

AN ABSTRACT OF THE THESIS OF

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Title: DETERMINATION OF EQUILIBRIUM PARTIAL PRESSURE OF  
AMMONIA GAS ABOVE ANAEROBICALLY DIGESTED SEWAGE  
SLUDGE

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Abstract approved: Dr. J. R. Miner

A laboratory study of anaerobically digested sewage sludge was performed to measure equilibrium constants for ammonia in the sludge. Measured constants describing the solution and dissociation of ammonia in sludge were compared to theoretical constants obtained from thermodynamic data. No significant difference was found between these two sets of constants. Corrections for activity effects due to ionic strength were necessary but no effect of the organic content of the sludge was noted.

Another laboratory experiment with sludge samples was performed to investigate the behavior of the pH of sludge upon exposure to air. The pH was found to rise in roughly a logarithmic manner with most of the increase occurring in the first day following exposure. The variation of pH with the concentration of carbonate system species was examined.

Increase in pH was seen to be related to a decrease in dissolved carbon dioxide concentration.

A procedure was developed to predict volatile losses of ammonia following surface application. Expected losses for typical conditions were examined using this method and found to be significant. Suggestions were made for the application of the results and procedures to wastes other than sludge.

The effects of several factors on loss rate were examined. Liquid temperature was seen to exert a major effect on loss potential.

Determination of Equilibrium Partial Pressure of  
Ammonia Gas Above Anaerobically Digested  
Sewage Sludge

by

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# DETERMINATION OF EQUILIBRIUM PARTIAL PRESSURE OF AMMONIA GAS ABOVE ANAEROBICALLY DIGESTED SEWAGE SLUDGE

## I. INTRODUCTION

Current methods of municipal sewage treatment have proven very effective in removing dissolved and suspended contaminants from wastewater, thus helping to improve water quality. The old axiom that matter cannot be created or destroyed, but only concentrated or dispersed remains valid, however, and reducing water pollution has increased sewage sludge disposal problems. One method of disposal that, when appropriate, is very attractive is application of sludge to cropland. This technique not only allows disposal, but also provides a means to utilize sludge as a fertilizer and soil conditioner.

Proper applications of anaerobically digested sewage sludge to agricultural lands can supply the nitrogen and phosphorus requirements of crop production. Overapplications are to be avoided because of potential hazards due to toxics and excess nitrogen. The best management technique appears to be to apply enough sludge to just satisfy the nitrogen demand of the crop. This nutrient requirement is met by the available nitrogen in the sludge. This refers to the total amount of nitrogen in the sludge minus that amount lost from the system or not available to

plants. To obtain proper application rates, then, expected nitrogen losses from the sludge must be predicted.

One potential source of loss from surface applied sludge that is thought to be very serious is volatilization of ammonia. It was felt that the volatile loss of ammonia from sludge should be describable as a convective mass transfer process. To predict ammonia volatilization using a mass transfer expression the equilibrium partial pressure of ammonia gas above the sludge must be known. This cannot be easily measured under field conditions, but can be calculated from easily obtainable quantities and easily determined characteristics of the sludge providing that two conditions are met.

First, theoretical equilibrium constants for the dissolution and dissociation of ammonia must be applicable for use with sludge. Values for these constants are tabulated or they can be calculated from thermodynamic data. Secondly, it must be possible to predict a value of pH that is appropriate to describe the average conditions of the sludge during volatilization. These conditions allow calculation of the partial pressure from equilibrium considerations. It was not known if these conditions would be met for the case of sludge applied to land, however.

This investigation was undertaken with the overall objective of determining whether a convective mass

transfer relationship could be used to predict volatile losses of ammonia from surface-applied sewage sludge.

Specific objectives were

1. To determine if theoretical equilibrium constants for ammonia dissolution and dissociation were valid for use in sludge.
2. To determine the behavior of the pH of sludge after application to land and to see if an appropriate value to describe pH can be predicted.
3. To identify factors related to behavior of the pH.
4. To see if the mass transfer model can explain the effect of various environmental factors on the volatilization of ammonia.

## II. BACKGROUND AND LITERATURE REVIEW

### Application of Sewage Sludge to Land

There are several types of sludges associated with common sewage treatment schemes. Primary sludge is the solid material that settles out of sewage under fairly quiescent conditions. Secondary sludge consists mainly of waste microorganisms from biological treatment to remove dissolved organics. Tertiary sludge usually refers to the chemical precipitates from advanced wastewater treatment. Anaerobically digested sludge is primary or primary and secondary sludge that has undergone biological stabilization through anaerobic fermentation. In common practice, and for this thesis, the term "sludge" will be used to signify anaerobically digested sewage sludge.

Anaerobic digestion is a process employed to stabilize high strength organic wastes such as primary and secondary sludges. The process basically occurs in two stages, the first being the fermentation of organic matter to volatile acids and the second being the conversion of these acids to methane gas. Carbon dioxide is a product of both reactions. Typical characteristics of anaerobically digested sewage sludge are given in Table 1. The atmosphere in the digester above the sludge is

Table 1. Typical composition of anaerobically digested sewage sludge (28).

Item	Range	Typical
Total dry solids (TS) %	6.0-12.0	10.0
Volatile solids (% of TS)	30-60	40
Nitrogen (N, % of TS)	1.6-6.0	3.0
Phosphorus ( $P_2O_5$ , % of TS)	1.5-4.0	2.5
Potash ( $K_2O$ , % of TS)	0-3.0	1.0
pH	6.5-7.5	7.0
Alkalinity (mg/l as $CaCO_3$ )	2500-3500	3000
Organic acids (mg/l as HAc)	100-600	200

typically 60 percent methane and 40 percent carbon dioxide with traces of other gases.

While other alternatives exist for treatment of primary and secondary sludges, anaerobic digestion is the most popular. Favorable economics, effective waste stabilization, volume reduction, and energy recovery through methane production all support this popularity. A city with a population of 100,000 having a conventional secondary sewage treatment plant with anaerobic sludge digestion will typically generate about 20,000 lb/day (9,000 kg/day) of digested sludge solids. This represents a volume of 12,000 to 60,000 gal/day (45,000 to 220,000 l/day) depending on the moisture content of the sludge. It should be apparent that this poses a significant disposal problem.

Alternatives for disposal of sludge include application to cropland, incineration, land reclamation, landfilling, and ocean disposal. The method deemed most appropriate, of course, depends largely on the geography of the disposal area.

If adequate cropland is available nearby, agricultural application of sludge is especially attractive. Not only is the disposal aspect taken care of, but the sludge may have significant economic value as a fertilizer and soil conditioner. Concentrations of common plant nutrients are included in Table 1.

The Willamette Valley of Oregon seems to be an excellent place to practice cropland disposal of sludge. The cities are small to medium in size and located in agricultural areas. Grasslands account for much of the agricultural activity.

Application to land is not without potential deleterious effects, however. Sludge may contain minute amounts of toxic matter, usually in the form of trace organic compounds and heavy metals. The long-term effects of the application of these substances to food crops are not well known. The concern over application to cover crops and grasslands is less significant.

Metal uptake by plants may be beneficial or harmful. The actual process of plant uptake of heavy metals following sludge application is very complicated. Certain

metals in organic wastes tend to move readily to plant tops after application to soil (Mn, Zn, Cd, B, Mo, Se). Others move less easily (Ni, Co, Cu) and others still rarely reach the tops or remain in the soil (Cr, Pb, Hg) (8).

Most concern is usually voiced over the fate of applied cadmium. Levels of cadmium found in plants following sludge treatments have been found to be substantially lower than in plants exposed to airborne cadmium or grown in media containing added inorganic cadmium. Also, cadmium found in foods of plant origin tends to be less digestible, and so less hazardous, than equal amounts of cadmium in soluble inorganic forms (8).

Copper is another metal which is of interest because of possible food chain effects. Applications of sludge have not been found to produce toxic levels of copper for plant consumers. Copper should exert a phytotoxic effect before accumulations become toxic to animals, with the possible exception of sheep. Other metals, such as zinc, nickel, and cobalt will cause phytotoxicity before hazardous levels are reached in plants (41).

On the beneficial side, sludge applications can provide needed micronutrients to crops. Commonly, these elements include iron, zinc, copper, manganese, boron, and molybdenum. Sewage sludge tends to be high in zinc, which is often found to be deficient in animal forages.



The nutrient of prime concern when disposing of sludge on agricultural land should be nitrogen. Sludge application rates should be based on crop nitrogen requirements if nitrogen is found to be the limiting nutrient.

The limiting nutrient is the nutrient whose requirement will be satisfied last by a fertilizer application. For example, suppose a crop requires 400 lb/acre (450 kg/ha) of nitrogen, 100 lb/acre (100 kg/ha) of phosphorus, and 200 lb/acre (220 kg/ha) of potash and the fertilizer to be applied is 10 percent nitrogen, 10 percent phosphorus, and 10 percent potash by weight. This means that 1000 lb/acre (1120 kg/ha) of fertilizer will supply the required phosphorus, 200 lb/acre (2240 kg/ha) the potash, and 4000 lb/acre (4480 kg/ha) the nitrogen. In this case nitrogen is the limiting nutrient since just satisfying its requirement exceeds the requirements of the others.

Nutrient utilization of common grass crops for given yields is shown in Table 2. Using these values and the typical concentrations of the nutrients in sludge, it is possible to determine the sludge application necessary to supply nutrient demands. This is given in Table 2. These values are based on the assumption that all nutrients in the sludge will be available to crops.

The values shown in Table 3 would suggest that potash is the limiting nutrient for sludge application. While

Table 2. Nutrient utilization by crops (29).

Crop	Yield (T/acre)	N (lb/acre)	P <sub>2</sub> O <sub>5</sub> (lb/acre)	K <sub>2</sub> O (lb/acre)
Alfalfa	8	450	80	480
Orchard Grass	6	300	100	375
Brome Grass	5	166	66	254
Tall Fescue	3.5	135	65	185
Bluegrass	3	200	55	180

Table 3. Typical sludge application rate to supply nutrient requirements (T/acre).

	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
Alfalfa	150	32	480
Orchard Grass	100	40	375
Brome Grass	55	26	254
Tall Fescue	45	26	185
Bluegrass	67	22	200

this is true in a strict sense, supplying the potash requirements will exceed the nitrogen requirements by about four times and the phosphorus requirements by about ten times. Some concern should be raised with this much over-application of nitrogen. Excess nitrogen may be detrimental when transformed into its more mobile forms. Since potassium requirements can be met cheaply using commercially available potash, nitrogen should be treated as the limiting nutrient. Applying for nitrogen requirements

gives roughly a three-fold excess of phosphorus. This is not of great consequence since phosphorus is very stable in the soil. The lower application to supply nitrogen demand instead of potassium demand also greatly reduces the amount of toxics applied, thereby reducing the opportunity for adverse side-effects. The desirable strategy when approaching sludge applications, then, is to satisfy fertilizer needs as efficiently as possible while keeping application rates at a minimum, thus minimizing the deleterious effects of overapplication. This is best accomplished by considering nitrogen as the limiting nutrient.

Various guidelines have been examined to discover acceptable application rates to meet toxicity limits. Application rates varying over orders of magnitude for the same soil-sludge system have resulted. In nearly all cases, however, nitrogen instead of toxics was found to limit applications (13).

If sludge is to be applied as a fertilizer it is necessary to determine the available nitrogen in the sludge. To determine available nitrogen there must be some understanding of the nitrogen transformations occurring after sludge is applied. Almost all nitrogen in the sludge is present as organic nitrogen, ammonia, or ammonium. The ammonical nitrogen, ammonia and ammonium, is found in the liquid phase of the sludge and the organic nitrogen in the solid phase (31). Organic nitrogen should

be slowly made available to plants by biological conversion to ammonia. Soluble nitrogen species may be carried into the soil as the sludge liquid infiltrates. Nitrogen in the ammonium form may be bound to the clay fraction of the soil after infiltration through the process of cation exchange. After this interaction it may be considered stable and available (50). Dissolved free ammonia gas, however, is subject to loss through volatilization if it is exposed to the atmosphere. This loss may occur immediately upon application and continue as long as there is ammonia in contact with the atmosphere. Considering that up to 50 percent of the total nitrogen in sludge may be in the ammonical form, volatilization may be responsible for a serious loss of fertilizer value. The severity of the loss is compounded by the form of the nitrogen being lost as well as the amount. Excess ammonical nitrogen that is not volatilized or taken up by plants may be biologically oxidized to nitrate within several weeks. While nitrate is an excellent fertilizer, it is also extremely mobile in the soil and is easily leached into groundwater where it may cause toxicity problems. Excess nitrate may, under the right conditions, be biologically reduced to nitrogen (denitrified) and lost to the atmosphere. This is a more long-term effect, however. Proper applications should result in very slight loss of

nitrogen availability due to nitrate leaching or denitrification.

Early results of sludge applications to forage crops seem to indicate that nitrogen is being lost. Comparisons between sludge nitrogen and commercial nitrogen show that after one year the sludge is about one fourth as effective. This increases to one-half as effective after two years, and almost as effective after three years (1). To obtain proper application rates, then, loss of available nitrogen due to ammonia volatilization must be predicted.

#### Ammonia Volatilization from Sewage Sludge

Several investigations have been made to measure ammonia volatilization losses from sewage sludge under both laboratory and field conditions. These studies were not concerned with developing a means of predicting losses, but rather with measuring the magnitude of the loss.

Molina, et al. (31) exposed sewage sludge to air in a laboratory investigation. Almost 60 percent of the original ammonical nitrogen was lost within six days. King and Morris (21) applied sludge to both bare and grassy soil in laboratory columns. The average volatile loss of ammonia was more than 30 percent of the applied ammonical nitrogen. This loss was essentially complete after three to five days. A similar laboratory study concluded that 11 to 60 percent of the ammonical nitrogen in sludge applied to soil can be lost by volatilization (37). An

earlier laboratory study of sludge applied to soil concluded that volatilization accounted for only about one percent of the original nitrogen added (38). This earlier investigation was more concerned with long-term effects, however, and did not begin measuring volatilization until after the first week. A laboratory study using a synthetic sludge found average losses of 20 to 30 percent of the added ammonia after seven weeks. Most of the loss occurred during the first few days, however, and losses were virtually complete after ten days (45).

Field experiments have also reported substantial losses due to volatilization. Stewart, et al. (44) applied sludge treatments of 1.25 to 5.0 cm to land planted in corn. The amount of ammonia volatilized was estimated to be 30 percent of the original ammonical nitrogen applied. Another field study showed ammonia losses of around 60 percent within five to seven days of application of the sludge to bare soil (4).

#### Factors Affecting Volatile Losses

The expression for the gaseous concentration of ammonia above the liquid phase developed later is

$$P_{A,S} = \frac{[TAN_{(aq)}] \gamma_{NH_3}}{K_S \left[ 1 + \frac{\Gamma' \{H^+_{(aq)}\}}{K_a} \right]}$$

To use this expression to predict losses it would be

beneficial to know if any of the terms in it are likely to undergo sudden changes upon application of the sludge to land. All of the terms depend to some degree on various concentrations and, therefore, can be affected by changes in moisture content.

In the case of sludge, however, the moisture content is typically so high that small changes in moisture content have little effect on concentration. Ryan and Keeny (37) observed no difference between the amount of ammonia volatilized from sludge into dry air and into humid air. Moisture losses, on the other hand, were much higher to the dry air. Air with relative humidities of 30, 70, 90, and 100 percent was drawn over laboratory sludge samples by Terry, et al. (45). No difference in ammonia loss among the different humidities was noted until several days after aeration began. Eventually, higher losses occurred to the driest air.

The activity coefficients depend upon the ionic strength. Changes in ionic strength can come about from loss of ionic constituents as well as from changes in moisture content. The only constituents expected to undergo significant loss are those subject to volatilization. Inorganic nitrogen and inorganic carbon were both seen to decrease as sludge dried while other constituents, including organic nitrogen and organic carbon, were conserved (11). This suggests that both ammonia and carbon dioxide are volatilized from sludge after application. Changes in

activity would then appear to depend on the relative magnitude of the volatile species to the non-volatile species.

Loss of ammonia and carbon dioxide should also cause changes in pH, which would be of concern in using the expression for gaseous concentration. Equilibrium considerations suggest that the pH would be lowered by ammonia loss (since ammonia acts as a weak base) and raised by carbon dioxide loss (since carbon dioxide acts as a weak acid). Srinath and Loehr (43) reported a linear decrease of pH with time as ammonia was desorbed from a solution of an ammonium salt. The pH of sludge, however, was seen to increase with aeration (5). Forced aeration produced an increase of one pH unit in one day, while gentle surface aeration caused an increase of 1.3 units over a period of six days (31). An increase in pH may mean that carbon dioxide loss exerts a greater influence than ammonia loss. Significant carbon dioxide loss should be expected since the sludge goes from a partial pressure of carbon dioxide of about 0.3 atm in a digester to about 0.0003 atm under normal environmental conditions.

While it has not been studied explicitly, there appears to be evidence from some studies that a mass transfer model may be applicable to describe volatile losses from sludge. Mass transfer theory holds that the mass transfer coefficient should increase with increasing wind velocity and decrease with increasing temperature. Also, the rate of ammonia volatilization should be highest initially and follow a logarithmic drop off, since the



model is based on a first order equation.

King and Morris (21) observed lower ammonia losses from sludge applied to grass than from sludge applied to bare soil in a laboratory study. Presumably this was due to the lower wind velocity caused by restriction of air movement by the grass stubble. Other investigators found that increasing the air flow over laboratory sludge samples increased losses (45).

Results of a study by Ryan and Keeny (37) include a logarithmic plot of ammonia loss versus time. Similar results were obtained by Terry, et al. (45). This suggests that the loss is described by a first order equation.

Other laboratory results show that much lower losses will occur when sludge is incorporated rather than left on the surface (20, 45). Possibly this shows the effect of reduced surface area and wind velocity.

Beauchamp, et al. (4) noted the effect of several factors upon ammonia loss in the field. A diurnal flux of ammonia was observed after application of sludge and appeared most closely related to air temperature. There was no apparent relationship between windspeed and ammonia flux. Observation of ammonia losses with time indicated a first order loss.

Calculation of mass transfer coefficients from field data was done by Koelliker and Miner (22). Losses measured were from an anaerobic lagoon, however, and not

from sludge. The coefficients calculated agreed with those developed by Haslam, et al. (15) from studies with a counter-current ammonia absorber. This transfer coefficient was seen to vary with wind velocity to the 0.8 power and absolute temperature to the negative 1.4 power.

### Equilibrium Constants

Strictly speaking, Henry's Law is applicable only for gases which do not combine chemically with the solvent. The ammonia-water system does not meet this requirement and whether Henry's Law applies to ammonia dissolved in water is a matter of debate.

Hougen and Watson (18) describe aqueous solutions of ammonia as systems whose behavior deviates widely from that predicted by Henry's Law except at low pressures. Srinath and Loehr (43) also warn that great care must be used when using Henry's Law with a gas such as ammonia.

