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PRODUCTION AND TRANSPORT OF GASEOUS NH_3 AND H_2S ASSOCIATED WITH LIVESTOCK PRODUCTION

Robert S. Kerr Environmental Research Laboratory
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PRODUCTION AND TRANSPORT OF GASEOUS NH_3 AND H_2S ASSOCIATED WITH LIVESTOCK PRODUCTION

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ABSTRACT

Current livestock production techniques release a large variety of volatile organic compounds to the atmosphere. This release results in complaints due to the odorous nature of the compounds and has been identified as a source of surface water pollution as these compounds are absorbed from the air. Ammonia has been identified as the compound of greatest concern relative to water pollution and of considerable interest relative to odor complaints because of its ease of measurement and its relationship to more odorous gas evolution.

Gas sampling and measuring schemes based upon the use of solid absorbents were investigated. The use of an absorbent suspended in a stainless steel screen container which could be exposed in an atmosphere to be sampled showed promise. The large number of volatiles absorbed compounded identification procedures. Trimethylamine was identified as a nitrogen-bearing volatile of particular odor importance.

The evolution of ammonia, hydrogen sulfide, and odorous volatiles was investigated as a function of beef cattle ration. The addition of an essential oil, mint oil, was found to alter the odor of fresh manure by masking. The mint oil odor was carried in the urine. Ammonia evolution from fresh manure was largely from urine. Fecal contributions became significant only after considerable decomposition had occurred.

A technique was devised for measuring the ammonia evolution rate from surfaces within and associated with livestock production enterprises. Included were barn floor surfaces, corral surfaces, and land to which manure had been applied. This measurement proved to be an accurate reflection of anaerobic biological activity and to provide a quantitative means for comparing treatment procedures designed to minimize volatile material evolution rates. Evolution rates for a variety of surfaces associated with livestock production enterprises were measured.

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SECTION I

CONCLUSIONS

The production, evolution, transport and perception of volatile compounds associated with livestock production involves a complex series of phenomena. Manure management has the potential for drastically modifying the overall process. Ration formulation, facility design, and specific treatment processes may also be used where appropriate to modify the system behavior to reduce volatile component production, alter the release process, modify the transport system, or, in certain instances, change the perception process.

Solid absorbents developed for use in gas-liquid chromatography have great capacity for absorption and retention of organic compounds. Although not fully perfected in this study, a sampling device fabricated of these materials has great potential for characterizing atmospheres containing manure-produced volatiles.

Ammonia evolution from fresh beef cattle manure is largely from urine. The fecal contribution occurs only after significant anaerobic activity has become established. An essential oil added to the feed ration was carried in the urine and successfully altered the fresh manure odor by masking.

The ammonia evolution rate sampling box designed in this project successfully met the need for a device to quantitatively measure evolution rates of volatile compounds. It has been used to measure ammonia nitrogen release rates from a variety of surfaces. Due to the relationship which exists between ammonia release rate and odor production, the device is useful in evaluating odor control procedures which have previously been dependent upon qualitative judgments.

SECTION II

RECOMMENDATIONS

This project was designed to identify areas suitable for full exploitation in the control of volatile organic emissions from livestock production enterprises. It is recommended that those aspects of the project showing greatest potential be further developed.

The use of solid absorbents fabricated to allow convenient exposure in an atmosphere of interest has potential as a quantitative measuring scheme. When perfected, such a system will allow inexpensive surveillance of suspected emission sources and allow definitive measurement of conditions in downwind areas.

Mint oil was effective in masking the odor of fresh manure. Other lower cost essential oils should be sought as feed ingredients.

The ammonia evolution rate measuring system perfected as part of this project has widespread application in measuring the evolution of ammonia from agricultural activities but may serve as a model for other measurement systems. It has immediate application in evaluating the effectiveness of feedlot odor control programs.

SECTION III

INTRODUCTION

Confinement livestock production schemes have been adopted for most species throughout the country. They have sufficient economic advantage over the more dispersed systems of the past to assure their continued importance in the overall food production complex.

Water pollution attributable to runoff from livestock production areas and discharge of animal manures has been well documented and means for its control investigated. The discharge of potential pollutants into the air has been less well studied and control procedures are not in widespread use. Two effects of airborne pollutant release have been identified: odor complaints and transport of water pollutants via air movement to surface waters. This project was designed to open this area of concern and to quantify release rates for the most pertinent compound, ammonia.

VOLATILE COMPOUNDS OF INTEREST

Ammonia

The presence of ammonia as a component of our atmosphere was noted 100 years ago by Scholssing.[1] Some of the physiological disorders specifically caused by ammonia were described by Weatherby[2] with the primary effect noted on the lungs, eyes, and mucous membranes. Ammonia was found to reduce chicken resistance to Newcastle disease and increase air sac lesions in turkeys.[3] It was shown by Charles and Payne[4] that elevated levels of ammonia in chicken houses had an adverse effect on the growth of chickens. Boyd *et al.*[5] studied the effect of ammonia gas poisoning on rabbits and cats.

The increased nitrogen concentration of surface waters in close proximity to livestock production units has generally been attributed to surface runoff from these units. The absorption of nitrogenous compounds directly from the atmosphere by surface acid traps was found, however, to be 20 times greater for traps located in close proximity to a beef feedlot as compared to those some distance away.[6] In more recent work (Luebs et al.[7]), the ammonia concentrated in air was measured and found to be increased 20-30 times in a concentrated dairying area as compared to nonagricultural areas. It was also noted that rainfall delivered three times the amount of ammonia inside a dairying area as outside.

Ammonia has been demonstrated to be the primary nitrogen compound volatilized from feedlots.[8] It has also been demonstrated that, under typical conditions, the ammonia will be present in quantities below its odor threshold.[9] Miner and Hazen[10] found this to be the case in swine building gases; they detected ammonia, but below its published threshold.

Between 11 and 60 percent of the ammonia from sewage sludge applied to crop land was lost during the first one to two days.[11] As much as 65 percent of the nitrogen added in the form of animal waste to an anaerobic swine lagoon was found to be volatilized.[12] The nitrogen in excreted urine was studied by Stewart[13] under simulated feedlot conditions; he found approximately 90 percent was converted to ammonia. The rate of ammonia release from a feedlot surface was increased when the surface was disturbed, such as would occur in manure mounding.[14] When the moisture content of manure was increased from 60 to 90 percent and the temperature from 10° C to 25° C, an increase in the amount of nitrogen volatilization was noted, with losses approaching 50 percent of the nitrogen content of the samples.[15] Diluted poultry manure has been shown to produce more ammonia, but the undiluted sample volatilized more ammonia.[16] In a densely populated dairying area, a diurnal fluctuation in the atmospheric ammonia concentration was noted, with low concentrations in the afternoon and high concentrations at night.[17]

The pH of the medium has a direct effect upon the form in which the ammonia is found; under acidic conditions, it is in the nonvolatile (NH_4^+) form and under basic conditions, in the volatile (NH_3) form.[18] A direct correlation between soil pH and ammonia volatilization was found when manure was mixed with different soil types.[19]

Urea in urine has been indicated as the primary precursor of ammonia from animal wastes.[13] It has been estimated that half of the nitrogen eliminated under normal conditions is in the form of urea.[20] Ammonia was consistently identified in the gaseous exhaust products from anaerobically and aerobically stored dairy wastes.[21]

Amines

The production of amines as by-products of decomposition of animal wastes has been proposed as a reaction between ammonia, an end product of protein and urea breakdown, and alcohols, products of carbohydrate degradation.[22] The odor thresholds for the amines are very low, with trimethylamine having a threshold that is 100,000 times less than ammonia.[23] Thus, a relatively small quantity of amines present as products of animal waste decomposition could play a major role in the odor intensity and offensiveness associated with livestock production units.

Amines have been detected in the atmosphere associated with livestock confinement units. Trimethylamine was identified as the major amine present in the gases generated from cattle feedlots.[9] This was supported by White et al.[24] who also identified methylamine and ethylamine in gases associated with dairy animal wastes. Low concentrations of amines in swine manure have also been identified by Miner and Hazen.[10]

Luebs et al.[25] indicated that less than 5 percent of the volatilized nitrogen compounds absorbed from a large dairy area were not ammonia. The amine content of poultry manure was found to increase and the uric acid decreased with the length of storage.[26]

Mosier,[27] using Chlorella ellipsoidea, a typical algae found in streams and lakes, studied the effect of amines volatilized from cattle feedyards on the growth of algae if absorbed by surface waters. Results indicated that growth was inhibited.

Hydrogen Sulfide

The presence of hydrogen sulfide as one of the volatile gases generated from animal wastes has been reported by Day et al.[28] and Hammond et al.[29] Hydrogen sulfide was found to be produced during the putrefaction process of swine manure; minimum concentrations for identifiable odor were 0.7 ppm. The assumption can be made that hydrogen sulfide is one of the gaseous products generated during the decomposition of animal wastes and that its precursors would be proteins and inorganic sulfur compounds.

When swine were exposed to 8.5 ppm or 2 ppm of hydrogen sulfide in combination with 50 ppm of ammonia under confinement conditions, it was shown that hydrogen sulfide had little effect on the rate of gain or feed efficiency.[30] The description of the effects of hydrogen sulfide by Taiganides and White[31] on poultry, swine, and cattle gives the symptoms associated with different levels and exposure periods. Chromatographic analyses of gases from accumulated liquid poultry manure by Burnett[32] indicated that the odor-causing pollutants were identified as hydrogen sulfide, ammonia, diketones, mercaptans, sulfides, organic acids, indole and skatole. Merkel et al.[22] performed odor evaluations, using selective absorbent solutions to alter the odor from swine wastes, and concluded that amines and sulfides were the major odor constituents.

In bovine confinement operations, hydrogen sulfide has been found as a component of the volatile gas mixture generated during the process of waste decomposition. Stephens[9] developed gas chromatographic techniques for the analysis of cattle feedlot odors and identified amines, sulfur-containing compounds, and low molecular weight organic acids in the gases. White et al.[24] found that similar effects with dairy animal waste indicated the presence of sulfides, disulfides and the esters of organic acids. Bethea and Narayan[33] detected hydrogen sulfide as the only sulfur-containing compound when beef cattle wastes were maintained under aerobic conditions by bubbling air through the samples.

In studies with swine, the production of hydrogen sulfide was found to be highly correlated with temperature, ratio of pit area to building volume, air retention time of the building, and daily sulfur intake of the animal.[34]

PROJECT OBJECTIVES

The first objective of this project was the preparation of a comprehensive state-of-the-art review concerning livestock waste odors. This material was compiled and a 125-page report based upon the work published in 1974. That publication continues to be of interest and requests are frequently received.

The effect of cattle ration on ammonia and hydrogen sulfide release from manure under various treatment schemes was investigated. Those results are included in this report.

A simple technique for identifying and measuring odorous compounds released from decomposing animal manures was sought. Solid absorbents were utilized in a variety of physical configurations. The successes and difficulties involved in this approach are recounted in Section IV.

A technique was needed to quantitatively measure the evolution of pertinent volatile compounds from specific surfaces associated with livestock production. A sampling box was designed and constructed to facilitate these measurements, which are summarized in this report.

SECTION IV

IDENTIFICATION OF AIRBORNE VOLATILES FROM A SWINE CONFINEMENT BUILDING USING POROUS POLYMERS

Odors associated with livestock production are generally related to manure; however, other odors from the animals themselves, dead animals, feed, or cleaning compounds and medicines may also contribute to the total atmospheric load.

Manure is a mixture of carbohydrates, fats, proteins, and their products and, as such, is a natural growth substrate for microorganisms. When manure undergoes decomposition as a result of microbial growth, volatile metabolic end products and their intermediates escape into the atmosphere. This is a prime source of odorous gases.

The main products in carbohydrate decomposition are acids, aldehydes, alcohols, ketones, carbon dioxide, methane, and water. Lipids are degraded into fatty acids and glycerol; the fatty acids break down into acetyl CoA, plus numerous smaller chained fatty acids, by beta-oxidation.

Proteins are hydrolyzed, cleaving the large molecules into amino acids. The amino acid decomposition can proceed in many ways depending on the organisms present and the environment. General reactions of amino acids include transamination, decarboxylation, racemization, and deamination. Many end products and intermediates are possible from amino acid decomposition including ammonia, hydrogen sulfide, acids, amines, mercaptans, sulfides, alcohols, aldehydes, ketones, esters, and alkyl ring structures.

The decomposition of manure is a stepwise process in which complex organic compounds are degraded into smaller molecules. Any combination of these is possible, and the observed odor represents the sum of the individual constituents. Research to identify the chemical compounds present has yielded about 45 compounds.[18] This list is undoubtedly incomplete, but does indicate the complexity of the problem.

Until recently, the measurement of volatile gases at extremely low concentration levels by the usual analytical methods has not been possible. However, recent developments in gas chromatography, mass spectrometry and methods of concentration and trapping have enabled researchers to separate and identify volatile compounds with relative ease.

BACKGROUND

Direct sampling was used at Cornell University by Burnett and Sobel[35] for identifying odors from poultry manure. The manure was filtered and centrifuged and the supernatant injected directly into gas chromatographs. The low concentration of compounds and the differences in concentrations of components from the liquid waste and the air make this method undesirable.

