the liquid phase contained the highest level of acetic acid, whereas, the ammonia content of the liquid phase in this treatment was significantly lower than that in Treatments A and B. The mean concentrations of H_2S and NH_3 were less in Treatments C and D; however, there were no statistical differences between these two treatments and Treatment A.

Since the gas samples were not analyzed for these compounds in the liquid phase, no data were available to indicate whether low concentrations in the liquid phase resulted in high concentrations in the gas phase or that the production rates were lower. Similarily, high levels of a compound in the liquid phase may have indicated low levels in the gas phase if the compounds accumulated within the liquid phase. Ammonia was analyzed in both the liquid and gas phases; however, the analyses were not concurrent. The NH_3 concentrations in the gas phase were time-dependent. Therefore, one could not conclude that a low concentration of ammonia in the liquid phase resulted in a high concentration in the gas phase.

Ammonia appears in the liquid pig manure as un-ionized ammonia (NH_3) and ammonium ion (NH_4^+). Un-ionized ammonia (NH_3) and NH_4^+ fractions in liquid pig manure are controlled by pH and temperature-dependent equilibrium (Yake and James, 1983). The decimal fraction of total ammonia in liquid pig manure present in the un-ionized form is given in Equation 6.1 (Yake and James, 1983):

$$f = 1/(10^{(pKa - pH)} + 1) \qquad (6.1)$$

where, f = decimal fraction of total ammonia in un-ionized form

$$pKa = 0.09018 + \frac{2729.92}{T}, \text{ and}$$

T = K of liquid pig manure.

For a given temperature and a pH value of liquid pig manure, the fraction of NH_3 can be calculated using Equation 6.1. This fraction of ammonia becomes available to be transferred to the gas phase under certain condition, such as agitation. Since no pH measurement was carried out during the experiment, decimal fraction of total ammonia in un-ionized form can

not be calculated.

Generally, the use of additives (Bio-gest and Nature-aid) tended to increase the concentrations of organic acids (Table 6.1 and Figures 6.2 to 6.12) in the liquid phase while, at the same time, reducing the ammonia levels. These observations in concert may indicate the fixation of carbon and nitrogen into biological material such as microbial cells. However, these observations also may indicate that more NH_3 was transfered into the gaseous phase above the liquid and greater levels of organic acids remain within the liquid phase organic material.

6.3.1 Other General Observations

Settleable solids were measured at the beginning of the experiment. However, no settleable solids were observed in the pig manure samples. When the samples were diluted with water, solids began to settle. However, the results were not consistent. Possibly, the particles contained in the liquid manure samples had different charges on the surfaces, physical interactions among these particles reached to an equlibrium of suspension of solids, instead of settling down. After adding dilution water, physical interactions among particles were broken down, then solids began to settle.

The mean gas production rate was highest in Treatment D (14.9L/pig.day), followed by Treatment C (14.8 L/pig.day), Treatment A (14.5 L/pig.day) and Treatment B (13.1 L/pig.day) (Table 6.8). These results imply that the mean gas production rate (litre of gas produced per pig per day) was increased slightly due to the addition of Bio-gest and Nature-aid, and the mean gas production rate was slowed down due to the introduction of the olygolysis treatment. The introduction of Bio-gest and Nature-aid may increase the microbial activity of the pig manure. However, there was no significant difference among mean gas production rates among these treatments. Methane concentrations in the gas phase did not reach flammability even though the concentrations of methane in the gas phase exceeded 5% among the four treatments. When gases contain more than 5% of methane, the gases will be flammable (Pearson, 1988). Gas production rates are temperature-dependent. When outside

temperature dropped, gas production rates decreased accordingly (Figure 6.19).

The colors of the treated pig manure varied among treatments (Table 6.4). The color of the treated manure from the oligolysis treatment appeared black. Bio-gest treatment produced the lightest color of the four treatments. Nature-aid and the control treatments yielded similar colors that were in-between that of oligolysis and Bio-gest treated pig manure. No further explanation was available to explain the differences in color.

The Total Nitrogen content in the liquid was not significantly different among the treatments (Table 6.4). The highest value appeared in the oligolysis treatment (0.764%), while the lowest value appeared in the Nature-aid treatment (0.735%).

The statistical analysis did not indicate any significant temperature differences among the treatments. The observed barn temperature (20.4°C), based on seven measurements) was lower than that of the treated liquid manure (21.2°) since the anaerobic degradation reactions are exothermic. An average temperature of 16.5°C was observed in the raw manure prior to adding it to the bio-reactors.

6.4 The Validation for the Odour Indicator Models

The odour indicator models as summarized in Section 2.7 of Chapter 2 could not be applied to results obtained from the oligolysis treatment. The reason for this is best explained by example. When using Eqation 2.14 as an odour indicator, an H_2S concentration value of zero as obtained from the oligolysis treatment would yield the odour intensity index (OII) value of zero. Equations 2.12 and 2.14 also yield zero values. A zero value of OII indicates no odour, which is not releastic. If NH_3 were eliminated, Equations 2.10, 2.13 and 2.14 would all give a result of zero. Therefore, the application of those models appeared to be limited. The models may be useful if models in Equations 2.10 to 2.14 are developed in other mathematical forms, such as a certain form of the summation of each item.

