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Title: THE EFFECT OF RATION FORMULATION ON THE

SUBSEQUENT GENERATION OF VOLATILE GASES AND

ODORS FROM BOVINE WASTE

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The objective of this study was to determine the effect that

ration formulation has on volatilization of gases and offensiveness of

the odor associated with the wastes produced from Holstein replace-

ment heifers. Six separate experiments were conducted to study the

relationships between different variables on the release of hydrogen

sulfide, ammonia, total nitrogenous gases and amines.

The rate of hydrogen sulfide evolution was increased as the

cereal grain level of supplementation was increased from 50% to 75%

of the diet. Ammonia was volatilized at between 1,000 and 10,000

times that of hydrogen sulfide during the initial storage period, but

no differences were found between the three levels (25%, 50%, 75%)

of the supplementation of the cereal grains.

The pH of the mixture of urine and feces obtained from animals

maintained on the various grains and levels (25%, 50%, 75%) indicated

that there was a difference between the grain sources with milo causing the lowest pH and barley the highest.

Amines were found to compose about 0.11% of the volatile basic nitrogenous gases that were initially volatilized from the waste. There was a positive correlation between the ammonia release and the amine evolution rate.

The urine fraction was found to be a major contributor to the amount of ammonia volatilized. The rate of ammonia volatilization was highest during the first five days of storage for the samples containing urine, the rate then declined; the samples containing feces only released less ammonia and the release rate continued to increase as the storage period increased. The results indicated, under anaerobic storage conditions, that urea is rapidly hydrolyzed to form ammonia. The moisture content of the waste samples were negatively correlated with the volatilization of the nitrogenous gases.

The Effect of Ration Formulation on the Subsequent
Generation of Volatile Gases and Odors
from Bovine Waste

by

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LITERATURE REVIEW

The centralizing of livestock production units and areas has

caused concern as to what effect they are having on the environment,

specifically with respect to surface water, soil, and atmospheric

pollution. Other factors that have caused this concern are: (1) an

increase in human population and urbanization of farm lands and

(2) the emphasis to identify polluting sources by environmentalists.

Atmospheric pollution from animal excreta is a major problem

associated with confined production systems. Animal waste manage-

ment has been discussed recently, with one author describing it as a

"national problem" (Loehr, 1969). Considerable research has been

directed towards animal waste management; some of it has been sum-

marized in a review by Miner and Jordan (1971) and several symposia

have specifically dealt with this topic (Amer. Soc. Agr. Eng., 1966,

1971; Cornell Univ. Conf. on Agr. Waste Management, 1969, 1970,

1971).

The effect on domestic animals of the various gases that are

commonly associated with the decomposition of animal wastes is cov-

ered in extensive reviews by Taiganides and White (1969), Lillie

(1970), and Aschbacher (1973). A critical look at the current

regulations and methods used to establish standards for odor limits associated with industrial sources was given by Leonardos (1974). The same basic methods could be used in the future for setting standards for the agricultural community.

Atmospheric pollution and how it relates to livestock production in confinement units and highly concentrated livestock areas will be reviewed with specific emphasis being given to ammonia, hydrogen sulfide, amines, and odors.

Ammonia from Livestock Production Units

The increased density of beef and dairy operations with respect to animal numbers and the large quantities of waste that are generated, specifically the nitrogen fraction, has the potential to be a major contributor of nitrogenous compounds to the surrounding environment. This section will primarily be concerned with the atmospheric contamination caused by the release of ammonia from livestock production units and factors that alter this release.

The presence of ammonia as a component of our atmosphere was noted 100 years ago by Schlossing (1875). Some of the physiological disorders specifically caused by ammonia were described by Weatherby (1952) with the primary effect being on the lungs, eyes, and mucous membranes. Ammonia was found to reduce the resistance of chickens to Newcastle disease and to increase air

sac lesions in turkeys (Anderson et al., 1964, 1966, 1968). It was shown by Charles and Payne (1966) that elevated levels of ammonia in chicken houses had an adverse effect on growth. Boyd et al. (1944) studied the effect of ammonia gas poisoning on rabbits and cats.

The direct enrichment of surface waters with nitrogenous compounds in close proximity to livestock production units has generally been thought to be due to surface run-off from these units. The absorption of nitrogenous compounds directly from the atmosphere by acid traps was found to be 20 times greater for traps located in close proximity to a beef feedlot as compared to those some distance away (Hutchinson et al., 1969). In more recent work (Luebs et al., 1973a), the ammonia concentration in air was measured and found to be increased by 20-30 times in a densely populated dairying area as compared to an urban area. It was also noted that rainfall delivered three times the amount of ammonia inside the dairying area as compared to outside.

Ammonia has been demonstrated to be the primary nitrogen compound that is volatilized from feedlots (McCalla and Viets, 1969). It has also been demonstrated that, under typical conditions, the ammonia will be present in quantities below its odor threshold (Stephens, 1971). Miner and Hazen (1968) found this to be the case in swine building gases; they detected ammonia, but below its published olfactory threshold.

In one study 11-60% of the ammonia from waste water sludge was lost during the first one to two days (Ryan and Keeney, 1975). They also indicated that as much as 65% of the nitrogen that was added in the form of animal waste to an anaerobic swine lagoon was volatilized. Excreted urine was studied by Stewart (1970) under simulated feedlot conditions and approximately 90% of the nitrogen content 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 (Elliott et al., 1971). When the moisture content of manure was increased from 60 to 90% and the temperature from 10°C to 25°C, an increase in the amount of nitrogen that was volatilized was noted, with losses approaching 50% of the nitrogen content of the samples over an 18 day period (Adriano et al., 1974). Diluted poultry manure has been shown to produce more ammonia, but the undiluted sample volatilized more ammonia (Ludington et al., 1969). In a densely populated dairying area a diurnal fluctuation in the atmospheric ammonia concentration was noted with low concentrations being present in the atmosphere in the afternoon and high concentrations at night (Luebs et al., 1974).

The pH of the media has been indicated to have a direct effect upon the form in which ammonia is found; under acidic conditions it is in the non-volatile (NH_4^+) form and under basic conditions in the volatile (NH_3) form (Miner, 1973). A direct correlation between

soil pH and ammonia volatilization was found when manure was mixed with different soil types (Chao and Kroontje, 1964).

The primary precursor of ammonia from animal wastes has been indicated to be urea in urine (Stewart, 1970). It has been estimated that half of the nitrogen that is eliminated under normal conditions is in the form of urea (Viets, 1970). Ammonia was consistently identified in the gaseous exhaust products from both anaerobically and aerobically stored dairy wastes (Barth and Polkowaski, 1974b).

