DENITRIFICATION IN A SOIL COLUMN WITH INCORPORATED BEEF MANURE AND APPLIED ANAEROBIC LAGOON WATER

by 613.8302

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INTRODUCTION

Pollution has been an important topic for debate for the last few years. Since the realization that not all things being produced by a manufacturing process are necessarily good, a large effort has gone into researching means for at least minimizing the pollution, or degradation of the environment, caused by waste products.

One of the major sources of wastes which has received considerable attention has been the beef industry. Because of the demand for this industry's final product, the necessity for good waste management is not only a current need, but can be expected to be a greater need in the future. According to Ahalt and Hairon (1970), the per capita consumption of beef is expected to rise from 112 to 130 pounds for the decade after 1970. Along with the expected increase in population, the significance of feverishly searching out solutions as readily as possible should be apparent.

One possible approach to manure management would be to convert it from a waste to a source of energy. Anderson (1972) has indicated that the Bureau of Mines currently has a method developed for converting organic wastes into oil with a low sulfur content. They also have a procedure developed which will produce methane gas from organic wastes. Due to predicted shortages in energy, these processes would appear to be very appealing. However, Anderson also indicates that of the total organic wastes currently being generated in manure, only 13% might be available for these conversions. Only a small portion of the problem, therefore, would be solved in this manner.

One solution which is receiving considerable attention is the disposal of beef feedlot wastes on the soil. The appeal for a manager of an agri-business to consider land disposal is that the manure may have potential value as a crop nutrient and that land disposal is the most convenient method available. However, as the manager expands and land becomes limiting, he may be forced to apply amounts well in excess of the optimum amount for fertilizer value. These heavy amounts create a good potential for groundwater pollution. In field studies where solid and/or liquid manures from dairies were applied on cropland in rates ranging from 20 to 45 T/A per year, plus some commercial fertilizers, Adriano, Pratt and Bishop (1971) reported nitrate nitrogen values in the groundwater averaged 45 ppm. Since the U.S. Public Health Service's upper limit for nitrate nitrogen is 10 ppm, it can be seen that much care needs to be taken in the application of heavy manure loads on the land. One of the more serious consequences that can result if this limit is exceeded is the potential for nitrate to cause the disease infant methemoglobonemia.

It is therefore evident that in order for the spiral of beef production to be sustained, all aspects of this enterprise must be thoroughly investigated. Since land disposal is currently the most practical means of waste management, investigations are needed to determine its effects and to determine means of controlling the processes associated with its implementation.

LITERATURE REVIEW

Mitrogen Cycle

Since the discovery of the denitrification process, considerable research has been conducted attempting to determine the details of the process. Only in the last few years has this research been directed to denitrification as a possible pollution control or waste disposal process. The initial concern of researchers was for the economic losses involved in losing nitrogen to plant consumption. Intimately involved with the research of denitrification has been work concerning mineralization and nitrification. Since there are many excellent reviews of these three processes, only brief descriptions will be given here.

Also to be described are redox potentials followed by a synopsis of the work done by George (1970) and Booram (1971).

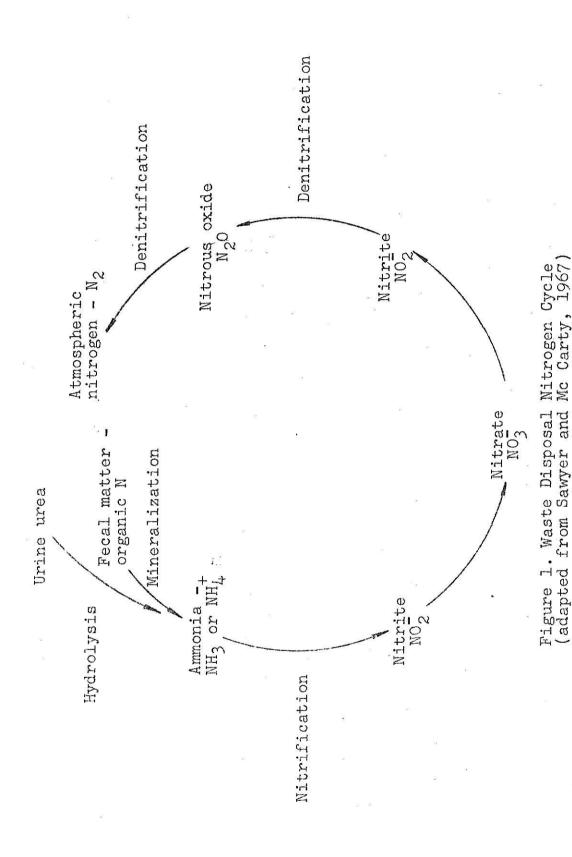
The portion of the nitrogen cycle which is of primary concern in this research is shown in Figure 1. This cycle was adapted from Sawyer and McCarty (1967).

The beginning of the nitrogen cycle in terms of waste disposal occurs with the depositing of fecal matter and urine urea in the feedlot. The urine urea is rapidly hydrolyzed to ammonia. The mineralization of fecal matter converts organic nitrogen to ammonia. This microbiological transformation is effected by several environmental factors. These factors are summarized in Table 1 along with the factors effecting nitrification and denitrification.

After the conversion of organic nitrogen to ammonia,

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Summary of Environmental Factors Effecting Mineralization, Nitri-fication and Denitrification. * Table 1.

Environment	Wineralization	Nitrification	Dentrification
Aeration state	Aerobic and anaerobic	Aerobie	Anaerobic or aerobic with pockets of anaerobiosis
Нď	Neutral - acid conditions depress	6 - 2	Constant above 6
Moisture content	Optimum conditions are at 50 - 75% of the water holding capacity	Same as for mineralization	Highest for water- logged soils with increasing rates up to 450% of the water holding
Temperature	0°09 - 04	30 - 35° C	25° C and above
Microorganism type	No specific group	Primarily autotrophic	Facultative anaerobic bacteria
Organic matter	The main effects of orghydrogen donor and an i	organic matter are as an end n influence on the aeration	energy souce, a ion of the soil
* Summerized	from Alexander (1961), A	Alexander (1965), Broadbe	Broadbent and Clark (1965)

exander (1905), broadbent and Clark (1965) and Bartholomew (1965)

nitrifying bacteria continue the nitrogen cycle. In a very general sense, nitrification has been defined by Alexander (1965) simple as "the specific process in which there occurs an increase in the oxidation state of nitrogen." This definition allows for the possibility of the conversion of inorganic as well as organic forms of nitrogen to a more oxidized state, Denitrification, then, is the biological reduction of nitrate and nitrite to volatile gases. These gases are primarily acknowledged to be nitrous oxide and nitrogen gas. In order for denitrification to be used as a pollution control or a waste disposal process, all three of the above phases of the nitrogen cycle must be considered as a chain of events.

The environmental variables listed in Table 1 are the main factors which have a controlling effect on the three processes of interest. The final end product of waste disposal research is to determine means of controlling the environment for the desired result. A primary variable for study, therefore, is the moisture content of the soil. Another major control possibility is the pH of the soil.

Aeration of the soil primarily determines which processes are occurring in the soil. The main factor which controls aeration is the moisture content of the soil. There appear to be two means by which the soil moisture content could be used as a control measure. The most difficult would be the maintenance of a soil profile such that all processes are occurring simultaneously. This is possible where nitrification is occurring in one portion of the soil profile with subsequent movement of nitrates to zones of anaerobiosis. A control measure which might be somewhat more

predictable is the cycling of the entire profile between a water-logged state and the moist conditions as indicated in Table 1.

The problem of control then is the determination of the aeration status of the soil. One means of measuring this condition is with the measurement of redox potentials.

Redox Potentials

Oxidation-reduction, redox, potentials are an indication in natural systems of the opposing result of electron donation and acceptance rates. These rates are related to the microbial activity (Bohn, 1971). Since nitrification is an oxidation process and denitrification is a reduction reaction, redox potentials have the possibility of indicating which reaction is taking place. From this it can be seen that the redox potential is intimately related to the aeration status of the soil.