7. CONCLUSIONS

The following conclusions are drawn from this study:

1. Bio-gest and Nature-aid increased the concentration of organic acids in the liquid phase of treated pig manure.

2. There was no statistical difference in concentrations between the control and oligolysis treatments with the exception of propionic acid being lower in the oliglysis treatment.

3. Bio-gest and Nature-aid decreased the concentration of ammonia in the liquid phase of treated pig manure.

4. Oligolysis treatment reduced the odour nuisance of the treated pig manure in both the liquid and gas phases.

5. Nature-aid decreased the concentration of hydrogen sulfide in the gas phase of the treated pig manure.

6. Oligolysis treatment eliminated hydrogen sulfide in the gas phase of the treated pig manure.

7. No settleable solids were found in the liquid treated pig manure unless they were diluted with water.

8. Gas production rates and temperatures are not significantly different among the treatments. Mean gas production rate was 14.3 L/pig.day and mean temperature was 21.2°C.

8. RECOMMENDATIONS

Since odours are the volatile fractions of compounds, the gas phase of treated pig manure should be studied carefully. The thirteen compounds should be measured concurrently in both liquid phase and gas phase. The results should explain whether a lower concentration of a specific compound in the liquid phase yields a higher concentration in the gas phase.

The measurement of the pH value is recommended at the same time as for the compounds, since pH can effect the volatility of the compounds.

Hydrogen sulfide was eliminated in the oligolysis treatment. The fixation of sulfide appears to be in the form of sulfate. Therefore, a sulfate measurement also is recommended for future study. Ferrous sulfide identification should be carried out in the treated liquid pig manure, since no hydrogen sulfide was found in the oligolysis treatment, and the black color observed from the oligolysis treatment also may attribute to the formation of ferrous sulfide.

The gas collection system should be improved since it is unknown whether the generated gases from the manure are corrosive to the plastic material. If there were reactions between the plastic bag and the gases, leakage may occur. A displacement gas collection system would be an alternative.

For a complete odorous compounds evaluation, attention also should be paid to other suspect odorous compounds, such as sulfur compounds and amines.

An odour panel should be set up to evaluate the effectiveness of each treatment on odour control. The studies for individual odorous compound can not evaluate the total odour. A correlation study between the odorous compounds and the panel judgment will provide certain information between the the odorous compounds and the total odour, so that a odour prediction model can be developed.

A combination of oligolysis treatment, Bio-gest treatment and Nature-aid treatment may yield interesting results. Odour control has been extensively concentrated to only one single treatment. No information is available on the combinations of two or several treatments.

Electrical consumption is recommended as a parameter be studied in the oligolysis treatment in the future. The economical feasibility of this treatment will depend on the energy consumption, as well as the capital cost.

9. REFERENCES

American Society for Testing and Materials. 1971. Standard method for measurement of odour in atmospheres (dilution method). ASTM D 1391-57. ASTM. 23:301

Barber, E.M. and J.B. McQuitty. 1974. Hydrogen sulfide evaluation from anaerobic swine manure. Publ. Faculty of Agriculture and Forestry, University of Alberta. Edmonton, Alberta. pp. 69.

Barth, C.L., L.F. Elliot and S.W. Melvin. 1982. Using odour control technology to support animal agriculture. Paper No. 82-4035. ASAE, St. Joseph, MI.

Barth, C.L. and D.T. Hill. 1976. Methods for treating odours: Problems and consequences. Paper No. 76-4015. ASAE, St. Joseph, MI.

Barth, C.L. and L.B. Polkowski. 1972. Correlation OII and odorous components in stored dairy manure. Paper No. 72-950. ASAE, St. Joseph, MI.

Barth, C.L. 1972. Using Odour intensity limits in air quality standards. Paper No. 72-441. ASAE, St.Joseph, MI.

Barth, C.L and L.B. Polkowski. 1974. Identifying odourous components of stored dairy manure. Trans. of the ASAE, 17(3):737.

Bosch, V.D. and L.C. Buchanan. 1975. The effect of ozone treatment on swine manure. Paper No. 75-207. CSAE, Ottawa, ON.

Carney, P.G. and V.A. Dodd. 1988. The measurement of agricultural odours. Paper No. 88-340. International Conference on Agricultural Engineering. Paris, France.

Chang, A., G.L. Riskowski, M.P. Steinberg and D.L. Day. 1988. Evaluation of swine manure odour control additive. Paper No. 88-4045. ASAE, St. Joseph, MI.

Chiumenti, R., L. Donantoni and S. Guercini. 1987. First trials of swine manure odour control with depth aeration and "olygolyse". Latest Development in Livestock Housing Seminar of the 2nd Technical Section of the CIGR. ASAE, St. Joseph, MI.

