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Identifying Sources of Subsurface Nitrate Pollution with Stable Nitrogen Isotopes

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IDENTIFYING SOURCES OF SUBSURFACE NITRATE POLLUTION WITH STABLE NITROGEN ISOTOPES

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques, and new technologies through which optimum use of the Nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate, and management of pollutants in ground water; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows; (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control or abate pollution from the petroleum refining and petrochemical industries; and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

This report contributes to that knowledge which is essential in order for EPA to establish and enforce pollution control standards which are reasonable, cost effective, and provide adequate environmental protection for the American public.

William C. Galegar

William C. Galegar
Director

ABSTRACT

This report describes the methods, results, conclusions, and recommendations of an investigation of a technique to identify sources of nitrate ions in ground water. A discussion of the theoretical basis of the technique is also provided. Over 300 soil and ground-water samples were collected for this study. The samples are from numerous sites from within the United States, representing a variety of environmental conditions. The nitrate ions in 66 of these samples were separated from other nitrogen species, converted to nitrogen (N_2) gas, purified, and analyzed to determine the nitrogen-isotope ratio ($^{15}N/^{14}N$). These data were combined with the results of analyses performed previously by Jones (1) and Kreitler (2). Standard statistical techniques were used to analyze the observed variations in $\delta^{15}N$ values, with respect to several nitrate-ion sources and various environmental factors. It was found that nitrate ions from feedlots, barnyards, and septic tanks can be distinguished from natural soil nitrate ions on the basis of the $\delta^{15}N$ values. These nitrate ions from various sources cannot, however, be distinguished from each other. Environmental factors contributed to the observed variation in $\delta^{15}N$ values.

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SECTION 1

INTRODUCTION

GOALS AND APPROACH OF THIS STUDY

This report describes the results of an investigation of a technique to identify sources of nitrate (NO_3^-) in ground water. The investigation was funded by the U.S. Environmental Protection Agency.

The technique under investigation was developed previously by Radian Corporation under EPA Grant 16060 HNI (1). It is based on the premise that nitrate in soils and ground water will have a nitrogen-isotope ratio ($^{15}N/^{14}N$) that is determined by (a) the series of reactions which formed the nitrate, and (b) the nitrogen-isotope composition of its precursors. Previous work (1, 2) has indicated that soil and ground-water nitrates that were derived from animal wastes can be distinguished from other soil nitrates on the basis of their nitrogen isotope ratios. A detailed description of the technique is presented in Section 4 of this report.

The overall objective of this study was to assess the general feasibility of using stable nitrogen isotope ratios to identify the source(s) of nitrate pollution in ground water. Within this context, two key questions were addressed:

1. For a given waste source, are the isotope ratios of nitrate-nitrogen statistically equivalent in different geographic and climatic

regions of the country? and

2. For different waste sources, is the variance of the isotope ratio means adequate to differentiate between these sources?

Particular emphasis was placed on evaluating the technique with respect to its ability to differentiate between domestic septic tank, animal feedlot, and municipal wastewater land-application (irrigation) sources of nitrate.

In pursuing this study, soil and ground-water samples were obtained from numerous sites around the United States. Emphasis was placed on acquiring sufficient numbers of samples to obtain statistically significant results. Samples were prepared and analyzed using equipment and procedures previously developed by Radian under EPA Grant 16060 NHI (1). These procedures are described in Section 5 of this report. Isotopic ratio determinations were performed at the mass spectrometer facility of the Center for Research in Water Resources, University of Texas at Austin. Standard statistical procedures were then used to evaluate the results of the analyses.

SIGNIFICANCE OF THE NITRATE PROBLEM

The presence of excessive nitrate in drinking water supplies is a well-recognized public health hazard. The best known health problem arising from nitrate consumption is methemoglobinemia, a cyanosis which is brought about by the reduction of nitrate (NO_3^-) to nitrite (NO_2^-) by bacteria in the digestive tract, followed by absorption of the nitrite into the bloodstream. There, the nitrite oxidizes the ferrous ion (Fe^{++}) in hemoglobin to ferric ion (Fe^{+++}), thereby preventing the transport of oxygen by the hemoglobin. This results in a gradual suffocation (cyanosis). It is noteworthy that infants are most

susceptible since the acidity of their stomach is considerably less than that of adults, resulting in a more favorable environment for the nitrate-reducing bacteria. The digestive system of animals such as cattle (ruminants) also is conducive to this bacterial action. Therefore, when a nitrate problem occurs, it is first reflected in health problems of cattle or human infants

It should also be noted that the whole problem of methemoglobinemia is poorly understood. The nitrate or nitrite concentration at which methemoglobinemia becomes a problem may vary widely, and is most likely influenced by some as yet unidentified factor or factors. Because of the methemoglobinemia problem, the U.S. Environmental Protection Agency has established a maximum contaminant level (MCL) for nitrate (as nitrogen) of 10 milligrams per liter (mg/ℓ). This MCL was established for drinking water supplies, under the National Interim Primary Drinking Water Regulations (3).

Another potential health effect of nitrate relates to cancer. Nitrate and/or nitrite can react with secondary amines to form nitrosamines, many of which are carcinogenic. Numerous studies indicate a possible link between nitrate and cancer (4, 5,6).

If ground waters become contaminated with nitrate as a result of man's activities, a public health hazard could arise. Moreover, some ground waters naturally contain high levels of nitrate. The technique under investigation in this study has been proposed as a means of identifying the source(s) of nitrate in ground water. This investigation was aimed toward identifying any limitations and potential applications of the technique.

SECTION 2

CONCLUSIONS

1. Nitrates from septic tanks, feedlots, and barnyards can be distinguished from natural soil nitrates on the basis of the isotopic compositions.

2. Nitrates from septic tanks, feedlots, and barnyards cannot be distinguished from each other.

3. The average nitrogen isotope ratio del value ($\delta^{15}N$) of nitrates from municipal wastewater irrigation sites falls between the average for feedlots and septic tanks and the average for natural soil nitrates.

4. The range of $\delta^{15}N$ values of nitrates from municipal wastewater irrigation sites overlaps the range for feedlots and septic tanks and the range for natural soil nitrates.

5. Therefore, nitrates from municipal wastewater irrigation sites cannot be distinguished from nitrates derived from septic tanks, feedlots, barnyards, or from natural soil nitrates.

6. The isotopic composition of nitrates from municipal wastewater irrigation sites suggests that these nitrates are a mixture of nitrates derived from the waste and nitrates derived from natural soil processes.

7. Environmental factors influence the $\delta^{15}N$ value of soil and ground-water nitrates.

8. Only about 30 percent of the observed variation in $\delta^{15}N$ can be attributed to the environmental factors assessed in this study.

9. Identifying causal relationships between $\delta^{15}N$ values and specific environmental factors will require additional research.

10. The ranges of $\delta^{15}N$ values for specific nitrate source categories overlap.

11. Distinguishing between nitrates from animal or human wastes and natural soil nitrates will therefore require a comparison of mean $\delta^{15}N$ values.

12. Analysis of large numbers of samples will improve the ability to distinguish between mean $\delta^{15}N$ values.

13. The isotope technique for identifying sources of nitrate is not suitable for use as a "routine" procedure, because:

    a. sophisticated analytical equipment, which is not commonly available, is required to prepare and anlyze samples; and

    b. a high level of familiarity with the technique, the chemistry of nitrogen, and nitrogen isotopic systematics is required on the part of the investigator, in order to insure the proper analysis of samples and interpretation of results.

SECTION 3

RECOMMENDATIONS

Additional information is needed to make the nitrogen isotope ratio technique a generally applicable tool for tracing nitrate sources. Studies should be performed to determine whether variables such as soil oxidation-reduction potential (Eh), pH, and bacteria exert a major influence on the del value.

These studies also should include variables considered in this program, e.g. precipitation, elevation, soils, etc. Correlation studies similar to those used in this study should be performed on the larger data base to determine whether variations in del value can be explained.

If these expanded studies are successful in explaining the del values, the results must be studied to develop a practical scheme which would permit the sampling of a location to identify the source of subsurface nitrate. This might require on-site measurements of parameters such as soil Eh and pH.

SECTION 4

RATIONALE FOR TRACING NITRATE VIA STABLE ISOTOPE RATIOS

NITROGEN ISOTOPE ABUNDANCE

There are two naturally occurring, stable (non-radioactive) isotopes of nitrogen, ^{14}N and ^{15}N. The nucleus of a ^{14}N atom contains seven protons and seven neutrons, while the nucleus of a ^{15}N atom contains seven protons and eight neutrons. The nitrogen gas in air is composed of 99.632 percent ^{14}N and 0.368 percent ^{15}N. Junk and Svec analyzed air samples from many localities and found no significant variation in the isotope composition of atmospheric nitrogen (7). In other nitrogen-containing compounds the ^{15}N occurrence may be different from that in air, however.

The ^{15}N content of any particular nitrogen species is expressed in terms of the nitrogen isotope ratio del value (δ), in parts per thousand (ppt), defined as follows:

$$\delta^{15}N = \frac{^{15}N/^{14}N\ (\text{sample}) - {}^{15}N/^{14}N\ (\text{air})}{^{15}N/^{14}N\ (\text{air})} \times 1000$$

It can be seen that the nitrogen isotope ratio in air is used as a reference, and therefore has a δ value of zero. Substances with a higher ^{15}N content than air will have a positive δ value, while substances with a lower ^{15}N content than air will have a negative δ value. Del values of naturally occurring substances generally range from -20 to +20. Selected nitrogen isotope ratios determined for various substances are shown in Table 1

TABLE 1. NITROGEN ISOTOPE RATIOS FOR VARIOUS SUBSTANCES*

Sample (Source)	$\delta^{15}N$ (ppt)
Inorganic Nitrogen	
Chile nitratite (Chile)	-2.6
Sal ammoniac (Mexico)	+13.0
Rocks and Minerals	
Pitchblende (Canada)	-2.3
Granite (Maine)	-0.2
Oil and Gas	
Bitt No. 1 Oil (Oklahoma)	-11.5
Natural Gas (Arkansas)	-5.9
Plaisted No. 1 Oil (Oklahoma)	-3.5
Peat and Coal	
Peat (New York)	-2.8
Bituminous coal (Pennsylvania)	-0.9
Peat (Eire)	+1.9
Animal Protein	
Rat liver (Unknown)	-3.3 to +9.3
Lamb flesh (Unknown)	+5.0
Clam flesh (Atlantic Ocean)	+7.3
Marine zooplankton (Unknown)	+10.0
Marine fish flesh (Unknown)	+15.0
Plant Protein	
White Clover leaves (Local)	-6.5
Dandelion leaves (Local)	-2.8
Oats (Unknown)	+6.2
Seaweed (Unknown)	+7.0

*From Jones (1) and Kreitler (2).

An isotope ratio mass spectrometer is used to measure δ values.

ISOTOPE FRACTIONATION MECHANISMS

Differences in the nitrogen isotope ratios of different species occur because of the difference in mass between ^{15}N and ^{14}N atoms. Since an atom of ^{15}N contains an extra neutron, it has a mass approximately 7 percent greater than a ^{14}N atom. This greater mass causes ^{15}N atoms to behave slightly differently from ^{14}N atoms in physical and chemical processes. These behavioral differences can produce variations in the $^{15}N/^{14}N$ ratios of different nitrogen compounds (isotopic fractionation).

The isotopic ratio of a nitrogen compound is the result of:

1. Physical fractionation;
2. Chemical equilibrium fractionation;
3. Chemical kinetic fractionation; and
4. The original isotopic composition of the material from which the compound was formed.

Physical fractionation, chemical equilibrium fractionation, and chemical kinetic fractionation are all important in the isotopic fractionation of nitrogen in natural biogeochemical systems. However, their relative importance is only beginning to be understood.

Physical fractionation can occur through diffusion, evaporation, and sublimation. In diffusion the light isotope (^{14}N) will have a higher velocity. In evaporation and sublimation the lighter isotope will have a higher vapor pressure.

Chemical equilibrium fractionation (isotope exchange equilibrium) is the tendency of an isotope to concentrate in one species of a chemical equilibrium reaction. When two chemical species

are in equilibrium, the isotopic distribution also reaches an equilibrium (i.e., the isotopic ratio in one species may not be the same as the ratio in the the other species). The distribution of isotopes between the species is dependent on the different energy levels of the molecules, and is described by the isotope equilibrium constant (K or α). Isotope equilibrium constants may be calculated or determined experimentally.

The calculated isotope equilibrium constant is "K", where

$$K = \frac{[\text{Products}]}{[\text{Reactants}]}$$

The experimentally determined isotope equilibrium constant is "α". K and α are related as follows:

$$\alpha = K^{1/n},$$

where n is the number of equivalent exchangeable atoms in the reaction.

Isotope equilibrium constants have been calculated from partition functions and/or determined for several nitrogen equilibrium reactions relevant to surface or near-surface conditions. These are listed in Table 2.

The meaning of the isotope equilibrium constant may be illustrated using the second reaction in Table 2:

$$^{14}NH_{4(aq)} + {}^{15}NH_{3(g)} = {}^{15}NH_{4(aq)} + {}^{14}NH_{3(g)}$$

This is the nitrogen isotope exchange equilibrium reaction when ammonium is in chemical equilibrium with gaseous ammonia (ammonia volatilization). From the equation for the calculated equilibrium

TABLE 2. ISOTOPE EQUILIBRIUM CONSTANTS*

Reaction	T°K	Isotope Equilibrium Constant	
		Calculated (K)	Experimental (α)
$^{14}NH_4 + \frac{1}{2}(^{15}N_2) = {}^{15}NH_4 + \frac{1}{2}(^{14}N_2)$	298.1	1.023	- -
$^{14}NH_{4(aq)} + {}^{15}NH_{3(g)} = {}^{15}NH_{4(aq)} + {}^{14}NH_{3(g)}$	298.1	1.035	1.034 ± 0.002
$^{14}NH_4 + {}^{15}NO = {}^{14}NO + {}^{15}NH_4$	298.1	1.038	- -
$\frac{1}{2}(^{14}N_2) + {}^{15}NH_3 = \frac{1}{2}(^{15}N_2) + {}^{14}NH_3$	298.1	1.012	- -
$^{14}NH_{3(aq)} + {}^{15}NH_{3(g)} = {}^{15}NH_{3(aq)} + {}^{14}NH_{3(g)}$	298.1	- -	1.005
$^{15}NH_{3(aq)} + {}^{14}NH_{4(aq)} = {}^{14}NH_{3(aq)} + {}^{15}NH_{4(aq)}$	298.1	- -	1.029

*From Kreitler (2).

constant, the second reaction in the table is written:

$$K = 1.035 = \frac{(^{15}NH_4)_{(aq)} \quad (^{14}NH_3)_{(g)}}{(^{14}NH_4)_{(aq)} \quad (^{15}NH_3)_{(g)}} = \frac{(^{15}NH_4/^{14}NH_4)_{(aq)}}{(^{15}NH_3/^{14}NH_3)_{(g)}}$$

This equation states that there should be a 35 parts per thousand (ppt) enrichment of ^{15}N in aqueous ammonium compared to ammonia gas.

In the equations in Table 2 there is only one exchange atom (i.e., n = 1), and the relation between K and α is therefore:

$$\alpha = K.$$

For the second reaction in Table 2,

$$\alpha = 1.034 = \frac{^{15}N/^{14}N\ (NH_4)}{^{15}N/^{14}N\ (NH_3)}$$

This equation states that a 34 ppt enrichment of ^{15}N in ammonium compared to ammonia, was determined.

Chemical kinetic fractionation describes the tendency of the two isotopes to react at different rates when undergoing the same reaction. If all the reactants are not converted into products (because of side reactions or incomplete reactions) the nitrogen isotope ratio will differ between the reactants and products. The particular isotope ratio for the products will depend on (a) the initial isotope ratio of the reactants, and (b) the particular reaction which occurred.

It should be noted that environmental parameters can affect isotope fractionation. For example, high temperatures (hundreds of degrees) tend to lessen the tendency of the two isotopes to react at different rates. Thus, less isotope fractionation would be expected at high temperatures. This is because the slight differences in energy levels (due to the slightly different masses of the nitrogen atoms) become less important as the total energy of the system is increased by the added heat (molecular motion). Bacterially-aided reactions are another example of environmental influence on isotope fractionation. Such reactions often exhibit significant fractionation.