Merkel[36] used a salting-out technique to identify volatiles from swine manure. Anhydrous inorganic salts are added to a sample solution. The mixture is then shaken and heated to 60° C to release the dissolved gases. A sample of the headspace gas is then injected into the chromatograph. This method is easily and quickly conducted. Heating, however, may alter the normal conditions of the waste and the efficiency of the salting-out effect is undefined.

Selective absorption techniques involve contacting gases with specific reagents in which they are either soluble or form stable nonvolatile products. This concentration method was used to isolate alcohols, amines, carbonyls, and sulfur derivatives by Merkel *et al.*[22] Nitrogen was bubbled through a liquid manure sample and through a series of tubes containing the selected absorbents. The absorbed compounds were regenerated by various means and the expelled gases or distilled liquids were injected into the chromatograph. Some of the procedures are tedious and time consuming and may not be representative of those odors characteristic of the barn atmosphere.

Frus et al.[37] used a flask containing potassium dichromate-sulfuric acid solution to trap gases from a sample of manure. The gases from the manure were bubbled through the solution for chemical oxygen demand (COD) analysis. The COD technique was sensitive to individual organic gases believed to contribute to manure odor, but whether air COD is an overall measure of the level of organic gases is unknown.

Atmospheric ammonia has been measured by absorption in dilute acid. Ammonia absorption rates measured near feedlots were as much as 20 times greater than controls.[6] Ammonia was measured in a swine building atmosphere by absorbing in a 2% boric acid solution and then using Nessler's reagent to form a typical color whose intensity can be measured at a wavelength of 420 mμ.[10]

Absorption techniques have been tried in the detection of amines in the air from an animal chamber bubbled through 5% acetic acid. After 12-48 hours of aeration the liquid was subjected to chromatographic analysis.[11] Several amines were detected; however, the chromatographic identifications were questionable and results were not verified by an alternate method. The dilute acid trap technique has also been used to absorb basic compounds volatilized from cattle feedlots. The collected trappings were returned to the laboratory, filtered and evaporated to dryness at 50° C under vacuum. The resultant residue was taken up on a few milliliters of the dilute acid and analyzed for amines by gas chromatography.[38] Ten different amines were identified by this procedure.

The biggest drawback to direct sampling, salting-out and some selective absorption techniques is that the compounds identified may not be physiologically responsible for the odors detected by the nose, or for those which occur naturally in the vicinity of the barnyard, especially if samples are taken under laboratory conditions. These dilute acid traps at the feedlots and subsequent chromatographic analyses may not be detecting the same compounds as the nose. Further tests are needed to substantiate this.

Vapors can be condensed at various temperatures. This method was used in identifying the volatile components of skim milk.[39] The condensate from various traps may be injected into the chromatograph. However, transfer of the condensate requires special handling methods and has been little used.

Air can also be sampled by circulation through cold traps in dry ice or liquid gas;[36,40] however, this method is troublesome unless the moisture has been removed. Desiccants may be used to remove moisture, but they often absorb odor as well. The optimum system depends on the selection of an appropriate cryogen. For this purpose liquid oxygen has been found to be the best since it does not liquefy the major component of air and efficiently freezes out low molecular weight compounds.[40] Dry ice is readily available and the easiest to work with but does not retain hydrogen sulfide efficiently. Cryogenics may prove to be the most efficient method for collecting volatiles, though not the simplest.

Zlatkis et al.[41] adsorbed headspace gas of volatile organic metabolites in human urine by heating, then letting the vapors pass through a short water condenser, and finally onto a porous polymer trap. The trap was then inserted into a modified injector port of a gas chromatograph. Fifty-one compounds were identified by this method.

Miller[42] identified methyl mercaptan, dimethyl disulfide, dimethyl trisulfide, 3 methyl-1-butanol, and a trimethylamine produced in fish muscle by certain bacteria. The volatiles were collected on Porapak Q traps for subsequent condensation in a capillary column and then volatilized for gas chromatographic-mass spectral analysis. Porapak Q was also used to entrain any organic volatiles emitted from female fir beetles as a sexual attractant.[43]

A combination of selective absorption and headspace trapping was used by Hartung et al.[44] to identify carbonyl compounds in a swine building. Sample air was pulled through a column packed with silica gel impregnated with aqueous acidic DNPH solution. Carbonyl compounds in the air samples were converted to DNPHs (2,4-dinitrophenylhydrazones) and eluted from the column with hexane. The elute from the reaction column was evaporated to a small volume and spotted on thin layer chromatography plates.

MATERIALS AND METHODS

Air samples were taken from inside the Oregon State University swine barn from a platform 2.5 m above the floor.

The 150-175 swine in the barn were being fed a corn-based ration through the sampling period. The partially slotted floor building was washed completely once a week with

manure, wash water, and liquid manure from the under-floor storage pit going into an anaerobic lagoon about 50 m from the confinement area. The water from this pond is pumped out and used for crop irrigation.

Initial Traps

Volatile compounds were trapped on Porapak Q (80/100 mesh ethylvinylbenzenedivinylbenzene polymers) and Tenax GC (35/60 mesh 2,6-diphenyl p-phenylene oxide polymers) packed inside stainless steel traps 103 mm by 6 mm outside diameter (O.D.) by 3 mm inside diameter (I.D.). Air to be sampled was drawn through a glass manifold holding four traps for 24 hours using a small Dyna-Vac pump. The traps could then be run immediately or stored in refrigeration without any loss of volatiles. All sample traps were purged with nitrogen (30 ml/min) for one and a half hours. The traps were first heated to 55-60° C for one hour to remove traces of water and then reversed and reheated to remove the trapped volatiles. The traps were first heated to remove excess water because water interferes with the spectrum and is harmful to the ionizing tube in the mass spectrometer. Excessive water in the gas chromatograph has a tendency to broaden the peaks and run them together. The Porapak Q traps were then heated to 150-160° C for thirty minutes, while being purged with nitrogen, to transfer the entrained volatiles to an open tubular stainless steel trap 150 mm by 1.25 mm I.D. immersed in dry ice. The Tenax traps were heated to 200° C. The small cold traps were connected to the gas chromatograph by a modified inlet system. The cold traps were transferred to the mass spectrometer in dry ice and connected by a modified inlet system. In both instances the cold traps were heated with a heat gun that reaches 500° C to volatilize the entrained odor constituents.

Over 30 Swine Center samples were studied using the initial sampling traps. The technique involved a 24-hour sampling period and about four hours of sampling preparation and gas-liquid chromatography (GLC) separation. By using multiple traps several samples were simultaneously taken and/or stored for later analysis. The traps were purged for 24 hours with helium or nitrogen at 200° C before re-use.

Cold traps were checked in the lab for odor retention before being run on the chromatograph. After purging 103 mm traps loaded from both the Swine Barn and OSU campus into the open tubular stainless steel traps in dry ice, the cold traps were removed from the dry ice and heated to let the trapped volatiles escape into the atmosphere. The escaping volatiles were then smelled by several people in the lab to obtain a relative comparison of the two odors.

Revised Traps

In order to overcome the difficulties inherent in long packed columns as a volatile gas collection device, an alternate trap was devised. The new traps were constructed from 150 mesh stainless steel screen and silver soldered into 180 mm x 6 mm tubes. A small wire hook was soldered to one end. These tubes were cleaned with a brush and pipe cleaner inside and out with hot water, dried in an oven at 176° C for one-half hour, rinsed with dimethylchlorosilane and anhydrous methanol, and dried in an oven again at 176° C overnight. With proper cleaning, conditioning, and handling (no grease or direct contact with chemicals or sewage) tubes do not need this rigorous cleaning again. Dust is shaken or blown off with clean filtered air.

Using clean gloves or forceps to prevent contamination, the fabricated tubes were packed with 0.85 ± 0.05 grams of a 50:50 mix by volume of Tenax GC (60/80 mesh 2,6 diphenyl-p-phenylene oxide polymers) and Porapak Q (ethylvinylbenzene-divinyl benzene polymers) held in place with silane treated glass wool. Tubes thus filled are placed in pyrex sample tubes and plugged with teflon cylindrical septums.

Filled traps were placed in sample tubes and conditioned for 24 hours at 200° C in a co-distiller tube oven with a flow of purified nitrogen (O_2 and H_2O removed) at 30 ml/min. Conditioned traps sealed in glass sample tubes under purified nitrogen were transferred to the sampling site. Traps in glass tubes are either connected directly to manifold or vacuum pump for flow through sampling or are withdrawn from tubes with a wire hook and then placed on hoods inside plastic dust and water protective containers with clean gloves or forceps. A flow rate of 310 ml/min/trap (930 ml/min for a manifold holding three traps) was preset and checked at the site with a flow meter. Sample periods used were from 1 to 24 hours (18.6 to 446 liters of air) for pumped-in sampling. After sampling, traps were transferred to the laboratory in the plugged glass sample tubes.

Samples can be stored in sample tubes in a refrigerator at -5° C for several days without volatilization loss or noticeable contamination. Loaded traps were purged with helium at a flow rate of not more than 20 ml/min at a temperature of 150° C for 2 hours. If samples were to be analyzed by mass spectrograph, the small amounts of water present in the traps were removed by first purging the traps with purified nitrogen at 50° C for 1 hour. Volatiles were

collected in a 1-meter long 0.16-cm I.D. stainless steel capillary tube which had luer-lok syringe devices silver soldered to each end. This appartus was immersed in liquid nitrogen at -196° C and purged with helium. The outlets were equipped with miniert teflon shut-off valves with luer-lok attachment. When samples were collected, the valves were shut and plastic disposable 10-ml syringes filled with 8 ml of purified helium were attached to the inlets of four traps (3 for sample replicates and 1 for reference control). With syringes attached and valves shut, the traps were gas tight and could be pressurized for direct injection.

Pressurized direct injection on column was found to be the most efficient and gave the best resolution. Two chromatographic columns were used, one for amine separation and one for aliphatic acids separation. Dual column-detector set-up and settings were used for all analyses to remove column bleed or ghost peaks coming from the packings and stationary phases used at high temperatures.

Chromatography

The analyses were made on an F & M Model 402 gas chromatograph fitted with a dual flame ionization detector (FID), a Honeywell strip chart recorder, and a Hewlett-Packard 3370A integrator. A Beckman GC2A with a thermal detector was used to identify fixed gases. A Finnigan 1015C mass spectrometer in conjunction with a Varian Aerograph series 1440 GLC was used for mass spectral analysis.

The following chromatographic columns were used: a 1.83 m x 3.18 mm O.D. stainless steel tubing packed with a 5% Triton X305 coated on 100/120 mesh Chromosorb W; a 1.83 m x 3.18 mm O.D. stainless steel tube packed with 4% Carbowax 20 M + 0.8% KOH on Carbopack B; a capillary column 30.5 m x 0.75 mm I.D. stainless steel coated with 5% Ethylene Glycol Succinate (EGS); a 61 m x 0.75 mm I.D. capillary stainless steel column coated with 5% Triton X305; and a 153.8 m by 0.75 m I.D. capillary stainless steel column coated with 8% Carbowax 20M. Carrier gas flow rates were: 30 ml/min of helium for the 3.18 mm columns and 12-15 ml/min of helium for the capillary columns.

The columns used with the thermal detector were run isothermally at 40° C. The Carbopack B column was run isothermally at 90° C. The Carbowax capillary column was operated at 70° C for five minutes and then temperature programmed

to 150° C at 2° C/min. The Triton X305 capillary column was programmed to operate at 60° C for five minutes and raised to 150° C at 4° C/min and held. The EGS column was programmed to run at 110° C for four minutes and raised to 175° C at 4° C/min and held.

The 3.18-mm Porapak Q and Triton X305 columns were used with the thermal detector for free gas identification. The Triton X305 and Carbowax 20M capillary columns were used for general identification, the EGS column was used for free acids and the Carbopack B column was used for amines with the FID system.

Selective absorption was used to identify alcohols and carbonyls. Nitrogen was bubbled through a manure slurry in a three-liter flask and then into a collecting tube containing 25 ml of propylene glycol for absorbing alcohols. Any carbonyls absorbed were removed in carbon tetrachloride by successive steps of liquid extraction using the technique described by Suffis and Dean.[45] The solutions were distilled and injected into the gas chromatographs.

RESULTS AND DISCUSSION

Initial Traps

Table 1 shows the compounds identified, the traps and columns used, and the compounds' retention times. Many of the compounds were detected from more than one column, but for convenience, only listed once. There were two xylene isomers and several alkyl benzene isomers seen, hence the variation in retention times. This is in agreement with recent work done by Hammond et al.[46] using a similar trapping method with Chromosorb 102 as the collecting agent. The major organic constituents they collected were a series of alkylated aromatic hydrocarbons. Junk and Svec[47] also found many alkylated aromatic compounds plus the aliphatic acids hexanal and diacetal in air, using macroreticular resins as trapping materials.

Table 2 shows the compounds detected by selective absorption. The alcohols of greatest concentration were ethanol and butanol.