Redox potentials are based on the reactions of redox couples. The Nernst equation had been used to calculate these potentials. Bohn, Penn and Moore (1969) have indicated that this equation can only be used in equilibrium or steady state conditions or in the improbable circumstance of completely reversible couples for all redox couples present. The Nernst equation is an electrochemical approach to the ratio of the concentrations of the reactants in an oxidation-reduction situation (Sisler, VanderWerf and Davidson, 1967). Therefore, in a pure mixture of one couple at equilibrium, this equation might be used as a quantitative measure. This situation does not exist in a soil system. Bonner and Ralston (1968) have indicated that a soil system is a complex mixture of metals, organic compounds and gases. This was reflected upon

also by Bohn (1971) when he referred to a weighted average of all redox couples in a system as being a first approximation of a mixed potential. He expanded on this by indicating that negative potentials are produced not only by oxygen deficiencies but also by "increased solubility of iron, aluminum and manganese, and by accumulation of hydrogen sulfide, methane and hydrogen." Since redox potentials cannot be used quantitatively, the remaining use for them is in a qualitative sense. This is emphasized by Baas Becking, Kaplan and Moore (1960) in their conclusion that redox potential and pH measurements may give an indication of the ecology of the environment.

Bohn (1968) has defined electrode potentials (Eh) as "the electrochemical potential of the electrons exchanged at equilibrium between the redox couples and between the couples and an inert electrode." This definition again refers to the equilibrium condition. It also refers to inert electrodes. The problem of inert electrodes is that no metal is completely inert with respect to redox systems in the soil. Platinum is one metal which approaches this inert quality. With reference to these "inert" electrodes, Bohn (1971) indicates that they are influenced in proportion to the redox couple's ability to exchange electrons with the electrode surface. It is acknowledged then that Eh is a rough measurement of oxidation-reduction conditions (Bohn, 1968).

The difference between pure and mixed potentials was shown by comparing calculated values and experimental values. Bohn, Fenn and Moore (1969) used the Nernst equation for calculating some Eh-pH diagrams. For the nitrate to nitrite reduction system, an electrode potential of +435 mv was determined for pH 7.

For the same pH value, several researchers have reported values in the range of +200 to +250 mv at which nitrate is being reduced to nitrite (Bailey and Beauchamp, 1971; Patrick and Delaune, 1972; Patrick and Mahapatra, 1968; Patrick, 1960; Pilot and Patrick, 1972; Bell, 1969). Meek, Grass and MacKenzie (1969) found large nitrogen losses at +300 mv or less. In a soil column equipped with electrodes at several depths, Lance and Whisler (1972) attributed a rise in redox potentials from negative values to values in the range of +200 to +400 mv to a short period of apparent nitrate reduction. These values help to point out the differences between the pure, calculated potentials and the actual mixed potentials.

In reference to these differences, it is now possible to be concerned about some general guidelines. Patrick and Mahapatra (1968) have set up some redox potential ranges for indicating oxidized or reduced conditions. At a pH of 7, greater than +400 my is an oxidized zone; moderately reduced is from +100 to +400; -100 to +100 indicates a reduced condition; highly reduced potentials are from -100 to -300 mv. The limiting redox potentials for an aqueous system are indicated by Baas Becking, Kaplan and Moore (1960). Oxidizing conditions have the oxidation of water to molecular oxygen as an upper boundary. Reducing conditions are lower bounded by reduction of the hydrogen ion to molecular hydrogen. A generally accepted relationship between Eh and pH is Eh7=Eh+59(pH - 7) where Eh7 is the potential corrected to pH7, Eh is the measured potential, and pH is the pH at the measured potential. The value 59 is calculated from the Nernst equation (Sisler, VanderWerf and Davidson, 1967). One exception to this

was the use by Bohn (1968) of the value 40 which was taken from some unpublished TVA data.

The equipment necessary for redox can be accumulated with some ease. Most researchers construct the necessary microelectrodes because commercial probes are somewhat expensive. A quite good description of the construction and standardization is given by Mann and Stolzy (1972). The reference electrode used is a saturated calomel electrode. When using this reference electrode, the conventional procedure is to add 244 mv to all readings in order to standardize redox potentials to the hydrogen electrode (Sawyer and McCarty, 1967). In order to take readings, a pH meter can be used with an appropriate recorder if desired.

One use for redox potentials was an application by Patrick and Delaume (1972) to determine the thickness of the oxidized zone in a soil submerged by one inch of water. Using their device, it was possible not only to determine an initial thickness, but also to see the zone become thicker with a decrease in the available organic matter. An indication of the possibilities for redox potentials was the determination that nitrates in a system poised the system at +200 mv. Bell (1969) observed that this poising was followed by a decline in the redox potential to a -300 mv with a concurrent evolution of methane. The addition of nitrate to the system at this point repoised the system at +200 mv with a cessation in methane production. Bell concluded from this that it might be possible to eliminate the methane part of the cycle if sufficient nitrate were present to completely utilize the substrate by nitrate respiration. Another possible

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use of this observation would be to control the redox at an above some level such as +150 or +100 mv. This would help to maximize the nitrification-denitrification chain by conserving energy that would otherwise be used for methane production. Redox potentials, if utilized carefully, would appear, then, to have considerable possibility as a monitoring and/or a control procedure.

George (1970)

George's main contribution to the research of feedlot waste disposal was the groundwork of assimilating the three basic types of soil nitrogen studies. His attempt at combining "the total soil profile of a lysimeter, the closed gas collection system of an incubation apparatus and the soil solution sampling ability of a percolation apparatus" was moderately successful. George apparently was able to develop an excellent soil solution sampling apparatus. This enabled him to profile the changing conditions within the soil column. The two main objectives that were not accomplished were the ability to monitor the soil moisture conditions and the qualitative and quantitative analysis of the gases. The soil moisture problem arose out of some apparent equipment faults. He suggested that possibly the best approach to this problem might be the use of tensiometers. The gas analysis was the major problem, however. In George's study, atmospheric air was used. In attempting to quantify and qualify the gases, a wet test meter was used to measure the influent air volume and a wet test meter plus a gas chromatograph were used to analyze the effluent gases. Because of the large amount of nitrogen in the influent gas, plus some leakage that occurred, it was impossible for George to attempt a nitrogen balance for

his system. His suggestion for gas quantification was the possible use of a water displacement system. By making these modifications, George felt that the system would be workable.

Booram (1971)

Booram used basically the same system as that designed by George. He made one major change, following George's suggestion. In order to obtain gas quantification, oil displacement reservoirs were set up for both influent and effluent gases. Using this system, Booram ran two different tests. In his first test, atmospheric air was used as the influent air. He again suffered the problem that George had of trying to determine the difference between the quantity of nitrogen in the incoming gas and the nitrogen added through denitrification. This led him into the second experiment where the use of an artificial atmosphere was attempted. Instead of using atmospheric air as the influent gas, a mixture of 85% helium and 20% oxygen was used. Because of some apparent leaks, which may or may not have caused large differences in the input and output volumes, the gas analysis was again invalid. Booram's conclusion was that the present gas chromatograph was incapable of the accuracy required for a nitrogen balance. He suggested either replacing the present gas chromatograph with a more sophisticated one or using a mass spectrometer. This was suggested in addition to making the analysis on a batch basis rather than on the basis of analyzing the gases as they are drawn from the column.

By way of summary, the system which has been developed would appear to have considerable potential. Aside from some minor problems, the apparatus has given some quite excellent water sampling and with some modification the gas analysis would appear

to have some potential. If the gas analysis can be further refined, a nitrogen balance should be in the offing. Using the available techniques of redox potential measurement and possibly tensiometer use along with pH measurement, control of a soil column could be possible also.

INVESTIGATION

Purpose

The prime objective of this research was to continue the work of George (1970) and Booram (1971). They attempted to develop equipment with which a nitrogen balance could be obtained for a soil profile.

A secondary objective was to study the effect of applying anaerobic lagoon water to a soil profile with two zones of heavily applied feedlot manure.

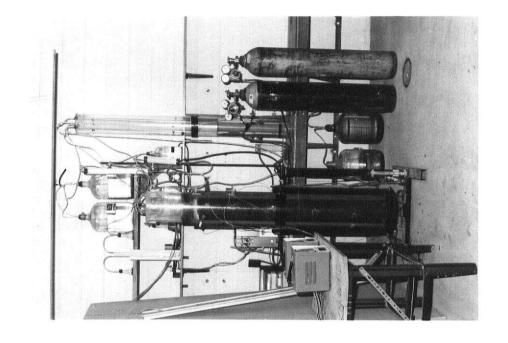
Materials and Equipment

After considering the recommendations of George (1970) and Booram (1971), the system shown in Figures 2 and 3 was decided upon. The main idea behind this system was to try to simplify the previous systems as much as possible in order to obtain a better analysis of the gas.