The kinetic fractionation factor B is used to describe isotopic fractionations in nonequilibrium reactions. Table 3 lists the values for B that have been determined for several nitrogen reactions, as summarized by Kreitler (2). Since no single convention for the usage of B has been established, the equation defining B is given for each of the reactions listed in Table 3. For example, the equation for B for the first step of the nitrification process (oxidation of ammonia to nitrite; reaction #2 in Table 3) is written:

$$B = \frac{^{15}N/^{14}N\ (NH_3)}{^{15}N/^{14}N\ (NO_2)} = 1.026$$

The value given for B, 1.026, indicates that there is a 26 ppt enrichment of ^{15}N in ammonia relative to nitrite.

NITROGEN IN THE ENVIRONMENT

The Nitrogen Cycle

The earth may be viewed as having a natural "metabolism", in which materials are continually circulated through the atmosphere; to the oceans via streams; in and out of the biota via

TABLE 3. KINETIC FRACTIONATION FACTORS FOR VARIOUS NONEQUILIBRIUM REACTIONS*

Reaction	Equation for B	Measured Values of B
1. Nonsymbiotic bacterial nitrogen fixation.	$B = \frac{^{15}N/^{14}N \text{ (atmospheric } N_2)}{^{15}/^{14}N \text{ (fixed nitrogen)}}$	1.0022-1.004
2. Nitrification: two-step bacterial oxidation of ammonia to nitrate. Only the first step has been measured.	$B = \frac{^{15}N/^{14}N \text{ } (NH_3)}{^{15}N/^{14}N \text{ } (NO_2)}$	1.026
3. Denitrification: bacterial reduction of nitrate to nitrogen gas.	$B = \frac{^{15}N/^{14}N \text{ } (NO_3)}{^{15}N/^{14}N \text{ } (N_2)}$	1.0173-1.02
4. Cation exchange of ammonium with exchange resins or kaolinitic clay.	$B = \frac{^{15}N/^{14}N \text{ (solution } NH_4)}{^{15}N/^{14}N \text{ (adsorbed } NH_4)}$	0.99926-0.99922
5. Anion exchange of nitrate with exchange resin.	$B = \frac{^{15}N/^{14}N \text{ (solution } NO_3)}{^{15}N/^{14}N \text{ (adsorbed } NO_3)}$	1.0021

*Reported by Kreitler (2).

photosynthesis, growth, and decay; and through the lithosphere via sedimentation, weathering, and erosion. Each element follows a particular path or set of pathways through the natural system. The paths are determined by the biogeochemical and physical properties of the elements. Each has its own natural biogeochemical cycle.

The global nitrogen cycle is extremely complex, and many of its aspects are poorly understood. A simplified schematic of the nitrogen cycle is shown in Figure 1. The figure shows the various nitrogen reservoirs (e.g., the atmosphere, the biosphere, sedimentary rocks, etc.) and the gross aspects of nitrogen transfer between these reservoirs.

The major nitrogen reservoir is the atmosphere. In this respect, nitrogen is somewhat unique. Other elements for which global cycles have been investigated (e.g., carbon, sulfur, and phosphorus) have their major inventories in the sedimentary rock reservoir (8). Several nitrogen species are significant in the atmosphere. Of these, however, nitrogen gas is by far the most abundant, accounting for more than 99.999 percent of all atmospheric nitrogen. Ammonia, ammonium, and oxides of nitrogen are also present, but together they account for less than 0.001 percent of the atmospheric nitrogen (8).

The transfer of nitrogen from one reservoir to another is indicated in Figure 1 by the various arrows. The mechanisms by which nitrogen is transferred are very complex, involving a large number of pathways and many nitrogen species. Many of the mechanisms are only beginning to be understood. The situation is complicated by such factors as the recycling of nitrogen in the biosphere, the complex photochemical reactions involving nitrogen oxides in the atmosphere, and the influence of man's

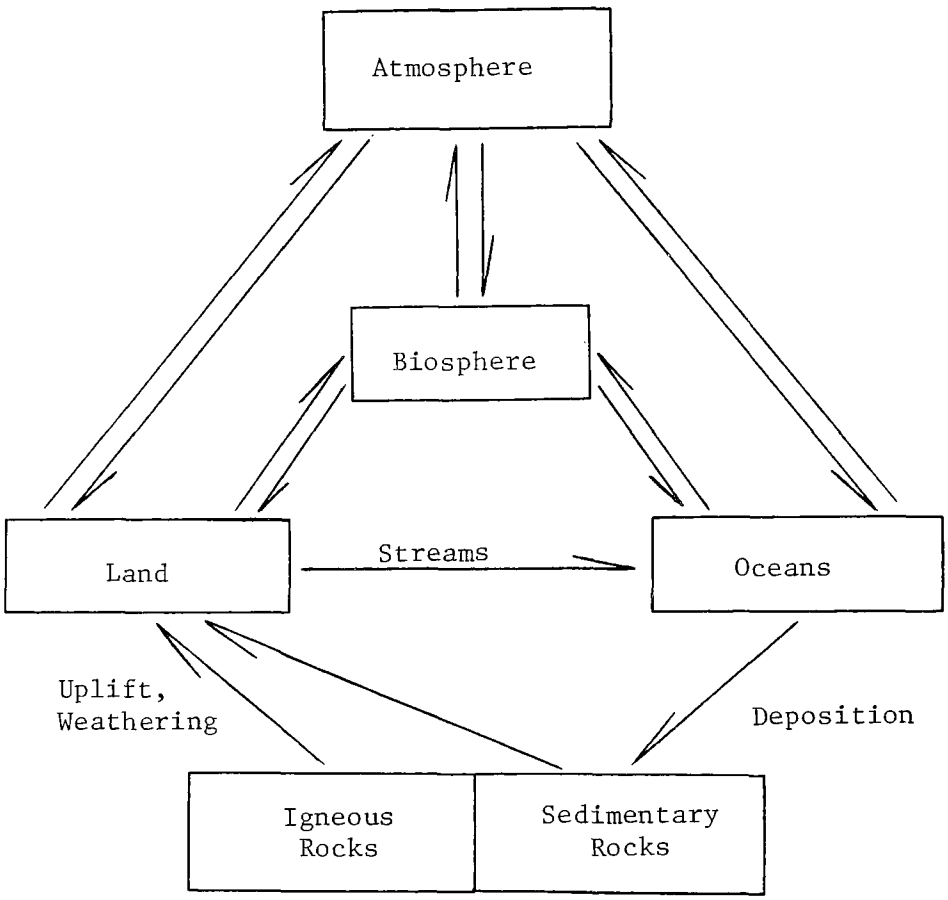

Figure 1. Simplified Schematic of the Nitrogen Cycle.

activities (e.g., fixation of atmospheric nitrogen gas for fertilizer manufacture).

Nitrate In the Terrestrial Environment

In the context of this study, the significant portions of the nitrogen cycle are those that lead to the presence of nitrate (NO_3^-) in soils and ground waters.

The major input of nitrogen to the soil-water-biomass subsystem of the nitrogen cycle is the fixation of atmospheric N_2. This is accomplished primarily through natural bacterial fixation. Within the last 100 years, however, the demand for fixed nitrogen compounds as fertilizers has grown to the point where the amount of industrially fixed atmospheric N_2 nearly equals the amount fixed naturally (8).

Other somewhat less important inputs to the soil-water-biomass system also exist. Ammonium and nitrate are directly deposited on the land surface by rainout of both natural and pollutionally derived ammonium nitrate and ammonium sulfate. Estimates of the rate of addition of nitrogen by this mechanism are very uncertain, but some estimates suggest that it may be significant.

Nitrogen may also enter the soil-water-biomass system via the weathering of nitrogen-bearing rocks. This appears to be a very minor source, however. The rate of input, estimated on the basis of global weathering rates and the average nitrogen contents of rocks, is only about 2 percent of the rate of input from atmospheric sources (8).

Assuming the atmosphere to be the important source of nitrogen, several reaction paths for the production of nitrate can be visualized. The most reasonable paths are shown in Figure

2. These include (a) nitrate from fertilizer, (b) nitrate due to fixation by free-living bacteria, (c) nitrate from decayed plants, (d) nitrate from legumes, (e) nitrate from animal wastes, and (f) nitrate from human wastes. Not all possible paths are shown, e.g., rainout of atmospheric ammonium nitrate.

An examination of Figure 2 shows that the overall reaction schemes can be very complex due to possible recycling of the nitrate. This is only true at depths within the root zone of plants, however. Once the nitrate is flushed beyond the root zone it should be unavailable for further recycling. It should be noted that many of the reactions shown are caused or aided by bacteria.

It can be seen in Figure 2 that the ammonia and nitrate from human and animal wastes are not assumed to participate in recycling. This is because these wastes are concentrated at particular sites (e.g., barnyards or septic tanks) where plants either do not grow or are not numerous enough to consume significant amounts of the nitrate.

NITRATE SOURCE DETERMINATION

The technique under investigation in this study relies on the dependence of the nitrogen isotope ratio of a particular compound (specifically, nitrate) on the type of reaction or series of reactions which formed that compound. A complete knowledge of all possible nitrate formation pathways, and of the nitrogen isotopic fractionations that occur along those pathways, would enable one to predict the isotopic composition of any particular nitrate sample. Such detailed information on the nitrogen isotope behavior of nitrate and its precursors does not exist, however.

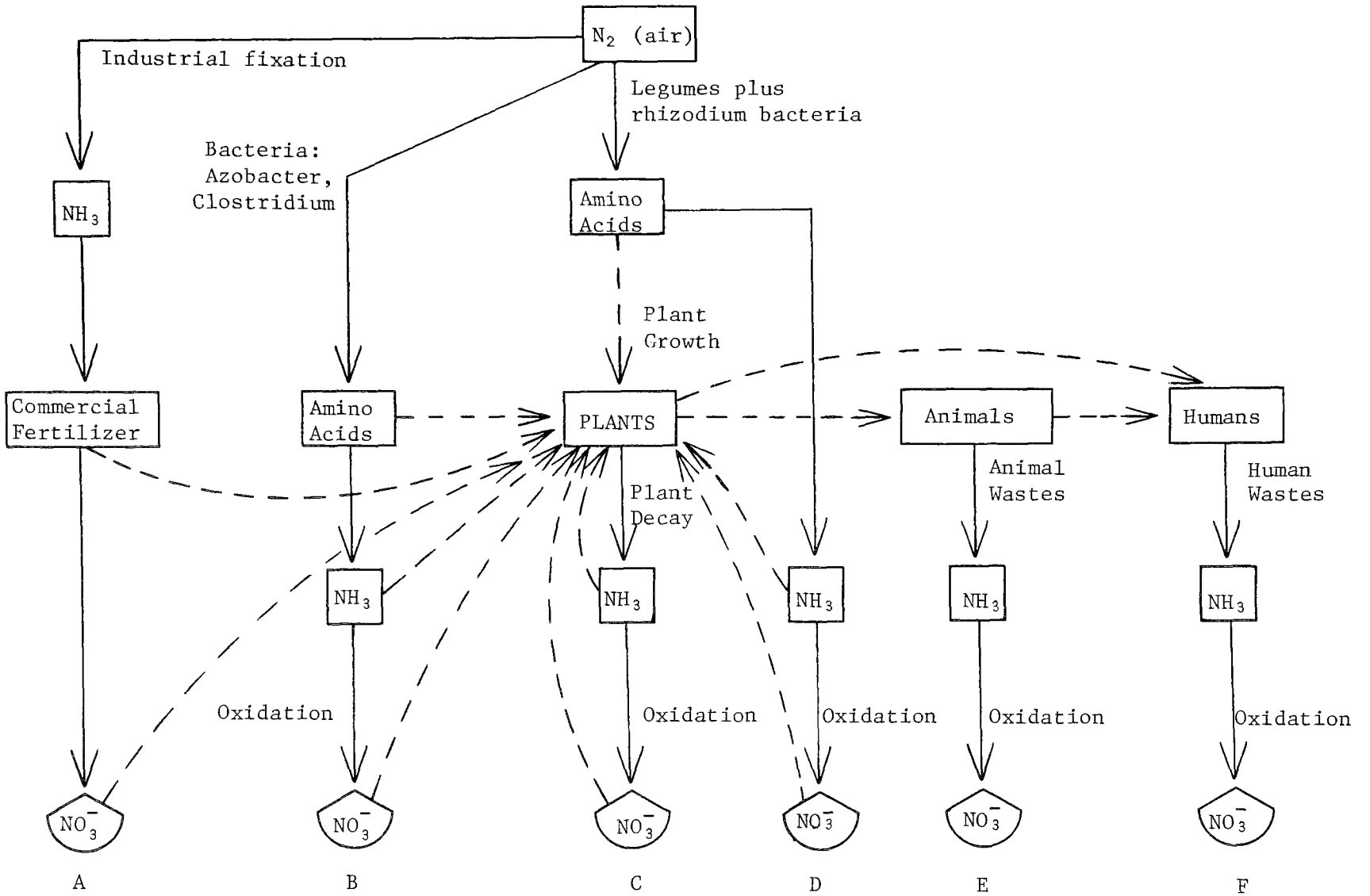

Figure 2. Mechanisms of Nitrate Formation.

The technique for identifying sources of nitrate in ground water is based on more of a "black box" approach. It is sufficient to know (a) that isotopic fractionations exist for various reactions (such as those presented in Tables 2 and 3), and (b) that nitrate may be formed by different reaction pathways (such as those shown in Figure 2) that depend, at least in part, on the source of the nitrogen. As an example, nitrate formed during the manufacture of fertilizer should go through a different series of reactions than nitrate formed from animal wastes, and should therefore exhibit a different nitrogen isotope ratio.

Jones (1) and Kreitler (2) tested this hypothesis in Runnels County, Texas. They found that nitrates derived from septic tanks and animal wastes had a different nitrogen isotope ratio from nitrates derived from "natural" processes (i.e., bacterial fixation and plant uptake, growth, and decay). This was demonstrated by obtaining samples of soil nitrate from sites where the source of the nitrate could be reasonably predicted. Nitrate derived from the decomposition of animal wastes (including human wastes) was found to have a characteristic isotopic composition ($\delta^{15}N$) of from +10 ppt to +22 ppt, while nitrate derived from natural soil-bacteria-vegetation systems had an isotopic composition of from +2 ppt to +8 ppt.

It is possible that these results are applicable only to the particular systems studied in Runnels County, Texas. Environmental factors, such as climate and soil type, could affect the isotopic composition of a soil nitrate sample by affecting the types of bacteria present and the reaction pathways leading to nitrate formation.

One purpose of this study is to determine whether environmental factors influence the isotopic composition of nitrates derived from a particular waste source category (e.g., septic tanks). This is accomplished by analyzing soil and ground-water

samples obtained from various sites across the country, representing a range of environmental conditions.

The other major goal of this study is to determine the extent to which nitrates from various sources can be differentiated on the basis of their isotopic composition. The work of Kreitler and Jones indicated that for one geographic area nitrate from animal and human wastes can be distinguished from nitrate derived from "natural" soils or fertilizers. This study addresses the question of whether or not nitrate from various sources can be distinguished on the basis of nitrogen isotope ratio for the country as a whole.

OTHER STABLE ISOTOPES AS TRACERS

It may be possible to identify sources of ground-water contamination using stable isotopes of elements other than nitrogen. In the case of nitrate (NO_3^-), there is only one other element (oxygen) to consider. Other contaminants (e.g., phosphates, sulfates and sulfides, detergents, and other organic compounds) contain elements for which isotopic studies may prove useful, however. These elements include hydrogen, oxygen, carbon, sulfur, chlorine, and some trace metals.

The usefulness of these elements as waste-source indicators is difficult to assess. It should be remembered that for stable isotope identification of waste sources to be successful, it is necessary that relatively unique isotope fractionations exist for given waste types or waste sources. This has not been established for the elements mentioned above.

A complete theoretical evaluation of the potential for using stable isotopes of elements other than nitrogen is beyond the scope of this study. Rather, brief discussions are provided

for several elements that are considered to be "possible candidates" for this use.

Hydrogen

There are two stable isotopes of hydrogen, ^{1}H and ^{2}H (^{2}H is commonly called deuterium, and is designated by the symbol "D"). The nucleus of a ^{1}H atom contains a single proton, while the nucleus of a D atom contains a proton and a neutron.

The relative mass difference between ^{1}H and D is larger than that of any other pair of stable isotopes of other elements: the mass of the ^{1}H nucleus is essentially half that of the D nucleus. Because of this, hydrogen exhibits the largest fractionations of any stable isotopes. Fractionations of several hundred parts per thousand have been observed for various earth materials (9).