Chiumenti, R., L. Donantoni and S. Guercini. 1988. The olygolytic treatment of swine liquid manure: results of current tests. In: Storing, handling and spreading of

manure and municipal waste. Proceedings of the seminar of the 2nd and 3rd Technical Section of the C.I.G.R.. Swedish Institute of Agricultural Engineering. Uppsala, Sweden. 1988(8):1-11.

Dale, A.C.. 1967. Prairie Farmer Article. Purdue University Coorperative Extension Service. Lafayette, IN.

Day, D.L. 1965. Gases and ofours in confinement swine buildings. Ill. Agr. Expt. Sta. Pub. AS-624. 4p.

Day, D.L.. 1966(c). Liquid hog manure can be deodorized by treatment with chlorine or lime. Ill. Res. 8(3):16. (as cited by Muehling, 1966).

Demuynck, M., E.J. Nyns and H.P. Naveau. 1985. A review of the of anaerobic digestion on odour and on disease survival. In J.K.R. Gasser (Ed.),Composting of Agricultural and Other Wastes, Elsevier Applied Science Publishers. London. pp. 120-126.

Evans, M.R. and F.E. Thacker. 1985. Aeration and odour control. Agricultural waste utilization and management, Proceedings of the fifth International Symposiom on Agricultural Wastes. Publication of ASAE. Chicago, IL. pp. 454-460.

Faith, W.L. 1964. Odour control in cattle feedlot. Journal of Air Pollution Control Association. 14:459.

Frijters, J.E.R. 1978. A critical analysis of odour unit number and its use. Chemical Senses and Flavour, 3:227-233. (Cited by Miner, 1982)

Ghaly, A.E. and N.R. Bulley. 1988. Odour production, measurement and control. Paper No. 88-109. CSAE, Ottawa, ON.

Goodall, S.R., S.E. Curtis and J.M. McParland. 1988. Reducing aerial ammonia by adding Micro-aid to poultry diets: Laboratory and on-farm evaluations. Proceedings of the Third International Livestock Environmental Symposium. ASAE, St. Joseph, MI. pp. 286-290.

Gunn, J.D. and H.W. Kolstee. 1974. Controlling odour from hog manure lagoon storage using floating plastic cover. Paper No. 74-218. CSAE, Ottawa, ON.

Hammond, E.G., C. Fedler and G. Junk. 1979. Identification of dust-borne odours in swine confinement facilities. Trans. of ASAE. 22:1186-1189, 1192.

Hammond, E.G., P. Kuczala, G.A. Junk, and J. Kozel. 1974. Constituents of swine house odours. In: Livestock Environment (Proceedings, International Symposium). ASAE, St. Joseph, MI. pp. 364-372. (Cited by Miner, 1982)

Hartung, L.D., Hammong E.G. and J.R. Miner. 1970. Identification of carbonyl compounds in a swine-building atmosphere. Proceedings of the International Symposium on Livestock Wastes, ASAE, St. Joseph, MI. pp. 105-106.

Hill, D.T. and C.L. Barth. 1976. Quantitative prediction of odour intensity. Trans. of the ASAE. 19:939-944.

Hill, D.T. and C.L. Barth. 1976(b). Removal of gaseous ammonia and methylamine using ozone. Trans. of A.S.A.E. 19,5:935.

Hobson P.N. and A.M. Robertson. 1977. Waste Treatment in Agriculture. Applied Science Publishers Ltd., London.

Hoek, V.D. and J. Oosthoek. 1985. Composting: Odour emission and odour control by biofiltration. In K.J.R. Gasser (Ed.), Composting of Agricultural and Other Wastes, Elsevier Applied Sciece Publishers. London. pp. 70-76.

Klarenbeek, J.V. 1985. Odour emissions of Dutch agriculture. Agricultural Waste Utilization and Management. Proceedings of the Fifth International Symposium on Agricultural Wastes. ASAE, St. Joseph, MI.

Licht, L.A. and J.R. Miner. 1978. A scrubber to reduce livestock confinement building odours. Paper No. PN 78-203. ASAE, St. Joseph, MI.

Lindvall, T., D. Noren and L. Thyselins. 1974. Trans. of the ASAE. 17(3): 508-512.

McFarland, A.R., J.E. Sorel and D.L. Reddell. 1982. Design of a 1-butanol scale dynamic olfactometer for ambient odour measurement. Paper No. 82-3085. ASAE, St. Joseph, MI.

Merkel, J.A., T.E. Hazen and J.R. Miner. 1969. Identification of gases in a confinement swine building atmosphere. Trans. of the ASAE. 12(3):310-315.

Miner, J.R. and R.C. Stroh. 1975. Controlling feedlot surface odour emission rates by application of commercial products. Paper No. 75-4566. ASAE, St. Joseph, MI.

Miner, J.R. 1982. Controlling odours from livestock production facilities. Research Results in Manure Digestion, Runoff, Refeeding, Odour. North Central Regional Research Publication No. 284. Midwest Plan Service, Iowa State University, Ames, IA 50011. pp. 30-35.

Moncrieff, R.W. 1967. The Chemical Senses. Leonard Hill, London. pp. 208-213. (Cited by Barth, 1972)

Muehling, A.J. 1969. Swine housing and waste managment. Publ. AEng-873, University of Illinois, Urbana-Champaign, IL. pp. 27-28.