Since the water sampling system was functioning quite well, as a first step toward simplifying the system, this part was eliminated to a large extent. Water samples were initially collected at the bottom of the column only. The bottom of the column was made by sealing a Coors porcelain plate, I, into a plexiglass plate. This porcelain plate had a maximum pore diameter of 0.5 micron. Except at a very high vacuum, this plate would not allow the passage of any gas when the plate was saturated. The plate was fastened to the bottom of the column in a manner which would allow its removal. The bottom was sealed, as were all seams in the system, with Formica Brand

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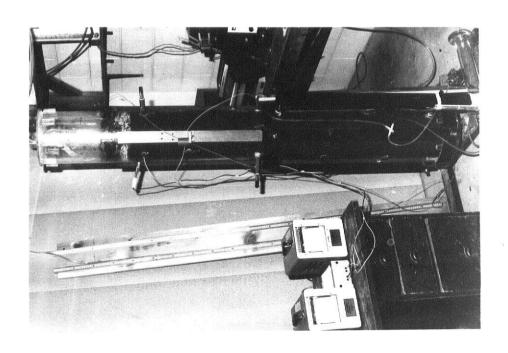


Figure 2. Soil Column with Soil and Manure in Place

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Legend for Figure 3.

- A. Soil column
- B. Drierite column
- C. Oil manometer
- D. Oil storage
- E. Hand clamp
- E_{Ω} Hand clamps on the oil lines
- F. Soil tensiometer
- G. Reference electrode
- H. Platinum electrode
- I. Porcelain plate
- J. Sulfuric acid scrubber
- K. Sodium hydroxide scrubber
- L. Mercury manometer
- M. Fritted glass sampler
- N. Collection flask
- P. Gas chromatograph
- R. Tubing pump
- S. Atmosphere storage column
- T. Oxygen source

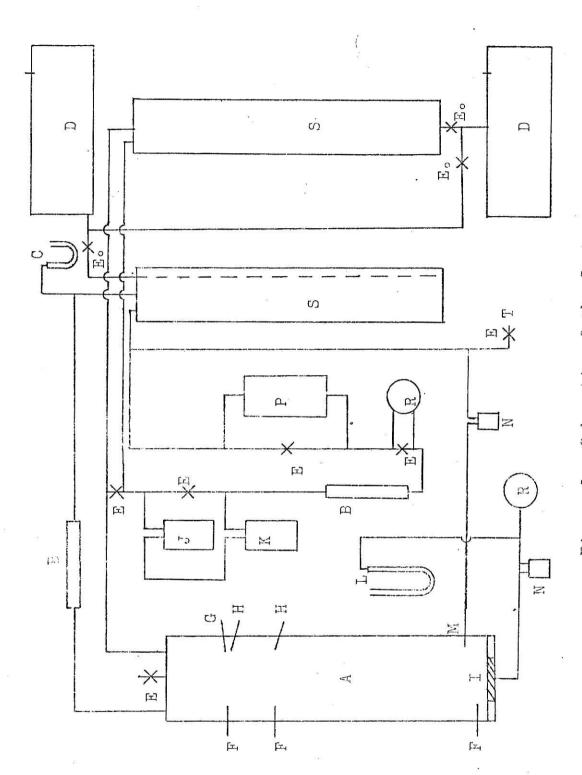


Figure 3. Schematic of the System.

140 adhesive. The use of this porcelain plate allowed the application and maintenance of a vacuum on the plate. By varying this vacuum, it was expected that the soil moisture tension could be controlled. This system also precluded any movement out of the soil profile of gas except at the soil surface.

By the 72nd day, water movement through the porous plate had become slow enough that a fritted glass sampler, M, was placed into the soil column 18 cm above the porous plate. This will be discussed in greater detail in the results. Because this sampler would allow gas movement out of the soil, the sampler was vented to the gas storage columns. All water samples were preserved by the addition of adequate sulfuric acid to stop any microbiological activity.

There were two major changes in the gas analysis system. Following Booram's suggestion, a batch approach to the analysis was decided on. Since no gases were to be drawn from the soil profile, the gases were circulated through the top of the column, A, from the atmosphere storage columns, S. The initial atmoshere was made up of 80% helium and 20% oxygen. Provision was also made for admitting oxygen, T, as needed to maintain the 20% oxygen level.

The gas circulation in the system was accomplished with a tubing pump, R. This pump would pull gas from the top of the soil column. The gas would then flow through a sulfuric acid solution, J, to scrub out any ammonia. It would then pass through a sodium hydroxide solution, K, where carbon dioxide would be scrubbed out. Following this, the gas was dried before entering the gas chromatograph, P, by passing it through a small column

containing Drierite, B. The gases then flowed back to the soil column by way of the storage column and another Drierite column.

Gas circulation was carried out only for mixing purposes prior to analysis or for scrubbing when the carbon dioxide level became high. For the remainder of the time, the by-pass clamps, E, were opened up in order to allow the gases to diffuse between storage and the soil column.

The second major change in the gas system was the removal of the automatic mode of operation. Booram accomplished the regulation of atmospheric pressure through the use of solenoid valves in the oil lines. These valves were activated by mercury manometers. Since there was some trouble during Booram's work with these solenoid valves used for pressure equalization, they were removed. The gas pressure was held at atmospheric, instead, by the hand clamps $E_{\rm O}$, on the connecting hoses. The pressure in the system was monitored by an oil manometer, C, with a specific gravity for the oil of 0.827. Using this system, some pressure would build up overnight, but not usually over 10-15 inches of oil.

As indicated from the synopsis of the work by Booram, it was suggested that the gas chromatograph be replaced. However, since only one attempt had been made with this instrument on a batch basis, and since there were other problems concurrently, it was not felt that this instrument had been given a sufficient trial. Therefore, the Fisher-Hamilton Model 29 Gas Partitioner with a strip chart recorder was kept in the system.

The characteristics of this gas chromatograph, according to the instruction manual, are as follows:

The standard Model 29 employs a dual-detector chromatographic system to separate and measure carbon dioxide, oxygen, nitrogen, methane and carbon monoxide.

The standard Model 29 uses in position No. 1 a 6 foot long by 1/4 inch diameter column packed with Di-2-ethylhexylsebacate on 60-80 mesh Columnpak. This is a liquid phase known as DEHS. In the No. 2 position is a 6½ foot long by 3/16 inch diameter column packed with 42-60 mesh Molecular Sieve.

This gas chromatograph has an integral gas sampling valve with a 0.25 ml sample loop. In order to get automation in his system, George (1970) designed an electrical circuit which would control a solenoid valve which he attached to the sampling valve's plunger. For the current system, this circuit was altered for manual activation. When the system was activated by a 110 volt source, the solenoid depressed the sampling plunger. A time delay tube would then deactivate the solenoid after 5 seconds, allowing the sampler to return to its normal position. This system allowed samples to be taken with very good duplication.

When a gas sample was analyzed, a peak was drawn by the recorder which was proportional to the concentration for that particular gas. This concentration was calculated from the following equation:

$$C_s = \frac{H_s}{H_{std}}(C_{std})$$

Where: C_s = Concentration of sample component, % by volume.

Cstd = Concentration of standard
component, % by volume.

H_S = Peak height of sample component, in chart divisions.

H_{std} = Peak height of standard component, in chart divisions.

The standard components which were calibrated were oxygen and nitrogen. The calibration was accomplished with atmospheric air.

Methane and carbon dioxide were not calibrated. Therefore, peaks corresponding to these gases were used as indicators of their presence only.

In order to measure redox potentials, some commercial probes were obtained from Leeds and Northrup. Two Std. 1199-60 platinum electrodes and one calomel reference electrode, electrode No. 117105, were used. The reference electrode and one of the platinum electrodes were placed in the soil at a depth of approximately 12 cm. The other platinum electrode was placed approximately 63 cm deep in the soil. These electrodes were placed in the soil through the side of the column and were sealed to the column with adhesive. The shallower electrodes were positioned just under the manure containing surface soil. The lower probe was placed slightly below a deep manure layer, which is described later.

Since two Cole Parmer Mark VI Potentiometer Recorders were available for this project, a system was constructed for use with these recorders. A schematic of this system is shown in Appendix A. Using this apparatus, it was possible to manually control the recording of redox potential measurements.

Because of the use of a saturated calomel reference electrode, 244 mv were added to all readings. Corrections for pH were based on the initial and final soil pH measurements. Only the final redox readings were corrected according to the final soil pH. These corrections were made as indicated by the equation given in the literature review.

Tensiometers were used for the measurement of the soil moisture tension. Some modifications to the tensiometers specified by Henderson and Rogers (1963) were made in order to adapt them

to a laboratory soil profile. One tensiometer was placed at each of the levels of the redox probes. These instruments were attached to water manometers. One additional tensiometer was placed approximately 9 cm above the porous plate at the bottom of the column. This probe was attached to a mercury manometer.

