

AN ABSTRACT OF THE THESIS OF

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A conceptual model was developed to further the understanding of the evolution and fate of volatilized ammonia in the atmosphere. Recent trends in livestock rearing have been toward confinement facilities in which high animal concentrations are maintained. One of the impacts of these facilities has been increased local concentrations of ammonia in the atmosphere directly resulting from surface volatilization associated with the facility.

The various components of the model serve as sinks for the atmospheric ammonia and subsequently, under the right conditions, will also emit ammonia. Depending upon the degree of influence which each component will display, atmospheric ammonia can become a serious pollutant. The most significant of these potential pollution situations is the eutrophication of surface waters resulting from the direct absorption of atmospheric ammonia. Ammonia evolution

is also related to odor emission which is a major social concern relative to livestock production.

A knowledge of the system described by the model and the interaction of the system components serve as the basis in developing a pollution management philosophy. The environmental impact of a livestock facility upon surface water bodies can be predicted by estimating the potential ammonia absorption rate, and the impact can be lessened by modifying the other system components. This approach takes advantage of nature's assimilative capacity.

Fate of Ammonia Volatilized From a Confinement
Livestock Facility

by

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FATE OF AMMONIA VOLATILIZED FROM A CONFINEMENT LIVESTOCK FACILITY

I

Introduction

Recent trends in livestock production have been responsible for local increases in atmospheric concentration of barnyard related odors and gases. Particular interest has been centered upon ammonia which is a primary odor constituent. In addition to its odor properties, ammonia is subject to absorption by surface waters and a potential contributor to surface water eutrophication. This factor has raised a question concerning the fate of airborne ammonia.

Obviously, all of the ammonia released into the atmosphere does not remain there nor is it removed via a single mechanism. A system, which is believed to be responsible for the cycling of ammonia, was developed. A diagram of the major active components of the system is presented in Fig. 1. The reference point for the system is the surface volatilization of ammonia from the source. Sources will be restricted to manure covered surfaces and liquid manure storage pits related to livestock production facilities.

Once ammonia enters the atmosphere it interacts with a variety of system components. Some of these components are active in character and others are passive. The significant active components are folial absorption, soil

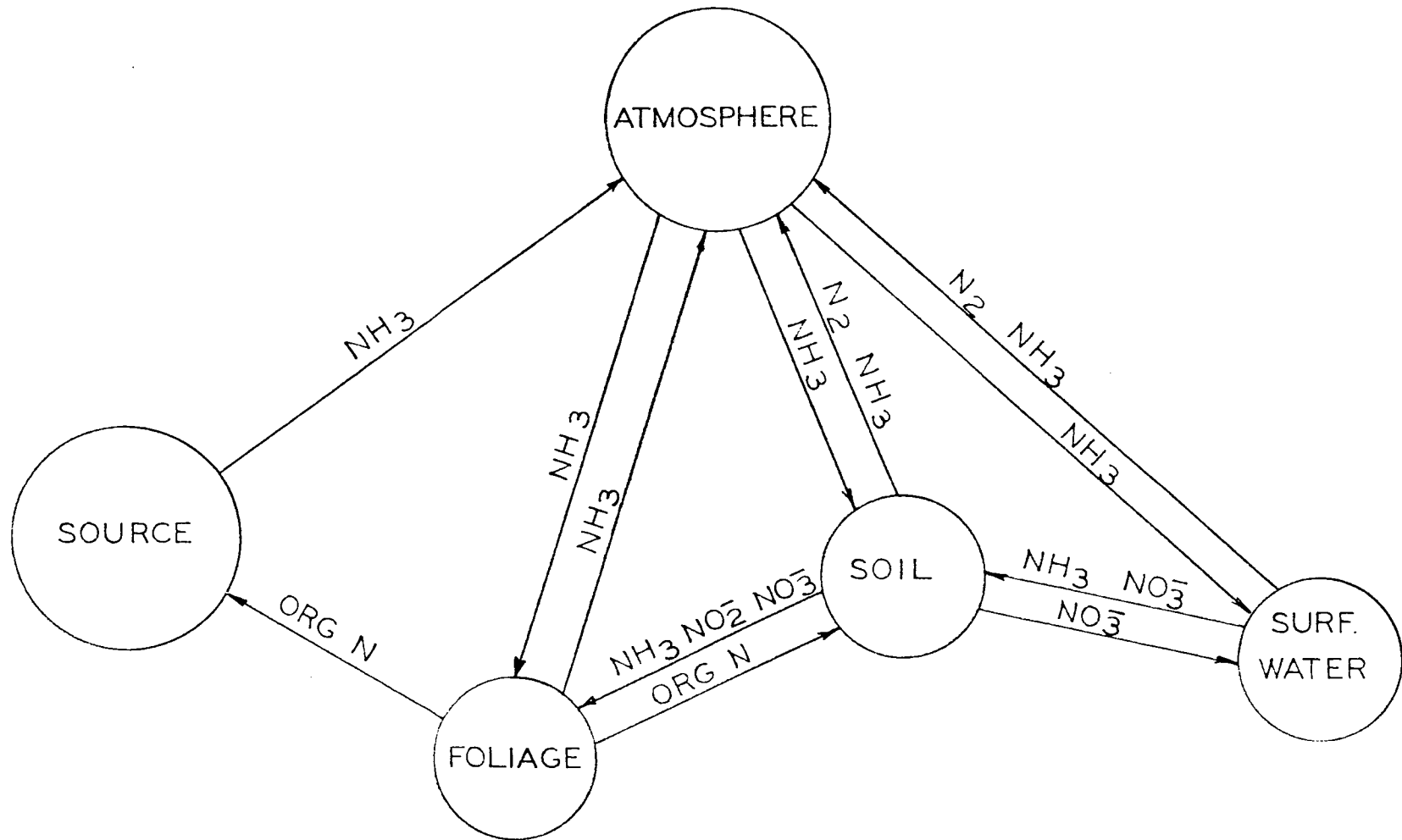


Fig. 1. Surface volatilized ammonia nitrogen system and the relationship between major system components.

absorption, and surface water absorption. These will be discussed in more detail in separate sections of the text. An example of a passive component would be ammonium particle fallout upon solid surfaces such as a concrete wall. The passive system components are not considered to play a significant role within the system.

II

SOURCE AND PRODUCTION OF ATMOSPHERIC $\text{NH}_3\text{-N}$

Bacterial decomposition of organic substances is a significant biological activity in our world. Living organisms require from 30 to 40 elements for normal development and, because there is only a finite supply of these elements, continuation of life requires recirculation. The total nitrogen cycle is a typical natural recirculation system. Bacteria play an important role in the nitrogen cycle (Sutton et al., 1973).

Most commercial livestock animals can be classified as herbivores in the food chain illustrated in Fig. 2. The wastes produced by this level of consumer are energy-rich but unusable by higher life forms. Decomposers are capable of utilizing this energy and in the process can reduce the compounds for reincorporation into the system. This chapter will be primarily concerned with the decomposition of animal waste and more specifically with the conversion of organic nitrogen into inorganic $\text{NH}_3\text{-N}$ and its subsequent volatilization into the atmosphere.

Bacterial Conversion of Organic-Nitrogen to Inorganic $\text{NH}_3\text{-N}$

Animal waste or manure includes fecal matter and urine. The composition of manure is highly variable due to the non-

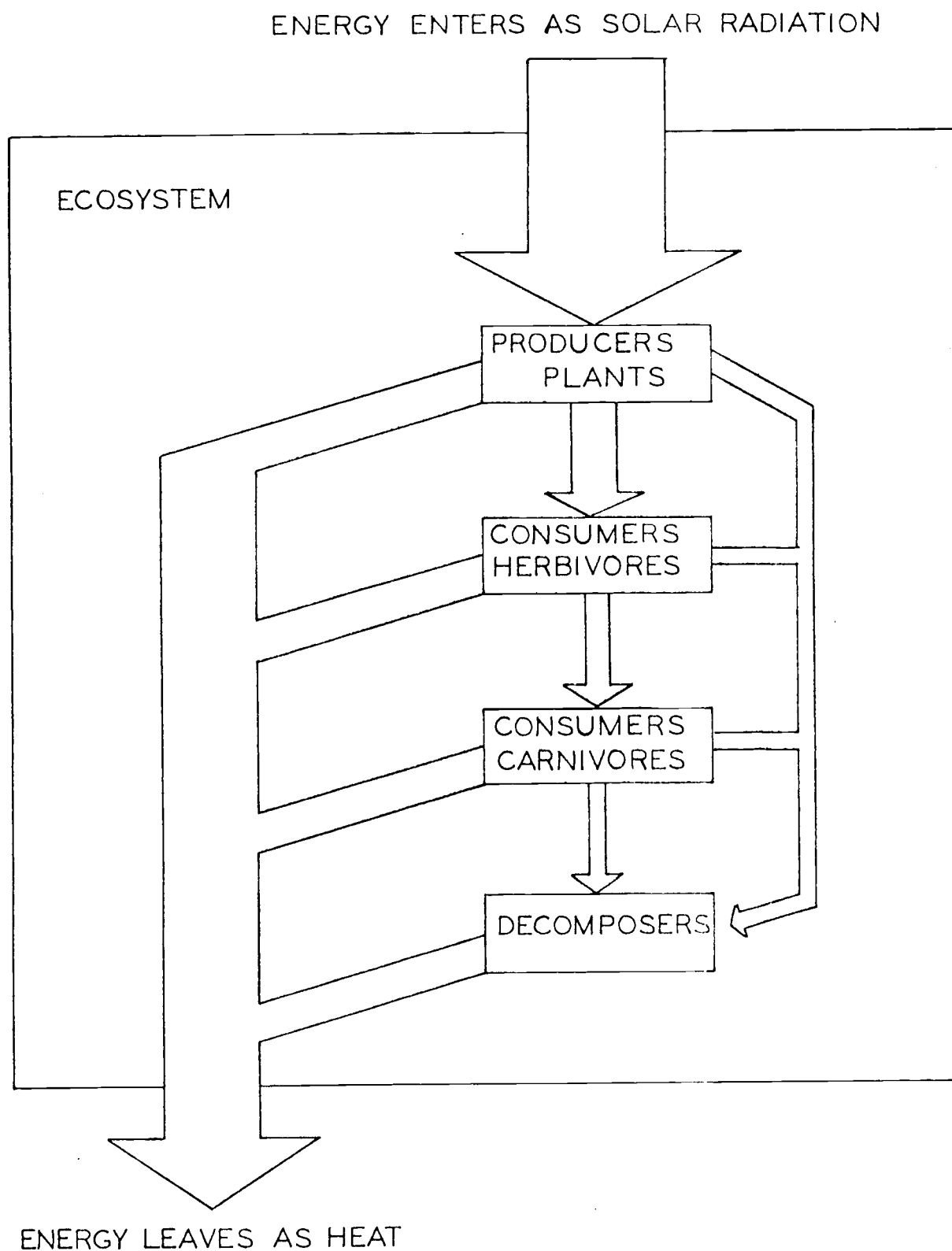


Fig. 2. Energy flow through an ecosystem -- a food chain (Sutton and Harmon, 1973).

uniformity in feeding and waste management practices. Some general chemical characteristics of manure from a variety of livestock animals are shown in Table 1. The data show that about 5% of the total solids in a typical manure is nitrogen. As much as 90% of the nitrogen in urea is readily converted into $\text{NH}_3\text{-N}$ (Stewart, 1970), and approximately 90% of the dry fecal matter is undigested organics of which 60 to 75% is biodegradable (McCalla et al., 1970). Chang and Johanson (1975) found that, in a ten week study period, up to 66% of the total nitrogen in a dairy animal waste was lost due to volatilization from an open feedlot surface.

Aerobic, anaerobic, and facultative microorganisms are all capable of decomposing organic-nitrogen compounds. In most cases though, the free $\text{NH}_3\text{-N}$ in decomposing animal waste can be attributed to anaerobic decomposition (Miner and Hazen, 1969). Organic-nitrogen in manure exists in two principle forms: proteins and uric acid. Two separate processes are involved in the breakdown of these compounds.

Proteins consist of long chains of amino acids linked together. Many bacteria are involved in the various steps of the breakdown process which is shown in Fig. 3. Fungi may play an important role in the initial breakdown of the protein to the peptide form since bacteria cannot easily attack pure proteins (Thimann, 1955). Uric acid is a purine and can be anaerobically broken down into ammonia, carbon

Parameter	Quantities	Dairy cow	Beef feeder	Swine feeder	Sheep feeder	Poultry		Horse
						layer	broiler	
Raw Manure (RM)	Wt./day	82	60	65	40	53	71	45
Feces:urine	Ratio	2.2	2.4	1.2	1.0	--	--	4.0
Total Solids	Wt./day	10.4	6.9	6.0	10.0	13.4	17.1	9.4
(TS)	% RM	12.7	11.6	9.2	25	25.2	25.2	20.9
Volatile Solids	Wt./day	8.6	5.9	4.8	8.5	9.4	12.0	7.5
(VS)	% TS	82.5	85	80	85	70	70	80
BOD ₅	Wt./day	1.7	1.6	2.0	0.9	3.5	--	--
	% TS	16.5	23	33	9.0	27	--	--
COD	Wt./day	9.1	6.6	5.7	11.8	12.0	--	--
	% TS	88	95	95	118	90	--	--
Nitrogen	Wt./day	0.41	0.34	0.45	0.45	0.72	1.16	0.27
(Total, as N)	% TS	3.9	4.9	7.5	4.5	5.4	6.8	2.9
Phosphorus	Wt./day	0.073	0.11	0.15	0.066	0.28	0.26	0.046
(as P)	% TS	0.7	1.6	2.5	0.66	2.1	1.5	0.49
Potassium	Wt./day	0.27	0.24	0.30	0.32	0.31	0.36	0.17
(as K)	% TS	2.6	3.6	4.9	3.2	2.3	2.1	1.8

Table 1. Manure production and characteristics of domesticated livestock per 1000 liveweight units (lb or kg).

Source: American Society of Agricultural Engineers, data adapted from Structures and Environment Committee 412 report AW-D-1, revised 14 June 1973.

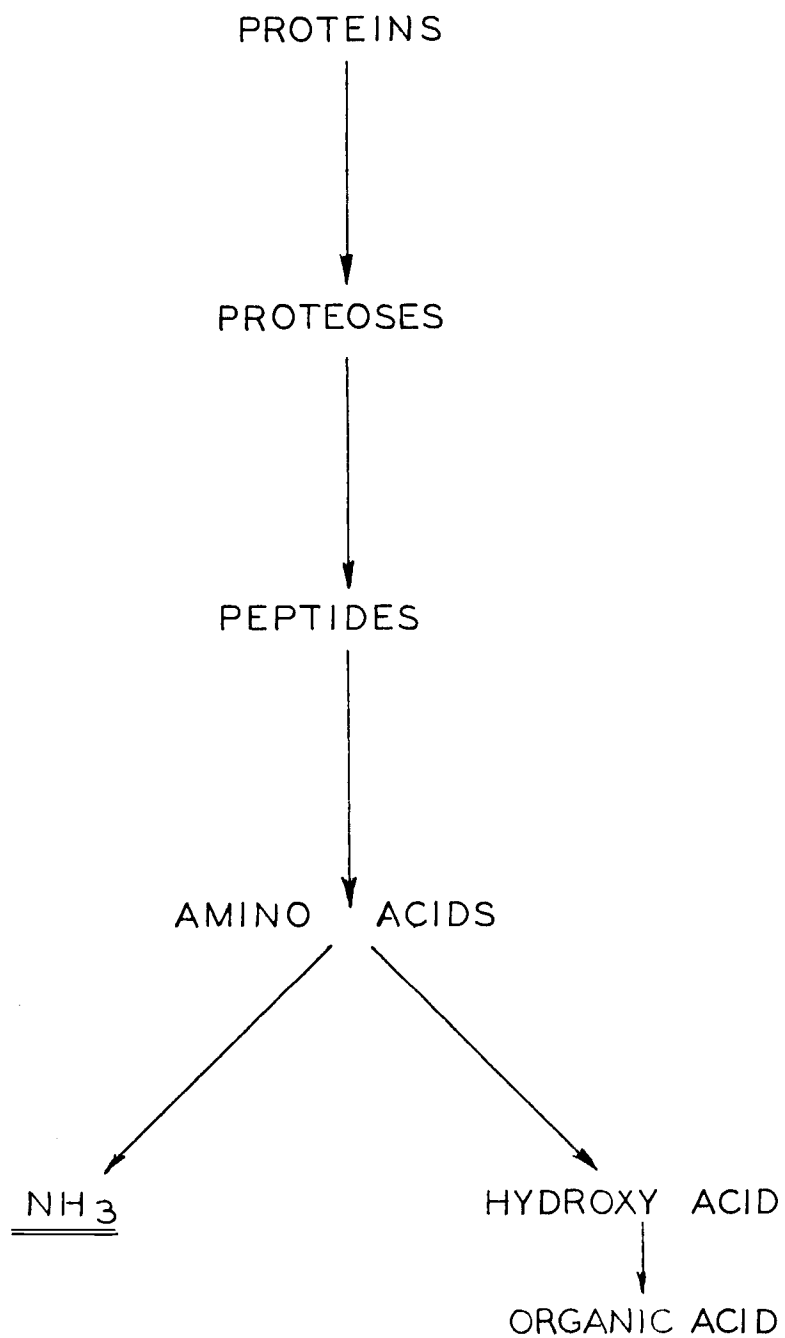


Fig. 3. The anaerobic breakdown process of proteins in animal manure (Miner et al., 1969).

dioxide, and acetic acid according to the process shown in Fig. 4. Anaerobic bacteria which produce the enzyme urease can perform this breakdown.