Muller, W.. 1985. Erfahrungen mit einem gullebehandlungsverfarhen (OLYGOLYSE). Tierarztliche Umschau, 40 (5): 343-350.

Pearson, C.G.. 1988. Air cleaning for livestock production building. Farm Building & Engineering, 5(2): 13-17.

Philips, V.R. and Le Roux N.W.. 1984. The control of odour nuidance from livestock building in the UK. PMP/WE/84/014074/P, NIAE/WARREN spring laboratory project paper.

Schaefer, J. 1980. Development of instrumental methods for measuring odour levels in intensive livestock buildings. In: Effluents from livestock (Gasser, J.K.R.(Ed.)). Applied Science Publishers, London, UK. pp. 513-535

Schirz, S. 1977, Odour removal from the exhaust air of animal shelters. pp. 207-216. In: Agriculture and Environment, Special issue - Odour Characterization and Control, F. de Soet, etc., Associated Scientific Publishers, Amsterdam, The Netherlands. (Cited by Licht and Miner, 1978)

Sweeten, J.M.. 1975. Odour perception and measurement. Presented at Pollution Effects on Vegetation Workshop, Texas Agricultural Extension Service, Galveston County, TX.

Sweeten, J.M., D.L. Reddell, R.O. Gauntt and J.E. Sorel. 1982. Field measurement of ambient agrucultural odours with a butanol olfactometer. Paper No. 82-3086. ASAE, St. Joseph, MI.

Thacker, F.E. and M.R. Evans. 1985. BOD_5, TOA and odour offensiveness. EEC/FAO Seminar. Silsoe, UK.

The Furrow. 1979. John Deere Limited, Grimsby, Ontario. Vol. 5, p. 22.

Tchobanoglous, G.. 1979. Wastewater Engineering: Treatment Disposal Reuse (2nd Edition). McGraw-Hill Book Company, Metcalf and Eddy, Boston, MASS.

van Geelen, M.A. and K.W. van der Hoek. 1977. Odour control with biological washers. Agriculture and Environment, 3:217-222. (Cited by Miner, 1982)

Voermans, J.A.M. 1985. Biogas productivity on livestock farms. Agricultural Waste Utilization and Management. Proceedings of the Fifth International Symposium on Agricultural Wastes. Publ. of ASAE, St. Joseph, MI.

Warburton, D.J., J.N. Scarborough, D.L. Day, A.J. Muehling, S.E. Curtiss, and A.H. Jensen. 1981. Evaluation of commercial products for odour control and solids reduction of liquid swine manure. In: Livestock waste: a renewable resource (Proceedings, International Symposium). ASAE, St. Joseph pp. 309-313.

Welsh, F.W., D.D. Schulte, E.J. Kroeker and H.M. Lapp. 1976. The effect of anaerobic digestion upon swine manure odours. Paper No. 76-206. CSAE, Ottawa, ON.

Williams, A.G. 1984(a). Indicator of piggery slurry odour offensiveness. Agric. Wastes. Elsevier Applied Science Publishers Ltd, England. 10: 15-36.

Williams A.G. 1984(b). Control of piggery slurry odours by aerobic treatment. NIAE and SIAE. BSRAE Association, Silsoe, Bedford.

Yake, W.E. and R.K. James. 1983. Setting effluint ammonia limits to meet in-stream toxicity criteria. J. WPCF. 55(3):303-309.

Yasuhara, A. and K. Fuwa. 1977(a). Odour and volatile compounds in liquid swine manure: Carboxylic acids and phenols. Bulletin of the Chemical Society of Japan. 50(3): 731-733.

Yasuhara, A. and K. Fuwa. 1977(b). Odour and volatile compounds in liquid swine manure: Steam-distillable substances. Bulletin of the Chemical Society of Japan. 50(11): 3029-3032.

Yasuhara, A. and K. Fuwa. 1978. Hydrogen sulfide and dimethyl sulfide in solid swine manure. Chemosphere Vol. 10, Pergamon Press Ltd., London, UK. pp. 833-838.

Yasuhara, A. and K. Fuwa. 1979(a). Volatile and odourous components in solid swine manure. Agric. Biol. Chem., 43(2): 313-316.

Yasuhara, A. and K. Fuwa. 1979(b). Quantification of Phenols in gas from rotten liquid swine manure by computer-controlled gas chromatography-mass spectrometry. Bulletin of the Chemical Society of Japan. 52 (11): 3311-3313.

Yasuhara, A. and K. Fuwa. 1979 (c). Odour and volatile compounds in liquid swine manure: Volatile and odourous components in anaerobically or aerobically digested liquid swine manure. Bulletin of the Chemical Society of Japan, 52 (1): 114-117.

Yasuhara, A.. 1980. Relation between odour and odourous components in solid swine manure. Chemosphere Vol. 9, Pergamon Press Ltd., London, UK. pp. 587-592

Yasuhara, A. and K. Fuwa. 1980. Isolation and characterization of odourous componenets in solid swine manure. Agric., Biol., Chem., 44 (10): 2379-2385.

