EVALUATION OF SPHAGNUM MOSS AND CHEMICAL COMPOUNDS FOR MANAGEMENT OF ODOR AND USE OF LIQUID HOG MANURE

by

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ABSTRACT

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M.Sc. Food Science and Agricultural Chemistry

EVALUATION OF SPHAGNUM MOSS AND CHEMICAL COMPOUNDS FOR MANAGEMENT OF ODOR AND USE OF LIQUID HOG MANURE

Liquid hog manure (LHM) obtained from the Macdonald College farm was used in experiments aimed at (a) reducing the odor associated with LHM during handling and (b) conserving the fertilizer capacity of LHM. Various chemical treatments and sphagnum moss (SM) were evaluated to achieve the above objectives. Direct acidification to < pH 5.0, sphagnum moss (SM) and its combination with aluminum sulfate (AS) resulted in significant ($p < 0.05$) reduction in ammonia losses during storage of LHM. The SM and SM/AS combination also significantly ($p < 0.05$) reduced both odor presence and offensiveness. Gas chromatographic (GC) and GC/mass spectrometry (GC/MS) analysis indicated the absence of certain malodor compounds and lower peak areas of certain compounds in the SM and SM/AS treatments when compared to the controls. Investigations with barley seeding revealed that treatments which reduced the malodor of the LHM did not significantly ($p < 0.05$) affect the nitrogen fertilization capacity of the LHM, as indicated by plant dry matter yield.

RESUME

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M.Sc. Science des Alimants et de la Chimie Agricole

EVALUATION DE LA TOURBE DE SPHAIGNE ET DE COMPOSES CHIMIQUES POUR LE CONTROL DES ODEURS, ET UTILISATION DU LISIER DE PORC

Du lisier liquide de porc (LLP) obtenu de la ferme du College Macdonald fut utilise dans des experiences visant a (a) reduire les odeurs associees au LLP et (b) conserver sa valeur fertilisante. Pour atteindre les objectifs ci-dessus cites, differents traitements chimiques et de la tourbe de sphaigne furent examines. L'acidification direct a un $\mathrm{pH} < 5.0$, la tourbe de sphaigne et sa combinaison avec du sulfate d'aluminium ont permit de reduire de maniere significative ($p < 0.05$) les pertes d'ammoniac durant l'entreposage. La tourbe de sphaigne et sa combinaison avec le sulfate d'aluminium ont aussi permit une reduction significative ($p < 0.05$) et de la presence des odeurs et de leur offensivete. Pour ces deux traitements, des analyses chromatographiques en phase gaseuse (CG) et CG/spectromety de mass (CG/MS) ont revele l'absence de certains composes malodorants. Des experiences de germination de l'orge ont revele par la mesure du taux de matieres seches, l'infime contribution ($p < 0.05$) des traitements efficaces a reduire les odeurs aux capacites fertilisantes du LLP

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May God bless you all.

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I. INTRODUCTION

Concern for the environment is presently a major issue for the general population. Environmental contamination from use of industrial chemicals, from industrial and farm wastes and from consumer disposable wastes has become an ordeal.

Forty or fifty years ago, handling of wastes and related materials was termed "offensive trade" (McCord 1949) and was considered a menial task. Presently, handling of wastes requires some form of management. This has resulted from the efforts of environmentalists who have convinced our society of the dire concequences of irreversible, global pollution.

Animal farming in general creates a critical and hence waste management pollution problem due to the manure[1] generated. Recently, several factors has added to this problem; these include increased animal confinement for high rates of production of meat, milk and eggs; operation of animal farms within limits of residential areas and the absence of cropland for spreading of manure. This often results in a critical problem of odor pollution in populated areas. Consequently, properly designed animal facilities and land-use policies with consideration of waste management are needed.

1; The term manure denotes the fecal and urinary excretions of animals and combined with such material as bedding, feed, soil and other contaminants. This term will be used interchangeably with animal waste in this thesis.

The use of animal wastes for crop production necessitates its incorporation to soil by some spreading or injection technique. The risks associated with this practice include surface and ground water contamination, soil overloading and air pollution by odors. The odors result from biological breakdown of organic compounds in the manure. The challenge, therefore is to overcome these risks so that the availability and low cost of wastes become a viable alternative to chemical fertilizers. The recognition that chemical fertilizers can be damaging to the environment, provides support for the use of animal wastes as nutrient source for crops.

The overall objective of this research is to investigate methods for reducing the odor of hog manure to an acceptable level while at the same time conserve its fertilizer value. The specific objectives are to:

1. Evaluate the use of sphagnum moss (<u>Sphagnum fuscum</u>) and chemical treatments for odor reduction
2. Evaluate the interaction of aeration and acidification on odor reduction
3. Identify chemical compounds which are associated with odor reduction
4. Evaluate the fertilizer value of the treated waste.

II. LITERATURE REVIEW

2.1. THE PROBLEM OF ANIMAL WASTE DISPOSAL

With mounting pressures to conserve the environment in areas where there is intense livestock production, odor control has become an important issue. This is reflected in the increased frequency of odor-based complaints along with circumstances leading to law suits (Willrich and Miner, 1971; Jongebreur, 1977). Odor emission from animal farming facilities is regarded as odor pollution and as a nuisance, and is a particular problem associated with handling and disposal of manure. The disposal of manure without its polluting effects on air, soil or water, presents a challenge to agriculturalists and government agencies. In Canada, there is extensive land area available for the integration of manure disposal with crop and livestock production; however, the climate and crop requirements dictate that the manure be stored for up to six months (Townshend and Reichert, 1969). This storage time represents a high risk for environmental contamination.

2.1.1. Environmental problems

While domestic refuses and human wastes are continuously removed and treated before released into the environment, animal wastes are generally applied to farm lands without any treatment. This practice has generated concern regarding the environment and a number of safety questions have been raised regarding soil and water contamination (Jongebreur, 1977; Spoelstra, 1980; McGrath, 1977).

Animal manure can be detrimental to the environment and poses a hazard to the health of both humans and animals (Glock and Shwartz, 1975; Waston and Friend, 1987). Hence, an awareness of the problems and potential hazards, and an understanding of the overall situation can help to minimize the risks associated with pollution by animal manure. Water and soil pollution, gases generated by manure, odor emission and associated health hazards represent some of these risks.

2.1.1.1 Water and Soil pollution

Several researchers have reported on the improvement of soil physical properties (infiltration rates, hydraulic conductivity, bulk density, water holding capacity and aggregate stability) after application of animal wastes. This was attributed to the organic matter content of manures (Wallingford et al. 1975). However, when manure is applied to soil, the amount of plant nutrients available from the manure is frequently in excess of those removed by the crop; thus results in an accumulation of nutrients and in certain cases reduced soil fertility due to buildup of salts (Loerh, 1974).

Manure can contaminate groundwater by various ways e.g. direct dumping of manure into surface water, animals gaining direct access to rivers or streams for drinking, runoff from feedlots, overflow from manure storage tank, wind transport of volatiles (Jewell and Loehr, 1978)). Other less obvious sources of contamination include surface runoff from winter application on frozen soil leaning towards a stream (Phillips et al., 1981), and infiltration from high application on land and from lagoon and ground detention tank constructed in porous soil (Culley and Phillips, 1989). Culley and Phillips (1989) noted the contradictory results obtained by different workers investigating groundwater quality changes under pits. Miller et al. (1985) reported that soil sealed itself within 12 weeks of liquid manure introduction, however, high level of chloride was found in the groundwater beneath the storage and the level of nitrate nitrogen was reduced due to denitification. On the other hand, Sewell (1978) observed a rapid flush of Chloride and nitrate nitrogen in groundwater after loading a pit. The differences in the results can be attributed to factors such as variation waste composition, management practices, soil types and weather.

Nitrogen content of manure is often used as the basis for determining application rates of manure to croplands, because (a) nitrogen is a limiting factor in plant growth and (b) nitrogen compounds pose the greatest threat to ground water contamination. The amount of waste needed for a specific cropland can be accurately determined only after the soil is tested, the decay rate of the waste estimated, and the waste analyzed for contents of nitrogen, phosphorus, potassium, sodium, calcium and magnesium (Pratt et al. 1973).

2.1.1.2 Gas and odor from manure

Of the gases that accumulate in enclosed piggeries, carbon dioxide (CO_2), carbon monoxide (CO) and methane (CH_4) are asphyxiating, while ammonia (NH_3) and hydrogen sulfide (H_2S) are irritating and toxic (Agriculture Canada, 1979). Fatalities and near fatalities, involving humans and animals, and property damage and loses resulting from high concentration of manure gases have been reported.

Incidence of CO_2 accumulation in animal housing is not common, however, death of animals have been reported due to carbon dioxide buildup as a result of ventilation machinery failure . Other investigations have demonstrated that livestock death results from a combination of oxygen deficiency and heat stress rather than CO_2 asphyxiation alone (Donham et al. 1977).

The significance of methane gas lies in it flammable and explosive properties. This gas tends to build up in head spaces of anaerobic manure tanks (Agriculture Canada, 1979).

Ammonia is believed to be the main cause of the noxious odor character of manure. Studies has linked the volatilization of NH_3 to the presence and offensiveness of objectionable odors (Pain et al.,1990; Williams, 1984; Paul and Beauchamp, 1989). Other chemicals such as p-cresol, skatol and indol have been found to contribute to the odor of manure even though they are produced in minute amounts (Spoelstra, 1980).

2.1.1.3 Odors and the environment

Mass production generates large quantities of waste which could readily be odorous (e.g. fishery industries) or which undergo microbial decomposition with production of noxious and offensive odors (e.g. animal manure). When this odor is discharged in the atmosphere, pollution results.

Socioepidemiological studies have dealt with the possibility that odor may be linked to diseases. No conclusive evidence has yet been found. However, the conclusion that odor is harmless cannot be reached at the moment and probably will never be reached if, among other things, one consider the definition of "well-being" proposed and adopted by the World Health Organization (W.H.O.). It stressed that welfare involves a state of complete physical, mental and social well-being, not merely the absence of disease or infirmity (Ludwig and Naegel, 1990). Nevertheless, the presence of offensive odor is known to induce depression and affect other psychological attitudes.

2.1.1.4 The health risks

Ironically, the most practical and efficient ways of hog manure storage, e.g. lagoon and pit, were shown to be a spreading source of pathogenic organisms. Glock and Shwartz

(1975) in their investigation on a swine waste lagoon isolated four serotypes of Salmonella. It was suggested that the organisms can cause dysentery and diarrhea (Taylor and Alexander, 1971) . The studies indicated that Salmonella isolated from swine manure can survive for an undetermined time in anaerobic lagoons which serve as storage facility. The Salmonella tend to be host-adapted by causing infection, (Glen. and Van, 1975) but the many serotypes and their environmental adaptability have so far made it impossible to completely control Salmonella. Pathogenic microorganisms from manure enter the environment by way of urine and fecal wastes as well as secretion from the mouth and respiratory tract. These pathogens can infect water, soil, plant, animal or man in certain situation. Waston and Friend (1987) reported on studies which show that workers in enclosed piggeries have high levels of respiratory diseases, apparently caused by contaminated air in their work place; the contaminants are gases, dust and infectious bacteria.

Manure lagoons are also used by insects, such as mosquitoes and flies, as reproduction sites because of the high organic matter content. This represents a potential source of both diseases transmission and annoyance from insects bites.

2.2 ODOR CONTROL

Odor sensation comprises a number of subjective attributes which cause subjective dimensional odor variations (McCord, 1949; Wright, 1968). Duration and intensity are the two easiest sensations to study. Among the difficult sensations is the pleasantness because parameters for odor quality definition are not well understood or not well known; much less understandable is the combination pattern leading to any complex odor quality. Amos et al. (1974) observed that what may be a pleasant odor in one context can produce a repulsive effect in another, that the variation of odor quality does not follow a single subjective dimension, hence odor concentration can influence quality. Intensity is the main concern in olfaction and sensory evaluation, and this has been demonstrated in a number of investigations which have been used to establish basic theories and techniques of sensory measurement (Berglund et al., 1986).

Odor control is aimed at the prevention of osmogens formation or their reduction after they are formed. To achieve an efficient control, at least three aspects must be considered : (a) the origin, (b) the measurement and (c) the transport dispersal of the odor material (Berglund et al., 1986).

a. Origin of odor

The source of livestock odor emission originate from the volatilization of gaseous malodor compounds resulting from bacteria, mainly anaerobic bacteria, activities in animal manures (Spoelstra, 1980). Studies by Paul et al. (1989) and by Williams (1984) have quantitated the relationship between the offensiveness of the odor and the volatile fatty acids (VFA) concentration in piggery slurry.

b. Scales for measurement

Stevens (1959) in an attempt to standardize odor measurement, reported the following four psychological scales: the nominal, ordinal, interval and ratio scale. Despite the efficiency of these scales, lack of agreement on what may constitute a valid unit magnitude still poses a problem.

c. Transport and dispersal of odor

Transport, dispersal and dilution of odor is achieved by winds and turbulences on the ground (Stork, 1977). These phenomena depend on five main factors: the source of emission, the transport, dispersion and chemical processes and the physical separation. Their effects on odor will depend on the constituents of the odorous material and the atmospheric conditions at the time of release (Stork, 1977).

2.2.1 Methods for odor control

Odor control has for centuries posed a problem. The earlier techniques of accommodation can no longer be applied today. Methods for control include ventilation (which is a physical mean), chemical and biological means.

2.2.1.1 Chemical methods of odor control

Combustion of the odor source or the odorant air by combining it with oxygen and a combustible matter is one method of control (Rajinder and Kachru, 1974). This method is used extensively in the meat by-products rendering industry.

Masking of odor is defined as the coverage of an offensive odor by a more pleasant or easily associative odorant. A person inhaling the mixture may experience a sensation of "no odor" (Summer, 1971). The mechanism of control is either the predominance of the masking agent or the paralysis of the olfaction system caused by the presence of masking agents. The method is also referred to as neutralization of odors (Summer, 1971). While masking works well in a confined room, it is not efficient in open air, where winds carry the masking agent and the odorant at different velocities, making it impossible to inhale the correct ratio of the mixture. The health hazard associated with the masking agents may also be a problem. Nevertheless, masking, deodorizing or neutralization is part of everyday life in many industries as well as in the home.

Chemical treatment of odor or the odor source is a well used procedure in industries and in animal farming. Animal manure is chemically treated to reduce the emission of malodors. Odor from livestock production follow a complex release mechanism, transport system and receptor reaction (Miner, 1980). However, odor control techniques are based on a limited number of principles. Paul and Beauchamp (1989) reported on the effect of pH on the reduced volatility of some volatile compounds. Barrington and MacKenzie (1989) reported on the use of cement kiln dust to enrich swine manures and have shown a reduction in odor emission when a 5% solids (w/w) swine manure is treated with the cement dust. Earlier work by Carroll et al., (1964) demonstrated the benefits of incorporating cement kiln into soil. Fenelon and Mills (1980) reported reduced odor by addition of 1% lime (CaO) to swine slurries. Ingram (1973), and Kellems et al., (1979) found no significant change in fecal odor by using sagebrush as an additive

Abatement techniques to control odors (Jean, 1977) include ozonization of the air, deodorization with chemicals, scraping, absorbing filtering and electrostatic filtering. The mode of action of these techniques is to influence the odor material after its release into the atmosphere. Materials preventing the release of odorous compounds by inhibiting their formation, are most effective in odor control (Miner 1980). Faith (1964) used potassium permanganate as an oxidizing agent to control odor and found that an application rate of 28g permaganate per Kg of manure totally suppressed the release of odorous compounds. Other oxidizing chemicals such as potassium nitrate, hydrogen peroxide, paraformaldehyde have been investigated (Miner, 1980). Enzymes and other digestive aids have also been considered.

Modern confinement livestock farming rely heavily on design and management practices in an attempt to control the odor (Miner, 1980; Phillips et al.,1981). This include initial site selection, the design and construction of the production facility, management of the facility, location and frequent service of manure retention tanks and lagoons, choice of adequate manure disposal technique and timing (Miner, 1980).

2.2.1.2 Bacteriological methods for odor control

Livestock producers generally manage animal waste as liquids, stored in pits, tanks, or lagoons before subsequent land disposal. The pits can be either anaerobic or aerobic depending on the management systems and the end use of the liquid waste. Foul smelling products are generated by biological decomposition during storage (Spoelstra, 1980). However, the odor problem can be controlled if the biological decomposition products can be converted to less odoriferous end products (Cole ,1975).

Biological control is based on inhibiting the action of microorganisms responsible for the break-down of protein, carbohydrate and lipids. This leads to the formation of volatiles such as fatty acids, phenols and sulfur compounds in the case of hog manure (Spoelstra, 1980).