Volatization of Free $\text{NH}_3\text{-N}$ From Source

Once the decomposition process begins the $\text{NH}_3\text{-N}$ content of the manure begins to increase. Within a livestock confinement facility manure ranges from a suspended liquid slurry to a semi-dry form. Most facilities will have a variety of forms. Miner et al. (1975) found the highest NH_3 evolution rates to come from a manure-covered aisle in a freestall dairy barn ($50\text{-}100 \text{ mg/dy-m}^2$) and somewhat lower rates from an anaerobic hog manure lagoon surface ($20\text{-}40 \text{ mg/dy-m}^2$).

Anaerobic storage pits have been shown to be sources for atmospheric $\text{NH}_3\text{-N}$ in a swine building (Merkel, 1969). Koelliker et al. (1973) gave the following equation to describe the $\text{NH}_3\text{-N}$ desorption:

$$\frac{d(\text{NH}_3\text{-N})}{dt} = KA(P_l - P_g). \quad \text{Eq. 1}$$

In this equation $\text{NH}_3\text{-N}$ is the weight of $\text{NH}_3\text{-N}$ transferred (kg), t is the time (dys), A is the area of liquid-gas interface (m^2), K is the over-all transfer coefficient ($\text{kg/dy-m}^2 \text{ atm}$), P_l is the partial pressure of $\text{NH}_3\text{-N}$ in liquid (atm), and P_g is the partial pressure of $\text{NH}_3\text{-N}$ in air (atm). The mass transfer coefficient is defined by the equation

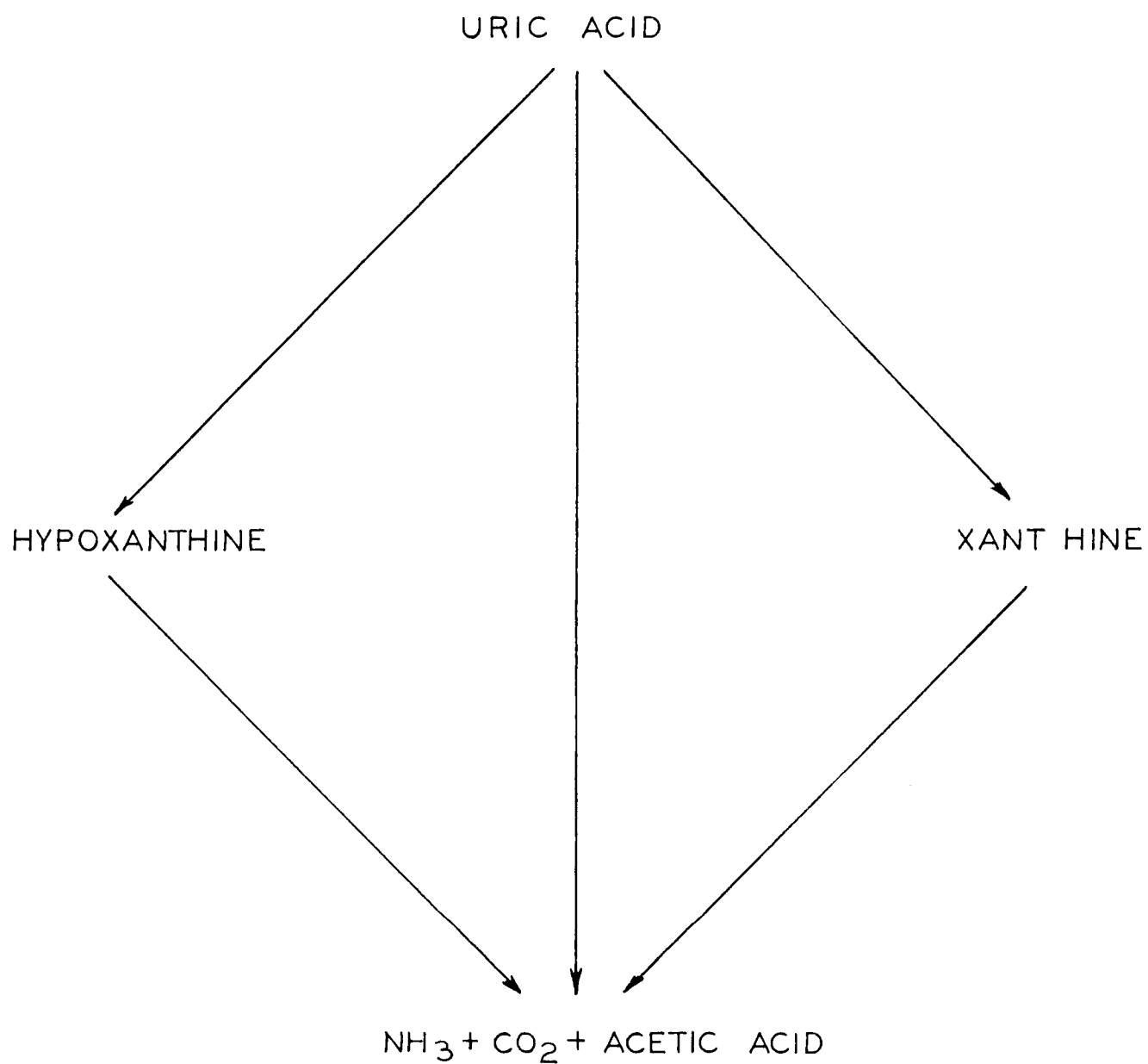


Fig. 4. The anaerobic breakdown process of uric acid in animal manure (Stephenson, 1949).

$$K = 3.3 \times 10^6 V^{0.8} T^{-1.4} \quad \text{Eq. 2}$$

Where V is the air velocity across the surface (ft/sec) and T is the ambient air temperature (deg K).

Manure stored in the semi-dry state is considered to be comprised of three layers: 1) the aerobic surface; 2) an anaerobic manure pack; and 3) a hard packed humified layer (Elliot et al., 1971). The hydrolysis of urea in the anaerobic portion produces $\text{NH}_3\text{-N}$ and raises the pH. Both of these factors will increase the NH_3 volatilization rate.

Influences Affecting the NH_3 Evolution

Bacterial activity is dependent upon the accessibility of water, necessary substrates and elements, and a suitable environment. Most manures are not limited with respect to necessary substrates and elements so that bacterial decomposition will occur (Alexander, 1971). The important step in NH_3 production at the source is not the bacterial decomposition, but the volatilization.

The moisture status of the manure has been proven to be very important. Manure maintained at higher moisture contents consistently displays higher NH_3 volatilization rates (Chang, 1975, Adriano et al., 1974). The highest evolution rates appear to occur, though, during periods of rapid drying (Hutchinson and Viets, 1969). Stewart (1970) found that

a dry soil dosed with urine every four days lost 90% of the total nitrogen added. When urine was added every two days to an initially wet soil, less than 25% of the total nitrogen was lost.

Another important factor influencing the volatilization rate is the pH. Ammonia must exist in the non-ionized (NH_3) form before it can become available for volatilization. As the pH of a manure increases the fraction of ammonia present as NH_3 will increase. At a temperature of 20°C and a pH of 7, about 0.4% of the ammonia exists as NH_3 . Whereas at pH 10 about 80% of the ammonia is in the volatile form (Miner, 1973).

A recent study in Michigan found that a manure maintained at 10°C and 60% moisture lost an average of 25% of its total nitrogen after 16 weeks of incubation (Adriano et al., 1974). When the temperature was increased to 25°C the loss increased to 40%. There is not enough information available, though, to fully establish the relationship between the temperature and evolution rate. The same study also showed that the rate of manure addition to a surface does not appreciably affect the percentage of NH_3 lost.

The effects of wind upon the evolution rate will depend upon the situation. Increases in wind will tend to decrease the liquid-gas film layer resistance. This is evidenced in Eq. 2; an increase in V will increase K . Wind will also increase the drying rate of manure which will increase the

evolution rate.

Summary and Conclusions

Bacteria play a very important role in manure decomposition, and the production of NH_3 is a by-product of this decomposition. Most manures have the necessary nutrients and conditions for high NH_3 production. Highest rates have been found under conditions of rapid surface drying and temperatures in the vicinity of 25°C . Usually a manure covered surface will show a higher evolution rate than liquid lagoon surface.

III

AMMONIA NITROGEN COMPOUNDS IN THE ATMOSPHERE

Atmospheric ammonia was reported as an air constituent in the early 1800's by De Saussure (Eriksson, 1952). One of the first attempts to measure the concentration was made by Schlessing (1875) who reported an average atmospheric concentration of 0.02 mg/m^3 . Later work, as cited by Eriksson (1952), shows a range of 0.007 to 0.087 mg/m^3 . In 1960 the average NH_3 content of New York City's atmosphere was found to be 0.028 mg/m^3 .

The primary source for atmospheric NH_3 is biological activity (Robinson and Robins, 1970) as is shown in Table 2. The importance of combustion processes is not as significant. Because the majority of the NH_3 is attributed to biological activity, the average global emission rate is usually assumed to remain relatively stable over a period of years (Junge, 1958). Local increases in NH_3 concentration, however, are significant. Beef cattle feedlots have been shown to produce local increases in atmospheric NH_3 concentrations (Hutchinson and Viets, 1969) and certain industries have also been reported as making significant contributions (Healy et al., 1970).

The data shown in Table 3 reveals that the bulk concentration of NH_3 is not nearly as high as predicted by an extrapolation of the emission rates shown in Table 2. This

Compound	Source	Source (tn/yr)	Estimated emissions (tn/yr)	Emissions as nitrogen (tn/yr)
NO ₂	Coal combustion	3,074 x 10 ⁶	26.9 x 10 ⁶	8.2 x 10 ⁶
	Petroleum refining	11,317 x 10 ⁶	0.7 x 10 ⁶	0.2 x 10 ⁶
	Gasoline combustion	379 x 10 ⁶	7.5 x 10 ⁶	2.3 x 10 ⁶
	Other oil combustion	894 x 10 ⁶	14.1 x 10 ⁶	4.3 x 10 ⁶
	Natural gas combustion	20.56 x 10 ⁶ (ft ³)	2.1 x 10 ⁶	0.6 x 10 ⁶
	Other combustion	1,290 x 10 ⁶	1.6 x 10 ⁶	0.5 x 10 ⁶
	Total		52.9 x 10 ⁶	16.1 x 10 ⁶
NH ₃	Combustion		4.2 x 10 ⁶	3.5 x 10 ⁶
NO	Biological action		501 x 10 ⁶	234 x 10 ⁶
NH ₃	Biological action		1,160 x 10 ⁶	957 x 10 ⁶
N ₂ O	Biological action		592 x 10 ⁶	378 x 10 ⁶

Table 2. Estimated annual global emissions of nitrogen compounds, (Robinson and Robbins, 1970).

Compound	Ambient Concentration	Atmospheric mass as N (tons)
N_2O	0.25 ppm	1500×10^6
NO		
Land (65N-65S)	2 ppb	2.2×10^6
All other areas	0.2 ppb	
NO_2		
Land (65N-65S)	4 ppb	4.0×10^6
All other areas	0.5 ppb	
NH_3	6 ppb	30×10^6
NO_3	0.2 g/m^3	0.2×10^6
+		
NH_4	1.0 g/m^3	4.1×10^6

Table 3. Global background concentrations of nitrogen compounds (Robinson and Robbins, 1970).

suggests the presence of a significant scavenging system. Estimates have been made that the atmosphere is capable of a turnover period of about one week (Robinson and Robbins, 1970). The diagram shown in Figure 5 is presented as the system which is responsible for the introduction, circulation, and removal of atmospheric ammonia.

Introductory, Circulatory and Removal Pathways

Generally, the introduction of NH_3 into the atmosphere results from the surface volatilization of gaseous NH_3 . In the vicinity of concentrated animal populations the volatilization rate is high because of increased biological activity upon the animal wastes (Healy et al., 1970).

Once in the atmosphere, the NH_3 is mixed with the air by three mechanisms: convection, advection, and diffusion (Lowry et al., 1967). The analytical equations describing these mechanisms will not be introduced, since the theory is quite complex and their inclusion is not deemed necessary to the development and understanding of the conceptual model. Instead the important variables of each mechanism will be presented and discussed.

Two basic types of turbulent eddy motion exist which are caused by two different processes. Mechanical turbulence occurs when air moves past an object which protrudes vertically into the wind stream. Wind speed and the size and

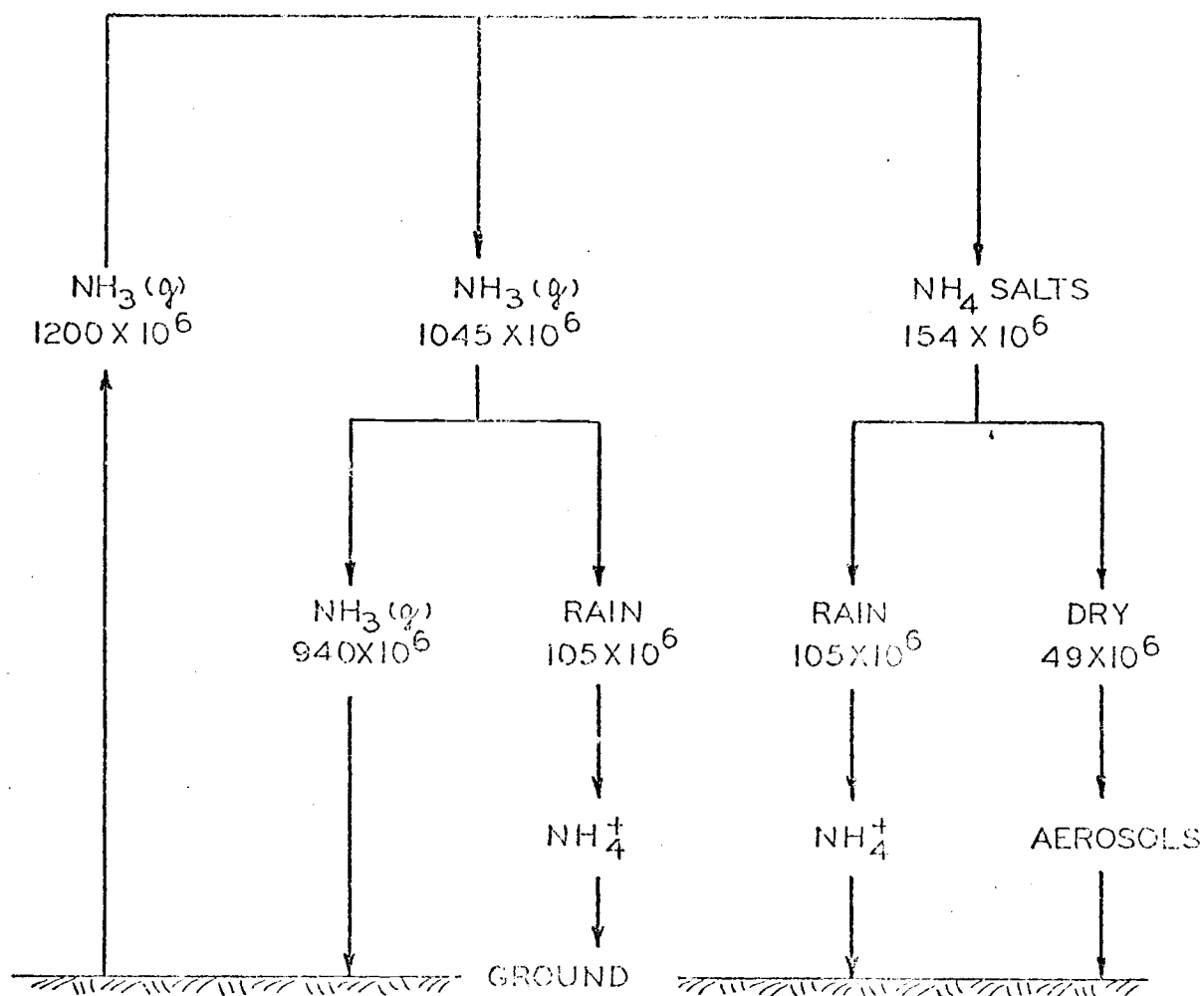


Fig. 5. System diagram for atmospheric ammonia compounds, showing introductory, circulatory, and removal pathways (tn/yr).

shape of the object determine the eddy size. The rising of warm air from the earth surface and the motion of cool air replacing the warm results in thermal turbulence. Most turbulence can be attributed to a mixture of both types. Turbulent eddies are of interest because they represent the mechanism for the vertical movement of air masses. This movement is called convection and results in the vertical flux of the air mass and its constituents (Lowry et al., 1967). In the case of NH_3 transport the vertical motion sets up a vertical concentration gradient and the NH_3 laden air mass is transferred upwards.

Meteorologists refer to the horizontal transport of air mass as advection. The horizontal wind velocity component is directly proportional to the advection rate with respect to time. In atmospheric mass transport the direction of advection is considered to proceed in alignment with the horizontal component of the wind.