10. APPENDICES

APPENDIX A: Odorous Compounds Detected.

Compounds Identified in the Solid, Liquid Swine Manure and Gases from Anaerobic Decomposition and in Dust.

Catalog	Researchers identified odorous compounds in				Compound
	Solid	Liquid	Gas	Dust	
Organic		4,5	1	8	Acetic acid
Acid	2	4	1	8	Propoinic acid
	2,3,6	4,5	1		iso-butyric acid
	2,3,6	4,5		8	Butyric acid
	2,3,6	4,5	1		iso-Valeric acid
	2,3,6	4,5		8	Valeric acid
		4			2-Methylbutyric acid
		4			2,2-Dimethylpropionic acid
	2				Caproic acid
	4	4,5		8	Hexanoic acid
		4		8	Heptanoic acid
		4		8	Octanoic acid
		4			Nonanioc acid
	2	4,5		8	Benzoic acid
				8	Decanoic acid
				8	Undecanoic acid
				8	Dodecanoic acid
				8	Tridecanoic acid
				8	Tetradecanoic acid
	2	4,5		8	Phenylacetic aci
				8	Hydrocnnamic acid
	3				4-Methylvaleric acid
		4			4-Methylhexanoic acid
	2	4,5			3-Phenylpropionic acid
Alcohol			1,7		Methanol
	3		1,7		Ethanol
	3,6	4			Propanol
			1		2-Propanol
			1,7		n-Propanol
	4,7				
		4			Butanol
			1,7		n-Butanol
			1,7		iso-Butanol
			1,7		iso-pentanol
	2				Diacetone alcohol
	3				Isomayl alcohol
Amines			1		Methylamine
			1		Ethylamine
			1		Trimethylamine
			1		Triethylamine
		5			Aniline
		5			Methylquinazoline
		11			Quinazoline
		5			Dimethyl- or ethylquinazoline
Fixed gas		2	1		Ammonia
			1		Hydrogen sulphide
Carbonyls			1,7		Acetaldehyde

			1,7		Propanaldehyde
			1		Byturaldehyde
			1,7		iso-Butyraldehyde
			1,7		Formaldehyde
			1,7		Heptaldehyde
			1,7		Valeraldehyde
			1,7		Octaldehyde
			1,7		Decaldehyde
				8	Bensaldehyde
			12		Ethanal
			12		Propanal
				8	Butanal
				8	2-Butanal
			1		Hexanal
					2-Henxanal
				8	Pentanal
				8	2-Pentenal
		12	1,13	8	Acetone
				8	Butanone
		12			2-Butanone
	6				3-Nethyl-2-Butanone
				8	Pentanone
			1		3-Pentanone
				8	1-Octene-3one ÷ Octanone
		11			2-Pentadecanone
		11			2-Hexadecanone
		5			o-Aminoacetophenone
				8	2-Heptenal
				8	2,4-Heptadienal
				8	Decanal
				8	2,4-Nonadienal
				8	2,4-Decadienal
	6				3-Methylbutanal
			1		Triacetyl (2,3-Diketo-Butane)
		11			Trithiapentane
		11			Triapentane
		11			3,3-dimethyl-2-thiapentane
Ester			1		Methyl formate
			1		Methyl acetate
			1		iso-Propyl acetate
			1		iso-Butyl acetate
			1		iso-Propyl propionate
			1		Propyl acetate
			1		n-Butyl acetate
Sulfur	3	9	1		Dimethyl sulfide
Compound			1		Diethyl sulphide
			1		Methyl disulfide
		11			Benzothiazole
		5			Dimethylsulfoxide
Phenol	2,6	5,10			Phenol
		10			o-Cresol
		10			m-Cresol
	2,6	5,10			p-Cresol
		11			2,6-Di-t-butyl-p-cresol
	5	4,9			p-Ethyl-Phenol
Heterocycle	3,6	2	1		Indole

	3,6	2	Skatole
		1	Pyrazines
		8	Trimethylpyrazine
		8	Tetramethylpyrazine
Mercaptan		1	Methyl mercaptan

1. Miner and Stroh, 1975
2. Yasuhara and Fuwa, 1979(a)
3. Yasuhara, 1980
4. Yasuhara and Fuwa, 1977(b)
5. Yasuhara and Fuwa, 1979 (c)
6. Yasuhara and Fuwa, 1980
7. Merkel et al., 1969
8. Miner, 1982
9. Yasuhara and Fuwa, 1978
10. Yasuhara and Fuwa, 1979(b)
11. Yasuhara and Fuwa, 1977(a)
12. Hartung et al., 1970

APPENDIX B: Feed Ration for the Pigs.

wheat	25.0%
barley	55.1%
soybean	6.0%
iodized salt	0.4%
biofox	1.5%
limestone	1.0%
premix	1.0%

The premix consisted of:

zinc oxide	7.8%
copper sulphate	2.4%
manganese sulphate	2.2%
iron sulphate (ferrous)	25.85%
sodium selenite	25.0%
ground limestone	36.75%

(courtesy of Sinclair Swine Research Center, University of Alberta)

APPENDIX C: Kjeldahl Method.