The complex organic compounds in animal manure are reduced to principally carbon dioxide and methane also called biogas (Spoelstra, 1977). The first step in the breakdown of animal wastes is marked by the rapid desapearence of the available oxygen. The oxygen is used to oxidize urea, ammonia and other putrefactive compounds causing the waste to become anaerobic. The second phase is anaerobic putrefaction. Proteins are broken down to form urea, ammonia, the foul-smelling mercaptans, hydrogen sulfide, aliphatic and aromatic acids, amines and amides. Fats are converted to fatty acids, water, carbon dioxide, hydrogen, methane and other substances. Carbohydrates turn to alcohols, aldehydes together with carbon dioxide, hydrogen and methane. The last step, the nitrification step, is marked by the production of nitrates and nitrites from the putrefactive products. Nitrates and nitrites are stable compounds and usable forms of nitrogen as plant nutrients. Other compounds such as phenols and sulfur compounds are also produced in the case of hog manure.

2.2.1.2.1 Anaerobic storage

Anaerobic digestion combined with energy recovery has been used for many years as a disposal method (Klinger and Marchain, 1986; Hobson et al. 1974). From the bacteriological point of view (Klinger and Machaim, 1986), temperature is used as a means to change the active population of mesospheric bacteria. Other factors influencing the process are pH, nutrient content, level of oxygen and level of substances toxic to methane producing bacteria. Klinger et al.(1986) indicated that anaerobic digestion is efficient in reducing odor, reducing the organic load from the environment, recycling of the volatile phase as biogas, recycling of the solid phase as peat, recycling of pathogen free waste water and inactivation of infective agents in the waste. The use of the solid as peat, called "cabutz" in green house cultivation lately, has become the main purpose of anaerobic digestion process (Hobson et al. 1974).

Estaban et al.(1986) produced methane from the anaerobic digestion process. A similar system was used on a large scale by Cortellini et al.(1986) to evaluate the efficiency and cost. The anaerobic process was found to be stable and the biogas yield was estimated as significant.

2.2.1.2.2 Aerobic storage

Aerobic treatment is a way of controlling odor from manure prior to spreading. Organic matter under aerobic conditions, is oxidized by bacteria supported by oxygen from surface aeration or algae as a result of photosynthetic reactions. The intensive method is to use a floating electrically driven aeration device which agitate the liquid, bringing it into close contact with air (Jean, 1977). Oxygen dissolved in the slurry oxidizes carbon and nitrogen compounds in the presence of suitable microorganisms with the production of heat. The optimum condition is control by the organic matter supply and dissolved oxygen. The two concerns of odor control by aeration are the energy requirement of the process and the nitrogen loss through ammonia volatilization. Van Der Hoek (1977) reported that up to 70 % of the nitrogen content of manure can be lost during aeration storage.

2.3 Odor measurement

The characteristic odor of animal waste is mainly due to the emission of volatile crganic compounds which are end products of bacteriological breakdown of constituent proteins and carbohydrates and other organic compounds (Spoelstra, 1980). The odor produced has a nuisance value which is related to both the odor compounds presence and offensiveness. While, most odor compounds create nuisance at high concentrations, at low intensity, nuisance is most frequently associated with offensiveness. Arguing that complete odor suppression is nor feasible or necessary, several workers (Bell, 1970; Sobel, 1972; Hashimoto, 1974; Cole et al., 1976; Welsh et al, 1977) have favoured the subjective assessment of odor offensiveness rather than the objective test of intensity. Both the terms odor control and odor prevention implies odor measurement because their goal is to change the perceived odor of ambient air (Berglund, 1986).

An understanding of the nature of odor and the parameters which affect its production is essential to odor measurement. Odorous compounds are often physiologically, biologically and chemically complex (Wright 1968). It was observed (Wright, 1968) that an odor can be the result of a combination of individual compounds, each of which if taken separately exhibits very far different odor character. This fact tends to explain the change of odor quality with intensity. When the intensity of an odor is reduced, the separate chemical constituents, each of which have different thresholds, drops out individually. The residual odor still has character, but is extremely different from the original odor. Since threshold is defined as the smallest concentration that will generate a sensation, one must differentiate between detection and identification thresholds. Thus the nose can perceive an odor without being able to associate the sensation.

Dyson (1935) concluded that no chemical data either from the viewpoint of reactivity or chemical structure would give a rational, quantitative interpretation of odor phenomena. The use of the nose as an evaluating device results in subjective responses measured. After fifty-six years, the above statement is still valid, although many attempts have been made at quantitative evaluation of odor.

2.3.1 Methods of odor measurement

Human appraisal of odor rely on the olfactory mucosa. The nose is frequently used to locate the source of various odors and to establish preferences. Berglund (1974) reported that acceptability is based on not only the perceptual information but on social values as well. Thus, psychological research is needed to provide meaningful relationships between technically measurable conditions and human odor perception (Berglund 1974).

Odor responses conform to the Weber-Fechner psychological law (McCord, 1949) applicable to all sense organs, in that a change in intensity is not recognizable unless the alteration is sufficient to constitute a definite functional increment of the stimulus, furthermore, the response of sensory stimulation is proportional to the logarithm of the stimulus (Williams, 1984). To overcome the subjectivity of the olfaction, recent years have seen the introduction of more sophisticated analytical methods for the measurement of odor.

2.3.1.1 The olfaction

The nose was the first odor detector known to man; however the lack of objectivity in interpreting sensations has limited it use in many area of odor research. Early investigations were based solely on human and lower animal olfaction system. Numerous devices have been developed in an attempt to produce objective measurements. At the beginning of the nineteenth century, instruments such as scentometers, olfactometers, odorimeters osmoscopes, stinkometers were developed (McCord 1949) and have been useful in establishing the basis of osmogenic researches. The methods associated with these instruments can be divided in two main groups :

1- determination of minimal identifiable odor (MIO) which later was termed odor threshold; an example of this device is the olfactometer developed by Zwaardemaker in 1895 as reoerted by Moncrieff (1972).

2- chemical methods for odor determination which relate the odor intensity to the concentration of the odorivector; an example is the stinkometer.

The olfactometer is widely used because sufficient degrees of representativeness and reliability can be achieved (Berglund, 1986).

Numerous authors have attempted to associate the concentrations of specific compounds or conditions with odor. William (1984) has demonstrated the relation between the fifth day biological oxygen demand (BOD_5) of the supernatant of piggery slurry and its odor offensiveness. This work was later updated by Thaker et al.(1985) using a wider range of offensiveness values. BOD is a measure of oxygen required by bacteria to decompose organic content of a waste under aerobic condition to stable compounds. The test is based on determining the amount of oxygen that has been consumed in a 300 mL sample bottle at 20°C for a period of 5 days (Merkel, 1982). The five days incubation period is to limit the error on BOD measurement caused by the presence of nitrifying bacteria which become very active after 8 or 10 days. Volatile fatty acids, hydrogen sulfide and ammonia were correlated with odor intensity by Barth et al.(1974). Bell (1970) also found a close relationship between volatile fatty acids and odor offensiveness. Sobel (1972) has found an inverse logarithmic relationship between total solids and odor offensiveness. Scheafer (1977) proposed that p-cresol, phenol, indole, skatole, n-buturic acid and 2,3-butanedione were mainly responsible for the stench of piggery wastes, and later on (Scheafer, 1977) correlated p-cresol with odor intensity; these researchers also stated that ammonia, volatile amines and sulfur compounds are miner importance. However, Kowalewsky et al (1980) correlated ammonia with odor strength (p = 0.001). Williams (1984) found ammonia misleading as odor offensiveness indicator under aerobic conditions as ammonia is likely to be more volatile but the odor less offensive. Spoelstra (1980) listed the following five criteria that a substance must fulfill in order to be a suitable odor indicator:

(1) The component must be a product of protein or carbohydrate degradation.

(2) The component must be stable under normal farm storage conditions.

(3) The formation of the product must reflect the kinetics of manure degradation.

(4) The component must respond in a representative way to environmental changes, e.g. aeration, methane formation.

(5) The concentration must be suitably large for easy measurements.

2.3.1.2 Physical methods

More recently, physical or instrumental analytical methods have been introduced for the evaluation of the quality and intensity of odor, and for the separation, characterization and quantitation of each constituents of odor. Many of these techniques are adapted versions of existing physical methods e.g. high performance liquid chromatography (HPLC), gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). However, no single objective technique which gives a complete sensory profile of odors is available.

2.4 Analysis of odor

Emission of objectionable odors is one of the negative environmental sides of the intensification of livestock production (Spoelstra 1980). The importance of the problem has give rise to numerous methods of odor control, e.g. aeration techniques and addition of chemicals. The effectiveness of any of these methods is dependant on the odor material (Dravnieks 1972).

Russell and Richard (1917) has used chemical analysis to assess waste composition (proximate analysis), bacterial decomposition of protein and the rate of other changes.

Roustan et al. (1977) has used colorimetric techniques to determine ammonia. Primary and secondary amines were also determined by Roustan et al. (1977).

The advent of gas chromatography has enhanced the prospect of relating subjective responses to instrumental measurements. The analysis of odor (flavor, volatile) implicate a highly critical step which is the sample collection and introduction to the chromatograph.

Odor analysis by analytical methods have been hindered by the low concentration of odorous compounds at their threshold, and by the difficulty in separating and identifying odorous compounds (Sobel, 1972). Development in gas chromatography have provided methods of separating and identifying those compounds. The principal problem remains sampling, because of the low concentration at which substances are odorous, and the additional dilution by the carrier gas in the analysis. Several sampling techniques have been developed to overcome these problems.

2.4.1 Sampling techniques

The methods of odors sampling can be conveniently classified as follows (White and Taiganides, 1969):

(1) direct sampling, in which small air within the odor source environment or a sample of the waste is taken for immediate analysis for the odorant components.

(2) cumulative sampling, in which the odorants are isolated from larger volume of air.

(3) selective sampling, in which only specific chemical or odorant groups are collected for analysis.

2.4.1.1 Direct sampling

This method was used for determining odor from poultry wastes (Burnett, 1969). Poultry manure from pits under cage layers was filtered and centrifuged. The supernatant was injected directly in to the gas chromatograph. The major drawback of the method is that the relative concentration of components in the liquid waste is likely to be different from that in the air above the waste (White and Taiganides, 1969).

2.4.1.2 Cumulative sampling

2.4.1.2.1 Salting out

The vapor pressure of odorants in an aqueous solution is increased by addition of anhydrous organic salts (sodium sulphate) to saturate the water. The mixture is heated ($60^{\circ}C$) to release dissolved gases. A sample of the head space is injected into the gas chromatograph (Bassette, 1960). A disadvantage of this technique is that the heat can alter the normal condition of the odorous mixture (White, 1969).

2.4.1.2.2 Cryogenic Collection

In this method of gas sampling, a cold trap of dry ice in acetone and/or a cold trap of liquid nitrogen is used. Microgram amounts of highly volatile materials can be trapped in a coiled tubing immersed in a Dewar flask (Benoza, 1964). A sampling valve is used to transfer the collected sample directly to the chromatograph. This method is very useful when odorous gases need to be concentrated (White and Taiganides, 1969).

2.4.1.2.3 Equilibration or adsorption sampling

In this procedure, volatiles from the source being sampled, are passed over a stationary liquid or solid collecting phase until the collecting phase reaches full equilibrium with the volatiles. The stationary or collection phase is usually polymeric beads. The amount of any one volatile dissolved in the collecting phase is directly proportional to the concentration (of the volatile) in the sample (White and Taiganides, 1969; Dravnieks, 1972) is given by the following equation :

$$(N_i)_c = 6.02 \text{ x } 1023 \, (Q)(1 / g_i) \, (N_a) \, / \, (N_i)_o = K(N_i)_a$$

where :

$(N_i)_c$ = the concentration of the ith component in the collecting phase (molecules/cm^3)
$(N_i)_a$ = the concentration of the ith component in sample
$(N_i)_o$ = the concentration of the ith component in saturated vapor above pure the ith component at the same temperature
Q = a coefficient dependent of molecular weight and density of the collecting phase, and = d/M

g_i = the activity coefficient of the solution of the ith component in the stationary phase
K = the partition coefficient of the ith component between the collecting phase and the sample

A drawback of this method is that the more volatile components will tend to saturate the collecting phase (White and Taiganides, 1969).

2.4.1.3 Selective sampling

2.4.1.3.1 Chemical absorption and regeneration

Volatile organic compounds with similar functional groups or molecules from a gas stream can be absorbed in a solution that reacts with the particular group of compounds.

The absorption procedures are useful in ascertaining the presence of functional groups and help in identification of the compounds. A major drawback in relation to odor analysis is the inability to correlate concentration in the sample and those indicated by the chromatographic analysis of the regenerate volatiles (White and Taiganides, 1969).

Cryogenic and adsorption sampling are the two most common sampling techniques used in odors and volatiles research.

2.4.2 Correlation of gas chromatographic and sensory measurements

2.4.2.1 General considerations

Although gas chromatography is being extensively used in odor analysis, the following short comings have been identified (Moncrieff, 1967):

(a) not all compounds separated by gas chromatography are odorous

(b) the presence of some odorous substances may not be detected by gas chromatography. This is due to their low threshold; however, their contribution to the overall character may be significant.

(c) although many compounds possess characteristic odor, they may not contribute malodorous notes to the total odor.

As a result, characterization by odor is needed in order to achieve identification of constituents.

2.4.2.2 Basic characteristics of the olfaction

The quality of the air (atmospheric environment) is readily monitored by smelling. Besides water, glycol, dimethyl formamide and some gases (H_2, CO, NO, N_2O), the shorter chain saturated aliphatic hydrocarbons and CO_2, there are very few vaporizable substances whose odor cannot be perceived by the nose. This sensory organ is highly sensitive and is able to detect odors at concentrations as low as ppm to ppb (Moncrieff, 1967). It has a rapid, quite instantaneous response when an odor compound is brought to its vicinity and equally rapid disappearance of odor when the substance is taken away. But it lacks reliability due to fatigue and selectivity as it measures the sum of odorous substances present, and responds subjectively.

2.4.2.3 Techniques of correlation

The advent of gas chromatography has enhanced the prospect of relating subjective responses to instrumental measurements. Gas chromatographic "exit-port" organoleptic evaluation has become an important method for determining which of the many chemicals present in a mixture are actually responsible for the interacting or unusual aroma that gives a compounds its character (Fuller et al. 1964). The technique for correlating gas chromatography and organoleptic measurement in general is as follows:

> The effluent from the gas chromatographic column is split between an electronic detector and a heated transfer line that leads outside the gas chromatographic column (Moto, 1987). In some cases a fine aerosol of water is added in front of the outlet in order both to cool the effluent and to provide humidity, this aids in the perception of odor. The characteristic description of each fraction is recorded as the peak develops. Since chemical odor character can

change when mixed with other chemicals, the "exit port" can be modified to provide for the recombination of two or more peaks. In this way, each set of peaks can be mixed individually and their relationship studied (Moto, 1987).

Guadagni et al. (1966) used the above method in evaluating apple volatiles. The characteristic apple or apple-like aroma fractions were identified and peaks responsible for such odors were isolated. Some of the adjectives use to describe the various fraction were: alcoholic, burnt, rancid, butyric, oily, ester, fruity, floral, grassy, caramel, apple-like, apple, green apple, etc. Fractions with the most intense odor were present in the least amount.

Similar work by Burnett (1969) identified components such as mercaptans, sulfides, indole, skatole and some organic acids, as chemicals responsible for the offensive and noxious odor of poultry manure; in some cases, odors noticed by panelists were not detected by the gas chromatograph.

2.5 Animal manure utilization

Methods used for animal wastes management in livestock production include concentration and/or relocation, e.g. source separation, biological treatment, incineration and land disposal (Loehr, 1974). The common method of utilization of animal waste is to return it to the land.

However, this approach may not be economically feasible because of the cost of handling and the availability of inexpensive chemical fertilizers. In animal production operations, waste management may require as much as one-fifth of both manpower and the total investment (Jewell and Loehr,1978). Higher costs are expected when the waste has to be further conditioned prior to land application.

Investigations on other methods of disposal have resulted in some reduction of agricultural wastes. For instances, fruit and vegetable wastes are being utilized as stockfeed; solid wastes of canning industries are dehydrated and used as part of animal feed; animal manure are composted, dried, and pelletized for soil conditioners, animal feed supplement and fertilizer base (Loehr, 1974). While these methods offer the possibility for waste utilization, they rarely solve the problem since only relatively small quantity of the material is removed. The utilization processes include composting, drying and dehydration, by-product development, energy recovery (Jewell, 1978) and water reclamation. In the light of results obtained from the above processes, use of animal waste as fertilizer is the most promising means of utilization. All activities in this direction must be directed at effective and economically feasible solutions.

2.5.1 The fertilizer value of animal wastes

Application of animal manure, sewage sludge, municipal waste waters on land for both disposal and fertilizer value has been practiced for centuries. The challenge is to maintain or improve the chemical, physical, and biological properties of the soil to which the waste is applied with minimum undesirable effect (a) on the crop grown on the soil, (b) on the characteristics of the soil, and (c) on the quality of groundwater and surface runoff (Loehr, 1974). Existing information on soil assimilative capacity (maximum waste loading) originated with the use of chemical fertilizers and followed by manures to increase crop yield. Data is also available on the quantity of nutrients and trace elements used by the crop from organic wastes such as animal manures. However, the fate of remaining organic and inorganic compounds is still a preoccupation to soil scientists. Loehr (1974), suggested that contribution from various disciplines, such as agronomy, soil science, agricultural engineering and sanitary engineering are needed to develop the criteria that will permit the use of the land as a resource to accommodate animal wastes.