The average natural abundances of the stable hydrogen isotopes are as follows:

^{1}H: 99.9844%
D: 0.0156 %.

Hydrogen is an extremely abundant element in natural biogeochemical systems. It occurs in water, clay minerals, dissolved inorganic compounds and organics. Appreciable fractionations have been observed in isotope exchange equilibrium reactions, and significant kinetic fractionations seem possible in biochemical processes (e.g., photosynthesis and bacterial production of H_2 and CH_4)(9).

Carbon

Carbon has two stable isotopes: ^{12}C and ^{13}C. Carbon-12 accounts for 98.89 percent of natural carbon. Natural frac-

tionations of greater than 10 percent have been observed (9). Extensive fractionations take place in the biosphere, during photosynthesis and metabolism. Environmental factors (e.g., temperature and pH) have also been observed to influence carbon isotope fractionations (9).

Carbon occurs extensively in the environment as organic compounds, carbon dioxide (CO_2)gas, and bicarbonate (HCO_3^-) and carbonate (CO_3^-) ions. Kinetic fractionations are significant in the system: atmospheric CO_2 - dissolved HCO_3^- ions - Calcium carbonate ($CaCO_3$) (9).

Oxygen

Oxygen has three stable isotopes. Their natural abundances are as follows:

^{16}O: 99.763%
^{17}O: 0.0375%
^{18}O: 0.1995%

In oxygen stable isotope studies the $^{18}O/^{16}O$ ratio is usually measured, due to the higher abundance and greater mass difference (9).

Oxygen plays a critical role in natural biogeochemical processes. It is the most abundant element on earth and occurs in gaseous, liquid, and solid compounds. Natural variations in the $^{18}O/^{16}O$ ratio of up to about 10 percent have been measured.

Isotope equilibrium exchange fractionations are significant in inorganic geochemical systems. The $^{18}O/^{16}O$ ratios of mineral pairs are temperature sensitive, and oxygen isotope studies have been used extensively to estimate the "temperature of formation" of various mineral samples. Chemical kinetic fractionations of

oxygen isotopes occur during biochemical processes (e.g., photosynthesis and respiration)(9).

Sulfur

There are four stable isotopes of sulfur: ^{32}S, ^{33}S, ^{34}S, and ^{36}S. ^{32}S and ^{34}S are most abundant:

$$^{32}S = 95.02\%$$
$$^{34}S = 4.21\%$$

These are the isotopes that are generally of interest in sulfur isotope studies.

Sulfur is present in nearly all biogeochemical environments, in a number of forms including sulfides, organic substances, elemental sulfur, and sulfates. Natural variations in $^{34}S/^{32}S$ ratios on the order of 15 percent have been measured. Kinetic effects and isotope exchange reactions both produce isotope ratio variations. Kinetic effects are particularly noticeable in biochemical reactions, such as the bacterial reduction of sulfate to hydrogen sulfide (H_2S). Isotope exchange between sulfate and sulfide and between different sulfide species is significant in geochemical systems (9).

Chlorine

The natural abundances of the two stable chlorine isotopes are:

$$^{35}Cl: \quad 75.53\%$$
$$^{37}Cl: \quad 24.47\%$$

The chloride ion is a major anion in natural waters, and is present in relatively high concentrations in waste materials

(see, for example, the analysis of septic tank effluent in Table B-1, Appendix B). Theoretically one might expect to see small variations in the isotopic composition of chlorine. No significant fractionations have been observed, however (9).

Trace Elements

Many of the more environmentally significant trace elements have more than one stable isotope: chromium (4 isotopes), iron (4 isotopes), nickel (5 isotopes), copper (2 isotopes), zinc (5 isotopes), selenium (6 isotopes), silver (2 isotopes), cadmium (7 isotopes), tin (10 isotopes), mercury (7 isotopes), and lead (3 isotopes). Some of these may be useful in tracing pollution sources. Little, if any, previous work has been done in this area with these elements, however.

Summary

From a theoretical standpoint, stable nitrogen isotopes appear to be most useful for identifying pollutant sources that contribute nitrate to subsurface water-soil systems. The restricted sources of nitrogen and the better defined pathways reduce the uncertainty inherent in this approach. Especially helpful in this regard is the fact that most of the nitrogen in natural soils is ultimately derived from a single source (the atmosphere) which has a uniform nitrogen isotopic composition.

SECTION 5

EXPERIMENTAL PROCEDURES

The procedures followed in selecting sampling sites and in collecting, preserving, transporting, storing, and analyzing samples are discussed below.

SELECTION OF SAMPLING SITES

Samples of soil and/or ground water were obtained from numerous sites across the United States (see Section 6). The process of selecting these sites was based primarily on a review of published literature relating to nitrate contamination of ground waters. Over 300 references were assembled in the course of this review. To the extent possible, these references were subdivided as to suspected, presumed, or known sources of the nitrate and as to their geographic distribution within the source categories. The objective of the geographic classification was not to select sampling sites in all areas of the country, but to identify sites that were representative of a wide range of environmental conditions (e.g., climate, soil type, latitude, elevation). This classification enabled numerous candidate sites to be identified.

Final site selection was based on an assessment of how well the candidate sites met the set of selection criteria described below. In some cases, inquiries were directed toward cognizant local personnel to better define the suitability of a site for sampling.

In order for a candidate site to be selected for sampling, the site must first have been characterized as having a single, identified source of environmental nitrate. Three sources of nitrate were of primary interest: domestic septic tanks, animal feedlots, and municipal wastewater land application operations. Particular emphasis was placed on finding sites where domestic septic tanks were considered to be the known or probable source of any environmental nitrate.

Additional criteria were that the final choice of sites should provide a wide geographic representation and that the geologic and soil conditions at the sites be well-characterized. Finally, the sites had to be accessible for sampling.

Fourteen sites were chosen for intensive sampling. Samples of soil and ground water were collected from these sites by Radian personnel according to the procedures discussed below. An additional five sites were selected, to be sampled by local personnel of the United States Geological Survey, various state agencies, or universities. These sites were selected primarily to provide additional geographic coverage, and were sampled less intensively than the others.

Data on five other sites were obtained from Kreitler (personal communication, 2). These data provided additional geographic coverage and enlarged the final data base, particularly for the animal waste source category. They also provided coverage of "natural" sources, i.e., sites where the nitrates were derived from the natural growth and decay of plants.

The various sites and the samples obtained from them are discussed in Section 6. More detailed descriptions of the 14 intensively sampled sites are given in Appendix B.

SAMPLING PROCEDURES

Ground-Water Samples

Ground-water samples were collected from existing wells in the vicinity of the sites whenever wells were available for sampling. In a few cases, water samples were also obtained from augered soil sampling holes. At two sites, well points were driven to collect ground-water samples.

The procedure for collecting samples from wells was straightforward. Samples were collected from points as near to the wellhead as possible. The presence of any treatment or storage systems (e.g., water softeners or pressure tanks) between the wellhead and the sampling point was noted, along with any other information about the well that was available (such as well type, use, date installed, diameter, and depth). Prior to collecting a sample, the well was pumped for a period of at least five minutes to assure the collection of a fresh water sample.

Information on well construction is needed because the manner of well completion can affect the observed $\delta^{15}N$ value of nitrate in the well water. For example, a well completed in two distinct aquifers may yield water containing nitrate from two distinct sources.

In many cases, however, details of well construction were lacking. All wells sampled were assumed to tap a single aquifer, based on observations of depth, well diameter, use, and pump size.

Water samples from augered soil sampling holes were obtained with a small peristaltic pump or by bailing with a small bucket. The holes were bailed out several times before a sample was collected. Water samples obtained with well points were collected

with a small peristaltic pump. The pump was run for several minutes before a sample was collected to flush the pump and hoses. All water samples were collected into one-liter polyethylene bottles.

Soil Samples

Most soil samples were collected using a 4-inch diameter soil auger. Some near-surface samples were obtained using a shovel. The depth intervals from which the samples were collected were recorded. Soil samples were placed in plastic bags for shipping and storage.

At one site, a set of 1.25-inch diameter cores was obtained. These samples were obtained by driving a core-barrel fitted with a tapered cutting bit. The core barrel was lined with 1.25-inch thin-wall PVC pipe. When the maximum depth had been reached, the PVC pipe, with the core-sample inside, was extracted. The core was cut into convenient lengths, and the ends of the PVC tube were sealed.

Sampling Kits

Sampling kits were sent to local personnel at the five sites not visited by Radian personnel (see Section 6). These kits were designed to supply all of the materials required for collecting a sample. Each kit consisted of a styrofoam-lined shipping container, water sample bottles, labels, data sheets, vials of sample preservative, plastic soil sample bags, and an instruction sheet.

Sample Preservation, Transport, and Storage

Water samples were preserved by adding 10 milliliters (ml) of 1 normal (N) sulfuric acid (H_2SO_4) to each liter of sample. The

samples were refrigerated, frozen, or placed on ice as soon after collection as possible. Deviations from this procedure are noted in the descriptions of the sampling sites given in Appendix B.

No preserving agents were applied to the soil samples. These samples were refrigerated and/or frozen as soon after collection as possible. Usually this was within an hour, and in no case were samples left unrefrigerated for more than eight hours. Coolers and dry ice were taken to the sites when cold storage facilities were unavailable.

The samples were shipped , by either air or surface carrier, packed in dry ice. Upon receipt in Austin some frozen samples were found to have thawed in transit, but no samples had reached ambient temperature.

All samples were kept frozen after they reached Austin. Samples were not thawed until immediately prior to analysis. Frozen samples were stored for up to nine months before being analyzed.

SAMPLE PREPARATION AND ANALYSIS

Isotope analysis is most conveniently performed on nitrogen gas (N_2). This means that all nitrate samples must be reduced to nitrogen gas, and this conversion must be performed without introducing any isotope fractionation during the sample preparation. Once the nitrate is converted to nitrogen gas, the gas must be purified to remove species such as oxygen which might damage the filaments in the mass spectrometer. The techniques which were developed for sample preparation were as follows.

Soil Sample Leaching

Prior to analysis, the soluble nitrogen species were extracted from the soil samples by leaching. A one-kilogram

aliquot of soil was placed in a 4.2 liter polyethylene wide mouth bottle. One liter of deionized water was added and the bottle was placed on an orbital shaker table for four hours.

After four hours of shaking, the sample was removed and allowed to settle for 15 to 20 minutes. A 50 ml aliquot of the supernatant liquid was analyzed for nitrate with a specific-ion electrode. Approximately 65 milligrams (mg) of silver sulfate were added to minimize chloride interference during the nitrate concentration determinations.

Those samples that yielded a leachate nitrate concentration of less than 5 mg/ℓ were not analyzed further. A concentration of at least 5 mg/ℓ was found to be necessary in order to obtain a sufficiently large nitrogen gas sample for isotopic analysis.

Those soil samples yielding a leachate nitrate concentration greater than 5 mg/ℓ were filtered using an 11-centimeter Buchner funnel and a 1,000-ml vacuum flask attached to an aspirator. Diatomaceous earth was added as a filter aid. The subsequent sample preparation procedures were identical for soil sample leachates and ground-water samples.

Sample Preparation

The procedures followed in preparing samples for nitrogen isotopic analysis were essentially the same as those described by Krietler (2). Since only the isotopic ratio of the nitrate was of interest, other species of nitrogen had to be removed. These included ammonia and organic nitrogen. Removal of these species and extraction of nitrate was accomplished using a two-stage distillation process. The apparatus used for this process is illustrated in Figure 3.

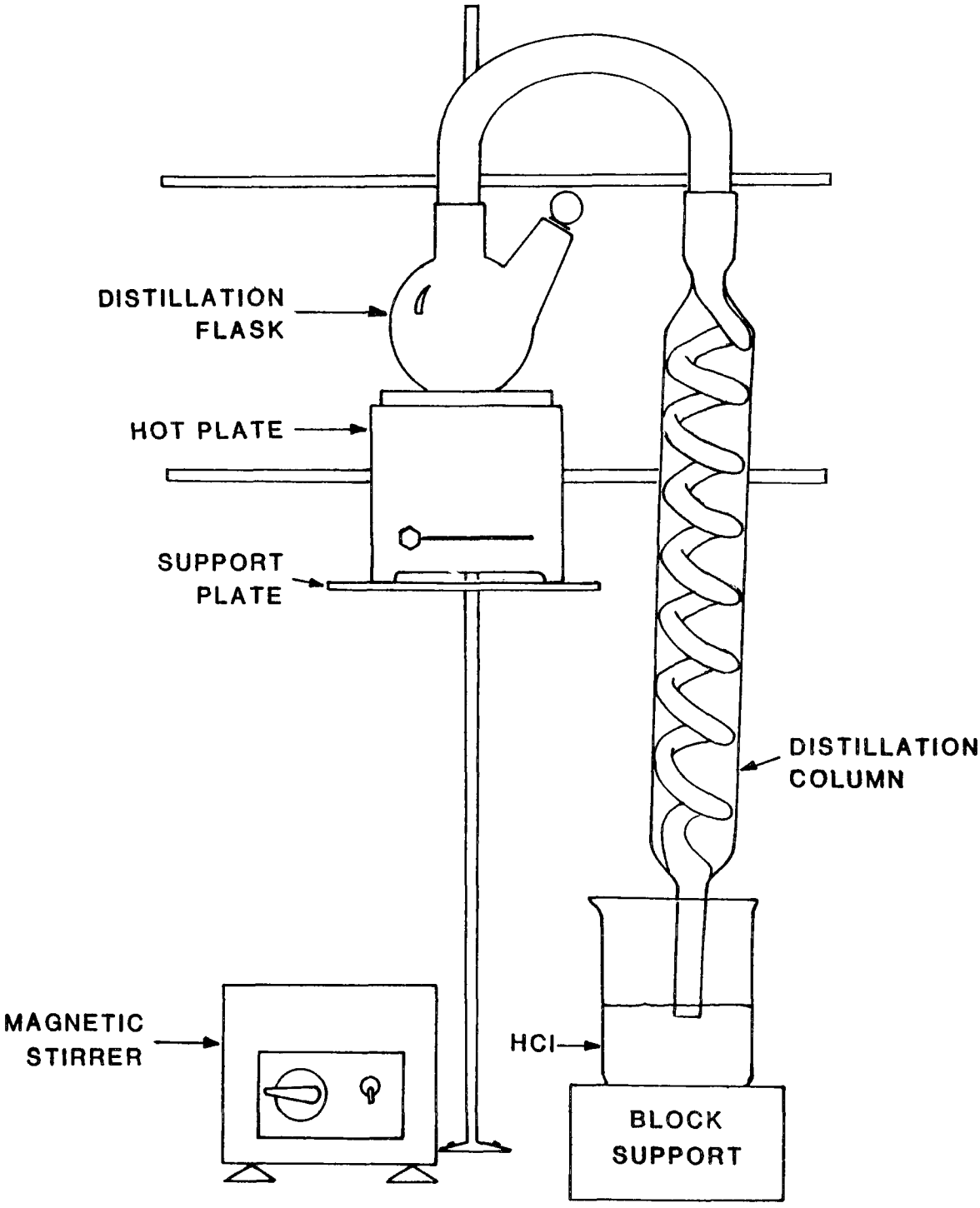

Figure 3. Distillation Apparatus Used for Removal of Interfering Nitrogen Species.

The pH of the sample (soil leachate or ground water) was first raised to between 9.5 and 10.0 by addition of powdered magnesium oxide (MgO). The solution was agitated to suspend the MgO (see Appendix A), transferred to a two-port round bottom distillation flask, and distilled until 50 ml of distillate were collected. This caused the conversion of NH_4^+ to NH_3 and the breakdown of any labile organic compounds to ammonia. At this stage, interfering forms of nitrogen were removed from the sample, having been collected in the distillate.

The hot plate was then replaced with the magnetic stirrer, and the exit port of the water-jacketed distillation column was immersed in a beaker containing 50 ml of 0.1 normal hydrochloric acid (HCl) (see Appendix A). Five grams of finely ground Devarda's Alloy (see Appendix A) were added through the side port of the flask. The flask was immediately restoppered and the solution magnetically stirred for 10 minutes without heating. This step reduced the nitrate in the sample to ammonia. Finally, the solution was redistilled until 75 ml of distillate were collected in the 0.1 HCl solution. Relatively concentrated HCl was used to insure that all ammonia was absorbed, producing an acidic ammonium chloride solution. The volume of this solution was reduced to 5 to 10 ml by heating on a hot plate at 70°C to 80°C.