The soil column was the same column that Booram used. The dimensions of the plexiglass column were 21.6 cm for the inside diameter by approximately 183 cm in length.

Procedure

Soil for this experiment was obtained from the Kansas State University Evapotranspiration Site. This soil was a silt loam: 25% clay, 60% silt and 15% sand. The soil was allowed to become air dry before placing it into the column. Placement of the soil into the column was accomplished in increments with concurrent mechanical compaction. Compaction was obtained by dropping a five pound weight from a height of one foot. Total compaction amounted to approximately 1000 ft-lbs per cubic foot. Tensiometers and microelectrodes were placed and sealed into the column as the soil reached their respective depths.

After the placement of the middle probes, a shallow layer of soil was added before placing the manure layer. This manure layer was added to the soil column in order to test the effect of deep plowing. The manure which was placed in the column at this depth was first ground to remove any large chunks and was then oven dried. After drying, the manure was stored in a freezer in an airtight container along with a small amount of Drierite. Placement into the column was accomplished by removing the manure from the freezer, weighing out an amount equivalent to 100 tons per

acre on an oven dry basis and placing the manure in a layer in the column. This layer of manure was uncompacted as was the soil which was placed immediately above it. The depth of this manure layer was from 55.9 to 61.5 cm.

Soil placement and compaction was begun again and continued up to the level of the upper probes. The upper probes were again sealed in place and covered by a thin layer of soil. Manure to be placed in the upper zone of soil was treated as before. In order to complete the soil profile, sufficient manure was measured out to equal 50 tons per acre, oven dry. This manure was mixed with a quantity of soil capable of providing an uncompacted soilmanure surface layer of 11.2 cm in depth. The total depth of the soil profile then amounted to 155.9 cm. Upon completion of the soil and manure placement, the top lid which had previously been connected to the remainder of the system, was sealed onto the column.

In order to obtain an initial soil analysis, a composite sample of the soil was collected concurrent with the soil placement. Samples were also taken for soil moisture analysis. An initial manure analysis was obtained by using manure that remained in the freezer after manure was taken for placement into the column.

Following the sealing of the column, a check was run to determine if there were any leaks in the column. This was accomplished by placing some commercial gas leak detector on all parts of the system where leakage might occur. A light pressure was then applied to the system. This procedure indicated a satisfactorily sealed system.

After completely sealing the system, the next step was to purge the system of atmospheric nitrogen. This was accomplished by applying a vacuum to the system followed by the admittance of helium to restore atmospheric pressure. This helium was the same as that which was being used as a carrier gas for the gas chromatograph. Using this procedure, the nitrogen content was lowered to 3.1% of the original storage volume. The original volume of nitrogen present in the storage atmosphere could have been lowered more. However, it was felt that this level would be sufficient.

At this point, the column was ready to begin a test.

Anaerobic lagoon water was then applied to the soil. This water was collected from a beef feedlot east of Manhattan. Anaerobic lagoon water was used instead of distilled water in order to test the soil profile as a disposal site for all feedlot wastes. Over a period of three days, 27 liters of water were added to the column. This water was added by way of a tube through the top of the column. This tube was attached to a glass tube which had a bulb on one end. There were holes in the bulb which would allow water passage but would reduce the velocity in order to control erosion. The amount of water applied was equivalent to approximately 74 cm of depth in the column. All of the water except for one liter was applied the first two days. Since this amount was sufficient to saturate the soil profile, the last liter served to provide approximately 3 cm of ponded water.

A vacuum was not applied to the bottom porous plate until the seventh day. At that time, a 10 cm mercury vacuum was applied. Since the bottom tensiometer was indicating 12.6 cm of mercury pressure, this meant that there was a 22.6 cm pressure drop across

the porous plate.

The intent for this research was to use a combination of the tensiometer and redox potential data to determine appropriate times for adding more anaerobic lagoon water to the system. Along with this intent was the hope that water could be drained by percolation through the column rather quickly for the first run. Because of this, the first water sample was not collected until the 18th day. The next sample was collected on the 50th day followed by weekly sampling for the duration of the test. No further additions of water were made after the initial addition. A further explanation of this situation can be found in the results. The sampler which was added on the 72nd day was also sampled weekly.

Readings from the tensiometers were not recorded. The tensiometers were, however, monitored daily in order to maintain a knowledge of the moisture conditions in the soil. Redox measurements were recorded, but not on a regular basis, throughout the test.

It was necessary to analyze the column atmosphere almost daily in the initial stages. Toward the end of the test, carbon dioxide production had decreased enough that daily monitoring was not necessary. It was necessary to run the circulation pump daily in order to maintain a low carbon dioxide content. This was due to high production rates of this gas through a major portion of the experiment.

Termination of this project occurred on the 101st day.

After the final water collection was made along with the final gas analysis, the column was opened. Soil samples were taken from the two manure layers as well as at intervals throughout the soil

profile. Two soil samples were taken at each location. One set of these samples was transported to the Soil Test Lab immediately after collection where they were placed in a forced air oven. This even is set at a temperature which is low enough so that ammonia tests may be run accurately. The other set of samples was used for soil moisture analysis.

Soil and Water Analysis

Soil chemical analysis was run by the Kansas State Soil Testing Laboratory. Tests run were for nitrate nitrogen, ammonia nitrogen, total nitrogen, pH and organic matter. As mentioned above, the drying oven is set for ammonia analysis. As the results will relate, the soil profile was entirely acid (below pH7) so that any ammonia that might have been driven off in the oven was insignificant. Soil tests which will not be commented on in this thesis were salts and alkali analysis. Complete soil and water analysis may be found in Appendix B.

Anaerobic lagoon water analysis for electrical conductivity and soluble sodium percentage was also conducted by the Soil Testing Laboratory. All other water analysis were carried out in the Sanitary Engineering Laboratory. Nitrites were analyzed using a Hach Kit. Anaerobic lagoon water only was analyzed for pH. Nitrates were tested using the Brucine method and ammonia was determined by distillation (see Standard Methods). A micro-Kjeldahl test was used for ammonia plus organic nitrogen where the ammonia from the digestion was determined by direct nesslerization and the chemical oxygen demand was determined also.

RESULTS AND DISCUSSION

Although a nitrogen balance was not attained (Table 2) it was possible to account for nitrogen in all phases of the system. The problem of gas analysis still remains, though, despite some improvement in the potential for an accurate analysis of this phase.

This experiment has shown two areas which are the main trouble with gas analysis. The largest problem was the containment of gases evolving from the soil profile. During the course of the experiment, approximately 75 liters of gases were produced, not including the large amount of carbon dioxide scrubbed out in the sodium hydroxide scrubber. (Most of the gas build-up toward the end appeared to be caused by an accumulation of methane. Methane was first detected on the 33rd day of operation with continued production thereafter.) This 75 liters plus the original 37 liters was well over the system's maximum capacity of approximately 70 liters. Some of this extra gas was lost when the gas pressure built up overnight on one occasion sufficiently to exceed the 18 inch capacity of the oil manometer. The remainder of the gas was purged from the system on a few occasions when the system's capacity was being used to near the limit.

A concurrent problem which was encountered was the ability to maintain the 20% oxygen level in the atmosphere. Some oxygen was added throughout the test, which would have temporarily added to the volume problem. However, this oxygen was converted to carbon dioxide soon after its addition and was subsequently scrubbed out.

Table 2. Nitrogen Balance Sheet

Location	of Nitrogen at the start:		æ
	Soil	63.99	grams
	Manure - 50 T/A plus soil layer 100 T/A layer	13.33 24.46	
	Atmosphere	1.32	grams
	Anaerobic Lagoon Water	6.48	grams
38	Total	109.58	grams
Location	of Nitrogen at the finish:	2	
	Soil	83.60	grams
3.7	Manure - 50 T/A plus soil layer 100 T/A layer	2.90 2.52	grams grams
	Atmosphere	8.57	grams
	Water removed from the column	.57	grams
	Total	98.16	grams
Unexplain	ned difference	11.42	grams
Percent t	that was accounted for	89.6%	¥
Nitrogen	gained by the soil	19.61	grams
Nitrogen	lost by the manure, 50 T/A plus soil layer 100 T/A layer	10.43	

flow rate had decreased to approximately 23 ml/day. The vacuum on the plate had been gradually increased up to 20 inches of mercury where it remained for the final 37 days of operation. Since there were still 5 to 7 cm of mercury pressure indicated by the bottom tensiometer, the minimum pressure drop accross the procelain at any time toward the end was 25 cm of mercury. The decrease in water movement with an almost constant potential for movement was attributed to two possible causes. Since the soil used contained a significant amount of clay, it may have been possible that the porcelain plate was acting as a filter and simply became plugged with soil fines. The other possible contributing factor might have been bacterial growth on the surface of the plate. The fritted glass sampler which was added on the 72nd day indicated similar problems. From an initial 93 ml/day, the flow reduced to a level of 12 ml/day by the final week.