Solid, slurry or liquid animal manures have been studied for their fertilizer value on bermuda grass (Burns et al. 1990). Municipal wastes have also been considered (King et al. 1985). These studies revealed varying crop yields related (a) to the plant variety used to evaluate the organic nutrient content (Burns et al. 1990), (b) the accumulation of nutrients as a result of time period of application, (c) the type of soil and (d) the type of treatment used to stabilize the waste, e.g. aerobic , anaerobic digestion or compost.

2.5.2 Reactions and transformations in the soil.

An understanding of reactions and transformations that take place in the soil after waste application may be essential to the development of a successful program of waste incorporation to land (Agri.Canada, 1979). Loehr (1974) pointed out that soil is composed of inert rock, gravel, sand, reactive clay minerals, organic matter, living and dead vegetative and animal matter, plus a wide variety of microorganisms. Hence, various types of transformation mechanisms could take place. These include, oxidation, ion-exchange, adsorption, precipitation processes and the assimilation of chemical compounds by living organisms.

The use of a soil for waste disposal is dependent of its biochemical and physical characteristics. Alexander (1961) reviewed the ecological relationships and microbial transformations that occur in the soil. Kolliker and Miner (1969) demonstrated the ability of soil to remove organic matter from anaerobic lagoon effluent and found that the microbial activity of the soil decreases with depth. It was found that this decrease reached a maximum at a soil depth of 1 foot in sandy soils. Loehr (1974) suggested that the decrease of microbial activity with depth could be due to the fact that organisms in a waste material face competition for food supply and antibiotic materials from other microorganisms and from predation by indigenous soil organisms. Competition and predation are greatest in the surface soil layer since oxygen is more abundant and rates of decomposition are greater (Loehr, 1974).

Organic compounds present in wastes applied to land will exist as slowly degradable soil humus, and as carbon dioxide released to the atmosphere (Loehr, 1974). Organic residues are not considered as environment quality concern in the conventional waste treatment systems (Loehr, 1974).

Oxygen, one of the important component of soil system is a limiting factor of microbial activity (Loehr, 1974) and its presence or absence will dictate respectively aerobic and anaerobic conditions.

As a key nutrient, nitrogen undergoes transformations involving organic, inorganic and gaseous compounds. Until the advent of adequate quantities of inorganic fertilizers, nitrogen management was one of the major factors limiting crop yields (Nelson, 1972; Parr, 1973). Waste management and environment quality agencies are concerned about the quantity of excess nitrogen that is not incorporated into plant and microbial growth or held in the soil. A list (Loehr, 1974) of the main pathways of nitrogen transformation in soil includes mineralization, immobilization, nitrification, and denitrification; further, mineralization, (conversion to mineral nitrogen available to plants) and immobilization (during which organic nitrogen is obtained) occur simultaneously and are dependent on carbon and nitrogen content of the medium. Other researchers (Fyles et al. 1990) explained that nitrogen is mineralized when the level of nitrogenous matter is high and immobilized at high level of carbonaceous matter.

III. MATERIALS AND METHODS

3.1 Materials

All odor reduction experiments were carried out using liquid hog (Sus scrofa domesticus) manure (LHM) containing 4% solids (w/w, wet basis). Manure was collected fresh, as produced by fattening hogs at the Macdonald College experimental farm.

Sampling of manure was done between the barn and the storage tank. The manure was homogenized by stirring. Total solid content was determined by an oven drying method (Pomeranz, 1987). The sample was then diluted to a total solid content of 4 % (w/w, wet basis) by adding distilled water according to Agri. Canada (1979). This solids content is desirable since it approximates the solids content of manure in farm storing tanks. At the farm this dilution is achieved by rain, floor washings and animal urine.

Sphagnum moss (Sphagnum fuscum) was purchased from Tourbiere premiere du Quebec (Quebec, Canada), reagent grade elemental sulfur, aluminum sulfate, monocalcium monophosphate, sulfuric acid and phosphoric acid were obtained from Anachemia (Montreal, Canada). Calcium carbonate and calcium oxide (lime) were purchased from Fisher Scientific (Montreal, Canada).

3.2 INCUBATION OF LHM

3.2.1 Incubation with aeration

Clean air was introduced into a 2.7 L glass bottle containing 1000 g of LHM (Figure 1). The tap air was cleansed by bubbling through a NaOH solution (7N), then through $Ba(OH)_2$ solution (0.1N), through a H_2SO_4 solution (2N), and finally dried by passing through a silica gel bed (Figure 1) . The cleansed air was then introduced into the incubation vessel at a flow rate of 5L/min (MacKenzie and Tomar, 1989).

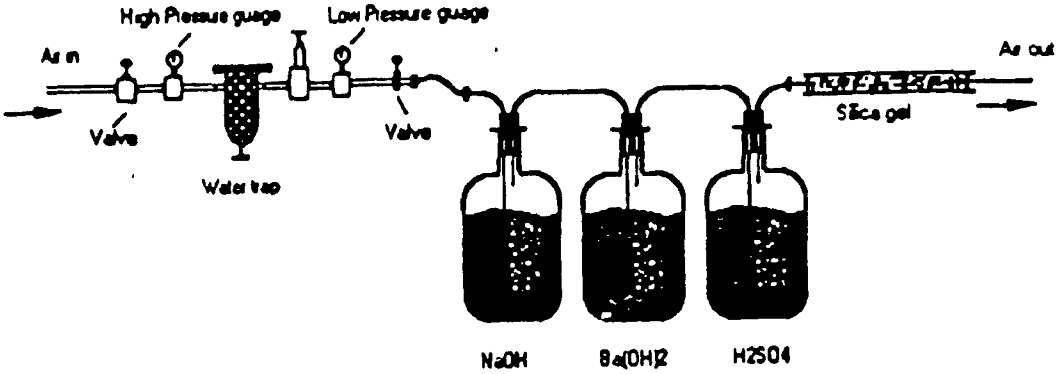


FIGURE 1 : DIAGRAM OF THE AIR CLEANSING SYSTEM

3.2.2 Incubation without aeration

Stoppered glass bottles containning the LHM samples were left on the bench for the required period of incubation (usually 4 days). The bottles were opened daily to release pressure build-up resulting from microbial activity. This set up was considered to simulate anaerobic incubation.

3.3 Treatments

i. Experiment 1

An initial experiment was carried out to determine how best acidification to pH 4.0, 5.0 and 6.0 can be achieved by direct addition of acid without significantly affecting the volume of the system.

LHM containing 4% solid (w/w, wet basis) was acidified with 1.5 N H_2SO_4 to pH levels of 4.0, 5.0 and 6.0. Quantities (1 Kg) LHM were placed in clear glass jars (2.7 L capacity, Figure 2) which were connected to the air train apparatus shown in Figure 1. The sample jar (incubating vessel) was aerated as described in Section 3.2.1. The effluent gas from the incubation vessels, which represent nitrogen loss by volatilization, was bubbled into 100 mL of 2% boric acid to absorb ammonia . The experiment was carried out over a 14-day period with sampling done on a daily basis. On the basis of results from this experiment, it was decided that a 3 N H_2SO_4 solution would be appropriate to use for acidification without affecting the sample volume..

ii. Experiment 2

LHM was treated with the chemical compounds and with sphagnum moss (Sphagnum fuscum) as shown in Table 1. In selecting the treatments and the levels, the objective was to reduce the pH of the slurry to an acid value of pH 4.0, 5.0 and 6.0 and to investigate this effect of acidification on ammonia volatilization (MacKenzie and Tomar, 1987). This experiment was carried out under aeration condition as described in Section 3.2.1 over a 14-day period, with sampling done on a daily basis.

iii. Experiment 3

On the basis of the results from Experiment 2, a third set of experiments was carried out using treatments and levels shown in Table 2, to investigate the odor presence and offensiveness as described in Section 3.8. The experiment was carried out under aeration conditions over a 30-day period. Sampling was done after 2, 24, 96 and 720 hours. CO_2 was measured in the effluent gas as described in Section 3.5. Gas chromatographic analysis was also done according to the procedure described in Section 3.6.

iv. Experiment 4

In this experiment, the effects of different levels of the treatments shown in Table 3 were investigated. The effects of aeration and non-aeration on odor presence and offensiveness were investigated. Gas chromatographic/mass spectrometry (GC/MS) analysis was performed using LHM and LHM treated with 8 % (w/w) sphagnum moss.

TABLE 1 TREATMENTS USED IN EXPERIMENT 2

Treatment	Level of use (%, w/w)[1]	pH
sulfuric acid 3 N	3.9	4.0
	2.6	5.0
	1.4	6.0
phosphoric acid 5 N	7.1	4.0
	5.1	5.0
	0.6	6.0
aluminum sulfate	2.0	4.3
	0.5	5.2
	0.06	6.4
MCPM[2]	4.1	4.3
	1.1	5.1
	0.1	6.2
powdered sulfur	4.1	6.9
	16.2	7.2
	40.5	7.1
sphagnum moss (SM)	2.0	6.1
	4.0	5.8
	8.0	5.6
SM + $Al_2(SO_4)_3$[3]	2:2	6.8
	8:0.5	5.8
control	----	6.6

1; fresh weight basis
2; monocalcium phosphate monohydrate
3; sphagnum moss, aluminum sulfate combination

TABLE 2 TREATMENTS USED IN EXPERIMENT 3

Treatment	Level of use (%, w/w)[1]
sulfuric acid 3 N	4.0
phosphoric acid 5 N	7.0
aluminum sulfate	2.0
MCPM[2]	4.0
sphagnum moss (SM)	8.0
SM + $Al_2(SO_4)_3$[3]	2:2
control	---

1; fresh weight basis
2; monocalcium phosphate monohydrate
3; sphagnum moss, aluminum sulfate combination

TABLE 3 TREATMENTS USED IN EXPERIMENT 4

Treatment	Level of use (%, w/w)[1]
aluminum sulfate	1.0
	2.0
	4.0
sphagnum moss (SM)	1.0
	2.0
	4.0
	8.0
	12.0
	24.0
SM + $Al_2(SO_4)_3$[2]	12:2
SM + MCPM[3]	12:2
control	---

1; fresh weight basis
2; sphagnum moss, aluminum sulfate combination
3; sphagnum moss, monocalcium phosphate monohydrate combination

v. Experiment 5

A fifth set of experiments was carried out based on the results obtained from Experiment 4. Sensory evaluation was done using the treatments and levels shown in Table 4. The calcium carbonate treatment and calcium oxide (lime) treatment were expected to react with sulfur-containing odorous compounds not affected by sphagnum moss.

The nitrogen content of the treated LHM was determined according to Section 3.5iii, iv and v. The fertilizer value of treated and untreated LHM was evaluated as described in Section 3.9, using the treatments shown in Table 5.

TABLE 4 TREATMENTS USED IN EXPERIMENT 5

Treatment	Level of use (%, w/w)[1]
sphagnum moss (SM)	1.0 4.0 8.0
calcium carbonate ($CaCO_3$)	2.0
SM + $CaCO_3$	1:2 8:2
Calcium oxide (CaO)	2.0
SM + CaO	1:2
pyridine	1ppm 10ppm 100ppm 1000ppm 10000ppm
control	---

1; fresh weight basis

3.4 Sampling

The outlet from each incubating vessel was divided into two streams as shown on Figure 2. One of the streams was connected to a Teflon lined aluminum bag (250 mL) to collect gases for GC analysis and for sensory evaluation. The second stream was bubbled into a 2% boric acid solution (100 mL) to collect ammonia evolving from the incubating vessel.

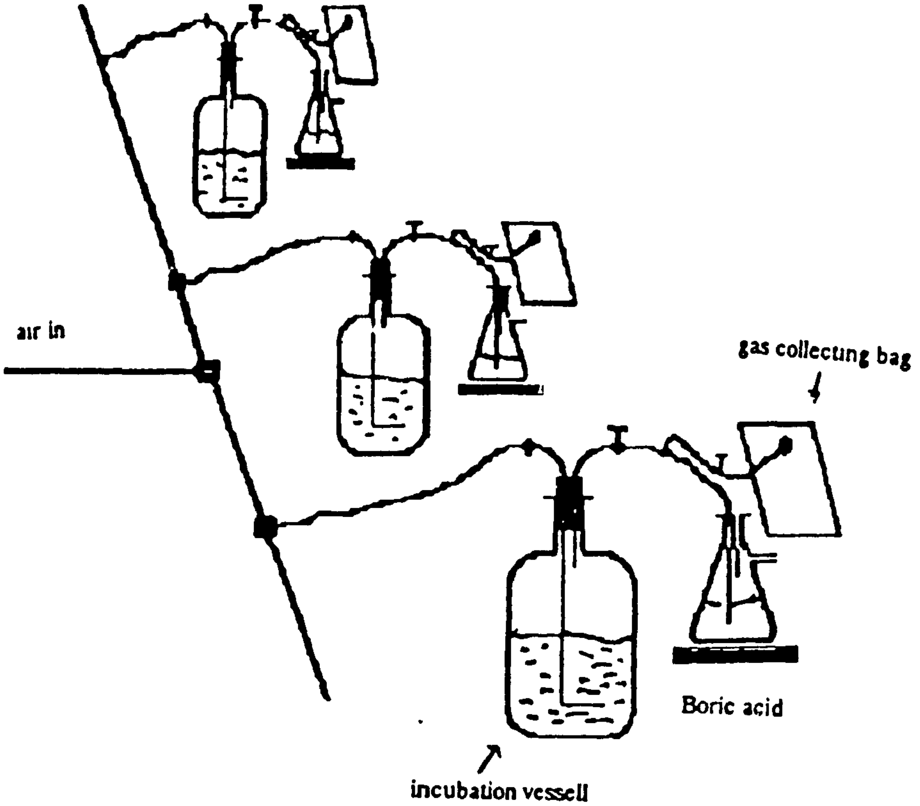


FIGURE 2 : DIAGRAM OF THE SAMPLE COLLECTING SYSTEM

3.5 Chemical analysis

i. Dry matter

Total solid content of LHM was determined by an oven drying method as described in Section 3.1. The samples were heated at 85°C to a constant weight using an air oven (Fisher Scientific, Montreal, Canada)

ii. pH

The pH of treated and untreated LHM was determined using a Mettler DL20 Compact pH-meter. The pH measurement were made before incubation and at specified time intervals during the incubation period.

iii. Ammonia analysis

The 2% boric acid which was used to absorb ammonia, was titrated with a standardized 0.1 N H_2SO_4 solution. The titration was performed using a Metler DL20 automatic titrator (Section 3.5ii) which stops dispensing the sulfuric acid solution when the preprogrammed pH is reached.

iv. CO_2 analysis

Carbon dioxide in the effluent gas from the incubating vessel was determined using the procedure described by Tiessen et al. (1983). The pH of a NaOH solution (0.5N) containing the dissolved CO_2 was adjusted to < pH 11 by dropwise addition of HCl solution (2N). Bovine carbonic anhydrase solution (Sigma Chemical, St Louis, USA) was added

(1mg/mL, 5 drops), and the pH was adjusted to pH 8.3. The solution was titrated with HCl solution (0.1N) to pH 3.7.

v. Total nitrogen

Total nitrogen (TN) was determined by the macro-Kjeldahl procedure using an automated system (Labconco Rapid Still III). A sample (1g) was digested in the conc. H_2SO_4 in presence of K_2SO_4/HgO catalyst at 410°C for 30 minutes. The clear liquid digest, was allowed to cool and the digestion tube attached to the Labconco steam distillation unit which was programmed to deliver 55 mL of distilled water and 40 mL of 10 N NaOH into the tube. The ammonia liberated was steam distilled into boric acid solution. The distillate was titrated with a 1.0 N sulfuric acid solution.

vi. Ammonium

A saturated solution of KCl (10 mL) along with 0,2 g of MgO was added to the sample which was subjected to direct distillation of ammonium as described by Bremner (1965).