Nitrogen Gas Generation

A special nitrogen gas generation and purification apparatus was required to further prepare a sample for isotopic analysis. A schematic of the apparatus is shown in Figure 4. The apparatus consists of the following: a nitrogen gas generation tube, a freeze-thaw manifold, two furnaces (containing copper and copper oxide, respectively), a Toeppler pump, a gas collection flask, two mechanical vacuum pumps, and a mercury diffusion pump.

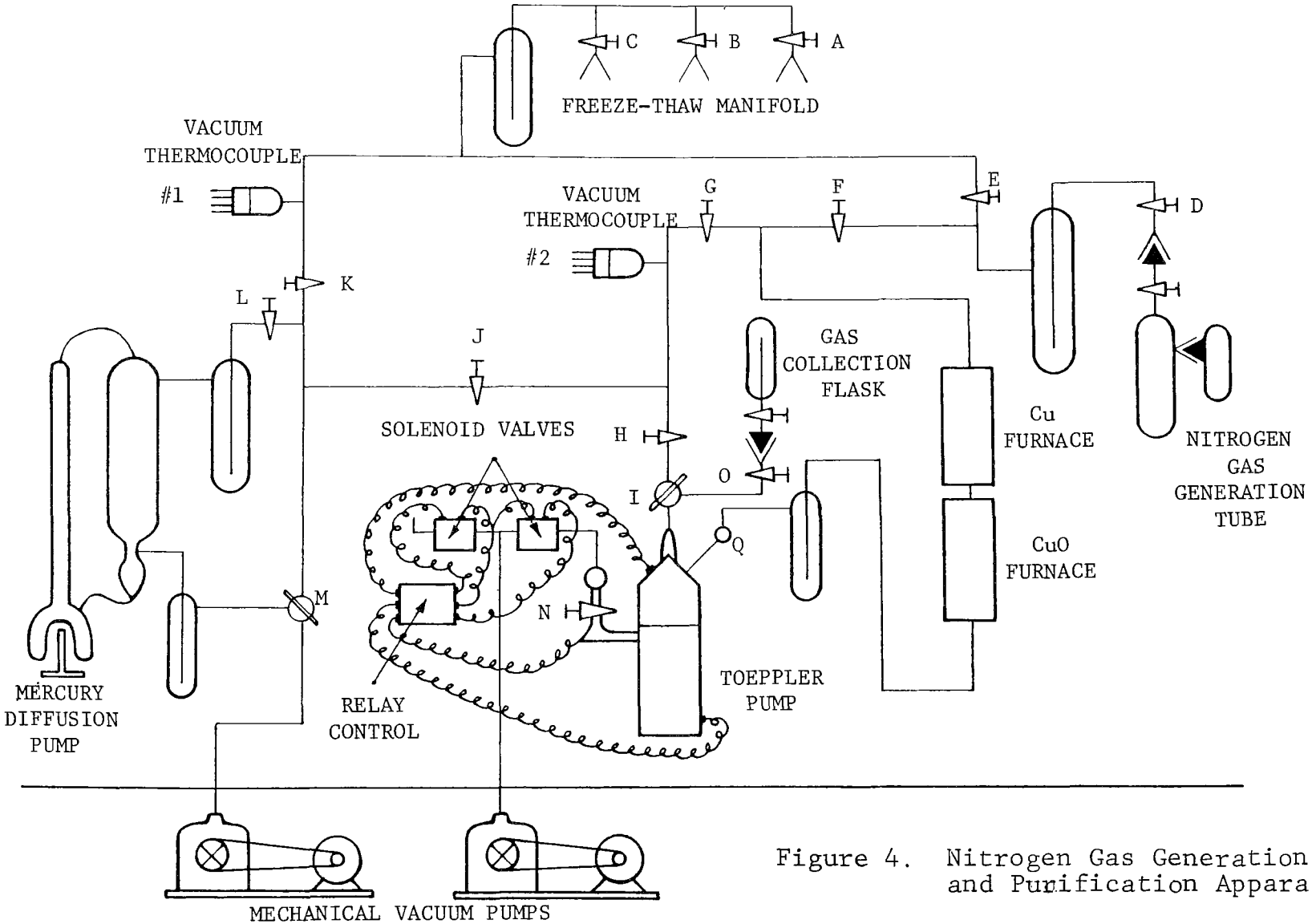

Figure 4. Nitrogen Gas Generation and Purification Apparatus.

After the ammonium chloride solution was concentrated to an appropriate volume (5 to 10 ml), as described above, it was transferred to the large volume side of a nitrogen gas generating tube (see Figure 5). Approximately 5 ml of sodium hypobromite (NaOBr) solution (see Appendix A) were added to the small side-arm. This assembly was attached to the freeze-thaw manifold of the vacuum preparation apparatus.

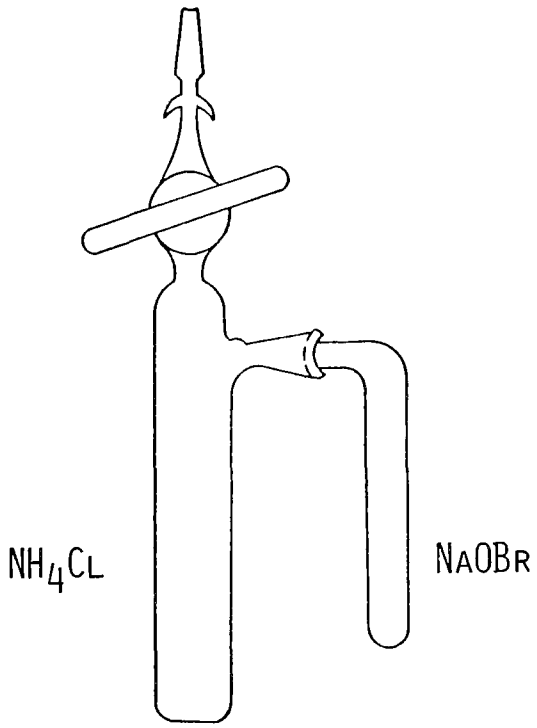

Figure 5. Nitrogen Gas Generation Tube

The two separate solutions were frozen by immersing the generating tube in an equilibrated dry ice-acetone mixture. Once frozen, the stopcock on the reaction tube was opened to the vacuum system allowing the atmosphere above the frozen solutions to be withdrawn. The stopcock was reclosed, and the

solutions were allowed to thaw. This sequence was carried out three times to completely degas the solutions and thereby eliminate atmospheric nitrogen contamination.

The nitrogen gas generation tube was transferred to the sample injection port below stopcock D (see Figure 4). With the gas generation tube isolated from the rest of the system (i.e., stopcock D closed), the side-arm was rotated 180° to drain the sodium hypobromite solution into the ammonium chloride solution. The resulting reaction liberates nitrogen gas:

$$2NH_3 + 3NaOBr \leftrightharpoons 3NaBr + 3H_2O + N_2$$

N_2 Gas Purification

When the N_2 gas generation reaction was complete, stopcocks D and F were opened and the Toeppler pump was activated (stopcocks E, G, and J closed). The nitrogen gas was pumped from the generation tube, through the furnaces, and into the tubing segment bounded by stopcocks G, I, and J. When a pressure of 3 to 5 mm Hg was accumulated (as indicated by vacuum thermocouple #2), stopcock F was closed and stopcock G was opened. A closed loop was thus created through the furnaces and the Toeppler pump.

The nitrogen gas was circulated through the hot copper furnace (T = 400°C), the hot copper oxide furnace (T = 800°C), and a liquid nitrogen cold trap for one hour. This eliminated any oxygen, carbon monoxide, and gaseous oxides of nitrogen that may have been present.

To collect the purified nitrogen sample the three-way stopcock I was turned, which redirected the purified sample into the gas collection flask. The stopcock on the collection flask as well as the stopcock on the collection port (0) were then closed and the gas collection flask removed.

Isotopic Analysis

Purified nitrogen gas samples were analyzed for their nitrogen isotope compositions by personnel of the Center for Research in Water Resources of the University of Texas at Austin. The isotope ratio was measured by comparing mass 28 ($^{14}N^{14}N$) to mass 29 ($^{15}N^{14}N$) in a double-collector, gas-source, mass spectrometer, using atmospheric nitrogen as a standard.

ANALYSIS OF STANDARDS

The analytical technique used in this study was perfected by Kreitler (2), who found that the experimental error in the technique was about ±1 ppt. Careful adherence to the details of the procedure is necessary to achieve this level of precision, however. Deviations from the procedure can introduce isotopic fractionations in the sample.

An additional check on the reliability of the analytical procedures was made in this study by running standards of known isotopic composition. A set of potassium nitrate (KNO_3) standards was supplied by Kreitler. Four of these were run through a distillation, preparation, and purification system. The resulting nitrogen gas samples were returned to Kreitler for isotopic analysis. Kreitler compared the $\delta^{15}N$ values of the investigator's standards with the results of a set of analyses that were performed on the same material in Kreitler's laboratory. Kreitler concluded that the $\delta^{15}N$ values were in agreement, within the limits of the mass spectrometer, and that the investigator's preparation techniques were acceptable.

Additional standards were periodically run during the course of the program. These standards were prepared from a stock solution of KNO_3 provided by Kreitler. A sample of atmospheric nitrogen was also run.

All of these standards, except one, yielded $\delta^{15}N$ values within ±0.5 ppt of the known $\delta^{15}N$ values. The one exception was a KNO_3 standard ($\delta^{15}N$ = -0.7) which yielded an apparent $\delta^{15}N$ value of -10.7 ppt. Calculations involving the mass of nitrogen in the standard, the mass of Devarda's Alloy in the nitrate-to-ammonium reaction, and the mass of NaOBr in the ammonium-to-nitrogen gas reaction indicated that incomplete conversion reactions were <u>not</u> the cause of this discrepancy. This data point is viewed as an analytical "outlier," since none of the known opportunities for isotopic fractionation in the analytical procedures could be blamed for the discrepancy.

As an additional check on the procedure, the measured $\delta^{15}N$ values of the samples prepared by Radian were examined as a function of the time during the program in which the samples were analyzed. Most of the analytical difficulties experienced (see Section 7) occurred in the early stages of the program. The examination of $\delta^{15}N$ versus time was to determine whether there was any consistent and/or progressive error in the procedures as the program progressed. No relationship was found between $\delta^{15}N$ and the time a sample was analyzed.

SECTION 6

SAMPLING SITES

The intensive field sampling program carried out by Radian personnel resulted in the acquisition of 324 discrete soil and water samples, plus a total of about 45 feet of 1¼-inch core. Two hundred forty-three of the discrete samples were soils; eighty-one were water samples.

Fourteen sites were visited in the intensive program:

1. Texas A&M University (TAMU) at College Station, Texas;
2. Rockdale, Texas;
3. Tampa, Florida (2 sites);
4. Indian Hills, Colorado;
5. Pueblo, Colorado;
6. Houghton Lake, Michigan (2 sites);
7. Tallahassee, Florida;
8. Abilene, Texas;
9. Michigan State University (MSU) at East Lansing, Michigan;
10. San Angelo, Texas;

11. Greeley, Colorado; and

12. Dimmitt, Texas

These sites are associated with three nitrate source categories: domestic septic tank systems (7 sites), municipal wastewater land application systems (5 sites), and cattle feedlots (2 sites). A breakdown of the samples collected from each of these sites is given in Table 4.

Sampling kits were sent to an additional 5 sites, all of which are associated with septic tank nitrate sources. Provision was made in each kit for the collection of 3 samples.

In addition to these 19 sites, data were obtained from Dr. C.W. Kreitler, of the Texas Bureau of Economic Geology, for samples that he obtained from 5 other sites. The Queens County, New York, and Grand Cayman Island sites are believed to represent septic tank sources of nitrate. The Macon County, Missouri, and Lockhart-Taylor, Texas, sites are believed to represent animal-waste nitrate. In Runnels County, Texas, data for septic tank, animal waste (barnyards), and natural nitrate sources were obtained. The geographic locations of the 24 sites are shown in Figure 6. A key identifying each site shown in the figure is given in Table 5.

Environmental factors were assessed for each of the 24 sites. The environmental variables considered were related to climate and soil type:

- mean annual precipitation,
- mean annual air temperature,

TABLE 4. SUMMARY OF SAMPLES COLLECTED IN RADIAN'S INTENSIVE SAMPLING PROGRAM.

Location	NO_3^- Source	No. of Soil Samples	Total Combined Depth Interval	No. of Water Samples
TAMU	Septic Tank	8	2.0-4.5 ft.	12
Rockdale	Septic Tank	23	1.0-5.0 ft.	0
Tampa	Septic Tank	64	0.0-11.5 ft.	8
Indian Hills	Septic Tank	5	0.5-5.1 ft.	6
Houghton Lake (A)	Septic Tank	8	0.0-4.9 ft.	0
Houghton Lake (B)	Septic Tank	11	0.0-5.7 ft.	0
Pueblo	Septic Tank	10	0.1-10.9 ft	1
Tampa	Wastewater	21*	0.0-20.0 ft.	29
Tallahassee	Wastewater	19	0.0-9.5 ft.	6
Abilene	Wastewater	16	0.0-7.2 ft.	6
San Angelo	Wastewater	15	0.5-6.4 ft.	4
MSU	Wastewater	16	0.0-6.2 ft.	7
Greeley	Feedlot	13	0.0-6.0 ft.	1
Dimmitt	Feedlot	14	0.0-10.3 ft.	1
		243		81

*Plus four 1 1/4-inch cores from the surface to a maximum depth of 20 feet.

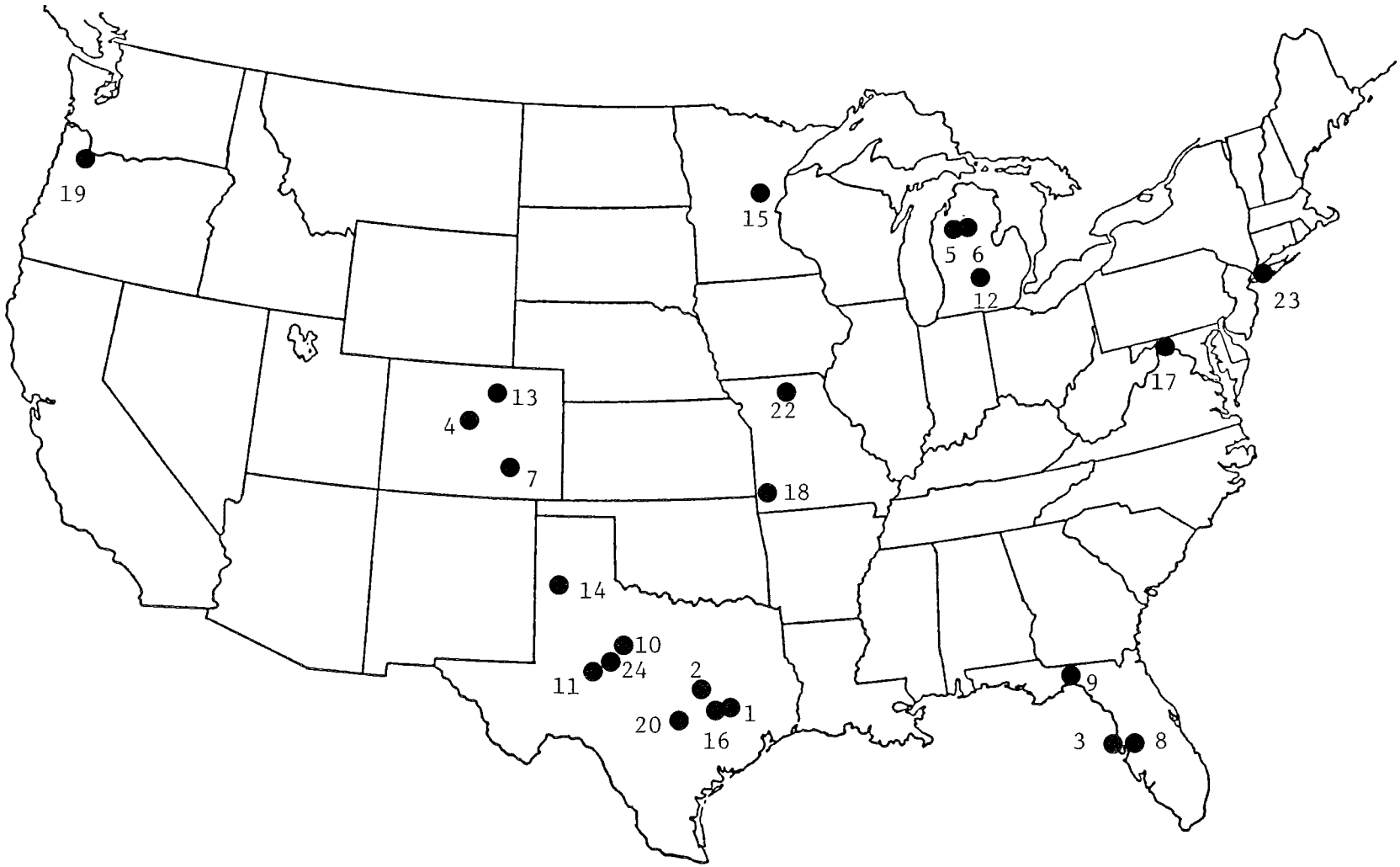

Figure 6. Locations of sampling sites (see key in Table 5).