Amines from Animal Wastes

The production of amines as by-products of decomposition of animal wastes has been proposed as a reaction between ammonia that is an end product of protein and urea breakdown and alcohols that are products of carbohydrate degradation (Merkel et al., 1969). The odor thresholds for the amines are very low, with trimethylamine having a threshold that is 100,000 times less than ammonia (Leonardos et al., 1969). 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 that were being generated from

cattle feedlots (Stephens, 1971). This was supported by White et al.

(1971) who also identified methylamine and ethylamine in gases

associated with dairy animal wastes. Very low but significant con-

centrations of amines in swine manure have also been identified by

Miner and Hazen (1968).

Luebs et al. (1973) indicated that less than 5% 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 concentration to decrease with the length of storage

(Burnett and Dondero, 1969).

Basic organic N-compounds volatilized from a cattle feedlot and

collected in dilute acid traps have been characterized (Mosier et al.,

1973). The direct gas chromatographic analysis (GLC) of the acid

solutions and separation of pentafluorobenzoyl derivatives of the

malodorous volatiles were used in their identification. Methyl,

dimethyl, ethyl, n-propyl, isopropyl, n-butyl, and amylamines were

among the basic N-compounds emanating from a high density cattle

feedlot.

Mosier (1974), used Chlorella ellipsoidea, a typical algae

found in lakes and streams, in a pure culture study. He studied the

effect amines volatilized from cattle feedyards would have on the

growth of algae if absorbed by surface waters. Results indicated that

growth was inhibited with the primary amines being more effective

than the secondary amines. This suggested that enrichment of surface waters by amines generated from feedyards could have an inhibitory effect instead of improving growth as would be expected with nitrogen enrichment of surface waters.

Effect of Ration Formulation

Only limited research has been done on the effect of ration formulation on the subsequent odor and generation rates of the volatile gases associated with animal wastes. The work of Ingram (1973a) indicated that the addition of Lactobacillus acidophilus, yeast, and activated charcoal to a swine ration had no effect on the olfactory evaluation of the fecal samples. Activated charcoal was the most effective of the treatments tried in reducing the volatile matter, but the reduction was not detected by the olfactory panel. The yeast and Lactobacillis reduced skatole and indole content of the feces, but these changes were not detected by the olfactory panelists (Ingram, 1973b).

The addition of sagebrush to the ration of beef feedlot animals at the rate of 1 to 2 pounds per day was found to reduce the manure odor associated with these units (Anonymous, 1972).

Hydrogen Sulfide from Animal Wastes

Hydrogen sulfide has been identified as one of the volatile gases generated by animal wastes (Day et al., 1965; Hammond et al., 1968). The assumption can be made that hydrogen sulfide is one of the gaseous products that is being generated during the decomposition of animal wastes and the precursors for it 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 (Curtis, 1975). The description of the effects of hydrogen sulfide by Taiganides and White (1969) on poultry, swine, and cattle gives the symptoms associated with different levels and exposure periods. The results of chromatographic analyses of gases from accumulated liquid poultry manure by Burnett (1969) indicated that the odor-causing pollutants were primarily a mixture of hydrogen sulfide, ammonia, diketones, mercaptans, sulfides, organic acids, indole, and skatole. Merket et al. (1969) performed odor evaluations, using selective absorbants solutions to alter the odor from swine wastes, and concluded that amines and sulfides were the important constituents.

In bovine confinement operations hydrogen sulfide has been found as a component of the volatile gas mixture that is generated during the process of waste decomposition. Stephens (1971) 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. Similar results with dairy animal waste by White et al. (1971) indicated the presence of sulfides, disulfides and the esters of C3 and C4 organic acids. Bethea and Narayan (1972) detected hydrogen sulfide as the only sulfur containing compound when beef cattle wastes were maintained under aerobic conditions by bubbling air through the samples and trapping in $HgCl_2$ and $Hg(CN)_2$. The two solutions were then mixed and acidified with HCl followed by chromatographic analysis.

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 the daily sulfur intake of the animal (Avery et al., 1975).

Odors Associated with Livestock Production

The subject of odors from livestock production units has been an area of considerable research interest in the past decade. The production of odorous gases is a bacterial process (Deibel, 1966). The most frequent complaint registered against livestock producers

are those that are associated with odors. Many odorous gases have been identified as products of manure storage (Miner, 1973). Actual physiological damage has not been proven for livestock odors; however property damage and nuisance have been proven in court (Miner, 1970). The need to set standards for odor emission has been stifled by our current inability to accurately measure odor quality or intensity. The basic cause for the increase in complaints is related to increasing animal and human populations (Russell, 1965). A bibliography on gases and odors generated from poultry manure, which contains information on microbiological and chemical changes that are associated with its decomposition, implicated certain organisms as producers of odorous gases and showed an apparent correlation between increasing storage time, concentration of volatile organic acids, ammonia, sulfides, and odor intensity (Burnett, 1971).

Atmospheric pollution is being traced more and more to liquid manure handling systems. It has been indicated that air contaminated from liquid manure under confinement conditions has resulted in the suffocation of animals and humans (Cooper et al., 1969). Industrial methods for the treatment of odors; namely, dilution, absorption, masking, counteraction, and burning, could possibly be used to control the odors from stored manure (Muehling, 1970).

Detection of Odors

The nose is the most sensitive odor detecting device that is currently available. Gas chromatographic techniques have been developed that can detect compounds in quantities as low as 10^{-12} g. Compounds with low odor thresholds can be readily detected by the nose below concentrations detectable by GLC (Freeman, 1967). When liquid manure gaseous decomposition products were subjected to both chromatographic and organoleptic evaluations, it was noted that odors were present that caused no chromatograph responses. The following considerations are indicated by Sobel (1972) as being important when evaluating odors: (1) the use of a rating method utilizing the human nose for odor evaluation provides the most accurate information for manure samples; (2) the ratings for odor presence and odor offensiveness are very similar; (3) descriptive terms help in categorizing odors; (4) olfactory observations along with visual observation produce a different rating in comparison with olfactory observation only; and (5) since there is no right answer to an olfactory test, the test must be conducted so that comparisons can be made.

Odormeters of various forms have been developed to assist in odor evaluation work. The meters make the necessary dilutions of the odorant with an odor-free medium prior to inhalation by the person evaluating the sample. The meters have been given such names

as "olfactoscope", "odormeter", and "osmometer". Descriptions and use of these instruments have been outlined by Moncrieff (1967), Stone (1964), and Sobel (1969). The forced-choice triangular olfactometry method provides more definitive data and is free of problems connected with the use of Scentometers in an odorous environment (Dravnieks et al., 1975). A summary of sampling methods, analytical techniques, and odor evaluation procedures has been reviewed by Dravnieks (1974). The comparisons of four common procedures for the determination of the odor threshold values of an odorant in odor-free water dilution were performed, including two multiple-bottle and two serial dilution techniques (Baker, 1964).