Diffusion theory involves the molecular movement of the air mass constituents where convection and advection were concerned only with the bulk movement of the air mass itself. The diffusion model most widely accepted in the United States is the Gaussian plume model (Lowry et al., 1967). It is based upon the concept that each molecular particle moves in a random fashion through continuous time and space, independent of the presence of any other particles. The distribution is based upon the probability of

finding a given particle at a given point at a given time. The concentration at any point is directly proportional to the generation rate at the source and inversely proportional to the standard deviation of the spatial distribution and the wind velocity. Increases in horizontal and vertical distances from the source reflect exponential decreases in the concentrations. Generally, lateral diffusive movement will be more pronounced than vertical movement (Lowry et al., 1967).

Circulation of atmospheric NH_3 involves the interaction of all three of these transport mechanisms. The mixing process, resulting from this circulation, moves towards a minimization of concentration gradients. As was pointed out earlier, though, the atmospheric NH_3 -N system is dynamic and in a constant state of turnover so that very little storage of NH_3 -N occurs. This means then, that the atmosphere never reaches a well-mixed state with respect to NH_3 . The scavenging mechanisms responsible for this turnover consist of two basic pathways; gaseous deposition and aerosol formation (Robinson et al., 1970).

Gaseous deposition, consisting of both surface absorption and adsorption, accounts for about 75% of the turnover (Robinson et al., 1970). Vegetation, soil, and water surfaces are all capable of absorbing NH_3 from the atmosphere (Junge, 1963). Specific rates and process pathways will be

discussed later in the text. Most of the nonabsorbing surfaces are capable of adsorption. Robinson et al. (1970) estimates a deposition velocity of 1 cm/sec for the adsorption process.

Approximately 60% of the remaining nitrogen chemically reacts to form ammonium salts (Healy et al., 1970). These salts, when first formed, are crystalline in structure and are principally in the large particle range ($0.2\text{--}1\mu$ diam.) (Junge, 1953). About one third of these particles are removed by gravitational fallout. The remainder of the crystalline particles become condensation nuclei and form rain droplets. Investigation has shown that only about half of the $\text{NH}_4^+\text{-N}$ in precipitation can be attributed to the dissociation of ammonium salts (Junge, 1958). Gaseous adsorption of the free NH_3 into the water droplets must therefore account for the remaining portion of $\text{NH}_4^+\text{-N}$ found in precipitation.

Some authors have contended that NH_3 is photochemically oxidized to form nitrate in the atmosphere (Feth, 1966, Hutchinson, 1954). This has been done to account for the unexplained presence of nitrate in precipitation. There is, however, no known reaction that will satisfactorily perform this conversion (Robinson et al., 1970). Robinson has presented a pathway, based upon the biological production of nitric oxide, which accounts for the nitrate in the atmosphere. This theory seems more reasonable and was included

in the development of the atmospheric NH_3 model.

Influences Upon The System

An obvious influence upon the system is the NH_3 source release rate. The relationship between the concentration and the release rate is not readily determined, though, because of the nature of the scavenging system. Adsorption deposition rates and adsorption rates are directly proportional to the NH_3 release rate. This means that whenever the system inputs are increased the system outputs will also increase. Available data suggest that usually local atmospheric concentrations will be higher in areas close to sources with high release rates. Luebs et al. (1974) found that large concentrations of dairy animals caused a distinct increase in the local atmospheric NH_3 concentration.

Wind velocities can effect an important influence upon the mixing mechanisms in the atmospheric system. Mixing proceeds faster and becomes more complete at higher wind velocities (Lowry et al., 1967). The direction of the wind also plays an important role in establishing the primary direction for advection. Somewhat related to the wind influence are the land formation and physical presence of protruding obstacles. These will influence the mechanical turbulence responsible for convection (Lowry et al., 1967). Hilly terrain and the presence of trees and buildings will conceivably result in greater vertical motion than flat,

barren land.

Thermal turbulence is determined by the presence and severity of temperature gradients. Areas which experience rapid temperature changes will probably experience high thermal turbulence (Priestly, 1959). Temperature inversions tend to cause pollution traps in local areas (Lowry, et al., 1967). The importance and nature of temperature inversions must be determined for each specific situation.

Shutt et al. (1925) found that, while the amount of rainfall is a necessary influence upon the amount of nitrogen removed by precipitation, there is no direct relationship between the two. Further work in the area has revealed that the duration of a particular storm is an important factor (Angstrom, 1952) (Junge, 1963). The NH_3 concentration in rainfall becomes less as the precipitation progresses. The form of precipitation is also important. Snow has been shown to have a $\text{NH}_3\text{-N}$ content approximately half that of rain. (Shutt et al., 1925).

Summary Conclusions

Although the bulk mass of $\text{NH}_3\text{-N}$ in the atmosphere changes little with time, the development of concentrated industrial districts and larger animal rearing facilities can cause serious local increases in $\text{NH}_3\text{-N}$ concentration. The effects of these high concentrations usually remain local because of the tremendous capacity of the atmosphere to

dilute and remove pollutants. Much work remains to be done in the area of developing theories and models which can better explain the system.

IV

FOLIAL INTERACTION WITH NH_3 SYSTEM

Until recently, interactions between atmospheric NH_3 and plant life have been regarded as having negligible importance with respect to the NH_3 system as a whole. Research conducted within the last few years, though, has shown that the folial absorption of NH_3 is indeed significant. Interaction with surfaces can account for 82% of the loss from the atmosphere of pollutants having relatively short half-lives (Hill, 1971). Since vegetation covers 90% of the land surface in the United States (Frey, 1964), vegetation seems to be a logical object of study.

Many different atmospheric pollutants are absorbed by foliage surfaces. A direct relationship has been shown to exist between the non-steady state rate at which a plant will absorb a compound and the solubility of that compound in water (Hill, 1971). Table 4 shows this relationship for various gases. Steady state absorption rates are dependent upon the ability of the plant to metabolize, translocate, or remove the compound from the absorbing solution. Thus, the study of folial absorption involves a system consisting of relationships more complex than just NH_3 solubility.

Observation has shown that soybean plants are capable of absorbing amounts of NH_3 in excess of their saturation

Compound	Uptake Rate at 5 ppm l/min/m ²	Solubility at 20 C, 1 atm cc gas/ccH ₂ O
CO	0	0.02
NO	3	0.05
CO ₂	10	0.88
O ₃	50	0.26
NO ₂	57	Decomposes
Cl ₂	62	2.30
SO ₂	85	39.4
HF	113	446

Table 4. Comparison of the folial uptake rate and solubility in water for various compounds (Hill, 1971).

levels without showing signs of approaching a saturation equilibrium (Hutchinson et al., 1972). Additional research has shown that plants previously exposed to an atmosphere containing labeled NH_3 , have ^{15}N -enriched compounds distributed throughout the cell structures in excess of what would normally be present (Porter, 1972). In this particular study the soil was isolated from the enriched atmosphere so that the only pathway available to the labeled NH_3 was folial absorption. The conclusion drawn from these studies is that plants are capable of metabolizing NH_3 after absorbing it from the atmosphere.

Absorption Pathway

The feasibility of a plant's metabolizing atmospheric NH_3 can be determined by an examination of the pathway which the NH_3 molecule must follow. The diagram illustrated in Fig. 6 shows the transport pathway.

Gaseous NH_3 in the bulk air is carried to the outer edge of an obscure boundary layer by convection. Molecular diffusion is responsible for transporting the molecule across this boundary layer, through an open stomate and across the leaf's intercellular air space to the outer cell wall. At this point the assumption is made that the wall of the leaf mesophyll cells can be treated as a rigid matrix of inert cellulose fibers bathed in a water milieu (Hutchinson, 1973).

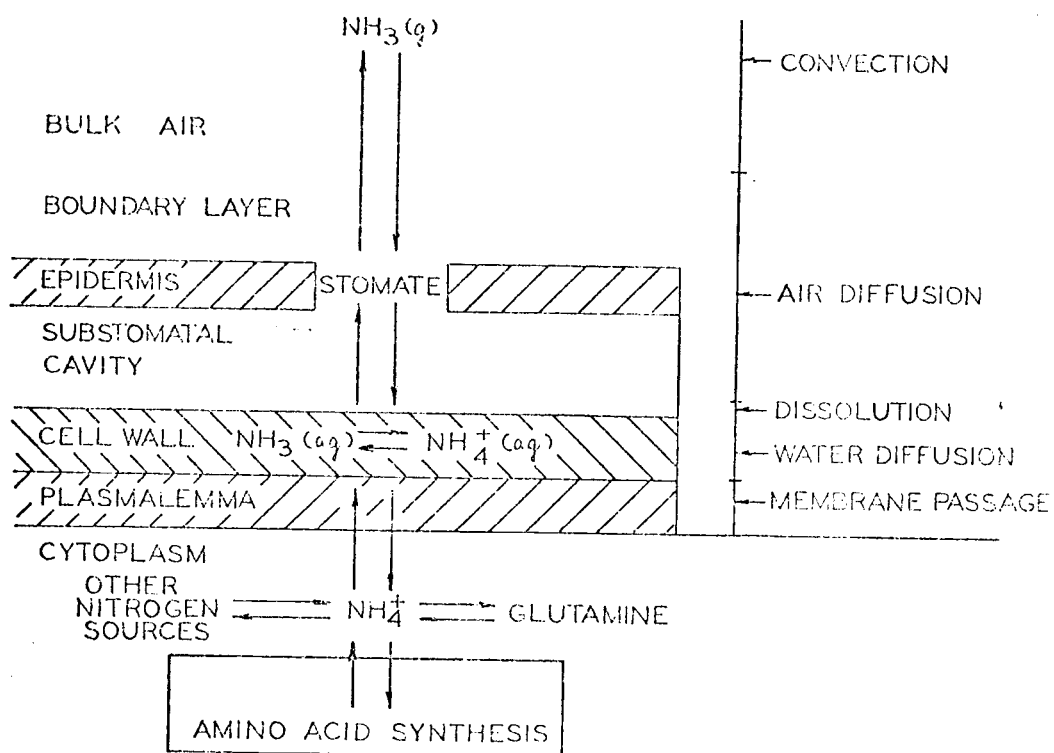
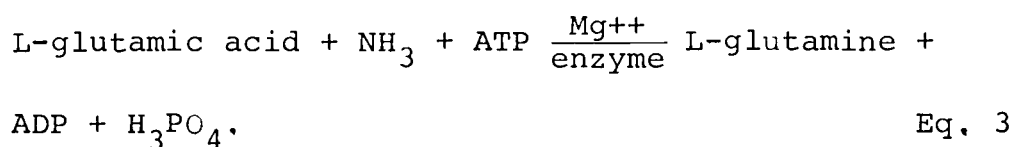


Fig. 6. The transport pathway and transport process involved in folial uptake and assimilation of atmospheric ammonia (Hutchinson, 1973).

The NH_3 then dissolves in the cell wall liquid where it diffuses through the aqueous phase of the cell wall and across the plasmalemma to the cytoplasmic fluid. Once the NH_3 enters the aqueous phase an equilibrium is reached with the ionic form.

After entering the cytoplasmic fluid, the NH_3 (or NH_4^+) is either utilized in the metabolic process or stored for future use. Almost immediately upon entering the cytoplasm, NH_3 is converted to an amide form in the compound glutamine (Fowden, 1965). The equation describing this process is



This reaction, Eq. 3 allows storage of nitrogen within the plant without the danger of NH_3 toxicity. Reversal of the reaction yields NH_3 for amino acid production as the need arises. Because the catalyzing enzyme for this reaction is widely distributed, has a low Michaelis constant and a high turnover number, the suggestion is made that the concentration of free NH_3 in the cytoplasm is maintained at essentially zero (Hutchinson, 1973).

The rate of gas transport can be written in equation form by taking a ratio of the driving force to the physical resistance that the molecule encounters. Rate of gas transport or flux is then

$$F = \frac{c_a - c_o}{r} \quad \text{Eq. 4}$$

where c_a and c_o are the gas concentrations (mg/cm^3) in the external air and at the site of assimilation inside the cell, respectively, and the flux, F (mg/cm^2). Resistance to molecular movement, r , is

$$r = r_a + r_s + r_m \quad \text{Eq. 5}$$

where r_a is the resistance of the boundary layer surrounding the leaf, r_s is the resistance encountered through the stomate and across the intercellular air space up to the cell wall, and r_m is the mesophyll resistance which impedes movement across the cell wall, the plasmalemma and a variable length of cytoplasmic fluid.

Literature shows that an average value of 2 sec cm^{-1} can be used for the sum of r_a and r_s (Hutchinson, 1973). Values for the mesophyll resistance, r_m , cannot be measured independently and are usually obtained by manipulation of Eq. 2. Calculations show that for NH_3 transport, $r_m = 0.001 \text{ sec cm}^{-1}$ is a reasonable value (Hutchinson, 1973). This is negligible in comparison to r_a and r_s and can therefore be disregarded. Previously the suggestion was made that the free NH_3 level within the cytoplasm was essentially equal to zero. Incorporating these ideas then gives

$$F = \frac{c_a}{r_a + r_s} \quad \text{Eq. 6}$$

Hutchinson utilizes this equation for predicting folial uptake rates. Comparisons of the actual experimental values to the predicted values showed good correlation with deviations ranging from 0% to 36%.

Influences Upon System

Most work in this particular area is done under controlled laboratory conditions because of the unpredictable impacts which can influence the process. Some understanding of these impacts, though, must be attempted in order to allow the laboratory model to assume a useful role in pollution work.

The flux equation, Eq. 6, may be viewed as the ratio of the atmospheric concentration to the resistance. Under conditions where the resistance to molecular movement remains constant, the equation would predict that an increase in concentration will yield an increase in the flux. Two experimenters, Hutchinson (1973) and Porter (1972), found the relationship between concentration and flux to follow the general trend shown graphically in Figure 7. Therefore, within the bounds of normal atmospheric concentrations, one can expect that an increase in NH_3 concentration will result in a corresponding linear increase in the rate of folial uptake.

Included in the resistance term, r_s , is the effect of

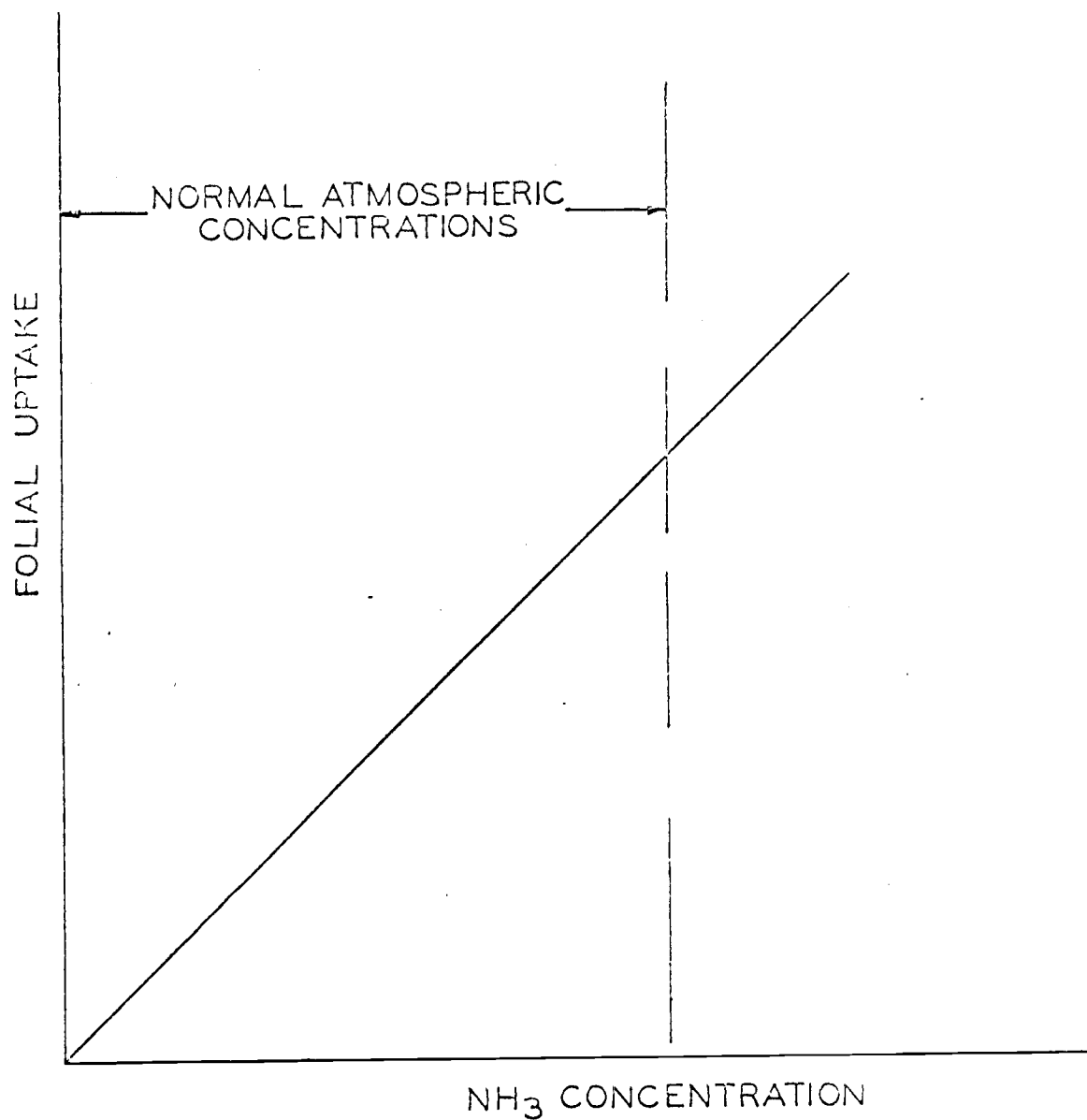


Fig. 7. Relationship of atmospheric ammonia concentration to folial uptake rate (Hutchinson, 1973 and Porter, 1972).

the size of the stomatal opening on the leaf surface. These stomates respond to light intensity by opening in the presence of light and closing in the absence of it. As would be expected, the rate of folial uptake of atmospheric NH_3 is greater during daylight hours than during the night. This phenomenon is shown graphically in Fig. 8, which plots data from a 24 hour period taken under controlled conditions. The actual difference between night and day uptakes is somewhat obscured. The flow of NH_3 was constant with time so that the lower uptake rate occurred in the presence of an NH_3 concentration much larger than the day concentration.