There were two major results of not being able to move enough water out of the soil profile. The primary effect was the soil profile being in a somewhat static, anaerobic state for the entire length of the experiment. The soil mositure tension at the top tensiometer was approximately 40 cm of water by the end of the test, allowing the soil to begin opening up. However, by that time the gas confinement problems were becoming so acute that there was little oxygen available for the soil microflora. The other major effect was the inability to determine the results of adding additional water to the system.

The effect that this system did have on the nitrogen can be seen in the nitrogen balance, Table 2, and in the water and soil analysis, Figures 4 through 10. The main effect indicated by the

As a result of the massive gas production, after the first few weeks of operation, it became very difficult to add oxygen to the system. This resulted in oxygen levels as low as one percent on a few occasions with 20% being attained for only brief periods.

The other major problem of gas analysis was the sensitivity of the gas chromatograph. Since the chromatograph was calibrated using air as a standard, it was necessary to use the least sensitive of the nine possible settings on the chromatograph. Analysis of air at this setting gave a nitrogen peak on the recorder of approximately 50. This compares with a maximum reading during the experiment of approximately 5 for nitrogen. Therefore, although it was possible to detect a nitrogen gas build-up, the accuracy of the analysis is questionable. Despite the lack of a nitrogen balance, the gas analysis does indicate that denitrification occurred. The batch analysis approach was therefore successful in that respect.

Aside from the limited success of the gas analysis, there was little improvement in this system over the previous two systems. Because of an inability to move water out of the soil profile, there was very little that could be done to control the system. As a result, the tensiometers and the redox probes were not satisfactorily tested. The cause for this inability appeared to be an interaction between the type of soil used and the porcelain plate at the bottom of the column.

During the first eleven days of operation, the average rate of water movement through the porcelain plate was close to 200 ml/day. This was with the previously mentioned 22.6 cm mercury pressure drop across the plate. By the end of the test, the water