The evaluation of odors from swine waste, using selective absorbants to alter the odors, showed that alcohols and carbonyls were probably unimportant, whereas the amines and sulfides were considered the major malodorous constituents (Merket et al., 1968). Burnett (1969), using a combination of gas chromatography and organoleptic techniques, indicated that there was some correlation between the quantitative measurements and the olfactory evaluation.

Instrumental techniques for odor evaluation have been proposed by Hemeon (1968) and Gruber et al. (1960). Specific procedures for the identification of malodorous compounds from animal wastes were studied by White and Taiganides (1969). Similar reports of the use of gas liquid chromatography for analysis of volatile gases generated

from animal waste have been published by Burnett (1969), Merket

et al. (1969), and Miner and Hazen (1968).

The organic acid, ammonia, and hydrogen sulfide content of

gases generated from animal waste were correlated with odor

intensity by Barth et al. (1974a); the volatile organic acid concentra-

tions were the most highly correlated, followed by hydrogen sulfide

and then ammonia. Similar results of Bell (1971) showed a relation-

ship between the volatile organic acid content of poultry manure and

the odor level. Sobel (1972) related odor strength and quality to an

"offensiveness" rating and judged poultry manure odor on this basis.

In a series of experiments designed to secure criteria for tolerable

concentrations, it was found that the fatty acid content, while not

necessarily the cause of the odor, was an excellent indicator of odor

strength (Bell, 1970).

An excellent review by Barth (1973) describes procedures that

can be employed for specific odor determinations and, even more

important, highlights the phenomena important in analysis of odor

quality and intensity.

The theories for the various proposed models for the perception

of odors is beyond the scope of this literature review; for information

pertaining to this subject there is an excellent summary given by

Miner (1973). Procedures that can be employed for spcific odor

determination and the phenomena important in analysis of odor quality

and intensity of animal wastes are outlined in detail by Barth (1973).
The basic principles of sensory evaluation and sensory testing ,
methods are explained in these two publications (ASTM, 1968a,b).

Research with mixtures of odorants of known odor intensity
proves that it is not possible to predict the intensity of a mixture of
even two components (Rosen et al., 1962). The interaction of odor-
ants produces results indicative of addition, independence, counter-
action and synergism. The additive effect of subthreshold concentra-
tions of some organic compounds has been studied by Guadagni et al.
(1963).

The perception of odors is primarily based on a subjective
evaluation at the present time. With improvements in analytical
techniques and a better understanding of the olfactory process, it
should be possible to develop an objective evaluation based on the
composition of the gases produced from animal wastes.

SECTION I

EXPERIMENTAL PROCEDURE

The nuisance complaints associated with animal production units are primarily the result of the offensive odors which they generate. Considerable research effort has been directed towards developing waste management techniques and procedures for handling the wastes after they have been produced, but only limited research has been directed towards modifying rations with additives to control the odors associated with the subsequent wastes produced.

An experiment was designed to evaluate the effect of supplementing the rations of replacement heifers with two essential oil sources to determine the effect the oils had on the offensiveness of the initial odor of the wastes produced from these animals. In a second experiment, the effect of different combinations of feces, urine, and water were studied to determine what relationship they would have on the initial release of ammonia and their olfactory evaluations.

Experiment I

Three separate olfactory evaluations were conducted using a group of five Holstein replacement heifers. The heifers were maintained on a basal ration of 25% barley (rolled) and 75% alfalfa hay

(chopped) mixed to form a complete ration to which two levels (1% and 1.5%) of ground mountain big sagebrush (Artemisia tridentata sp. vaseyana form xericensis)[1] 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 (Appendix Table 1).

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 minimize 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 (Figure 1 of the Appendix) was carried out and composition of the oil was determined to be: 49.6% menthol, 22.5% menthone, 6.6% menthyl acetate, 2.5% menthofuran, and a number of other components in lesser concentrations.

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[1] This taxon of big sagebrush, although not officially recognized, was encountered by Winward (1970).

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 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 of the groups.

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 hr prior to being evaluated by an olfactory panel. The samples were removed from the water bath, dried, wrapped in paper, and allowed to equilibrate with the ambient temperature for approximately 30 min prior to being evaluated. 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 triangular testing procedure in which two of the samples were duplicated; this procedure is similar to the olfactory evaluation methods reported by Amerine (1965) and ASTM (1968a, b). The rating scale ranged from 0-15 with 15 being the most offensive and 0 the least offensive. Samples were also ranked as to their offensiveness with the value of 1 being given to the most offensive and 3 to the least offensive.

Experiment II

Feces and urine samples were collected from each of five

Holstein replacement heifers that were being fed a ration of 25%

barley and 75% alfalfa hay, with composition given in Table 1 of the

Appendix.

The procedure for urine and feces collection was the same as in

Experiment I. The collected urine and feces were then returned to

the laboratory and immediately the following samples were prepared

from a composite sample of the 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 in the same manner for each

of the subsequent evaluations. The samples were allowed to incubate

in a 30°C water bath for 24 hr prior to being evaluated by an olfactory

panel. The same procedure as outlined in Section I of the experimen-

tal procedures was used to prepare the samples prior to being pre-

sented to the olfactory panel for evaluation.

The rating was based on a scale of 0-10, with 10 being the most

offensive, and 0 the least offensive. An example of the judging form

used is shown in Figure 1. The panels ranged in size from 19 to 29

members.

Rates of ammonia release for each of the various samples were

determined just prior to being presented to the olfactory panel for

Rating Scale

15 ——————————— Most objectionable

15

14

13

12

11

10

9

8

7

6

5

4

3

2

1 ——————————— Least objectionable

Sample Numbers ___   ___   ___

Name _____

Date _____

Figure 1. Rating form for olfactory evaluation of manure odors.

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 evolved ammonia. The head space gases were replaced at the rate of 30 cu in/min for a 3 hr period and ammonia was quantitated using the nesslerization method (APHA, 1970). The results of the olfactory rating and ranking evaluations were correlated with the ammonia release rates to determine the relationships between these various measurements.