Table 1. VOLATILES IDENTIFIED FROM THE SWINE CENTER ATMOSPHERE USING THE TRAP METHOD AND COMBINED GLC MASS SPECTRAL ANALYSIS

Compound	Column[a]	Trap[b]	Retention time, seconds
2 butanol	T	T,P	75
Sec-butanol	T	T,P	81
Hexanal	T	T,P	97.5
Dimethyl disulfide (DMDS)	T	T,P	105
3 amino pyridine	T	T	120
n-butanol	T	T,P	140
Dimethyl trisulfide (DMTS)	T	T	450
Toluene	T	T,P	130
Xylenes	T	T,P	variable
Alkyl benzenes	T	T,P	variable
2,3 butanediol	T	T,P	170
Acetoin	T	T,P	180
Indane	T	T	345
Benzaldehyde	T	T,P	540
Me-naphthalene	T	T	1440
Diacetyl	C	T,P	240
2-octanone	C	T	210
Acetic acid	E	T,P	85
Propionic acid	E	T,P	115
N-butyric acid	E	T,P	150

Table 1 (continued). VOLATILES IDENTIFIED FROM THE SWINE CENTER ATMOSPHERE USING THE TRAP METHOD AND COMBINED GLC MASS SPECTRAL ANALYSIS

Compound	Column[a]	Trap[b]	Retention time, seconds
Valeric acid	E	T,P	210
Acetophenone	E	T	240
Caproic acid	E	T	275
Enanthic acid	E	T,P	300
Phenol	E	T,P	455
P-cresol	E	T,P	515
2-ethoxy-1-propanol	E	P	195
Et-phenol	E	P	580
Benzoic acid	E	P	645
Trimethyl amine (TMA)	B	T,P	75

[a]Column packings were:
- T - 5% Triton X305 on 100/120 mesh Chromosorb W
- C - 4% Carbowax 20M plus 0.8% KOH on Carbopack B
- E - 5% Ethylene glycol succinate on a stainless steel capillary column
- B - 8% Carbowax 20M on a stainless steel capillary column

[b]Trap packings were:
- T - Tenax GC
- P - Porapak Q

Table 2. COMPOUNDS DETECTED BY SELECTIVE ABSORPTION AND GLC

Compound	Column	Absorbent
Methanol	Triton	Propylene glycol
Ethanol	"	"
N-propanol	"	"
Iso-propanol	"	"
N-butanol	"	"
Iso-butanol	"	"
Formaldehyde	Carbowax	Carbon Tetrachloride
Acetaldehyde	"	"
Propionaldehyde	"	"
Iso-butyraldehyde	"	"
Heptaldehyde	"	"
Valeraldehyde	"	"
Octaldehyde	"	"
Decaldehyde	"	"

Table 3 shows the fixed gases found over a slurry of manure and water. Samples were taken in a gas tight syringe and injected directly into a column of a gas chromatograph equipped with a thermal detector. The Triton X305 column was used for sulfides and the Porapak Q column for methane, carbon dioxide, nitrous oxide, and nitrogen. No satisfactory column was found for the identification of ammonia; consequently, the Nessler's chemical test was used to confirm its presence. Carbon dioxide and methane were the most abundant gases found.

Traps were also set up outside Nash Hall on the OSU campus about one and a half miles from the Swine Center. Compounds identified on the Triton X305 column were very similar between the swine barn and the OSU campus. The alkyl benzene isomers were common to both locations, the only difference being that the concentrations were slightly higher from the Swine Center. However, the chromatographic results on the EGS column in similar locations were very different. The acid and phenolic compounds were absent from traps exposed on campus. The chromatographic results from the Carbopack B column for amines were surprising.

Table 3. FIXED GASES FOUND OVER A SLURRY OF MANURE AND WATER. GAS SAMPLES INJECTED DIRECTLY INTO CHROMATOGRAPH WITH A THERMAL DETECTOR

Gas	Column	Relative Retention Time
N_2	Porapak	30 seconds
CH_4	"	36 seconds
CO_2	"	85 seconds
H_2S	Triton	70 seconds
NH_3	Chemical absorption	

The campus chromatograph showed more peaks than the one of the Swine Center. Trimethylamine was the only compound positively identified and was most prominent in the Swine Center. Isopropyl amine was tentatively identified in both places. Dimethylamine was tentatively identified from the Swine Center and ethylamine from the campus sample.

By using a gas chromatograph equipped with an integrator, a quantitative check could be made on various compounds. One microliter of standard solution was injected into the gas chromatograph giving concentration readings in millivolts. By using the formula:

1 µl of known = 3500×10^3 mvolts (standard value)
X µl of unknown = integrator presentation in mvolts
X (3500×10^3) = (1 µl) (integrator presentation of unknown)

The amount of unknown was determined in microliters and was converted to micrograms. Approximately 720 liters of air passed through each Tenax trap and 500 liters through each Porapak Q trap in 24 hours; the fraction of unknown volatiles is given in µg/l (Table 4). Two traps were set up in a series to see if any acids were being missed. The chromatogram from the second trap was either negative or too small to measure for the acids. It was, however, found that not all of the aromatic hydrocarbons were retained on one trap alone. The values determined for acids by this method were well below threshold limit values.[18]

Table 4. CONCENTRATION OF VOLATILES IN 500 l OF SWINE CENTER AIR PASSED THROUGH PORAPAK Q TRAPS IN 24 HOURS

Compound	Date	Recorder Presentation in Millivolts	µg x 10^{-4}	µg/l x 10^{-7}
Acetic	5/03/74	1140	3.42	6.84
"	5/10/74	1333	4.0	8.0
"	5/17/74	3996	12.0	24.0
"	5/24/74	3990	12.0	24.0
Propionic	5/03/74	910	2.6	5.2
"	5/10/74	500	1.43	2.86
"	5/17/74	8738	25.0	50.0
"	5/24/74	8610	23.0	46.0
Butyric	5/03/74	1065	2.92	5.84
"	5/10/74	800	2.2	4.4
"	5/17/74	286	0.79	1.58
"	5/24/74	5660	17.3	34.6
Valeric	5/03/74	2663	7.17	14.34
"	5/10/74	3863	10.4	20.8
"	5/17/74	485	1.32	2.64
"	5/24/74	1700	4.6	9.2
Phenol	5/03/74	2942	9.0	18.0
"	5/10/74	5667	17.4	34.8
"	5/17/74	1910	5.46	10.93
"	5/24/74	5660	17.3	34.6
Cresol	5/03/74	3580	10.6	21.2
"	5/10/74	8863	26.0	52.0
"	5/17/74	7878	23.4	46.8
"	5/24/74	8610	23.0	46.0
DMDS	5/17/74	5040	15.2	30.4
"	5/24/74	2663	7.17	14.34
Xylene	5/17/74	6995	17.6	35.2
"	5/24/74	8738	25.0	50.0

Revised Traps

Problems previously encountered in multiple sampling -- handling of several traps simultaneously, reproducibility, resolution, and efficiency of gas chromatographic analysis -- have been reduced or eliminated. With a larger quantity of adsorbent in each trap, a greater number of volatiles are adsorbed in a shorter time period and theoretically reduce the possibility of selectivity.

The new holder for the adsorbent (made from stainless steel, 150-mesh screen silver soldered into a tube with wire hook at one end and plugged with silane treated glass wool) promises to be a simple way to trap air pollutants. When the traps were placed in volatile contaminated atmospheres, they trapped as many or more volatiles by adsorption than by forced pumping of air through them.

Changing the method of sample injection from indirect diversion through a sample loop to direct pressurized injection avoided disruption of carrier gas flow through the column, which gives an off-scale deflection on chart for up to 30 seconds while restabilization of instrument and column flow takes place. The pressurization of sample gives better resolution due to the recommended fast plug injection rather than the slower diffused injection from sample loops. The modified cold traps are used as syringes after warming with a heat gun to revolatilize the collected samples. The units are sealed at the outlets with miniert valves after collection. Then 10-ml plastic disposable syringes filled with 2-8 ml of helium are connected to the inlets via luer-loks. The plastic components of the system appear not to have introduced any plasticizer contaminants in high enough levels to be of any significance, as all properly conditioned blank traps run under the same conditions and sensitivities on the gas chromatograph showed only traces of air and water.

The short chain aliphatic primary amines (methyl, dimethyl, ethyl, isopropyl, and trimethyl) have been tentatively identified in animal house air as well as in countryside odor-free air by comparison with known amines, using a column specific for amine separation. None of the individual amines could be clearly identified as unique to individual types of animal house odors monitored (swine, dairy, and poultry). All reference controls of samples taken in odor-free air seven miles from the city limits of Corvallis, Oregon, and about eight miles from any animal feedlots show

identical peak patterns and comparable quantities of volatile material. Blank traps have always shown clean traces, so it appears that the odorous compounds are not being collected in sufficient amounts or are masked by the larger amounts of other organic compounds present in so-called "clean odor-free air."

SUMMARY

The main difference between the air of the Swine Center and OSU campus was the dimethyl disulfide (DMDS), the mixed acids, and the trimethylamine (TMA). All would result in a marked odor. DMDS and TMA have a putrid smell and the acids are pungent. The major organic constituents collected at both locations are alkylated aromatic hydrocarbons. Most hydrocarbons have a relatively high odor threshold and do not leave odors characteristic of swine rearing facilities. Exceptions are the naphthalene compounds, which have a mothball odor, and the cresols, which have a preservative smell.

Many of the compounds identified are well known flavor constituents in food such as diacetyl, butyric acid, and p-cresol, which occur in dairy products, and hexanal, a common constituent of vegetables and their fats.[48]

Both organic absorbents used, Porapak Q and Tenax, selectively retain those compounds having at least two-carbon atoms and are useful as adsorbents for volatile organic compounds. Most one-carbon compounds probably are not retained or may be lost during the water purge. Miller et al.,[42] however, did identify methyl mercaptan, a one-carbon compound produced from fish muscle by a bacteria, using a Porapak Q trap following a water purge of one hour at 55° C. Another method may be required in order to efficiently trap one-carbon compounds.

The large number and complexity of compounds of potential importance in odorous air account for the difficulty encountered in odor analysis. It also helps explain the variability in the detected odors commonly found in wastes. The objection to manure odors arises from the particular concentration and combination of volatiles present. The compounds found in the Swine Center were each individually below danger threshold for man; however, this does not mean that they are not an odor nuisance. Air in other confinements in which wastes are handled differently may have different odorous constituents.

The work with the modified traps was designed to find a simple means of using gas sampling and analysis of complex mixtures by gas chromatography to discover unique odorous indicator compounds which might allow quantitative and routine monitoring of odorous air associated with concentrations of animals. A major problem encountered was interference from other relatively nonodorous organic volatiles (carbonyls, alcohols, and aromatics) present in larger concentrations which must be removed for clear routine monitoring of the odorous volatiles. A method to selectively adsorb or desorb volatiles on traps is needed. Mixtures sometimes showing compounds that had retention times identical to amines or acids could not be confirmed by mass spectral analysis. Quantitation of individual compounds (peaks on the chromatogram) could not be made without reservation.

Total amounts of volatiles trapped were quantified and resulted in concentrations 2-3 magnitudes below perceptible concentrations of highly volatile and odorous compounds (trimethylamine-14.0 x 10^{-2} µg/l and ethyl seleno mercaptan-18.0 x 10^{-4} µg/l *vs.* highest *total* volatile concentration measured at 37.0 x 10^{-5} ml/l). Quantities were calculated using an internal standard of known quantity (1 µl amine mixture and 1 x 10^{-3} µl acid mixture).

Variations in temperature, humidity, wind velocity, and number and activity of animals from hour to hour make it difficult to correlate odor intensity with volatile profile and quantity. Since exchanges can occur on the adsorbent, short trapping periods are probably best. No patterns could be seen in longer exposures. Many times it was noted that the quantity of volatiles trapped would decrease after extended exposure.

SECTION V

EFFECT OF RATION FORMULATION ON THE EVOLUTION OF VOLATILE AMMONIA AND HYDROGEN SULFIDE FROM CATTLE MANURE

The nuisance complaints associated with animal production units are frequently due to odors. Considerable research effort has been directed toward developing waste management techniques and procedures for handling wastes after they have been produced. Only limited research has been directed toward modifying rations to control the odors associated with the subsequent wastes.

SUPPLEMENT WITH ESSENTIAL OILS

Background

Supplementing swine rations with Lactobacillus acidophilus, yeast activated charcoal, and sagebrush (5%) was shown to have no significant effect upon the olfactory evaluation of the wastes produced.[49,50] Research conducted at Colorado State University indicated that a beef feedlot ration supplemented with sagebrush at a rate of 0.5 to 1 kg/day-animal (1 to 2 lbs/day-animal) was effective in reducing feedlot odors.[51]

Methods

An experiment was designed to evaluate the effect of supplementing the rations of replacement heifers with two essential oils to determine their effects on the odors of the animal wastes. The materials tested were sagebrush and peppermint oil.

Three separate olfactory evaluations were conducted using a group of five Holstein replacement heifers. The heifers were maintained on a basal ration of barley and alfalfa hay mixed to form a complete ration (Table 5) to which two levels (1% and 1.5%) of ground mountain big sagebrush (Artemisia

Table 5. BASAL RATION OF HEIFERS DURING THE ESSENTIAL OIL SUPPLEMENTATION EXPERIMENT

Ingredient	Proportion
Barley	0.250
Chopped alfalfa	0.696
Cane molasses	0.050
Cottonseed meal	0.004

tridentata ssp. vaseyana form xericensis) and one level (0.25%) of peppermint oil were added. A control group of five replacement heifers was maintained on the basal ration during the experimental period. All rations were fed ad libitum with free access to trace mineralized salt and water.

Sagebrush was collected approximately 15 miles northeast of Bend, Oregon, in June of 1974. It was allowed to air dry to a moisture content of approximately 11%. The leaf portion was then ground in a Wiley mill equipped with a 1-mm screen. The ground sagebrush was frozen until the day it was added to the ration to reduce the loss of essential oils.