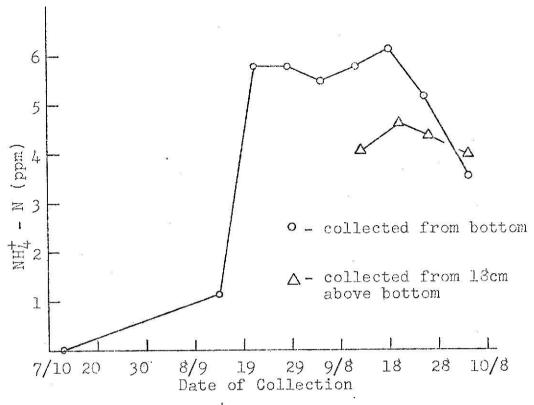


Figure 4. NH_4^+ - N of Water Samples

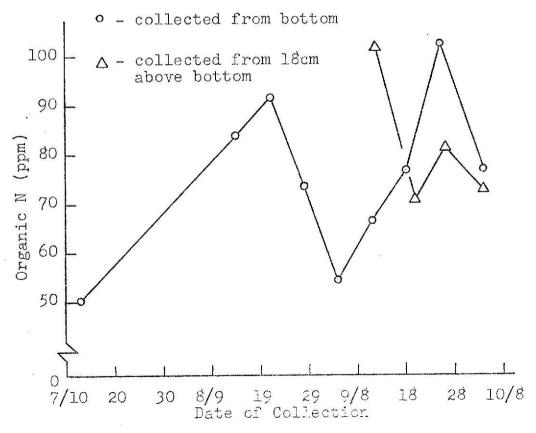


Figure 5. Organic N of Water Samples

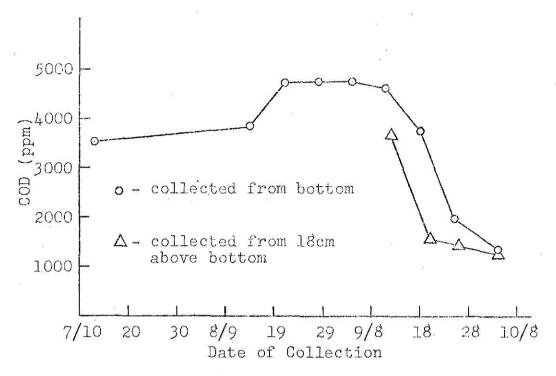


Figure 6. COD of Water Samples

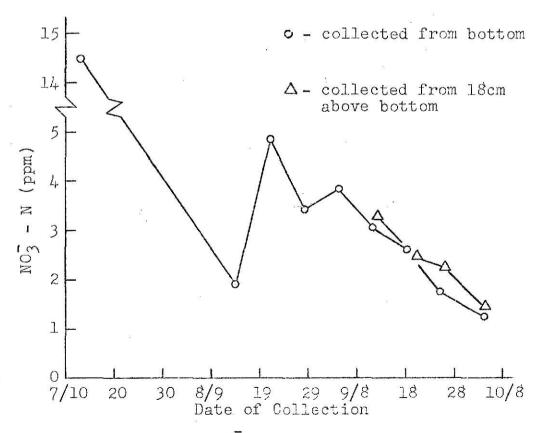


Figure 7. NO_3^- - N of Water Samples

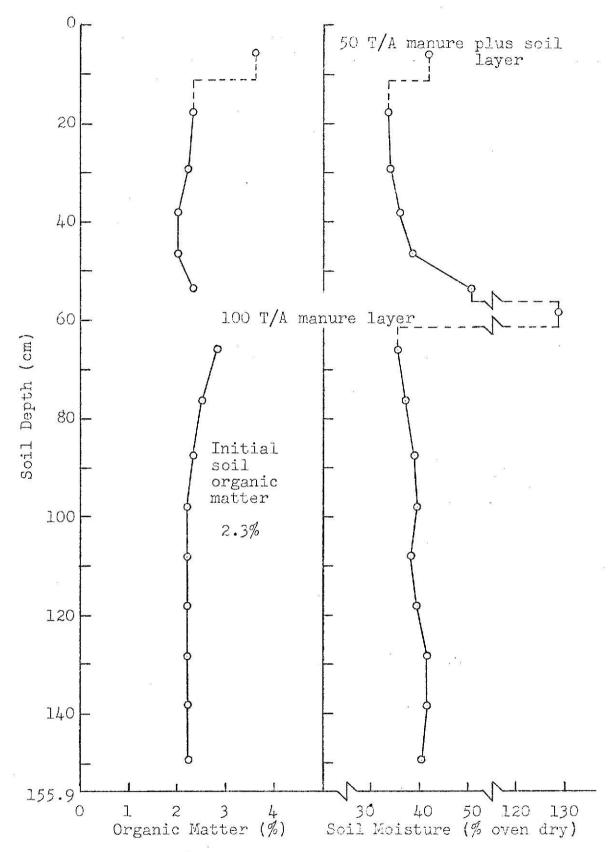


Figure 8. Organic Matter and Soil Moisture in the Final Soil Analysis

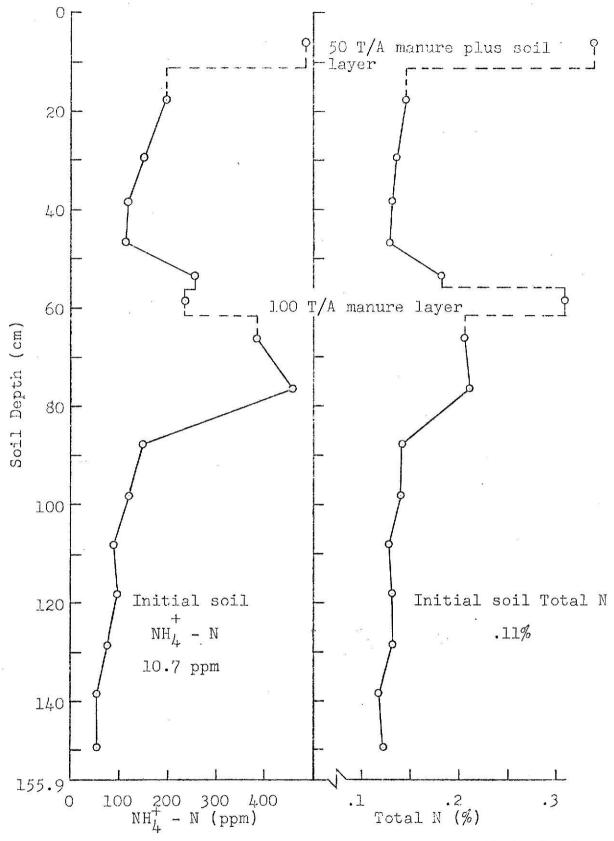


Figure 9. Ammonium-N and Total-N in the Final Soil Analysis

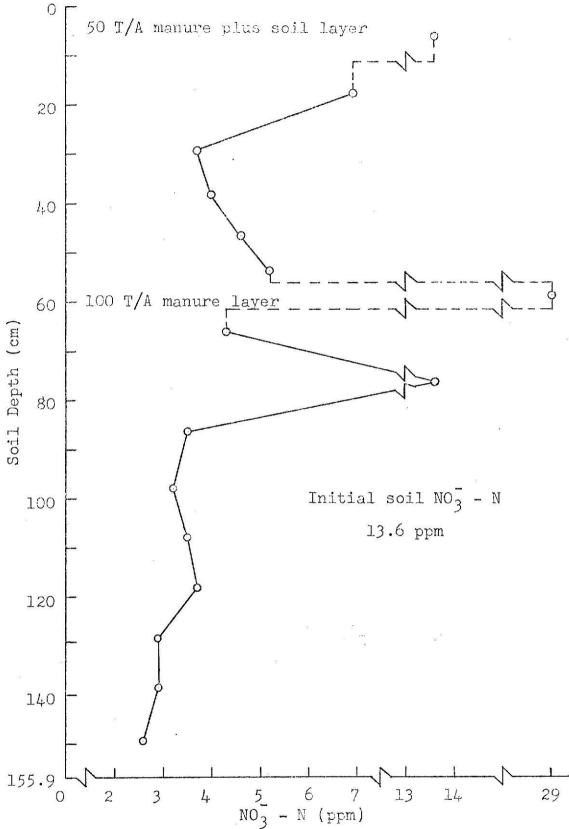


Figure 10. Nitrate - Nitrogen in the Final Soil Analysis

balance sheet was a redistribution of the nitrogen out of the manure and into the soil. A total of 32.37 grams of nitrogen was lost by the two manure layers while the soil gained 19.61 grams. Only .57 gram was lost through the leachate. A very good indication that denitrification had occurred was shown by the addition of 7.25 grams of nitrogen to the system's atmosphere. This left an unaccounted for amount of 11.42 grams or 10.4% of the original total for the system.

Of the nitrogen collected in the leachate, most was in the organic form. The range of concentrations for organic nitrogen, Figure 5, was from 50.25 to 102.56 ppm. The closest nitrogen concentration of any other constituent was an initial 14.48 ppm for nitrate nitrogen with the remaining NO₃ - N concentrations below 5 ppm, Figure 7. Nitrite nitrogen was detected only in the initial sample at a concentration of 5.70 ppm. From an initial ammonium nitrogen concentration of 0.0 ppm, Figure 4, a peak concentration of 6.10 ppm was reached.

An overview of what occurred during the test can be seen in Table 3. According to this table, in order for the system to have produced the 7.25 grams of nitrogen which accumulated in the atmosphere, 6.72 grams of nitrogen had to be nitrified in addition to the initial .89 gram of NO_3^- - N. Since the conditions were not suitable for nitrification until perhaps near the end, it is assumed that any significant nitrification occurred within a short period after water was added to the dry soil.

Table	3.	Forms	of	Nitrogen	in	the	System
	6.5	_	O	11 - 0 - 0 - 0 - 11		Caro	2,000

Form (Grams)	Organic N	NHţ-N	(NO3+NO2)-N	N ₂
Initial	102.27	5.10	.89	1.32
Final	79.25	9.98	<u>.36</u>	8.57
Change	- 23.02	+4.88	53	+7.25

Table 3 also indicates that mineralization was occurring from the beginning since the 5.10 grams of ammonium nitrogen that was present initially was less than the 6.72 grams needed for the nitrification. However, unlike nitrification which slowed down considerably, mineralization continued throughout the test. Evidence of these opposing changes is evident in the final soil analysis, Figures 9 and 10, and in the water quality analysis, indicates no ammonium nitrogen in the initial water with an increase up to 6.10 ppm before declining the final two weeks. final soil analysis for ammonium nitrogen indicates a buildup of nitrogen from the initial soil analysis. Whereas the initial content was 10.7 ppm, the lowest concentration in the final analysis was 53.1 ppm NHL-N. In contrast to this, the water analysis for NO3-N originally was 14.48 ppm and generally declined thereafter. The final soil analysis indicates agreement with this, as the soil was generally less than 5.2 ppm in contrast to the original content of 13.6 ppm. This nitrate data would also seem to be further evidence that denitrification was occuring throughout the soil profile.

The COD data in Figure 6 indicates that the water was picking up a considerable amount of organic matter. Only the last sample

collected fell below the original water content of 1294 ppm. The remainder of the water samples had a COD of between 3500 and 4700 ppm, indicating that there was a large amount of energy available in the system.

One unexpected analysis of the final soil was the pH. Whereas the soil at either end of the profile had a pH increase of 6.3 to approximately 6.7, the pH just below the 100 T/A manure layer decreased from 6.3 to 4.8. This may have resulted from acid forming bacteria lowering the pH before methane forming bacteria could keep up with the formation of acids. This low pH, then, would have suppressed the formation of the methane forming bacteria. This low pH would also have severely suppressed any nitrogen reaction, as indicated in Table 1 in the literature review.

The soil tensiometers appeared to work quite well. One problem incurred in their use was the susceptability they indicated to changes in atmospheric pressure within the column. For the greater part of the experiment, the two upper tensiometers gave identical readings. However, after the addition of the fritted glass sampler, a soil separation occurred 25-30 cm below the soil surface. Thereafter, the two tensiometers gave widely varying readings. The final readings were 47 cm of water tension for the upper tensiometer and 22 cm for the middle probe.

The redox potential data which was gathered is presented in Appendix C. There were no clear trends similar to those reported in the literature review. There was evidence that the probes were responsive to the system. On one particular occasion when a concerted effort was made to bring the atmospheric oxygen content up to 20%, within a couple of days the shallower probe indicated a

moderately reduced condition as defined in the literature review. This only lasted for one day. For the remainder of the experiment the probes gave an indication of reduced to strongly reduced conditions. When the experiment was terminated, the top was left off the column. Within one week, the shallower probe was indicating oxidized conditions and the lower probe was indicating moderately reduced conditions. The probes, therefore, were apparently still functional.

This investigation has shown the gas chromatograph to be potentially capable of an accurate atmosphere analysis. analysis remains dependent upon further refinement in the system. The batch approach would appear to be the best method of analysis if the confinement problem can be solved. Since this investigation had an extremely heavy loading of nitrogen and organic matter, this problem might not be too difficult to solve for a lesser loading. The present system was, however, capable of producing good evidence that denitrification had occurred without using the chemistry-by-difference approach. The redox probes and the tensiometers gave evidence of satisfactory performance despite not being able to test them thoroughly. The porcelain plate was a questionable addition to the column. If the plugging problem can be solved, this plate should be useful in controlling the moisture content of the soil profile. The soil and water analysis produced evidence of nitrification taking place in the early stages. Mineralization appeared to be happening throughout the investigation with denitrification apparently starting several days after the beginning and continuing for the duration of the investigation. Nitrates were quite low in the leachate, well below the USPHS

standard for a major portion of the test. COD and organic nitrogen were higher than might be desired.

SUMMARY

For the purpose of studying the use of land as a disposal site for feedlot cattle wastes, this investigation dealt with a laboratory soil column. The soil used was a silt loam obtained from the KSU Evapotranspiration Research site. Manure was applied to the soil profile in two zones. In the upper zone, 50 T/A oven dry manure was mixed with soil for a total depth of approximately 11 cm. The lower zone was a 100 T/A oven dry layer placed 56 to 62 cm below the surface. All of the soil and manure was placed in the column in a dry state. Anaerobic lagoon water from a beef feedlot was then applied in a quantity sufficient to waterlog the soil profile. In order to gain a nitrogen balance for the system, all nitrogen was quantified prior to the investigation and again at the termination. Gases were analyzed on a batch basis with a gas chromatograph. Water drawn from the bottom of the column was analyzed for different nitrogen forms as was the soil profile.

From this analysis, a determination was made as to what had occurred during the investigation. The analysis indicated that nitrification happened in the early stages of the experiment. However, due to the soil profile becoming anaerobic, this reaction did not occur to a significant extent through a major portion of the investigation. There was also evidence that mineralization proceeded throughout the test with denitrification beginning with the advent of anaerobiosis and continuing for the duration of the investigation. A nitrogen balance was not possible although 89.6% of the initial nitrogen was accounted for in the final analysis.