Boric Acid
or
Cadmium Hydroxide

Water Bath

Sample

Cadmium Hydroxide
Solution

HCl (dilute)

Air Source
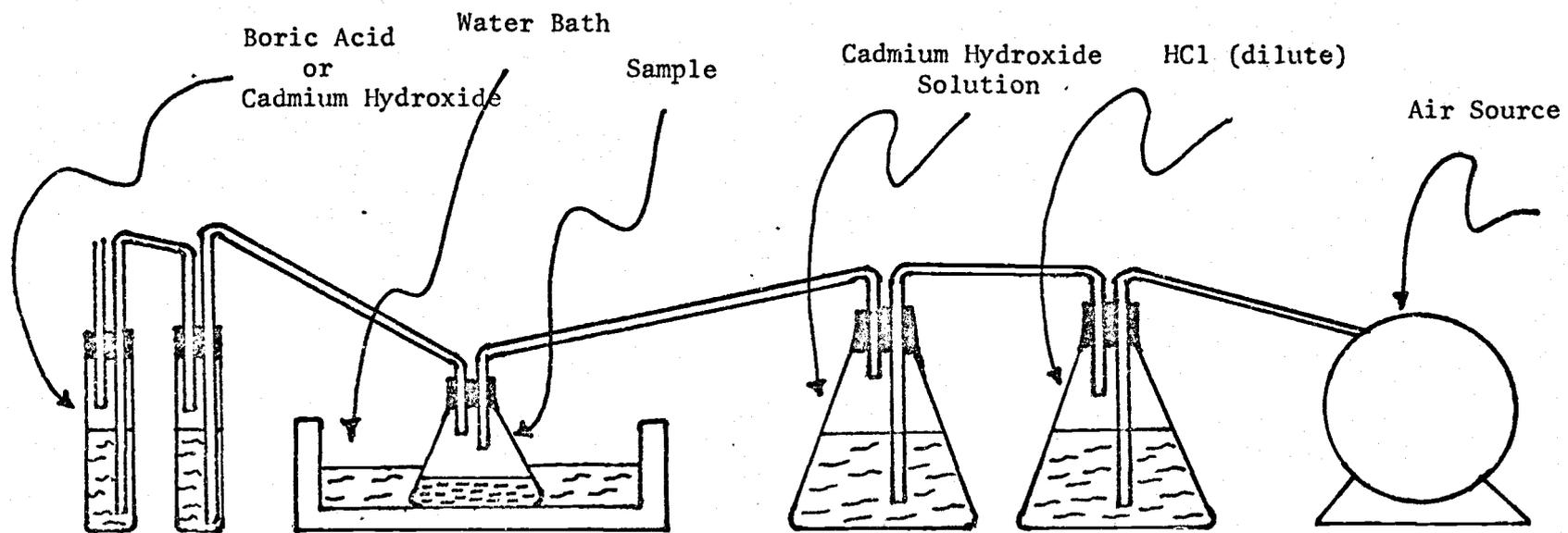
Figure 2. Ammonia and hydrogen sulfide trapping apparatus.

RESULTS AND DISCUSSION

Experiment I

Due to the subjective nature of the olfactory evaluation, a comparative rating and ranking of the samples must be made. Each panelist gave a numerical rating value between 1 and 15 with 15 being the most offensive for each of the three samples evaluated. The samples were then ranked giving the value of 1 to the most offensive as determined by the rating value, and 2 to the second most offensive, and 3 to the least offensive sample. 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 1.

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

The peppermint supplemented ration was evaluated with and without the urine fraction being added, 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 fecal plus water. When the fecal waste from the peppermint supplemented animal was combined with distilled water and compared to

Table 1. Olfactory evaluation of manure produced from replacement heifers receiving rations supplemented with sagebrush and peppermint oil.

Description of Sample[a]	Rating[b]	Std. Error of Mean	Ranking[c]	Std. Error of Mean
1% sagebrush + urine[d]	7.87[a]	1.008	2.13[a]	0.192
Basal[d]	7.87[a]	1.241	1.93[a]	0.228
Basal[d]	8.67[a]	1.058	1.67[a]	0.188
1.5% sagebrush + urine[d]	7.46[a]	1.163	1.77[a]	0.231
1.5% sagebrush + urine[d]	7.15[a]	0.799	1.461[a]	0.215
Basal[d]	6.62[a]	0.605	2.07[a]	0.239
0.25% peppermint w/o urine[e]	8.5[a]	1.108	1.6[a]	0.221
0.25% peppermint w/o urine[e]	6.9[a]	1.005	2.2[a]	0.20
Basal[d]	7.4[a]	1.284	2.0[a]	0.30
0.25 peppermint + urine[d]	6.00[a]	0.697	2.65[a]	0.170
Basal[d]	10.65[b]	0.702	1.53[b]	0.151
Basal[d]	9.68[b]	0.920	1.50[b]	0.158

Means in each column with different superscript letters are significantly different (P < .05).

[a]Indicates ration that animals are receiving and level of supplementation of essential oil source.

[b]Numerical scoring of samples with a rating of 0 having no offensiveness associated with it, expressed as means.

[c]Numerical value for the order of offensiveness for each of the respective samples; based on a scale of 1-3 with 1 being the value given to the most offensive, and 3 to the least. Values expressed as means.

[d]Samples contained 50 g of feces + 50 g urine.

[e]Samples contained 50 g of feces + 50 g distilled water.

that from the basal fed group plus urine, this 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.

Experiment II

The initial numerical rating and ranking values for relative offensiveness were not found to be noticeably different (P > .10) for the samples evaluated (Table 2). This would indicate that the relative portions of feces, urine, and water of the samples have little effect upon the initial release of odoriferous compounds.

The correlation coefficients for the various interactions are given in Table 3 of the Appendix. 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 were observed.

Table 2. Ammonia generation rates and olfactory evaluation ratings and rankings for various combinations of urine and feces collected from Holstein replacement heifers receiving a 25% barley + 75% alfalfa ration.

Sample Size	Sample[c]	Rating[d]	Std. Error of Mean	Ranking[e]	Std. Error of Mean	Ammonia[f]	Std. Error of Mean
19	100% urine	5.20[a]	0.48	2.47[a]	0.21	276.7[a]	68.32
19	50% fecal + 50% urine	3.95[a]	0.51	1.84[a]	0.17	116.94[a]	31.99
29	50% fecal + 50% water	4.13[a]	0.44	1.83[a]	0.16	8.26[b]	3.91
22	25% fecal + 75% water	4.04[a]	0.43	1.77[a]	0.13	0.18[b]	0.08

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

[c]Feces and urine samples were combined with distilled water added as indicated to form samples having a total weight of 100 g.

[d]Numerical scoring of samples with a rating of 0 having no offensiveness and 10 being highly offensive, expressed as means.

[e]Numerical value for the order of offensiveness for each of the respective samples; based on a scale of 1-3 with 1 being the value given to the most offensive, and 3 to the least, expressed as means.

[f]Ammonia generation rate expressed as means ($\mu g/hr$).

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.

This indicated that the initial olfactory evaluation of bovine manure would be affected by the relative proportions of urine, feces, and water that it contained. The urine fraction seemed to be responsible for the initial odors associated with manure. This indicates, during the initial phase of gas and odor production from bovine waste, that ammonia generation rates would be a good indicator of the offensiveness of the odors associated with the waste.