In the Kjeldahl method, nitrogenous compounds are reduced to ammonia by digestion with sulfuric acid and an appropriate catalyst. The resulting digestion mixture is then made basic and the ammonia is collected in a boric acid solution by steam distillation. The quantity of ammonia is determined by titration with a standard solution of a strong acid.

Reagents:

1. Concentrated H_2SO_4
2. Catalyst packs: each contains 9.9 g K_2SO_4, 0.41 g HgO, and 0.08 g $CuSO_4$
3. 40% NaOH
4. 4.0% boric acid and indicator
5. Zinc metal, 20 mesh
6. Standard H_2SO_4 (about 0.1 N)

Procedures:

Digestion:

1. Weigh approximately 5 g of sample on a filter paper, wrap and drop into a 800 ml Kjedahl flask as a package. Run a blank by leaving out the sample.

2. Add 1 catalyst pack and 30 ml concentrated H_2SO_4 to each flask. Put the flasks on the digestion rack and turn on fan and heat.

3. Digest for about 30 minutes after clearing has occurred, and then let flasks cool to room temperature.

Distillation:

4. Add 300 ml of tap water to each flask.

5. Add 1 g of zinc metal (20 mesh) to each flask.

6. Measure 50 ml aliquots of 4% boric acid solution into 500 ml Erlenmeyer flasks and place under the delivery tubes of the distillation rack.

7. Turn on condenser water and heat.

8. Add 110 ml of 40% NaOH to the Kjeldahl flask, swirl and place on the distillation rack.

9. Distill until the receiving flask contains 250 to 300 ml of liquid.

10. Lower the receiving flasks so the distillate will not suck back and turn off the heat.

Titrate the ammonia with the standard H_2SO_4. End point was a light pink color.

11. Calculate the final results on the MTS.

APPENDIX D: Original Data from the Liquid Phase

Treat.	Week	Rep.	Concentration of Odour Causing Compound (ppt)												
			Acet. Acid	Prop. Acid	Isob. Acid	Buty. Acid	Isov. Acid	Vale. Acid	Capr. Acid	Hept. Acid	Phen.	p-Cr.	Indo.	Skat.	Ammo.
A	2	1	5.595	3.209	0.411	3.159	0.769	0.499	0.046	0.008	0.032	0.068	0.000	0.000	7.398
A	2	2	5.828	3.243	0.430	3.089	0.783	0.384	0.042	0.004	0.028	0.064	0.000	0.000	7.398
A	2	3	5.959	3.213	0.416	2.769	0.771	0.574	0.038	0.006	0.026	0.062	0.000	0.118	7.099
B	2	1	5.758	3.179	0.464	3.267	0.894	0.518	0.060	0.004	0.035	0.092	0.000	0.068	7.681
B	2	2	5.100	2.813	0.422	2.788	0.795	0.453	0.054	0.000	0.035	0.072	0.000	0.072	6.785
B	2	3	6.428	3.033	0.430	2.845	0.816	0.544	0.080	0.008	0.032	0.080	0.000	0.000	7.071
C	2	1	8.048	3.900	0.513	3.979	0.966	0.530	0.062	0.008	0.032	0.092	0.000	0.000	6.929
C	2	2	5.700	3.703	0.522	4.032	1.207	0.591	0.072	0.006	0.041	0.106	0.000	0.000	6.134
C	2	3	5.038	3.307	0.485	3.345	0.935	0.670	0.236	0.038	0.035	0.098	0.000	0.000	6.389
D	2	1	7.360	3.890	0.519	4.028	0.939	0.501	0.132	0.006	0.028	0.106	0.000	0.000	6.482
D	2	2	6.923	3.530	0.471	3.627	0.857	0.457	0.062	0.000	0.063	0.138	0.000	0.000	5.722
D	2	3	6.723	3.628	0.507	3.721	0.923	0.591	0.268	0.042	0.028	0.104	0.000	0.000	5.722
A	4	1	7.269	3.253	0.399	2.748	0.705	0.510	0.038	0.002	0.024	0.058	0.000	0.000	7.247
A	4	2	5.522	3.646	0.445	3.422	0.845	0.729	0.252	0.045	0.032	0.148	0.000	0.000	6.954
A	4	3	4.656	2.640	0.339	2.360	0.644	0.495	0.088	0.006	0.024	0.310	0.000	0.020	6.813
B	4	1	4.652	2.492	0.386	2.497	0.730	0.459	0.050	0.000	0.028	0.072	0.000	0.000	7.071
B	4	2	3.931	2.875	0.441	3.029	0.841	0.556	0.142	0.015	0.028	0.086	0.000	0.000	7.071
B	4	3	5.780	2.601	0.367	2.389	0.689	0.203	0.068	0.028	0.030	0.072	0.000	0.000	6.785
C	4	1	7.757	3.898	0.570	4.229	1.113	0.715	0.096	0.008	0.045	0.124	0.004	0.000	6.389
C	4	2	7.440	3.683	0.528	3.755	0.992	0.650	0.170	0.000	0.041	0.098	0.000	0.000	6.134
C	4	3	6.905	3.735	0.536	3.759	0.998	0.623	0.102	0.000	0.037	0.100	0.000	0.000	6.653
D	4	1	8.405	4.177	0.594	4.376	1.103	0.670	0.138	0.004	0.037	0.144	0.000	0.040	5.965
D	4	2	8.117	4.083	0.602	2.108	1.164	0.769	0.356	0.049	0.043	0.152	0.000	0.000	5.722
D	4	3	9.278	4.147	0.608	4.219	1.058	0.666	0.216	0.021	0.048	0.192	0.036	0.034	5.722
A	6	1	6.661	3.473	0.418	3.015	0.779	0.652	0.264	0.042	0.043	0.064	0.000	0.070	6.813
A	6	2	4.597	3.204	0.352	3.184	0.633	0.631	0.308	0.053	0.024	0.060	0.034	0.042	6.674
A	6	3	5.824	3.246	0.407	2.943	0.828	0.646	0.156	0.025	0.028	0.082	0.000	0.000	6.538
B	6	1	4.142	3.485	0.384	2.453	0.748	0.528	0.244	0.040	0.028	0.070	0.000	0.000	6.785
B	6	2	4.881	3.004	0.428	3.063	0.830	0.589	0.392	0.061	0.030	0.072	0.000	0.000	6.510
B	6	3	5.729	2.999	0.439	2.762	0.822	0.591	0.188	0.000	0.026	0.076	0.000	0.000	6.510
C	6	1	5.169	3.330	2.507	3.364	0.984	0.731	0.432	0.000	0.037	0.112	0.000	0.000	6.653