3.6 Gas chromatographic analysis

A 500 uL of gas sample from the gas collecting bag (Fig 2) was analyzed on a Varian Model 3700 gas chromatograh equipped with a flame ionization detector. The injection port of the gas chromatograph was specially adapted for gas sample injection. Conditions for separation were as follow: fused silica capillary column [30m length x 0.32mm i.d. with

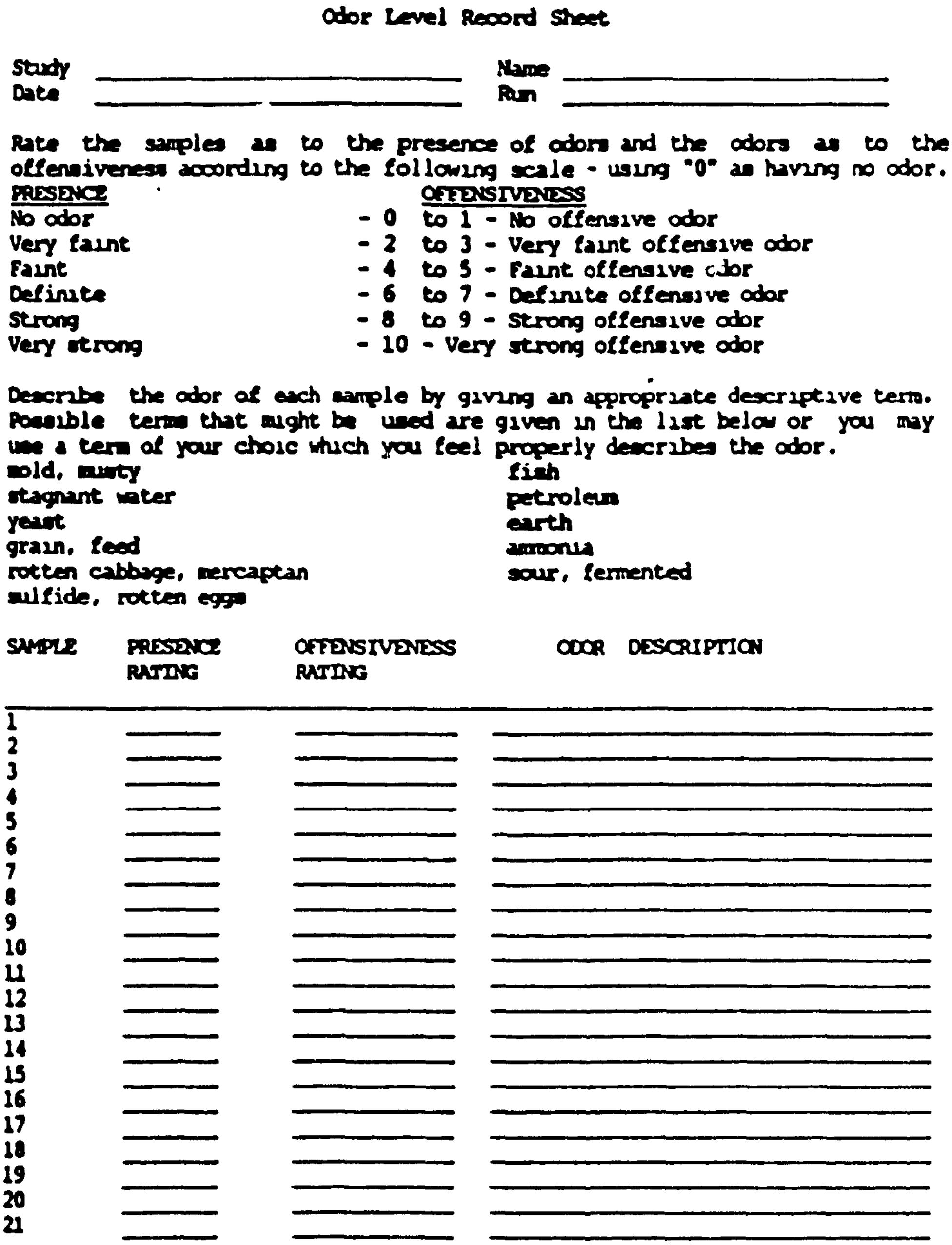
0.1 u film thickness, DB5 (Chromatographic Specialities)]; constant temperature of 40°C; helium carrier gas flow rate, 0.8 mL/min; injector port temperature, 100°C; detector temperature, 150°C. Chromatograms were recorded and integrated with a Hewlett-Packard Model HP-3390A integrator.

3.7 Gas chromatographic/mass spectrometry analysis

Gas chromatography/mass spectrometry (GC/MS) analysis was carried out at the Food Research and Development Centre of Agriculture Canada in St Hyacinthe using a HP-5890 gas chromatograph coupled to a VG-7070 medium resolution mass spectrometer equipped with a VG-11-250 data system linked to NBS data library. The ionization energy was 70 eV, and Helium was used as carrier gas at a flow rate of 0.8 L/min.

3.8 Sensory evaluation

Organoleptic measurements were carried out according to the procedure by Sobel (1972) with some modifications. Gas collecting sample bags (Figure 2) were presented to volunteer untrained panelists (10 to 14 persons). The samples were smelled or sniffed and rated for odor presence and odor offensiveness using a numerical scale of 0 to 10 (Figure 3). Words were suggested to describe the odors and panelists were also instructed to provide words that best describe the odor. A total of 15 to 24 samples were evaluated by each panelist per session. To minimize habituation and fatigue of the nose, a 2 to 3 min rest period was observed between samples. Odor free air and a reference odor chemical (pyridine) (Table 4) were included as odor reference samples. In some case, the panelists were asked to evaluate odors emanating directly from the incubation vessels.



Odor Level Record Sheet

Study ____________________ Name ____________________
Date __________ __________ Run ____________________

Rate the samples as to the presence of odors and the odors as to the offensiveness according to the following scale - using "0" as having no odor.

PRESENCE		OFFENSIVENESS
No odor	- 0	to 1 - No offensive odor
Very faint	- 2	to 3 - Very faint offensive odor
Faint	- 4	to 5 - Faint offensive odor
Definite	- 6	to 7 - Definite offensive odor
Strong	- 8	to 9 - Strong offensive odor
Very strong	- 10	- Very strong offensive odor

Describe the odor of each sample by giving an appropriate descriptive term. Possible terms that might be used are given in the list below or you may use a term of your choic which you feel properly describes the odor.

mold, musty
stagnant water
yeast
grain, feed
rotten cabbage, mercaptan
sulfide, rotten eggs
fish
petroleum
earth
ammonia
sour, fermented

SAMPLE	PRESENCE RATING	OFFENSIVENESS RATING	ODOR DESCRIPTION
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			
20			
21			

FIGURE 3 : SENSORY EVALUATION SHEET

3.9 Fertilizer value of treated samples

A growth experiment was carried out in the growth chamber of Renewable Resources Department of Macdonald College. Treatments and levels used are shown in Table 5. KH_2PO_4 was purchased from Anachemia, the loamy soil from Chicot, Quebec was obtained from the Renewable Resources Department of McGill University and sandy soil was sampled from the Morgan Arboretum (Upland Macdonald). Chicot and Upland soils have different characteristics based on their composition e.g. 30 % clay, 0.2 % nitrogen, and 5 % organic matter for chicot, compared to 9 % clay, 0.1 % nitrogen and 2 % organic matter for Upland (Day, 1965; Bremner, 1965; Allison, 1965). Barley seeds (Hordeum vulgare L.) were obtained from the Department of Plant Science of McGill university.

TABLE 5 TREATMENTS USED IN EXPERIMENT 5

Treatment	Level of use (%, w/w)[1]
sphagnum moss (SM)	1.0 4.0 8.0
calcium carbonate	2.0
SM + calcium carbonate[2]	1:2
control	---

1, fresh weight basis
2, sphagnum moss, calcium carbonate combination

3.9.1 Soil preparation and seeding

Basic application of fertilizers to the two soils types were as follows; potassium (K) as KCl applied at a rate of 300 Kg K / ha, phosphorous (P) was applied as KH_2PO_4 at a rate of 100 Kg P_2O_5 / ha. The experimental design was a randomized complete block design with 4 replicates and 3 levels of treatment as follows; 0, 150 and 300 Kg of LHM /ha corresponding to 0, 17 and 34 mg of nitrogen/pot, respectively. The soil was brought to field capacity by addition of distilled water prior to treatment application. For each replicate of each treatment, 250 g of soil was weighed into a pot (8 cm i.d. x 8 cm depth). A top layer of 30 g of soil was removed from the pot and LHM was applied to the remaining soil. Ten barley seeds (Hordeum vulgare L.) were placed in 5 equidistant holes (2 seeds per hole) and the top layer of soil was replaced in the pot to cover the treatment and the seeds. The seeds were allowed to germinate in a growth chamber. The pots were watered every day at random to simulate rain fall. After germination, the plants were thinned so that 5 plants remained per pot and, preferably one plant per hole . Conditions of germination and growth were as follows:

- day time period: 16 hours
- day temperature: 26°C
- night temperature: 16°C

3.10 Statistical analysis

Statistical analysis was carried out using the SAS statistical software (SAS, 1982) to compare odor tests (presence and offensiveness versus treatment) and to evaluate treatment effects on dry matter yield of the barley plant. Means were compared using the Duncan' new multiple range test and, different effects were evaluated using the analysis of variance (AOV) feature of SAS.

IV. RESULTS AND DISCUSSION

4.1 EXPERIMENT 1: The effect of aeration and pH on ammonia loss

The results of Experiment 1 (Table 6) show an increase in pH for both treated and control LHM. For the control, the increase was from pH 7.2 to pH 8.5; for the acidified treatments, the increases were to pH 5.87, 7.20 and 7.91 from the initial pH of 4.0, 5.0 and 6.0 respectively (Table 6). As a result of microbial fermentation, of carbohydrates, it would be expected that volatile fatty acids, e.g. acetic, propionic and butyric acids, would be produced in the LHM; the acids have been reported to release H^+ in the slurry at near neutral pH (Georgacakis et al., 1982) and this was suggested to be responsible for the noxious odor of slurries. In LHM, pH is dependent not only on the concentration of the volatile fatty acids but also on the strength of $HCO_3^-/CO_3^=$ and NH_4^+/NH_3 buffer systems. Consequently, the final pH attained is the net effect of these ionic equilibria. The increase of pH observed in this experiment is in agreement with the results of Stevens and Cornforth (1974), Cooper and Cornforth (1978) and Paul and Beauchamp (1989). Under aeration the NH_4+/NH_3 equilibrium favors the formation of NH_3. In addition, the removal of VFA by enzymatic oxidation which releases hydroxy groups may also contribute to an increase of pH (Williams, 1983).

Table 6 also shows the effect of pH on ammonia loss from LHM. In general, ammonia volatilization was reduced at low pH. These results are in agreement with those reported by MacKenzie and Tomar (1987). In the present study, initial acidification to pH 4.0 resulted in a reduction of ammonia loss from 366.8 mg/Kg to 0.16 mg/Kg from LHM.

Ammonia losses from LHM acidified initially to pH 4.0 remained extremely low throughout the 14 days of incubation suggesting a low accumulation of free NH_3 (Figure 4). Despite the straight line shown by the graph, the data could not be adequatly described by a linear equation (Figure 4). The LHM acidified initially to pH 5.0 showed an abrupt increase in ammonia loss at day 10 of the incubation period. The increase of NH_3 loss with time was characterized by an exponential regression (Figure 4) which satisfies the equation $y=a.e^{b.x}$. LHM acidified initially to pH 6.0 also showed an exponential increase of ammonia loss with time and is characterized by the same general equation as above. The control (pH 7.2) started losing ammonia after the first day of the incubation period with a linear regression satisfying the equation $y=a+bx$ (Figure 4). The above equations are detailled in Appendix A. In general, the onset of ammonia losses, (day 6 for all treatments), might be related to the activation time of nitrifying bacteria (Merkel, 1982). This could favor ammonia formation and its subsequent loss.

TABLE 6 Effect of pH of LHM on ammonia loss after 14 days of incubation

	Initial pH	Final pH	NH_3 losses (mg/Kg)*
Treated	4.0	5.87	0.16
	5.0	7.20	28.30
	6.0	7.91	159.20
Control	7.2	8.50	366.80

*, mg/kg of LHM

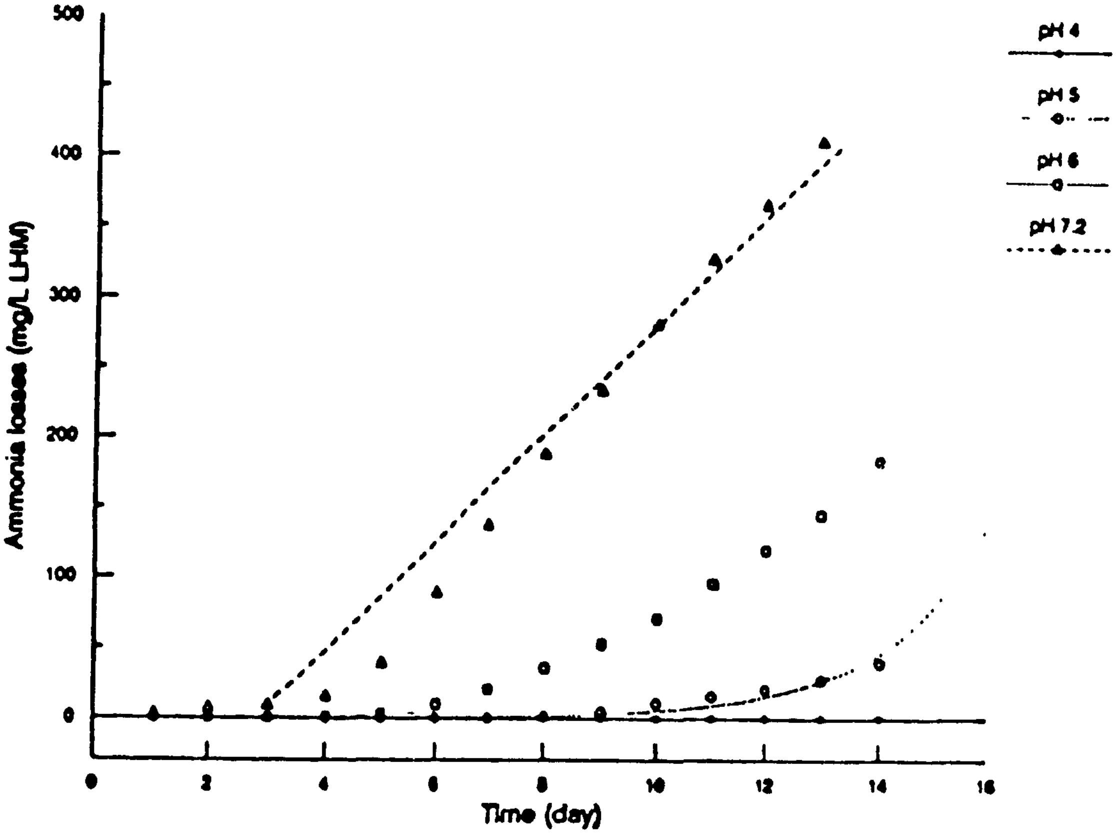


FIGURE 4: EFFECT OF PH ON AMMONIA LOSS DURING INCUBATION

4.2 EXPERIMENT 2 : Effect of acidification with chemicals and sphagnum moss on ammonia loss from LHM

The results shown in Table 7 suggest a relationship between the pH of LHM at time of incubation and loss of ammonia with the following treatments : sulfuric and phosphoric acids, aluminum sulfate, monocalcium monophosphate and sphagnum moss. The results are in agreement with those reported by Stevens and Cornforth (1974), Cooper and Cornforth (1978), Paul and Beauchamp (1989). This suggests that, under conditions of aeration the, NH_4+/NH_3 equilibrium favors liberation of NH_3. Williams (1983) reported that the removal of volatile fatty acids could contribute to the increase of pH which in turn can favor the release of NH_3. Our results show that in general, ammonia volatilization is reduced considerably at low pH values e.g. in the range of pH 4.0 to pH 5.0. With the LHM acidified to pH 4.0, the ammonia loss after 14 days of incubation was negligible regardless of the type of chemical treatment used (Table 7).

Sphagnum moss and sphagnum moss/aluminum sulfate combination also produced a significant ($p < 0.05$) reduction in ammonia loss (Table 7). The reduction in this case was not related to the pH of the incubated material. Mathur et al.(1985) suggested that sphagnum moss can retain ammonia by forming ammonium carbonate [$(NH_4)_2CO_3$]; the carbon provided by sphagnum moss along with its porous nature is considered to increase the relatively low C/N ratio in LHM slurries and allows oxygen circulation in the waste, respectively. This combination renders aerobic bacteria more efficient in transforming the malodorous compounds into NO_3^-, $SO_4^=$, CO_2 and H_2O (Miner and Hazen, 1969, 1977; Mathur et al., 1990).

As a binding material, sphagnum moss is reported (Peltola, 1986) to be more efficient than saw dust and rice straw, for odor reduction and moisture (urine) retention.

The powdered sulfur treatment increased the ammonia loss (Table 7). It was hypothesized that upon exposure to oxygen by aeration, the added sulfur would be oxidized to form H_2SO_4 and therefore could reduce the pH of LHM and subsequently reduce NH_3 volatilization. It likely that the microbiological conditions required for this oxidation were not well developed and that the LHM treatment with sulfur may need to be inoculated with thiobacillus bacteria for adequate conversion of sulfur to sulfuric acid (MacKenzie, 1990).

The results from this experiment supports the finding of other workers (MacKenzie and Tomar, 1987; Stevens and Cornforth, 1974; Cooper and Cornforth, 1978; Paul and Beauchamp, 1989; Mathur et al. 1990) in that the initial pH of the LHM is a critical factor which affects ammonia loss from the LHM during storage under aeration; furthermore, the results also indicate that sphagnum moss can also reduce ammonia loss considerably without affecting the pH of the LHM in a significant way.