SECTION II

EXPERIMENTAL PROCEDURE

This section describes five separate experiments. In the first experiment different sources of cereal grains (corn, milo, and barley) and amounts in the ration (25, 50, and 75%) were related to volatilization rate of ammonia and hydrogen sulfide from the respective wastes. The relationship between the grain fed (corn, milo, or barley) and the pH of the manure produced was studied in the second experiment when concentrates provided 75% of the ration. Samples containing 95% and 99% moisture with the same amounts of feces and urine were evaluated in the third experiment to determine the effect moisture has on the release of volatile ammonia and amines. Experiment four determined the effect the relative portions of feces, urine, and water have on the volatilization rate of ammonia. The fifth experiment was designed to evaluate the relationships between several variables (urea content, pH, storage period, crude protein content, dry matter, and specific gravity of urine) associated with animal wastes on the initial volatilization rate of ammonia and other volatile nitrogen containing gases.

Effect of the Grain Source on the Volatilization of Ammonia and Hydrogen Sulfide

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 increasing levels of concentrations (25, 50, and 75%) in a complete ration (Appendix Table 1). The animals were housed in the beef confinement units at Oregon State University during the experimental period.

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. The 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 min. 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 20 cu.in./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 20 cu.in./min.

for a period of 22 hr. The boric acid traps were then combined and

the ammonia content was determined using the nesslerization method

(A.P.H.A., 1970). A diagram of 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] for a period of 48 hr. 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 (Hach, 1970).

Relationship Between Grain Source and pH of Animal Waste

Corn, milo, and barley based rations were fed to groups of five

Holstein replacement heifers. Each grain composed 75% of a com-

plete ration; the composition of the rations is given in Appendix Table

1. 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 were 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 hr, during which time the head space gases were being replaced at the rate of 20 cu. in./min. After the trapping 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 Keenley (1965).

Effect of Moisture on the Volatilization of Ammonia and Amines

Samples of feces were collected from a group of Holstein replacement heifers maintained on a ration with 25% barley and 75% alfalfa. 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 hr) 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 samples containing 95% and 99% moisture. The 95% moisture samples contained 50 g feces, 24 g urine and 75 g distilled 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 required to be adjusted back to their original volume on a daily basis by adding distilled water to replace evaporative losses.

A diagram of 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 present. The head space gas of each of the samples was replaced at the rate of 20-25 cu. in. /min. and then bubbled through a boric acid trap to remove the ammonia and amines; traps were changed every 24 hr. Total volatile nitrogen and amine evolution rate of each of the samples was then determined.

The method described by Ekladius and King (1957) 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 Keenley (1965) and expressed as ammonia.

Effect of Feces, Urine, Water, and Storage Period on Ammonia Release

Fresh feces and urine were collected as described previously from heifers which were fed a base ration containing 25% barley and 75% alfalfa hay (Appendix Table 1). A composite sample was made for both the urine and feces. Duplicate samples of the following combinations 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
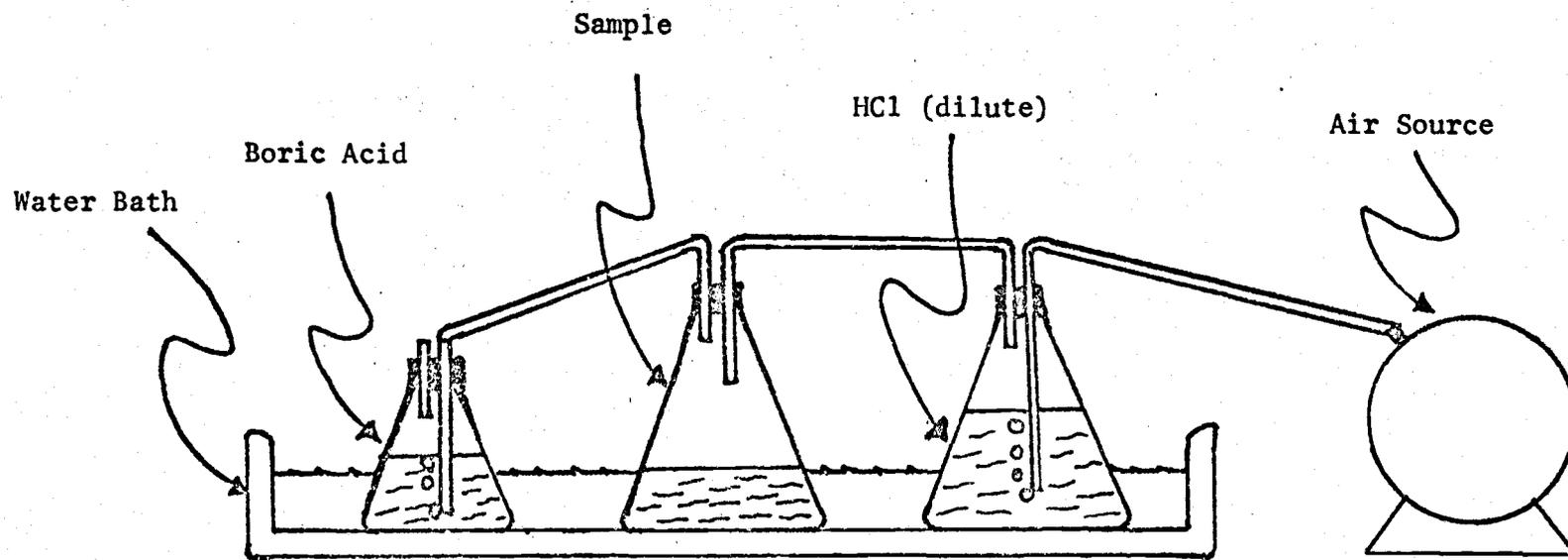
Figure 3. Ammonia and amine trapping apparatus.

contained a total weight of 100 g.

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 20 cu. in. /min. and trapped for a period of 3 hr; 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 Keenley (1965) and expressed as ammonia.

Effect of Various Variables Associated with Animal Waste on the Evolution of Ammonia and Volatile Nitrogen Gases

Two groups of five Holstein heifers were fed barley based rations that contained three levels of barley (25, 50, and 75%) formulated into complete rations (Appendix Table 1). 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 and maintained at 30°C. The trapping procedure has been described previously. The ammonia released from the samples was trapped for a period of 3 hr.

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 (expressed as ammonia) on each of the combined boric acid traps. The dry matter content was determined by drying a fecal sample for a period of 24 hr at 100° C. The crude protein was determined by using the micro-Kjeldahl method 42.016 (A.O.A.C., 1970). The ammonia was determined by taking a 10 ml portion of the combined boric acid traps from 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 (Anonymous, 1964) was used to measure the urea content of the urine samples. A urinometer was used to measure the specific gravity of the urine samples.

RESULTS AND DISCUSSION

Effect of the Grain Source on the Volatilization of Ammonia and Hydrogen Sulfide

The hydrogen sulfide evolution rates were similar (P > .10) between samples from cattle fed the corn, barley, and milo based rations (Table 3). 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 were similar with each of them being appreciably higher (P < .05) than their respective 20% and 50% levels.

Table 3. Hydrogen sulfide generation rates from mixtures of 50 g feces and 50 g urine collected from Holstein replacement heifers fed various levels of corn, milo, and barley.