Many of the difficulties encountered with use of Henry's Law and ammonia seem to stem from a misuse of the law. As it is defined, Henry's Law relates the mass of gas dissolved in a given amount of solvent for a given partial pressure (39). For ammonia, the mass of gas dissolved per unit volume of solution would equal the concentration of dissolved ammonia gas plus ammonium ion. There exists, as will be shown later in this thesis, a thermodynamic equilibrium between the partial pressure of

ammonia and the dissolved ammonia gas in the liquid. There also exists an equilibrium between the dissolved ammonia gas and ammonium ion. As the concentration of total ammonical nitrogen increases, activity effects cause the ammonium ion to become an increasingly greater percentage of the total ammonical nitrogen in the liquid. This, coupled with the equilibrium between the dissolved ammonia gas and partial pressure, cause the ratio of partial pressure to total ammonia plus ammonium in solution to decrease as concentration increases. A strictly defined Henry's Law constant would then decrease with concentration for ammonia, and Henry's Law would not appear valid.

Henry's Law may be used with ammonia-water systems for several specific cases. In dilute solutions the activity effects should be small enough that Henry's Law will be valid over a wide range of low concentrations. This range of concentrations can be increased if the solutions are at high pH. In this case virtually all of the ammonical nitrogen is present as dissolved ammonia gas which, as an uncharged molecule, is less subject to activity effects. For this same reason, one can define an "apparent Henry's Law" constant as the ratio of activity of dissolved ammonia gas to partial pressure, which should remain constant over a wide range of concentrations. This constant is referred to in this thesis as a gas solubility constant. One should be careful when looking through the literature

that such a constant is not mistakenly called a Henry's Law constant.

Kowalke, et al. (23) developed an expression giving the equilibrium partial pressure of ammonia and the molality of dissolved ammonia gas as a function of temperature. This derivation was based on the molal heat of solution, molal change in free energy, and molal change in entropy for the dissolution of ammonia gas. This expression compared well with experimental results using pure ammonia-water solutions up to a concentration of 3.5 molar. While two studies involving animal wastes apparently used this expression successfully to relate partial pressure to ammonia concentration (22, 43), the assumptions used in its derivation apply to dilute aqueous solutions of ammonia.

Problems were also discovered in the use of a dissociation constant for ammonia in organic wastes. Srinath and Loehr (43) presented an expression showing the dissociation constant to vary inversely with the logarithm of the temperature. While this expression was developed from dilute aqueous solutions of ammonia in water it was used for several organic wastes. Some mention was made, however, of the possible effects of concentrated organic matter on the constant. Beauchamp, et al. (4) stated that the physical and chemical nature of sludge may significantly reduce the proportion of the ammonical nitrogen in the

ammonia form from that predicted for very dilute aqueous systems.

Hashimoto and Ludington (14) reported that ionic strength, dielectric constant, and organic content are all factors which can change the dissociation constant for ammonia. They measured the dissociation constant in a concentrated chicken manure slurry and found it to be about one sixth of the value for dilute ammonia solutions. While this constant, based on concentrations rather than activities, should have been slightly lower due to the salting out effect on dissolved ammonia, such a large difference is surprising.

### Measurement Techniques

Common methods of measuring the concentration of ammonia in a gas involve removing the ammonia from the gas with some type of trap and then analyzing the trap to determine the amount of ammonia present. Several different techniques exist for trapping the ammonia. All of them make use of the fact that ammonia contacting an acid becomes ammonium ion, which is non-volatile.

Perhaps the easiest technique involves placing an open container of acid in contact with an atmosphere containing ammonia. This method was used by Ryan, et al. (38) to measure ammonia volatilized from sludge. A disadvantage of this method is the very long time required to

absorb the ammonia from the gas into the liquid (theoretically, an infinite amount of time would be required). It was reported by another author that this method would not accurately measure ammonia volatilization rates (24).

By far the most common approach noted was to draw the gas through some sort of trap. This usually involved bubbling the gas sample through an acid. Examples of acids reported include sulfuric acid (8, 19, 21, 24, 25, 26, 30, 32, 37, 45), distilled water (22), and boric acid (20). The strength of the mineral acids ranged from 0.02 to 1.0 normal, depending on the amount of ammonia expected to be trapped. Flow rates through the traps of 20 to 2000 ml/min were cited.

Okita and Kanamori (33) presented evidence to show that such impinger traps are inefficient in removing ammonia from air, especially at low concentrations. Sampling efficiency was seen to improve as the sampling time was reduced. Axelrod and Greenburg (3) mentioned that these inefficiencies were due to contamination and gave a procedure for cleaning the scrubbers in an alkaline cleaner. This was then shown to result in 100 percent sampling efficiency, even at low concentrations.

A different type of liquid trap used was a vessel almost filled with glass beads containing a small amount of weak phosphoric acid. The gas sample was then drawn through this bed of beads. Denmead, et al. (9) used such

a trap to measure atmospheric concentrations of ammonia. Beauchamp, et al. (4) attempted to use a similar trap, but discovered inefficiencies at concentrations much above ambient and had to apply a correction factor.

Various means were given for measuring the concentration of ammonia in the traps. These were steam distillation (24, 25, 37, 38, 45), direct titration (8, 19, 20, 26), Nesslerization (22, 30), an ammonia specific electrode (32), and the use of the phenate method in a Technicon AutoAnalyser (4).

Using titrametric methods to analyze traps from samples obtained over organic wastes presents the problem that any non-ammonical basic nitrogen compounds trapped may be measured as ammonia. According to Miner, et al. (30) these compounds may be measured specifically by analyzing part of the trap using direct Nesslerization and part using Nesslerization after Kjeldahl digestion. Direct titrametric methods seem to be the least sensitive of all the methods in measuring ammonia.

Shendrikar and Lodge (40) reported the Nessler colorimetric method to be sensitive to numerous variables including the stability of the reagents and did not recommend it for routine analysis if an alternative existed. The same report cited the phenate method as more specific and less subject to interferences than Nesslerization. Disadvantages of close control over pH, reagent concentration, and

length of time for analysis were reported. Rossum and Villarruz (36) warned that any appreciable delay before adding the phenate reagent or too rapid an addition of the reagent will cause erratically low results.

Another method cited was the trapping of ammonia on acid impregnated filters. Shendrikar and Lodge (40) presented results of several attempts to use filters to trap ammonia. Glass fiber filters impregnated with standard sulfuric acid were found to have very poor efficiency of absorption under field conditions. It was found that efficiency could be improved to almost 100 percent using glass fiber filters impregnated with 5  $\text{NH}_2\text{SO}_4$ . Due to the hygroscopic nature of such concentrated acid, however, difficulties were foreseen in handling the filters in humid atmospheres. The best results were obtained with Whatman No. 1 or 41 filters which had been impregnated with an ethanolic solution of oxalic acid and allowed to dry. These filters were reported to combine high efficiency of absorption with ease of handling.

Methods of measuring the amount of ammonia trapped by the filters varied with the type of filter. Okita and Kanamori (33) used filters impregnated with sulfuric acid. After collection, the filter was washed and the resulting solution analyzed for ammonia with the pyridine-pyrazolone method. Microdetermination of ammonia in the nanogram and microgram range was developed by Shendrikar and



Lodge (40) using oxalic acid impregnated filters. Analysis was done using the ring oven technique developed by Weisz (47).

The ammonical nitrogen concentration in sludge can be easily determined using the techniques presented in Standard Methods for the Examination of Water and Wastewater (2). Due to the large amount of interfering substances present, steam distillation is required as part of the determination. Distillate can be analyzed for nitrogen using either colorimetric or titrametric techniques. Because of the variable nature of sludge it is advised to report ammonia concentration as a percentage of the wet weight of the sludge.

An alternative technique is the use of the ammonia specific electrode. Such an electrode was used by Moore, et al. (32) to measure the ammonia concentration in concentrated animal manure slurries. The manufacturer of the electrode warns of interference caused by surface active agents such as may be found in sewage (34).

Alkalinity in sludge can be determined using the procedure given in Standard Methods (2). Brovko, et al. (6) reported that the total alkalinity measured this way represents alkalinity due both to the carbonate system and volatile acids. The simplified technique developed by DiLallo and Albertson (10) is suggested for measuring

volatile acids so that total alkalinity can be corrected to bicarbonate alkalinity.

## III. THEORY

Methods of predicting volatile losses have not been adequately developed. It should be expected, however, that volatilization would fall into the realm of convective mass transfer. In this case volatile losses could be described by use of an appropriate mass transfer model.

A general form of the convective mass transfer model is

$$N_A = K_G (P_{A,S} - P_{A,B}) \quad (1)$$

where  $N_A$  is the areal mass flux of volatile component A leaving a surface ( $\text{kg/m}^2\text{-hr}$ ),  $K_G$  is an overall mass transfer coefficient ( $\text{kg/m}^2\text{-hr-atm}$ ),  $P_{A,S}$  is the gaseous concentration of A right at the surface (atm), and  $P_{A,B}$  is the bulk or ambient concentration of A above the surface. (atm).

Regardless of the exact model employed, all make use of a concentration gradient to characterize the driving force responsible for loss. In this case the concentration gradient is the difference between the partial pressure of ammonia at the surface of the sludge and the partial pressure in the ambient air. These concentrations must be known to predict loss of ammonia.

The partial pressure of a dissolved gas above a gas-liquid interface is extremely difficult to measure in situ. Therefore, it is generally determined from the liquid phase

concentration by use of an equilibrium constant. This constant defines the equilibrium relationship between the concentration of a dissolved gas in the liquid phase and the concentration of the gas in the atmosphere above the liquid.

The value of the constant depends on the thermodynamics of the dissolution of the gas and the physical and chemical nature of the solvent. Constants are tabulated for pure ammonia-water systems but it is not known if these are valid for use with sludge because of its complex nature (4).

In order to use conventional mass transfer models to describe losses of ammonia an equilibrium constant relating the gas and liquid phase concentrations of ammonia must be determined. Once this has been found it will be possible to define the gaseous concentration of ammonia at the sludge surface in terms of easily determined characteristics of the sludge.

There are two reactions of interest involving ammonia. First is the dissolution of ammonia in an aqueous solvent represented by



The equilibrium constant for this type of reaction is commonly referred to as the Henry's Law constant. For the reasons explained earlier, the term Henry's Law constant may not be appropriate for ammonia-water systems. Therefore, the term gas solubility constant,  $K_g$ , will be used.

$$K_S = \frac{\{NH_3(aq)\}}{\{NH_3(g)\}} \quad (3)$$

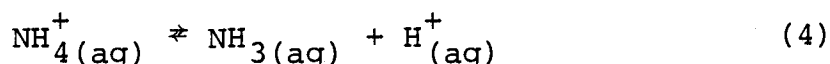
The brackets denote the activities of the enclosed species.

The symbol  $\{NH_3(g)\}$  is also interchangeable with  $P_{A,S}$ ,

which is found in the mass transfer model. The second

reaction of concern is the dissociation reaction of

ammonium represented by



The equilibrium constant for this type of reaction is known as the acid dissociation constant,  $K_a$ .

$$K_a = \frac{\{H^+(aq)\}\{NH_3(aq)\}}{\{NH_4^+(aq)\}} \quad (5)$$

Common analytical techniques suitable for use with sludge allow determination only of the concentration of total ammonical nitrogen (ammonia plus ammonium) and not of the individual species concentrations. Also, to measure equilibrium constants directly, the activities of the individual species must be known. In dilute solutions the activity can be assumed to equal the concentration. This assumption should not be made with sludge, however. There appears to be no direct method of measuring the activity of ammonical species in sludge.

Determinations that can be made easily with sludge include:

- i) the concentration of total ammonical nitrogen present in the liquid phase,  $[TAN_{(aq)}]$

- ii) the activity of the hydrogen ion in the liquid phase,  $\{H^+_{(aq)}\}^{1/}$
- iii) the activity of ammonia in the gas phase  $\{NH_{3(g)}\}^{2/}$

The ratio of the concentration of ammonia to the concentration of total ammonical nitrogen is denoted by F

$$F = \frac{[NH_{3(aq)}]}{[TAN_{(aq)}]} \quad (6)$$

The activity of dissolved ammonia in the liquid phase is equal to the concentration times an activity coefficient,  $\gamma_{NH_3}$ . This activity can then be written as

$$\{NH_{3(aq)}\} = \gamma_{NH_3} [NH_{3(aq)}] = \gamma_{NH_3} F [TAN_{(aq)}] \quad (7)$$

This can be substituted into the gas solubility expression to yield

$$K_S = \frac{\gamma_{NH_3} F [TAN_{(aq)}]}{\{NH_{3(g)}\}} \quad (8)$$

The solubility constant should vary only with the temperature of the system. Expression (8) can be written as

$$\frac{K_S}{[TAN_{(aq)}]} = \frac{\gamma_{NH_3} F}{\{NH_{3(g)}\}} \quad (9)$$

For samples of the same sludge at identical temperatures and moisture contents and assuming a closed system

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<sup>1/</sup> The activity of the hydrogen ion is determined by use of a pH meter since electrometric pH measurements determine the activity, not concentration, of hydrogen ions.

<sup>2/</sup> Since the gas phase is at low pressure, the ideal gas law is assumed valid. In this case, the concentration of the gas is assumed equal to the activity of the gas.

exists with respect to ammonia, the quantity  $K_S/[TAN_{(aq)}]$  should be constant. With such samples at different pH values the following expression should be true

$$\frac{\gamma_{NH_3 I}^{F_I}}{\{NH_{3(g)}\}_I} = \frac{\gamma_{NH_3 II}^{F_{II}}}{\{NH_{3(g)}\}_{II}} \quad (10)$$

where the subscript I denotes sludge at a pH below about 8.5 and the subscript II denotes sludge with the pH above 10.5. Since pH values above 10.5 are sufficiently high that essentially all of the ammonical nitrogen will be present as ammonia,  $F_{II}$  can be assumed to equal unity. Expression (1) can then be written as

$$F_I = \frac{\gamma_{NH_3 II} \{NH_{3(g)}\}_I}{\gamma_{NH_3 I} \{NH_{3(g)}\}_{II}} \quad (11)$$

If it is assumed that the activity coefficients at the two pH values are equal then expression (11) becomes

$$F_I = \frac{\{NH_{3(g)}\}_I}{\{NH_{3(g)}\}_{II}} \quad (12)$$

Therefore, measuring the gaseous concentration in equilibrium with the liquid at the two pH values will yield the dissociated fraction at the low pH. Rewriting the dissociation constant given by equation (5) in terms of  $F$  yields

$$K_a = \frac{F[TAN_{(aq)}] \gamma_{NH_3} \{H^+_{(aq)}\}}{(1-F)[TAN_{(aq)}] \gamma_{NH_4^+}} \quad (13)$$

which then simplifies to

$$K_a = \frac{F \gamma_{\text{NH}_3} \{ \text{H}^+_{(\text{aq})} \}}{(1-F) \gamma_{\text{NH}_4^+}} \quad (14)$$

A value of the ratio of  $\gamma_{\text{NH}_3}$  to  $\gamma_{\text{NH}_4^+}$  can be assumed within reasonable error over the range of ionic strengths expected for the sludge so that  $K_a$  can be calculated from the pH and F values.

The gas solubility constant has been given by

$$K_s = \frac{\gamma_{\text{NH}_3} F [\text{TAN}_{(\text{aq})}]}{\{ \text{NH}_3(\text{g}) \}} \quad (8)$$

A value of  $\gamma_{\text{NH}_3}$  can be assumed over the expected range of ionic strengths within acceptable error to allow calculation of  $K_s$ .

With values for the ammonia equilibrium constants it should be possible to express the gaseous concentration of ammonia above the sludge in terms of these constants and several easily determinable physical characteristics of the sludge.

Writing equation (5), the definition of the acid dissociation constant, in terms of concentrations and activity coefficients for the ammonical species yields

$$K_a = \frac{\gamma_{\text{NH}_3} [\text{NH}_3(\text{aq})] \{ \text{H}^+_{(\text{aq})} \}}{\gamma_{\text{NH}_4^+} [\text{NH}_4^+(\text{aq})]} \quad (15)$$



If the ratio of activity coefficients is defined by

$$\Gamma' = \frac{\gamma_{\text{NH}_3}}{\gamma_{\text{NH}_4^+}} \quad (16)$$

and this is substituted into expression (15), the ammonium concentration can be expressed by

$$[\text{NH}_4^+(\text{aq})] = \frac{\Gamma' [\text{NH}_3(\text{aq})] \{\text{H}^+(\text{aq})\}}{K_a} \quad (17)$$

Substituting the above expression into the definition of total ammonical nitrogen yields

$$\begin{aligned} [\text{TAN}(\text{aq})] &= [\text{NH}_3(\text{aq})] + \frac{[\text{NH}_3(\text{aq})] \Gamma' \{\text{H}^+(\text{aq})\}}{K_a} \\ &= [\text{NH}_3(\text{aq})] \left[ 1 + \frac{\Gamma' \{\text{H}^+(\text{aq})\}}{K_a} \right] \end{aligned} \quad (18)$$

This can be rearranged to give the concentration of ammonia as

$$[\text{NH}_3(\text{aq})] = \frac{[\text{TAN}(\text{aq})]}{\left[ 1 + \frac{\Gamma' \{\text{H}^+(\text{aq})\}}{K_a} \right]} \quad (19)$$

The above expression can then be substituted into expression (3) to obtain

$$P_{A,S} = \frac{[\text{TAN}(\text{aq})] \gamma_{\text{NH}_3}}{K_S \left[ 1 + \frac{\Gamma' \{\text{H}^+(\text{aq})\}}{K_a} \right]} \quad (20)$$

Using expression (20) it is possible to obtain the equilibrium concentration of ammonia above the sludge given other properties and characteristics of the sludge. The concentration of total ammonical nitrogen can be easily determined using analytical procedures described in this thesis. Activity coefficients may be estimated from a knowledge of the characteristics of the sludge. Values of equilibrium constants and pH will be investigated experimentally.

#### IV. METHODS AND MATERIALS

The experimental portion of this thesis was comprised of two main experiments. The objective of the first experiment was to determine the two equilibrium constants for ammonia described previously. The objective of the second was to obtain some knowledge of the behavior of the pH of the sludge following application.

The first experiment required determining the temperature, pH, aqueous concentration of total ammonical nitrogen, and equilibrium gaseous concentration for each of two sludge samples. The samples were to be identical except for pH; one sample being at a pH of at least 10.5 and the other in the neighborhood of 8.0 to 8.5. Since the pH of the sludge was thought to vary as carbon dioxide was lost, the second experiment required determination of the pH and carbonate species concentrations for sludge samples after various times of exposure to air.

Both experiments were performed in the laboratory. Sludge for the first experiment was obtained September 6, 1978 from the Willow Lake Wastewater Treatment Plant near Salem, Oregon and stored in a tightly stoppered container at 4°C until needed. Sludge samples for the first and second runs of the second experiment were obtained November 17 and November 28, 1978, respectively, from the

Albany Sewage Treatment Plant in Albany, Oregon.