TABLE 7 Effect of pH on ammonia loss after 14 days of incubation

Treatment	Level of use (%, w/w)[1]	Initial pH	Ammonia losses (mg/Kg)[1]
sulfuric acid 3 N	3.9	4.0	0.01 i
	2.6	5.0	22.73 e
	1.4	6.0	167.10 b
phosphoric acid 5 N	7.1	4.0	nd
	5.1	5.0	0.20 i
	0.6	6.0	61.80 d
aluminum sulfate	2.0	4.3	nd
	0.5	5.2	76.70 d
	0.06	6.4	90.10 d
MCPM[2]	4.1	4.3	0.10 i
	1.1	5.1	2.00 g
	0.1	6.2	78.90 d
sulfur flower	4.1	6.9	145.00 b
	16.2	7.2	189.30 b
	40.5	7.1	210.90 b
sphagnum moss (SM)	2.0	6.1	6.40 f
	4.0	5.8	3.50 g
	8.0	5.6	1.10 c
SM + $Al_2(SO_4)_3$[3]	2:2	6.8	2.40 g
	8:0.5	5.8	0.70 h
LHM (control)	----	6.6	151.00 b

1; mg/Kg of LHM, fresh weight basis
2; monocalcium phosphate monohydrate
3; sphagnum moss, aluminum sulfate combination
nd, not detected
a-i; values followed by the same letter are not significantly different at $p<0.05$ level

4.3 EXPERIMENT 3 : Effect of treatments on the presence and the offensiveness of odor from LHM, gas chromatographic analysis, and measurement of CO_2 for microbial activity evaluation.

4.3.1 Odor presence

Table 8 gives the results of sensory analysis for odor presence of the untreated and treated LHM samples. The results suggest that after the 2 h incubation period, only the 8 % sphagnum treatment produced a significant ($p < 0.05$) reduction in odor presence. After 24 h of incubation, sphagnum moss (8 %), the combination of sphagnum moss and aluminum sulfate and aluminum sulfate were the treatments which produced a significant ($p < 0.05$) reduction in odor presence. After 96 h and 720 h incubation periods, the sphagnum moss and the sphagnum moss/aluminum sulfate combination produced a significant ($p < 0.05$) reduction in odor presence. The phosphoric acid treatment also produced a significant reduction in odor presence after 96 h of incubation.

4.3.2 Odor offensiveness

Table 9 shows the results of sensory analysis for odor offensiveness in the untreated and treated LHM samples. After 2 h and 24 h of incubation, the aluminum sulfate, sphagnum moss and sphagnum moss/aluminum sulfate combination produced significant ($p < 0.05$) reduction in odor offensiveness. The latter two treatments along with sulfuric acid, phosphoric acid and monocalcium monophosphate treatments also produced a reduction in odor offensiveness after 96 h of incubation. Only the sphagnum moss and sphagnum moss/aluminum sulfate combination produced a significant reduction in odor offensiveness after 720 h of incubation.

The relationship between offensiveness and presence of odor (as affected by the incubation period) is shown in Figures 5a,b,c,d,e. In general, odor offensiveness increased as the odor presence increased. This increase satisfied different regression equations depending on the treatment and the time of incubation (Appendix B). With 8 % sphagnum moss, for instance, the logarithmic relationship between presence and offensiveness demonstrated after 2 h of incubation is changed to a linear relationship after 720 h, after a power and linear relationships following 24 h and 96 h of incubation, respectively.

Plots of odor offensiveness versus incubation period for different treatments (Figure 6a) show that odor offensiveness reached a stable level after 96 h of incubation. Similar behavior was observed for the odor presence (Figure 6b). Thus, sensory evaluation may be carried out after 96 hours and be representative of the treatment. This may also suggest that 96 hours is the time required to stabilize LHM in terms of odor development.

TABLE 8 EFFECT OF TREATMENTS ON ODOR PRESENCE

Treatment	Period of incubation			
	2 h	24 h	96 h	720 h
sulfuric acid (3N, 4%)	7.3a	7.9a	6.7a	7.6a
phosphoric acid (5N, 7%)	7.5a	8.2a	6.5b	7.8a
$Al_2(SO_4)_3$[1]	7.1a	6.4b	7.2a	7.5a
MCPM[2] (4%)	7.8a	8.1a	7.0a	7.6a
sphagnum moss (SM) (8%)	6.3b	5.0c	5.0b	5.5b
SM + $Al_2(SO_4)_3$[3] (2%+2%)	7.2a	6.7b	5.7b	6.8b
air (odor free)	0.4c	0.2d	0.2c	2.1c
control (LHM)	7.2a	7.5a	7.6a	7.9a

1, aluminum sulfate
2, monocalcium phosphate monohydrate
3, sphagnum moss and aluminum sulfate combination
a-d, values followed by the same letter within a column are not significantly different at $p<0.05$

TABLE 9 EFFECT OF TREATMENTS ON ODOR OFFENSIVENESS

Treatment	Period of incubation			
	2 h	24 h	96 h	720 h
sulfuric acid (3N, 4%)	6.5a	7.3a	6.6b	7.5a
phosphoric acid (5N, 7%)	6.9a	8.3a	6.4b	7.4a
$Al_2(SO_4)_3$[1] (2%)	6.3b	6.2b	7.1a	7.3a
MCPM[2] (4%)	7.2a	7.8a	6.6b	6.9a
sphagnum moss (SM) (8%)	5.6c	5.2c	4.7c	5.2b
SM + $Al_2(SO_4)_3$[3] (2%+2%)	6.4b	6.2b	5.1b	6.3b
air (odor free)	0.4c	0.2d	0.2c	2.1c
control (100% LHM)	6.6a	7.1a	7.3a	7.6a

1, aluminum sulfate
2, monocalcium phosphate monohydrate
3, sphagnum moos and aluminum sulfate combination
a-d, values followed by the same letter within a column are not significantly different at $p<0.05$