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TABLE 5. KEY TO FIGURE 6.

Map Number	Location	NO_3^- Source	Sampled By*
1	Texas A&M University	Septic Tank	A
2	Rockdale, Texas	Septic Tank	A
3	Tampa, Florida	Septic Tank	A
4	Indian Hills, Colorado	Septic Tank	A
5	Houghton Lake, Michigan, Site A	Septic Tank	A
6	Houghton Lake, Michigan, Site B	Septic Tank	A
7	Pueblo, Colorado	Septic Tank	A
8	Tampa, Florida	Wastewater	A
9	Tallahassee, Florida	Wastewater	A
10	Abilene, Texas	Wastewater	A
11	San Angelo, Texas	Wastewater	A
12	Michigan State University	Wastewater	A
13	Greeley, Colorado	Feedlot	A
14	Dimmitt, Texas	Feedlot	A
15	Wahkon, Minnesota	Septic Tank	B
16	College Station, Texas	Septic Tank	B
17	Jefferson County, West Virginia	Septic Tank	B
18	Joplin Area, Missouri	Septic Tank	B
19	Portland Area, Oregon	Septic Tank	B
20	Lockhart-Taylor Area, Texas	Barnyard	C
21	Grand Cayman Island	Septic Tank	C
22	Macon County, Missouri	Barnyard	D
23	Queens County, New York	Septic Tank	D
24	Runnels County, Texas	Septic Tank, Barnyard, and "natural"	D

*Samples by: A = Radian Intensive Sampling Program; B = Radian Kit Sampling Program; C = Kreitler (unpublished data); D = Kreitler (2).

- Köppen Climate Classification,
- regional soil type,
- elevation, and
- latitude.

The values of these parameters are listed in Table 6 for each of the sites. The Köppen Climate Classification system and Soil Classification system are described in Appendices E and F, respectively.

TABLE 6. SITE ENVIRONMENTAL CHARACTERISTICS

Site Location	Sampled By[@]	Average Annual Temperature (°F)	Average Annual Precipitation (Inches)	Köppen Climate Classification*	Elevation (Feet)	Latitude (Degrees)	Soil Type[+]
Texas A&M University	A	68	36	Caf	200	30.50	5
Rockdale, Texas	A	67	34	Caf	490	30.75	5
Tampa, Florida (2 sites)	A	72	52	Caf	50	28.00	3
Indian Hills, Colorado	A	42	24	H	7,200	39.75	10
Houghton Lake, Michigan, Site A	A	43	30	Dbf	1,150	44.25	1
Houghton Lake, Michigan, Site B	A	43	30	Dbf	1,270	44.25	1
Pueblo, Colorado	A	51	12	BSk	3,500#	38.25	6
Tallahassee, Florida	A	68	56	Caf	250#	30.25	3
Abilene, Texas	A	64	24	BSk	1,700	32.50	6
San Angelo, Texas	A	65	20	BSh	1,800	31.50	6
Michigan State University	A	47	31	Daf	870	42.75	2
Greeley, Colorado	A	46	12	BSk	4,630	40.50	6
Dimmitt, Texas	A	56	18	BSk	3,900	34.50	6
Wahkon, Minnesota	B	39	28	Dbf	1,500#	46.00	1
College Station, Texas	B	68	36	Caf	200	30.50	5
Jefferson Co., West Virginia	B	52	40	Daf	500#	39.50	2
Joplin Area, Missouri	B	57	40	Caf	1,500#	37.00	3
Portland Area, Oregon	B	54	48	Cb	250#	45.50	10
Lockhart-Taylor Area, Texas	C	68	32	Caf	500	30.25	5
Grand Cayman Island	C	82#	80#	Aw	50#	19.00	4
Macon Co., Missouri	D	52	36	Daf	750#	39.75	5
Queens Co., New York	D	50	44	Daf	100#	40.75	2
Runnels Co., Texas	D	66	24	BSh	1,600	31.75	6

[@]Sampled by: A = Radian Intensive Sampling Program; B = Radian Kit Sampling Program; C = Kreitler (unpublished data); D = Kreitler (2).

*See Appendix E for definitions of Climate Classes.

+See Appendix F for definitions of Soil Classes.

#Estimated value.

SECTION 7

RESULTS AND DISCUSSION

STATISTICAL ANALYSES OF THE DATA

The analytical data used in this study are tabulated in Appendix D. This data base includes the results of the isotopic analyses performed under this study, and also includes both published (2) and unpublished data provided by Dr. C.W. Kreitler of the Texas Bureau of Economic Geology. The distribution of the data by nitrate source category and site is presented in Table 7. It should be noted that not all of the samples collected in Radian's sampling program were analyzed, and that some sites are not represented in the data base. The reasons for this are discussed in the following subsection on Analytical Problems.

This data base was analyzed using several statistical techniques. These included an analysis of means and variances of $\delta^{15}N$ for the various waste source categories, preparation of histograms, and correlation and regression analysis.

Correlation, multiple correlation, and partial correlation analyses were performed for the entire data base and for each separate nitrate source category. The analysis of the entire data base examines the "behavior" of $\delta^{15}N$ (and of nitrate concentration) as a function of the various environmental factors.

Separate correlation analyses were performed within each of the nitrate source categories. The values of $\delta^{15}N$ will be shown to vary over fairly wide ranges in the discussion below. The

TABLE 7. SUMMARY OF SAMPLES INCLUDED IN THE FINAL DATA BASE, BY SOURCE CATEGORY AND SITE.

NO_3^- Source Category	Site	Number of Analyses	Analyzed By*
Septic Tanks	Houghton Lake, Michigan, Site A	6	A
	Houghton Lake, Michigan, Site B	4	A
	Pueblo, Colorado	6	A
	Tampa, Florida	13	A
	Indian Hills, Colorado	5	A
	Rockdale, Texas	4	A
	Texas A&M University	3	A
	Grand Cayman Island	4	B
	Macon County, Missouri	1	C
	Queens County, New York	2	C
	Runnels County, Texas	4	C
	Subtotal	52	
Animal Wastes (Feedlots and Barnyards)	Dimmitt, Texas	8	A
	Greeley, Colorado	7	A
	Lockhart-Taylor Area, Texas	11	B
	Macon County, Missouri	10	C
	Runnels County, Texas	16	C
	Subtotal	52	
Municipal Wastewater Irrigation	Abilene, Texas	2	A
	San Angelo, Texas	5	A
	Michigan State University	3	A
	Subtotal	10	
Natural Soil-Plant Systems	Runnels County, Texas	64	C
	TOTAL, ALL SOURCE CATEGORIES AND SITES	178	

*Analyzed by: A = Radian; B = Kreitler, unpublished data; C = Kreitler (2).

separate correlation analyses examine the extent to which this observed variation in $\delta^{15}N$ for specific nitrate sources can be explained in terms of the various environmental factors.

Descriptive Statistics for $\delta^{15}N$

The means and standard deviations of the isotope ratios of the samples were computed for each of the nitrate source categories. These statistics are presented in Table 8.

The means and variances of $\delta^{15}N$ for the different source groups were compared using a one-way analysis of variance (F-test) and other statistical tests (t-tests). This analysis indicated that the mean $\delta^{15}N$ values for the septic tank (+10.9), animal waste (+12.4), and municipal wastewater irrigation (+9.5) source categories do not differ significantly (i.e., these sources of nitrate cannot be distinguished on the basis of $\delta^{15}N$ values). Moreover, the mean $\delta^{15}N$ values for the irrigation source (+9.5) and "natural" nitrate sources (+7.3) do not differ significantly.

TABLE 8. MEANS AND STANDARD DEVIATIONS OF $\delta^{15}N$ FOR DIFFERENT NITRATE SOURCE CATEGORIES

NO_3^- Source	Mean (ppt)	Standard Deviation	Number of Data Points
Septic Tanks	+10.9	9.8	52
Animal Wastes (Feedlots and Barnyards)	+12.4	9.4	52
Municipal Waste Water Irrigation	+9.5	7.2	10
Other*	+7.3	5.4	64

*"Natural" soil systems: primarily unfertilized cultivated fields.

The analysis indicated, however, that the mean $\delta^{15}N$ values of both the septic tank (+10.9) and the animal waste (+12.4) source categories differ from the mean $\delta^{15}N$ value for "natural" soil nitrates (+7.3) at the 0.05 level of significance. (The "level of significance" is discussed below in the section on correlation analysis.) This supports Kreitler's conclusion (2) that nitrates derived from animal wastes (including human wastes) can be distinguished from natural soil nitrates on the basis of their nitrogen-isotope ratios.

The distribution of $\delta^{15}N$ values for the various NO_3^- source categories are plotted as histograms in Figure 7. These histograms (and the standard deviations given in Table 8) show that the isotopic composition for each source category varies over a wide range of values. These ranges overlap considerably (in contrast to Kreitler's (2) findings).

The variation in del within the source categories was examined using correlation analysis. This analysis was carried out to determine whether environmental factors associated with the sampling locations were the cause of the variations observed.

Correlation Analysis

Definition of Variables--

The environmental variables associated with the sampling sites were described in Section 6 (see Table 6). They cover such environmental factors as latitude, climate class, soil type, and elevation. Some of the variables are "continuous." For example, the mean annual precipitation at a site may logically assume any real number value, even though the actual values used were integers ranging from 12 to 80. Other variables are "binary." These variables are assigned a value of either zero or one. A value of "1" means that a sample is characterized by that variable. For example, climate zone Caf (see

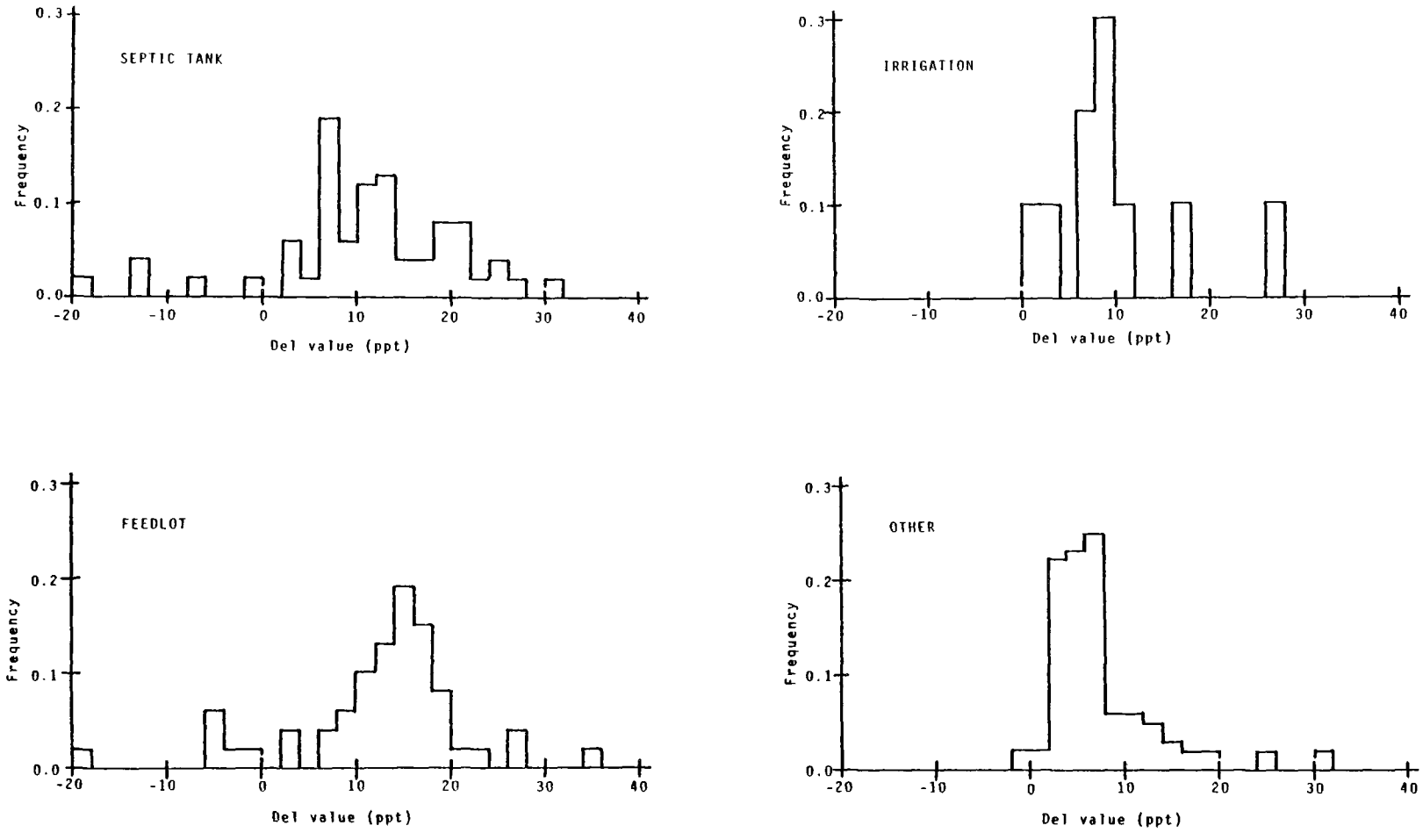

Figure 7. Histograms of Del Values by Source Category.

Appendix E) is designated by the variable name "C CAF." Thus, a sample acquired from a site located in climate zone Caf will have a value of C CAF = 1, while a sample acquired from a site located in climate zone Aw (see Appendix E) will have a value of C CAF = 0 The definitions of the variables used in the correlation analyses are given in Table 9. These definitions are provided because coded variable names (e.g., C CAF) are used in the following discussion of the results of the correlation analyses.

Meaning of the Correlation Coefficient--

The correlation coefficient is a very useful measure of the extent to which two variables are related. The correlation coefficient r is defined as follows:

$$r = \frac{\sum_{i=1}^{N} (X_i - \bar{X})(Y_i - \bar{Y})}{\sqrt{\sum_{i=1}^{N} (X_i - \bar{X})^2 \sum_{j=1}^{N} (Y_j - \bar{Y})^2}}$$

where

N = number of data points,
$\bar{X}$ = average of the X values, and
$\bar{Y}$ = average of the Y values.

TABLE 9. DEFINITIONS OF VARIABLES USED IN THE CORRELATION ANALYSES

A. Variables with Continuous Values

DEL	$\delta^{15}N$ value, in parts per thousand.
PPM	NO_3^- concentration, in parts per million (mg/ℓ).
D*SOIL	Depth from which a particular soil sample was obtained, in meters.
TEMP	Mean annual air temperature at a site, in degrees F.
PRECIP	Mean annual precipitation at a site, in inches.
ELEV	Elevation of a site, in feet above mean sea level.
LAT	Latitude of a site, in decimal degrees.
SEQNCE	Sequence number of samples analyzed in this study.

B. Variables with Zero-One Values*

1. Miscellaneous Variables

RADSAM	The sample was prepared by Radian under this study.
SOIL	The sample was a soil sample.

2. Nitrate Source Variables†

SEPTIC	The sample was from a septic tank site.
FEEDL	The sample was from an animal waste (feedlot or barnyard) site.
IRRIG	The sample was from a municipal wastewater irrigation site.

3. Climate Variables‡

C AW	The sample was from a site in climate zone Aw.
C BSK	The sample was from a site in climate zone BSk.
C CAF	The sample was from a site in climate zone Caf.
C DAF	The sample was from a site in climate zone Daf.
C DBF	The sample was from a site in climate zone Dbf.
C H	The sample was from a site in climate zone H.

(Continued)

TABLE 9. DEFINITIONS OF VARIABLES USED IN THE CORRELATION ANALYSES (Continued)

4. Soil Type Variables§

SOIL 1	The sample was from a site with type 1 soils.
SOIL 2	The sample was from a site with type 2 soils.
SOIL 3	The sample was from a site with type 3 soils.
SOIL 4	The sample was from a site with type 4 soils.
SOIL 5	The sample was from a site with type 5 soils.
SOIL 6	The sample was from a site with type 6 soils.
SOIL 10	The sample was from a site with type 10 soils.