### Experiment I

The first experiment required determination of temperature, pH, aqueous concentration of total ammonical nitrogen, and equilibrium gaseous ammonia concentration for samples of sludge. Temperature was measured directly using a mercury-filled thermometer. Hydrogen ion activity was determined directly using a Broadley-James flat surface pH electrode and a Corning Model 12 expanded scale pH meter. Efforts were made to measure the pH as near the surface of the sludge sample as possible in case gradients existed with depth. The liquid and gaseous concentrations of ammonia could not be measured directly. Procedures and apparatus had to be developed to make indirect determinations.

### Apparatus

Development of a suitable procedure and apparatus for determining the gaseous concentration of ammonia above liquid samples presented significant difficulties. A complete description of the development of the method is given in Appendix I to this thesis.

Briefly, the procedure involved sealing a sample of sludge inside of a jar. The air in the jar was allowed to come to equilibrium with the ammonia in the sludge. After

this the air was drawn out of the jar and through an ammonia trap. The trap was analyzed to determine the amount of ammonia removed.

Samples of sludge were placed in 100 ml plastic beakers and sealed in a one quart wide-mouth Mason jar. Air flowing into the jar was first directed through an ammonia scrubber and flowmeter. In the scrubber incoming air was bubbled through 5 N  $\text{H}_2\text{SO}_4$  to remove any ammonia that might cause contamination. The flowmeter was a Gilmont compact flowmeter capable of measuring air flows from 20 to 2100 ml/min. Air leaving the jar was directed through three ammonia traps connected in series. Each trap consisted of a vertical gas dispersion tube with a coarse fritted cylinder sealed in a 29 x 200 mm test tube. Each tube contained 50 ml of 0.001 N  $\text{H}_2\text{SO}_4$  to trap the ammonia. Air entered the jar near the bottom, away from the surface of the sludge, and exited near the top of the jar to promote good mixing of the gas in the jar. Air was drawn through the system by a rotary motor-mounted vacuum pump. Flow regulation was accomplished by a brass needle valve in the line between the exit of the traps and the entrance to the pump. Also, a Neptune Dyna-Pump having a flow rate of approximately 1500 ml/min was connected to the sample jar. The purpose of this pump was to recirculate the contents of the jar and promote transfer of ammonia out of the sludge while equilibrium was being

reached. All connections were made using either glass or teflon tubing. A schematic of the system is shown in Figure 1.

### Procedure

Seventy ml samples of sludge were placed in 100 ml plastic beakers. The pH of the sludge was adjusted to a desired value by addition of 10 N NaOH. The sample and beaker were then sealed in the sample jar and allowed to sit with the recirculation pump running for approximately 36 hours. The recirculation pump was then turned off and the apparatus was prepared for sample collection.

Temperature and pH were measured by inserting the thermometer and pH electrode through rubber seals in the lid of the jar. After these measurements were obtained the air inside the jar was collected for analysis. This was done by drawing air through the system at 1000 ml/min for five minutes using the vacuum pump.

After the gas sample had been collected the acid traps were removed and the impingers washed thoroughly with 0.1 N NaOH and ammonia-free distilled water. They were then dried by drawing ammonia-free air through them for 30 minutes.

Next, samples of the liquid sludge were collected for analysis. Three samples of approximately ten ml were drawn off for total solids determination. The remaining

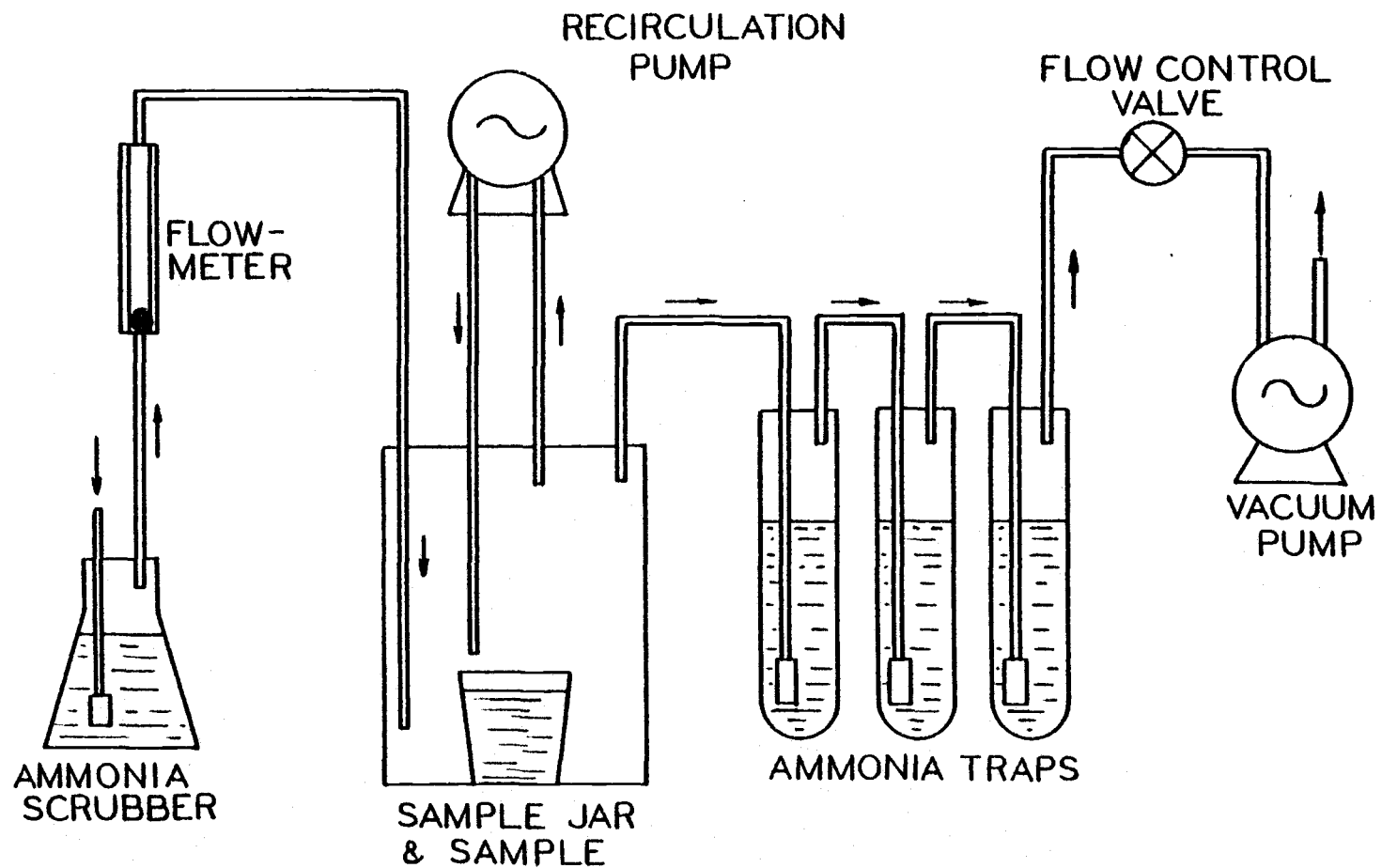


Figure 1. Gas sample collection apparatus.

sludge was then adjusted to a pH of approximately seven using 5 N  $\text{H}_2\text{SO}_4$ . This was done to prevent ammonia loss during storage and handling. Three samples of approximately one ml were then removed for determination of ammonia nitrogen. Twelve runs of two samples each were made.

Some variation of the moisture content of the sludge was made between runs. Moisture content of the sludge was decreased by lowering the pH of the sludge to approximately seven with concentrated  $\text{H}_2\text{SO}_4$  and evaporating moisture at  $40^\circ\text{C}$ .

#### Gas Sample Analysis

Gaseous ammonia concentration was obtained by analyzing the acid from the ammonia traps. The liquid concentration of ammonia nitrogen in the traps was determined using the phenate method. Samples from each of the traps were taken and diluted to a volume of 20 ml with 0.001 N  $\text{H}_2\text{SO}_4$ , if necessary, to be within the analytical range of the method. Analytical procedure followed was the same as that given in Standard Methods for the Examination of Water and Wastewater (2) except that all sample and reagent volumes were doubled. Because of instability with storage, fresh reagents were prepared before each run. Standards and a reagent blank were carried through every analysis. Colorimetric analysis was done using a Coleman Jr. II A Spectrophotometer. The amount of ammonia in each trap was



calculated by multiplying the trap concentration by the dilution factor and the trap volume of 50 ml.

### Liquid Sample Analysis

Liquid concentration of total ammonical nitrogen had to be obtained from values of total solids and total ammonia nitrogen. Total solids was determined using the procedure in Standard Methods (2) with the exception that smaller sample volumes were used. Triplicate determinations were made on all sludge samples. Total ammonia nitrogen was determined using a micro-distillation technique with an acidimetric finish. Reagents and procedures used were identical to those given in Standard Methods (2) except for proportionally smaller sample and reagent volumes. Triplicate determinations were made on all sludge samples.

### Experiment II

The second experiment required determination of pH and carbonate species concentrations of sludge samples. The procedure used called for exposing sludge samples to air for specified times and then performing analyses.

For the first run twenty-two 80 ml samples of sludge were placed in 100 ml beakers and left exposed to the air in the laboratory. Two samples were analyzed for pH, total alkalinity, and volatile acid alkalinity at the end

of each exposure period. Exposures of 0, 2, 4, 6, 8, 10, 24, 30, 36, 60, and 84 hours were made. The second run used 20 samples and exposures of 0, 11, 24, 35, 48, 72, 92, 120, 168, and 216 hours. A Corning Model 12 expanded scale pH meter with glass and calomel electrodes was used to measure pH. Alkalinities were determined using the procedure developed by DiLallo and Albertson (10).

## V. RESULTS AND DISCUSSION

### Introduction

The data of experiment I were used to calculate equilibrium constants for ammonia. Direct calculation with the results was not possible, however, and several intermediate steps had to be taken. These included calculating the various ammonia concentrations and estimating activity coefficients. With all of the necessary values obtained the equilibrium constants were calculated. The measured values of equilibrium constants were then statistically compared to the theoretical values expected. A review of the experimental procedure for possible sources of measurement error was made.

The data of experiment II were used to describe the behavior of the pH of sludge after exposure to the atmosphere. Part of the data were used to directly show the change of pH with time. The remaining data were used to investigate the variation of pH with carbonate system concentrations. This included estimating activity coefficients and calculating concentrations. The relationship between carbonate species concentration and pH was then examined. Possible explanations for the results were offered.

Finally, the practical significance of the results was examined. This included suggestions concerning possible use of the constants. The practical significance of the knowledge concerning the behavior of the pH was examined next. A mass transfer model to describe losses from applied sludge was then developed and a hypothetical case investigated. The expected losses were viewed in light of the results of actual cases. Factors that influence the loss of ammonia were then examined.

### Experiment I

#### Calculation of Ammonia Concentrations

The aqueous concentration of total ammonical nitrogen is calculated from the percent total solids and percent ammonia nitrogen using the following relationship

$$(\text{TAN}_{\text{(aq)}}) = \frac{\% \text{ TAN } (1,000,000)}{100 - \% \text{ TS}} \quad (21)$$

where  $(\text{TAN}_{\text{(aq)}})$  is the aqueous concentration of total ammonical nitrogen (mg N/l), % TAN is the percent total ammonia (gm N/100 gm sludge), % TS is the percent total solids (gm solid/100 gm sludge), and 1,000,000 is a conversion factor for gm N/gm water to mg N/l. This assumes that the liquid phase of the sludge is sufficiently dilute to have a specific gravity of 1.0.

The gaseous concentration of ammonia is calculated as the amount of ammonia present in the gas in the sample jar divided by the volume of gas in the sample jar. The amount of ammonia recovered from the traps is not, however, equal to the amount of ammonia originally present in the jar. The actual amount of ammonia originally present is estimated from the amount measured and the dissolved ammonia concentration by the following stochastic relationship.<sup>3/</sup>

$$\text{NH}_3 \text{ act} = \frac{\text{NH}_3 \text{ meas}}{4.74 - 0.912 \log(\text{NH}_3(\text{aq}))} \quad (22)$$

where  $\text{NH}_3 \text{ act}$  is the estimated actual amount of ammonia originally present in the jar ( $\mu\text{g}$ ),  $\text{NH}_3 \text{ meas}$  is the amount of ammonia measured in the traps ( $\mu\text{g}$ ), and  $(\text{NH}_3(\text{aq}))$  is the concentration of dissolved ammonia gas present in the liquid sludge ( $\text{mg}/\ell$ ).

For the samples of sludge at high pH,  $\text{NH}_3 \text{ act}$  can be calculated directly since  $(\text{NH}_3(\text{aq}))$  is assumed to equal  $(\text{TAN}(\text{aq}))$ . Problems arise with the samples at low pH, however. To calculate  $\text{NH}_3 \text{ act}$  the F value must be known since  $(\text{NH}_3(\text{aq}))$  is equal to the product of F and  $(\text{TAN}(\text{aq}))$ . However, the F value must be calculated from the gaseous concentration of ammonia, which is calculated from  $\text{NH}_3 \text{ act}$ . Therefore, an iterative procedure was devised. A value of

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<sup>3/</sup>For a discussion of the development of this relationship see Appendix I.

F was assumed and used to calculate  $(\text{NH}_3(\text{aq}))$  from  $(\text{TAN}(\text{aq}))$ . This was then used in expression (22) to obtain  $\text{NH}_3 \text{ act}$ . The gaseous concentration was calculated from this and a new value of F obtained. This value was used to calculate a new value of  $(\text{NH}_3(\text{aq}))$  and the procedure repeated until the initial and final values of F agreed closely.

The gaseous ammonia concentration is calculated as the quotient of the estimated actual amount of ammonia originally present and the gas volume in the jar. The volume inside the jar under sampling conditions was measured as 870 ml by finding the volume of water required to fill the jar. The gaseous concentration is then converted to a partial pressure using the Universal Gas Law.

#### Estimation of Activity Coefficients

To calculate activity effects the ionic strength of the liquid phase must be known. For sludge, it is assumed that the only anions of significant concentration are the carbonate species and volatile acids. The ionic strength of the sludge is then estimated from the alkalinity and pH. When the sludge was first obtained it was analyzed for total and volatile acid alkalinity and total solids. These were found to be 4920 mg/l as  $\text{CaCO}_3$ , 390 mg/l as  $\text{CaCO}_3$ , and 2.78 percent, respectively. It was assumed that the carbonate species and volatile acids were conserved during

storage. Therefore, the total carbonate system and volatile acid concentrations for the sludge samples can be obtained by adjustment for changes in moisture content due to loss of water. For samples at low pH the carbonate system alkalinity (the difference between total and volatile acid alkalinities) was assumed to be due only to bicarbonate ions. For high pH samples it was assumed that the bicarbonate and carbonate concentrations were equal for pH from 10.0 to 10.5 and that only carbonate ion was present for pH above 10.5. For each sample, then, an estimation of bicarbonate and carbonate ion concentrations was made. These were added to the volatile acid anion concentration to obtain the total anion concentration. It was assumed that half of the cations present in sludge are singly charged and half are doubly charged. A charge balance then gave an estimation of concentrations of plus one, plus two, minus one, and minus two species. Any acids or bases added to the samples were then accounted for and the approximate ionic strength calculated using the following relationship

$$I = 1/2 \sum_i c_i z_i^2 \quad (23)$$

where  $c_i$  is the molar concentration of ions having the charge  $z_i$ . With the ionic strength known the activity coefficients can be obtained using the approaches offered by Butler (7). Tabulation of activity coefficients for

various ionic strengths and species charges is given in Appendix II.

Under actual field conditions, however, the pH of the sludge will be well below 10.0. Therefore the only significant anions expected are bicarbonate and volatile acid anions. Since these both carry a charge of minus one, the ionic strength can be estimated directly from the total alkalinity. This alleviates the need to obtain bicarbonate and volatile acid alkalinities.

#### Calculation of Equilibrium Constants

A value of ammonium dissociation constant,  $K_a$  (moles/l), was calculated for each run of two samples using the expression

$$K_a = \frac{F \gamma_{\text{NH}_3} \{H^+_{(aq)}\}}{1 - F \gamma_{\text{NH}_4^+}} \quad (14)$$

All quantities in the above expression are for the low pH sludge sample. A value of ammonia solubility constant,  $K_s$  (mg/l-atm), was calculated for each sludge sample using the expression

$$K_s = \frac{\gamma_{\text{NH}_3} F (\text{TAN}_{(aq)})}{\{NH_3(g)\}} \quad (24)$$

Appendix III gives the measured data and calculated results for experiment I.



Theoretical values of the acid dissociation and gas solubility constants for dilute aqueous solutions at various temperatures were calculated from thermodynamic data. These are given in Appendix IV.

For each run the measured dissociation constant was compared to the theoretical constant for the temperature of the low pH sample. For each sample the measured solubility constant was compared to the theoretical constant for the temperature of the sample. These results are shown in Figure 2 and Figure 3, respectively. A least squares regression analysis was made with the results. This information is given in Table 4.

Table 4. Results of least squares regression analysis for experiment I.