C	6	2	5.431	3.339	0.473	3.263	0.886	0.627	0.598	0.076	0.028	0.086	0.000	0.000	6.389
C	6	3	6.643	3.577	0.513	3.422	0.947	0.725	0.440	0.074	0.035	0.108	0.000	0.000	6.134
D	6	1	7.229	4.231	0.630	4.594	1.214	0.857	0.696	0.134	0.043	0.172	0.000	0.032	6.218
D	6	2	6.465	3.962	0.566	4.259	1.082	0.735	0.642	0.114	0.026	0.118	0.000	0.000	5.722
D	6	3	7.051	3.952	0.562	4.183	1.093	0.771	0.564	0.104	0.037	0.136	0.000	0.000	5.722
A	8	1	4.980	3.115	0.377	2.807	0.742	0.607	0.146	0.023	0.024	0.066	0.000	0.000	6.538
A	8	2	6.042	3.125	0.384	2.820	0.746	0.603	0.100	0.011	0.035	0.088	0.018	0.218	6.954
A	8	3	5.132	2.863	0.409	2.733	0.783	0.599	0.142	0.017	0.030	0.072	0.000	0.000	6.674
B	8	1	5.234	2.826	0.407	2.599	0.777	0.542	0.234	0.032	0.032	0.076	0.000	0.000	6.510
B	8	2	5.879	3.162	0.447	3.034	0.861	0.635	0.214	0.028	0.035	0.078	0.000	0.000	6.246
B	8	3	5.678	3.016	0.481	2.919	0.939	0.666	0.262	0.093	0.030	0.078	0.000	0.000	6.246
C	8	1	5.456	2.823	0.348	2.841	0.633	0.546	0.398	0.059	0.026	0.070	0.000	0.000	3.203
C	8	2	5.631	3.399	0.471	3.339	0.896	0.719	0.366	0.061	0.030	0.094	0.000	0.000	5.890
C	8	3	6.166	3.305	0.479	3.133	0.910	0.717	0.200	0.078	0.041	0.096	0.000	0.000	5.890
D	8	1	7.633	4.031	0.568	4.378	1.125	0.853	0.576	0.114	0.028	0.160	0.000	0.000	5.051
D	8	2	7.014	3.819	0.536	4.039	1.035	0.757	0.462	0.089	0.032	0.112	0.000	0.000	5.265
D	8	3	6.763	3.569	0.528	3.875	1.056	0.806	0.520	0.117	0.028	0.148	0.036	0.026	5.265

Note: Treatment A: Cotrol
Treatment B: Oligolysis
Treatment C: Bio-gest
Treatment D: Nature-aid

APPENDIX E: Original Data from the Gas Phase

No. of Day	Concentration within Treatment (%)			
	Control	Olygolysis	Bio-gest	Nature-aid
		H_2S		
43	0.30	0.00	0.23	0.00
47	0.35	0.00	0.30	0.00
51	0.43	0.00	0.38	0.00
		NH_3		
40	0.043	0.077	0.049	0.048
41	0.046	0.074	0.064	0.064
47	0.100	0.109	0.088	0.113
59	0.049	0.084	0.093	0.086
		CH_4		
40	7.93	8.12	7.72	2.47
43	9.26	8.90	8.57	7.70
47	10.97	10.36	9.35	10.80
51	11.62	12.26	11.14	9.83
		CO_2		
40	81.06	78.59	74.93	31.38
43	79.95	80.76	73.15	69.82
47	77.70	77.38	69.69	79.32
51	73.80	76.96	74.62	76.05
		N_2		
40	11.01	12.71	17.35	66.14
43	10.48	10.34	18.05	22.48
47	10.98	12.25	20.66	9.88
51	14.15	10.78	13.86	14.05