	No. Obs.	Mean[a]	Std. Dev.
Corn[b]			
25%	8	0.390[c]	0.48
50%	37	1.121[c]	0.67
75%	72	4.96[d]	1.54
Barley[b]			
25%	19	0.616[c]	1.112
50%	50	0.653[c]	0.513
75%	59	4.87[d]	1.38
Milo[b]			
25%	6	0.498[c]	0.32
50%	34	0.741[c]	0.64
75%	76	4.531[d]	0.97

[a] Means expressed as μg/hr.
[b] Percentage of ingredient in complete ration.
[c,d] 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) between the different levels of supplementation and the grains, with the exception of the 75% milo and the 50 and 75% barley based rations that were different (P < .05) as shown in Table 4.

Table 4. Effect of corn, milo, and barley supplemented at the 25%, 50%, and 75% level in a complete ration on the initial evolution rate of ammonia from manure samples collected from animals maintained on each of these respective treatments.[1]

	Sample Size	Means[2]	Std. Error of Mean
Corn			
25%	24	3037.7^{ab}	424.3
50%	11	3467.5^{ab}	401.5
75%	26	3189.2^{ab}	269.3
Barley			
25%	26	3107.2^{ab}	527.9
50%	34	3921.1^{a}	470.3
75%	14	3833.0^{a}	322.2
Milo			
25%	14	2925.9^{ab}	543.2
50%	26	2855.3^{ab}	344.45
75%	34	2325.44^{b}	233.24

[1]Samples contained 50 g of feces and 50 g of urine.

[2]Means 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

Results indicate 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 5. There was a difference (P < .05) between the pH

of the samples for each of the grains as indicated in Table 6, but dif-

ferences in ammonia release were not (P > .05) noted between grains

in the pooled data.

Effects of Moisture on the Volatilization of Ammonia and Amines

The amines represented an average of 0.11% of the initial total

nitrogen volatilized (expressed as ammonia) with averages of 17.86

and 16.41 µg/day being volatilized from the 95% and 99% moisture

levels, respectively. Average ammonia evolution rates were 15.15

and 13.20 mg/day for the 95% and 99% moisture samples, respec-

tively. The ammonia and amine evolution rates had a significant nega-

tive correlation with the length of storage (Table 7) and ammonia and

amine release rates were found to be positively correlated (P <.01)

to each other. This would support the idea expressed by Merket

et al. (1969) that ammonia was a precursor of amines.

Table 5. Correlation between pH and ammonia evolution rate of manure eliminated from cattle receiving 75% of their ration as either corn, milo, or barley. [1]

Ration	Correlation Coefficients Between pH and NH_3	P[2]
Corn	0.5022[a]	.01
Milo	0.4204[b]	.05
Barley	0.3838[c]	.05

[1] pH was determined on samples composed of 50 g feces + 50 g urine from each of the respective groups.

[2] Correlation coefficients are significant at the probability level listed.

[a,b,c] Correlation coefficients are based on the following number of comparisons 28, 27, and 29 respectively.

Table 6. pH and ammonia evolution rates from feces and urine mixtures collected from cattle receiving 75% corn, barley, and milo rations. [1]

Ration	Average pH[d]	Std Error of Mean	Ave. Ammonia[d] (μg/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

[1] Samples composed of 50 g feces + 50 g urine from each of the respective groups.

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

[d] Expressed as means of 28 observations.

Table 7. Correlations between amine evolution rate and period of storage; and ammonia evolution rate and period of storage of manure samples containing 95% and 99% moisture. [1]

Relationship Correlated	Correlation Coefficient	P[2]
Length of storage vs Ave. amine 95% moisture	-0.771	.01
Length of storage vs Ave. amine 99% moisture	-0.538	.05
Length of storage vs Ave. ammonia 95% moisture	-0.727	.01
Length of storage vs Ave. ammonia 99% moisture	-0.783	.01
Ave. ammonia 95% moisture vs Ave. amine 95% moisture	0.903	.01
Ave. ammonia 99% moisture vs Ave. amine 99% moisture	0.822	.01

[1] Based on a 14 day storage period and duplicate samples.

[2] Correlation coefficients are significant at the probability levels listed.

Effect of Feces, Urine, Water, and Storage Period on Ammonia Release

Average ammonia evolution rates for the various samples are given in Table 8. Ammonia was evolved at a faster rate from samples containing urine (P < .05) than the samples containing only feces and water, with the exception of the 75% feces + 25% urine samples.

Correlation coefficients between the ammonia relase rates and length of storage for the various samples are given in Table 9. The samples containing feces only and feces + water were found to be positively correlated (P < .01) with the exception of the 5% feces + 95% water samples.

Table 8. Effects of various combinations of feces, urine, and water on the average initial ammonia evolution rates of manure from bovines.[1]

Sample	Ammonia[2] (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).

[1] Samples total weight was 100 g.

[2] Values expressed as means.

Table 9. Correlations between average initial ammonia release rate and length of storage of manure samples from bovines containing various combinations of feces, urine, and water.[1]

Sample	Correlation Coefficient[2]	P[3]
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] Samples contained 100 g of material.
[2] Calculated on the ammonia evolution rate vs the number of days of storage.
[3] Correlation coefficients are significant at the probability level listed.

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 + water samples showed no rapid initial release of ammonia but the release rate increased as the storage period increased. The combination of feces and urine samples showed a rapid release of ammonia initially, then a decrease at day 5 until day 15 and than a gradual increase starting at that time and continuing until the end of the 25 day period.

Urine was found to be primarily responsible for the initial release of ammonia; feces had little effect. 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 which was released. The results 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.

Effect of Various Variables Associated with Animal Waste on
the Evolution of Ammonia and Volatile Nitrogen Gases