5. Geographic Variables

HLMA	The sample was from Houghton Lake, Michigan, site A.
HLMB	The sample was from Houghton Lake, Michigan, site B.
PU	The sample was from Pueblo, Colorado.
TAM	The sample was from Tampa, Florida.
IH	The sample was from Indian Hills, Colorado.
RT	The sample was from Rockdale, Texas.
TAMU	The sample was from Texas A&M University.
ABL	The sample was from Abilene, Texas.
SNGLO	The sample was from San Angelo, Texas.
MSU	The sample was from Michigan State University.
DI	The sample was from Dimmitt, Texas.
GR	The sample was from Greeley, Colorado.
LOCTAY	The sample was from the Lockhart-Taylor area, Texas.
GNDCMN	The sample was from Grand Cayman Island in the Caribbean.
MACON	The sample was from Macon County, Missouri.
QUEENS	The sample was from Queens County, New York.
RUNLS	The sample was from Runnels County, Texas.

*A value of "1" indicates that sample is characterized by a particular variable; a value of "0" indicates that it is not.

†Samples of "natural" soil nitrate were indicated by a value of "0" for each of the three nitrate source variables.

‡Climate classifications are defined in Appendix E.

§Soil classifications are defined in Appendix F.

The correlation coefficient is a number between -1 and +1, and r^2 can be interpreted as the proportion of the variation in Y that can be "explained" or "predicted" in terms of X. For example, the correlation coefficient between DEL (Y) and ELEV (X) is (from Table 11)

$$r = .31.$$

Since

$$r^2 = (-.31)^2 = .096,$$

it follows that 9.6 percent of the total variation in DEL can be explained in terms of ELEV.

Figure 8 illustrates the meaning of a non-negative correlation coefficient. A negative correlation between two variables occurs if one increases as the other decreases.

The <u>multiple</u> correlation coefficient is a measure of the strength of the composite relationship between a single variable Y (e.g., DEL) and a <u>set</u> of predictor variables. The square of the multiple correlation coefficient is the proportion of the total variation in Y that can be explained in terms of the set of predictor variables. For example, consider the multiple correlation analysis of the data for the septic tank source category. The correlation coefficient between DEL and the set of predictor variables (D*SOIL, ELEV, and SOIL) is (from Table 17)

$$r = .56.$$

Since

$$r^2 = (.56)^2 = .314,$$

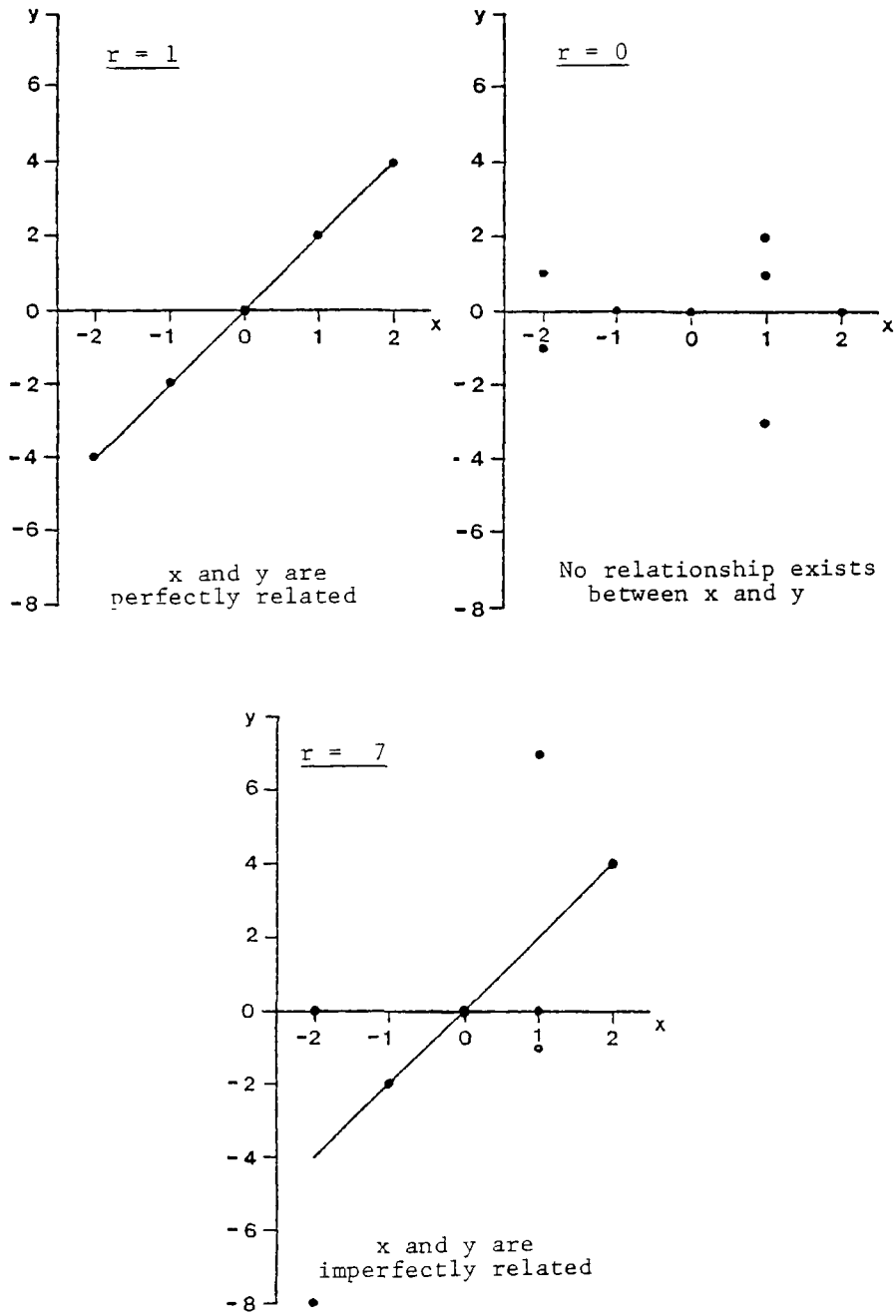

Figure 8. Illustration of the Meaning of Correlation Coefficient, r.

it follows that 3.14 percent of the variation in DEL can be explained in terms of the composite influence of D*SOIL, ELEV, and SOIL.

The partial correlation coefficient is a measure of the strength of the relationship between two variables given that one or more other variables are fixed.

Criterion for Choosing Variables Which Are Correlated--

If two variables had no true relationship, their correlation computed from a finite data sample would still almost certainly be non-zero. The question, then, is how large should the correlation coefficient be to indicate a true or repeatable relationship between the two variables?

There is a small chance (one in ten) that an r value as large as .123 in magnitude would be obtained if the two variables being considered were unrelated. (The threshold correlation .123 was computed as a function of the sample size, 178). Thus, if two variables have a correlation coefficient larger than .123 or less than -.123, there is a high probability that a true relationship exists between them. In this case, the correlation is said to be "statistically significant."

The probability (.10 in the example above) of erroneously concluding that a true correlation exists is called the level of significance, or "confidence" level. Values of the sample correlation coefficient (r) required to achieve statistical significance for different levels of significance and sample sizes used in this study are given in Table 10.

Correlation, multiple correlation, and partial correlation analyses were performed for the entire data base and for each separate nitrate source category. The analysis of the entire data base examines the "behavior" of DEL (and PPM) as a function of all other independent variables, including SEPTIC, FEEDL, and IRRIG (see Table 9).

TABLE 10. VALUE REQUIRED FOR A CORRELATION COEFFICIENT (r) TO BE SIGNIFICANT, AS A FUNCTION OF SIGNIFICANCE LEVEL AND SAMPLE SIZE.

Sample Size (N)	Value of r at Significance Level .10	.05	.01
10	.539	.619	.746
52	.231	.273	.354
64	.207	.246	.320
178	.123	.146	.191

Separate correlation analyses were performed within each of the four nitrate source categories. The values of $\delta^{15}N$ (DEL) were shown above to vary over fairly wide ranges (see Table 8 and the histograms in Figure 7). The separate analyses examine the extent to which this observed variation in DEL for specific nitrate sources can be explained in terms of the various environmental factors.

Correlations in the Entire Data Base

The most significant results of the correlation analysis of the entire data base are presented in Tables 11 and 12. Additional details of the statistical analyses are presented in Appendix G.

TABLE 11. VARIABLES WHICH HAVE STATISTICALLY SIGNIFICANT CORRELATIONS WITH DEL

	Correlation with DEL	Level of Significance
TEMP	.13	.10
PRECIP	.29	.01
ELEV	-.31	.01
FEEDL	.19	.05
C AW	.15	.05
C BSK	-.13	.10
C DAF	.18	.05
C H	-.18	.05
SOIL 4	.15	.05
SOIL 5	.27	.01
SOIL 6	-.26	.01
SOIL 10	-.18	.05
HLMB	-.13	.10
IH	-.18	.05
DI	-.19	.05
LOCTAY	.22	.01
GNDCMN	.15	.05
MACON	.15	.05
RUNLS	-.15	.05

TABLE 12. CORRELATIONS INVOLVING VARIABLES MOST CLOSELY RELATED TO DEL

	DEL	PRECIP	ELEV	SOIL 5	SOIL 6	LOCTAY
DEL	1.	.29	-.31	.27	-.26	.22
PRECIP	.29	1.	-.61	.21	-.69	.08
ELEV	-.39	-.61	1.	-.35	.35	-.21
SOIL 5	.27	.21	-.35	1.	-.58	.58
SOIL 6	-.26	-.69	.35	-.58	1.	-.33
LOCTAY	.22	.08	-.21	.58	-.33	1.

Table 11 lists the significant correlations with DEL and the levels of significance of those correlations. None of the other variables listed in Table 9 are significantly correlated with DEL in the entire data base. Table 12 presents the complete correlation matrix for DEL and the five variables which correlate most highly (at the .01 level) with DEL. Table 12 indicates the extent to which these independent variables are correlated with each other. Note especially the relatively high correlation between PRECIP and ELEV (-.61); these are the two variables with the highest correlations with DEL. These correlations suggest that, for the sites and samples considered in this study, $\delta^{15}N$ values tend to be higher in areas of high precipitation and/or low elevation.

It is impossible to determine, however, whether a true relationship exists between DEL and PRECIP, between DEL and ELEV, or between DEL and the combination (PRECIP + ELEV), solely on the basis of the correlations presented in Table 12. The fact that PRECIP and ELEV are correlated with each other may be causing the observed correlation between DEL and PRECIP or between DEL and ELEV.

For example, it is possible that a true relationship exists between DEL and PRECIP (i.e., that the mean annual precipitation influences the biogeochemical environment of soil/ground-water systems, and thereby influences the nitrogen isotope ratio). This would show up as a significant correlation. The relationship between DEL and ELEV, however, may be caused by the correlation of PRECIP and ELEV. This correlation may be real, or may be the result of a sampling bias (e.g., no samples were obtained from low elevation deserts). In either case, ELEV could be linked to DEL through PRECIP. The fact that sites with high precipitation are at relatively low elevations (in this study) would yield a correlation between DEL and ELEV,

even if the elevation, in and of itself, has no influence on $\delta^{15}N$. Additional research will be required to clarify the influence of these environmental variables on $\delta^{15}N$ in nitrates.

The most significant correlation in Table 11 is the positive (although small) correlation between FEEDL and DEL. The DEL value is higher in the feedlot (and barnyard) data than in the data for septic tank, irrigation, and natural ("other") nitrate sources as a whole. This difference is primarily due to the difference between feedlot DEL values and natural ("other") DEL values (see the earlier discussion of mean $\delta^{15}N$ values for the various source categories).

The correlation between FEEDL and DEL cannot be "explained" by other environmental factors. An analysis of partial correlations (see Appendix G) indicates that the correlation between DEL and FEEDL changes very little as the influence of other variables (including ELEV) is removed. Thus, a true relation between animal waste nitrate sources (feedlots and barnyards) and higher DEL values appears to exist.

The correlations between nitrate concentration (PPM) and various other variables were also examined. The variables which have significant correlations with PPM are listed in Table 13. Six variables are correlated with PPM at the .01 level: RUNLS (.36), RADSAM (-.36), FEEDL (.29), C CAF (.25), SEPTIC (-.25), and SOIL 6 (.23).

Thus, for the data examined in this study, higher nitrate concentrations were found in Runnels County, Texas; in feedlots and barnyards; in climate zone CAF; and in areas with type 6 soils (Runnels County soils are classified as type 6).

Samples collected for this study (RADSAM = 1) generally had lower nitrate concentrations than samples analyzed previously

TABLE 13. VARIABLES WHICH HAVE STATISTICALLY SIGNIFICANT CORRELATIONS WITH PPM

Variable	Correlation with PPM	Level of Significance
TEMP	.17	.05
PRECIP	-.14	.10
LAT	-.13	.10
RADSAM	-.36	.01
SOIL	-.16	.05
SEPTIC	-.25	.01
FEEDL	.29	.01
IRRIG	-.13	.10
C BSK	-.15	.05
C CAF	.25	.01
SOIL 3	-.14	.10
SOIL 6	.23	.01
TAM	.14	.10
RUNLS	.36	.01

by Kreitler (2). This situation had been observed prior to the statistical analyses: few sites had samples with nitrate concentrations as high as those found in Runnels County, Texas, by Jones (1) and Kreitler (2).

Finally, samples obtained from around septic tank laterals tended to have relatively low nitrate concentrations (compared primarily to samples from feedlots and barnyards).

Correlations Within Source Categories

Correlation analyses were also performed to determine whether any of the observed variation in DEL within a particular source category (see histograms in Figure 9) can be "explained" by environmental factors. Only the more significant results of these analyses are presented here. Additional details of the source-by-source analyses are presented in Appendix H.

Correlations With Del: Septic Tank Sources--

The significant correlations with DEL in the septic tank source category are listed in Table 14. The two variables that correlate most highly (at the .01 level) with DEL are TEMP (.35) and ELEV (-.39). These variables are also correlated with each other, and with some of the other variables that are less highly correlated with DEL (PRECIP and LAT). Thus, it appears that the $\delta^{15}N$ values of nitrates from septic tanks are higher in warm, moist, low elevation and low latitude areas than in cool, dry, high elevation, and/or more northerly areas. The specific causal relationship between DEL and these four factors cannot be identified. A true relationship may exist between DEL and any one of these variables, between DEL and a combination of these variables, or between DEL and a fifth unidentified variable which is also correlated with TEMP, PRECIP, ELEV, or LAT.

TABLE 14. VARIABLES WHICH HAVE STATISTICALLY SIGNIFICANT CORRELATIONS WITH DEL: SEPTIC TANK SOURCES

Variable	Correlation with DEL	Level of Significance
TEMP	.35	.01
PRECIP	.33	.05
ELEV	-.39	.01
LAT	-.31	.05
RADSAM	-.27	.10
C H	-.32	.05
SOIL 10	-.32	.05
HLMB	-.25	.10
IH	-.32	.05

NOTE: C H, SOIL 10, and IH occur simultaneously in this data subset and, therefore, are indistinguishable for the purposes of statistics.

It should be noted that the variables C H, SOIL 10, and IH occur simultaneously in the septic tank source category data. That is, the correlation between each of these three variables is r = 1.0. They are therefore indistinguishable in this analysis.

The variable RADSAM is negatively correlated with DEL (-.27) in this data subset. This means that the $\delta^{15}N$ values of samples collected by Radian in this study were generally lower than the $\delta^{15}N$ values for septic tank samples provided by Kreitler (2).

Correlation With DEL: Feedlot Sources--

The significant correlations with DEL in the feedlot (and barnyard) source category are listed in Table 15. The variables which correlate most highly with DEL are DI, RADSAM, C BSK, and ELEV. All of these correlations are negative (i.e., these variables are inversely related to DEL). These correlations are strongly influenced by the fact that six of the eleven

negative $\delta^{15}N$ values that were determined in this study are included in the feedlot data subset. Five of these six are associated with the DI (Dimmitt, Texas) site variable. It is interesting to note that nitrates from feedlots had the highest average $\delta^{15}N$ values of any source category (see the discussions of means and correlations in the entire data base above) in spite of this relatively high prevalence of negative $\delta^{15}N$ values

TABLE 15. VARIABLES WHICH HAVE STATISTICALLY SIGNIFICANT CORRELATIONS WITH DEL: FEEDLOT SOURCES

Variable	Correlation with DEL	Level of Significance
PRECIP	.32	.05
ELEV	-.37	.01
SEQNCE	-.30	.05
RADSAM	-.38	.01
C BSK	-.38	.01
C CAF	.25	.10
SOIL 5	.32	.05
SOIL 6	-.32	.05
DI	-.44	.01
LOCTAY	.27	.10

The negative correlation of climate class BSk with $\delta^{15}N$ can largely be attributed to the DI samples. The Dimmitt site is located in climate zone BSk.