Item	$K_a$	$K_s$
Intercept, $b_0$	0.240	0.421
Standard deviation of intercept, $S(b_0)$	0.626	1.90
Slope, $b_1$	1.03	1.03
Standard deviation of slope, $S(b_1)$	0.220	0.175
Coefficient of determination, $r^2$	0.68	0.61
95 percent confidence interval for $\beta_0$	$-1.52 \leq \beta_0 \leq 2.00$	$-3.53 \leq \beta_0 \leq 4.37$
95 percent confidence interval for $\beta_1$	$0.536 \leq \beta_1 \leq 1.52$	$0.668 \leq \beta_1 \leq 1.40$

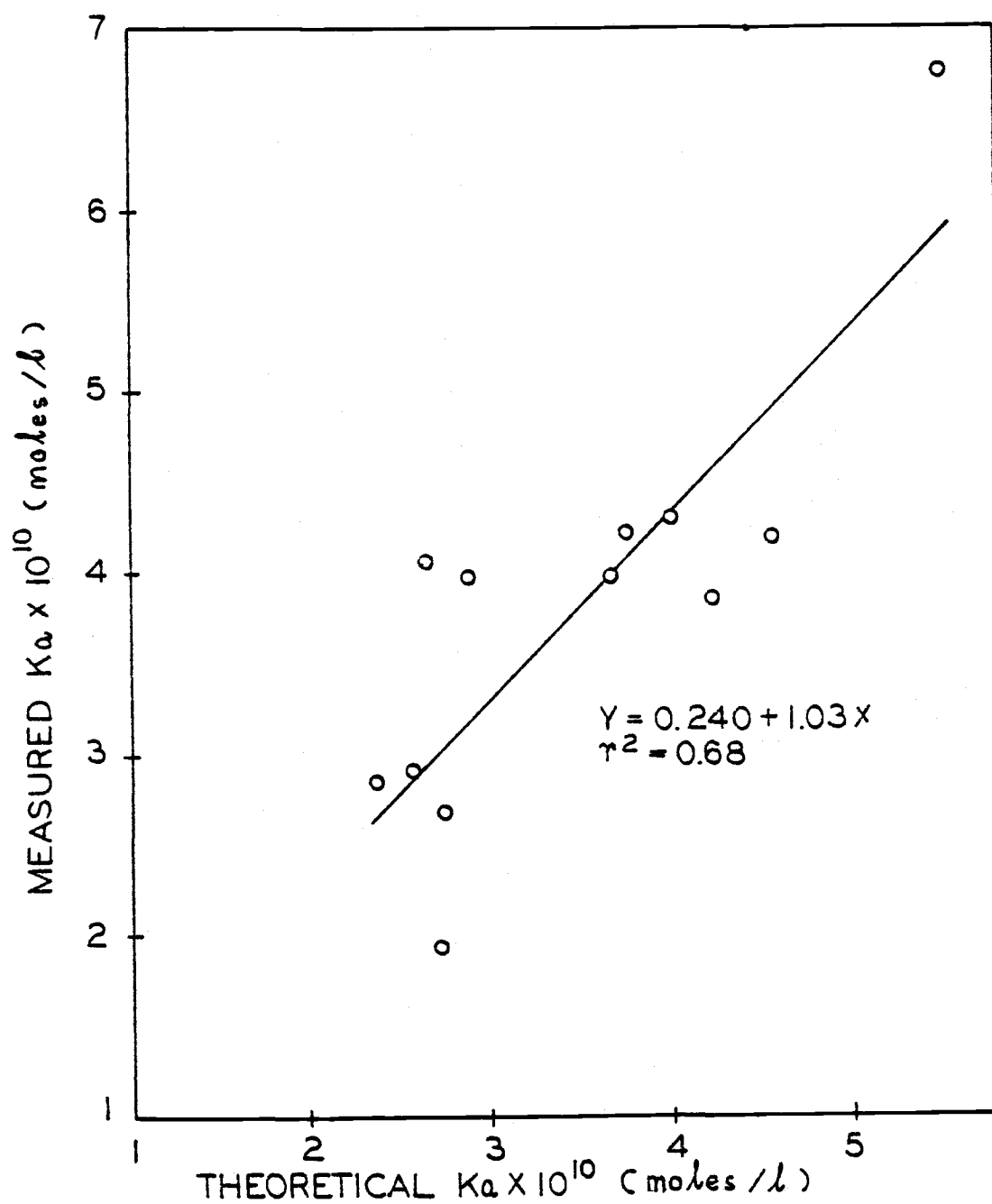


Figure 2. Acid dissociation constant for ammonia measured in sewage sludge versus theoretical value.

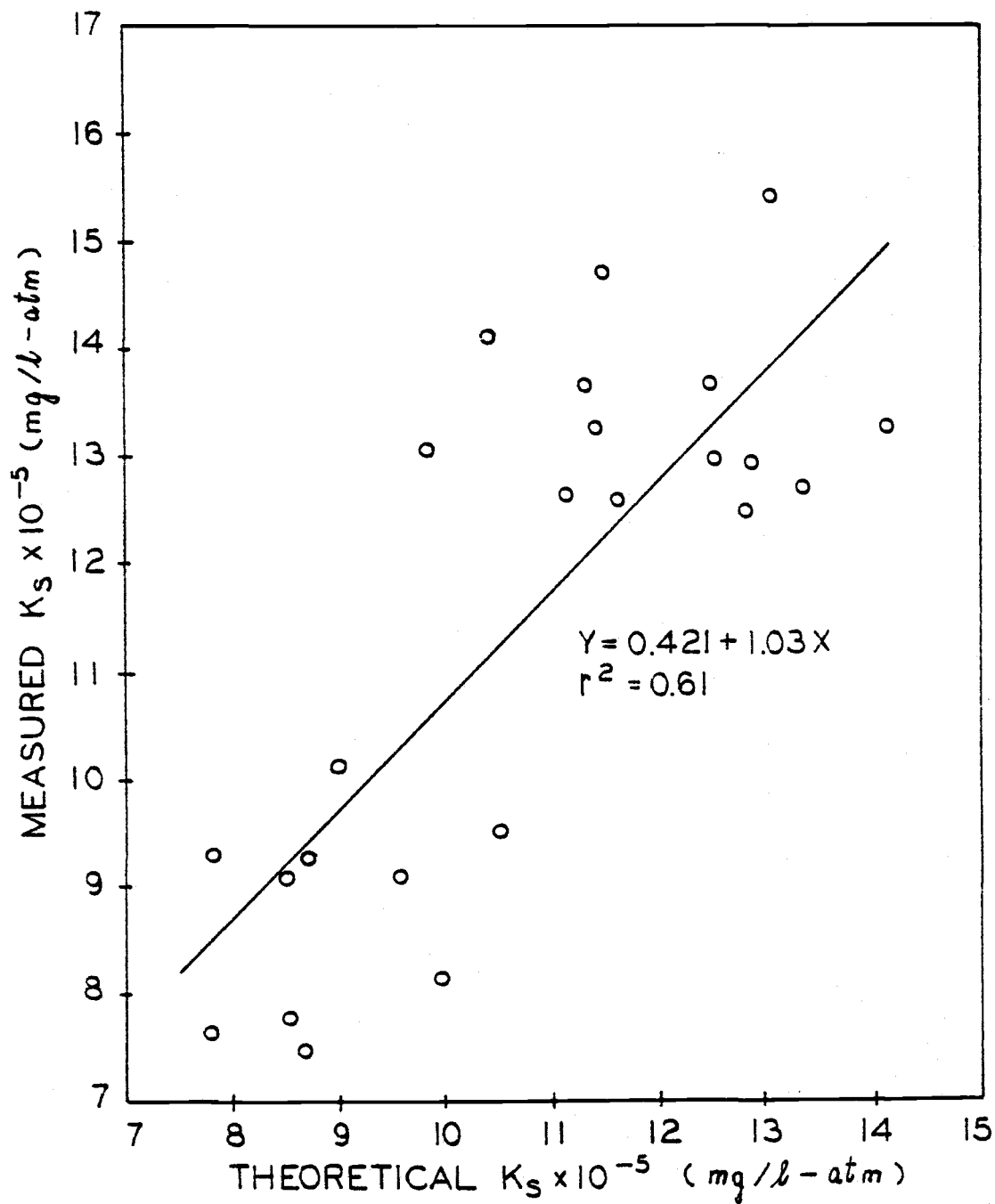


Figure 3. Gas solubility constant for ammonia measured in sewage sludge versus theoretical value.

## Discussion of Experiment Results

The statistical results show a fairly high degree of correlation between measured and theoretical constants. If the theoretical constants were actually valid for use with sludge the plot of measured constants versus theoretical constants should go through the origin and have a slope of unity. The 95 percent confidence intervals for intercepts and slopes include the values zero and one, respectively. The statistical inference at this significance level is that there is no significant difference between the measured and theoretical constants. There are, unfortunately, rather large standard deviations for the regression parameters.

There are several possible explanations for the scatter observed and the large standard deviations. The first of these concerns the sampling technique. The technique was not as refined as originally desired due to the difficulties encountered in developing it. A more direct method of determining the gaseous ammonia concentrations would have been desirable. Employment of the correction factor for the amount of ammonia recovered certainly introduced an opportunity for error.

The ammonia traps appeared to be very efficient in removing ammonia from the gas. The third trap in the series always revealed negligible amounts of ammonia and

the second traps only revealed detectable amounts of ammonia for the high pH samples. This would indicate that there was no appreciable amount of ammonia escaping detection.

The phenate method for determining the ammonia concentration in the traps seemed to work well. There were several occasions, however, when there was a noticeable difference between duplicate determinations for a trap. This probably resulted from errors in making the dilutions required to get down to the detectable range for the method. Dilutions of the first traps of 1:15 for low pH samples and 1:79 for high pH samples were usually required. Such dilutions also have the effect of multiplying any measurement errors when calculating the actual concentrations. The phenate method was, however, more reliable than any other technique investigated.

Perhaps the greatest opportunity for error is with the values of temperature and pH used in calculations and in obtaining the theoretical constants. The gaseous concentrations measured for the sludge samples reflect the average conditions present in the jar during the 36 hour period before sampling. The temperature and pH values measured were those at the time of sampling. The equilibrium gaseous concentration is highly dependent upon temperature and pH. Because of the slow kinetics of gas transfer, however, rapid changes in gaseous concentration could not be

made to reflect rapid changes in temperature or pH. If the temperature or pH measured did not reflect the average conditions in the jar before sampling they would not be the appropriate values to use.

The values for total solids were usually noticeably higher for the samples at high pH. This is probably because a drying temperature of 103°C was used. For such high pH samples a temperature of 180°C would have been better. Because of this, the solids value for the low pH sample was used in calculations for both samples for each run. It is possible, however, that the high pH samples should have had higher solids. This could have been due to the reduced solubilities of carbonate, hydroxide, or other metal complexes at high pH.

Errors could certainly have been made in estimating the ionic strengths. This is especially true for the high pH samples where strong base was added to adjust the pH and possible precipitation may have been occurring. It is fortunate, however, that only the activity coefficient for dissolved ammonia was required for these samples. As seen in Appendix II, this coefficient is not very sensitive to changes in ionic strength. Also, the value of the activity coefficient for the ammonium ion does not undergo extreme change for the values of ionic strength expected for the low pH samples.

## Experiment II

### Variation of pH with Time

The pH of the sludge samples was measured after various times of exposure to the atmosphere. The average pH of two samples was then plotted against time. These results are shown in Figure 4 and Figure 5 for runs one and two, respectively.

### Variation of pH with Carbonate System Species Concentration

For each sludge sample the bicarbonate alkalinity was calculated as the difference between the total and volatile acid alkalinities. The concentration of the bicarbonate ion was then calculated from the following expression

$$[\text{HCO}_3^-] = \frac{(\text{BA})}{50,000} \quad (25)$$

where  $[\text{HCO}_3^-]$  is the concentration of bicarbonate ion (moles/l), (BA) is the bicarbonate alkalinity (mg/l as  $\text{CaCO}_3$ ), and 50,000 is a conversion factor. Once the bicarbonate concentration is known the concentrations of the other carbonate system species can be calculated from the carbonate system acid dissociation constants, pH, and activity coefficients. The dissolved carbon dioxide concentration is calculated using the following expression

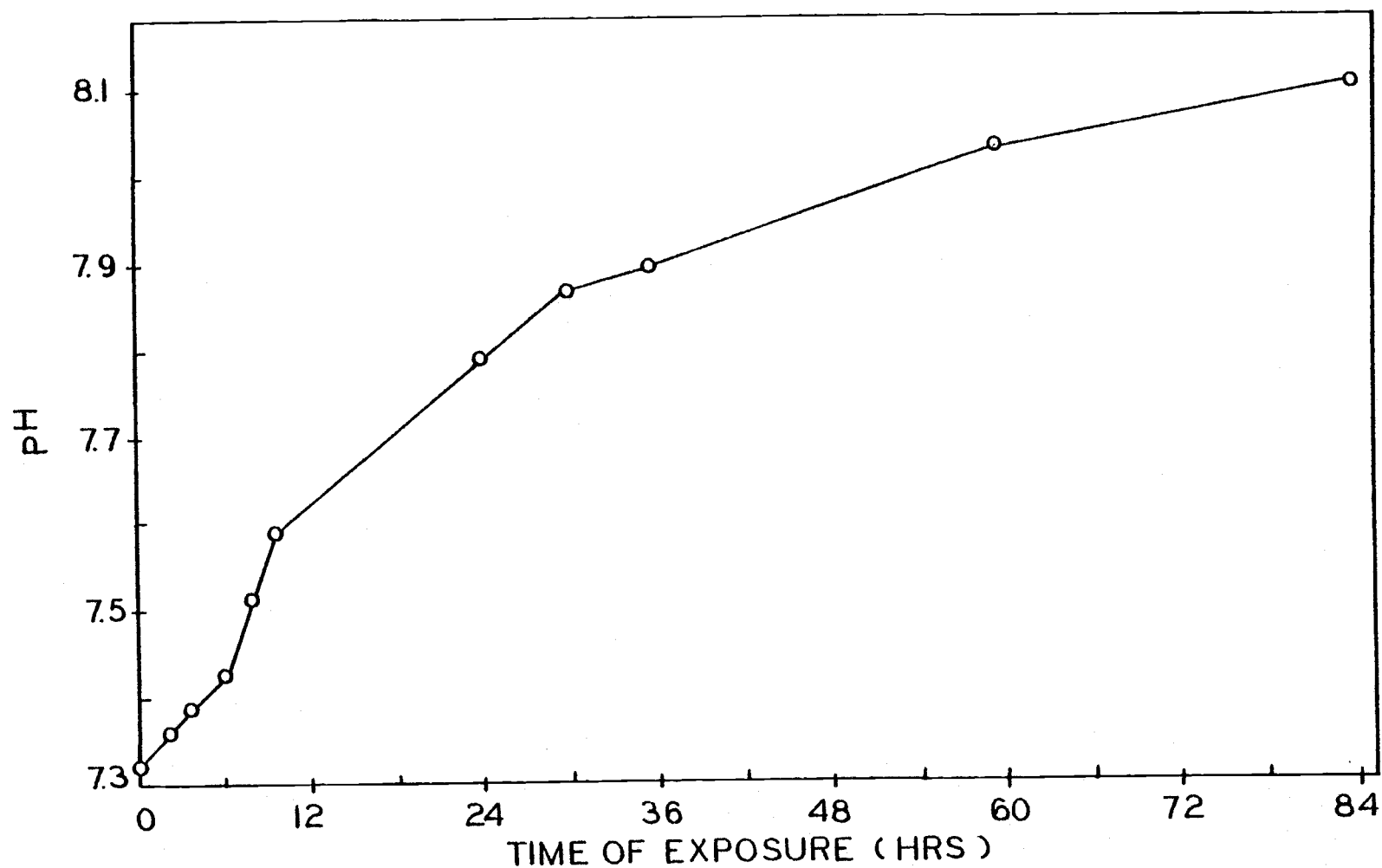


Figure 4. pH value of sludge samples versus time of exposure to air for run 1.



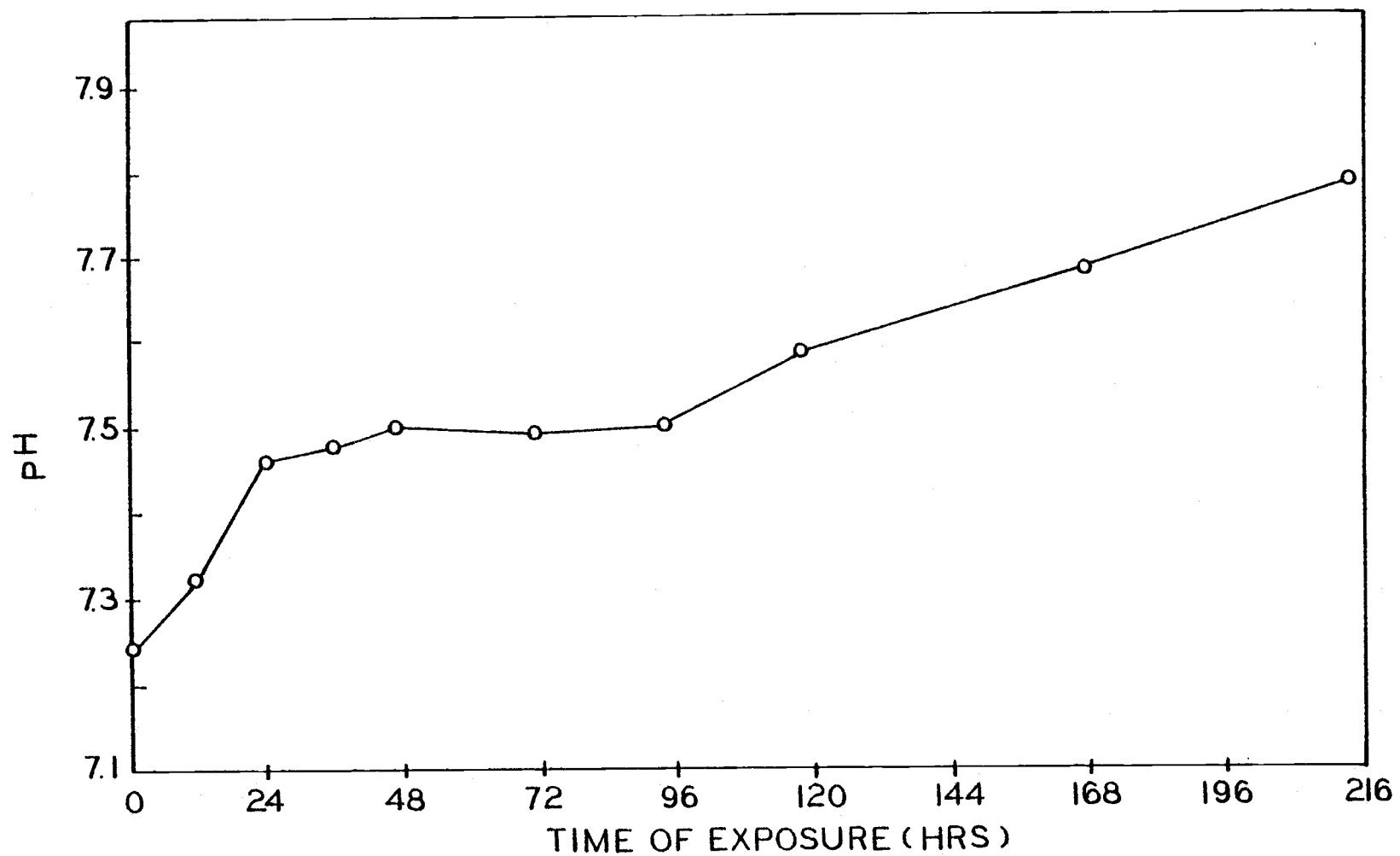


Figure 5. pH value of sludge samples versus time of exposure to air for run 2.

$$[\text{H}_2\text{CO}_3^*] = \frac{\{\text{H}^+\} [\text{HCO}_3^-] \gamma_{\text{HCO}_3^-}}{K_1 \gamma_{\text{H}_2\text{CO}_3^*}} \quad (26)$$

where  $[\text{H}_2\text{CO}_3^*]$  is the concentration of dissolved carbon dioxide (moles/l),  $\{\text{H}^+\}$  is the hydrogen ion activity (moles/l),  $\gamma_{\text{HCO}_3^-}$  is the activity coefficient for the bicarbonate ion,  $\gamma_{\text{H}_2\text{CO}_3^*}$  is the activity coefficient for dissolved carbon dioxide, and  $K_1$  is the first dissociation constant for the carbonate system (moles/l). Similarly, the second dissociation constant for the carbonate system can be used to calculate the concentration of carbonate ions

$$[\text{CO}_3^{=}] = \frac{K_2 [\text{HCO}_3^-] \gamma_{\text{HCO}_3^-}}{\{\text{H}^+\} \gamma_{\text{CO}_3^{=}}} \quad (27)$$

where  $[\text{CO}_3^{=}]$  is the concentration of carbonate ions (moles/l),  $K_2$  is the second dissociation constant for the carbonate system (moles/l), and  $\gamma_{\text{CO}_3^{=}}$  is the activity coefficient for the carbonate ion.