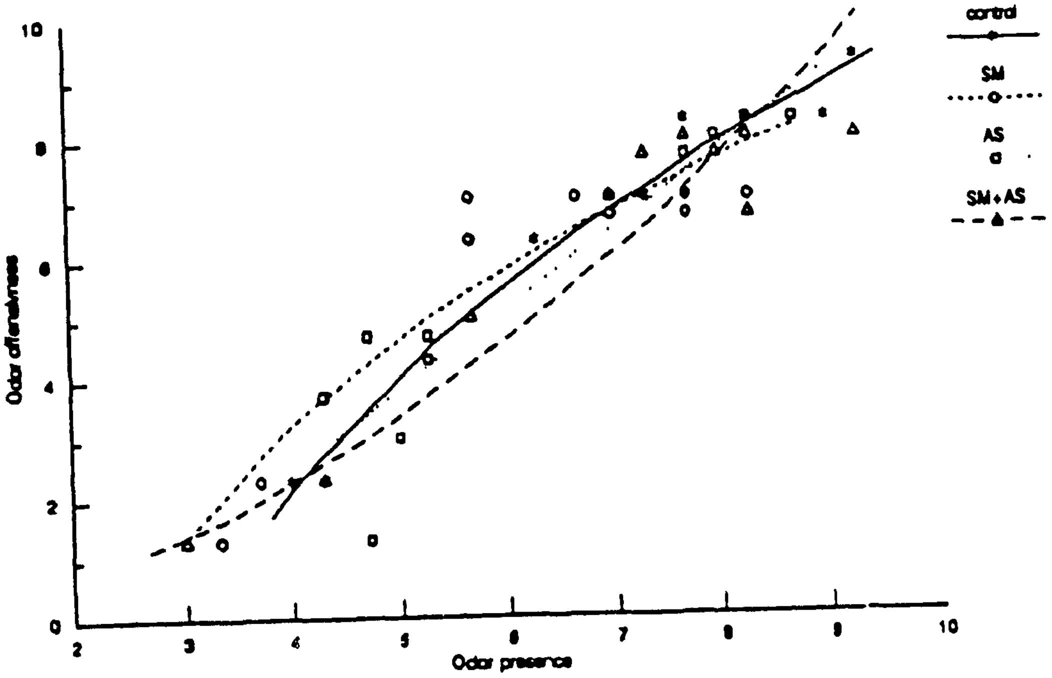


FIGURE 5a : EFFECT OF TREATMENT ON THE RELATIONSHIP BETWEEN ODOR OFFENSIVENESS AND ODOR PRESENCE AFTER 2 h INCUBATION

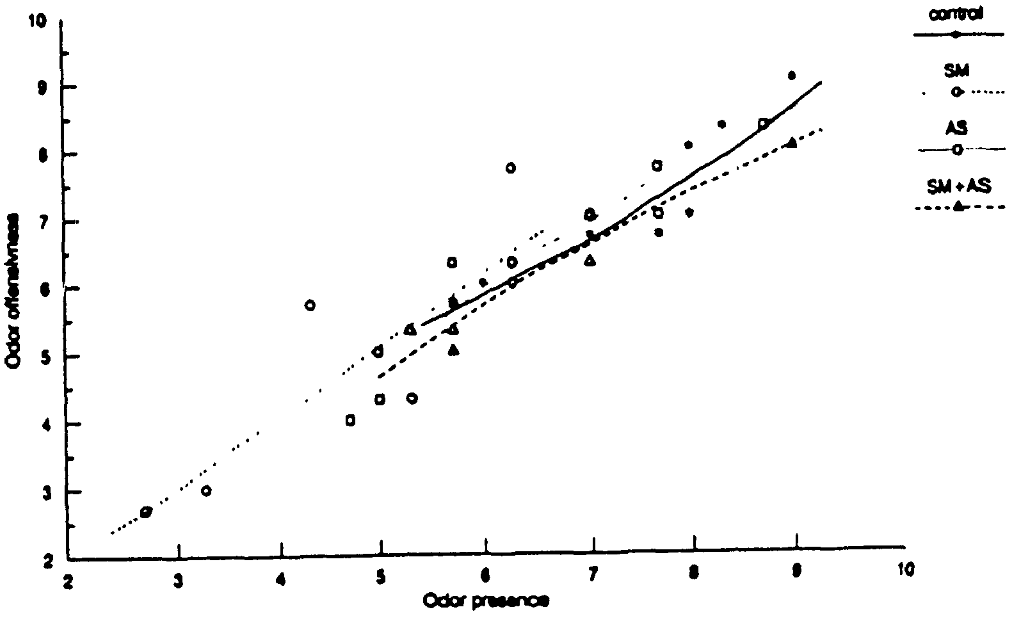


FIGURE 5b : EFFECT OF TREATMENT ON THE RELATIONSHIP BETWEEN ODOR OFFENSIVENESS AND ODOR PRESENCE AFTER 24 h INCUBATION

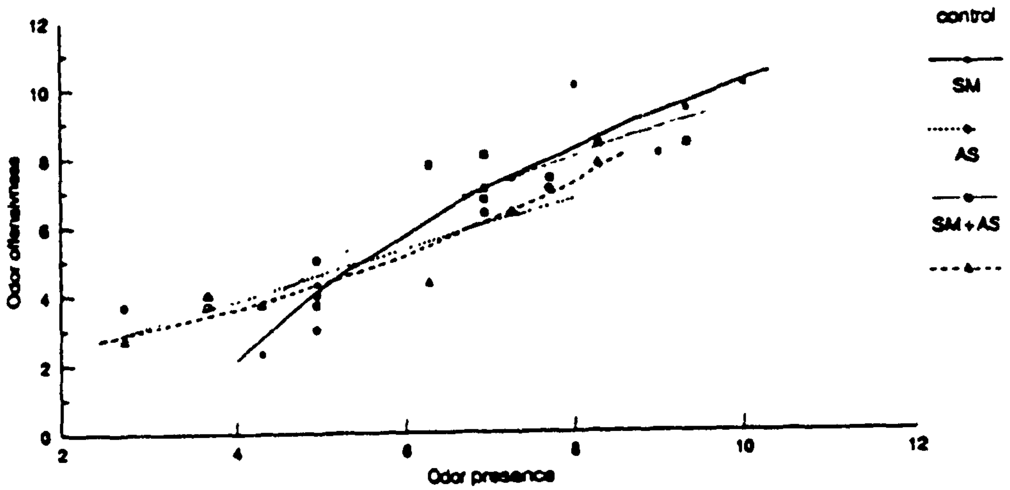


FIGURE 5c : EFFECT OF TREATMENT ON THE RELATIONSHIP BETWEEN ODOR OFFENSIVENESS AND ODOR PRESENCE AFTER 96 h INCUBATION

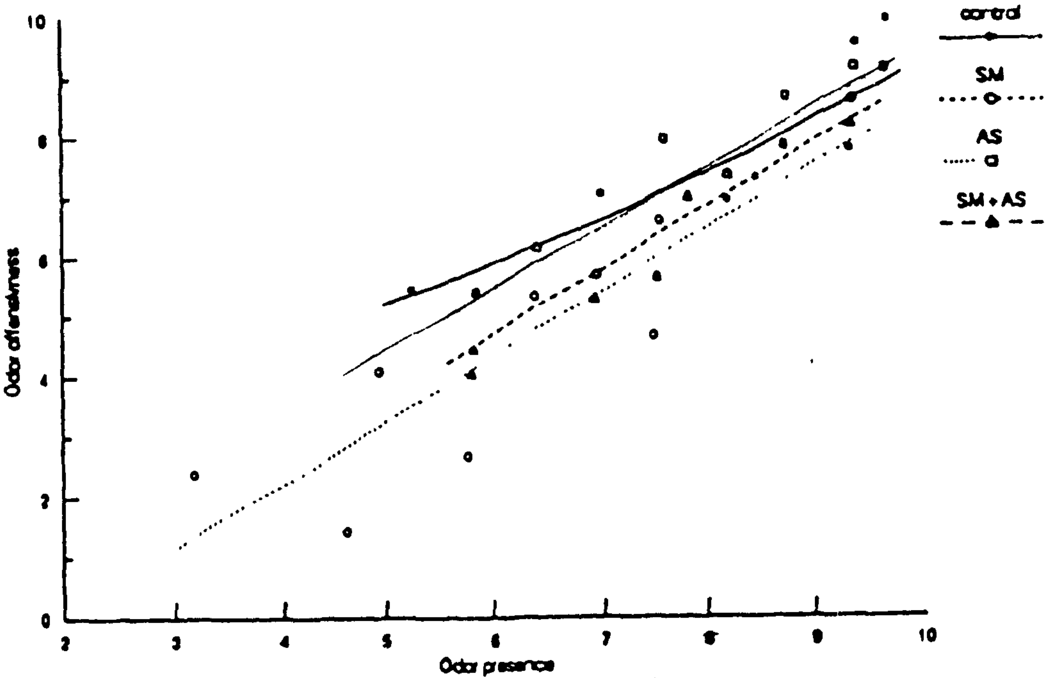


FIGURE 5d : EFFECT OF TREATMENT ON THE RELATIONSHIP BETWEEN ODOR OFFENSIVENESS AND ODOR PRESENCE AFTER 720 h INCUBATION

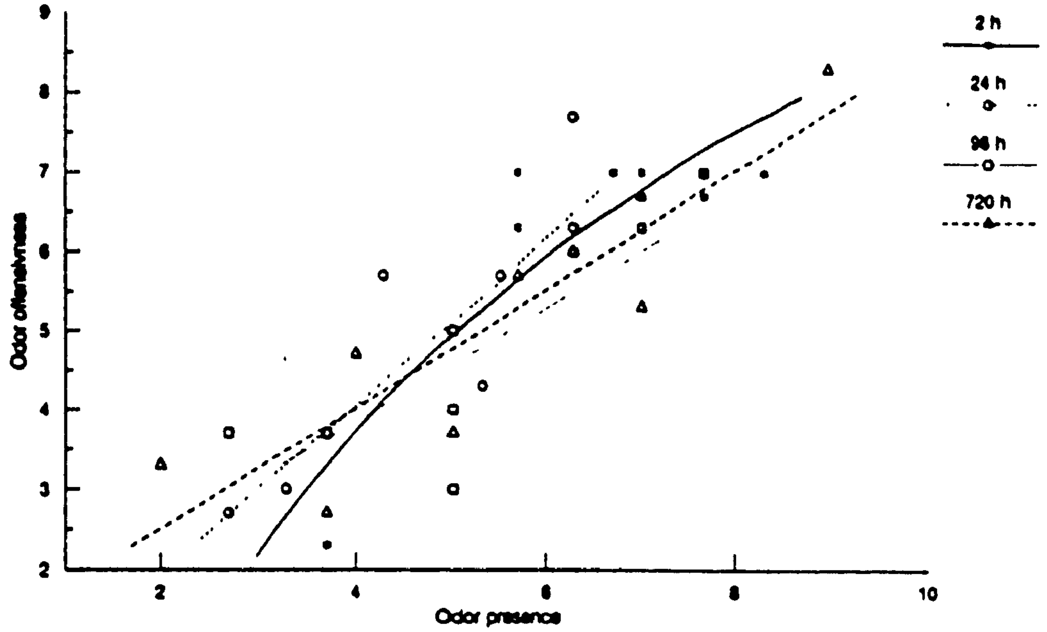


FIGURE 5e : EFFECT OF THE PERIOD OF INCUBATION ON THE RELATIONSHIP BETWEEN ODOR OFFENSIVENESS AND ODOR PRESENCE

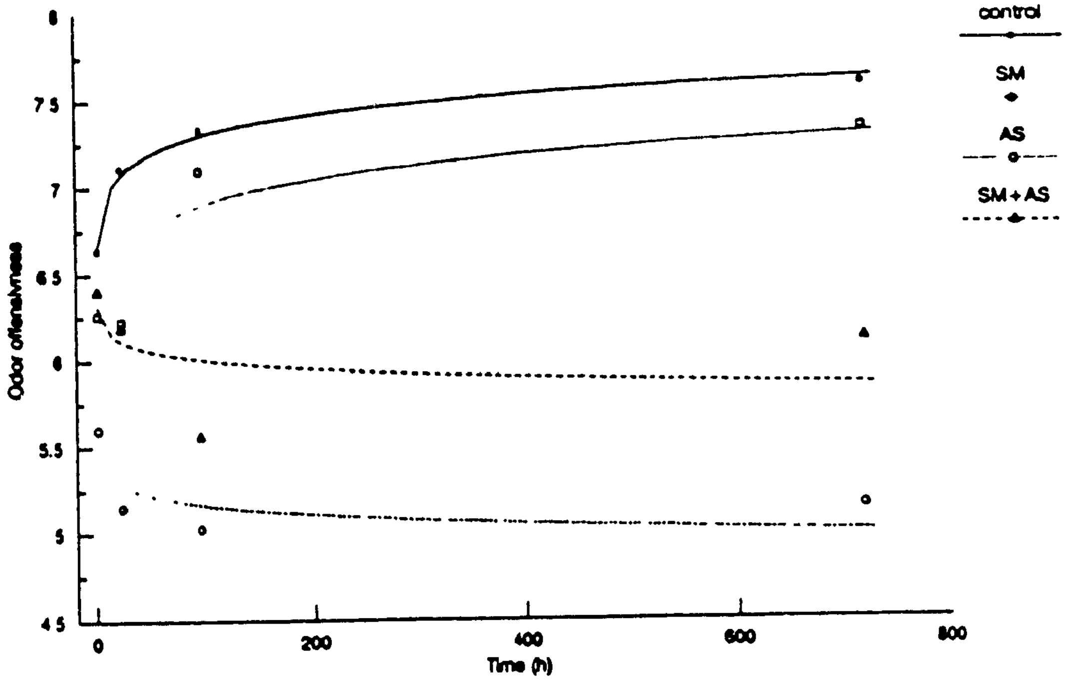


FIGURE 6a : EFFECT OF TREATMENT ON THE RELATIONSHIP BETWEEN ODOR OFFENSIVENESS AND PERIOD OF INCUBATION

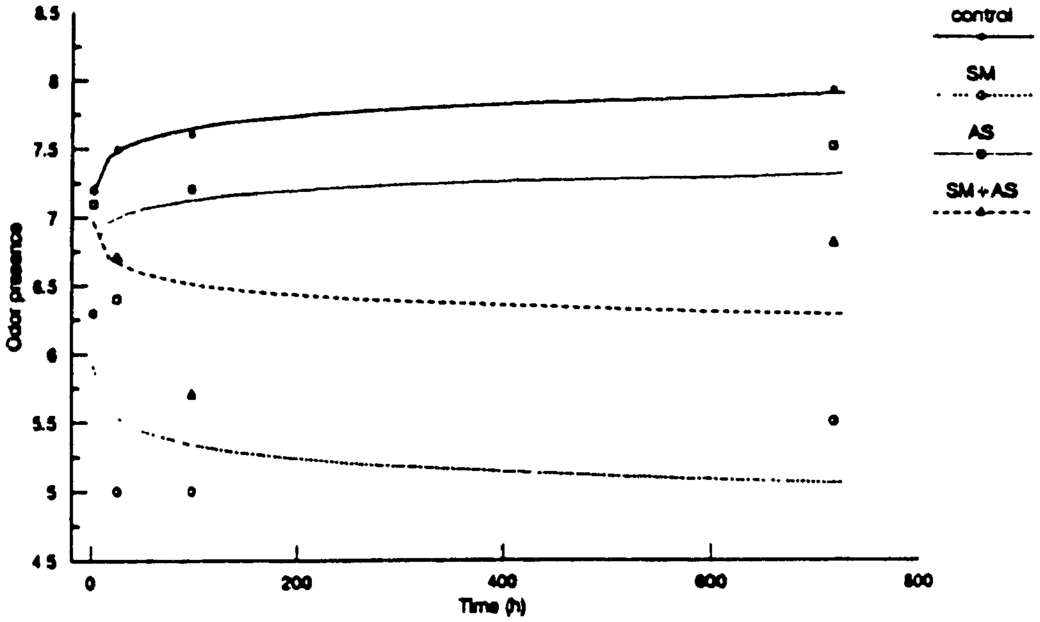


FIGURE 6b : EFFECT OF TREATMENT ON THE RELATIONSHIP BETWEEN ODOR PRESENCE AND PERIOD OF INCUBATION

4.3.3 Gas chromatography analysis of air from treated and untreated LHM

Figures 7 to 13 show the gas chromatograms obtained from the direct injection of air samples collected from the untreated and treated LHM during incubation.

In general, three peaks were obtained with the control and the treatments (Figues 7, 8, 9, 10 and 11), with the exception of sphagnum moss and sphagnum moss/aluminum sulfate combination which gave 2 peaks (Figures 12, 13). After 24 h of incubation, peak area measurements (Table 10) show that the peak areas,which reflects the quantities, of peak # 1 (P1) were lower in all treatments than in the control. After 96 h, the sphagnum moss and sphagnum moss/aluminum sulfate combination continued to produce a effect in that, peak # 3 (P3) was absent. This represents the absence of at least a single odorous compound. It will be recalled from the odor presence evaluation that sphagnum moss, sphagnum moss/aluminum sulfate combination treatments were also effective in reducing the presence of odor. It could be suggested that the reduced odor presence in these two treatments may be related to the volatile compounds represented by peak # 3 (P3) from the gas chromatography analysis.

TABLE 10 Peak areas from gas chromatographic analysis of gas from incubated LHM.

Treatment	Period of incubation								
	24 h			96 h			720 h		
	P1	P2	P3	P1	P2	P3	P1	P2	P3
H2SO4	108.0	8.8	31.7	148.0	3.5	26.3	41.0	---	---
H_3PO_4	100.0	7.3	40.4	119.5	21.4	---	43.7	---	---
MCPM[1]	86.7	6.2	44.8	143.0	4.0	53.0	55.0	---	---
AS[2]	87.4	4.0	23.5	106.2	8.0	32.0	40.2	---	---
SM[3]	120.4	16.8	---	143.7	25.0	---	32.5	---	---
SM+AS[4]	74.1	30.5	---	49.5	25.3	---	25.6	---	---
LHM	207.1	11.7	46.5	121.5	16.9	4.9	39.0	---	---

1, monocalcium phosphate monohydrate.
2, aluminum sulfate.
3, sphagnum moss.
4, sphagnum moss and aluminum sulfate combination.
P1,2,3, mean peaks areas in mm^2 from duplicate measurements and peak number as they appeared in the chromatograms (Figures 7 to 13).
--- represents the absence of peak

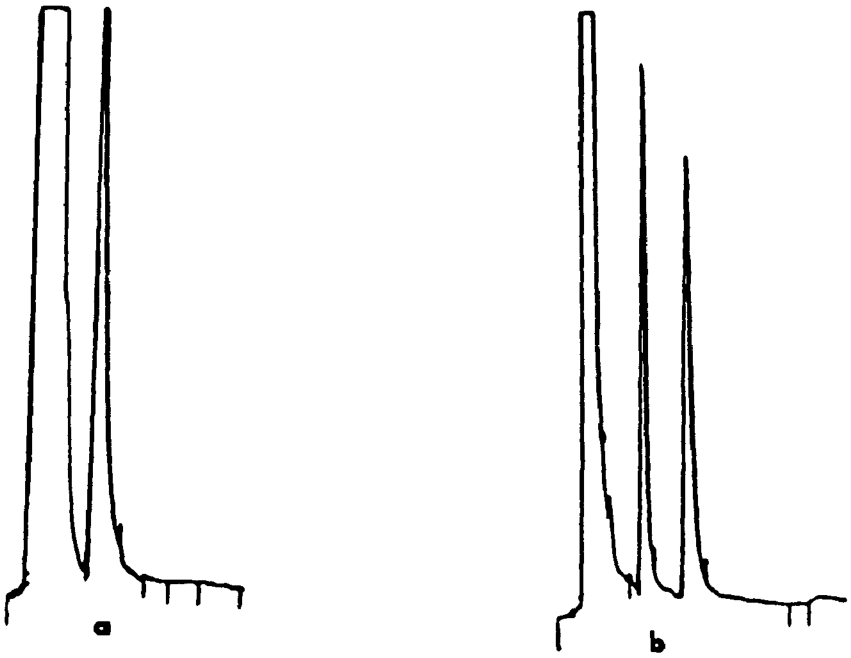


FIGURE 7 : CHROMATOGRAMS OF AIR FROM THE CONTROL LHM INCUBATED FOR (a) 22 h AND (b) 96 h

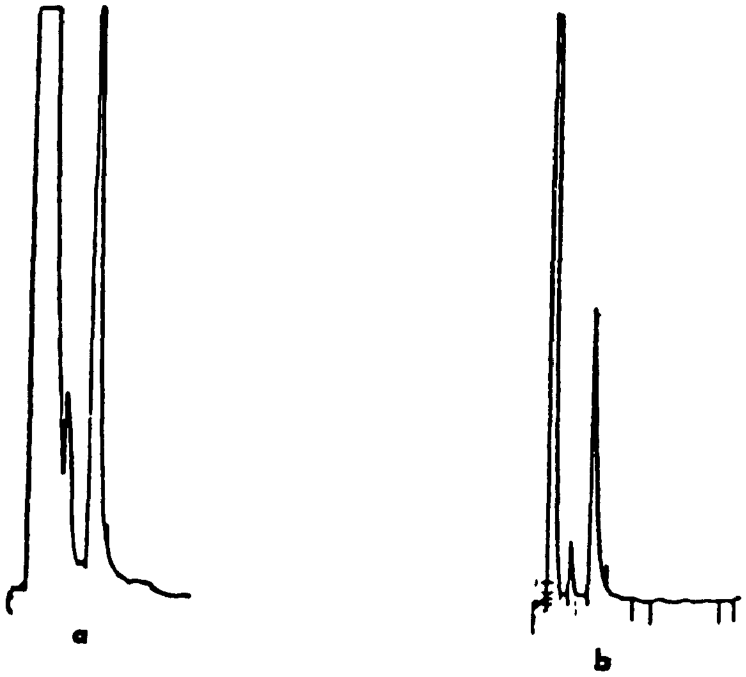


FIGURE 8 : CHROMATOGRAMS OF AIR FROM LHM TREATED WITH A SOLUTION OF 3 N H_2SO_4 (4 % w/w), INCUBATED FOR (a) 22 h AND (b) 96 h

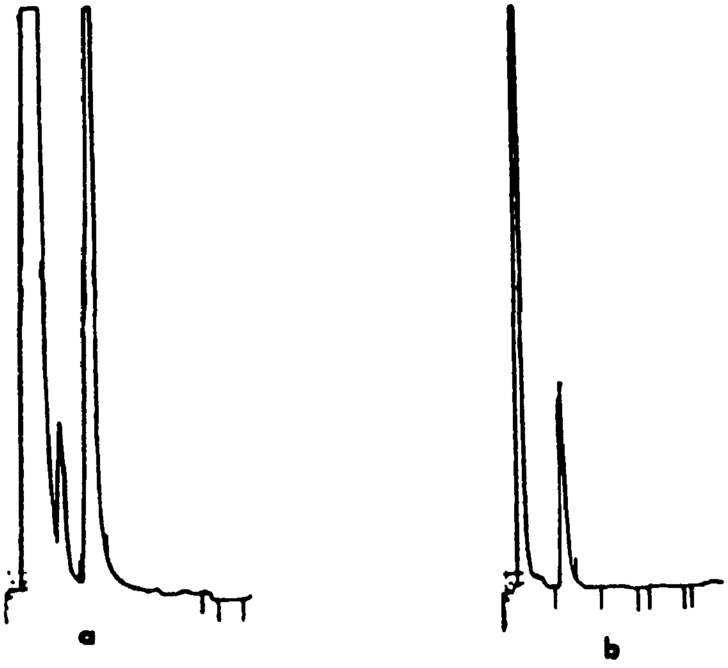


FIGURE 9 : CHROMATOGRAMS OF AIR FROM LHM TREATED WITH A SOLUTION OF 5 N H_3PO_4 (7 % w/w) INCUBATED FOR(a) 22 h AND (b) 96 h

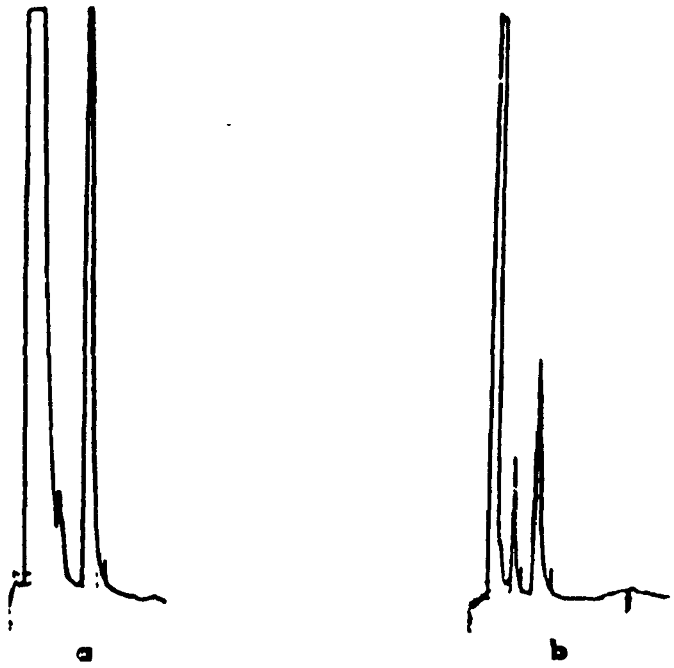


FIGURE 10 : CHROMATOGRAMS OF AIR FROM LHM TREATED WITH $AL_2(SO_4)_3$ (2 % w/w) AND INCUBATED FOR (a) 22 h AND (b) 96 h

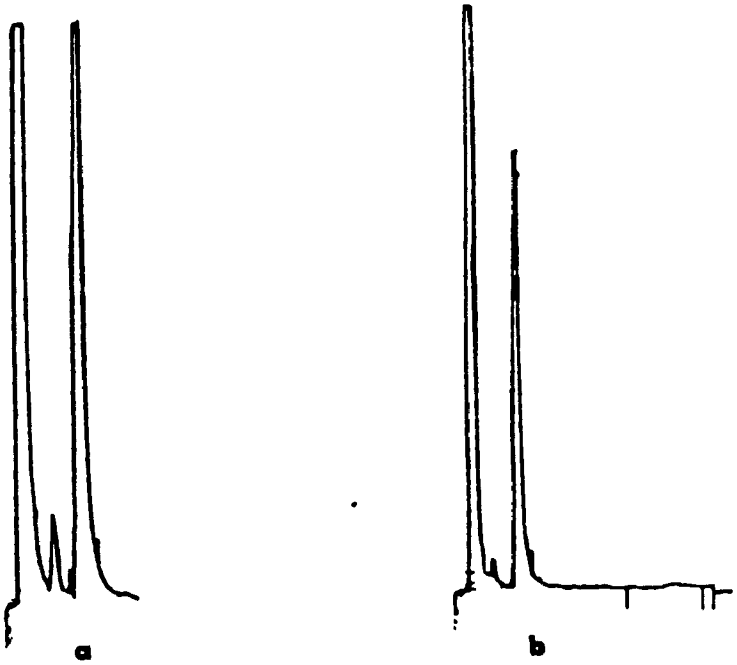


FIGURE 11 : CHROMATOGRAMS OF AIR FROM LHM TREATED WITH MONOCALCIUM PHOSOHATE MONOHYDRATE (4 % w/w), INCUBATED FOR (a) 22 h AND (b) 96 h