The negative correlation with RADSAM indicates that the del values of samples collected and analyzed for this study are lower than the del values reported by Kreitler for barnyards in Runnels County, Texas, the Lockhart-Taylor Area, Texas, and Macon County, Missouri.

Correlations With DEL: Irrigation Sources--

Only one variable (SOIL) was correlated with DEL in the waste water irrigation data subset (see Table 16). This is a

fairly "weak" negative correlation (i.e., the level of significance is .10). It indicates the two water samples had higher $\delta^{15}N$ values than the eight soil samples that were analyzed.

Correlations With DEL: Other Sources--

There were no meaningful correlations of variables with DEL in the "other" nitrate source category. It is important to note that all of the points in this data subset are from Runnels County, Texas. Thus, the only meaningful variables that could be correlated with DEL are PPM, D*SOIL, and SOIL. The fact that no significant correlations were found indicates simply that the influence of environmental factors (e.g., PRECIP, TEMP, etc.) was not assessed for this source category in this study

TABLE 16. VARIABLES WHICH HAVE STATISTICALLY SIGNIFICANT CORRELATIONS WITH DEL: IRRIGATION SOURCES

Variable	Correlation with DEL	Level of Significance
Soil	-.55	.10

NOTE: This data set included only 10 points, so a correlation of at least .54 was required for significance at the .10 level.

Regression Models for DEL--

Multiple regression models for DEL were constructed for each of the nitrate source categories. The regression models were developed by using stepwise regression analysis. This method adds variables to and deletes variables from a model one at a time until no further significant improvement in the predictive accuracy can be made.

The primary purpose of this analysis is not to develop equations to be used to estimate DEL, but to investigate the strength

of the relationship between DEL and the prediction variables. The set of candidate predictor variables included all except the site variables (HLMA, HLMB, etc.), RADSAM, and SEQNCE.

The variables that were included in the final regression model equations are not necessarily the ones that are most highly correlated with DEL in Tables 14, 15, and 16. If two predictor variables are highly correlated with each other, it is unlikely that both variables will be selected for inclusion in the equation. This is due to the fact that if one of the two variables is already in the equation, the other variable will make very little additional contribution to the predictive accuracy.

When there are many candidate predictor variables which are correlated with each other (as is the case in this analysis) the set of variables which is included in the equation is a complicated function of the nature of the correlations. The variables included in an equation for DEL and the list of variables which have the highest correlations with DEL may therefore be very different.

The results of the multiple regression analyses are summarized in Table 17. Additional details of the analyses, including the forms of all four equations for DEL and the analysis of variance tables, are given in Appendix H.

It is seen from Table 17 that the multiple correlations for septic, feedlot, and irrigation sources are all between .54 and .56; thus, only about

$$(.55)^2 = .30$$

or 30 percent of the total variation in DEL can be explained in terms of the predictor variables used in this study. In the

TABLE 17. COMPOSITE RELATIONSHIPS BETWEEN DEL AND PREDICTOR VARIABLES

Source	Terms in Model†	Multiple Correlation	Significant at Level	Standard Error
Septic	D*SOIL ELEV SOIL	.56	.01	8.3
Feedlot	ELEV SOIL C BSK SOIL 5	.54	.01	8.3
Irrigation	SOIL	.55	.10*	6.4
Other	PPM SOIL	.23	.25	5.4

†These variables were selected for inclusion in the equations by using the stepwise regression procedure.

*Borderline. The small sample size (10) accounts for the lower level of significance in this case.

case of other sources, only about 5 percent can be explained. It should be remembered that the only meaningful predictor variables in the "other" data subset are PPM, D*SOIL, and SOIL.

Correlations With PPM By Source--

The correlations between nitrate concentration (PPM) and the various environmental factors were also examined. Complete tables of the significant correlations with PPM are included in Appendix H. A summary of the variables which correlate most highly with PPM is presented in Table 18.

TABLE 18. VARIABLES WHICH CORRELATE MOST HIGHLY WITH PPM (AT THE .01 LEVEL OF SIGNIFICANCE) FOR THE VARIOUS SOURCE CATEGORIES

Source	Variable	Correlation with PPM
Septic Tank	RADSAM	-.41
	SOIL 6	.39
	RUNLS	.64
Feedlot	TEMP	.46
	LAT	-.40
	SEQNCE	-.38
	RADSAM	-.40
	C BSK	-.40
	C CAF	-.52
	RUNLS	.63
Irrigation	SNGLO	.77†
Other	D*SOIL	-.34
	SOIL	-.33

† This data set included only 10 points, so a correlation of at least .75 was required for significnace at the .01 level (see Table 10).

ANALYTICAL PROBLEMS

When sample analysis activities began, several problems occurred with the preparation and purification apparatus (the

"prep-line" is described in Section 5. The problems, which were related to equipment failure, included a ruptured Toeppler pump, a cracked mercury diffusion pump, and numerous leaks. Leaking stopcocks were repeatedly troublesome.

These various problems led, in some cases, to the loss of samples. Cumulatively, these problems resulted in considerable lost time. Because of this, although over 320 discrete soil and ground-water samples were obtained in our intensive sampling program, only about 140 samples were leached and had their nitrate concentrations determined. Only 87 of these (62 percent) contained sufficient nitrate to warrant further processing and isotopic analysis (see below). Of these 87, only 66 were successfully analyzed for their isotopic compositions. The remainder were either contaminated with interferring species such as carbon monoxide (CO) or atmospheric nitrogen (N_2) gas, or produced too little N_2 gas for a successful isotopic analysis.

Another problem was that none of the samples obtained via sampling kits were received in time to be analyzed in this study. The exclusion of these samples from the final data base reduced the geographic coverage and the size of the "septic tank" source data subset.

Another problem was related to the nitrate concentration of the samples. The configuration of the preparation apparatus, and the size of the samples, were such that a nitrate concentration of at least 5 mg/ℓ was required in the soil leachates and ground-water samples in order to generate sufficient N_2 gas for an isotopic analysis. Because of this constraint, none of the samples obtained from the Tallahassee, Florida, or Tampa, Florida spray irrigation sites were analyzed. This limited both the size of the data base and the geographic coverage for the "Irrigation" waste source category.

Table 7 presented a summary of the numbers of samples successfully analyzed for each site, according to nitrate source category. Also included in the table are the numbers of samples for which data was provided by Kreitler.

A final problem is a limitation of the method of study rather than an analytical problem. It is possible that the total history of a sample is unknown. Thus, the nitrate in a sample could conceivably have been derived from a variety of sources. During the sampling, every effort was made to minimize this possibility by sampling as close to the waste source as possible (e.g., within an active pen of a cattle feedlot). The results of the nitrate concentration and $\delta^{15}N$ analyses are tabulated in Appendix D.

Profiles of nitrate concentration and $\delta^{15}N$ versus depth were examined for the various sampling holes. An example of such a profile is presented in Figure 9. As can be seen in the figure, both nitrate concentration and del value vary over a fairly wide range with depth. This degree of variation was fairly typical for the profiles developed in this study. In the previous work by Kreitler (2), however, the profiles of del value were much more constant with depth. A representative profile prepared by Kreitler is reproduced in Figure 10 for comparison.

This difference in the behavior of $\delta^{15}N$ between different sites with similar waste sources can be accounted for by two possible explanations. The first explanation is that some unidentified deviation from the standard analytical procedure produced a variation in $\delta^{15}N$ values. Due to the time losses discussed above, duplicate analyses of samples were not performed. Standards of known isotopic composition were run, however. The results of these analyses did not indicate any systematic analytical errors (see Section 5).

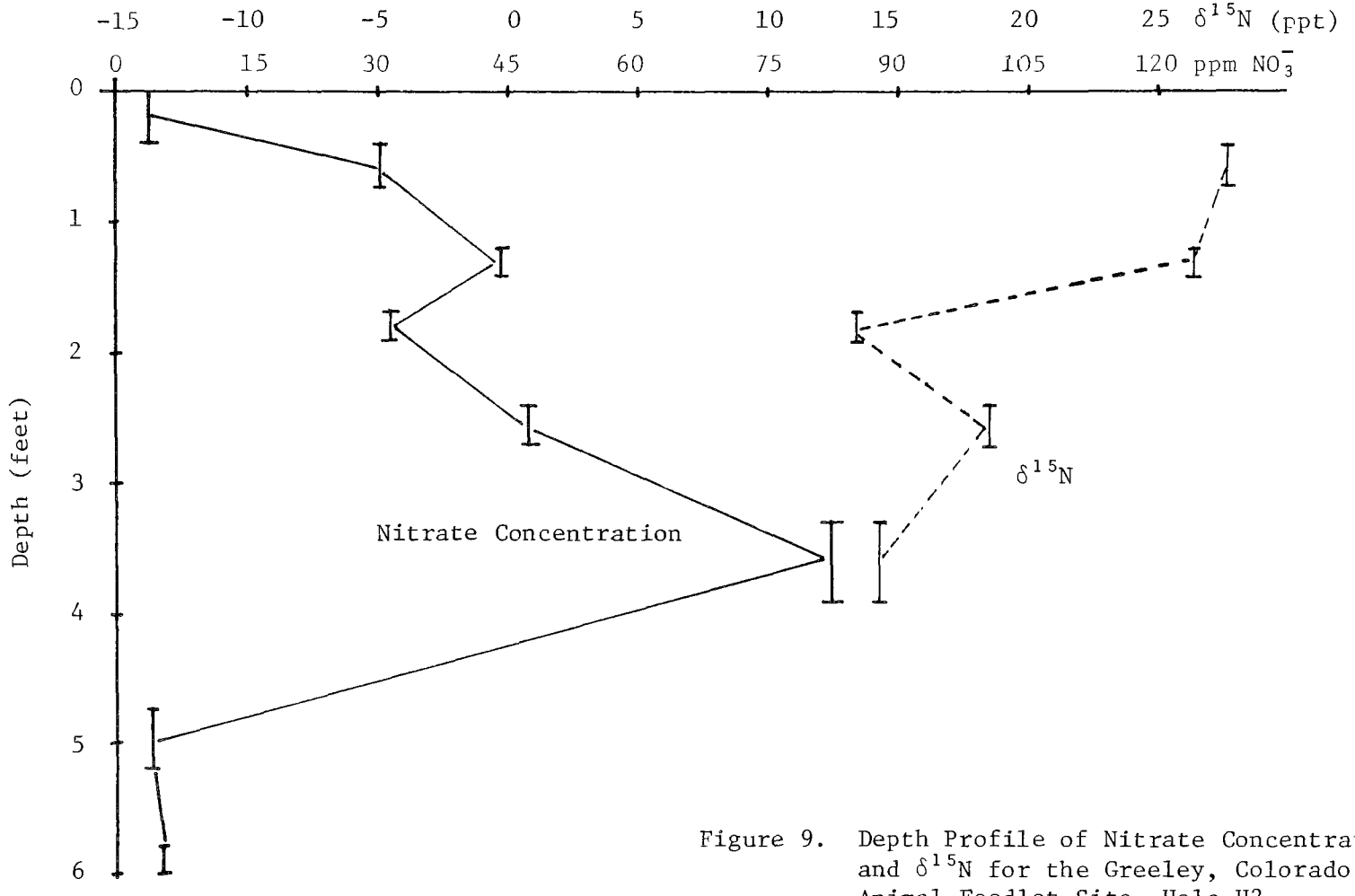

Figure 9. Depth Profile of Nitrate Concentration and $\delta^{15}N$ for the Greeley, Colorado, Animal Feedlot Site, Hole H2.

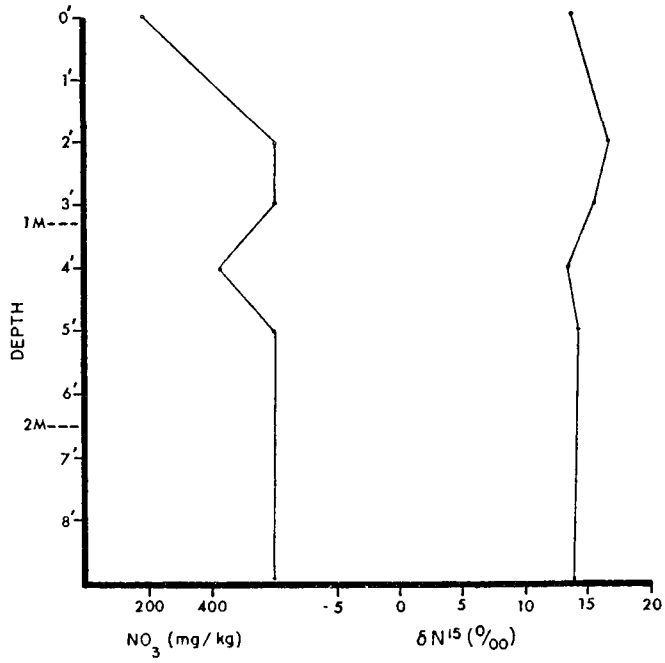

Figure 10. Nitrate and $\delta^{15}N$ Versus Depth Beneath a Barnyard With a Definite Animal Waste Contribution of Nitrogen, In Runnels County, Texas [From Kreitler (2)].

The second explanation is that the differences are real. Differences in the biogeochemical environments of the sites could be causing the observed variations in isotopic behavior.

Several depth-related factors could be involved. In particular, variations in the Eh-pH conditions of the soil column could have a strong influence on the depth distribution of both nitrate concentration and $\delta^{15}N$ value. The variations could also be related to changes or differences in soil bacteria populations, clay content or mineralogy, chemical composition, or soil texture.

It is impossible to explain the differences in isotopic behavior illustrated in Figures 9 and 10 with the data generated in this study. Detailed, site-specific studies, conducted under a variety of biogeochemical conditions, will be required to fully explain the N-isotope fractionations which occur in soil columns.

SUMMARY AND CONCLUSIONS

The objectives of this study were to:

1. determine whether $\delta^{15}N$ values of nitrates derived from a given waste source are consistent in different geographic regions of the country and to

2. determine whether $\delta^{15}N$ values of nitrates from different waste sources are sufficiently different to discriminate between the sources.

In order to meet these objectives, samples of soil- and ground water-nitrate were obtained from different regions of the country, from sites where the source of the nitrate could be reasonably predicted. Four nitrate source categories were examined:

1. nitrates from domestic septic tanks;

2. nitrates from feedlots and barnyards;

3. nitrates from municipal wastewater irrigation sites; and

4. "natural" nitrates from unfertilized soil-bacteria-vegetation systems (primarily cultivated fields).

The nitrate contents and the N-isotope compositions of these samples were determined. The results were examined using standard statistical procedures.

The means and standard deviations of the $\delta^{15}N$ values were computed for each of the nitrate source categories. These statistics were compared using a one-way analysis of variance (F-test) and other tests. This analysis indicated that nitrates from septic tanks, feedlots, and barnyards can be differentiated from natural soil nitrates on the basis of their isotopic compositions. The mean $\delta^{15}N$ values for septic tank nitrates and for feedlot/barnyard nitrates were +10.9 and +12.4, respectively, while the mean $\delta^{15}N$ value for natural soil nitrates was +7.3.

The analysis of variance of the means also indicated that nitrates from septic tanks and from feedlots and barnyards cannot be differentiated from each other. Finally, nitrates from municipal wastewater irrigation sites cannot be distinguished from nitrates from any of the other sources. The mean $\delta^{15}N$ value for irrigation nitrates was +9.5.

It should be remembered when considering these results that the data for natural soil nitrates are all from Runnels County, Texas, samples. Additional research is required to verify that the mean $\delta^{15}N$ value for natural soil nitrates (+7.3) is representative for other regions of the country.

The finding that nitrates from wastewater irrigation sites cannot be differentiated from nitrates from natural soils, septic tanks, or feedlots and barnyards may be attributable to the particular set of conditions that occur at wastewater irrigation sites. Wastewater irrigation operations are oriented toward removal of nutrients from the wastewater, via uptake by plants. The water generally receives some treatment before irrigation, and is then sprayed or flooded over the land surface. Two of

the three sites included in the irrigation data base were actively cultivated. The one site which was not had the highest $\delta^{15}N$ values. These factors tend to suggest that the nitrates at wastewater irrigation sites represent a mixture of nitrates derived from the waste and nitrates derived from natural soil-plant interactions.