The activity coefficients were obtained for the ionic strength of the sludge from the values in Appendix II. The ionic strength was estimated using the procedure described earlier in the discussion of Experiment I.

The data and calculated results of the experiment are tabulated in Appendix V. Since pH is defined as the negative of the log of the hydrogen ion concentration, the negative of the log of the carbonate system species was

plotted versus pH. These results are shown in Figure 6 and Figure 7 for runs one and two, respectively. A least squares regression analysis was performed for each set of data points to obtain the straight lines shown. The intercept,  $b_0$ , slope,  $b_1$ , and coefficient of determination,  $r^2$ , for each regression are given in Table 5.

Table 5. Results of least squares regression analysis for experiment II.

	Parameter	Run 1	Run 2
$\text{H}_2\text{CO}_3^*$	$b_0$	-5.46	-7.80
	$b_1$	1.11	1.38
	$r^2$	0.998	0.989
$\text{HCO}_3^-$	$b_0$	0.372	-2.16
	$b_1$	0.155	0.453
	$r^2$	0.799	0.912
$\text{CO}_3^{=}$	$b_0$	9.96	6.85
	$b_1$	-0.802	-0.428
	$r^2$	0.986	0.874

### Discussion of Experiment Results

Observation of the pH variation with time reveals that there is an increase with time, as was reported in the literature. The increase observed was similar to, but slightly less than that observed by Molina, et al. (31). They observed the pH to increase similarly but then start

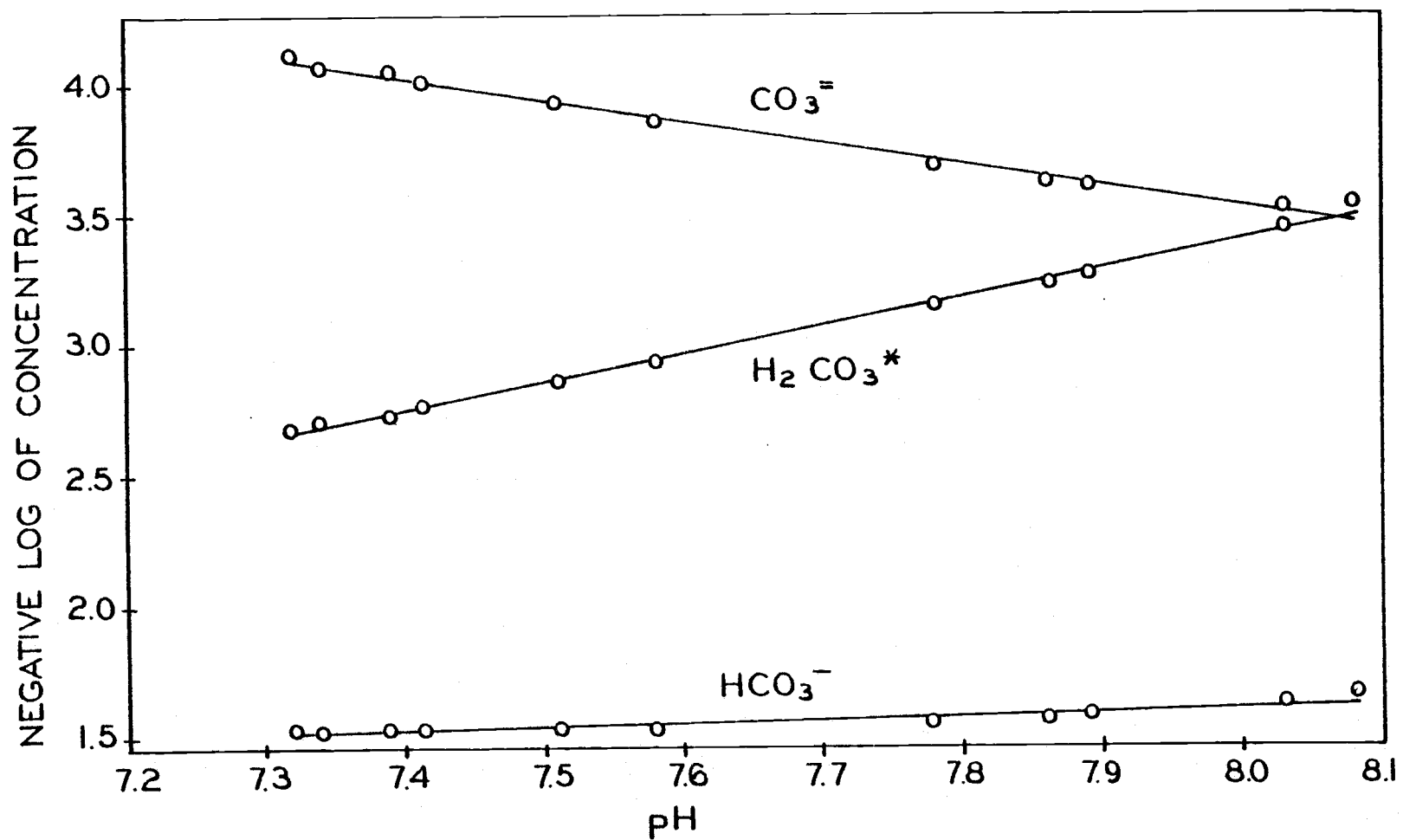


Figure 6. Negative log of carbonate system species concentration versus pH of sludge sample for run 1.

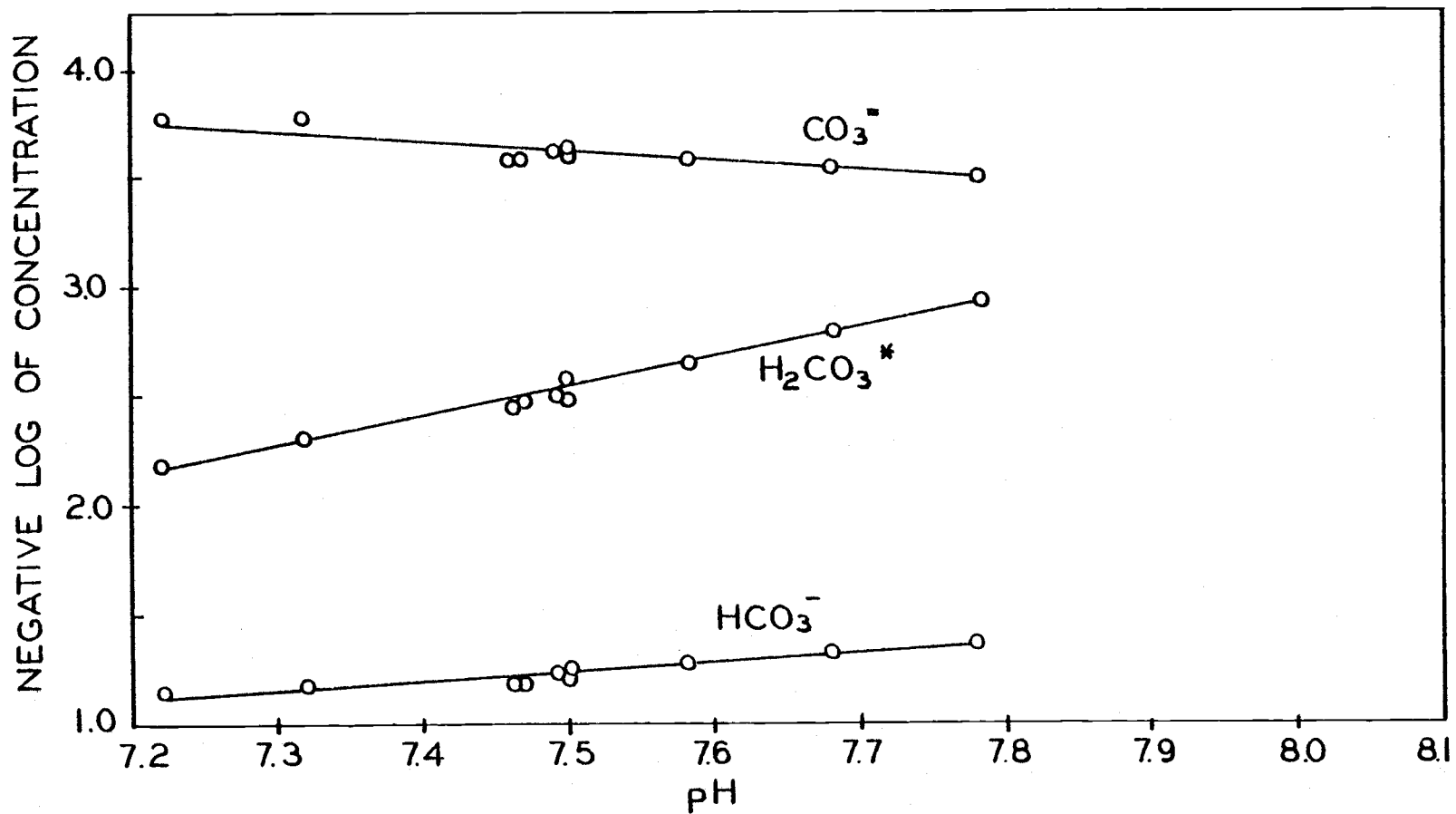


Figure 7. Negative log of carbonate system species concentration versus pH of sludge sample for run 2.

to decrease gradually after two days. This might reflect a difference in moisture or ammonia losses encountered.

The regression parameters reveal a high degree of correlation in all cases. The general tendency observed in both runs is that the dissolved carbon dioxide concentration decreases markedly, the bicarbonate ion concentration decreases slightly, and the carbonate ion concentration increases as the pH rises. In the range of pH encountered the bicarbonate ion is by far the dominant species present and the bicarbonate ion concentration would be essentially equal to the total carbonate carbon concentration.

These results are in agreement with the concept of pH increase due to loss of carbon dioxide. As carbon dioxide is lost the pH should increase and the bicarbonate concentration should decrease slightly. An increase in carbonate ion concentration should occur as the pH increases. Analysis of the exact expected slopes for the log C-pH plots would be extremely difficult due to the number of equilibria involved. The carbonate ion should certainly be in equilibrium with several solid phases. The system is open as far as dissolved carbon dioxide is concerned, but dissolved carbon dioxide is not in equilibrium with the atmosphere. Because of the slow kinetics of carbon dioxide dissolution it is not known whether to treat the system as open or closed. Since alkalinity was not conserved, the system did not behave strictly as a closed system. However, since

equilibrium between dissolved and atmospheric carbon dioxide was not present, the system cannot strictly be considered as open.

The analytical technique employed seemed to give good results. Close agreement between duplicate samples analyzed was obtained in all cases. In calculating the results some error may certainly have been made in estimating ionic strength because of the assumptions made and the possible loss of moisture during the exposure period. For the scope of this experiment, however, this error should not have been significant.

#### Significance and Application of Results

The goal of this investigation was to gain information needed to be able to predict the equilibrium gaseous concentration of ammonia above sewage sludge after application to cropland. Specifically, it was not known if theoretical equilibrium constants could be used with sludge or how stable the pH of sludge was following exposure to air. Determination of the gaseous concentration would allow a mass transfer equation to be used to describe volatile ammonia losses. Prediction of ammonia losses was judged to be important from the standpoint of determining the application rate of sludge to cropland. Knowledge of the fate of applied nutrients allows application of sludge to meet the nutrient requirements of the crop.

## Experiment I

The results of experiment I indicate that theoretical equilibrium constants can be used with sludge. Consideration must be made for activity effects due to ionic strength, however. A simple technique for estimating ionic strength was developed and used successfully. Use of estimated activity coefficients and tabulated equilibrium constants allows description of equilibrium conditions within the accuracy required for engineering application.

These results show that the concentration of organic matter in sludge apparently exerts no significant effect on the equilibrium distributions. It should be appropriate, therefore, to apply these results to organic wastes other than sludge. Anaerobic lagoons offer a great potential for surface losses of ammonia as do open storage facilities for manure slurries.

Koelliker and Miner (22) used theoretical equilibrium constants without activity corrections to calculate ammonia concentrations for an anaerobic lagoon. Similar determinations were made by Srinath and Loehr (43) with manure slurries and oxidation ditch mixed liquor. These wastes should have a lower ionic strength than sludge so that activity corrections might be unnecessary for the accuracy desired.

Hashimoto and Ludington (14) measured the dissociation constant for ammonia in a concentrated chicken manure



slurry. The values measured were approximately one sixth of the theoretical values. The solids concentration in this case was from 3.5 to 8.5 percent. It is not known whether the organic content was responsible for these results. It should be noted, however, that no correction was made for activity effects and that the experiments were run at high pH.

### Experiment II

The results of experiment II indicate that the pH does not vary widely in the first few hours after application of sludge. This is of importance for agronomic applications of sludge since it is during the first few hours after application that ammonia is most available for loss. After this the sludge should have infiltrated into the soil. It should be possible, therefore, to estimate a value of pH for use in calculating equilibrium concentrations.

The results also show that the increase in pH appears to be related to a loss of dissolved carbon dioxide. This is important for several reasons. Sludge handling techniques which minimize the loss of carbon dioxide are preferable since they will tend to minimize pH increases and the subsequent increases in volatile ammonia concentration. These techniques will also tend to minimize loss of ammonia since the mechanisms for loss of ammonia and carbon dioxide

are similar. The effect of good handling techniques then is especially important.

The high carbon dioxide concentration in sludge results from the conditions found within the digester. Similar conditions are not associated with lagoons or slurry storage tanks, however. The pH of these wastes should remain stable with time upon exposure to air. If the alkalinity of these wastes is low enough, a decrease in pH with ammonia concentration might be expected. Koelliker and Miner (22) found the pH of an anaerobic lagoon to be relatively stable throughout the year. The pH of a solution of an ammonium salt was seen to decrease regularly as ammonia was desorbed (43).

#### Mass Transfer Model for Ammonia Volatilization

Since the ammonia partial pressure can be determined, a mass transfer model can be used to describe losses due to volatilization. Mass transfer coefficients to describe field conditions for various wind velocities and temperatures were calculated from correlations given by Welty, et al. (48). An explanation of the development of these coefficients and tabulated results are given in Appendix VI.

A hypothetical case can now be examined to demonstrate the application of the results of this thesis. As an example, the sludge obtained for experiment I will be used. Initial properties of the sludge when it was obtained were

a temperature of 25°C, pH equal to 7.75, total alkalinity equal to 4920 mg/ℓ as CaCO<sub>3</sub>, total solids of 2.78 percent, and total ammonia nitrogen of 0.134 percent.

The total ammonical nitrogen concentration is calculated using expression (21)

$$(\text{TAN}_{(\text{aq})}) = \frac{(0.134)(1,000,000)}{100 - 2.78} = 1380 \text{ mg N/}\ell$$

The total alkalinity expressed in equivalents per liter is

$$\frac{(4920 \text{ mg CaCO}_3/\ell)}{(50,000 \text{ mg CaCO}_3/\text{eq})} = 0.0984 \text{ eq/}\ell$$

Since the anions present are assumed to be all singly charged, the concentration of anions is equal to the normality. The cations are assumed to be present half as plus one and half as plus two species. Two thirds of the cation charge will be due to the plus two species and one third to the plus one species. The cation concentrations are then calculated as

$$[\text{Cat}^+] = [\text{Cat}^{++}] = \frac{0.0984}{3} = 0.0328 \text{ moles/}\ell$$

The ionic strength can then be calculated

$$\begin{aligned} I &= 1/2[(0.0984)(1)^2 + (0.0328)(-1)^2 + (0.0328)(-2)^2] \\ &= 0.13 \text{ moles/}\ell \end{aligned}$$

From Table II-1 in Appendix II the activity coefficients

are obtained

$$\gamma_{\text{NH}_3} = 1.04 \quad \gamma_{\text{NH}_4} = 0.760 \quad \Gamma' = \frac{\gamma_{\text{NH}_3}}{\gamma_{\text{NH}_4^+}} = 1.37$$

For a temperature of 25°C the equilibrium constants listed in Table IV-1 in Appendix IV are

$$K_a = 5.63 \times 10^{-10} \text{ moles/l} \quad K_s = 7.88 \times 10^5 \text{ mg/l-atm}$$

For this example it will be assumed that liquid sludge will remain on the surface for four hours. A predicted increase in pH of one tenth of a unit over this period is reasonable. The average pH for the period would then be 7.80. Hydrogen ion activity is obtained directly from the pH

$$\{\text{H}_{(\text{aq})}^+\} = 10^{-7.80} = 1.58 \times 10^{-8} \text{ moles/l}$$

The equilibrium partial pressure of ammonia gas can then be calculated using expression (20)

$$\begin{aligned} P_{A,S} &= \frac{(1380 \text{ mgN/l})(1.04)}{7.88 \times 10^5 \text{ mgN/l-atm} \left[ 1 + \frac{(1.37)(1.58 \times 10^{-8} \text{ moles/l})}{(5.63 \times 10^{-10} \text{ moles/l})} \right]} \\ &= 4.62 \times 10^{-5} \text{ atm} \end{aligned}$$

Several values for ambient ammonia concentrations were given in the literature. Koelliker and Miner (22) measured an average value of  $1 \times 10^{-6}$  atm near an anaerobic lagoon. This was much higher than other values reported. Lauer, et

al. (24) measured an average of  $2.4 \times 10^{-8}$  atm above fields where manure was spread. Reddy, et al. (35) cited other values of  $1.4 \times 10^{-8}$  and  $5.0 \times 10^{-9}$  atm. For the case of sludge applications to land it will be assumed that the ambient concentration is negligible compared to the equilibrium partial pressure. The driving force then becomes equal to the equilibrium concentration.

For this example it will be assumed that one cm of this sludge is applied to a one hectare field. Assumed, also, is a wind velocity of six miles per hour and an air temperature of  $20^{\circ}\text{C}$ . From Appendix VI the mass transfer coefficient is obtained. This is  $29 \text{ kg/m}^2\text{-hr-atm}$ . The loss rate is then calculated from expression (1)

$$\begin{aligned} N_A &= (29 \text{ kgN/m}^2\text{-hr-atm}) (4.62 \times 10^{-5} \text{ atm}) \\ &= 1.3 \times 10^{-3} \text{ kgN/m}^2\text{-hr} \end{aligned}$$

The total expected loss can then be determined for the four hour period

$$L = (1.3 \times 10^{-3} \text{ kgN/m}^2\text{-hr}) (4\text{hr}) (10,000 \text{ m}^2) = 52 \text{ kg N}$$

If the specific gravity of the sludge is assumed to be equal to 1.00 the total ammonia nitrogen applied to the field can be calculated from the amount applied and percent ammonia nitrogen

$$\begin{aligned} A &= (10,000 \text{ m}^2) (0.01 \text{ m}) (1000 \text{ kg/m}^3) (0.00134 \text{ kgN/kg}) \\ &= 134 \text{ kg N} \end{aligned}$$

The percent of ammonia nitrogen lost is then calculated to be

$$\%L = \frac{52}{134} = 39\%$$

Since this loss is so significant the concentration of ammonia and, therefore, the driving force will decrease markedly during the four hour period. A more accurate approach would be to iterate losses over the four hour period. The loss during the first hour could be found and subtracted from the ammonia originally present to obtain a new concentration. This concentration could be used to predict losses for the second hour and so forth. For long periods it might be advisable to assign a new value of pH for each iteration.