Peppermint oil was obtained from a mint grower located in the Willamette Valley. A gas-liquid chromatographic analysis of the peppermint oil indicated it to be: 49.6% menthol, 22.5% menthone, 6.6% menthyl acetate, 2.5% menthofuran, and a number of other components in lesser concentrations.

Urine and fecal samples were collected from the control and the supplemented groups on an individual animal basis. Fresh urine samples were collected from each animal by manually stimulating it to urinate, at which time approximately a 200-ml sample was collected. Fecal samples were collected at the same time by removing a sample directly from the rectum of each animal. These samples were then returned to the laboratory where a composite sample was made for both the urine and feces from each group.

Samples containing 50 g of feces and 50 g of urine from the composite samples were mixed in 300-ml Erlenmeyer flasks and incubated at 30° C for 24 hours prior to evaluation by an olfactory panel. The samples were removed from the water bath, dried, wrapped in paper, and allowed to stand at ambient temperature for approximately 30 minutes prior to evaluation. The size of the olfactory panel varied from 13 to 30 members for each of the duplicate evaluations of the various treatments.

The samples were evaluated using a trianglar testing procedure in which two of the samples were duplicated; this procedure is similar to the olfactory evaluation methods reported by Amerine.[52,53,54] The rating scale ranged from 0 to 15, with 15 the most offensive and 0 the least offensive. Samples were also ranked by offensiveness with the value of 1 given to the most offensive and 3 to the least offensive.

Results and Discussion

Comparisons were only made between samples that were evaluated by an individual panelist at one given time. The means and standard error of the means were calculated for the rating and ranking values that were determined in this manner and are given in Table 6.

Addition of sagebrush to the ration at the 1% and 1.5% levels had no detectable effect upon ($P > .10$) the subsequent olfactory evaluation of the manure.

The peppermint supplemented ration was evaluated with and without the urine fraction, with an equal amount of distilled water replacing the urine. The samples containing both fecal and urine fractions were found to be less offensive ($P < .05$) than the basal plus urine. When the fecal waste from the peppermint supplemented animals was combined with distilled water and compared to the basal plus urine, a reduction in offensiveness was not observed ($P > .05$). This indicates that the urine fraction was responsible for the change in the offensiveness associated with the waste produced when peppermint was added to the ration. A characteristic menthol odor was noted to be present in the urine obtained from the peppermint supplemented animals. It apparently partially masked the normal odor of urine.

Table 6. SUMMARY OF DATA FROM THE OLFACTORY EVALUATION OF MANURE SAMPLES FROM ANIMALS FED RATIONS TO WHICH SAGEBRUSH AND PEPPERMINT OIL HAD BEEN ADDED

Ration	Rating	Std Error Mean	Ranking	Std Error Mean
1% Sagebrush				
Sagebrush 1%	7.87[a]	1.008	2.13[a]	0.192
Basal	7.87[a]	1.241	1.93[a]	0.228
Basal	8.67[a]	1.058	1.67[a]	0.188
1.5% Sagebrush				
Basal	6.62[a]	0.605	2.07[a]	0.239
Sagebrush 1.5%	7.46[a]	1.163	1.77[a]	0.231
Sagebrush 1.5%	7.15[a]	0.799	1.461[a]	0.215
0.25% Peppermint feces only				
Peppermint 0.25%	8.5[a]	1.108	1.6[a]	0.221
Peppermint 0.25%	6.9[a]	1.005	2.2[a]	0.30
Basal	7.4[a]	1.284	2.0[a]	0.30
0.25% Peppermint				
Peppermint 0.25%	6.00[a]	0.697	2.65[a]	0.170
Basal	10.65[b]	0.702	1.53[b]	0.151
Basal	9.68[b]	0.920	0.50[b]	0.158

[a,b] Means in each column with different superscript letters are significantly different ($P < .05$).

AMMONIA RELEASE AND OLFACTORY EVALUATION AS A FUNCTION OF FECES, URINE AND WATER RATIOS

Methods

Feces and urine samples were collected from each of five Holstein replacement heifers being fed a ration of barley and alfalfa hay. The composition of the ration is given in Table 5.

The procedure for urine and feces collection is the same as outlined in the previous trial. The collected urine and feces were then returned to the laboratory and the following samples were prepared immediately from a composite sample of urine and feces: 100 g urine; 50 g feces + 50 g water; 50 g feces + 50 g urine; and 25 g feces + 75 g water. Similar samples were prepared for each of the subsequent evaluations. The samples were allowed to incubate in a 30° C water bath for 24 hours prior to evaluation by an olfactory panel and presented to the olfactory panel for evaluation as described earlier.

The rating was based on a scale of 0 to 15, with 15 the most offensive and 0 the least offensive. An example of the judging form used is shown in Figure 1. Panels ranged in size from 19 to 29 members.

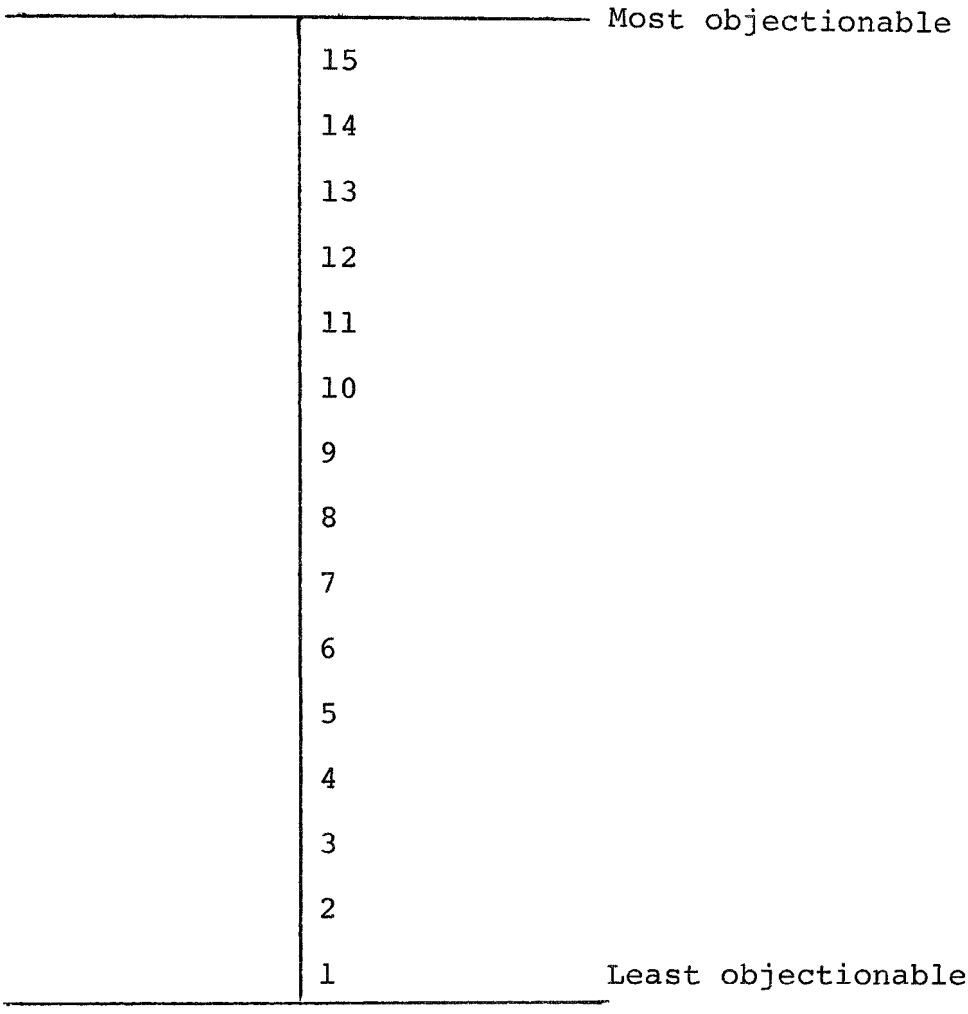
Rates of ammonia release for each of the various samples were determined just prior to presentation to the olfactory panel for evaluation. The trapping apparatus used is shown in Figure 2. A series of two dilute HCl (1:15 dilution with water) traps were used to trap the evolving ammonia. The head space gases were replaced at the rate of 0.5 l/min and ammonia quantities determined using the Nesslerization method.[55] The results of the olfactory rating and ranking evaluations were correlated with the ammonia release rates to determine the relationship between these measurements.

Results and Discussion

The initial numerical rating and ranking values for relative offensiveness were not found to be noticeably different ($P > .10$) for the samples evaluated (Table 7). This would indicate that the relative portions of feces, urine, and water of the samples have little effect upon the initial release of odorous compounds.

The correlation coefficients for the various interactions are given in Table 8. The numerical ratings were not found to be correlated ($P > .10$) with the fecal, urine, or water content of the samples. The rankings of the samples were not correlated ($P > .10$) with the water content. However, a negative correlation ($P < .05$) for the fecal content and a positive correlation ($P < .05$) for the urine with respect to ranking was observed.

Rating Scale



Sample Numbers _____ _____ _____

Name _____

Date _____

Figure 1. Rating form for olfactory evaluation of manure odors

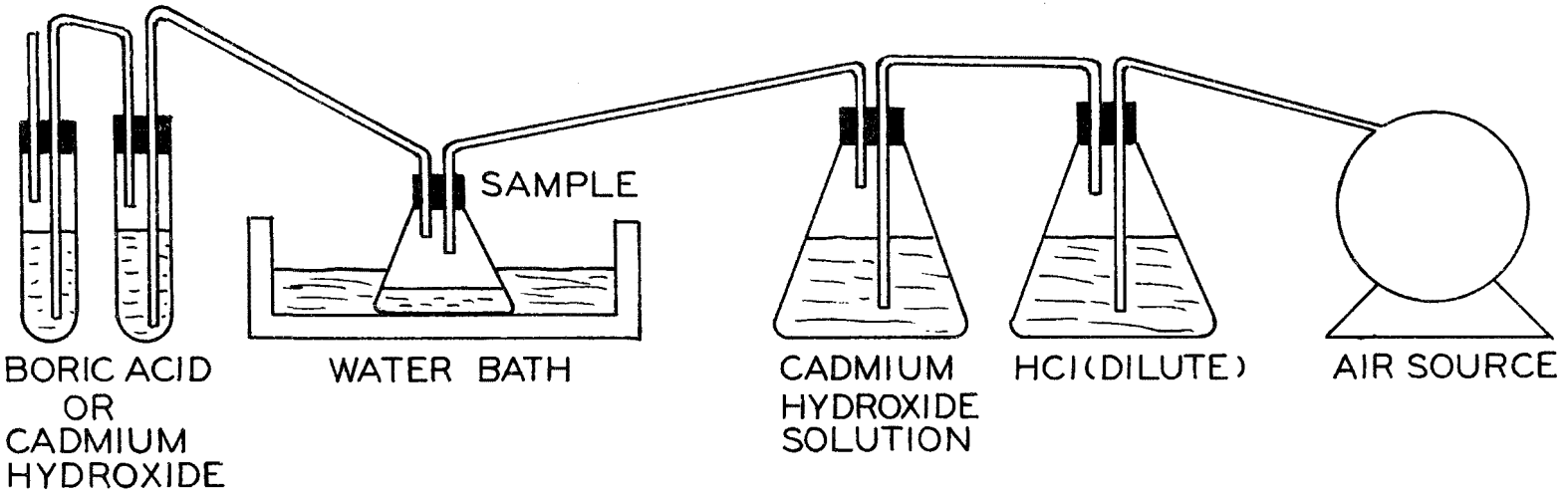


Figure 2. Apparatus for trapping evolved ammonia and hydrogen sulfide.

Table 7. OLFACTORY EVALUATION AND THE AMMONIA RELEASE RATE OF VARIOUS COMBINATIONS OF FECES, URINE, AND WATER

Item	Sample			
	1.0 urine	0.5 feces 0.5 urine	0.5 feces 0.5 water	0.25 feces 0.75 water
Offensiveness				
Mean rating[1,2]	5.21[a]	3.95[a]	4.13[a]	4.04[a]
Std. error	0.48	0.51	0.44	0.43
Mean ranking[1,3]	2.47[a]	1.84[a]	1.83[a]	1.77[a]
Std. error	0.21	0.17	0.16	0.13
Ammonia evolution				
Mean rate[1]	276.7[a]	116.9[a]	8.26[b]	0.18[b]
Std. error	68.3	32.0	3.91	0.08

[1]Means in each row with different superscript letters are significantly different ($P < .05$).
[2]Rating on a scale of 1-15, 15 most offensive.
[3]Ranking of 3 samples, 3 most offensive.

Table 8. CORRELATIONS BETWEEN WATER, FECES, URINE CONTENT AND RATING, RANKING AND AMMONIA RELEASE RATE FOR MANURE SAMPLES INCUBATED FOR 24 HOURS AT 30° C

	Correlation Coefficients	P
Rating Number		
Water	-0.045	NS
Fecal	-0.154	NS
Urine	0.109	NS
Ranking Number		
Water	-0.135	NS
Fecal	-0.234	.05
Urine	0.217	.05
Ammonia Release Rate		
Water	-0.498	.01
Fecal	-0.407	.01
Urine	0.584	.01

The ammonia release rates were positively correlated ($P < .01$) with the urine content of the samples. The water and fecal content were negatively correlated ($P < .01$) with the initial release of ammonia. The samples containing urine were observed to generate more ammonia ($P < .05$) than the samples containing only feces and water.