APPENDIX F: Original Data from Gas Production Rate Measurement

No. of Day	Gas Production Rate within Treatment (L/pig.day)			
	Control	Olygolysis	Bio-gest	Nature-aid
23	13.6	16.5	13.9	17.6
25	20.0	17.6	15.4	20.3
27	17.3	16.2	19.3	18.9
29	19.1	15.9	19.2	18.0
32	12.4	7.2	12.7	12.1
34	19.3	18.9	20.8	20.4
36	19.1	18.8	20.5	20.0
38	21.0	17.7	19.8	18.7
41	10.0	9.4	11.7	10.0
45	5.5	5.2	6.0	5.3

APPENDIX G: An Example of Analysis of Variance for the Liquid Phase.

```
      ⍝
      ⍝     ANALYSIS OF VARIANCE OF ACETIC ACID
      ⍝
      ACEDATA←□←4 3 4⍴DATA
 5.595 5.758 8.048 7.36
 5.828 5.1   5.7   6.923
 5.959 6.428 5.038 6.723

 7.269 4.652 7.757 8.405
 5.522 3.931 7.44  8.117
 4.656 5.78  6.905 9.278

 6.661 4.142 5.169 7.229
 4.597 4.881 5.431 6.465
 5.824 5.729 6.643 7.051

 4.98  5.234 5.456 7.633
 6.042 5.879 5.631 7.014
 5.132 5.678 6.166 6.763
      )COPY 700 HARDIN
SAVED 10:08:07 08/09/88
      'Y=M+C+A+AC+BAC+ε' AOV5 ACEDATA
C          3     31.47871     10.4929
A          3     4.66469      1.5549
AC         9     8.75308      0.97256
BAC        32     19.0732      0.59604
TOTAL      47     63.96968
```

APPENDIX H: An Example of Mean Comparisons for the Liquid Phase.

```
      ⍝
      ⍝       COMPARISON OF MEANS OF BUTYRIC ACID
      ⍝
      )COPY RGWE.DUNLN
SAVED 11:38:26 01/23/86
      DUNLN
HOW MANY MEANS ARE THERE?
□:
      4
GIVE THE 4 MEAN VALUES.
□:
      2.921 2.804 3.538 3.951
HOW MANY OBS. ARE THERE PER MEAN?
□:
      12
GIVE THE VALUE OF THE EMS.
□:
      .17065
GIVE THE 3 DUNCAN VALUES.
□:
      2.89 3.49 3.84


SEQUENCE OF MEANS:  2 1 3 4

2.804 2.921 3.538 3.951


  2  1  3  4
 ------
STANDARD ERROR OF THE MEANS:  0.1192511356
      )OFF
# 21:35:05  T=0.101  RC=0
# EXEC HELP:APL.BUFFER C
# $SET ECHO=OFF
```

APPENDIX I: An Example of Analysis of Variance for the Gas Phase.

```
      ⍝
      ⍝     ANALYSIS OF VARIANCE OF HYDROGEN SULFIDE
      ⍝
      H2SDATA←□←3 4⍴DATA
  0.3   0     0.23 0
  0.35  0     0.3  0
  0.43  0     0.38 0.19
      )COPY 700 HARDIN
SAVED 10:08:07 08/09/88
      'Y=M+B+A+AB+ε' AOV5 H2SDATA
B          3     0.28083     0.09361
A          2     0.02982     0.01491
AB         6     0.01412     0.00235
TOTAL      11     0.32477
      ⍝
      ⍝     B:TREATMENT, CALCULATED F=39.834 TABLE F
      ⍝                  CALCULATED F>TABLE F
      ⍝     TREATMENTS ARE SIGNIFICANTLY DIFFERENT
      ⍝
      )OFF
# 11:24:35  T=0.119  RC=0
# EXEC HELP:APL.BUFFER C
# $SET ECHO=OFF
```

APPENDIX J: An Example of Mean Comparisons for the Gas Phase.

```
      ⍝
      ⍝          AMMONIA
      ⍝
      DUNLN
HOW MANY MEANS ARE THERE?
□:
      4
GIVE THE 4 MEAN VALUES.
□:
      595.05 860.425 737.65 777.65
HOW MANY OBS. ARE THERE PER MEAN?
□:
      4
GIVE THE VALUE OF THE EMS.
□:
      13162.46
GIVE THE 3 DUNCAN VALUES.
□:
      3.2 3.95 4.42


SEQUENCE OF MEANS:  1 3 4 2

595.05 737.65 777.65 860.425


  1  3  4  2
    ---------
 ---------
STANDARD ERROR OF THE MEANS:  57.36388237
      )OFF
# 03:54:21  T=0.281  RC=0
# EXEC HELP:APL.BUFFER C
# $SET ECHO=OFF
```