The feeding trial was divided into five periods; 25% barley; adjustment period between 25% and 50% barley; 50% barley; adjustment period between 50% and 75% barley; and the 75% barley level.
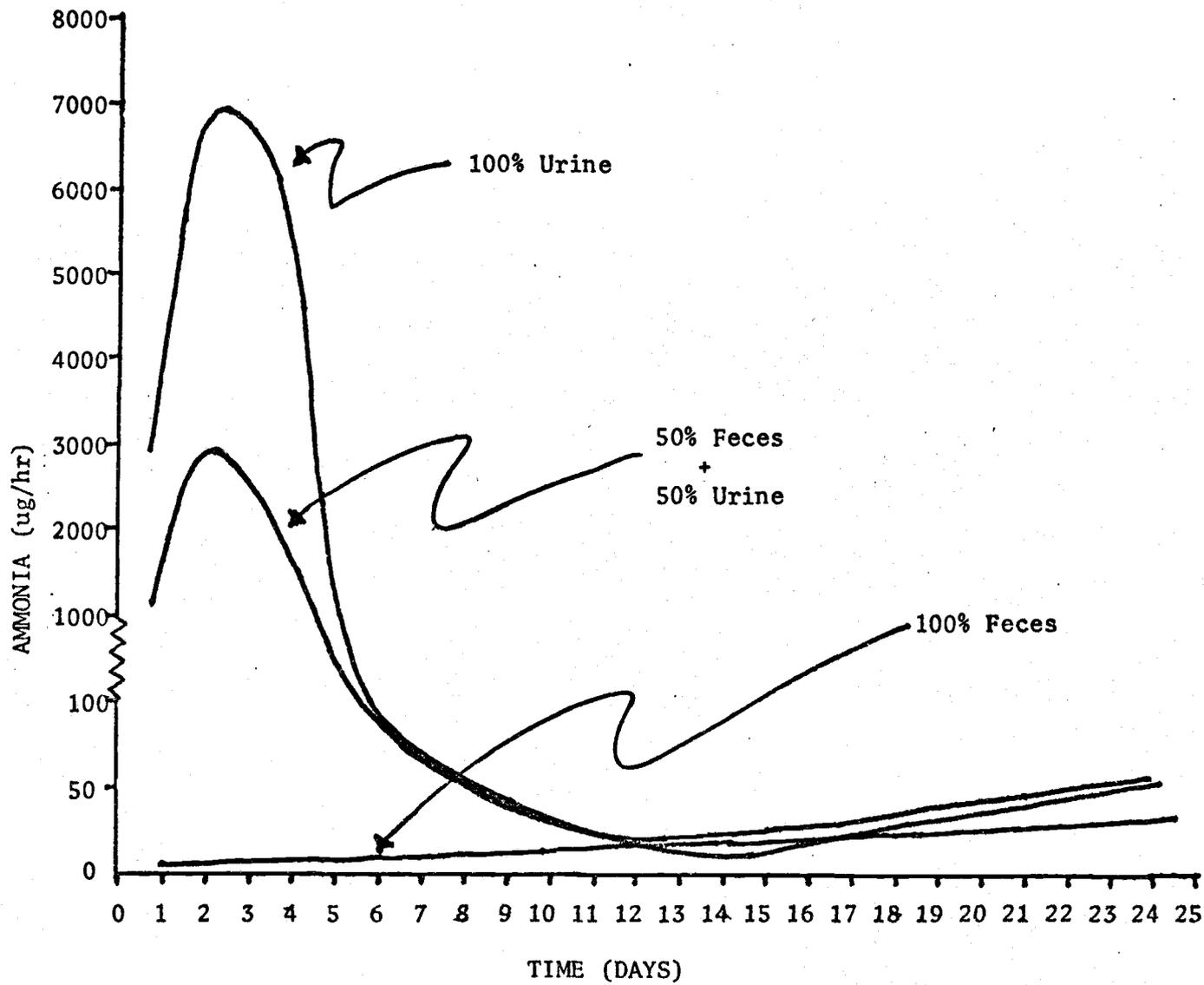
Figure 4. Evolution of ammonia from stored feces and urine.

The means and standard error of the means are given for each of

these periods in Table 4 of the Appendix. Correlation coefficients for

the interactions are shown in Table 5 of the Appendix along with the

probability levels that are significant. The correlations between the

various variables and total volatile nitrogen are given in Table 10.

The dry matter and crude protein content of the samples were found

to have no effect $(P > .10)$ on the initial release of ammonia.

Table 10. Correlations between the initial ammonia evolution rates
from manure samples and the dry matter, crude protein,
urea content, specific gravity of the urine of the samples;
and the total initial volatile nitrogen evolved. [1]

	Correlation Coefficient	No. of Comparisons	P^2
Ammonia vs dry matter content	0.0159	134	NS
Ammonia vs crude protein content	0.0081	81	NS
Ammonia vs volatile nitrogen	0.8783	178	.001
Ammonia vs urea content of urine	0.3124	108	.01
Ammonia vs specific gravity of urine	0.2700	132	.01

[1]Samples contained 50 g of feces + 50 g of urine.
[2]Correlation coefficients are significant at the probability level listed.

The ammonia and total volatile nitrogen values were highly

correlated $(P < .01)$. 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.

The averages for dry matter, crude protein, total volatile nitrogen, ammonia, urea content, and specific gravity of the urine are given in Table 11.

Table 11. Composition of manure samples collected from Holstein replacement heifers (dry matter, crude protein, urea content of urine and specific gravity of urine) and evolution rates of nitrogenous gases (total volatile nitrogen and ammonia).

Variable	No. of Obs.	Average	Std. Error of Mean
Dry matter	204	19.99%	0.1745
Crude protein	163	10.73%	0.3134
Total volatile nitrogen	210	13.73 µg/hr	0.5813
Ammonia	178	13.07 µg/hr	0.6177
Urea content of urine	174	855.9 mg%	43.189
Specific gravity of urine	205	1.027	0.00077

CONCLUSIONS

The olfactory evaluation of the waste produced by animals which were fed essential oils showed that the offensiveness of the odors associated with the 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 that was associated with the waste. This modification was thought to be a masking effect directly related to compounds that were excreted in the urine; it was not associated with the feces. The addition of sagebrush at 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 concentration of essential oils may have been different between the various sagebrush varieties; the sagebrush used in this experiment had an intermediate level of essential oils.

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 to be related to the pH of the wastes that are produced, which in turn affects the subsequent release of the basic volatile nitrogenous gases. The ammonia release rate was found to be approximately 1,000 times greater than that of hydrogen sulfide 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 that were evaluated were responsible for some differences in pH of the waste produced. The waste produced from the milo based (75% of the diet) ration 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 the ammonia release rate and pH.

Increasing the moisture content of the waste was found to reduce the evolution rate of ammonia and amines during the initial storage period. This was thought to be due to the capacity of the water phase to hold the ammonia and reduce its volatilization rate. The ammonia evolution rate was negatively correlated with the length of the storage period. This indicates that the 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 fraction of the waste. Approximately 100 times more ammonia was evolved from the urine portion than from the fecal portion. The evolution of ammonia from urine was rapid. The feces showed a more prolonged release and accounted for a small portion of the total ammonia that was volatilized from the waste.

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

Approximately 95%+ of the nitrogen content of the urine fraction was volatilized as ammonia when allowed to decompose alone or combined with fecal material. Less than 5% of the non-urea nitrogen was volatilized during the initial 25 days of storage. The urea fraction of the urine accounted for approximately 50% of the nitrogen that was secreted by the animal. Based on the above values, calculations based on nitrogen content of feces and urine samples and their subsequent generation rates of ammonia, a 1000 lb animal would produce approximately 100 grams of ammonia per day and would account for a substantial nitrogen enrichment of the surrounding environment in areas of high animal densities.