EFFECT OF THE GRAIN SOURCE ON THE VOLATILIZATION OF AMMONIA AND HYDROGEN SULFIDE

Methods

Twelve Holstein replacement heifers were divided into three groups of four animals each. These animals were then fed rations based on three different grain sources (milo, corn, and barley) at three concentrations (25%, 50%, 75%) in a complete ration (Table 9). The animals were housed in the beef confinement units at Oregon State University during the experimental period.

Table 9. COMPOSITION OF RATIONS[1] FED REPLACEMENT HEIFERS TO DETERMINE THE EFFECT OF GRAIN SOURCE ON AMMONIA AND HYDROGEN SULFIDE GENERATION

	25% Grain	50% Grain	75% Grain
Barley			
Barley	250	500	750
Alfalfa (chopped)	696	424	155
Molasses, cane	50	50	50
Cottonseed, meal	4	26	45
Corn (rolled)	250	500	750
Alfalfa (chopped)	695	416	142
Molasses, cane	50	50	50
Cottonseed, meal	5	34	58
Milo (rolled)	250	500	750
Alfalfa (chopped)	696	424	155
Molasses, cane	50	50	50
Cottonseed, meal	4	26	45

[1]Rations calculated to be isonitrogenous on DP basis (DP = 9.6%)

Fresh fecal samples were collected from the concrete floors of each of the respective pens and urine samples were collected from individual animals at random. Feces and urine from the same groups were then mixed in 300-ml Erlenmeyer flasks (50 g urine + 50 g feces) and incubated at 33° C in a water bath, and the volatilized ammonia and hydrogen sulfide were trapped. Duplicate samples were prepared for each of the feces and urine combinations.

The samples were allowed to equilibrate for a period of 30 minutes in the water bath prior to being connected to their respective traps. During this time the head space gases were replaced at the rate of 0.33 l/min. At the end of the flushing period the samples were connected to either the ammonia or hydrogen sulfide traps.

The ammonia traps consisted of a series of two 25 x 200 mm test tubes containing 25 ml of boric acid (4% w/v) through which the displaced head space gases were bubbled at a rate of 0.33 l/min for a period of 22 hours. The boric acid traps were then combined and the ammonia content determined using the Nesslerization method.[55] The apparatus used in trapping the ammonia is shown in Figure 2.

Hydrogen sulfide was trapped by bubbling the displaced head space gases through a series of two 25- x 200-mm test tubes, each containing 25 ml of $Cd(OH)_2$ [2.7 g $Cd(OH)_2$/l, pH 9.5]. The tubes were painted black to prevent photodecomposition of the hydrogen sulfide. The hydrogen sulfide content of the samples was determined using the methylene blue method.[56]

Results and Discussion

The hydrogen sulfide evolution rates were similar ($P > .10$) between samples from cattle fed the corn, barley, and milo based rations (Table 10). The hydrogen sulfide evolution rates from the 25% and 50% levels of supplementation of the three grains were not found to differ ($P > .05$). The 75% level of supplementation for each of the grains was similar with each of them being higher ($P < .05$) than their respective 25% and 50% levels.

Table 10. EFFECT OF GRAIN SOURCE AND LEVEL OF SUPPLEMENTATION ON HYDROGEN SULFIDE GENERATION RATE BY MIXTURE OF 50 g FECES AND 50 g URINE FROM REPLACEMENT HOLSTEIN HEIFERS FED VARIOUS GRAIN-BASED RATIONS

Corn	Mean[1]	Barley	Mean[1]	Milo	Mean[1]
25%	0.390[a]	25%	0.616[a]	25%	0.498[a]
50%	1.121[a]	50%	0.653[a]	50%	0.741[a]
75%	4.96[b]	75%	4.870[b]	75%	4.531[b]

[1]Mean values expressed as µg/hr.

[a,b]Means with different superscripts in the same columns are different ($P < .05$).

Ammonia was evolved at a much faster rate (approximately 1,000 to 10,000 times) than hydrogen sulfide. Ammonia evolution rates were not different ($P > .05$) among the different levels of supplementation and the grains, with the exception of the 75% milo and the three barley based rations ($P < .05$), as shown in Table 11.

Table 11. EFFECT OF GRAIN SOURCE AND LEVEL OF SUPPLEMENTATION ON AMMONIA EVOLUTION RATE BY MIXTURE OF 50 g FECES AND 50 g URINE FROM REPLACEMENT HOLSTEIN HEIFERS FED VARIOUS GRAIN-BASED RATIONS

	Mean[1]	Standard Error of Mean
Corn		
25%	3037.72[ab]	424.33
50%	3467.41[ab]	401.46
75%	3189.17[ab]	269.26
Barley		
25%	3107.16[a]	527.89
50%	3921.13[a]	470.27
75%	3833.02[a]	322.23
Milo		
25%	2925.89[ab]	543.23
50%	2855.32[ab]	344.45
75%	2325.44[b]	233.24

[1]Mean value expressed as µg/hr.

[a,b]Means with common superscripts are not significantly different ($P < .05$).

RELATIONSHIP BETWEEN GRAIN SOURCE AND pH OF ANIMAL WASTE

Methods

Three different grain-based rations (corn, milo, and barley) were fed to groups of five Holstein replacement heifers. Each grain was fed at the 75% level. The composition of the rations is given in Table 9. After an initial ten-day adjustment period, feces and urine were collected from each of the groups. Samples containing 50 g of urine and 50 g of feces were prepared from each group. A total of 28 samples was evaluated for each of the groups at the rate of two samples/day.

The samples were maintained in a water bath at 30° C. The apparatus and procedures used to trap the ammonia are described in the previous section. The boric acid traps were connected for a period of 22 hours, during which time head space gases were replaced at the rate of 0.33 l/min. After the incubation period the pH of the samples was determined using a Fisher Accumet Model 310 pH meter. The ammonia content of the combined double traps was determined using the method of Bremner and Kenney.[57]

Results and Discussion

Results indicated that the grain source did alter the pH of the waste that was produced, and there was a significant correlation between the pH of the waste and the evolution rate of ammonia as shown in Table 12. There was a difference ($P < .05$) between the pH of the samples for each of the grains as indicated in Table 13, but differences in ammonia release were not ($P > .05$) noted between grains in the pooled data.

Table 12. CORRELATIONS BETWEEN pH AND AMMONIA EVOLUTION RATES FOR CORN, BARLEY, AND MILO RATIONS

Sample	Correlation between pH and ammonia evolution rate	P[1]
Corn	0.5022	.01
Milo	0.4204	.05
Barley	0.3838	.05

[1]Correlation coefficients are significantly different at the probability level listed.

Table 13. pH AND AMMONIA EVOLUTION RATES FROM FECES AND URINE MIXTURES FROM CORN, BARLEY, AND MILO RATIONS

Sample	Average pH	Std error of mean	Ave. ammonia evolution rate, mg/hr	Std error of mean
Corn	7.21[a]	.0634	2731.96[a]	304.72
Milo	6.78[b]	.0839	2602.03[a]	302.56
Barley	7.65[c]	.0871	3182.48[a]	241.63

[a,b,c]Means in the same column with different superscripts differ significantly ($P < .05$).

EFFECT OF MOISTURE ON THE VOLATILIZATION OF AMMONIA AND AMINES

Methods

Samples of feces were collected from a group of Holstein replacement heifers. The samples were then combined and subdivided into two portions; one was immediately frozen and the dry matter (DM) content was determined (100° C for 24 hours) on the other (14.8% DM). A fresh urine sample was then collected which was later determined to have a nitrogen content of 0.28%. The fresh urine and feces with DM of 14.8% were then mixed to form duplicate samples containing 95% and 99% moisture. The 95% moisture samples contained 50 g feces, 24 g urine, and 75 g water. The 99% moisture samples contained 50 g feces, 24 g urine, and 670 g water.

The samples were maintained in a water bath at 37° C for the 14-day experimental period. The total volumes were adjusted to their original volume on a daily basis by adding distilled water to replace evaporative losses.

The apparatus used for trapping the ammonia and amines is shown in Figure 3. Air from a laboratory air outlet was bubbled through a dilute HCl trap (1:15 conc. HCl to distilled water) before displacing the head space gases of the samples to remove any ammonia or amines that might be

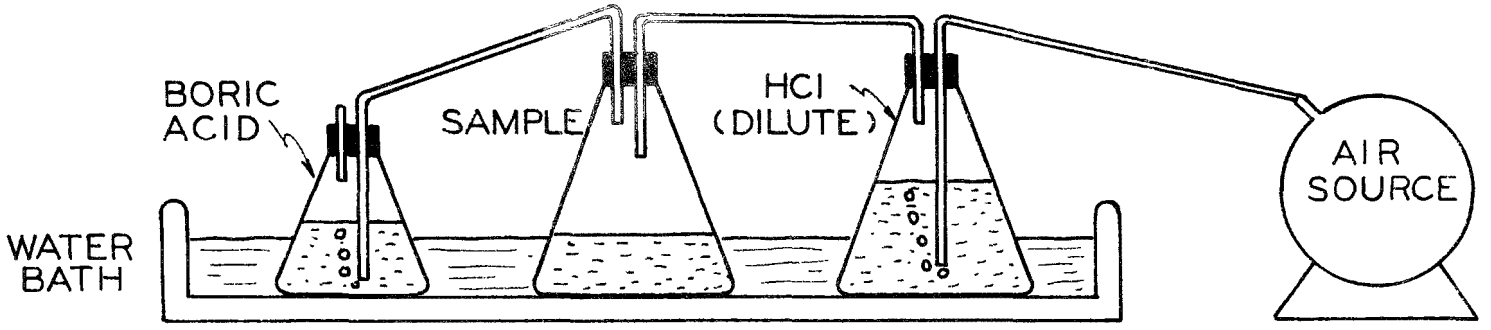


Figure 3. Apparatus used to trap evolved ammonia and amines.

present. The head space gas of each of the samples was replaced at the rate of 0.33 to 0.4 l/min and then bubbled through a boric acid trap to remove the ammonia and amines. Traps were changed every 24 hours. Total volatile nitrogen and amine evolution rate were then determined for each sample.

The method described by Ekladius and King[58] using butylamine as a standard was used for the amine assay. The total nitrogen was determined by the semi-micro-Kjeldahl method of Bremner and Kenney[57] and expressed as ammonia.

Results and Discussion

Amines were evolved at the rates of 17.86 and 16.41 µg/day for the 95% and 99% moisture levels, respectively, which was 0.11% of the total nitrogen volatilized. Ammonia evolution rates were 15.15 and 13.20 µg/day for the 95% and 99% moisture samples, respectively. The ammonia and amine evolution rates had a significant negative correlation with the length of storage (Table 14) and ammonia and amine release rates were found to be positively correlated ($P < .01$) to each other. This would support the idea expressed by Merkel *et al.*[22] that ammonia was a precursor of amines.

EFFECT OF FECES, URINE, WATER, AND STORAGE PERIOD ON AMMONIA RELEASE

Methods

Fresh feces and urine were collected, as described earlier, from Holstein replacement heifers which were fed a base ration containing 25% barley and 75% alfalfa hay (Table 8). A composite was made for both the urine and feces. Duplicates of the following samples were then prepared: 100% feces; 100% urine; 50% feces + 50% urine; 75% feces + 25% urine; 75% feces + 25% water; 50% feces + 50% water; 25% feces + 75% water; and 5% feces + 95% water; all samples contained 100 g of material.

The samples were maintained in a water bath at 30° C for a period of 25 days. The trapping procedure was the same as described previously. The head space gases were replaced at the rate of 0.33 l/min and trapped for a period of 3 hours; two trapping periods were carried out each day on each of the samples. The ammonia evolution rate of the samples was then determined using the method of Bremner and Kenney[57] and expressed as ammonia.

Table 14. CORRELATIONS BETWEEN MEAN AMMONIA AND AMINE EVOLUTION RATES AND STORAGE PERIOD

Correlation			
Evolution rate (10^{-6} g/hr)	Other Variable	Correlation coefficient	P[1]
Amine 95% moisture	Storage time	-0.771	0.01
Amine 99% moisture	Storage time	-0.538	0.05
Ammonia 95% moisture	Storage time	-0.727	0.01
Ammonia 99% moisture	Storage time	-0.783	0.01
Ammonia 95% moisture	Amine evolution	0.903	0.01
Ammonia 99% moisture	Amine evolution	0.822	0.01

[1]Correlation coefficients are significant at the probability listed.

Results and Discussion

Average ammonia evolution rates for the various samples are given in Table 15. Ammonia was evolved at a faster rate from samples containing urine ($P < .05$) than the samples containing only feces and water.

Correlation coefficients between the ammonia release rates and length of storage for the various samples are given in Table 16. The samples containing feces only and feces plus water were found to be positively correlated ($P < .01$) with the time of storage except for the 5% feces + 95% water samples.

Table 15. EFFECTS OF VARIOUS LEVELS OF FECES, URINE AND WATER ON AVERAGE AMMONIA EVOLUTION RATES (µg/hr)

Sample	Average Ammonia evolution rate, µg/hr	Standard Error of Mean
100% Feces	3.15[a]	0.92
100% Urine	426.35[b]	90.39
50% Feces 50% Urine	119.43[c]	10.69
75% Feces 25% Urine	15.64[a]	4.96
75% Feces 25% Water	3.42[a]	0.79
50% Feces 50% Water	6.61[a]	1.25
25% Feces 75% Water	9.71[a]	1.45
5% Feces 95% Water	2.25[a]	0.87

[a,b,c]Means with different superscripts are different ($P < .05$).