Wind velocity variations can trigger changes in the uptake rate of atmospheric NH_3 . As is evidenced in most boundary layer theory, turbulent velocities tend to reduce the effective thickness of the outer boundary layer and thereby reduce the resistance, r_s , experienced by molecules passing through the boundary. A reduction of the resistance will result in an increase of the flux rate defined by Eq. 6. Studies performed with O_3 show, however, that this effect is limited. A wind velocity increase from about 0.5 to 3 mph triples the uptake rate, but it remains about the same for velocities over 3 mph (Hill, 1971).

Although changes in temperature have a profound influence upon folial transpiration rates, NH_3 uptake rates seem to be little effected. The minor changes that have been

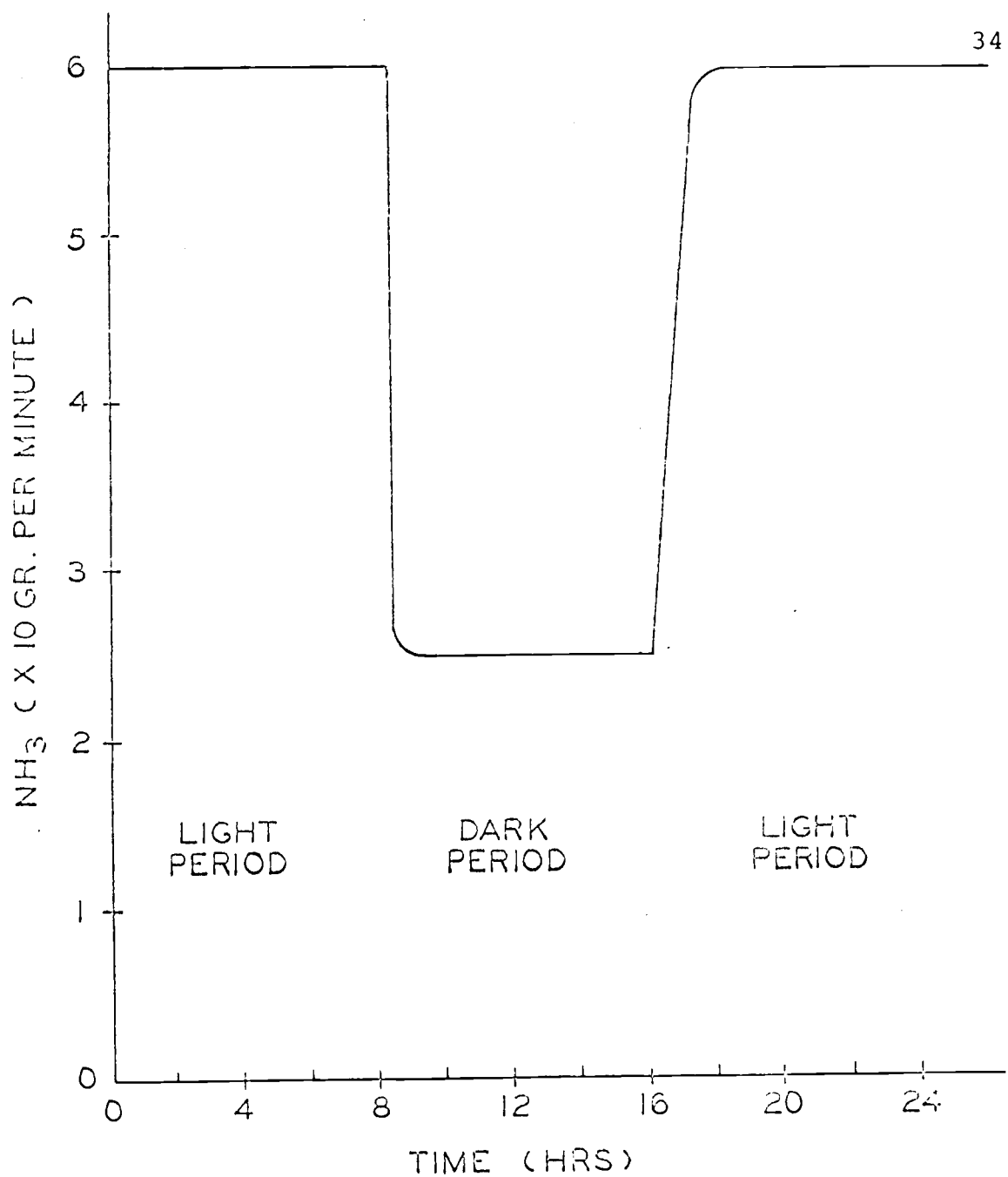


Fig. 8. Uptake rates of ammonia for soybean growing in soil containing 50 mg of nitrogen under simulated conditions of day and night (Hutchinson, 1973).

observed can be attributed to variations in the effective area of the stomatal opening.

The capacity to absorb and utilize atmospheric NH_3 does not seem to be dependent largely upon the previous nitrogen fertilization of the plant. Soybean plants, fertilized with 0, 5 and 20 mg of soil nitrogen showed no substantial differences in folial absorption rates (Hutchinson, 1972). Slight increases in NH_3 absorption was noted in corn samples fertilized with nitrate nitrogen (Porter, 1972).

Summary Conclusions

Accurate predictions of folial absorption rates cannot be made due to the complex interactions of the variables. However, the concepts can be utilized to gain a general understanding of a particular situation. Calculations based on available data indicate that under average conditions about 20 kg of NH_3 per hectare per year will be absorbed by a plant canopy which will supply as much as 10% of the total plant nitrogen requirement (Hutchinson, 1972). This particular parameter of the NH_3 system diagram can, in all conceivable situations, be considered to provide beneficial effects with respect to environmental management. The role of plant foliage in the NH_3 cycle plays a significant part and should be considered in the development of an overall model.

V

ATMOSPHERIC NH₃ ROLE IN SOIL FERTILITY

Conflicting theories concerning soil fertility have been developed. The result has been a somewhat obscure knowledge of the subject. In the early 1900's, fertility was believed to be an inherent property of the soil. Without an external input of fertilizer, a cropped field would become depleted of required plant nutrients.

The fallacy of this theory became evident by the work of Russell and Watson (1940). In 1865 the nitrogen content of an unfertilized soil, to a depth of 9 inches, was 0.1 per cent. After the harvesting of 70 successive annual high nitrogen crops, the soil nitrogen content was again found to be 0.1 per cent. The conclusion was that, if soil fertility was a static condition, the 70 year period would have been sufficient to deplete the available nitrogen. Since the nitrogen was not depleted, some replenishment system must exist. Ingham (1950b) also makes this conclusion based upon the fact that the natural vegetation of the South African veldt or the prairies of North America has persisted for thousands of years, giving sustenance to many millions of grazing animals. Even though a large portion of the nutrients would be returned to the soil, some would be bound in refractory compounds so that eventually one

would expect a soil nutrient depletion to occur. The opposite condition existed though as early settlers found a fertile soil rather than a sterile desert.

From this point, a general acknowledgement was made. Some system must exist by which restoration of plant nutrients is achieved so that soil fertility is maintained at a satisfactory level for an indefinite period of time (Ingham, 1950b). Initially, this system was believed to have been found in the fixation of atmospheric nitrogen by micro-organisms. Nitrogen fixing bacteria were first isolated in the early 1900's and since that time much debate has occurred over their actual contribution to soil fertility (Mortland and Walcott, 1965). Delwiche and Wajler (1956) observed very little nitrogen fixation under average field conditions. Considerable nitrogen fixation was reported by Allison (1955). The value of these findings has been discounted, though, because of the significant errors in soil sampling and analysis, and the general conclusion is now that, due to the physiological requirements of the nitrogen fixers, the contribution of nitrogen fixing bacteria to soil fertility is quite insignificant (Allison, 1965).

As the credibility of the nitrogen fixation theory was attacked, new methods of input were sought. In the mid 1800's, Liebig (1847) made the assertion that soil nitrogen fertility was maintained by the addition of NH_3 in rainwater

and by the direct absorption from the air of nitrogen compounds. This theory, which had previously been discredited, was reviewed by Ingham (1950a): and subsequent experiments gave evidence in support of the basic theory. Malo and Purvis (1964) continued the investigation and concluded that soils are capable of absorbing significant amounts of NH_3 from the atmosphere.

To a degree, soil fertility is maintained by the direct absorption of atmospheric nitrogen compounds and by the addition of NH_3 in rainwater. The significance of the process is still a much debated topic though, since not enough data have been collected to establish the importance (Allison, 1965). In order to understand the capacity and limits of this process, we must review the process and its parameters.

Soil Uptake of Atmospheric NH_3

According to Liebig's theory, two pathways exist for the introduction of atmospheric nitrogen into the soil. They are direct soil absorption and NH_3 laden precipitation as shown in the system diagram in Figure 9. The absorption process is the most significant of the two according to Liebig.

Soil absorption of atmospheric nitrogen compounds is a function of specific soil constituents. Three different factors are responsible: 1) organic colloids like humus, cellulose, and lignin, 2) inorganic colloids such as clay,

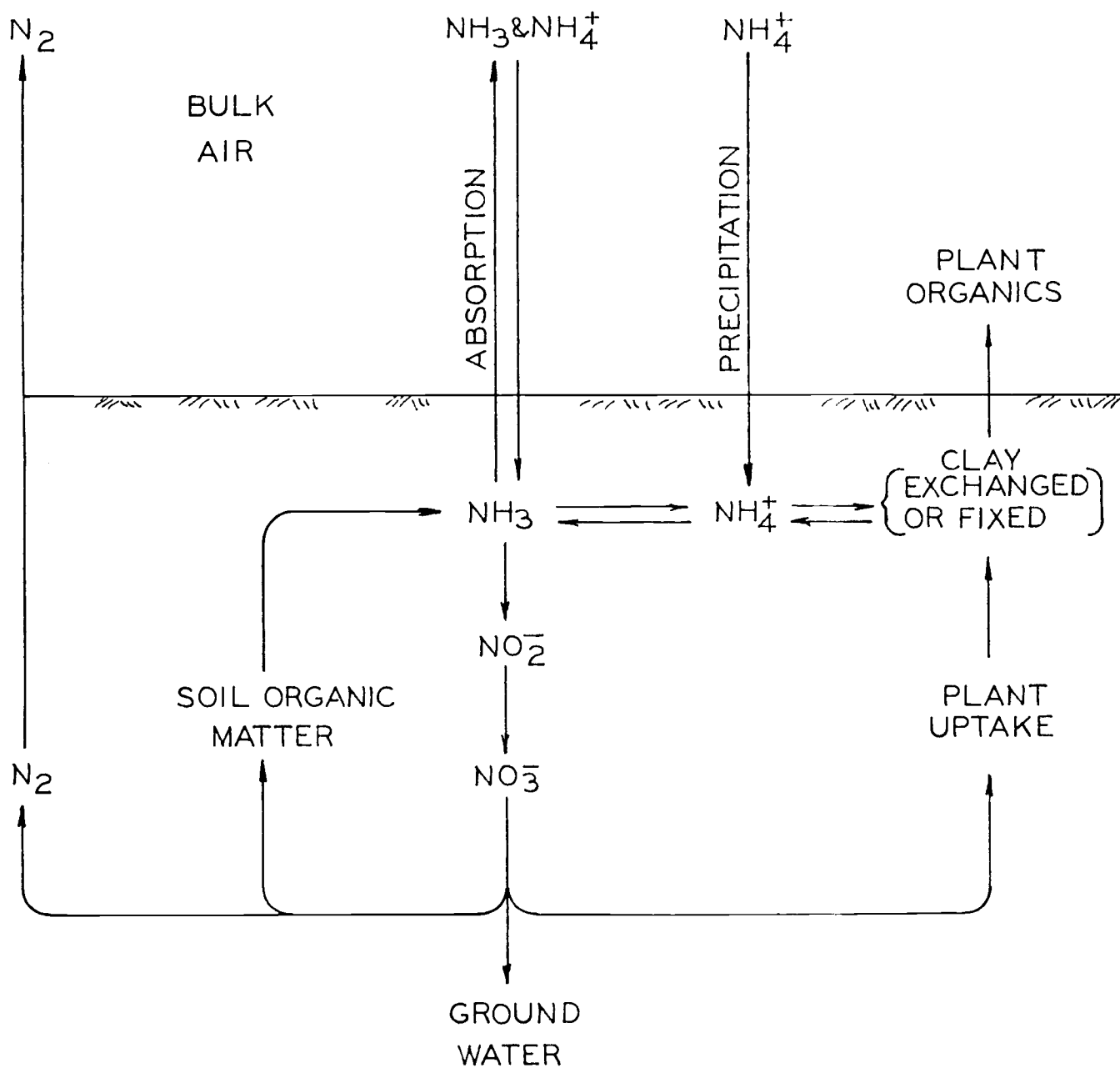


Fig. 9. The system diagram showing interaction between atmospheric ammonia and the soil.

and 3) water. The specific processes would be surface adsorption for organic and inorganic colloids and adsorption for water involving both NH_3 and ammonium aerosols.

Organic matter in soil is basically derived from the various plant residues which consist of cellulose, hemicellulose and lignin (Waksman, 1936). Colloids of these plant compounds are charged either positive or negative. Cellulose, the primary organic colloid involved, has a negative surface charge and has been shown to possess a capacity for adsorbing ammonia (Ingham, 1950a). Stevenson (1965) states that other organic colloids have also demonstrated a capacity for surface adsorption. The adsorption of NH_3 -nitrogen on inorganic colloids is quite similar to the adsorption on organic colloids (Ingham, 1950a), although it is not usually as extensive.

The adsorbed ammonia is readily washed from the colloid surfaces and enters the soil water. Malo and Purvis (1964) observed that the rate of adsorption decreases as the amount of adsorbed NH_3 increases. Pure cellulose also demonstrates this tendency to adsorb at a decreasing rate, but when washed in distilled water the original capacity to adsorb is completely restored (Ingham, 1950a). This suggests that soil colloids are capable of adsorbing NH_3 but at a decreasing rate. Intermittant rains, however, can restore the adsorption capacity to the original an indefinite number of times.

The extent of resotration will depend upon the rainfall duration.

Absorption of atmospheric ammonia by soil water is somewhat limited in actual occurrence. At normal soil pH water has a high capacity for solubilizing NH_3 . The amount of water available at the surface, though, is not sufficient to allow a significant role in soil nitrogen absorption (Ingham, 1950a, Allison, 1965).

Free NH_3 and ammonium aerosols are common constituents of precipitation (Junge, 1958). The introduction of nitrogen into the soil complex from this source has been demonstrated on numerous occasions (Allison, 1965). A typical range of values for nitrogen in precipitation would be 0.2 to 0.6 kg of N per hectare per year (Hutchinson, 1969, Collison, 1930). The comparison of this to the estimated range for soil absorption, 21 to 82 kg of N per hectare per year (Malo and Purvis, 1964), shows that the soil absorption process is, by far, the most significant pathway for the introduction of atmospheric nitrogen into the soil.

Soil Chemistry of Inorganic Nitrogen Compounds

The complete soil nitrogen system is much larger than the one presented in Fig. 1 because of the many influencing factors in addition to soil absorption. For this reason the attempt is not made here to present the complete interaction of system parameters. Instead of only those factors which

play a direct role in the absorption process will be discussed.

Absorbed NH_3 is temporarily held in storage by the exchange complexes of the soil. This exchange complex can be described as a nitrogen storehouse from which the NH_3 will eventually be released. The released NH_3 will enter the system where either oxidation to the nitrate form or direct plant utilization takes place. Equilibrium requirements will control the release rate. Some pilferage occurs from the storehouse by certain clays which are capable of fixing the nitrogen in the NH_4^+ form. These clays, usually vermiculite or illitic-types, have the capacity fix from about 233 to 1880 kg per hectare plow depth (Stevenson and Wagner, 1973). Koalinitic type clays have demonstrated very little tendency to fix NH_4^+ . Nommic (1965) suggests that the relationship between the fixed and exchangeable NH_4^+ is a dynamic equilibrium. Theoretically then, the fixed NH_4^+ would be released when the exchangeable NH_4^+ level drops below a certain equilibrium. This release is a slow process and is greatly effected by the presence of various cations. Potassium is able to completely block the release of fixed NH_4^+ (Stevenson and Clark, 1973). In most cases, though, NH_4^+ fixation has not been shown to be a serious factor in limiting nitrogen availability (Nommic, 1965).

The nitrification of NH_3 produces NO_2^- , which is usually only a transitory state, and NO_3^- . Nitrate is of great

concern because of its demonstrated high mobility (Adriano et al., 1974). Leaching can cause a movement of nitrate into ground waters and thus a potential pollution problem. The nitrate can also be incorporated into plant organics, utilized by soil bacteria and denitrified to form N_2 .