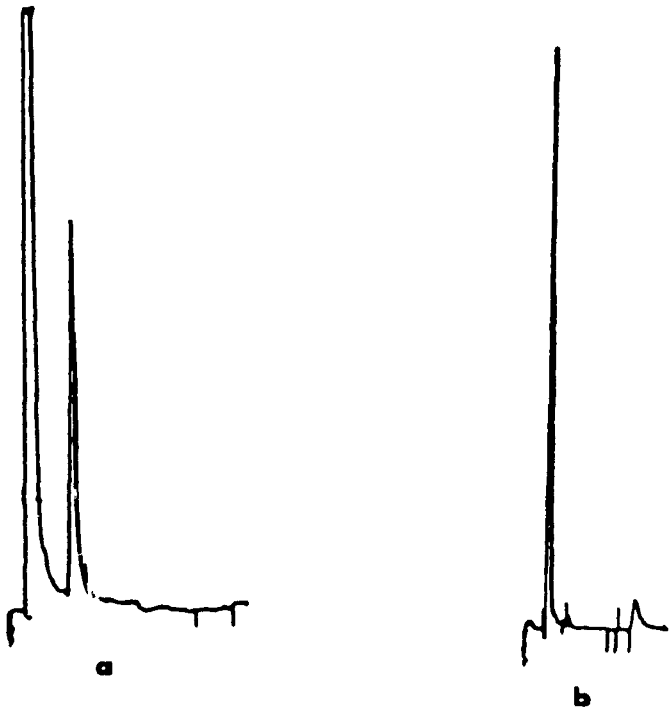


FIGURE 12 : CHROMATOGRAMS OF AIR FROM LHM TREATED WITH SPHAGNUM MOSS (8 % w/w), INCUBATED FOR (a) 22 h AND (b) 96 h

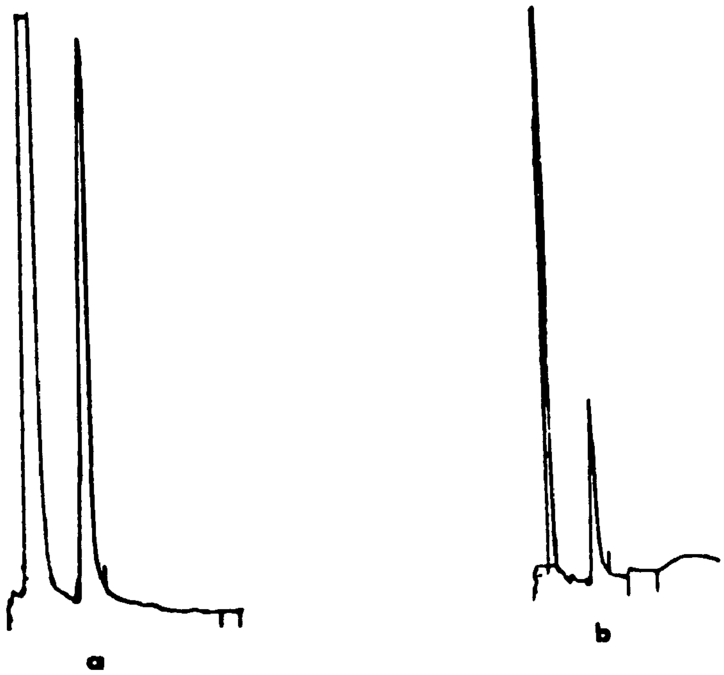


FIGURE 13 : CHROMATOGRAMS OF AIR FROM LHM TREATED WITH SPHAGNUM MOSS, ALUMINUM SULFATE (2:2 % w/w) COMBINATION, INCUBATED FOR (a) 22 h AND (b) 96 h

4.3.4 CO_2 measurement

CO_2 volatilization was determined with the LHM and the 8 % sphagnum moss treated LHM (Figure 14). The sphagnum moss treatment resulted in a reduction in CO_2 lost as compared to the control LHM treatment, the magnitude of the reduction was 61.5 % relative to the untreated manure. This result is in agreement with results obtained by Mathur et al.(1990) who suggested that CO_2 is occluded within the slurry by forming $(NH_4)_2CO_2$. This occlusion is particularly favored by the high viscosity that is conferred to the slurry by sphagnum moss.

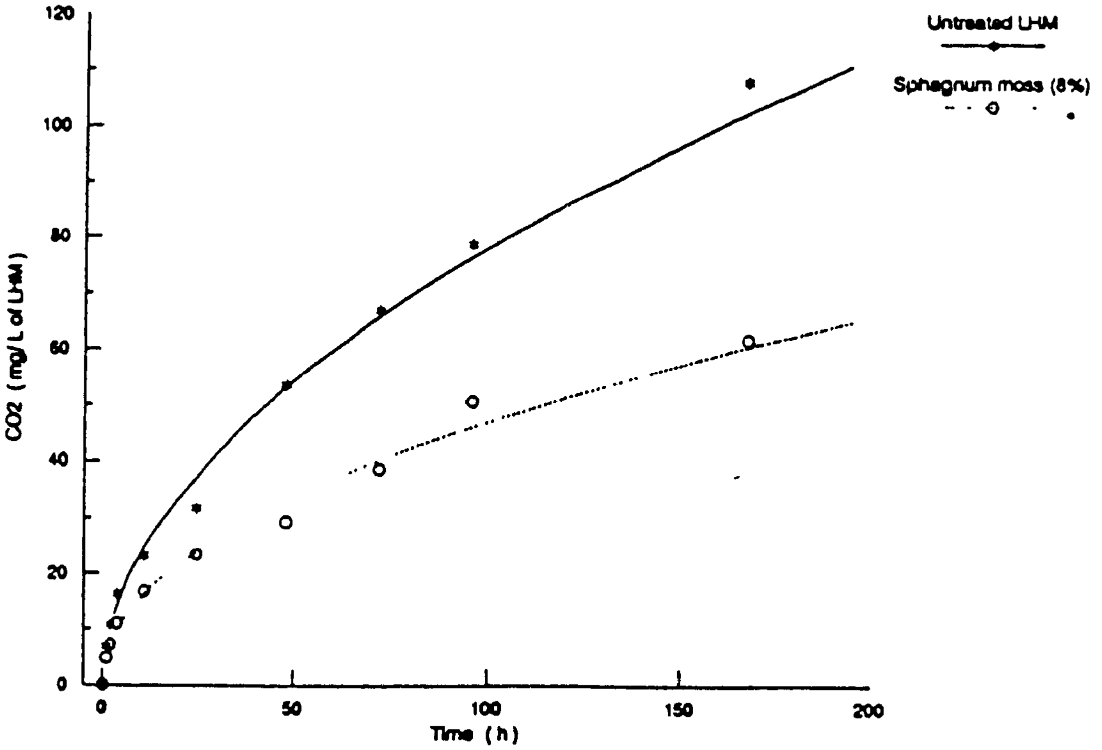


FIGURE 14 : CO2 EVOLUTION FROM LHM AS AFFECTED BY THE TREATMENTS DURING INCUBATION.

4.4 EXPERIMENT 4: Effects of levels of treatment and aeration on odor form LHM, and gas chromatographic/mass spectrometry analysis

4.4.1 The effects of treatment level

The results from Experiment 3 demonstrated the that sphagnum moss, aluminum sulfate and sphagnum moss/aluminum sulfate combination were effective in reducing odor presence and odor offensiveness. In Experiment 4, the effects of various level of these two materials were determined.

Table 11 shows the effects of the different levels of the treatments on odor presence and offensiveness. The results indicate that when sphagnum moss is use alone, a level of 8 % (w/w) significantly ($p < 0.05$) reduced odor presence and odor offensiveness. Levels of sphagnum moss above 8 % did not result in any further reduction of odor presence or offensiveness. Use of aluminum sulfate at 2 % and 4 % resulted in significant odor reduction. In addition, the sphagnum moss/monocalcium phosphate mohydrate treatment also produced significant reduction in odor presence and odor offensiveness.

TABLE 11 EFFECT OF LEVEL OF TREATMENTS ON ODOR PRESENCE AND ODOR OFFENSIVENESS

Treatment	Level of use (%, w/w)[1]	Odor			
		P		Of	
aluminum sulfate	1.0	5.0	a	5.1	a
	2.0	4.7	ab	4.8	ab
	4.0	4.4	ab	4.6	ab
sphagnum moss	1.0	5.0	a	5.1	a
	2.0	5.1	a	4.8	ab
	4.0	4.9	a	4.9	a
	8.0	3.8	c	3.4	c
	12.0	4.0	b	3.6	c
	24.0	3.9	c	4.0	b
SM + $Al_2(SO_4)_3$[2]	12:2	3.8	c	4.1	b
SM + MCPM[3]	12:2	4.3	b	4.4	ab
LHM (control)	----	6.3	a	5.7	a
Air (odor free)	----	0.4	d	0.9	d

1, fresh weight basis

2, sphagnum moss, aluminum sulfate combination

3, sphagnum moss, monocalcium monophosphate monohydrate combination

P for presence and Of for offensiveness

a-d, values follow by the same letter within a column are not significantly different at p=5%

4.4.2 Influence of aeration on odor presence and offensiveness.

Table 12 shows the effect of aeration on odor presence and offensiveness of LHM. The results indicate that odor presence and offensiveness of the aerated systems are significantly ($p < 0.05$) lower than those of the non-aerated systems. These results agree with those reported by Stevens and Cornforth (1974). This reduction in odor could be due to the activation of aerobic bacteria, to oxidation of volatile fatty acids which may have been formed, and to the dilution caused by the volume of air introduced in the incubation vessel. Aeration is efficient as a method to control odor of LHM (Miner, 1980), but its energy requirement makes it expensive (Mathur et al., 1990). The results obtained with the non-aerated 8 % sphagnum moss treatment (Table 12) shows that significant odor reduction ($p < 0.05$) is possible without aeration e.g 33.9 % reduction (non-aerated) and 17.6 % reduction (aerated) with 8 % sphagnum moss when compared to the respective controls (Table 12). On the basis of these results, it was decided that for mainly economic considerations, all further experiments should be carried out without aerating.

TABLE 12 ODOR PRESENCE AND OFFENSIVENESS AS INFLUENCED BY AERATION

Treatment	(%)[1]	Aeration		Non-aeration	
		P	Of	P	Of
AS[2]	2.0	5.10	4.97	7.24	7.10
SM[3]	1.0	5.00	5.10	7.80	7.66
	2.0	5.10	4.80	6.10	5.90
	8.0	4.20	3.70	5.00	4.67
SM+AS[4]	2:2	4.10	4.13	5.67	7.33
MCPM[5]	4.0	4.30	4.43	6.86	6.62
LHM	----	5.10	5.13	7.57	7.33

1, fresh weight basis
2, aluminum sulfate
3, sphagnum moss
4, sphagnum moss, aluminum sulfate combination
5, monocalcium mophosphate monohydrate
P, odor presence
Of,odor offensiveness

4.4.3 Gas chromatographic / Mass spectrometry analysis

Table 13 gives a list of compounds identified in the gas samples from LHM using gas chromatograpy-mass spectrometry (GC/MS). The results provide a comparison of actual chemical compounds which were identified in the air from untreated LHM to compounds identified in the air from LHM treated with sphagnum moss (8 %). A total of eleven compounds were identified in the untreated LHM; these include amines and other nitrogen containing compounds (1,2-

ethanediamine; N-methyl methanamine; 3-methyl,2-butanamine; methylhydrazine), sulfur containing compounds (hydrogen sulfide, carbon disulfide, thiobis-methane, methanethiol, ethanethioic acid) and alcohols (3-methyl,1-butanol; ethanol). Several of these compounds (hydrogen sulfide, methanethiol, N-methyl methanamine, ethanol, 3-methyl,1-butanol) have been reported in the air of LHM (Schaefer, 1977; Yasuhara and Fura, 1979; Branwart and Bremmer, 1975; Miner and Hazen, 1969; Merkel et al. 1969; Hartung et al. 1971). It is evident from Table 13 that sphagnum moss was effective in reducing the presence of the amines and nitrogen containing compounds as well as methanethiol and ethanethioic acid. It will be recalled that the sphagnum moss treatment also reduced odor presence and odor offensiveness as determined by a sensory panel. It could be suggested that the absence of these compounds (Table 13) might be related to the reduction of odor presence and odor offensiveness of LHM as indicated by the sensory panel. It should be mentioned that the alcohol 3-methyl,1-butanol with a characteristic foul odor was present in the air from the sphagnum moss treated LHM but not in the air from the untreated LHM.

TABLE 13 IDENTIFICATION OF ODOR COMPOUNDS IN AIR FROM UNTREATED LHM AND LHM TREATED WITH SPHAGNUM MOSS.

Compound	Presence(+) or Absence(-)		Odor[3] Characteristic
	Control[1]	8 % SM[2]	
Hydrogen sulfide[abc]	+	+	rotten egg
Carbon disulfide	+	+	foul
Thiobis-methane	+	+	putrid
Methanethiol[b]	+	-	rotten cabage
Ethanethioic acid	+	-	pungent
Methyl-Hydrazine	+	-	ammonia-like
1,2-Ethanediamine	+	-	ammonia-like
N-Methyl methanamine[d]	+	-	pungent
3-Methyl,2-Butanamine	+	-	ammonia like
Ethanol[e]	+	+	alcohol
3-Methyl,1-Butanol[f]	-	+	foul

1, untreated LHM
2, sphagnum moss treated LHM (8% w/w, fresh weight basis)
3, The Merck index, 1976
a, Scheafer ,1977
b, Brunwart et al., 1975
c, Yasuhara et al., 1979
d, Miner et al., 1969
e, Merkel et al., 1969
f, Hartung et al., 1971

4.5 EXPERIMENT 5 : Effects of calcium carbonate, calcium oxide and their combination with sphagnum moss.

4.5.1 Odor evaluation

Table 14 shows the effects of calcium carbonate, calcium oxide and their combination with sphagnum moss on odor presence and offensiveness. In this experiment, calcium compounds were used with the objective of reducing the odor contribution from the sulfur containing compounds (Table 13) which were not removed by the sphagnum moss treatments. The $CaCO_3$ and CaO treatments alone did not produce any significant reduction in odor presence or odor offensiveness. A reduction was observed with the sphagnum moss/$CaCO_3$ and sphagnum moss/CaO combinations to an extent comparable to the reduction occured with sphagnum moss alone at the 1 % level of treatment.

In this experiment, an odor reference chemical, pyridine was used in order to estimate semi-quantitatively the degree of reduction of odor achieved. Table 14 shows that a pyridine solution of concentration 10000 ppm gave an odor presence and offensiveness slightly higher than that of the air from untreated LHM as determined by the sensory panel. Figure 15 shows the relationship between odor offensiveness and the odor reference (pyridine) concentration, along with the plotted points of the air of treated and untreated LHM. All samples fitted the offensiveness response curve of the pyridine (Figure 15), suggesting that the odor offensiveness of LHM samples could be comparable with the odor of a pyridine solution between 1 ppm and 10000 ppm concentration.

TABLE 14 EFFECT OF $CaCO_3$, CaO, SPHAGNUM MOSS AND THEIR COMBINATIONS ON ODOR PRESENCE AND OFFENSIVENESS

Treatment	(% w/w)[1]	Odor	
		presence	offensiveness
SM	1.0	5.82	5.96
	4.0	4.73	4.27
	8.0	4.18	4.82
$CaCO_3$	2.0	5.91	5.77
SM + $CaCO_3$[2]	1:2	5.60	5.50
CaO	2.0	6.27	6.19
SM + CaO[3]	1:2	5.68	5.86
control	---	7.00	7.09
pyridine	1ppm	0.27	0.73
	10ppm	0.82	0.64
	100ppm	1.55	1.82
	1000ppm	3.55	3.73
	10000ppm	8.10	7.50

1, fresh weight basis
2, sphagnum moss/calcium carbonate combination
3, sphagnum moss/calcium oxide combination

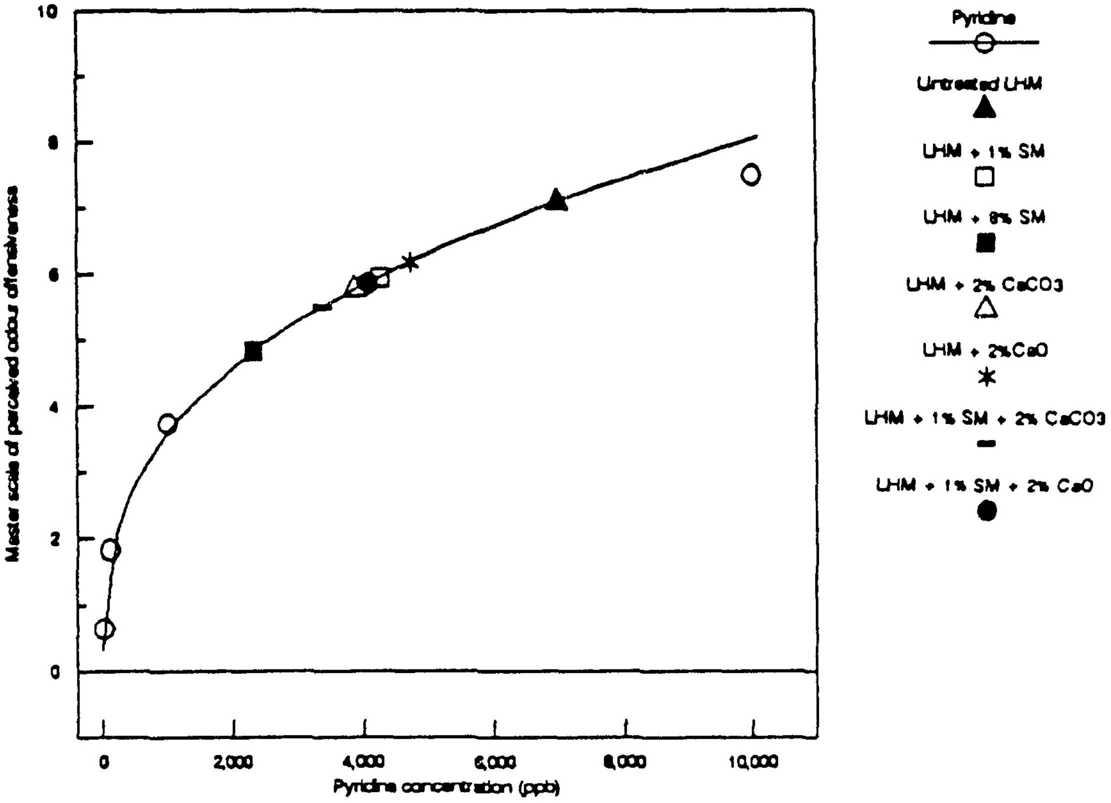


FIGURE 15 : COMPARISON OF ODOR OFFENSIVENESS OF AIR FROM LHM SAMPLES WITH THAT OF PYRIDINE.