Samples containing only urine were observed to have a rapid release of ammonia between the 2nd and 5th day of storage as shown in Figure 4. The feces plus water samples showed no rapid initial release of ammonia but increased as the storage period increased. The combination of feces and urine samples showed a rapid initial release of ammonia, then a decrease at day 5 until day 15, and then a gradual increase continuing until the end of the 25-day period.

Table 16. CORRELATIONS BETWEEN AVERAGE AMMONIA EVOLUTION RATE AND LENGTH OF STORAGE

Sample	Correlation Coefficient[1]	P[2]
100% Feces	0.572	.01
100% Urine	-0.192	NS
50% Feces 50% Urine	-0.152	NS
75% Feces 25% Urine	-0.680	.01
75% Feces 25% Water	0.635	.01
50% Feces 50% Water	0.503	.01
25% Feces 75% Water	0.636	.01
5% Feces 95% Water	-0.134	NS

[1]Calculated on the ammonia evolution rate vs the number of days on trial.
[2]Correlation coefficients are significantly different at the probability level listed.

Urine was found to be primarily responsible for the initial release of ammonia; feces had little effect. Approximately 100 times more ammonia was evoluted per gram from urine than from feces. The fecal material was found to increase the amount of ammonia released with increased time, but feces only accounted for a small portion of the total ammonia released. The results would indicate that urea is hydrolyzed more rapidly to ammonia than fecal proteins, and that urinary urea plays an important role in the volatilization of ammonia from animal wastes.

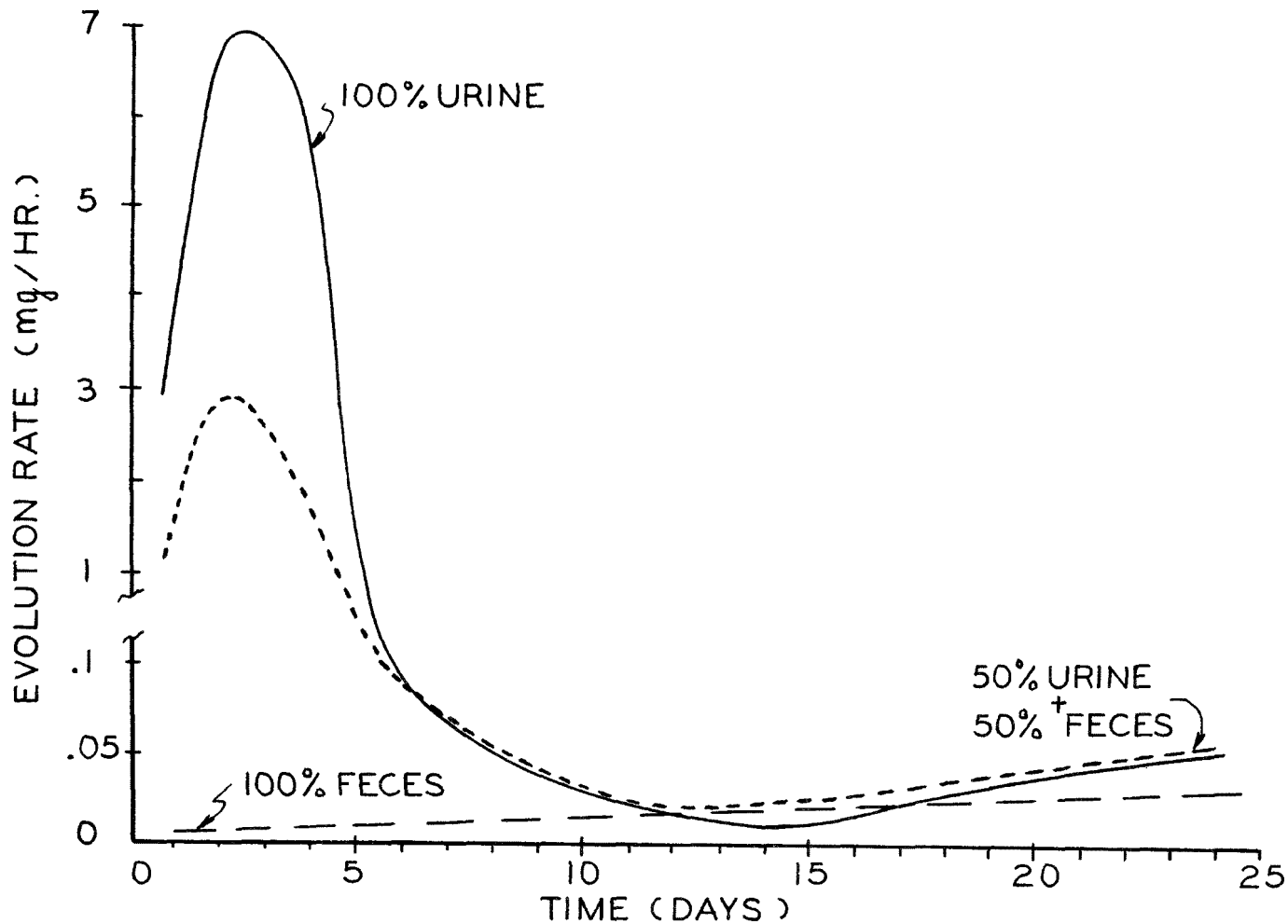


Figure 4. Ammonia evolution rate for urine, feces, and combination as a function of time.

EFFECT OF VARIOUS ANIMAL WASTE CHARACTERISTICS ON THE EVOLUTION OF AMMONIA AND VOLATILE NITROGEN GASES

Methods

Two groups of five Holstein replacement heifers were fed barley-based rations that contained three levels of barley (25%, 50%, 75%) formulated into complete rations (Table 8). The groups were started on the 25% ration, then changed to the 50%, and then to the 75%; each ration was fed ad libitum for a period of 15 days.

Urine and feces collected from each of the individual animals were combined (50 g of urine + 50 g of feces) and placed in a 300-ml Erlenmeyer flask and mixed thoroughly. These samples were placed in a water bath maintained at 30° C. The trapping procedure described previously was used. The ammonia released from the samples was trapped for a period of 3 hours.

The following analyses were performed: dry matter and crude protein content of the feces; specific gravity and urea content of the urine; and ammonia and total volatile nitrogen evolved. The dry matter content was determined by drying a fecal sample for a period of 24 hours at 100° C. The crude protein was determined by using the micro-Kjeldahl method.[57] The ammonia was determined by taking a 10-ml portion of the combined boric acid traps for each of the samples and using the micro-Kjeldahl method starting with the distillation step. Total volatile nitrogen (expressed as ammonia) was determined by taking a 5-ml aliquot of the boric acid trap and using the procedure as described for crude protein. The Hycel urea nitrogen method[59] was used to measure the urea content of the urine samples. The urinometer was used to measure the specific gravity of the urine samples.

Results and Discussion

The feeding trial was divided into five periods: 25% barley; transition period between 25% and 50% barley; 50% barley; transition period between 50% and 75% barley; and the 75% level. The means and standard error of the means are given for each of these periods in Tables 17, 18, and 19. The correlations between the variables and total volatile nitrogen evolution rates are given in Table 20. The dry matter and crude protein content of the samples were found to have no effect ($P > .10$) on the initial rate of ammonia release.

Table 17. RESULTS OF FECAL MATTER ANALYSES FOR TEN HEIFERS FED RATIONS OF 25, 50, and 75 PERCENT BARLEY

	Dry Matter		Crude Protein	
Percent barley	Mean percent	Standard error	Mean percent	Standard error
25	18.95	0.25	10.28	0.339
Transition 25-50	19.34	0.269	9.47	0.35
50	20.0	0.27	10.8	0.58
Transition 50-75	21.38	0.36	11.08	0.35
75	20.15	0.80	11.01	0.55

The ammonia and total volatile nitrogen evolution rates were highly correlated ($P < .01$) as determined by analysis of the boric acid traps. Urea content of the urine was related to the ammonia evolution rate ($P < .01$). The urea content of the urine was found to be correlated ($P < .01$) with the specific gravity values of the urine. This would explain why the specific gravity was correlated ($P < .01$) with the ammonia evolution rates for the samples.

SUMMARY

The olfactory evaluation of the waste produced by animals fed essential oils showed that the offensiveness of odors associated with fresh waste can be modified with the addition of an essential oil source. The addition of peppermint oil (0.25% of the diet) significantly reduced the relative offensiveness associated with the waste. This modification seemed to be a masking effect directly related to compounds excreted in the urine; it was not associated with the feces. Sagebrush supplemented at the 1% and 1.5% levels did not show any alteration of the olfactory evaluation. These results do not agree with the Colorado work, but the levels of supplementation were lower and the concentrations of essential oils in the sagebrush varieties used may have been different.

Table 18. AMMONIA AND TOTAL VOLATILE NITROGEN EVOLUTION RATES FOR MANURE SAMPLES FROM TEN HEIFERS FED RATIONS OF 25, 50, and 75 PERCENT BARLEY

Percent barley	Ammonia evolution rate		Total volatile nitrogen evolution rate	
	Mean 10^{-6} g/hr	Standard error	Mean 10^{-6} g/hr	Standard error
25	8.14	1.06	9.9	0.57
Transition 25-50	10.9	0.99	11.09	0.91
50	14.62	1.03	15.93	1.00
Transition 50-75	16.25	1.39	17.85	1.53
75	10.06	1.86	10.43	0.64

Table 19. RESULTS OF URINE ANALYSES FOR TEN HEIFERS FED RATIONS OF 25, 50, and 75 PERCENT BARLEY

	Urea content		Specific gravity	
Percent barley	Mean mg/l	Standard error	Mean	Standard error
25	848.9	46.5	1.032	0.00122
Transition 25-50	801.6	85.9	1.023	0.00184
50	737.7	49.9	1.028	0.00127
Transition 50-75	793	48.4	1.024	0.00129
75	896	177	1.025	0.00399

The results indicate that the cereal grain source and level in a ration does affect the initial volatilization of hydrogen sulfide and volatile nitrogenous gases. The primary effect of the grain source and level seems related to the pH of the wastes produced, which in turn affects the subsequent release of basic volatile nitrogenous gases. The ammonia release rate was found to be approximately 1,000 times greater than the hydrogen sulfide release rate at the 75% level of grain supplementation and 10,000 times greater at the 25% and 50% levels. This change in the relative amounts of hydrogen sulfide and ammonia was thought to be due to changes in the pH of the wastes.

The three different cereal grains evaluated were responsible for some pH differences. The waste produced from the milo-based ration (75% of the diet) was found to have a significantly lower pH than that from the barley or corn fed animals. This is important with respect to ammonia release because there is a direct relationship between ammonia release rate and pH.

Table 20. CORRELATIONS BETWEEN AMMONIA EVOLUTION RATES AND UREA, CRUDE PROTEIN, DRY MATTER, TOTAL VOLATILE NITROGEN AND SPECIFIC GRAVITY OF URINE SAMPLES AND BETWEEN UREA CONTENT AND SPECIFIC GRAVITY OF URINE

	Correlation coefficient	P[1]
Correlation between ammonia evolution rate and		
Dry matter content of feces	0.0159	NS
Crude protein content of feces	0.0081	NS
Total volatile nitrogen evolution rate	0.8784	.01
Urea content of urine	0.3123	.01
Specific gravity of urine	0.2700	.01
Urea content of urine		
Specific gravity of urine	0.2659	.01

[1]Correlation coefficients are significantly different at the probability level listed.

The addition of water to manure was found to reduce the evolution rate of ammonia and amines during the initial storage period. This was attributed to the capacity of water to absorb ammonia and reduce its volatilization rate. The ammonia evolution rate was negatively correlated with length of storage period for urine fecal matter mixtures. This indicates that major nitrogen enrichment of the atmosphere would occur during the first phase of the storage period.

The major contributor to the evolved ammonia is the urea content of the waste. Approximately 100 times more ammonia was evoluted per gram from urine than from feces. The evolution of ammonia from urine was rapid, while the feces showed a more prolonged release, accounting for a small portion of the total ammonia volatilized from the waste.

Of the variables measured, it was found that urea, specific gravity, and moisture content of the waste were the most highly correlated with volatilization of nitrogenous gases.

The modification of bovine rations has shown that changes in waste characteristics can be produced. Further research is needed to determine how practical this type of approach would be in controlling the volatilization of gases and odors from bovine confinement production units.