Influences Upon The System

Soil pH has been found to be an important factor in determining the absorption rate. Areas of the United States, which have low soil pH's, tend to demonstrate lower atmospheric NH_3 concentrations than normal (Junge, 1958). Ingham (1950a) found that twice as much NH_3 absorbed at a pH range of 5 to 6 as at a range of 7 to 8. Relationships between soil pH's and surface sorption characteristics of the soil particles are not clear because of the many variables which act concurrently (Mortland and Wolcott, 1965). Changes in pH, stimulated by agricultural activity, can cause NH_3 that has been absorbed to be volatilized (Harmsen and Lolenbrander, 1965). This can be a significant consideration when developing a soil nitrogen balance sheet.

Another important influence upon the absorption is precipitation. The amount of NH_3 contributed to soil will increase with higher rainfalls. Of more importance, though, is the effect that the rain will have in cleansing and restoring the absorption capacity of the soil colloids. Frequent, intermittent rain storms will allow a soil to

function at high absorption rates (Ingham, 1950b). The concentration of NH_3 in this water after the washing action is of possible importance. If the concentration exceeds equilibrium levels, then subsequent volatilization could occur. Hutchinson and Viets (1969) observed increased surface volatilization of NH_3 from a cattle feed lot following periods of rainfall.

The moisture content of the soil has not been shown to have a significant effect upon absorption rates. Malo and Purvis (1964) found, that up to field capacity the moisture content did not influence the absorption. Similar findings were recorded by Ingham (1950a). Malo also found that, within normal ranges, changes in atmospheric concentration had little effect upon the absorption rate. The reason for this is not yet clear.

Summary and Conclusions

Absorption of NH_3 by soil has been demonstrated to be a significant process activity in the atmospheric ammonia system. The importance of this process to soil fertility is debatable however, because the loss of nitrogen from NH_3 volatilization and NO_3^- denitrification could be an offsetting factor. The two factors which have the major influence upon soil absorption are soil pH and precipitation.

VI

NH₃-N ENRICHMENT OF SURFACE WATERS

Nitrogen enrichment of surface waters has long been of major concern. The focus of this concern for the most part has been centered upon nitrogen in runoff and nitrates in the percolating ground waters. Recently, though, attention has been given to the possible enrichment by atmospheric nitrogen, specifically airborne NH₃. Three mechanisms of transfer exist: 1) absorption of NH₃ into the surface water, 2) precipitation, and 3) particle fallout.

Upon entering the surface water, NH₃-N enters readily into the water nitrogen cycle and becomes available for aquatic growth. A diagram of this system illustrating both the transfer pathways and the nitrogen cycle is shown in Fig. 10. The various aspects of this system will be discussed in this section.

Transfer Pathways

Research has shown that the direct absorption of NH₃ into surface waters plays a definite role in nitrogen enrichment. Of the three modes for transferring NH₃ from atmosphere to surface water, direct absorption can be the most significant. Hutchinson and Viets (1969) have shown that in the vicinity of a cattle feed lot, a large surface

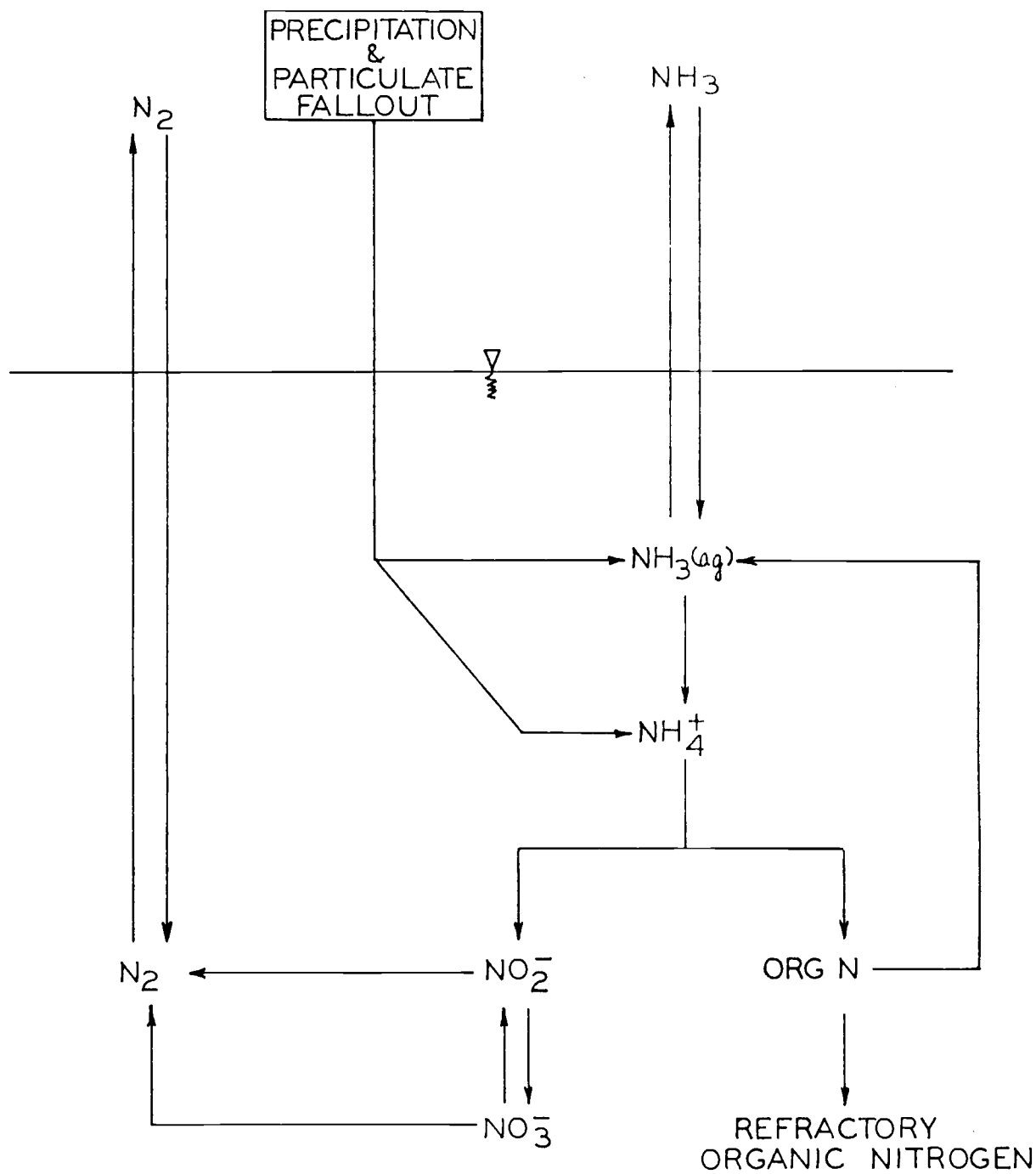


Fig. 10. The system diagram for interaction between atmospheric ammonia and surface water bodies.

water body can absorb enough NH_3 from the atmosphere to cause eutrophication. The estimated range of absorption is 4.0 to 75 kg per hectare per year.

The absorption of NH_3 by surface waters is a mass transfer operation. The absorption process is described by the failiar mass transfer relation

$$N = KA(P_g - P_l) \quad \text{Eq. 7}$$

where N is the mass transfer rate (kg/dy), K is the mass transfer coefficient for the gas phase (kg/dy-m²-atm), A is the area across which absorption is taking place (m²), and P_g and P_l are the partial pressures of the gas in the bulk gas phase and in the bulk liquid phase respectively (atm) (Rich, 1961). For low air velocities the mass transfer coefficient is expressed by

$$K = 3.3 \times 10^6 V^{0.8} T^{-1.4} \quad \text{Eq. 8}$$

where V is the surface wind velocity (ft/sec), and T is the air temperature (°K) (Halsam, 1924). These equations are based upon the assumption that the solubility of NH_3 is high enough that all of the resistance to mass flow is encountered in the gas film.

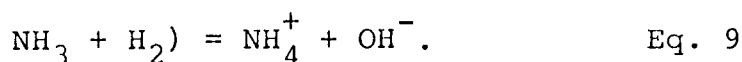
Precipitation washout of atmospheric nitrogen compounds in surface waters is the second most important transfer pathway. In agricultural areas, though, it is not nearly as significant as the absorption process (Hutchinson and

Viets, 1969). The nitrogen compounds which are of concern here are NH_3 and various ammonium salts. The process involves simple dilution of the precipitation liquid into the surface water body. Although some studies claim as much as 3.36 kg of N per hectare per year is introduced by precipitation (Goldberg, 1973), these have not attempted to delineate that portion which was introduced by direct surface absorption. More accurate studies, which have attempted to measure just the nitrogen in precipitation have produced values of about 0.2 to 0.6 kg of N per hectare per year depending upon the atmospheric concentration of NH_3 (Hutchinson, 1969, Collison, 1932).

The addition of NH_3 -N compounds to surface waters by particle fallout is of little significance when compared to the two previously mentioned pathways. These particles are composed of aggregates of ammonium salts which dissociate in water to give the ammonium ion (McCarty, 1968).

Nitrogen Water Chemistry

NH_3 is highly soluble in water and in aqueous solution it acts as a weak base according to the equation

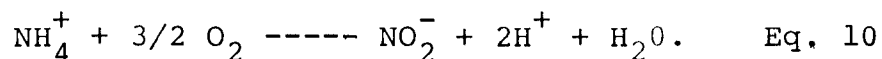


In the pH and temperature range encountered in most natural waters, this process proceeds to the right so that most ammonia exists in ionic form. This equilibrium is shown

graphically in Figure 11.

The chemical reactions which NH_4^+ can undergo in aqueous solution are somewhat limited because of the pH and temperature ranges normally encountered. Complexes can be formed with metal ions, but the formation of these complexes requires an ammonia concentration much higher than is usually found. In general the reactions between ammonia and metal ions are of little importance. In turbid waters the ammonium ion can become fixed within the lattice of clay minerals. Usually this fixation is strong enough so that the nitrogen is prevented from entering into further reactions.

In aqueous solution, the major NH_4^+ reactions involve the biological conversion to other nitrogen forms. The NH_4^+ may be incorporated into the organic-nitrogen fraction of both autotrophic and heterotrophic organisms, or it may be oxidized to nitrite nitrogen by the autotrophic bacteria, *Nitrosomonas*. The equation describing the nitrification process is



Nitrosomonas utilize the energy released by this reaction for growth. Most of the $\text{NH}_3\text{-N}$ entering a surface water body is converted to nitrite because of the long retention times. Under steady-state conditions the actual $\text{NH}_3\text{-N}$ concentration should remain quite low although in a few situations the opposite is evidenced. The reasons for these

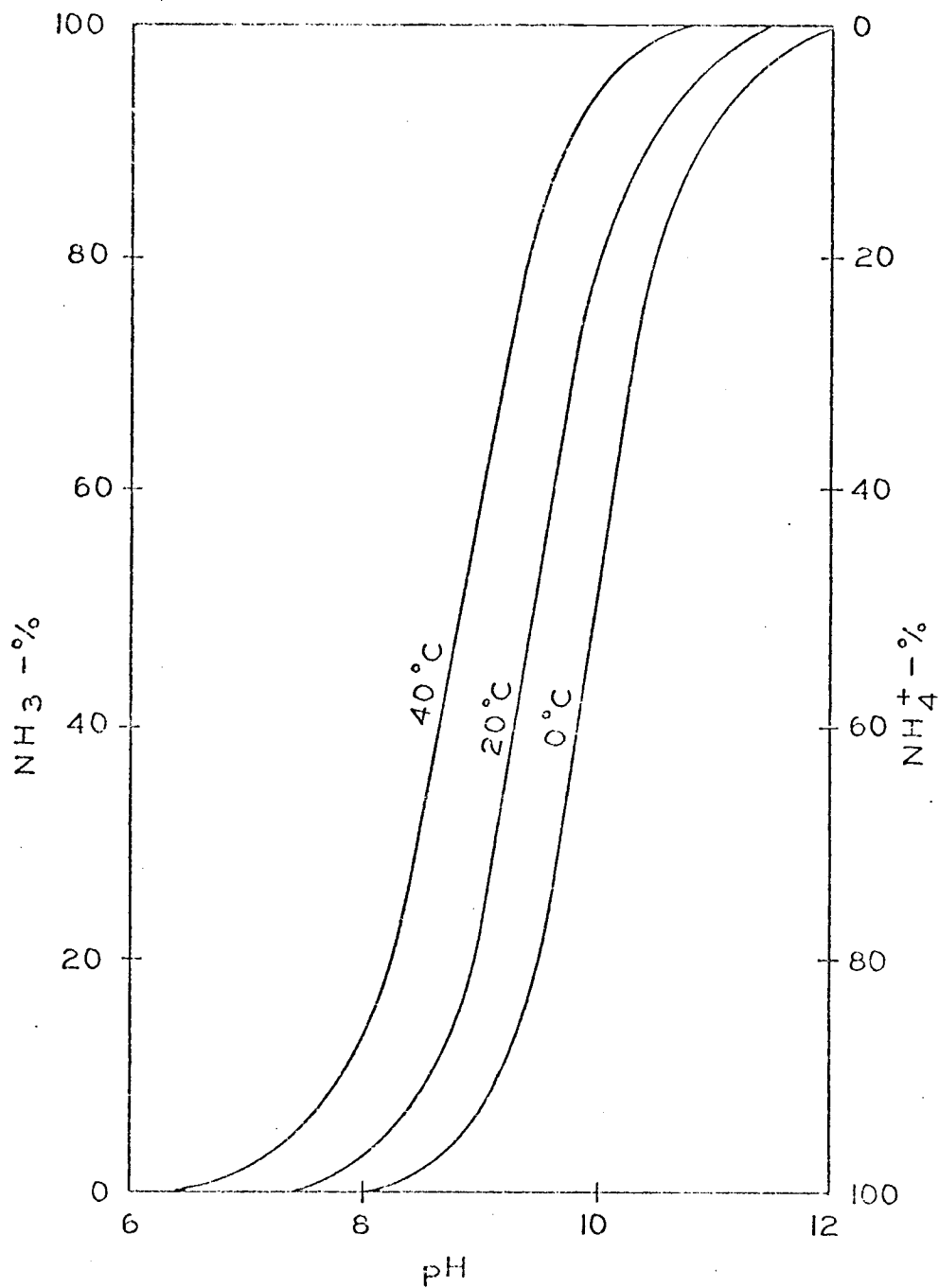


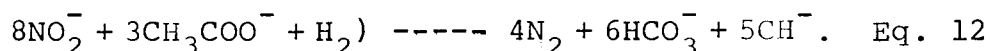
Fig. 11. Relationship between pH and the fraction of ammonia occurring as NH_3 with respect to temperature.

higher $\text{NH}_3\text{-N}$ levels than normally expected are not yet clear (McCarty, 1968).

Nitrogen in the nitrite form is relatively unstable and can be readily reduced or oxidized by either chemical or biological processes. Sulfide and ferrous ions are capable of reducing the nitrites, and chlorine can oxidize them. At the neutral pH found in most surface waters the major nitrite conversion involves either biological oxidation to the nitrate form under aerobic conditions or biological reduction to nitrogen gas under anaerobic conditions. The equation defining the oxidation process is



The bacterial species responsible for this conversion is Nitrobacter. Various groups of heterotrophic bacteria carry out the anaerobic denitrification process according to



Nitrate nitrogen is highly soluble in water, and is considered to be relatively chemically inactive. Therefore, the major transformation process to be considered, with respect to nitrate, is biological conversion. Both autotrophic and heterotrophic bacteria can utilize NO_3^- as nitrogen source thus incorporating the NO_3^- into organic-nitrogen forms. Under anaerobic conditions reduction to

either nitrite or nitrogen gas can occur (Brezonik, 1968).

The nitrogen gas formed by the anaerobic reduction of both nitrate and nitrite is released to the atmosphere. This release accounts for a majority of the available nitrogen that is lost from natural surface waters (Hutchinson, 1957).

Organic nitrogen exists mainly in the form of proteins and protein derivatives. The proteins can be divided into three main groups: fibrous proteins, globular proteins and conjugated proteins. Fibrous proteins and some of the conjugated proteins are resistant to biological degradation while the globular proteins are easily degraded biologically. The protein derivatives consist of purines, pyrimidiones, and urea. Urea is formed from the biological degradation of proteins and amino acids, and is the primary recycling pathway for returning nitrogen back into the biological process (McCarthy, 1968). Of major concern is that portion of the organic nitrogen which is refractory and accumulates as bottom sediment. Roughly 40% of all algal cell constituents are extremely resistant to biological degradation (Jewell, 1968). The proportion of nitrogen which is tied up in refractory bottom sediments is shown in relation to other nitrogen sources in Fig. 12.