An assumption in this example was that liquid sludge remained on the surface and available for loss for four hours. Even if liquid sludge was only on the surface for one hour, a loss of ten percent would have occurred. This example serves to illustrate how to calculate predicted losses and to show that ammonia volatilization from sludge can be very significant.

The results of this example compare well with results obtained by Beauchamp, et al. (4). In this case 60 percent of the ammonia in a 1.2 cm application of sludge to bare soil was volatilized. The loss occurred over six days, however. The peak flux measured was  $4.0 \times 10^{-4}$  kgN/m<sup>2</sup>-hr, roughly 30 percent of the flux calculated above. This flux was not measured, though, until over an hour after the sludge had been applied. In another field experiment

Stewart, et al. (44) measured 30 percent losses of ammonia from sludge applied to cornfields.

An average transfer coefficient calculated from the data of Lauer, et al. (24) for manure applied to a field is  $10 \text{ kgN/m}^2\text{-hr.}$  This is consistent with the values of transfer coefficient developed in this thesis. Koelliker and Miner (22) used mass transfer coefficients that were roughly one order of magnitude greater than those developed in this thesis to describe volatilization losses from an anaerobic lagoon. The expression for mass transfer coefficient they used, however, was developed from ammonia absorption measurements in a counter-current wetted wall column. Such apparatus would be expected to have greater transfer efficiency and, therefore, higher transfer coefficients than a lagoon surface. The application of such an expression to losses from a lagoon is questionable.

Examination of the mass transfer model to see what factors influence losses reveals that these factors must exert an influence on either the transfer coefficient, the concentration, or both. Examination of the transfer coefficients developed for this thesis shows that they tend to increase as wind velocity increases and decrease as air temperature increases. Theoretical considerations show that the mass transfer coefficient for a flat plate under turbulent conditions will be proportional to the gas velocity to the 0.8 power and the absolute temperature to the -0.7 power.

For a given amount of total ammonical nitrogen in solution the ammonia concentration can only be changed two ways. The equilibrium can be shifted by addition or removal of an acid or base or the equilibrium constant can change. The first phenomenon occurs when carbon dioxide is lost from the sludge. It should be governed by the same factors that govern ammonia loss. Chemical interactions with the soil will not be considered. Observation of the equilibrium constants reveals that their values are dependent upon temperature. The dissolution of ammonia is exothermic. Therefore, as the temperature increases at constant ammonia concentration the partial pressure will increase. The dissociation of ammonium is endothermic so an increase in temperature will cause an increase in the ammonia concentration. Both of these effects tend to increase the equilibrium partial pressure as temperature increases, and the combined effect is very significant. For example, increasing the temperature of a sample of sludge at a pH of 7.5 from 20°C to 25°C will increase the equilibrium partial pressure by about 80 percent. A five degree increase in air temperature will only decrease the transfer coefficient by about one percent. This should also illustrate the importance of accurately knowing the temperature of the sludge after application. Temperature control may also be an important management tool for reducing losses.



These considerations imply that sludge temperatures and wind velocity are the most important factors influencing loss. This is in agreement with many laboratory and field studies. Increased air flow or wind velocity was seen to increase losses in both laboratory (8, 15, 32, 43, 45) and field (9, 22, 32) investigations. Increased temperature was seen to cause increased losses in laboratory (26, 32, 43) and field (4, 32) experiments also.

Many other factors were mentioned in the literature as influencing ammonia losses in a variety of cases. These included soil texture, incorporation of nitrogen in the soil, vegetation, soil pH, soil moisture content, relative humidity of the air, clay content of the soil, cation exchange capacity of the soil, and application rates. It should be possible to explain the effects of all of these factors in terms of their effect on concentration and transfer coefficient, however.

## VI. CONCLUSIONS AND RECOMMENDATIONS

The goal of this thesis was to obtain information needed to apply a mass transfer model to quantitatively predict volatile losses of ammonia from surface applied sewage sludge. The results obtained allow conclusions to be drawn concerning not only sewage sludge but other nitrogen containing wastes as well.

The results show that theoretical equilibrium constants obtained from thermodynamic data are applicable for use with sewage sludge. Corrections must be made for activity effects due to ionic strength. The concentration of organic matter, however, does not exert an effect on the equilibrium. Therefore, use of the constants should be valid with other organic wastes having similar characteristics such as anaerobic lagoon liquor, dilute manure slurries, oxidation pond effluent, and so forth.

The pH was seen to increase upon exposure of sludge to the air, but not dramatically. Therefore an estimation of the pH of the sludge during the critical period after application can be made to predict losses. More importantly, this pH rise was seen to be related to a loss of dissolved carbon dioxide. Similar behavior of pH upon application should not occur for wastes lacking the high dissolved carbon dioxide concentration of sludge.

Calculations of expected loss are possible given the initial characteristics of sludge or other similar wastes. Calculations using typical values show that volatilization losses from sludge can be very significant. It was also concluded that the ambient ammonia concentration is negligible compared to the concentration of ammonia above the sludge.

Of all environmental factors examined, temperature of the sludge exerts the greatest effect on losses. Many factors have been investigated in the literature as to their effects on ammonia loss. The effect of any factor on loss should be explainable in terms of its effect on ammonia concentration and mass transfer coefficient.

Recommendations for further study are made with reference to the final conclusion drawn, namely the influence of various factors on concentration and transfer coefficient. The model as it exists now applies to losses from flat liquid surfaces under turbulent conditions. Since many cases of serious ammonia loss have been reported for other cases it would be desirable to be able to apply the model to these cases. The main area of concern involves interactions with the soil. Losses have been reported for sludge after infiltration into the soil. Likewise, losses have been reported for other ammonia sources applied to the soil, including commercial fertilizers. If one area should

be investigated it would be the area of obtaining concentrations to describe ammonia in contact with the soil.

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## APPENDICES

## APPENDIX I

Development of a Technique for Determining  
Gaseous Ammonia Concentration

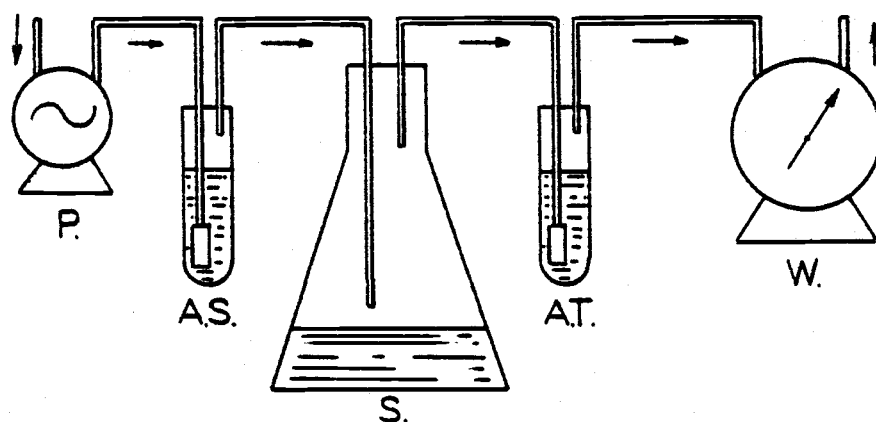
Identifying a direct and effective method of measuring the gaseous concentration of ammonia over a liquid sample proved to be very difficult. Much of this difficulty was apparently due to the low concentrations and small samples involved in this study. Common methods of measuring gaseous ammonia concentrations all involve removing ammonia from air with an acid trap. The most common trap described in the literature consists of a vertical gas dispersion tube with a fritted cylinder immersed in acid. The air sample is diffused through the porous glass with the ammonia remaining in the acid as ammonium ion.

The first method attempted utilized such a trap. Three hundred ml liquid samples were placed in a 1000 ml Erlenmeyer flask. Air was bubbled through 5  $\text{NH}_2\text{SO}_4$  to remove ammonia present in the atmosphere that might cause contamination. This ammonia-free air was then pumped into the sample flask where it mixed with the gas already in the flask. The resulting mixture flowed out of the flask and into the trap, which contained 25 ml 0.1 percent  $\text{H}_2\text{SO}_4$ . Gas and liquid temperatures as well as the pH of the liquid were recorded immediately after sampling. A Neptune

Dyna-Pump having a flow rate of approximately 1500 ml/min was used to pump the air. All connections were made with vinyl tubing. A schematic of the apparatus is shown in Figure I-1.

This approach assumes that the gaseous ammonia concentration inside the sample flask is at all times in equilibrium with the dissolved ammonia concentration in the liquid sample. This assumption requires a sufficiently long residence time for the air in the sample flask and rapid kinetics of gas transfer from the liquid to gas phase. The residence time in this case was approximately 30 seconds. Air entering the flask was directed onto the surface of the liquid to cause turbulence and increased gas transfer. For these reasons, equilibrium was assumed between the gas and liquid phases. Since equilibrium implies a constant gas concentration, the sampling time could be calculated from the flow rate of the pump and the volume of gas needed to give a detectable concentration of ammonia in the trap. Pump flow rates were checked using a Precision Scientific wet test meter.

Since reagents and apparatus were already available to analyze for ammonia by direct Nesslerization, this technique was used to measure the concentration of ammonia in the trap. The procedure used was that given in Standard Methods for the Examination of Water and Wastewater (2) except that reagent and sample volumes were halved and no



P.= PUMP  
 A.S.=AMMONIA SCRUBBER  
 S.= SAMPLE  
 A.T.= AMMONIA TRAP  
 W. = WET TEST METER  
 D.F.=DISPLACEMENT FLASK & COLLECTOR

Figure I-1. First gas sample collection apparatus tested.

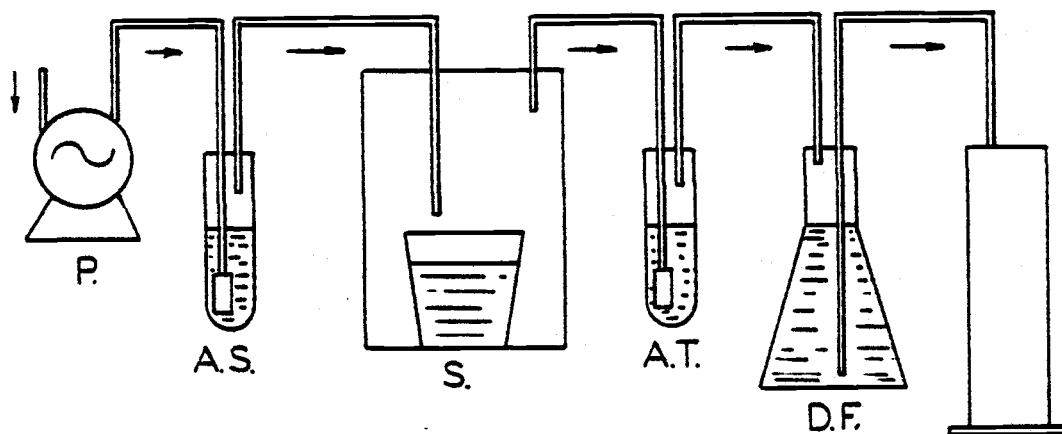


Figure I-2. Second gas sample collection apparatus tested.

pre-treatment was made for the removal of interferences. Analysis was done using a Coleman Jr. II A spectrophotometer. Past experience with this analytical technique and equipment indicated that concentrations from 0.4 to 1.1 mg/l as N could be measured. Gas sample volumes sufficient to give concentrations in the trap of approximately 0.5 mg/l as N were taken.

Multiplication of the trap concentration by the trap volume gives the amount of ammonia trapped. Division of this by the product of sample flow rate and sampling time yields the average gaseous concentration of ammonia in the sample flask. From the gaseous concentration and temperature the equilibrium partial pressure is calculated using the Universal Gas Law. The equilibrium partial pressure is then divided into the liquid concentration of ammonia to give the solubility constant for that temperature.

Initial trials using sludge as the liquid sample yielded results that were erratic as well as roughly one order of magnitude below values expected from thermodynamic data. At this time it was decided to modify the apparatus so that samples consisting of sludge applied to soil could be used if desired. This involved replacing the 1000 ml flask with a one quart wide-mouth Mason jar. Seventy ml liquid samples were placed in a 100 ml polyethylene beaker and sealed in the jar. As with the previous arrangement, air entering the jar was directed onto the surface of the

sample to promote rapid transfer. A schematic of this apparatus is shown in Figure I-2.

The combination of desired sample volumes and pump rate resulted in short sampling times which may have been a source of error. For this reason it was decided to reduce the flow rate using a brass needle valve on the pressure line leaving the pump. Sample volumes were measured by displacing water from a sealed flask with the gas coming out of the trap. It was also decided at this time to use a constant sample volume in all cases and dilute the traps before analysis if necessary.

Sludge samples were analyzed using this new apparatus. The pumping rate was reduced to about 150 ml/min and sample volumes of 500 and 2000 ml were used. Results were very erratic with almost one order of magnitude difference occurring between replicates.

To check the system standard ammonium chloride solutions of 10, 100, and 1000 mg/l as N were used as liquid samples. These samples were at a pH of at least 11 and their ionic strengths were adjusted with potassium chloride so that all were equal. Gas samples of 5000 ml were taken using flow rates in the neighborhood of 250 ml/min. Results were still low and erratic.

The low results were thought to be occurring because equilibrium conditions were not present inside the jar. It was decided to further reduce the flow rate to see if this

had an effect. Uniform flow rates below 100 ml/min were not possible with the pump and valve being used. For this reason the pump was replaced with a siphon which would draw air through the system. Flow was regulated by controlling the water flow out of the siphon reservoir. This flow was measured with a rotameter. As long as constant pressure was maintained in the sample jar the gas flow through the system was assumed to be equal to the liquid flow in the siphon. This was checked by attaching a U-tube manometer to the sample jar. Figure I-3 shows a schematic of this system.

Standard solutions were analyzed using this apparatus with flow rates of 25 ml/min and sample volumes from 2500 to 4500 ml. The results obtained were still erratic and many of the trap concentrations were too low to determine by direct Nesslerization. The high standard concentration gave better results than the low ones, but all were too varied to be of use.

It was felt that perhaps equilibrium conditions were still not being maintained in the jar. To promote transfer out of the liquid phase a magnetic stirring bar was placed in the liquid sample. As an alternative, a Neptune Dyna-Pump was attached to the jar to recirculate the contents of the jar and cause surface turbulence. Neither of these measures resulted in improved results. In addition, blanks run between samples indicated that contamination of



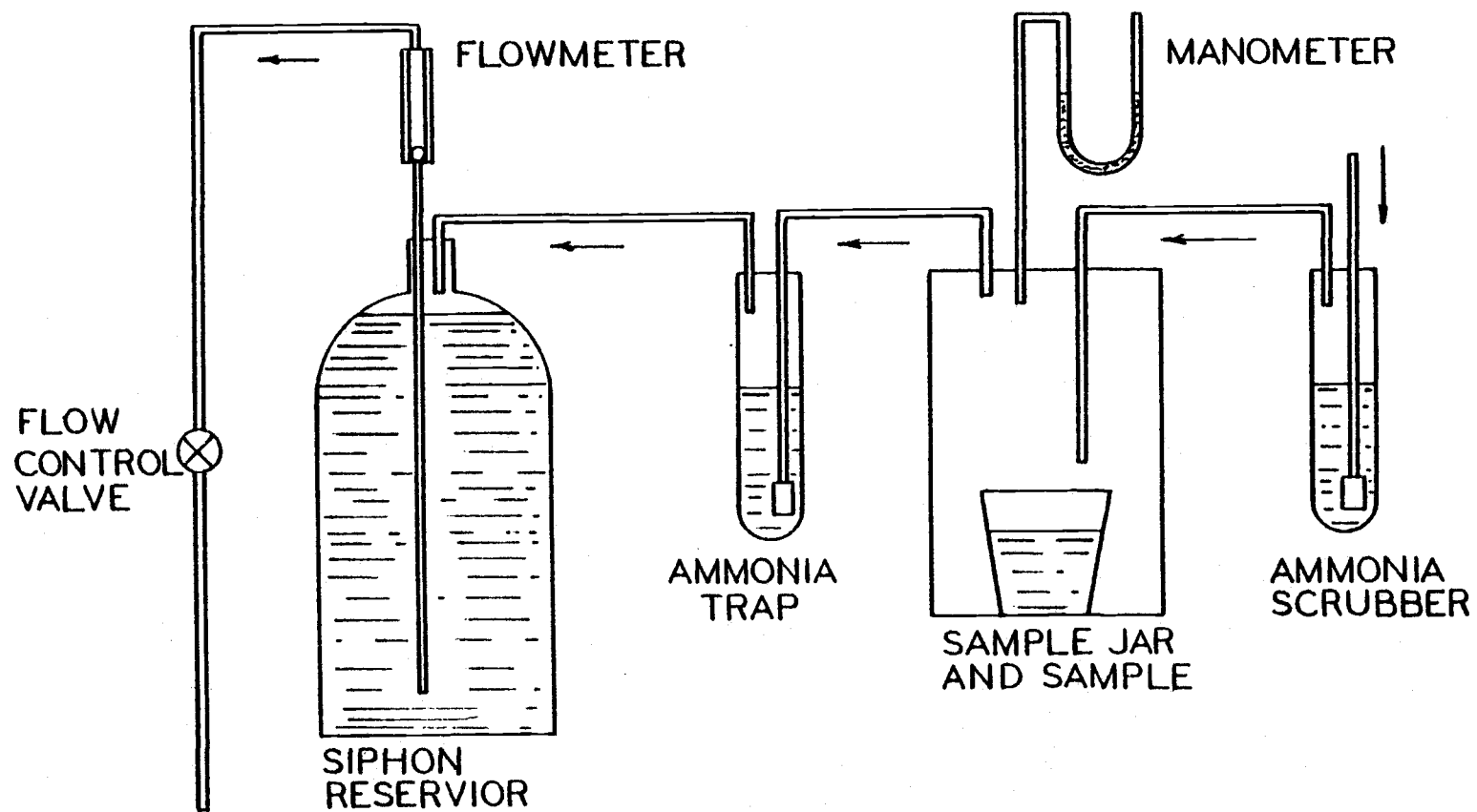


Figure I-3. Third gas sample collection apparatus tested.

the traps was occurring somehow. There was no consistency to the blank concentrations, however, that might indicate a systematic error.

Because of these difficulties, it was decided to abandon the liquid traps in favor of acid-impregnated filter traps. Filters were impregnated with three percent ethanolic oxalic acid as described by Shendrikar and Lodge (40). Because a ring oven was not available to analyze the filters an alternative had to be devised. This was to wash the filters in ammonia-free distilled water and measure the resulting liquid for ammonia. So that lower concentrations of ammonia could be analyzed, direct Nesslerization was abandoned in favor of the more sensitive phenate method. The phenate method was shown to be capable of measuring ammonia concentrations of 0.05 to 0.50 mg/l as N. The procedure used was the same as that given in Standard Methods (2) except that all samples and reagent volumes were doubled. Also, the reagents were found to be very unstable and so were prepared daily instead of weekly.