Because of a problem in drawing water from the soil profile, it was not possible to exercise any control over the column. This resulted in the inability to test the redox probes and the soil tensioneters satisfactorily. This also caused the extended anaerobic period which resulted in some gas confinement problems. These problems, along with the inadequate standardization of the gas chromatograph, led to the questioning of the accuracy of the gas analysis data. This data was sufficient, however, to indicate a buildup of nitrogen gas, confirming that denitrification had occurred.

The water drawn from the bottom of the soil profile indicated good treatment concerning the nitrate concentration. Only the initial concentration, 14.48 ppm exceeded the 10 ppm nitrate nitrogen maximum as specified by the United States Public Health Service. This water did contain a high content of organic nitrogen and had a high chemical oxygen demand (COD).

The overall results of this investigation in the cate that the apparatus has good potential. There are still problems which need to be solved. If these problems can be worked out, this apparatus should prove to be a useful tool for pollution control research.

SUGGESTIONS FOR FUTURE RESEARCH

In order for this apparatus to provide a nitrogen balance, the gas analysis system needs some improvement. The most important improvement would be the proper standardization of the gas chromatograph. This would require the use of some commercial gas mixtures with a nitrogen content of from 5 to 20% by volume in 5% intervals. These calibrated mixes could also contain nitrous oxide and ammonia along with carbon dioxide, methane and oxygen. However, for the nitrous oxide and ammonia to be useful, the column system on the chomatograph would need to be changed. Bell (1968) has reported the use of a Poropak Q column in conjunction with a mesh sieve which is capable of separating out these gases. It would need to be determined if this column arrangement is compatable with the current chromatograph. Even without this arrangement, the current system calibrated properly could give a satisfactory gas analysis. The batch gas analysis approach appeared to be satisfactory if the volume problem can be worked out. This might be accomplished by either enlarging the system's capacity or by restricting the quantity of organic matter in the system. Either way, the sodium hydroxide scrubber bottle should be kept in the system.

The tensiometers appeared to be satisfactory in their operation and should remain in the system also. The commercial redox probes should possibly be replaced with some probes made according to the reference in the literature review. This would allow a more detailed redox potential profile at considerably less expense.

Redox measurements could be better taken with a pH/mv meter also.

The porcelain plate could possibly be made more operational if graded sand was placed between it and the soil. However, if this did not work in the same trials, the plate should be replaced with a false bottom and sand. This system would not, however, have the potential for controlling the soil moisture content in the column that the porcelain plate has.

The fritted glass samplers should be returned to the system. The Formica Brand 140 adhesive appears to work satisfactorily enough that leakage around the samplers should not be a problem. These samplers are invaluable for two reasons. They can provide an ongoing analysis of the system's condition through the water analysis and they could be an invaluable means of controlling the aeration status of the column.

By the use of these techniques, unless further problems are encountered, a reasonable nitrogen balance should be attainable. If so, the equipment should be useful for many different types of trials. The use of anaerobic lagoon water versus pure water and whether the lagoon water provides enough energy to be useful might be one such trial. Different loading rates of manure versus different means of loading could be another.

BIBLIOGRAPHY

- Adriano, D. C., P. F. Pratt and S. E. Bishop. 1971. Fate of inorganic forms of nitrogen and salt from land-disposed manures from dairies. In: Proceedings of the International Symposium on Livestock Wastes. Livestock Waste Management and Pollution Abatement, American Society of Agricultural Engineers, St. Joseph, Michigan. p. 243-246.
- Ahalt, J. D. and J. J. Hairon. 1970. Agriculture in the seventies demand and price situation. U. S. Department of Agriculture, Economic Research Service, DPS 124, 31 pp.
- Alexander, Martin. 1961. Introduction to Soil Microbiology, New York and London. John Wiley and Sons, Inc.
- 1965. Nitrification. In: Soil Nitrogen, W. V. Bartholomew and F. E. Clark (Ed.), Agronomy No. 10, p.307-343.
- American Public Health Association Inc., Standard Methods for the Examination of Water and Wastewater. 12th ed., New York.
- Anderson, Larry L. 1972. Energy potential from organic wastes: a review of the quantities and sources. U. S. Department of the Interior, Bureau of Mines, IC 8549, 16p.
- Baas Becking, L. G. M., I. R. Kaplan and D. Moore. 1960. Limits of the natural environment in terms of pH and oxidation-reduction potentials. Journal of Geology. 68:243-284.
- Bailey, L. D. and E. G. Beauchamp. 1971. Nitrate reduction and redox potentials measured with permanently and temporarily placed platinum electrodes in saturated soils. Canadian Journal of Soil Science. 51:51-58.
- Bartholomew, W. V. 1965. Mineralization and immobilization of nitrogen in the decomposition of plant and animal residues. In: Soil Nitrogen, W. V. Bartholomew and F. E. Clark (Ed.), Agronomy No. 10, p. 285-306.
- Bell, R. G. 1968. Separation of gases likely to be evolved from flooded soils by gas chromatography. Soil Science. 105:78-80.
- 1969. Studies on the decomposition of organic matter in flooded soil. Soil Biology and Biochemistry. 1:105-116.
- Bohn, H. L. 1968. Electromotive force of inert electrodes in soil suspensions. Soil Science Society of America Proceedings. 32:211-215.
- 1971. Redox potentials. Soil Science. 112:39-45.

- Bohn, H. L., D. B. Fenn and W. J. Moore. 1969. Electrode potentials of nitrogen and sulfur half-reactions. Soil Science. 108:95-101.
- Bonner, F. T. and C. W. Ralston. 1968. Oxidation-reduction potential of saturated forest soils. Soil Science Society of America Proceedings. 32:111-112.
- Booram, C. V., Jr. 1971. Investigation of some factors influencing denitrification in a laboratory soil column with a surface loading of livestock wastes. Unpublished M. S. Thesis, Kansas State University.
- Broadbent, F. E. and Francis Clark. 1965. Denitrification. In: Soil Nitrogen, W. V. Bartholomew and F. E. Clark (Ed.), Agronomy No. 10, p.359-363.
- Fisher/Hamilton. Instruction Manual for Gas Partitioner Model 29.
- George, J. A. 1970. Development of a nitrogen balance in a laboratory soil profile with a heavy application of beef cattle wastes. Unpublished M. S. Thesis, Kansas State University.
- Hach Chemical Company. Engineers Laboratory Methods Manual.
- Henderson, D. W. and E. P. Rogers. 1963. Tensiometer construction with plastic materials. Soil Science Society of American Proceedings. 27:239-240.
- Lance, J. C. and F. D. Whisler. 1972. Nitrogen balance in soil columns intermittently flooded with secondary sewage effluent. Journal of Environmental Quality. 1:180-186.
- Mann, L. D. and L. H. Stolzy. 1972. An improved construction method for platinum microelectrodes. Soil Science Society of American Proceedings. 36:853-854.
- Meek, B. D., L. B. Grass and A. J. MacKenzie. 1969. Applied nitrogen losses in relation to oxygen status of soils. Soil Science Society of American Proceedings. 33:575-578.
- Patrick, W. H., Jr. 1960. Nitrate reduction rates in a submerged soil as affected by redox potential. Transactions of 7th International Congress of Soil Science. 2:494-500.
- Patrick, W. H., Jr. and R. D. Delaune. 1972. Characterization of the oxidized and reduced zones in flooded soil. Soil Science Society of American Proceedings. 36:573-576.
- Patrick, W. H., Jr. and I. C. Mahapatra. 1968. Transformations and availability of nitrogen and phosphorus in waterlogged soils. Advances in Agronomy. 20:323-359.

Pilot, Luc and W. H. Patrick, Jr. 1972. Nitrete reduction in soils: effect of soil moisture tension. Soil Science. 114:312-316.

Sawyer, Claire N. and Perry L. McCarty. 1967, second ed. Chemistry for Sanitary Engineers. New York, San Francisco, St. Louis. McGraw-Hill Book Company.

Sisler, Harry H., C. A. VanderWerf and Arthur W. Davidson. 1967, third ed. College Chemistry. New York. The Macmillan Company. p.455-458.

APPENDIX A.