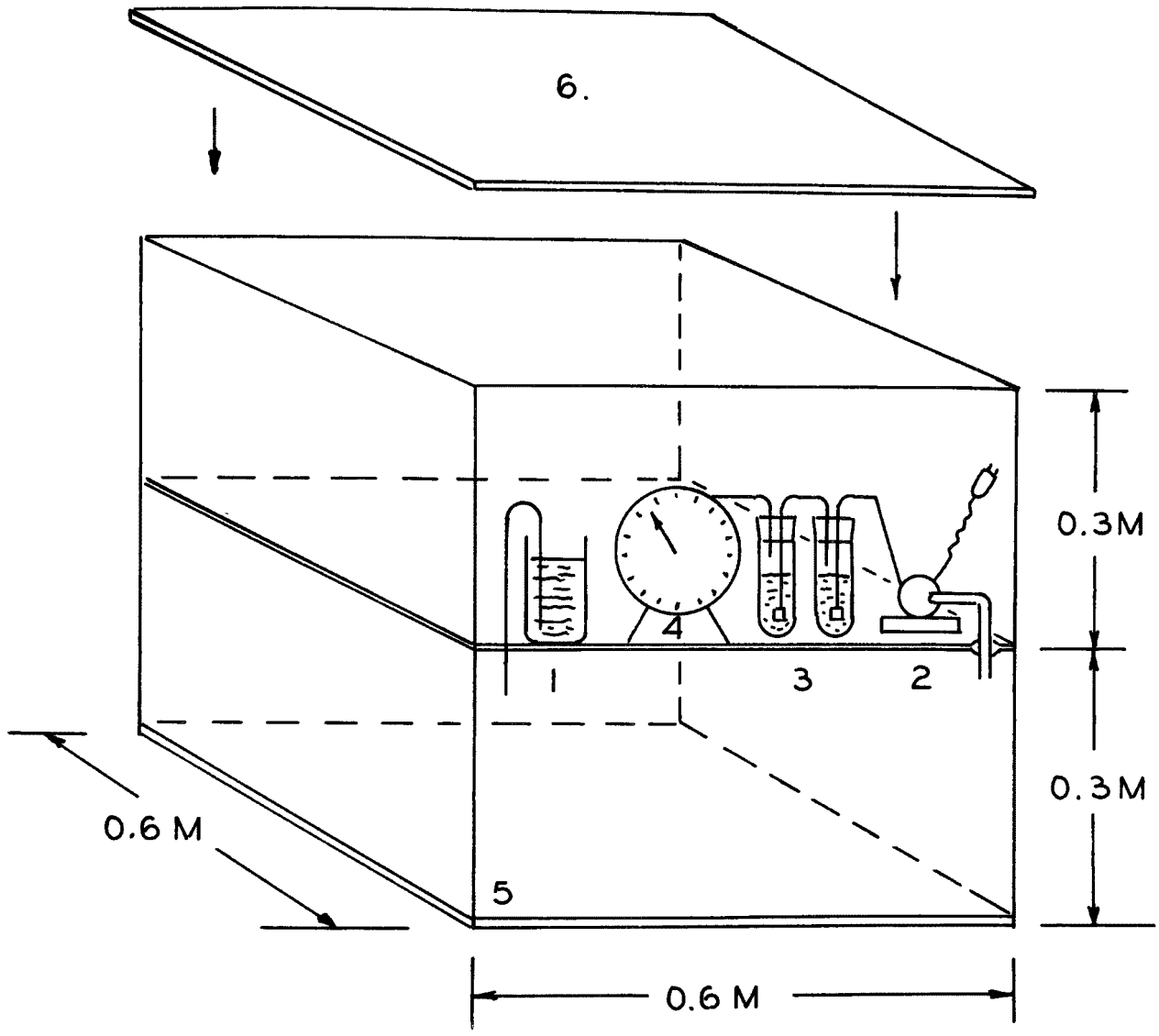
SECTION VI

AMMONIA EVOLUTION RATE FROM VARIOUS SURFACES ASSOCIATED WITH LIVESTOCK PRODUCTION

Ammonia release from manure-covered surfaces, or surfaces which are in the immediate proximity of livestock production facilities, has been demonstrated. Koelliker and Miner[12] documented the release of ammonia from an anaerobic swine manure lagoon surface. Ammonia concentrations in air near livestock feeding operations have been measured as significantly higher than those in other agricultural areas. Due to the solubility of ammonia in water, the potential exists for livestock production enterprises to make significant contribution to the nitrogen content of surface impoundments, thereby contributing to enrichment.

RATE MEASURING DEVICE

In order to quantify the rate of ammonia release from surfaces associated with livestock production systems, the sampling box shown schematically in Figure 5 was constructed. This box covers a square area 0.61 m on a side. There is a plywood deck 0.3 m from the bottom of the box. A diaphragm pump pulls air from beneath the deck through absorption tubes and finally through a wet test meter for air volume measurement. Air is admitted to the space beneath the deck through a copper tube which terminates in a can filled with activated carbon. The activated carbon insures that ammonia-free air enters the system. A metal strip attached to the lower edge of the sampling box prevents the entrance of unfiltered air. The air pump was driven by a 12-volt battery and DC-AC converter when other electrical connections were not accessible.



1. Activated carbon filtered air inlet.
2. Diaphragm air vacuum pressure pump.
3. Gas impinger tubes with absorption material.
4. Wet test meter.
5. Metal sealing strip.
6. Lid for rain protection.

Figure 5. Construction of the sampling box to capture the released volatile compounds from a soil surface previously exposed to animal manures.

Solid Surface Rate Measurements

The sampling box was used to measure ammonia release rates from a variety of surfaces associated with the OSU Dairy, Swine Center, and campus. Each of the sampling locations was subject to a variety of short-term variations and precise values were not reproducible. By collecting five or more samples from forty locations, useful information was obtained. Values were measured under summer conditions of 20° C to 30° C daytime temperatures during a period without rainfall. The results are summarized in Table 21.

Table 21. EVOLUTION RATE OF AMMONIA FROM SEVERAL DIFFERENT SURFACES IN THE VICINITY OF LIVESTOCK PRODUCTION FACILITIES

Surface description	Evolution rate, mg/day-m^2
On pasture grass and bare soil more than 30 m from dairy barn	1 - 2
On pasture with dried manure and on manure-free dairy barn surfaces	2 - 5
Pasture land after recent liquid dairy manure application	5 - 20
Manure-covered aisle in freestall dairy barn	50 - 100
Grassland near swine barn with no direct manure contact	2 - 3
Soil and grass with some previous manure application	2 - 5
Lagoon water	20 - 100
Campus sidewalk and lawn surfaces	0.5 - 1.5

A lagoon surface releasing 25 mg/m^2-day would release approximately 90 kg/ha. (80 lb/acre) annually. This value is considerably smaller than anticipated. This is best explained by the relatively low pH (7.9) of this lagoon for ammonia desorption. At this pH, less than four percent of the ammonia is present as NH_3 and exhibiting a vapor pressure. The same explanation - low soil pH - also explains the low ammonia release rates measured in this study. Nitrogen flux rates ranging from 25 to 80 mg/m^2-day have been reported from a grazed alfalfa pasture.

This technique offers a simple quantitative technique for the measurement of ammonia release rates from surfaces associated with livestock production. The values measured correlate well with observed odor release and lead to a prediction of the potential contribution of livestock feedings to airborne plant nutrients which can be absorbed by nearby surface waters.

Lagoon Surface Rate Measurements

At various times during the summer, the rate of ammonia volatilization was measured from an anaerobic swine manure lagoon. Apparatus for measurement consisted of a bucket 45 cm tall with an interior diameter of 30 cm, covered with a wooden plate. The bucket was filled approximately one-half full of lagoon water. Air was pumped from inside the bucket and bubbled through a weak acid solution to trap the ammonia. Air was replaced into the bucket one-half full of lagoon water. Results are shown in Table 22.

An intended goal of this experiment was to find how various additives and barriers affected the rates of ammonia volatilization of the swine lagoon water. Ten buckets, with interior diameter of 28.4 cm and height of 35 cm, were used. Five buckets were filled to 20 cm with lagoon water. The remaining five were filled with fresh water and manure.

Readings were taken using a sealed cover placed over each bucket. Air was pumped through a weak acid solution to trap the ammonia from within the bucket cover. Air was replaced through a charcoal filter. Results are noted in Table 23.

Table 22. AMMONIA EVOLUTION FROM ANAEROBIC LAGOON WATER MEASURED DURING THE SUMMER OF 1975

Date	Temperature, ° C	Ammonia evolution rate, mg/day-m^2
6-18	21	52
7-08	23	106
7-11	26	151
7-18	23	86
7-29	21	67
8-12	21	84
8-15	21	70
8-19	21	50
8-20	20	62
8-22	22	60

Table 23. AMMONIA EVOLUTION FROM ANAEROBIC LAGOON WATER AND FRESH MANURE AND WATER WHEN ADDITIVES ARE USED

Additive	Fresh influent		Lagoon water	
	mg/m^2-hr	% of control	mg/m^2-hr	% of control
Control	1.84	---	1.96	---
Acid added to bring pH to 6	0.85	46	1.17	60
Oil covering surface	0.41	22	0.40	20
Micro-aid (Odor control agent)	0.49	27	1.05	53
Styrofoam beads covering surface	0.91	49	1.29	66

Disposal Field Rate Measurements

Considerable interest exists in evaluating the nitrogen loss when manure is applied to crop land. To meet this need, anaerobic lagoon effluent was applied to a pasture plot at a rate equivalent to 200 kg of nitrogen per ha. Prior to application, the plot was evolving ammonia at a rate of 1.0 mg/m^2-day. The pH of the soil was 4.5. Immediately after application, the plot evolution increased to 4.0 mg/m^2-day for a six-hour period, then returned to the original value. The adjacent plot ammonia evolution rate also rose in response to the application of an equal volume of water. Thus, in this particular case, the nitrogen loss was very small.

Swine Enterprise Measurements

Atmospheric ammonia content was monitored in the vicinity of a 1,000-head commercial hog operation with surrounding land in grass seed production. The intended purpose was to look at the effects of several parameters on atmospheric ammonia.

Sulfuric acid sampling beakers were placed in covered stations in a pattern around the operation up to distances of one km. The ammonia level was determined by Nesslerization. Data was put in the form of $mg\text{-}NH_3/m^2$-day to express the amount of ammonia absorbed across the solution surface per day.

Growth of the rye grass correlated with ammonia concentration. During the early growth period, absorption rates ranged from 2 to 5 $mg\text{-}NH_3/m^2$-day. This increased to a range of 3 to 6 $mg\text{-}NH_3/m^2$-day. Immediately after the grass was cut, absorption rates jumped to a range of 4 to 11 mg/m^2-day.

Weather fluctuations seemed to influence ammonia level to some degree. Hot, humid weather seemed to cause higher levels than cold temperatures. Periods following rain showed the atmospheric ammonia levels to be slightly lower. Wind also seemed to disperse the ammonia so that lower atmospheric concentrations were experienced.

During the testing period, one area was sprayed with manure slurry from a storage pit. As expected, this area showed higher atmospheric concentrations. In general, the atmospheric concentrations became smaller in inverse proportion to the distance from the source.

EVOLUTION MEASUREMENTS IN THE LABORATORY

A series of laboratory experiments have been conducted in an attempt to document the production of gases by stored manure as well as the potential of various gas absorption techniques to remove odorants. Those results are reported below.

Effect of Moisture Content

Dairy manure samples of four solids contents (0.5, 1.5, 16, and 24 percent) were placed in flasks and air passed over the samples. The flask containing the nonadjusted moisture content (16 percent) produced the greatest concentrations of both ammonia and hydrogen sulfide. Addition of excess water appeared to absorb and retain the gases while drying inhibited their production.

Use of Water as an Absorbent

This experiment was designed to examine the hypothesis that water could be used to absorb odorants from air laden with gases from manure decomposition. The ammonia and COD concentration reductions achieved in the column were confirmed by personal observation of a decreased intensity when entering and exit stream odors were compared. The apparatus used is shown in Figure 6. Data collected during this experiment are presented in Table 24.

Use of Natural Ammonia Absorbents

This experiment was designed to demonstrate ammonia removal from air by normal environmental absorbents -- water, soil, and grass. A single carboy of manure was used as the odor source. Air was pumped from this carboy and split into absorbing flasks as shown in Figure 7. For absorption, odorous air was passed over the water and through the other two media.

This preliminary experiment indicated that all three media effectively reduced the ammonia content when first used. The grass rapidly lost effectiveness as it dried and began to release ammonia as it decomposed and as mold growth became evident (Table 25).

A second experiment similar to the above was made, except that the odorous air was passed over the absorbing media rather than through them. Again, as indicated in Table 26, all three media were initially effective in removing ammonia. As the soil and grass began to dry and decompose, their effectiveness decreased.