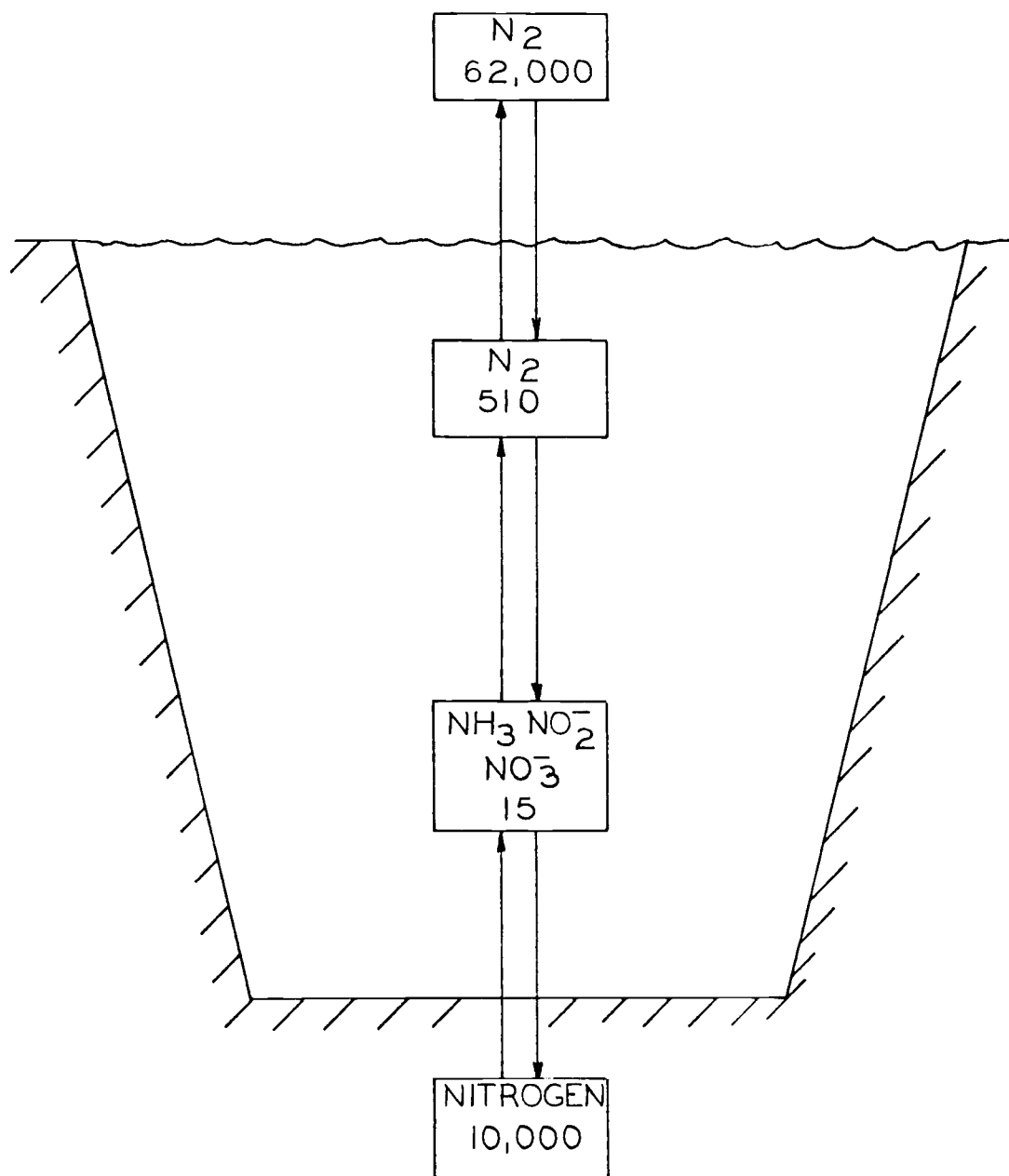


Fig. 12. Atom equivalents of nitrogen in its various forms in surface water bodies (McCarthy, 1968).

Influences Upon System

The rate at which NH_3 will be introduced into the surface water body is highly dependent upon the concentration of NH_3 in the atmosphere. An increase in the atmospheric concentration will cause a direct increase in the absorption flux according to Eq. 7, the mass transfer equation. Studies conducted in the vicinity of a cattle feedlot in Northeastern Colorado show that much higher absorption rates are experienced at locations of high atmospheric NH_3 levels than at low concentrations (Hutchinson, 1969). Logic would also seem to suggest that increases in air concentration would cause more NH_3 to be involved in precipitation washout and particle fallout. Evidence to support this is found in a study conducted by Junge (1958).

Mass transfer of NH_3 into water is dependent upon both temperature and wind velocity according to Eq. 9. The graphs shown in Figure 13 represent data collected by Halsam (1924). Correlations were made between the NH_3 transfer coefficient and various temperatures and velocities. The data suggests that velocity plays a greater role in determining the transfer coefficient, and hence the transfer rate, than does the temperature.

Once the NH_3 enters the water body the influences become much harder to define and describe. The pH of the water could have a profound effect upon the system

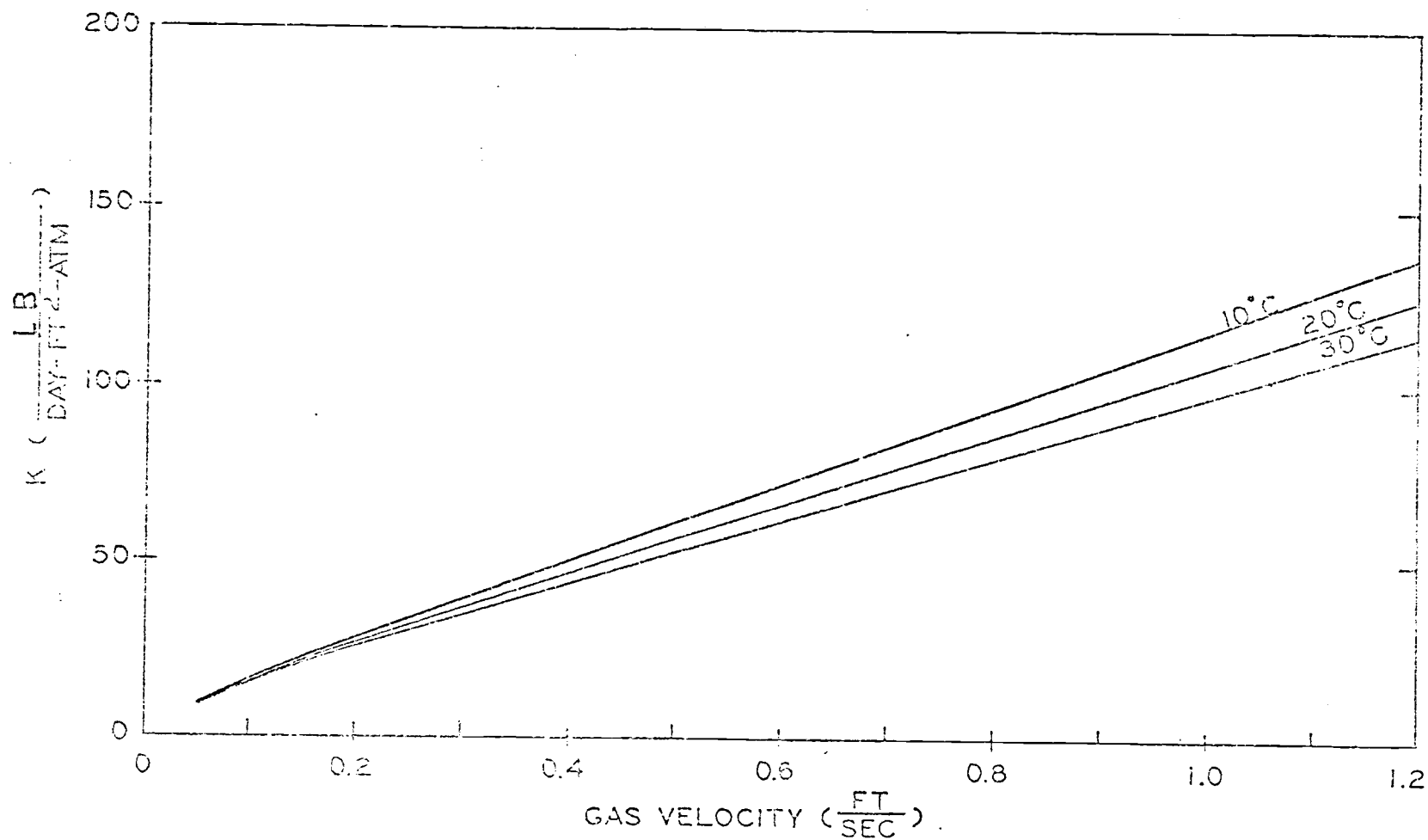


Fig. 13. Ammonia transfer coefficients versus gas velocity for ammonia absorption into water (Halsam, 1924).

processes. An abrupt increase in pH could cause the nitrogen to be volatilized as NH_3 . Most natural water bodies, though, display relatively stable pH levels so that impacts from changing pH are of little importance (Feth, 1966). The nitrification and denitrification processes can proceed relatively well in pH ranges of about 6.5 to 8.0 (Metcalf, 1972), which is about the range normally expected in natural water bodies.

Most of the bacteria that are involved in the nitrification and denitrification processes are facultative psychrophiles (Stanier, 1957). This means that, though their optimum temperature for growth is about 25°C , they are capable of functioning down to about 0°C . The growth rate does decrease with lower temperatures. A study conducted at Triangle Lake in Oregon revealed that a stratified lake experiences definite seasonal variations in temperature distributions (Smith and Bella, 1973). The data from this study is shown in Fig. 14. Even though the temperature ranges encountered display definite variations, the nitrification and denitrification processes are still able to proceed. The same study also revealed that changes in temperature usually discouraged one form of algae only to encourage another.

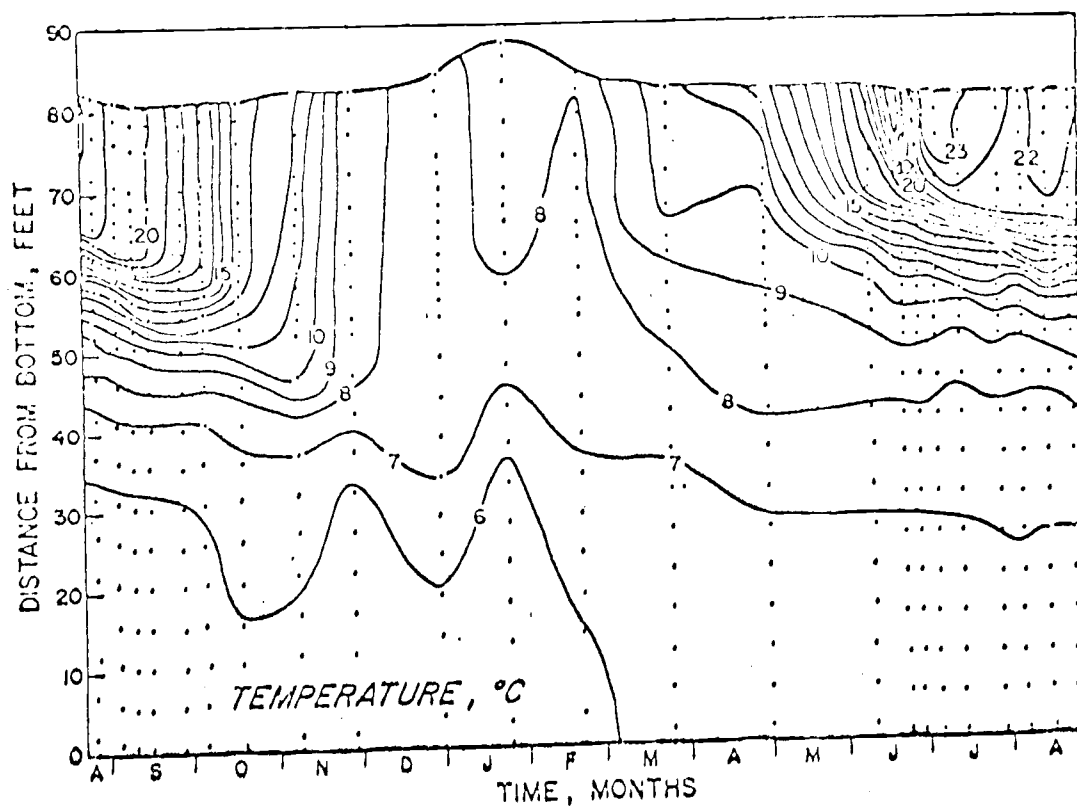


Fig. 14. Seasonal variations in temperature at a central sampling station in Triangle Lake, August 1969 through August 1970 (Smith and Bella, 1973).

SUMMARY CONCLUSIONS

Although the nitrogen water system is quite complex, the nitrogen enrichment of surface water bodies is a fairly straight forward process. Reasonable estimates of nitrogen enrichment can be made by making a careful study of the most significant influencing factors. Bulk air concentration, wind velocity and air temperatures are the major influences controlling the process. A general range of values to expect extend from about 4.0 kg NH_3 per hectare per year to about 75 kg NH_3 per hectare per year. The impact that this nitrogen can have once it enters the water can be quite significant. Nitrogen along with other important nutrients can lead to the eutrophication of the water.

VII

FIELD OBSERVATION OF COMPONENT INTERACTION

The purpose of a conceptual model is to develop understanding of the various complex processes occurring within a system. Usefulness of a particular model can only be determined from observance and collection of data under field conditions. These results cannot verify, but instead act as evidence, justifying the use of the model for a given situation.

An experiment was designed to observe the general overall effect of the component interaction within the atmospheric ammonia system. The presentation of this experiment will be divided into three sections: 1) method development, 2) analytical methods, and 3) discussion of results.

Method Development

In developing a meaningful experiment, my intent was to design one which would allow observation of the component interactions and yet remain simple in implementation. My initial effort was therefore concentrated upon finding the most significant aspects of the system. Once these aspects were identified, the experiment was designed around them.

For this project, the significant aspects will be defined as those which can cause deleterious effects within

the environment. As the model developed, it became apparent that detrimental environmental impacts were, for the most part, related to one particular component: the absorption of ammonia by surface waters. This was deemed the significant aspect of the system.

The system was viewed as follows. Ammonia is volatilized from manure covered surfaces into the atmosphere, and once in the atmosphere, the ammonia can be absorbed by surface waters. If the atmospheric concentration is high, enough ammonia can be absorbed to cause eutrophication. The other components of the system usually serve as sinks, and therefore, their significance is determined by the degree to which they can lower the atmospheric concentration. After this system view developed, the experimental method readily evolved.

An attempt was made to find a typical animal rearing facility. The criteria for selection was merely that it be as isolated as possible from other ammonia sources. A 1000 head confinement hog operation was found in Western Oregon which fit the criteria. A number of sampling stations were established around the facility, and the data collected were used to determine the surface water absorption potential. No attempt was made to alter the normal activities of the operation.

ANALYTICAL METHODS

The stations were placed in a grid surrounding the facility out to a distance of 2000 feet (609 meters). A layout of the experimental site is shown in Fig, 15. Since the predominant wind direction in the area is from the south, more stations were concentrated north of the facility.

A typical station consisted of a six foot steel fence post, a 50 ml plastic beaker, and a galvanized steel cover. The steel post, when driven into the ground to a depth of about one foot, supported the beaker at a height of five feet. About 30 ml. of 0.002 N H_2SO_4 was put into the beaker. The beaker was then put into position and remained in the field for three days. The cover protected the beaker from rain, birds and other such influences.

During the three days the beaker was in the field, it absorbed ammonia across its free surface. The low pH of the acid solution allowed all the absorbed ammonia to be held in the NH_4^+ form. After three days in the field, the samples were collected in stoppered test tubes and brought into the lab for analysis. The volume of each sample was recorded. Samples were then nesslerized according to Standard Methods (APHA, 1971), and ammonia concentrations were determined from a photometric measurement of the color. Once the ammonia concentration was determined the absorption

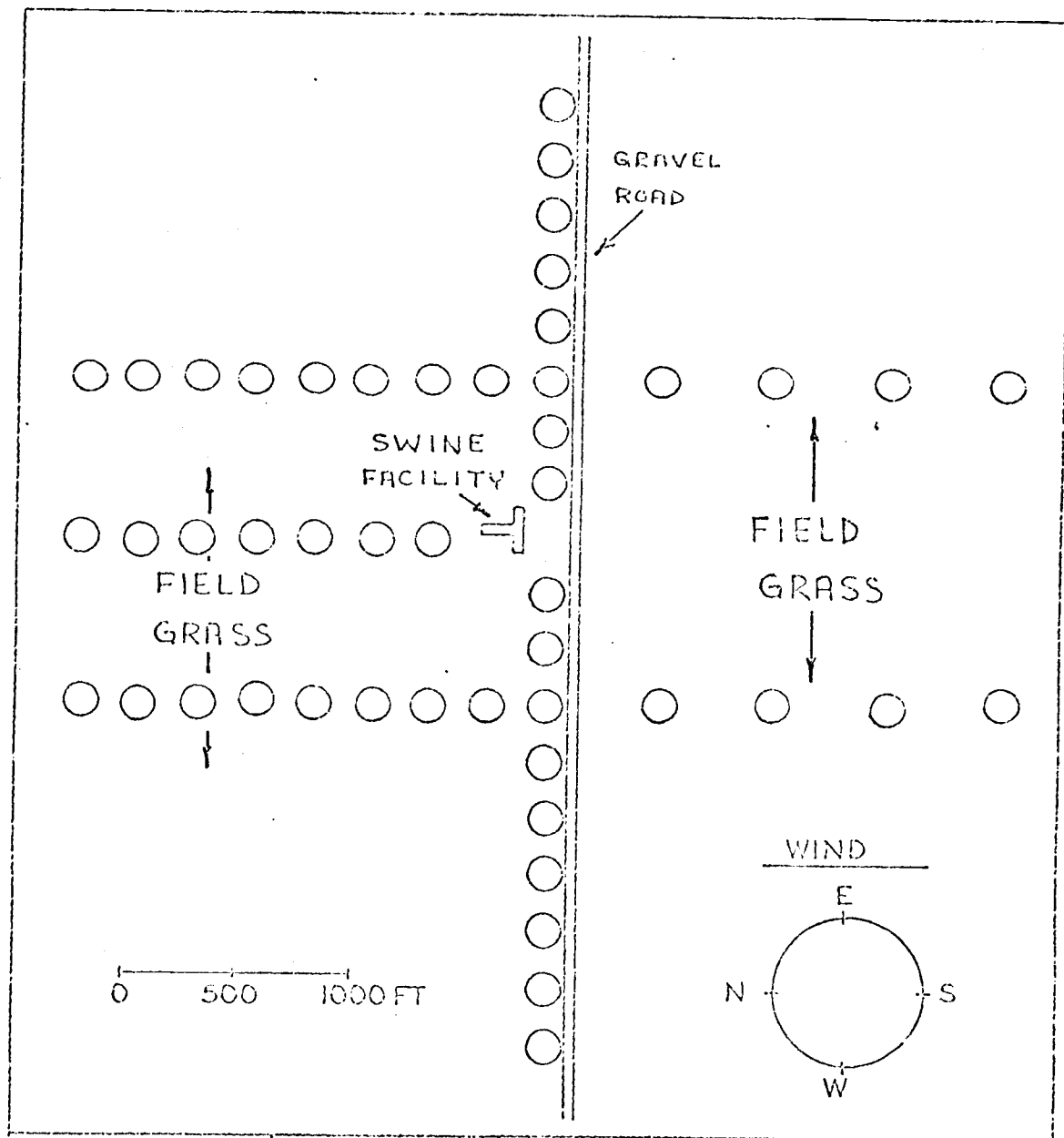


Fig. 15. plan view of sampling station layout at the experimental site.