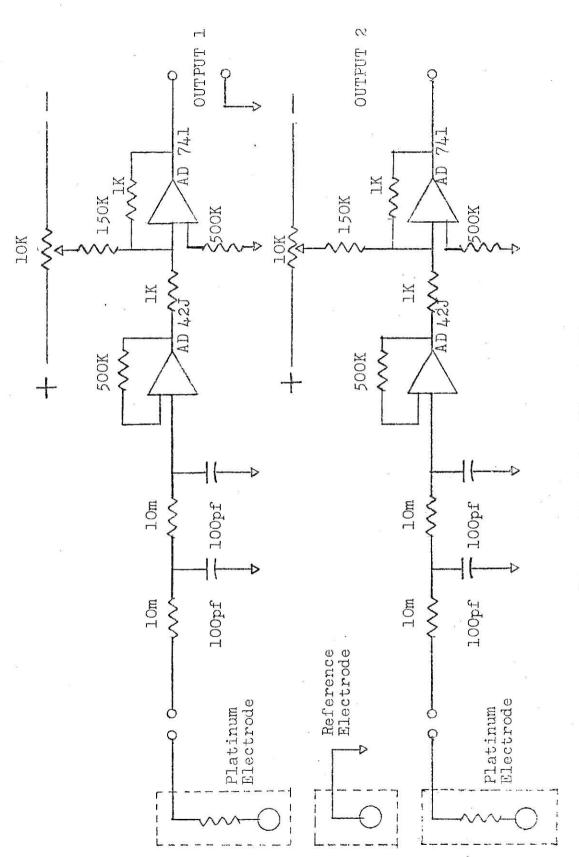


Figure 11. Redox Circuit Diagram

APPENDIX B.

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Table 4. Water Quality Analysis

anic N ppm	17	H						# #	101.76		70.53		81.08		72.58
Organic	192,17		50.25	83.73	91.23	73.50	24.07	66.38		76.53		102.56		76.75	
mdd N− [†] HN	45.6	II I		1.1	5.76	5.75	5.45	5.73	7.05	01.9	4.59	5.14	4.34	3.51	3.95
NO2-N	le Sour	Н	5.70			2			40						
NO3-N ppm	2.39 Final Sample Source		14.48	1.91	78.4	3.45	3.82	3.07	3.28	2.62	2.46	1.76	2.27	1.24	7.43
COD	1294		3523	3836	4727	4763	4771	7197	3643	3749	1577	1960	1413	1343	1243
Volume ml	0	*II							647.3		220.6	5	108.9		95.9
Vo		*	2156.4	2055.3	295.3	282.6	265.6	242.7		203.7		171.7		203.0	
Analysis	Anaerobic Lagoon Water	Date	7/13	8/14	8/21	8/28	4/6	9/11	9/12	9/18	9/20	9/25	97/56	10/1	77/01

 \ast I - From the porcelain plate on the bottom of the column. II - From the fritted glass sampler 18 cm. above I.

Table 5. Soil and Manure Analysis

Total soil in the column: 133.40 pounds (@ 4.47% soil moisture)

Average density in the column (including the manure): 1.14 grams/cubic centimeter

Table 6. Soil and Water Test for Salts and Alkalinity

Analysis	Anaerobic Lagoon Water	the contract of the contract o	12-20	Final S Depth (62-70	
		and white the state of the stat	managa (agasta ana ga Ana da manda da Manda ana Ana ana ana ana ana ana ana ana an	and the second of the second s	an an an an an
Electrical Conductivity (of the saturated extract for soil) mmho/c	2.42 m	1.50	1.87	4.62	2.36
Soluble Sodium (% for water or m.e./100gms for soil)	18.3	.017	.047	.087	.020
Exchangeable Sodium (m.e./100 gms)		.143	.40	.42	.18
Approximate Exchange Capacity (m.e./100 gms)		12.7	12.3	11.8	13.0
Exchangeable Sodium Percentage		1.13	3.25	3.56	1.38
Irrigation Hazard for Medium Soil Salinity Alkalinity	high low			£	
Salt Rank for Medium Soi		low	low	high	low
Alkali Rank for Medium S		low	low	low	low
THE CONTRACT OF THE CONTRACT C			30 60		

E. J.

APPENDIX C.

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Table 7. Redox Potentials (Eh7)

Date	Α×	B≯	Date	A	B
6/28	-205	-255	8/5	-200	-185
6/29	- 95	-115	3/8	25	-125
6/30	-165	- 95	8/9	15	-125
7/1	-115	-115	8/11	60	-185
7/2	-155	-155	8/14	0	-185
7/4	-235	-175	8/17	- 15	-185
7/6	-245	-195	8/21	-160 -120	-1.80
7/12	-245	-235	8/22	- 85	-175
7/14	-245	-215	0/ 22	100	
7/17	-185	-175	8/23	- 90 30	
7/19	-175	-165	8/25	-155	-170
7/21	-155	-155			
7/24	-205	-195	8/28	-225	-175
7/26	-215	-195	8/31	-245	-175
7/28	-205	-195	9/7	-305	-155
8/1	-165	- 190	9/20	-315	-125
0/1	- 15	-170	10/4	-260 ^a	-220 ^b
8/2	- 45	-190	10/9	240 ^{a,c}	5 ^b ,c
8/3	- 165	-190	10/11	. 245 ^{a,c}	75b,c

^{*} A - Redox probe at a depth of 12 cm

B - Redox probe at a depth of 63 cm a - Corrected from a pH of 6.7 b - Corrected from a pH of 4.8

c - Readings taken after termination of the investigation on 10/4, where the top of the column had been removed on the termination date. All readings but those noted by a and b above were corrected from a pH of 6.3.

DENITRIFICATION IN A SOIL COLUMN WITH INCORPORATED BEEF MANURE AND APPLIED ANAEROBIC LAGOON WATER

by

JIMMIE LEE GARTUNG

B.S., Kansas State University, 1971

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Agricultural Engineering

KANSAS STATE UNIVERSITY Manhattan, Kansas

1973

ABSTRACT

Because pollution is of such interest at the present time, all facets of society which might potentially contribute to pollution are being closely scrutinized. For that reason, this investigation was concerned with the aspect of beef feedlot disposal and the potential pollution that might be a side product, specifically to the ground water.

It is well known that the nitrate ion is a very mobile nitrogen form and is one that can cause disease. Through denitrification, this pollutant can be returned to the atmosphere in the form of nitrogen gas. In order to determine how nature might be controlled to enhance this process, a laboratory soil column was set up with the specific side intention of obtaining a nitrogen balance in order to know for certain where the nitrogen relocated to and in what form.

One of the problems of operating a laboratory soil column is to be able to monitor the conditions as they are changing. According to the literature, one method that would accomplish at least a part of this goal is the measurement of redox potentials. These potentials are capable of indicating the oxidation state of the soil as well as when denitrification might be occurring. The suggested guidelines for the oxidation status are: oxidized, above +400 mv; moderately reduced, +100 to +400 mv; reduced, -100 to +100 mv; highly reduced, -100 to -300 mv. The consensus level for the reduction of nitrate is from +200 to +250 mv.

For the purposes of this investigation, a laboratory soil

column was set up with a silt loam soil. The equivalent of 50 T/A oven dry manure was mixed into the top 11 cm of soil. In order to test the effect of deep plowing manure, an additional layer equivalent to 100 T/A was placed 60 cm into the soil, with a total depth of 156 cm. Redox probes and tensiometers were placed immediately below the manure layers with an additional tensiometer placed near to the bottom. In order to obtain a nitrogen balance, an artificial atmosphere was used initially consisting of 80% helium and 20% oxygen with the intention of measuring the gases evolved on a batch basis. In order to determine if it might be possible to treat all wastes from a beef feedlot, anaerobic lagoon water was applied to the soil profile in a quantity sufficient to initially inundate the soil profile. Water was drawn from the column through a porcelain plate at the bottom of the column throughout the 15 week test.

Quantification of the different nitrogen forms at the beginning and end of the investigation failed to produce a nitrogen balance. The gas analysis appeared to be questionable because of inadequate calibration and because of some gas confinement problems which resulted in some losses. The gas analysis did provide data which confirmed that denitrification had occurred. Approximately 7 gr of nitrogen gas was added to the atmosphere during the investigation.

Nitrate nitrogen in the leachate from the column was generally very low. After an initial concentration of 14.48 ppm, the level remained below 5 ppm. Organic nitrogen and chemical oxygen demand values were not quite as satisfactory, ranging from 50.25 to 102.56 ppm and 1243 to 4771 ppm respectively.

Ammonium nitrogen ranged from 0 initially to 6.10 ppm.

Due to plugging problems with the porcelain plate, insufficient water was drawn from the column to be able to add more water as had been hoped. This caused the column to be anaerobic for a major portion of the investigation. Consequently, the redox probes and the tensiometers did not provide much useful data, although they did appear to be operating.