This method was tested by applying a known amount of standard ammonia solution to filters, drying the filters, and then checking if the ammonia could be recovered and measured. Poor results were obtained at first because the filters tended to disintegrate during washing. The resulting fibers in the wash liquid interfered with colorimetric

analysis. To alleviate this, a new procedure was devised where the filter and wash water were steam distilled. The resulting distillate was then analyzed using the phenate method. To avoid the acidity interference associated with the phenate method, the distillate had to be collected in 0.001 N  $\text{H}_2\text{SO}_4$ . Approximately 15 ml of distillate were collected in 10 ml of acid. The volume of the resulting solution was determined by subtracting the empty weight of the collection beaker from the final weight of the beaker, acid, and distillate and assuming a specific gravity of 1.00. This volume multiplied by the ammonia concentration gives the amount of ammonia recovered. Figure I-4 shows the results of the distillation technique used directly with known amounts of standard solutions. These results show that the method is capable of recovering ammonia in the microgram range.

Next the technique was tested using known amounts of standard solution applied to filters. Because of difficulties in handling the rather fragile glass fiber filters, they were replaced with Staplex air sampling filters. Results of distillation of these filters with known amounts of ammonia are shown in Figure I-5. From these results it was concluded that ammonia in the microgram range trapped on filters could be recovered by distillation.

The sampling equipment was then modified so that the acid impregnated filters could be used as ammonia traps.

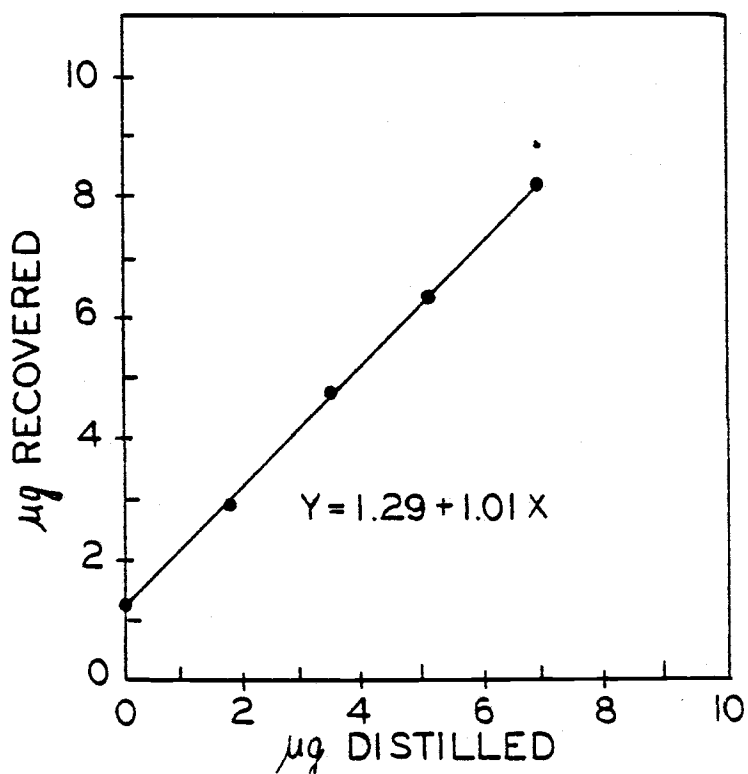


Figure I-4. Results of distillation of known amounts of ammonia standard.

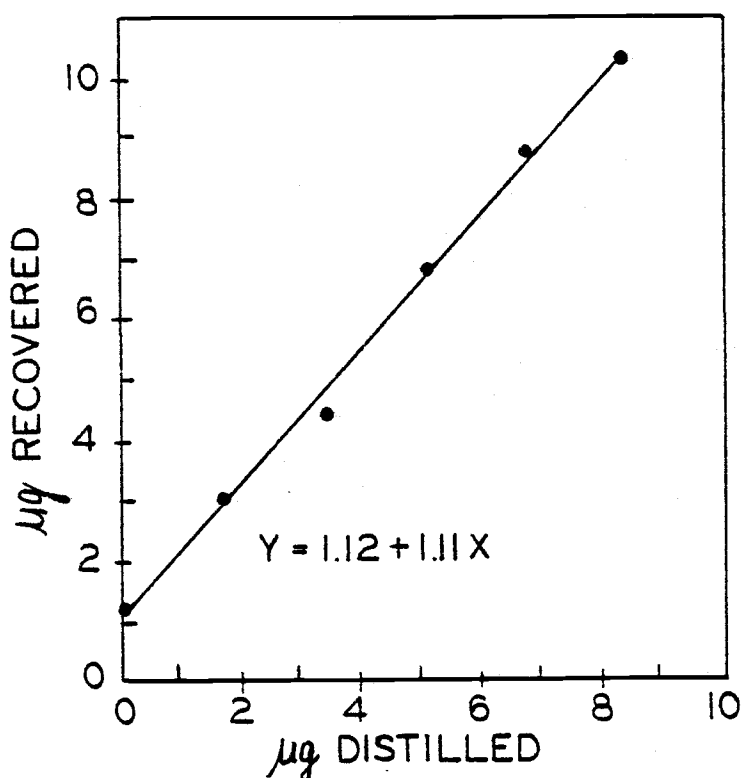


Figure I-5. Results of distillation of filters containing known amounts of ammonia standard.

Provisions were made so that samples could either be drawn directly from the sample jar or removed from the sample jar with a syringe and injected into the line ahead of the filter holder. A schematic of this apparatus is shown in Figure I-6. At this time also, all vinyl tubing carrying gas samples was replaced by teflon to prevent possible absorption of ammonia by the vinyl.

Numerous trials were made collecting samples of gas above standard solutions. Variations were made in sampling time, flow rate, ammonia flux through the filters, and ammonia concentrations. In no case could it be shown that any ammonia was being trapped on the filters. The apparatus was tested repeatedly to insure that there were no leaks in the system and that the samples were being directed through the filters.

Due to the many unexplainable difficulties encountered in collecting gas samples it was decided to review the fundamental assumptions made in designing the procedures. Of these, the most important concerned the kinetics of mass transfer of ammonia from the liquid sample into the atmosphere inside the jar. It had been assumed that the transfer was rapid enough to insure essentially equilibrium conditions several minutes after the sample was sealed inside the jar. Further, it was assumed that operation of the recirculation pump would maintain equilibrium conditions inside the jar during sampling. These assumptions

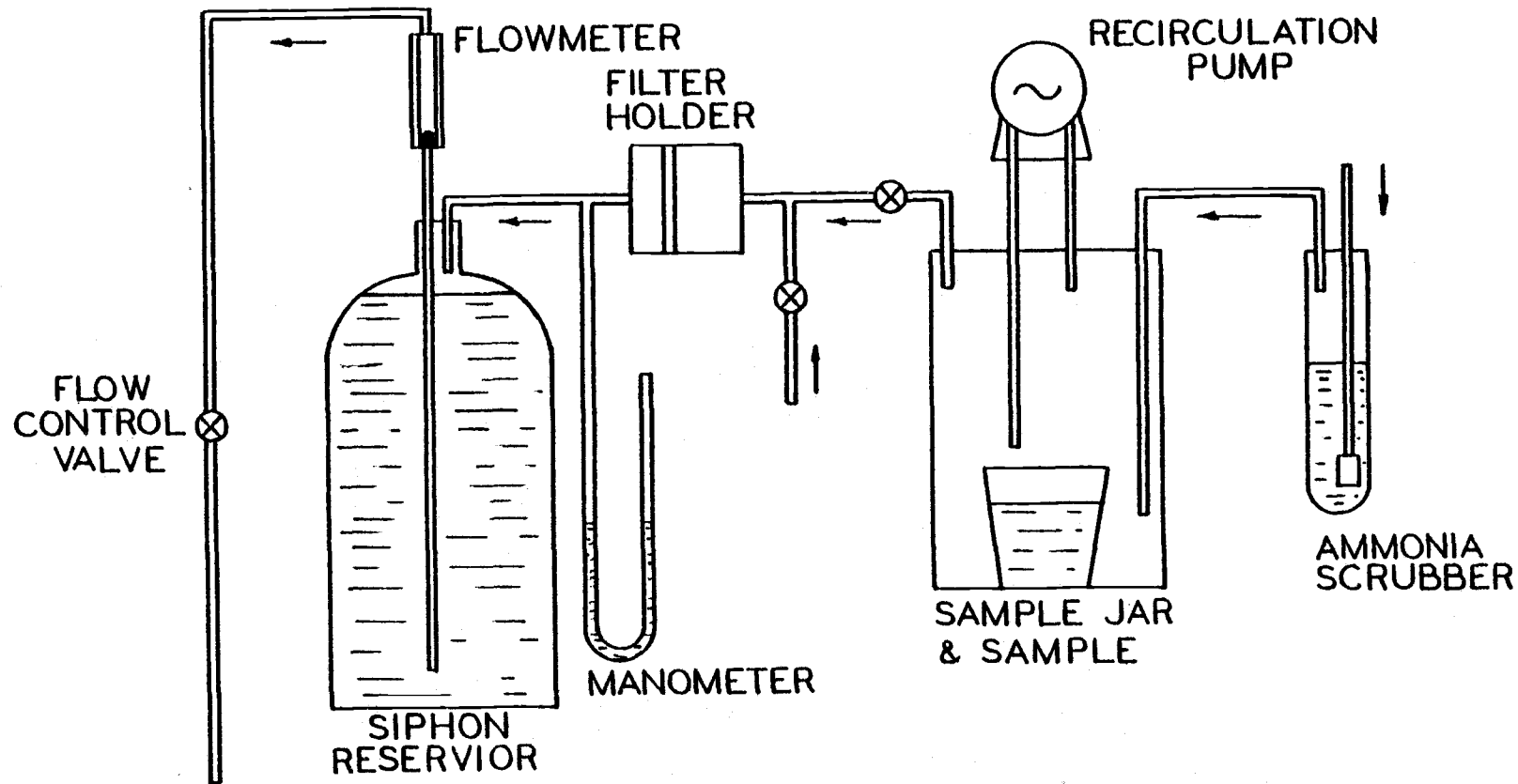


Figure I-6. Fourth gas sample collection apparatus tested.

had been made because of the difficulty in determining an appropriate mass transfer coefficient to describe conditions inside the jar. In light of the poor results that had been obtained with the equipment, however, an investigation of the mass transfer kinetics was undertaken. It was hoped that an approximate mass transfer coefficient could be obtained and that this could be used to make an order of magnitude check on the assumed kinetics.

Mass transfer correlations are given in Welty, et al. (48) for flow inside pipes and flow of gases parallel to flat plates. It was assumed that the value of a mass transfer coefficient describing conditions inside the sample jar would be between the values for the two above cases (49). The pipe flow and plate flow situations would be expected to yield conservative and liberal estimations, respectively. From the published data and knowledge of approximate conditions inside the sample vessel the two transfer coefficients were calculated. These coefficients are 0.00089 cm/sec for the pipe flow case and 0.0044 cm/sec for the parallel plate flow case.

Using these coefficients and Fick's second law values of the ratio of actual to equilibrium concentration,  $C_{A,B}/C_{A,S}$ , were obtained for various values of time. Since it is extremely difficult to explicitly solve for concentration as a function of time for the unsteady case with

Fick's Law, an iterative solution was used. Results are shown in Figure I-7.

These results show the kinetics of mass transfer to be far slower than originally assumed. The time required to reach a gas concentration inside the jar of 95 percent of the equilibrium value should be from 20 to 40 hours. Initially, only 10 to 30 minutes had been given. This is enough time to reach roughly only 10 percent of the equilibrium concentration. From these results it was decided to run the recirculation pump about 36 hours before sampling. It was felt that this would result in a concentration within five percent of the equilibrium value.

With values for transfer coefficients it is possible to do a mass balance on ammonia for the sample jar and solve for the unsteady-state ammonia concentration in the jar during sampling. This allows calculation of the amount of ammonia actually removed for a given sample volume. Using filter traps it was originally planned to use sample volumes that would yield approximately five  $\mu\text{g}$  of ammonia. With the difficulties inherent in taking small samples out of the jar and because of the slow transfer kinetics it was decided to collect the entire contents of the jar. From the material balance it was found that essentially all the ammonia would be removed with a sample volume of 2600 ml. Allowing for non-idealities and other sources of error, the sample volume was set at 5000 ml.



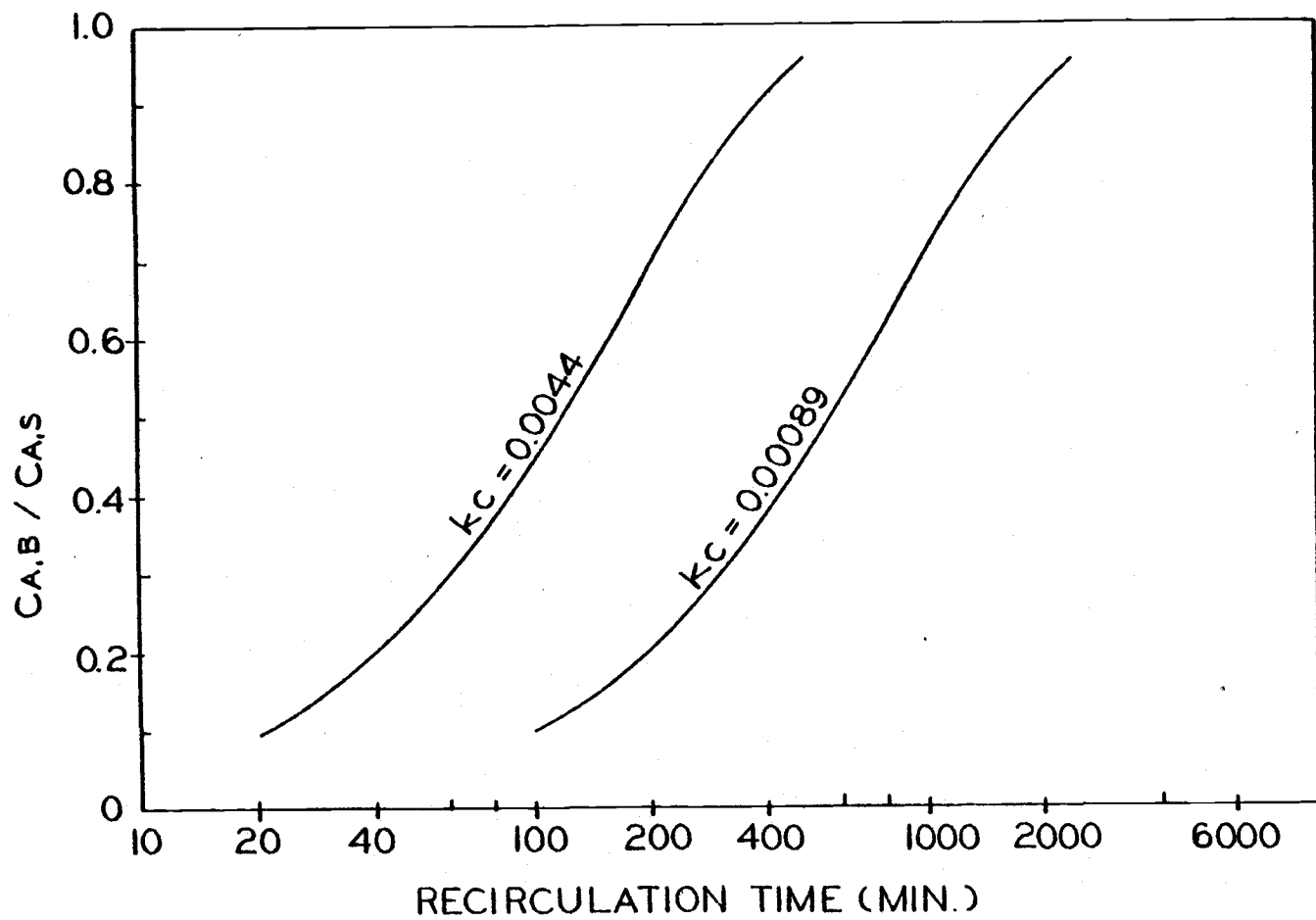


Figure I-7. Ratio of concentration of ammonia gas in sample jar to equilibrium concentration of ammonia gas versus recirculation time.

Filters could not be used for taking such large samples for several reasons. First, to collect such a large sample while maintaining a sufficiently low ammonia flux through the filter would require a very low sample flow rate. This would make the collection extremely time consuming. Secondly, large volumes of high concentration samples would probably exceed the capacity of the filters to trap ammonia. The filters had only been checked up to eight  $\mu\text{g}$  and amounts in the neighborhood of 1000  $\mu\text{g}$  were expected. Also, there is no way to "dilute" a filter trap when the sample exceeds analytical limits.

For the above reasons the gas impingers and liquid traps were again brought into use. The siphon was replaced with a rotary motor-mounted vacuum pump so that a sampling rate of 1000 ml/min could be obtained. Three traps were placed in series so that any inefficiencies in collection could be detected. Also, after each sample was collected the impingers were washed thoroughly in 0.1 N NaOH and ammonia-free distilled water to remove any traces of ammonia that might be present. A schematic of this apparatus is shown in Figure 1 in the Methods and Materials chapter of this thesis.

Standard solutions were run using this new procedure and equipment. After sealing the samples in the jar the recirculation pump was run for approximately 36 hours. Gas samples were collected by sampling at 1000 ml/min for

five minutes. Results with standard solutions were all higher than expected. The error appeared to be systematic, however, with the ratio of actual to expected amounts of ammonia decreasing as the liquid concentration increased. A least squares analysis showed a high degree of correlation between the ratio of actual to expected amounts of ammonia and the log of the liquid ammonia concentration. The linear regression parameters allow the actual concentration to be estimated from the measured concentration. Figure I-8 shows the results obtained with standard samples.

Results also show the impingers to be efficient in trapping ammonia when properly cleaned. At least 95 percent of the ammonia collected was found in the first trap. The high results may be due to too small a value of transfer coefficient being used in analyzing the unsteady-state concentration. However, it was felt that as long as a standard procedure was carried out, the regression parameters obtained from the standard samples would apply to the sludge samples. A complete description of the standard sampling procedure is given in the Methods and Materials chapter of this thesis.