The alteration of bovine rations has shown that changes can be produced in variables associated with the waste that are known to affect the generation of volatile gases. Further research is needed to determine how practical this approach would be in controlling the volatilization of gases and odors from bovine confinement production units.

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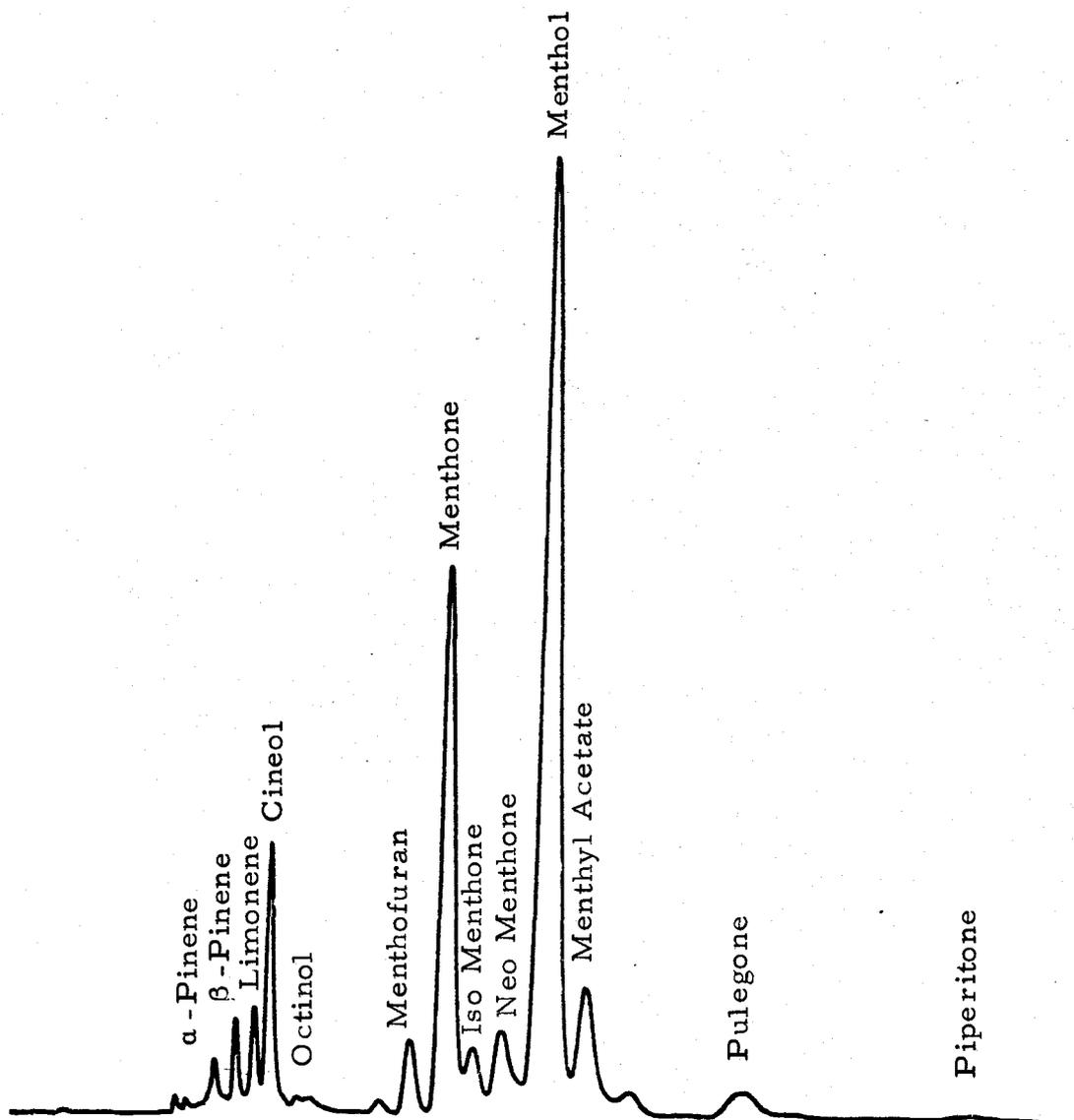
APPENDIX

Appendix Table 1. Ration composition[1] (lb/1000 lb).

	25%	50%	75%
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%).

Menthofuran   2.5%
Menthone + isomenthone   22.5%
Neo menthone + menthol   49.6%
Menthyl acetate (esters)   6.6%

Appendix Table 2.   Chromatogram of peppermint oil.

Appendix Table 3. Correlations between water, feces, urine content and rating, ranking and ammonia release rate.

	Correlation Coefficients	P
Number Rating		
Water	-0.045	NS
Fecal	-0.154	NS
Urine	0.109	NS
Number Ranking		
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

Appendix Table 4. Crude protein, dry matter, urea, and specific gravity of wastes from barley fed Holstein replacement heifers at the 25%, 50%, and 75% levels.

Sample	Dry Matter (%)	Crude Protein (%)	Ammonia (μg/hr)	Total Volatile Nitrogen (μg/hr)	Urea (mg%)	Specific Gravity
Barley 1	18.95±0.25	10.28±0.339	8.14±1.06	9.9 ±0.57	848.9±46.5	1.032±.00122
Between barley 1 & barley 2	19.34±0.269	9.47±0.35	10.9 ±0.99	11.09±0.91	801.6±85.9	1.023±.00184
Barley 2	20.0±0.27	10.8 ±0.58	14.62±1.03	15.93±1.00	737.7±49.9	1.028±.00127
Between barley 2 & barley 3	21.38±0.36	11.08±0.35	16.25±1.39	17.85±1.53	793 ±48.4	1.024±.00129
Barley 3	20.15±0.80	11.01±0.55	10.06±1.86	10.43±1.64	896 ±177	1.025±.00399

Appendix Table 5.   Correlations between crude protein, dry matter, urea, specific gravity and volatile nitrogen release of animal wastes.

Sample	Dry Matter vs Ammonia	P[1]	Crude Protein vs Ammonia	P[1]	Ammonia vs Total Volatile Nitrogen	P[1]	Urea vs Ammonia	P[1]	Specific Gravity vs Ammonia	P[1]	Urea vs Specific Gravity	P[1]
Barley 1	-0.2035	NS	0.2723	NS	0.7108	.01	0.2405	NS	0.2014	NS	0.5802	.01
Between barley 1 & barley 2	-0.0635	NS	0.2375	NS	0.9357	.01	0.2594	NS	0.3821	.05	0.2750	NS
Barley 2	-0.1259	NS	0.0606	NS	0.7406	.01	0.5106	.01	-0.0255	NS	0.2557	NS
Between barley 2 & barley 3	0.0774	NS	-0.0839	NS	0.9364	.01	0.4717	.01	0.5187	.01	0.5809	.01
Barley 3	-0.4317	.05	-0.3852	NS	0.8722	.01	0.5704	.05	0.2706	NS	0.4114	NS

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