rate was found by dividing the concentration by the time and the cross-sectional area and multiplying by the volume. The following is a sample calculation.

volume----19 ml
 cross sectional area---- $1.76 \times 10^{-3} \text{ m}^2$
 time----3 dys
 NH_3 conc.----1.44 mg/l

$$\text{abs. rate} = \frac{(19 \text{ ml}) (1.44 \text{ mg/l}) (10/100 \text{ ml})}{(3 \text{ dys}) (1.76 \times 10^{-3} \text{ m}^2)}$$

$$\text{abs. rate} = 6.8 \text{ mg/m}^2\text{-dy}$$

Results and Discussion

The data results are shown diagrammatically in Figs. 16 thru 21. The absorption rate for each station is shown, along with some general comments of the field conditions during the test period. Ammonia absorption rates are given in units of mg of $\text{NH}_3\text{-N}$ per square meter of surface area per day. Hutchinson and Viets (1969) found that ammonia absorption rates for H_2SO_4 are usually about twice what would be experienced for distilled water. If the values given are divided by two, an estimate can be made of the potential surface water absorption rate at a particular location. The data collection experiments will be discussed in particular first and then the general conditions will be examined.

The first experiment was conducted from June 23 to June 26, a period of three days. Surrounding fields had

been planted with field grass earlier in the spring and the grass was at a height of two feet. A slight tendency for the readings downwind of the facility to be higher is noticeable. The greatest factor in this particular experiment, though, results from the field application of the manure slurry. Stations in the immediate locale of the application area demonstrate high ammonia absorptions. This is expected due to the potentially higher atmospheric concentrations in this area.

The influence of the applied manure continued to be a factor through the second experiment which is shown in Fig. 17. Similar to the first experiment shown in Fig. 16, higher concentrations were experienced locally in the application area.

Approximately half of the stations were removed, prior to the third experiment, to facilitate the harvest of the field grass. The field application of the manure slurry was completed before this particular experiment began, and a slight decrease in the ammonia absorptions of the stations to the east of the facility is recorded. About 30 head of beef cattle were put into the enclosed area by the operator as shown in Fig. 18. As expected the stations in the vicinity demonstrated higher absorptions.

Ammonia absorption showed a general overall increase in the fourth experiment. The cause of this increase is somewhat obscure though due to the interaction of three

factors. An equipment malfunction delayed the scheduled emptying of one manure storage tank, and consequently, the tank overflowed into the area shown in Fig. 19. The grass crops to the east and to the south of the facility were harvested prior to the experiment, and the operator continued to feed the 30 beef cattle within the enclosed area. The manure spill and the beef cattle were probably responsible for the respective local increases while the grass harvest caused a slight increase in all of the absorptions.

The operator used a portable pump to empty the contents of the malfunctioning tank in the area shown in Fig. 20. This caused high local concentrations in the vicinity. The beef cattle had been removed prior to the beginning of this experiment, and the remaining grass crops had been harvested. Ammonia absorptions to the east of the facility were lower than those for the previous experiment. The influence of the spill was obviously short-termed. Overall, absorption rates continued to be higher than those taken prior to the grass harvest.

Data for the last experiment, shown in Fig. 21, continue to show a general overall increase from the values taken previous to the grass harvest. The effects of the manure, slurry dumped the week before, are rapidly diminishing. The data does not sufficiently establish whether wind is a factor or not.

The contribution of ammonia to the atmosphere by the swine operation is evidenced by the increased absorption rates downwind of the facility. Absorption rates ranged from 1.1 mg $\text{NH}_3\text{-N}$ per square meter per day to 16.1 mg $\text{NH}_3\text{-N}$ per square meter per day. These values are relatively low in comparison to data reported by other investigators. Miner and Stark (1976) measured ammonia absorption rates near a cattle feedlot in Idaho and found a range of 48 mg $\text{NH}_3\text{-N}$ per square meter per day to 950 mg $\text{NH}_3\text{-N}$ per square meter per day. These readings were all taken within 600 meters of feedlot pens. A study in California by Hutchinson and Viets (1969) found an ammonia absorption rate of 48 mg $\text{NH}_3\text{-N}$ per square meter per day at a site 400 meters distant from a large feedlot.

An estimate of the air concentration of ammonia in the vicinity of the facility can be determined from Eq's. 7 and 8. Assuming a temperature of 20°C , wind velocity of 2 feet per second, a partial pressure in the liquid phase of zero, and an absorption rate of 5 mg $\text{NH}_3\text{-N}$ per square meter per day, an atmospheric concentration of 2 ppb can be predicted. Robinson and Robins (1970) estimated a global ambient air concentration of 6 ppb $\text{NH}_3\text{-N}$. This estimate was based upon a collation of previous data and is shown in Table 3. The air concentration at the site is, then, well within the normal ambient range. The absorption rates experienced at the

site are probably not of a magnitude sufficient to cause nitrogen enrichment of a surface water body. This is especially true of locations more than 2000 feet (609 meters) distant from the facility.

The data does provide a basis for evaluating some of the system interactions. A slight influence upon the potential absorption rate was exerted by the seed grass crops. A decrease in absorption values seems to have occurred as the grass grew, though not enough data are recorded to establish a definite trend. When the grass was harvested, an overall increase in absorption rates was evidenced.

Wind direction played a role in the absorption rate, although the degree of influence is hard to determine. Locations downwind of the swine facility consistently showed a higher absorption rates than ones upwind. The wind velocities fluctuated between 0 and about 4 miles per hour, and consequently, a conclusion cannot be drawn with respect to its influence. The temperature and other weather conditions did not seem to influence the process to any degree.

Soil pH in the area is well within the acid range extending from about 5.0 to 6.4. This probably had some affect upon the absorption rates, although the extend of the influences was not determined. Since the soil pH does not fluctuate appreciably, attempts to determine its influence upon the system are difficult.

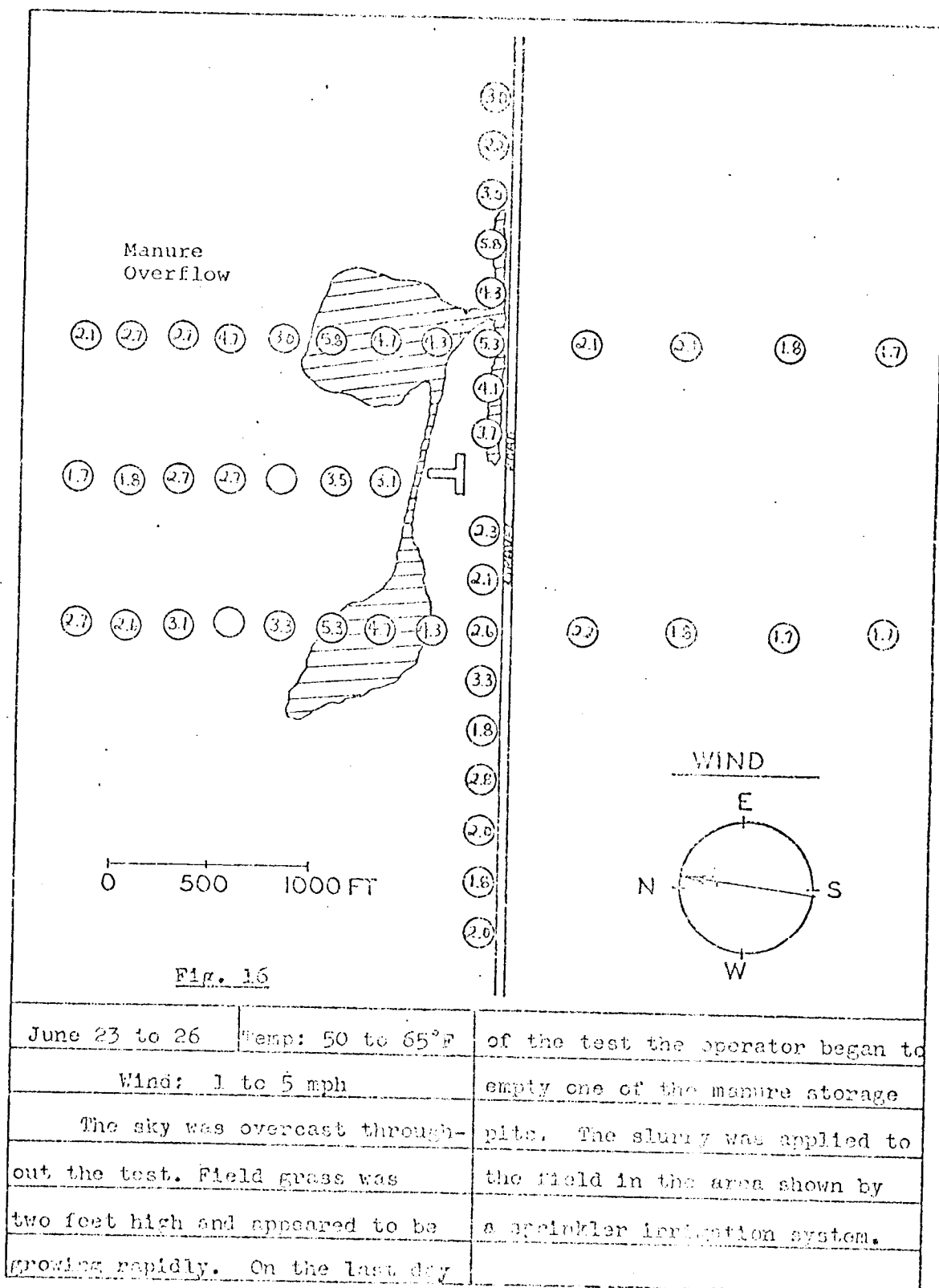
Two manure storage pits were located directly beneath the facility. These pits were scheduled to be emptied during the summer. The first of these pits was emptied over a two week period. The liquid slurry was spread onto the field via a liquid manure sprinkler. The affect that this had on the absorption rates is shown in Fig's. 16 and 17. Absorption was definitely higher at those stations within the affected area.

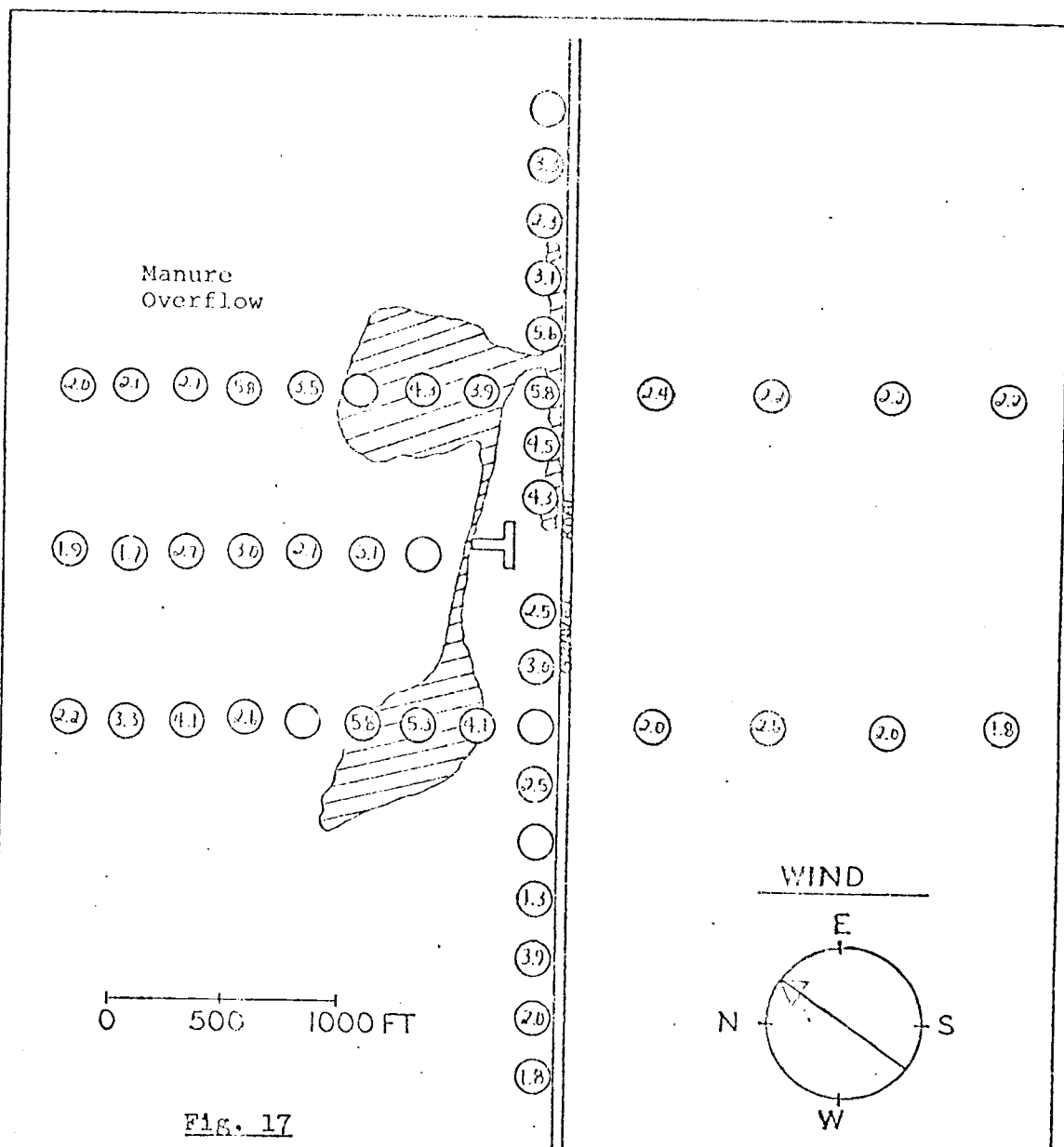
During the experimental testing period the facility experienced difficulty with one of the storage pits. A malfunction in the pumping equipment caused an overflow to occur which is seen in Fig. 19. To avoid a visible mess, the operator used a small pump to empty the liquid into a gully north of his buildings. This liquid manure slurry flowed along the gully and caused the high local concentrations shown in Fig. 20.

For two weeks during the summer the operator grazed about 30 head of beef cattle in the enclosed area shown in Fig.'s. 18 and 19. This caused a slight increase in the local concentrations.

The effects of these surface applications of ammonia do not seem to exhibit a long duration. A comparison of Fig. 20 to Fig. 21 shows that the high local absorptions experienced in Fig. 20 decreased appreciably in one week. This can be explained by the soil pH, which ranges from

about 5.0 to 6.4, values well within the acid range. At this pH, the majority of the ammonia would exist in the non-volatile state.





Jn 30 to July 3	Temp: 55 to 65°F	The sky remained overcast and a
Wind: 1 to 5 mph		small amount of rain fell during
The application of liquid		one day.
manure to the field was continued		
through this testing period. The		
grass was about 2½ feet high.		