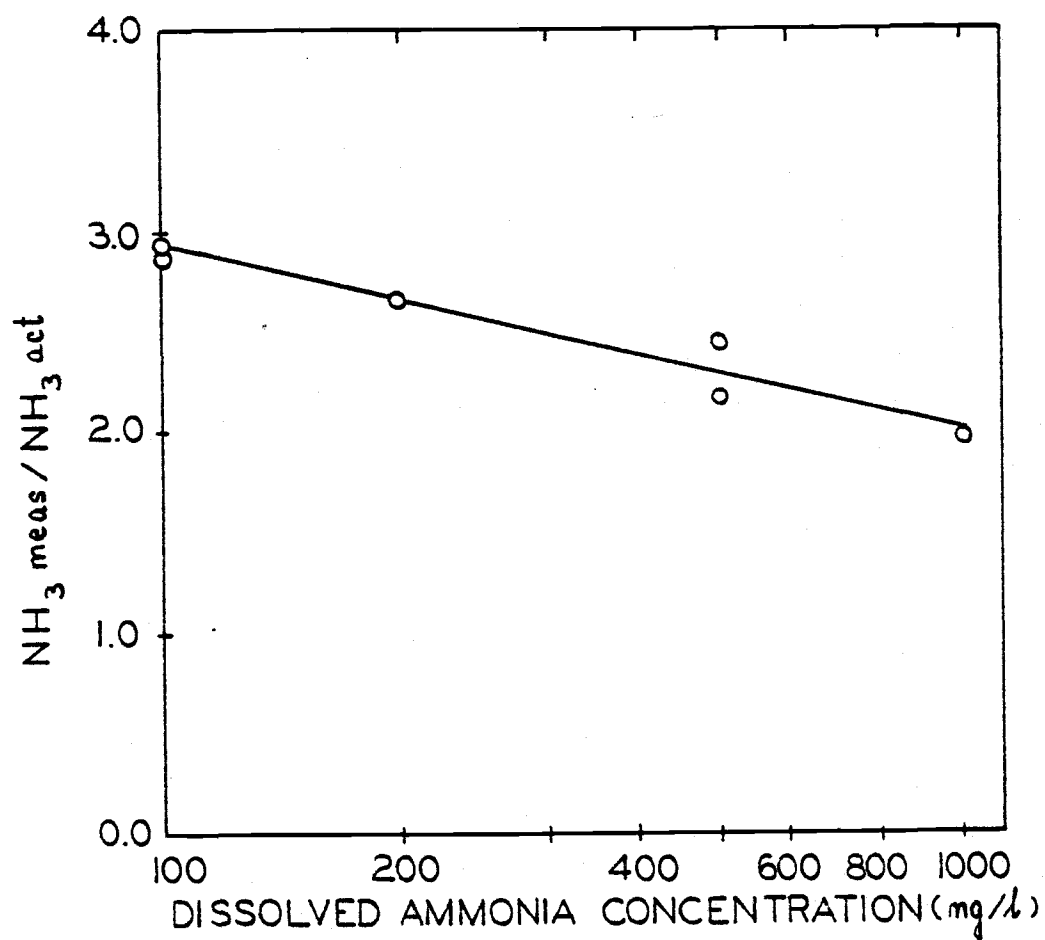


Figure I-8. Ratio of recovered to estimated theoretical amount of ammonia versus ammonia concentration.

## APPENDIX II

## Activity Coefficients for Equilibrium Expressions

The ionic strength of sludge was estimated based on alkalinity and pH. Butler (7) gives several expressions for calculating activity coefficients from ionic strength.

For charged species in solutions having ionic strengths of 0.01 molar to 0.10 molar the Guntelberg equation is recommended. For approximating activity coefficients in aqueous solutions the appropriate form of the Guntelberg expression is

$$-\log \gamma = 0.5 z^2 \frac{\sqrt{I}}{1+\sqrt{I}} \quad (\text{II-1})$$

where  $\gamma$  is the activity coefficient,  $z$  is the charge of the ion, and  $I$  is the ionic strength (moles/l).

For charged species in solutions having ionic strengths of 0.10 to 0.50 molar the empirical expression developed by Davies is suggested. To approximate activity coefficients in aqueous solutions the following form of the expression is used

$$-\log \gamma = 0.5 z^2 \left( \frac{\sqrt{I}}{1+\sqrt{I}} - 0.2 I \right) \quad (\text{II-2})$$

For charged species in solutions from 0.5 to 1.5 molar Butler (7) recommends that the Davies equation be used with

ionic strength set equal to 0.5 molar.

A single expression is given to approximate the activity coefficients of uncharged species in solutions having an ionic strength of less than 5.0 molar. This expression is

$$\log \gamma_0 = kI \quad (\text{II-3})$$

where  $k$  is a constant. In general, a value of  $k$  equal to 0.1 is suggested unless a specific value can be found for the species in question. For ammonia, a value of  $k = 0.12$  is given.

Activity coefficients for species of various charge over a range of ionic strengths were calculated using the above techniques. The values are given in Table II-1.

Table II-1. Activity coefficients for species of various charge for various ionic strengths.

I (moles/l)	$\gamma_0$	$\gamma_{\pm 1}$	$\gamma_{\pm 2}$	$\gamma_{\text{NH}_3}$
0.01	1.00	0.901	0.658	1.00
0.02	1.00	0.867	0.565	1.01
0.03	1.01	0.844	0.507	1.01
0.04	1.01	0.825	0.464	1.01
0.05	1.01	0.810	0.431	1.01
0.06	1.01	0.797	0.404	1.02
0.07	1.02	0.786	0.382	1.02
0.08	1.02	0.776	0.362	1.02
0.09	1.02	0.767	0.346	1.02
0.10	1.02	0.776	0.363	1.03
0.12	1.03	0.764	0.325	1.03
0.14	1.03	0.755	0.324	1.04
0.16	1.04	0.747	0.311	1.05
0.18	1.04	0.740	0.299	1.05
0.20	1.05	0.734	0.290	1.06
0.22	1.05	0.728	0.281	1.06
0.24	1.06	0.724	0.274	1.07
0.26	1.06	0.720	0.268	1.07
0.28	1.07	0.716	0.263	1.09
0.30	1.07	0.713	0.258	1.09
0.32	1.08	0.710	0.254	1.09
0.34	1.08	0.708	0.251	1.10
0.36	1.09	0.706	0.248	1.10
0.38	1.09	0.704	0.245	1.11
0.40	1.10	0.702	0.243	1.12
0.42	1.10	0.700	0.241	1.12
0.44	1.11	0.699	0.239	1.13
0.46	1.11	0.698	0.238	1.14
0.48	1.12	0.697	0.236	1.14
0.50	1.12	0.696	0.235	1.15

Table III-1. Data and calculated results of experiment I.

Sample No.	Date	Temp °C	pH	%TS	%TAN	(TAN(aq)) mg/ℓ	NH <sub>3</sub> meas μg	NH <sub>3</sub> act μg	I moles/ℓ
1-L	11-18-78	24.7	8.74	2.97	0.130	1340	482	193	0.14
1-H	11-18-78	23.0	10.61	4.02	0.115	1180	1760	908	0.64
2-L	11-20-78	21.0	9.08	3.13	0.137	1410	493	203	0.18
2-H	11-20-78	22.7	10.46	3.93	0.128	1320	1560	826	0.53
3-L	11-22-78	19.3	8.69	2.85	0.137	1410	186	69.7	0.12
3-H	11-22-78	21.0	10.67	3.68	0.115	1180	1020	525	0.50
4-L	11-29-78	22.0	8.65	3.91	0.133	1380	231	84.8	0.17
4-H	11-29-78	25.3	10.89	3.94	0.110	1140	1410	724	0.62
5-L	12- 1-78	19.0	8.62	3.61	0.145	1500	241	88.1	0.17
5-H	12- 1-78	23.0	10.81	5.06	0.109	1130	1640	840	1.07
6-L	12- 4-78	20.2	8.72	3.57	0.132	1370	327	123	0.17
6-H	12- 4-78	22.8	10.83	4.29	0.110	1140	1730	888	0.57
7-L	12- 6-78	15.7	8.43	4.44	0.163	1700	134	47.0	0.19
7-H	12- 6-78	17.6	10.12	4.96	0.151	1580	1230	677	0.52
8-L	12- 8-78	14.3	8.69	4.45	0.171	1780	188	68.8	0.21
8-H	12- 8-78	17.1	10.40	5.00	0.156	1630	1390	768	0.53
9-L	12-12-78	15.0	9.06	4.45	0.166	1740	253	97.9	0.21
9-H	12-12-78	17.6	10.85	5.03	0.153	1600	1340	737	0.67
10-L	12-14-78	15.2	8.78	5.29	0.163	1720	200	73.8	0.24
10-H	12-14-78	18.0	10.29	5.97	0.152	1600	1370	754	0.57
11-L	12-18-78	13.2	8.77	5.09	0.163	1720	197	73.0	0.24
11-H	12-18-78	15.6	10.16	5.56	0.155	1630	1310	723	0.42
12-L	12-20-78	14.8	8.77	5.11	0.166	1750	224	87.5	0.24
12-H	12-20-78	17.4	10.00	5.62	0.152	1600	1130	623	0.42



Table III-1 (continued)

Sample No.	$\gamma_{\text{NH}_3}$	$\gamma_{\text{NH}_4^+}$	$K_a \times 10^{10}$ moles/l	$K_s \times 10^{-5}$ mg/l-atm
1-L	1.04	0.755	6.74	7.63
1-H	1.19			7.75
2-L	1.05	0.740	3.85	9.06
2-H	1.16			9.30
3-L	1.03	0.764	4.22	14.1
3-H	1.15			13.0
4-L	1.05	0.744	4.19	10.1
4-H	1.19			9.32
5-L	1.05	0.744	3.97	9.54
5-H	1.34			9.04
6-L	1.05	0.744	4.30	8.17
6-H	1.17			7.53
7-L	1.06	0.737	3.98	13.7
7-H	1.15			13.7
8-L	1.06	0.732	2.91	12.7
8-H	1.16			12.6
9-L	1.06	0.732	1.93	12.9
9-H	1.20			13.3
10-L	1.07	0.724	2.66	12.6
10-H	1.17			12.7
11-L	1.07	0.724	2.82	13.2
11-H	1.12			13.0
12-L	1.07	0.724	4.08	15.4
12-H	1.12			14.7

## APPENDIX IV

Calculation of Theoretical  
Equilibrium Constants

Equilibrium constants can be calculated from thermodynamic data. The equilibrium constant,  $K$  of a reaction is related to the standard free energy change by

$$\Delta G^\circ = -RT \ln K \quad (\text{IV-1})$$

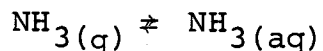
where  $\Delta G^\circ$  is the standard free energy change for the reaction (cal/mole),  $R$  is the universal gas constant which is equal to 1.99 cal/deg K-mole, and  $T$  is the absolute temperature in degrees Kelvin. This expression can be used to calculate the equilibrium constant at the standard temperature of 25°C.

If the standard enthalpy change of a reaction is assumed constant over the temperature range of interest the following expression can be used to calculate equilibrium constants at temperatures other than standard (39)

$$\ln\left(\frac{K_{T_2}}{K_{T_1}}\right) = \frac{-\Delta H^\circ}{R} \left(\frac{T_1 - T_2}{T_1 T_2}\right) \quad (\text{IV-2})$$

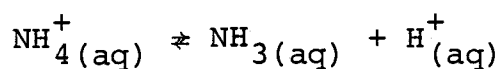
In the above expression,  $T_1$  refers to the standard temperature (deg K),  $T_2$  is the temperature of interest (deg K), and  $\Delta H^\circ$  is the standard enthalpy change for the reaction (cal/mole).

The reactions and standard free energy and enthalpy changes are given below (39).



$$\Delta G^\circ = -2390 \text{ cal/mole}$$

$$\Delta H^\circ = -8280 \text{ cal/mole}$$



$$\Delta G^\circ = 12,630 \text{ cal/mole}$$

$$\Delta H^\circ = 12,420 \text{ cal/mole}$$

The gas solubility constant calculated from the above data will have units of mole/l-atm. This is converted to mg/l-atm by multiplying by 14,000 mgN/mole. Equilibrium constants over the expected range of temperatures were calculated using the above technique and are given in Table IV-1.

Table IV-1. Theoretical equilibrium constants for ammonia dissociation and dissolution.

T°C	$K_a \times 10^{10}$ (mole/l)	$K_s \times 10^{-5}$ (mg/l-atm)
10	1.86	16.51
11	2.01	15.68
12	2.17	14.89
13	2.34	14.15
14	2.52	13.45
15	2.72	12.79
16	2.93	12.17
17	3.16	11.58
18	3.40	11.02
19	3.66	10.50
20	3.94	10.00
21	4.23	9.53
22	4.55	9.08
23	4.89	8.66
24	5.25	8.26
25	5.63	7.88
26	6.04	7.52
27	6.47	7.18
28	6.94	6.85
29	7.43	6.55
30	7.95	6.26
31	8.51	5.98
32	9.10	5.72
33	9.73	5.47
34	10.40	5.23
35	11.11	5.01

Table V-1. Data and calculated results of Experiment II.

Time hours	pH	Total alkalinity (mg/l as CaCO <sub>3</sub> )	Volatile acid alkalinity (mg/l as CaCO <sub>3</sub> )	log[H <sub>2</sub> CO <sub>3</sub> ]	log[HCO <sub>3</sub> <sup>-</sup> ]	log[CO <sub>3</sub> <sup>=</sup> ]
<u>Run 1</u>						
0	7.32	1600	120	-2.68	-1.53	-4.12
1.7	7.36	1620	120	-2.71	-1.52	-4.07
3.9	7.39	1610	120	-2.74	-1.53	-4.05
6.0	7.42	1600	120	-2.78	-1.53	-4.02
7.7	7.51	1590	120	-2.87	-1.53	-3.94
10.1	7.58	1580	120	-2.94	-1.53	-3.87
23.8	7.78	1520	120	-3.15	-1.55	-3.69
30.0	7.86	1480	120	-3.24	-1.57	-3.63
36.0	7.89	1440	120	-3.28	-1.58	-3.62
60.0	8.03	1320	140	-3.46	-1.63	-3.54
84.1	8.08	1200	120	-3.54	-1.67	-3.54
<u>Run 2</u>						
0	7.24	3880	260	-2.21	-1.14	-3.77
11.0	7.32	3690	250	-2.30	-1.16	-3.72
23.4	7.46	3590	250	-2.45	-1.18	-3.60
35.0	7.47	3470	260	-2.48	-1.19	-3.61
47.1	7.50	3380	270	-2.51	-1.21	-3.62
71.5	7.49	3220	270	-2.52	-1.23	-3.64
95.1	7.50	3040	280	-2.57	-1.26	-3.66
119.8	7.58	2940	280	-2.66	-1.27	-3.61
167.3	7.68	2640	280	-2.80	-1.33	-3.57
215.3	7.78	2440	300	-2.94	-1.37	-3.52

## APPENDIX VI

Development of Mass Transfer Coefficients  
for Field Conditions

Appropriate mass transfer coefficients were calculated from data presented in Fundamentals of Momentum, Heat, and Mass Transfer by Welty, Wilson, and Wicks (48). Presented in this work are results of mass transfer correlations for various cases. One of the cases analyzed is the flow of gases parallel to plates. This situation was thought to best describe the conditions expected in the field. Figure 30.1 in Welty, et al. (48) shows a plot of mass transfer  $j$  factor versus Reynolds number. These terms are defined, respectively as

$$j_D = \frac{k_{G^{P_{B, \ell m}}}(Sc)^{2/3}}{G_M} \quad (VI-1)$$

$$Re''' = \frac{\ell v \rho}{\mu} \quad (VI-2)$$

In the expression for  $j$  factor,  $k_G$  is the molar mass transfer coefficient (moles/hr-m<sup>2</sup>-atm),  $P_{B, \ell m}$  is the log mean partial pressure of the carrier gas (atm),  $Sc$  is the dimensionless Schmidt number, defined as the ratio of kinematic viscosity of the carrier gas to the diffusivity of the volatile component in the carrier gas, and  $G_M$  is the molar gas mass velocity of the carrier gas (moles/m<sup>2</sup>-

hr). In the expression for Reynolds number  $\ell$  is the characteristic length (m),  $v$  is the gas velocity (m/sec),  $\rho$  is the mass density of the gas ( $\text{kg/m}^3$ ), and  $\mu$  is the absolute viscosity of the gas ( $\text{kg/m-sec}$ ).

Conditions in the field are characterized by large distances, high velocities, and very low viscosities. The Reynolds number is expected to be very large. In other words, highly turbulent conditions exist. For this reason the exact value of the Reynolds number is not important. From Figure 30.1 in Welty, et al. (48) a  $j$  factor of 0.004 was chosen as being appropriate for high Reynolds numbers.

Rearranging expression (VI-1) results in

$$k_G = \frac{j_D G_M}{P_{B,\ell m} (Sc)^{2/3}} \quad (\text{VI-3})$$

The mass transfer coefficient of interest, however, is  $K_G$  having units of  $\text{kg/hr-m}^2\text{-atm}$ . Therefore  $k_G$  must be multiplied by the molecular weight of ammonia,  $MW_{\text{NH}_3}$ . The term  $G_M$  is defined as

$$G_M = \frac{\rho V_B}{MW} \quad (\text{VI-4})$$

where  $\rho$  is the mass density of the carrier gas, in this case air ( $\text{kg/m}^3$ ),  $V_B$  is the velocity of the carrier gas (m/hr) and  $MW$  is the molecular weight of the carrier gas ( $\text{kg/mole}$ ). The log mean partial pressure of the carrier

gas relates the partial pressure of the carrier gas in the bulk flow to the partial pressure of the carrier gas at the gas-liquid interface. In this case they are essentially the same and the value of  $P_{B,\ell m}$  becomes 1.00 atm. The Schmidt number is rewritten as

$$Sc = \frac{\nu}{D_{AB}} \quad (VI-5)$$

where  $\nu$  is the kinematic viscosity of air ( $m^2/sec$ ) and  $D_{AB}$  is the gas diffusivity of ammonia in air ( $m^2/sec$ ). The appropriate substitutions can be made to expression (VI-3) to obtain

$$K_G = \frac{(0.004) \rho_{air} V_{air}^{MW_{NH_3}}}{(1.00 \text{ atm}) \left( \frac{\nu_{AIR}}{D_{AB}} \right)^{2/3} MW_{air}} \quad (VI-6)$$

Appropriate values for the terms in expression (VI-6) were used to calculate mass transfer coefficients for various values of wind velocity and air temperature. These are given in Table VI-1.



Table VI-1. Mass transfer coefficients for field conditions ( $\text{kgN/m}^2\text{-hr-atm}$ ).

Air temperature (°C)	Wind velocity (mph)							
	2	4	6	8	10	12	15	20
0	10	21	32	42	53	63	79	105
5	10	21	31	41	53	62	77	103
10	10	20	30	40	50	60	75	100
15	10	20	30	39	49	59	74	99
20	10	19	29	39	48	58	72	97
25	9	19	28	38	47	57	71	95
30	9	19	28	37	46	56	70	93
35	9	18	27	36	45	55	68	91

## VITA

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In the fall of 1973, the author entered Oregon State University to study mechanical engineering. After two terms he elected to change his major to civil engineering because of a growing interest in the area of water resources. He received the degree Bachelor of Science in Civil Engineering in the spring of 1977. While an undergraduate, the author was elected to membership in Tau Beta Pi.

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