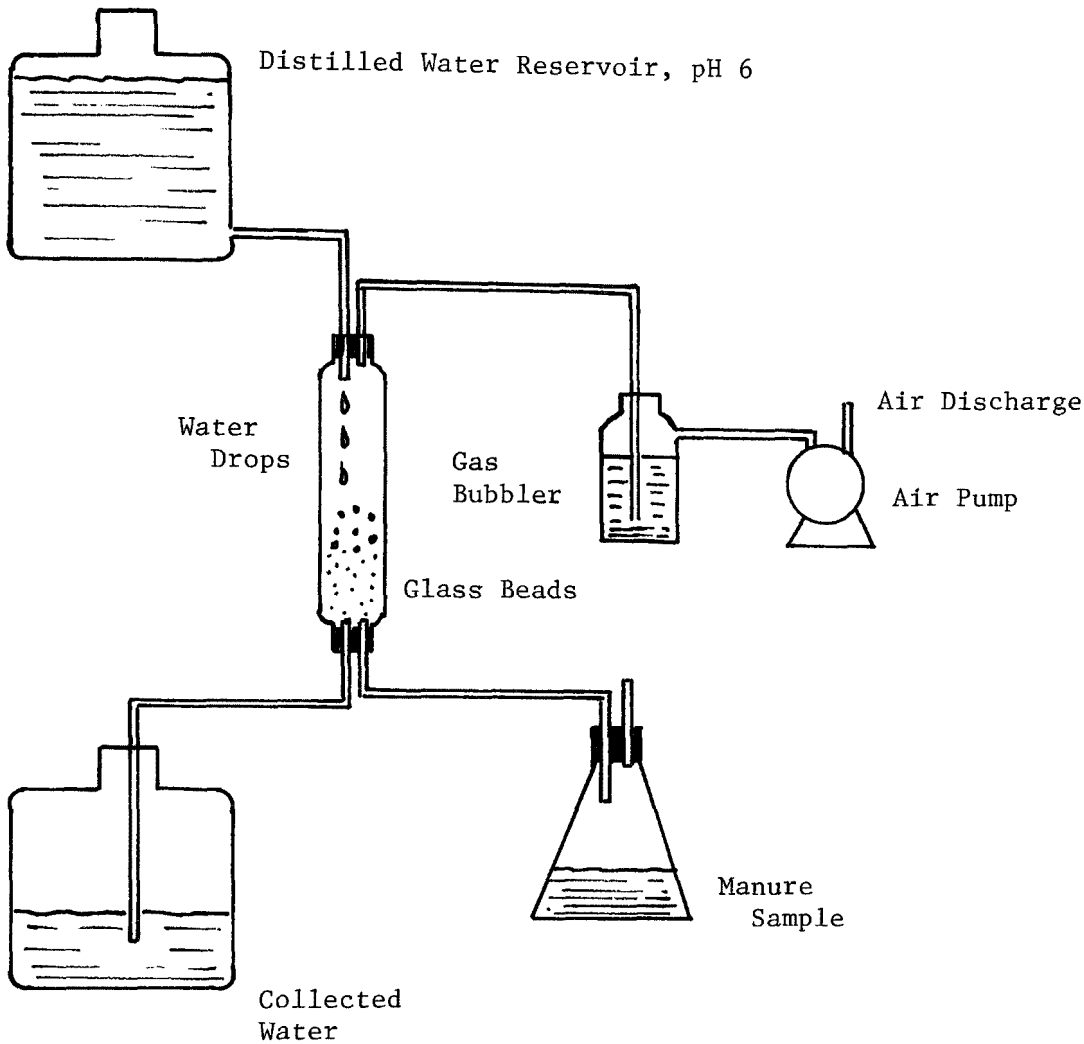


Figure 6. Laboratory apparatus used to evaluate the absorption of odorants using contact with water in a counter current exchange column.

Table 24. ABSORPTION OF AMMONIA FROM MANURE GASES BY WATER IN A COUNTER CURRENT EXCHANGE COLUMN

Date of observation	Air stream		Water stream	
	Ammonia concentration (% reduction)	COD concentration (% reduction)	Ammonia concentration in mg/l	Ammonia concentration out mg/l
11-28-73	28	8	.159	.206
11-29-73	7	-9	.283	.343
11-30-73	51	6	.172	.188
12-03-73	48	2	.089	.132
12-04-73	64	23	.150	.113
12-05-73	14	23	.137	.097
12-06-73	9	16	.083	.120
12-08-73	63	-132	.205	.130
12-10-73	55	44	.150	.230
12-11-73	56	21	.135	.177
12-12-73	18	22	.107	.123
12-13-73	9	24	.154	.218
12-14-73	32	18	.134	.203
12-17-73	50	14	.160	.175
12-18-73	40	-85	.160	.159

FEEDLOT ODOR STUDY

Ammonia evolution and absorption rate measurement techniques developed in pursuit of this project were utilized in a feedlot odor evaluation project conducted during the summer of 1975. The feedlot odor project was funded in part by the National Science Foundation, Research Applied to National Needs, Grant No. ESR 74-23211, the Idaho Department of Health and Welfare, and the host feedlot. A final report on this project has been published by the Idaho Research Foundation. That report is summarized below.

Alternate techniques for the control of odors from a cattle feedlot were evaluated at a southeastern Idaho site. Three separate odor sources were present: the feedlot surface, the runoff collection and storage ponds, and a potato waste

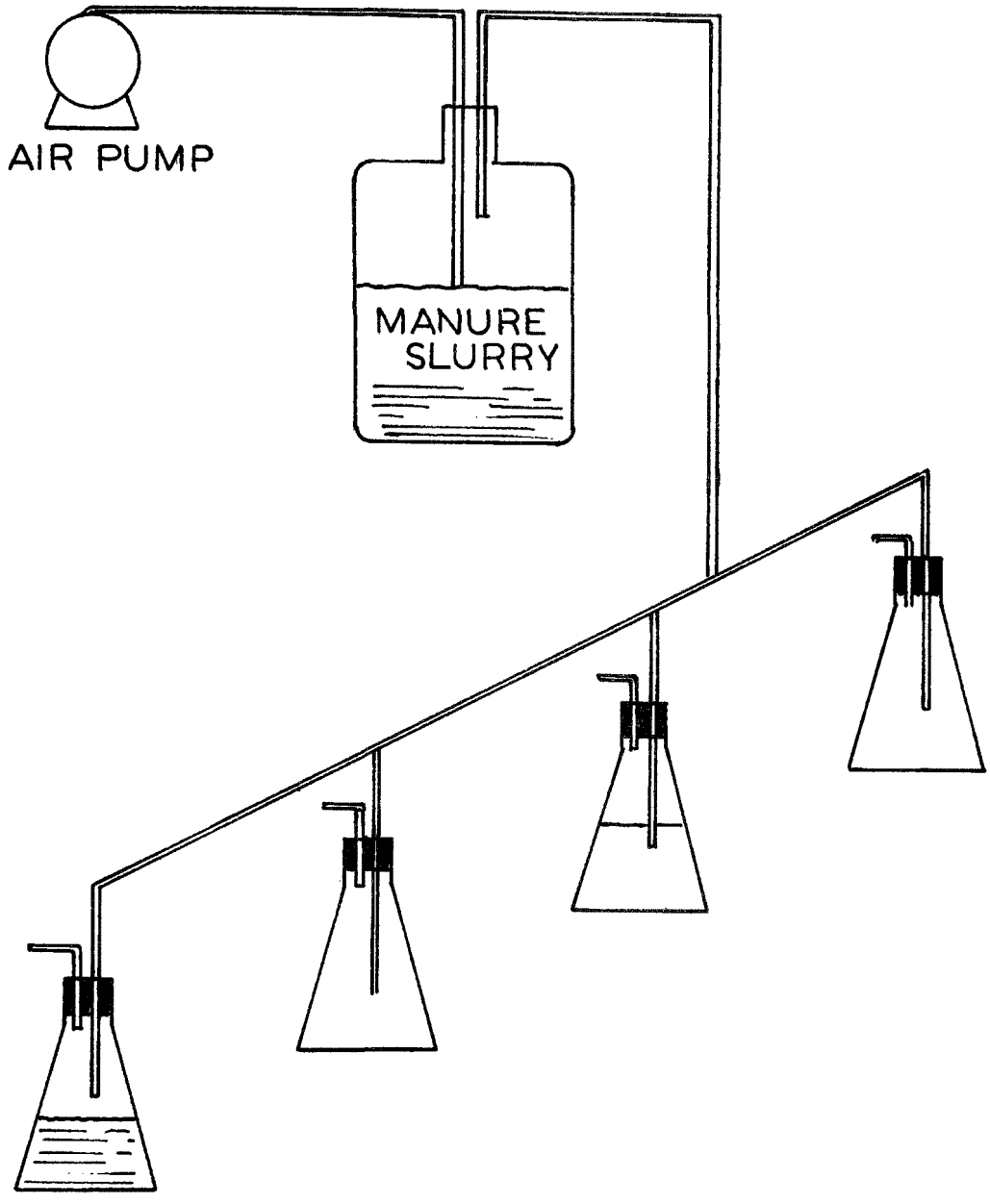


Figure 7. Laboratory apparatus used to evaluate the ability of various absorbing materials to remove ammonia from odorous air.

Table 25. AMMONIA IN AIR AFTER PASSING OVER WATER, THROUGH GRASS, SOIL OR NOTHING (mg/day)

Date	Absorbing media			
	Water	Grass	Soil	Nothing
3-18-74	0.11	0.29	0.16	0.11
3-19-74	-	0.13	-	1.12
3-20-74	-	1.08	-	2.80
3-21-74	-	1.00	-	10.08
3-22-74	-	1.12	-	3.08
3-25-74	-	4.44	0.124	3.96
3-26-74	-	62.4	-	5.20
3-27-74	-	58.8	-	4.64
Media replaced in all four flasks				
3-28-74	-	0.40	0.17	2.32
3-29-74	-	0.56	0.15	4.96
4-01-74	-	1.08	-	5.12
4-02-74	-	1.68	-	7.20
4-03-74	0.144	1.72	0.14	9.76
4-04-74	0.80	9.68	-	19.60
4-05-74	1.76	38.00	0.12	25.2
4-08-74	0.22	288.00	0.10	21.60

storage pit. Potato wastes from nearby processing plants were included in the ration at this feedlot after storage in a concrete-lined pit. The storage pit made a significant contribution to odor release but due to its unique character, was not included in the study.

Nine products were applied to various feedlot pen surfaces at rates and frequencies suggested by the respective manufacturers. Ammonia release rates and odor intensities of the feedlot litter were used as measures of success. Four of the products, sodium bentonite, ODOR CONTROL PLUS, and the two natural zeolites were found to consistently reduce the rate of ammonia release from treated areas when compared to nearby untreated areas. Odor intensity measurements confirmed the effectiveness of sodium bentonite. The ODOR CONTROL PLUS treated pen had a measurably less intense odor

Table 26. AMMONIA IN AIR AFTER PASSAGE OVER WATER, GRASS, SOIL, OR NOTHING (mg/day)

Date	Absorbing media			
	Water	Grass	Soil	Nothing
4-16-74	.11	0.19	0.16	13.2
4-17-74	-	0.36	0.40	9.6
4-18-74	.46	0.82	0.72	16.0
4-19-74	.22	1.92	0.48	2.64
4-22-74	.19	4.5	5.6	17.6
4-23-74	.12	3.8	2.4	9.6
4-24-74	.29	2.9	4.2	12.0
4-25-74	.29	9.8[a]	2.7	8.0
4-26-74	.26	18.4[a]	3.1	9.2

[a]Decomposition of the grass was evident, causing a release of ammonia.

five days after treatment but not ten. Only one of two observers was able to distinguish the zeolite treated pen litter from the control. The cost of the effective materials ranged from $150 to $300 per ha for treatment during the odor production season. Two materials were added to the feed ration as potential odor control techniques; however, neither material proved effective based upon the ammonia release rate or odor intensity measurements made.

A green belt odor barrier was established along the two sides of the feedlot where odor control is essential. Three species of trees and shrubs were planted in a typical wind-break manner. The success of this procedure will be evident only as the plantings mature and reach an effective height. A spray system was installed in the same area as the plantings. The spray system was designed to create a mist extending 6 m into the air along these borders. Although difficult to evaluate in a highly variable natural setting, the data suggested a more rapid decrease in ammonia absorption rate with downwind distance when the water spray was in operation than at other times. This system is effective only under low velocities, which is also the time of greatest odor transport.

The spray system was also used to dispense a dilute potassium permanganate solution. The first effort was to demonstrate the practice would not damage wetted vegetation. When applied at concentrations below 74 mg/l, no plant effects were noted. When added to the spray at 10 mg/l, potassium permanganate seemed to further speed the odor intensity reduction with distance; however, substantiation of that result will require considerably more data than it was possible to accumulate during this study.

Although not included in the original plan for this project due to the experimental difficulties anticipated, two chemicals were sprayed on the runoff retention ponds as an odor control effort. Ammonia absorption rates and hydrogen sulfide concentrations were the measurement techniques used. The close proximity of the ponds to one another and to the feedlot as well as the variability in climatic conditions made evaluation difficult; hence, no conclusions could be drawn. Further experimentation is necessary.

Examination of the climatic data indicate that for the Blackfoot, Idaho, area, climatic conditions would transport odor from the Harding Feedlot toward the Moreland community approximately three percent of the time. This frequency was, in general, confirmed by the odor records maintained by the residents of the area.

SECTION VII

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16. ABSTRACT

Current livestock production techniques release a large variety of volatile organic compounds to the atmosphere. This release results in complaints due to their odorous nature and has been identified as a source of surface water pollution as these compounds are absorbed from the air. Ammonia has been identified as the compound of greatest concern relative to water pollution and is of considerable interest relative to odor complaints due to its ease of measurement and its relationship to more odorous gas evolution.

Gas sampling and measuring schemes based upon the use of solid absorbents were studied. Use of an absorbent suspended in a stainless steel screen container which could be exposed in an atmosphere to be sampled showed promise.

The evolution of ammonia, hydrogen sulfide and odorous volatiles was investigated as a function of beef cattle ration. Addition of essential oil, mint oil, was found to mask the odor of fresh manure. Mint oil was carried in the urine. Ammonia evolution from fresh manure was largely from urine. Fecal contributions became significant only after significant decomposition had occurred.

A technique was devised for measuring ammonia evolution rates from surfaces. This measurement proved an accurate measure of anaerobic biological activity and provided a quantitative means for comparing treatment procedures designed to minimize volatile material evolution rates. Evolution rates for a variety of surfaces associated with livestock production enterprises were measured.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Cattle; Swine; Agricultural Wastes; Odors; Water Pollution	Ammonia Volatilization Rate; Ration Effects; Ammonia Absorption; Gas Sampling; Feces; Urine	02/A, B, C

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