4.5.2 Total nitrogen and Ammonia nitrogen contents of LHM

Table 15 shows total nitrogen (TN) and ammonia nitrogen (NH_3-N) contents of untreated and treated LHM after 25 days of incubation. The results indicate that the TN content of untreated LHM reduced from 66.84 g/Kg to 57.5 g/kg (dry matter basis) during the incubation period.This represented a loss of 13 % of the initial TN. (Vanderholm, 1975) reported that LHM on farms suffers from nitrogen losses, probably as a result of volatilization, during storage. Similar loss in TN were observed for the LHM treated with 1% sphagnum moss and the sphagnum moss/$CaCO_3$ combination. The 2% $CaCO_3$ treatment increased the loss of TN (21 % as compared to untreated LHM); this could be related to the relatively high pH of the CaCo3 treated slurry (Table 15). The LHM treated with 8 % sphagnum moss lost 3.7 % TN, suggesting the nitrogen conservation capability of the sphagnum moss. In general, the TN of all treatments decreased during the incubation, while the pH increased. The decrease in TN could be the result of ammonia loss by volatilization while, the increase in pH (Table 15) could be the result of (1) CO_2 accumulation due to microbial activity, (2) oxidation of volatile fatty acids and (3) NH_3 accumulation. According to Visser et al. (1973) and Kay (1978), bacterial uptake of acids and the subsequent release of OH^- could account for the increase in pH.

Ammonium nitrogen (NH_4-N) accounted for an average of 36 % of the TN in the treatments and showned no significant change during the 25 d incubation period

TABLE 15 EFFECT OF SPHAGNUM MOSS, $CaCO_3$, CaO AND THEIR COMBINATION ON TN AND NH_4-N DURING INCUBATION OF LHM.

Treatment	Fresh LHM			Incubated[a] LHM			NH_3-N volatilized after 25 d
	pH	TN	NH_4-N	TN	NH4-N	pH	
		g/Kg of LHM (DB)					
LHM	6.6	66.3	24.3	57.5	17.9	7.2	9.0
SM (1%)	6.4	68.8	26.0	48.5	17.6	6.9	10.6
SM (4%)	5.8	50.4	20.7	47.2	23.8	6.6	5.2
SM (8%)	5.6	48.9	20.9	44.5	19.8	6.2	1.7
CC (2%)	7.1	46.6	16.1	40.6	13.6	7.4	11.0
SM+CC	6.9	48.6	17.9	44.0	17.7	7.1	8.7
F	107.4**	5.7*	6.1*	5.1*	33.3**	ns	1103.3**
LSD	0.2	0.8	0.1	0.4	0.2		0.7

a, samples were incubated for a 25-day period at 23°C
SM, saphagnum moss
CC, calcium carbonate
SM+CC, sphagnum moss/calcium carbonate combination
DB, dry weight basis
F, F-value
ns, not significant
*,**, significant at $p<0.05$ and $p<0.01$ level, respectively

4.5.3 Nitrogen fertilizer potential of LHM

4.5.3.1 Plant dry matter yield

Table 16 shows the dry matter yield of barley (grown for 55 days) with treated and untreated LHM applied (three application rates) to 2 soil types. The results indicate that application of the untreatred LHM to the soil resulted in a significant ($p < 0.01$) increase in dry matter yield when compared to no application of LHM to the soil (Table 16). This suggests that N from LHM was utilized by plants. These response agree with results reported by Burns (1990). The dry matter from soil treated with LHM which was incubated with sphagnum moss was not statically different ($p < 0.05$) from that of the soil treated with the control LHM. In addition, higher rate of application (300 Kg N/ha) in the form of LHM treated with the combination of 1 % sphagnum moss and 2 % calcium carbonate actually resulted in lower dry matter yield than the same rate of application of untreated LHM. Figure 16 shows that the relationship between rate of N and dry matter yield was linear; the equations describing the relationships are shown in Appendix C. It appears that the yield response to nitrogen fertilizer was higher in the sandy upland soil than in chicot (Table 16). This is not surprising since the initial nitrogen content of the chicot soil was higher (Section 3.9) and could explain the lack of improvement in yield with this soil type.

TABLE 16: DRY MATTER YIELD OF BARLEY AS INFLUENCED BY THE RATE OF N APPLIED

Treatment	Amounts of LHM applied		Dry matter yield			
			Uplands		Chicot	
	Rate 2	Rate 1	Rate 1	Rate 2	Rate 1	Rate 2
	tonnes/ha					
soil[1]	----	----	6.79	----	17.72	---
LHM	7.32	14.63	15.83	23.87	21.95	28.05
SM(1%)	7.61	15.23	15.64	20.70	25.11	29.23
SM(4%)	6.52	13.04	13.56	21.39	26.57	27.89
SM(8%)	6.44	12.88	15.66	21.91	25.72	28.43
CC(2%)	12.93	25.86	16.71	23.65	26.57	25.40
SM+CC	11.28	22.56	14.22	21.19	21.50	21.37
F-value			29.95^{**}	55.28^{**}	5.02^{**}	3.84^{*}
LSD (0.05)			2.1	0.21	5.0	3.9

1, untreated soil
SM, saphagnum moss
CC, calcium carbonate
SM+CC, sphagnum moss/calcium carbonate combination (1%,2%)
*,**, significant at $p<0.05$ and $p<0.01$ level, respectinely

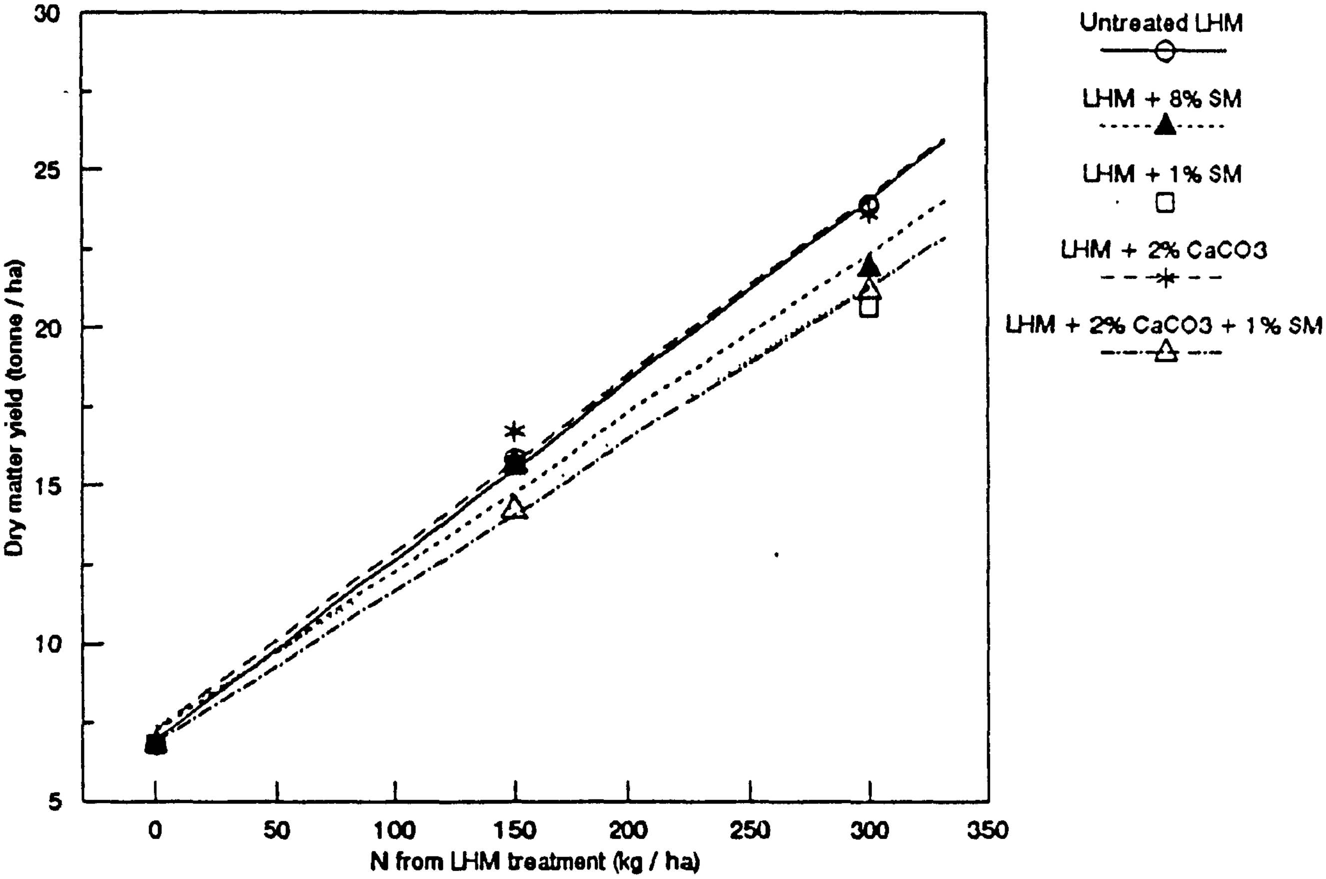


FIGURE 16 : EFFECT OF THE RATE OF APPLIED N ON THE DRY MATTER YIELD OF BARLEY

The analysis of variance (AOV) for dry matter showed significant interactions for treatments (T), rates (R) of N, and type of Soil (S) at $p<0.05$ level (Appendix D). The TxRxS and TxR interactions were not significant while TxS and RxS interactions were significant ($p<0.01$).

V. SUMMARY AND CONCLUSION

1. Direct treatment of LHM with sulfuric acid, phosphoric acid, monocalcium phosphate monohydrate and aluminum sulfate to $pH < 5.0$ resulted in a significant ($p < 0.05$) reduction in ammonia loss during storage of LHM over a 14-day period.

2. Treatment of LHM with sphagnum moss (SM) at levels of 2, 4, 8 % (w/w) and combinations of sphagnum moss and aluminum sulfate resulted in a significant ($p < 0.05$) reduction in ammonia loss during storage of LHM over a 14-day period; the reduction occurred without a marked reduction in the pH of the LHM.

3. Sphagnum moss (at 8 % application rate) and a mixture of sphagnum moss and aluminum sulfate (2% / 2% mixture) produced significant ($p < 0.05$) reduction of both odor presence and odor offensiveness in LHM during a 30-day storage period.

4. Gas chromatographic analysis of air from treated and untreated LHM indicated that sphagnum moss (8 % application rate) and a mixture of sphagnum moss (8% / 2% mixture) in the absence of certain odorous compounds as well as a reduction of quantities of some other odorous compounds.

5. Gas chromatographic/mass spectrometry analysis revealed that the use of 8 % sphagnum moss resulted in the absence of certain nitrogen containing malodorous compounds; these compounds were 1,2-ethanediamine, N-methyl methanamine, 3-methyl,2-butanamine and methyl hydrazine. In addition, two sulfur containing compounds methathiol and ethanethioic acid were present in the untreated LHM but were not in the sphagnum moss treated LHM.

6. The sphagnum moss treated LHM which showed reduced odor presence and reduced odor offensiveness, and which showed the absence of certain malodorous compounds, did not produce any improvement in plant dry matter yield when used as source of nitrogen fertilizer.

7. Sphagnum moss is potentially a satisfactory material for reducing the malodor of LHM as well as conserving the nitrogen fertilizer capacity of the LHM.

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APPENDICES

Appendix A : Equations describing the effect of pH on ammonia loss during incubation (Figure 4).

pH	Equation	R^2
4.0	-----	----
5.0	$Y = 0.02 . e^{0.55X}$	0.92
6.0	$Y = 0.11 . e^{0.61X}$	0.93
7.2	$Y = -105.8 + 38.6X$	0.96

Appendix B.1: Equations describing the effect of treatment on the relationship between odor offensiveness and odor presence after 2 h incubation (Figure 5a).

Treatment	Equation	R^2
control	$Y = -9.40 + 8.32 \ln X$	0.97
SM	$Y = -5.70 + 6.4 \ln X$	0.87
AS	$Y = -2.90 + 1.33 \ln X$	0.86
SM + AS	$Y = 0.21 . X^{1.74}$	0.95

Appendix B.2 : Equations describing the effect of treatment on the relationship between odor offensiveness and odor presence after 24 h incubation (Figure 5b).

Treatment	Equation	R^2
control	$Y = 2.70 . e^{0.13X}$	0.84
SM	$Y = 0.96 . X^{1.03}$	0.82
AS	$Y = -5.70 + 6.46 \ln X$	0.93
SM + AS	$Y = -4.70 + 5.78 \ln X$	0.94

Appendix B.3 : Equations describing the effect of treatment on the relationship between odor offensiveness and odor presence after 96 h incubation (Figure 5c).

Treatment	Equation	R^2
control	$Y = -9.90 + 8.71\ln X$	0.90
SM	$Y = 0.96 + 0.72X$	0.71
AS	$Y = -6.20 + 6.81\ln X$	0.71
SM + AS	$Y = 1.80 \cdot e^{0.17X}$	0.89

Appendix B.4 : Equations describing the effect of treatment on the relationship between odor offensiveness and odor presence after 720 h incubation (Figure 5d).

Treatment	Equation	R^2
control	$Y = 3.96 \cdot e^{0.08X}$	0.82
SM	$Y = 1.00 + 0.75X$	0.80
AS	$Y = 2.03 + 0.72X$	0.82
SM + AS	$Y = 1.27 + 0.75X$	0.90

Appendix B.5 : Equations describing the incubation period effect on the relationship between odor offensiveness and odor presence (Figure 5e).

Treatment	Equation	Time	R^2
control	$Y = -3.85 + 5.44\ln X$	2 h	0.76
SM	$Y = 0.96 \cdot X^{1.04}$	24 h	0.82
AS	$Y = 0.96 + 0.72X$	96 h	0.71
SM + AS	$Y = 1.00 + 0.75X$	720 h	0.80

Appendix B.6a : Equations describing the effect of treatment on the relationship between odor offensiveness and period of incubation (Figure 6a).

Treatment	Equation	R^2
control	$Y = 6.55 + 0.16\ln X$	0.99
SM	$Y = 5.50 - 0.09\ln X$	0.62
AS	$Y = 5.96 + 0.20\ln X$	0.78
SM + AS	$Y = 6.20 - 0.06\ln X$	0.27

Appendix B.6b : Equations describing the effect of treatment on the relationship between odor offensiveness and period of incubation (Figure 6b).

Treatment	Equation	R^2
control	$Y = 7.11 + 0.12\ln X$	0.99
SM	$Y = 5.98 - 0.14\ln X$	0.31
AS	$Y = 6.72 + 0.09\ln X$	0.22
SM + AS	$Y = 7.02 - 0.19\ln X$	0.19

Appendis C : Equation describing the relationship between dry matter yield of barley and rate of N applied to soil.

Treatment	Uplands		Chocot	
	Equation	R^2	Equation	R^2
control	$Y = 9.96 + 0.05X$	0.99	$Y = 17.41 + 0.03X$	0.99
SM 1%	$Y = 7.42 + 0.05X$	0.98	$Y = 19.39 + 0.03X$	0.74
SM 4%	$Y = 6.61 + 0.05X$	0.99	$Y = 18.26 + 0.04X$	0.97
SM 8%	$Y = 7.23 + 0.05X$	0.99	$Y = 18.60 + 0.04X$	0.93
Ca 2%	$Y = 7.29 + 0.06X$	0.99	$Y = 18.37 + 0.01X$	0.72
SM+Ca	$Y = 6.87 + 0.05$	0.99	$Y = 18.87 + 0.03X$	0.87

Ca, $CaCO_3$
SM+Ca, SM+$CaCO_3$ (2%, 2%)

Appendix D : Analysis of variance (AOV) of dry matter yield of barley

Source	DF	Mean square	F-value
Model	25	127.60	22.24^{**}
Treatment (T)	6	90.93	15.85^{**}
Soil (S)	1	1310.81	288.45^{**}
Rate (R)	1	502.79	87.63^{**}
T x S	6	28.58	4.98^{**}
T x R	5	13.00	2.27^{ns}
R x S	1	140.46	24.48^{**}
T x S x R	5	6.89	1.20^{ns}
Error	78	5.74	

ns, not significant
**, significant at $p < 0.01$ level