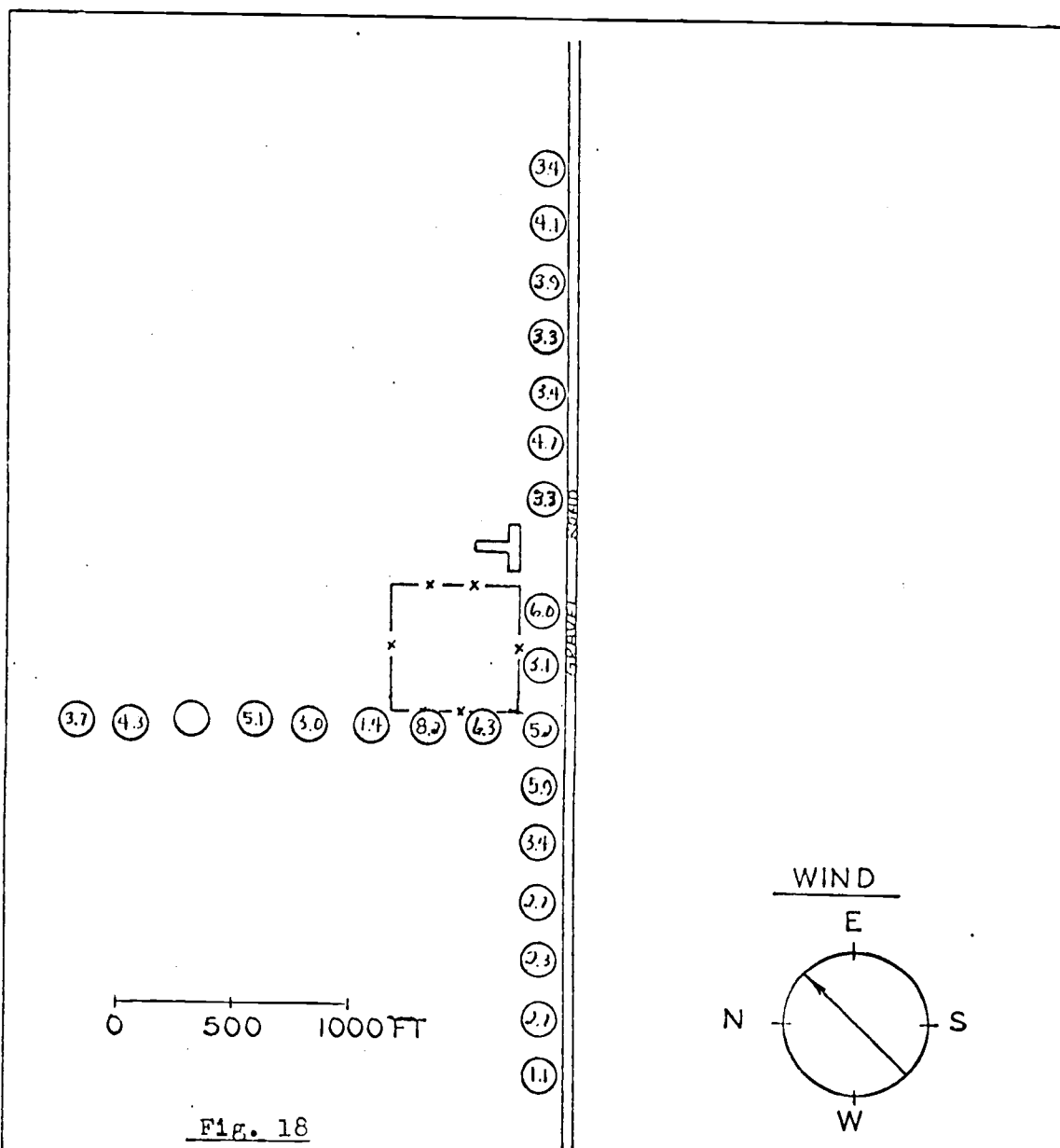
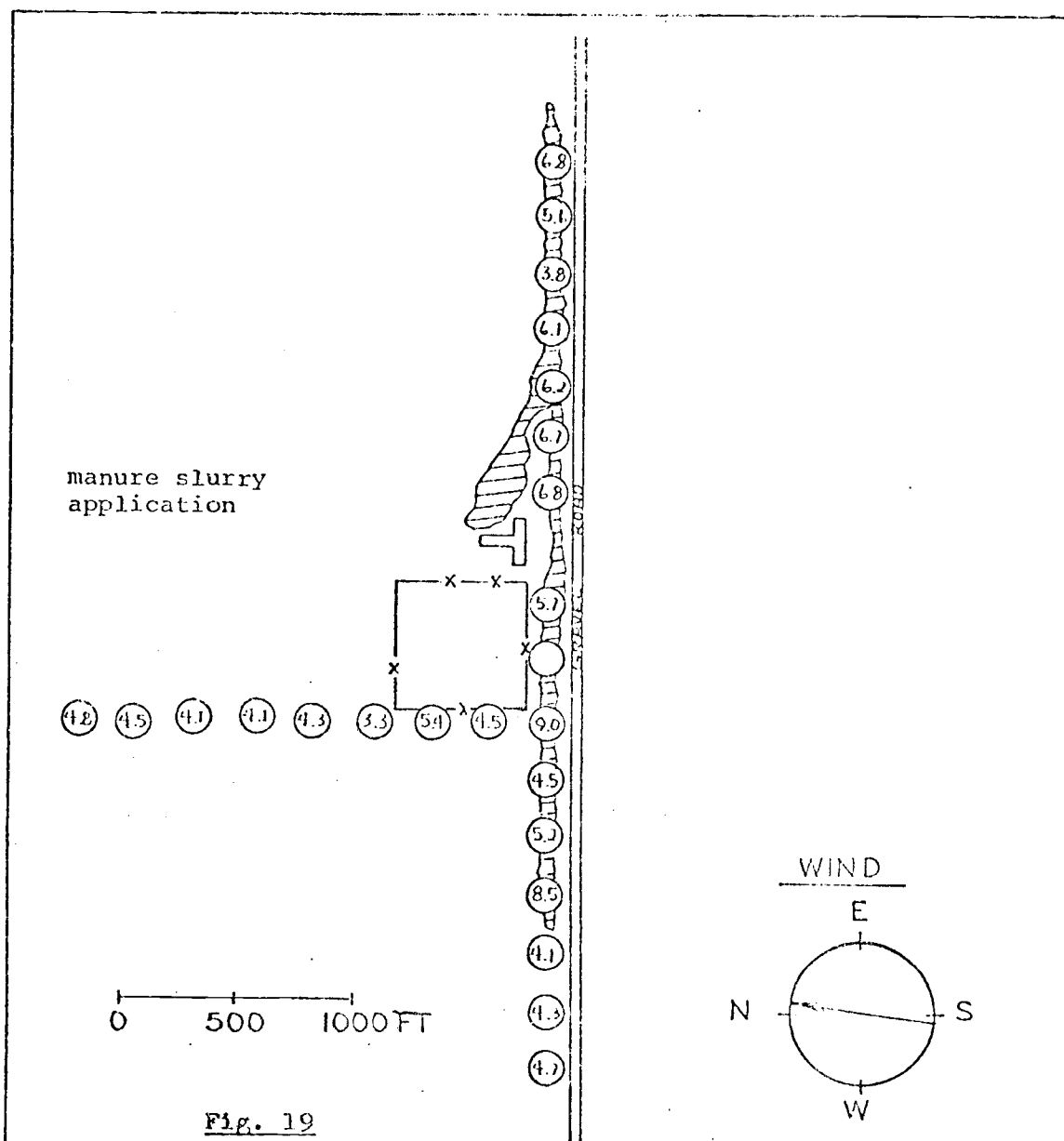
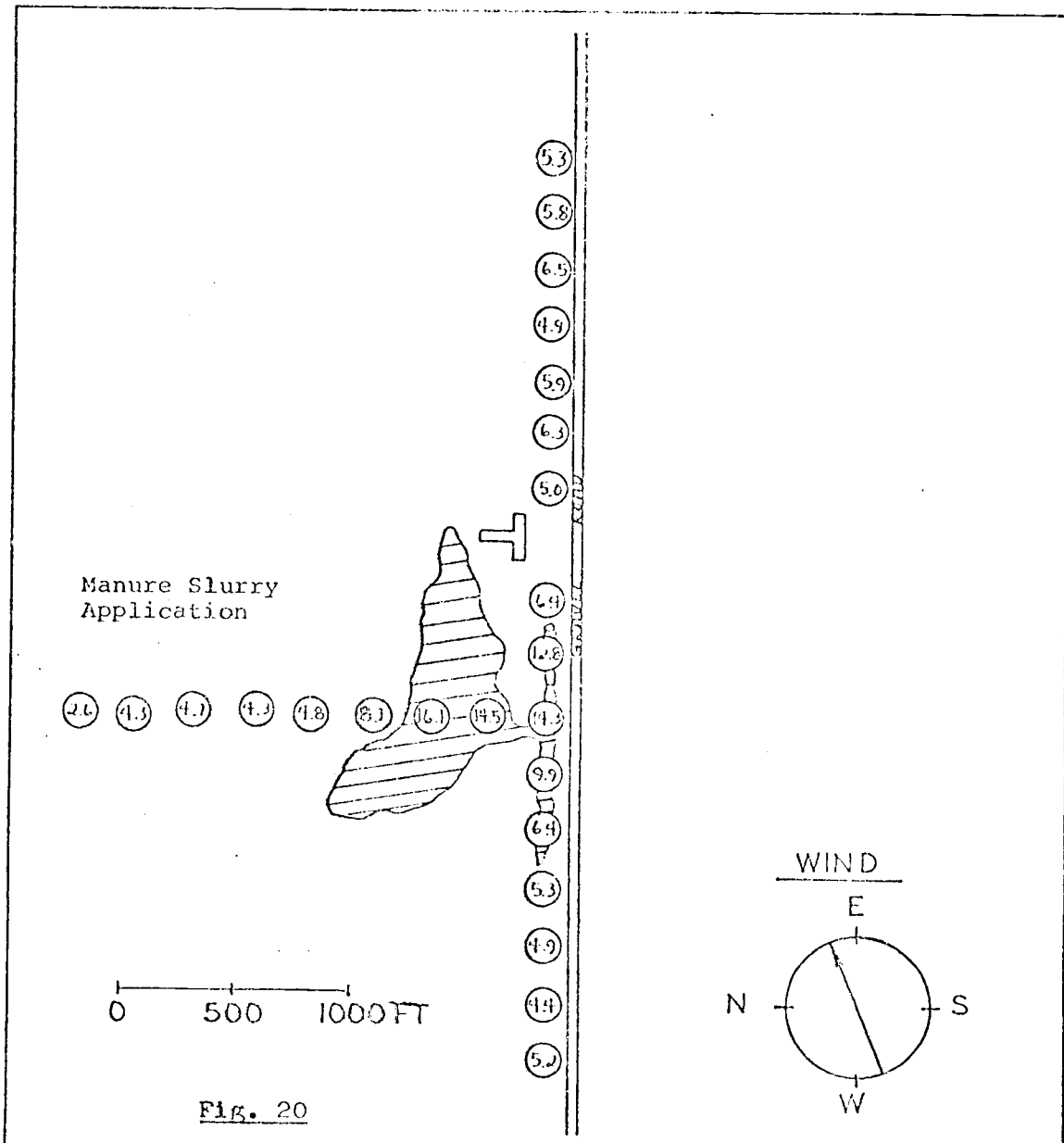


Fig. 18

July 7 to 10	Temp: 50 to 70°F	although occasional breaking up
Wind: 1 to 3 mph		of the clouds did occur.
The operator of the facility		
moved about 30 head of beef cattle		
into the enclosed area shown.		
Overcast conditions continued		



July 14 to 17	Temp: 65 to 75 F	pit overflowed into the area
All of the seed grass south of shown.		
the road and that east of the facil		
ity was harvested prior to this		
test. The cattle were still on the		
site. The remaining manure storage		



July 28 to 31	Temp: 55 to 75 F	small portable pump to empty
Wind: 0 to 3 mph		the contents into a gully north
Due to a malfunction in equip-		of his facility. The remaining
ment, the manure storage pit		grass was harvested during the
could not be emptied in the stand-		test.
ard manner. The operator used a		

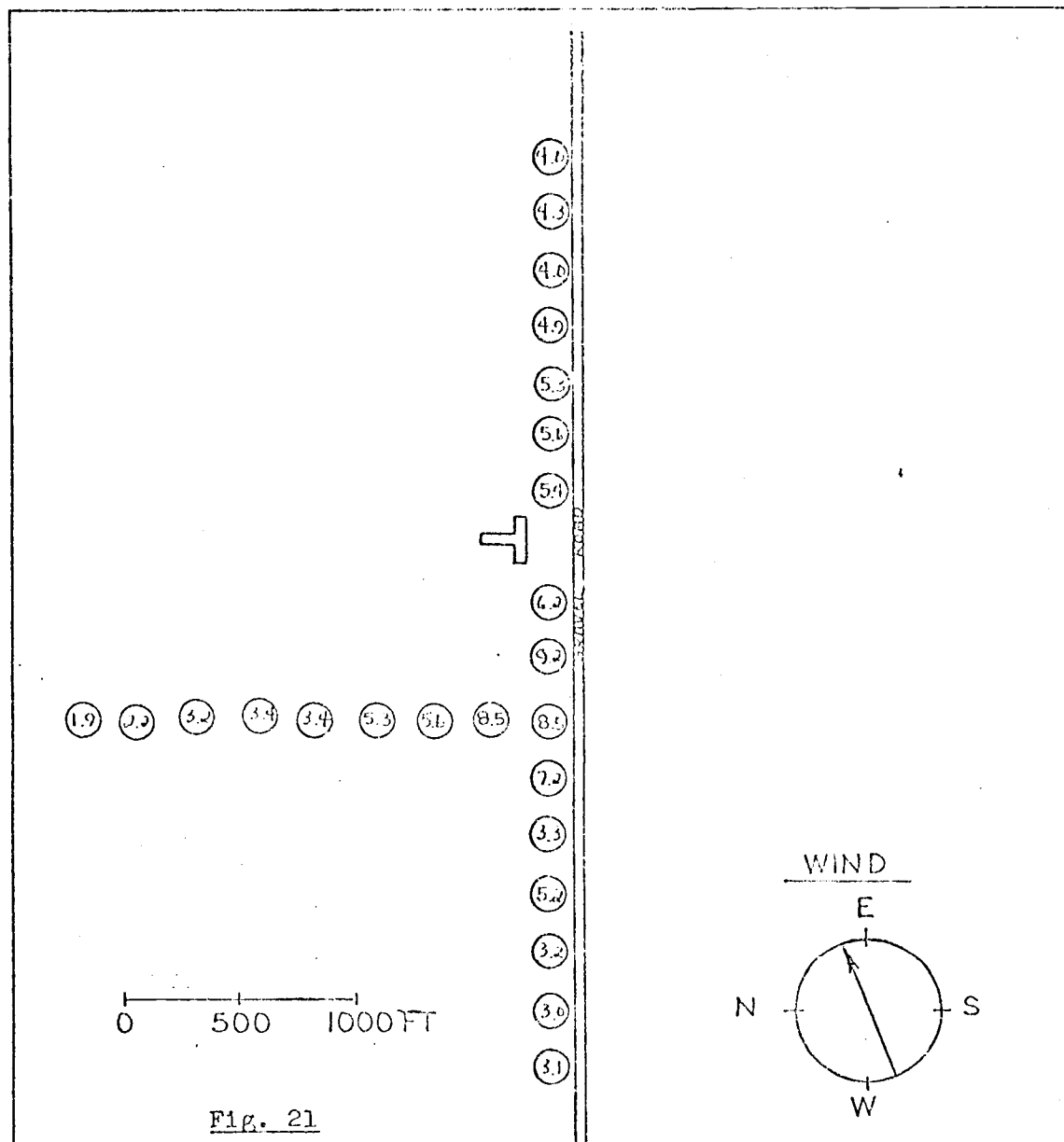


Fig. 21

August 4 to 7	Temp: 60 to 78 F	
Wind: 0 to 3 mph		
The sky was clear and sunny.		
Only stubble remained on all of		
the surrounding fields.		

VIII

SUMMARY AND CONCLUSIONS

Manure covered surfaces commonly associated with livestock production facilities are contributors to the ammonia content of the atmosphere. Ammonia is usually removed from the atmosphere via three basic pathways: 1) absorption by surface waters, 2) folial absorption, and 3) soil absorption. These elements are the basic components of a natural system through which the ecosystem cycles atmospheric ammonia.

The system is complex due to the presence of many interrelated factors. The effects of these factors upon the system components is of a dynamic nature, and thus, the system appears to be continually changing. An understanding of the system can be obtained, though, if the general characteristics of the system components are understood. A knowledge of the component characteristics helps establish the relative significance of the components and to develop an overall system view.

The conceptual view of the system is as follows. Ammonia is volatilized from manure covered surfaces into the atmosphere, and once in the atmosphere, the ammonia can be absorbed by surface waters. If the atmospheric concentration is high, enough ammonia can be absorbed to cause

eutrophication. The other system components usually serve as sinks, and therefore, their significance is determined by the degree to which they can lower the atmospheric concentration.

The basis for developing an environmental management philosophy evolves from this viewpoint. The pollution potential at any location is not merely related to the amount of ammonia which was volatilized from the source. Conceivably a greater pollution hazard could exist in the vicinity of a low ammonia volatilizing source than in similar proximity to a higher one. The activities displayed by folial absorption, soil absorption, atmospheric dispersion, and source production must be considered compositely.

Another factor which should be considered is time of day. When introducing an ammonia laden material into the environment the time of day could be crucial. Foliage and soil are capable of assimilating large quantities of ammonia during daylight hours, but in the dark this capacity diminishes. This would seem to suggest the best time of release to be early morning hours. Also to be considered, though, is the possibility of vertical mixing in the atmosphere during the night. After sundown, the upper atmosphere cools and warm air near the ground surface rises.

Existing facilities can be monitored by the methods set forth in this experiment. Surface water absorption

potentials can be determined from data collected from acid absorption traps, keeping in mind that acid will absorb approximately twice as much ammonia as distilled water. The absorption potential can be lowered by modifying the activity of the other system components. The effects of proposed facilities can be estimated by empirical methods. The activity of each component can be roughly determined from observation, and this, used in conjunction with data from similar situations, can be used to estimate the potential environmental impact.

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