Correlation analyses of the entire data base were carried out. The results of these analyses confirmed the ability to distinguish nitrates from feedlots and barnyards from natural soil nitrates (the variable FEEDL was positively correlated with DEL). This analysis also indicated that some of the variation in $\delta^{15}N$ values can result from environmental influences. The $\delta^{15}N$ value was correlated with mean annual precipitation (high $\delta^{15}N$ values occurred in areas of high precipitation) and negatively correlated with elevation (high $\delta^{15}N$ values occurred at low elevations). Identifying specific causal relationships between $\delta^{15}N$ and environmental variables will require additional study.

Correlation analyses were also carried out within each nitrate source category. These analyses explored the variation in $\delta^{15}N$ values determined for each nitrate source. The source-by-source analysis also included multiple regression analyses. These analyses indicated that about 30 percent of the variation in $\delta^{15}N$ for septic tank, feedlot and barnyard, and irrigation sources can be "explained" in terms of the environmental factors considered in this study.

As regards natural soil nitrates, only about 5 percent of the variation in $\delta^{15}N$ can be explained. The only meaningful variables in this source category are nitrate concentration (PPM), the depth from which soil samples were obtained (D*SOIL), and whether the sample was a soil sample or a ground-water sample (SOIL).

It is fairly clear that environmental factors influence $\delta^{15}N$ values. Additional research will be required to precisely identify the nature of this influence. It is also apparent, however, that this influence is not so great as to completely prevent the identification of nitrate sources by nitrogen isotope studies.

It is important to note that the mean $\delta^{15}N$ values of the nitrate from septic tanks and from feedlots and barnyards were statistically different from the mean value for natural soil nitrates. The ranges of $\delta^{15}N$ values overlap considerably. Thus, it will be impossible to identify the source of the nitrate in any single sample unless the $\delta^{15}N$ value is greater than about +24 ppt. This is the mean for natural soil nitrate, plus three standard deviations: $7.3 + 3(5.4) = 23.5$. The more samples that are analyzed, the more confident one would be of whether or not the samples represent contamination by a particular waste source or mixture of sources.

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APPENDIX A

REAGENTS USED IN ISOTOPIC ANALYSES

1. Magnesium Oxide - Finely ground "Baker Analyzed" reagent grade magnesium oxide was used directly from the bottle.

2. Devarda's Alloy - Reagent grade alloy from Baker composed of 50 percent copper, 44.5 percent aluminum, and 5.5 percent zinc was ground in a rotary ball mill using carborundum balls until it would pass through a 100-mesh screen and 75 percent would pass through a 200-mesh screen. In Radian's Norton rotary ball mill, two pounds could be processed to this specification after 48 hours of operation. It is absolutely necessary that the Devarda's Alloy be ground to a fine powder. If it is not, reduction of NO_3^- may be incomplete and isotopic fractionation may occur.

3. 0.1 Normal Hydrochloric Acid - This solution was prepared from a 0.1 normal hydrochloric acid Baker "Dilut-It" concentrate.

4. Silver Sulfate - Approximately 65 milligrams was added to minimize chloride interference during nitrate (NO_3^-) analyses with the specific ion electrode.

5. Sodium Hypobromite-Iodide Solution - 200 grams of sodium hydroxide were dissolved in 300 milliliters of deionized water and cooled to 0°C in ice-sodium chloride bath. Half of the cooled solution was transferred to a 500 milliliter Erlenmeyer flask immersed in crushed ice. Sixty milliliters

of bromine (Br_2) were added over a period of 30 minutes. The solution was stirred vigorously during the addition, and the rate of addition regulated so that the temperature of the solution did not exceed 5°C. When the addition of bromine was complete, the remainder of the sodium hydroxide solution was added and stirred. The solution was then stored in a refrigerator for six days. During the period of cold storage a precipitate of sodium bromide formed. The solution was then filtered through a glass-fibre filter and an equal volume of potassium iodide solution (2 grams KI in one liter of water) was added. The sodium hypo-bromite-iodide solution was stored in a tightly stoppered amber bottle at 4°C. One milliliter of this solution will oxidize five to six milligrams of NH_4^+ to N_2.

APPENDIX B

DESCRIPTION OF RADIAN'S INTENSIVE SAMPLING PROGRAM, BY SITES

TEXAS A&M UNIVERSITY EXPERIMENTAL SEPTIC TANK

The experimental septic tank system at Texas A&M was located on the TAMU Research Farm, about 12 miles west of the university campus. A plan of the site is shown in Figure B-1. Operation of the site ceased in 1977.

The site consisted of three tile fields and a lysimeter complex. These four basic elements were tied into a central effluent distribution system. The effluent was derived from a septic tank serving several houses located about a mile from the site. It was delivered to the site via pipeline. The average composition of the effluent is presented in Table B-1.

The lysimeter complex consisted of three lysimeters, each measuring about 7 feet long, 6 feet across, and 6 feet deep. Each lysimeter contained a different soil type: Lakeland sand; Norwood sandy loam; and Miller clay. Effluent was applied at a constant rate by peristaltic pumps.

There were three tile fields at the site: the dump field; the Norwood field; and the Miller field. The dump field consisted of four parallel laterals, each of which was 50 feet long. They were spaced about 10 feet apart. The dump field was in Norwood sandy loam soil and was used to dispose of excess effluent. No record was kept of the effluent application rate to this field.

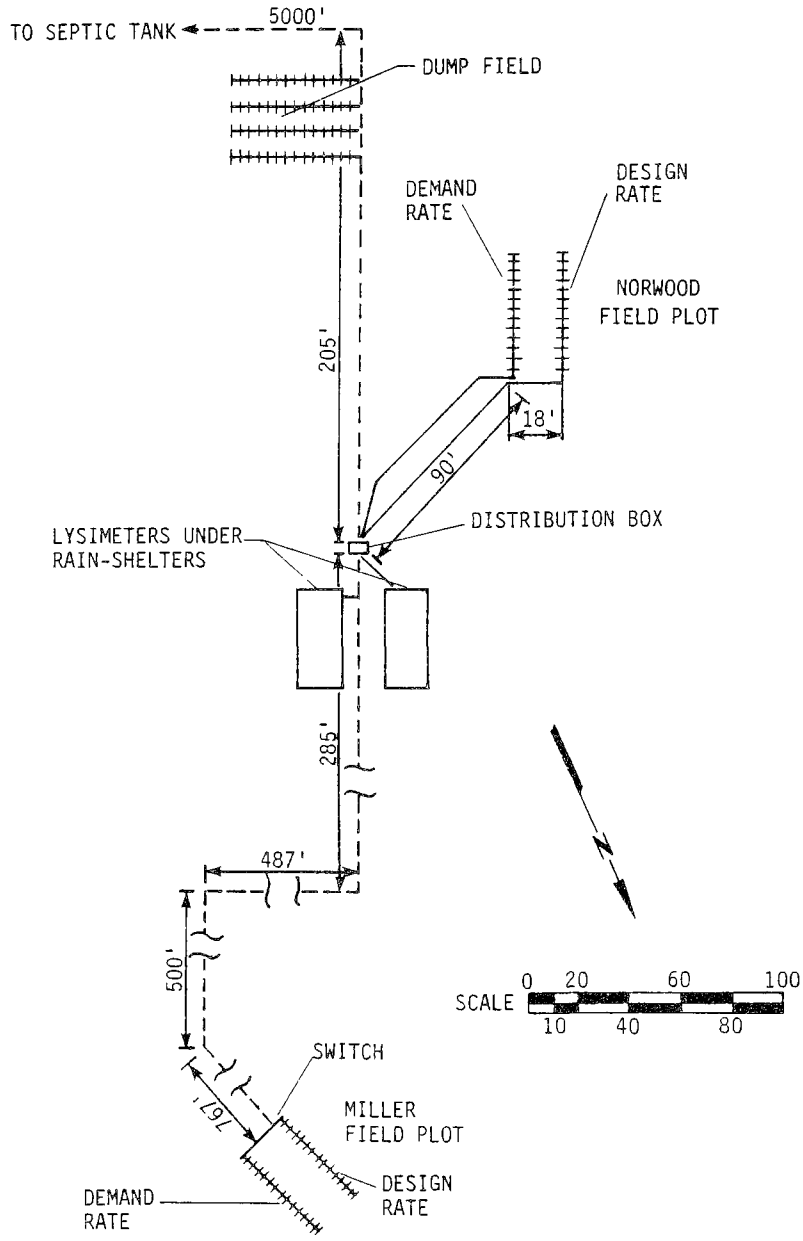

Figure B-1. Plan of TAMU Experimental Septic Tank System [From Brown (10)]

TABLE B-1. TAMU EXPERIMENTAL SEPTIC TANK EFFLUENT QUALITY FOR 14 MONTH PERIOD

	Mean		Standard Deviation
pH	7.5	±	0.3
T alkalinity	952	±	246 mg/l
Conductivity	2,346	±	438 mhos/cm
Hardness	42	±	30 mg/l
COD	292	±	212 mg/l
$T-PO_4-P$	8.3	±	4.5 mg/l
$O-PO_4-P$	6.6	±	3.0 mg/l
Organic N	9.2	±	9.5 mg/l
NH_3-N	23.4	±	9.4 mg/l
NO_3-N	1.55	±	0.44 mg/l
NO_2-N	< 0.55		
Cl	166	±	64 mg/l
SO_4	19	±	12 mg/l
TOC	128	±	81 mg/l
IOC	125	±	39 mg/l
Fecal Coliform	1.8×10^6	±	1.03×10^6 /100 ml
Total Coliform	1.8×10^6	±	1.03×10^6 /100 ml
TC	220	±	9.6 mg/l
TN	30.4	±	13.6 mg/l

Source: Brown, et al. (10).

The Norwood field consisted of two parallel, 50-foot long laterals in Norwood sandy loam. One lateral was a design rate line which received effluent at a standard 40 gallons per day. The other was a demand rate line. They were located about 50 feet apart at a depth of 45 cm. A stand pipe was connected to the demand field via a 2 cm diameter tube which was positioned below the level of the line so that the system remained sealed from the air. A water stage recorder was positioned on top of the stand pipe to record the changes in water level within the field. Three stainless steel rods were used in the pipe as electrodes. These activated the pump when the water level dropped to 5 cm from the bottom of the field and turned it off when the level rose to within 5 cm of the top of the field. This demand field began operation near the end of April, 1976.

The Miller field was set up the same as the Norwood field. It was located in Miller clay. The Miller clay is less capable of accepting effluent than is Norwood sandy loam. The Miller design field was therefore set at an application rate of 20 gpd.

Sampling of the various fields was accomplished in a variety of ways. The lysimeters contained tubes terminating in porous ceramic suction cups through which soil water samples were obtained. The cups were located in an array at different depths and distances from the line of inflow. Effluent was applied through a horizontal perforated pipe enclosed in a gravel pack. The pipe was located at a depth of 45 cm along one wall of the lysimeter. Soil water samples were obtained by applying a vacuum to the suction cup tubes.

Twelve water samples were obtained from lysimeters at TAMU. Three samples were obtained from a lysimeter containing Lakeland

sand, 4 were obtained from a lysimeter containing Norwood sandy loam, and 5 samples were obtained from a lysimeter containing Miller clay.

Sampling along a dump field lateral was achieved through hand augering. Eight soil samples were obtained from the dump field. The positions of the sampling holes are shown in Figure B-2. The depth intervals sampled from each hole are shown in Figure B-3. No samples were obtained from the Norwood field or the Miller field, because sampling these fields would have interfered with the TAMU experimental program.

ROCKDALE, TEXAS, SPETIC TANK SITE

A septic tank system located approximately 5 miles east of Rockdale, Texas, was sampled. The system has an overall length of 100 feet. The current effective length of the lateral is only about 30 feet, however.

The system was installed in April, 1966, and has been in continuous operation since then. The lateral extends to the southeast from the south side of a single residence. It is buried at a depth of about 18 inches and is surrounded by a gravel pack one foot thick.

At a distance of about 30 feet from the tank, there is a 3 foot break in the lateral. The tiles were removed from this section of the lateral in October of 1976, when they became clogged with roots. No effluent passes this break at present.

Twenty-three soil samples were collected from around the 30 feet section of lateral still in operation. They were collected using a 4-inch, hand operated soil auger. They were placed in plastic bags and frozen upon return to Austin (within 8 hours).

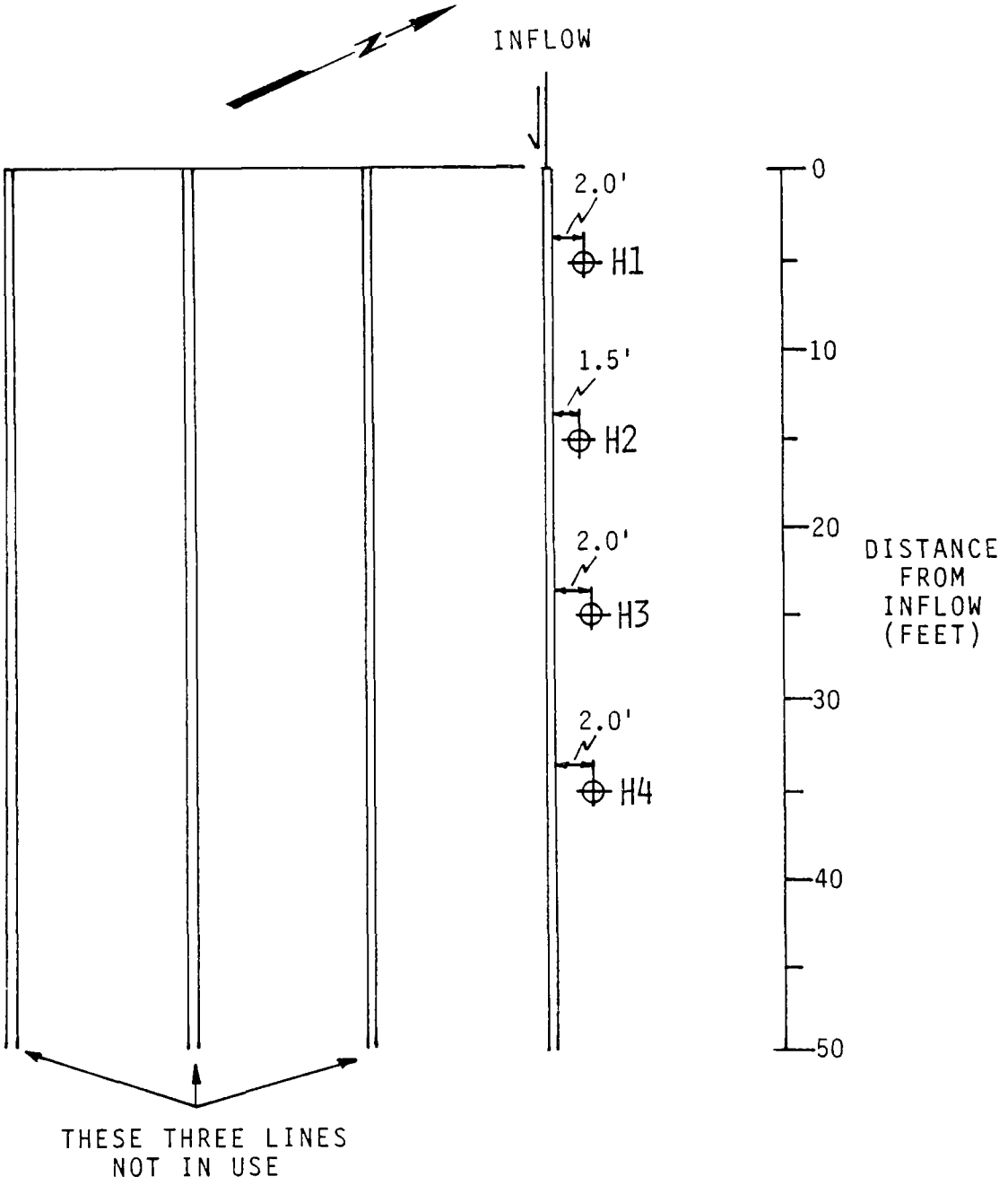

Figure B-2. Locations of Soil Sampling Holes H1-H4, TAMU Experimental Septic Tank Dump Field.

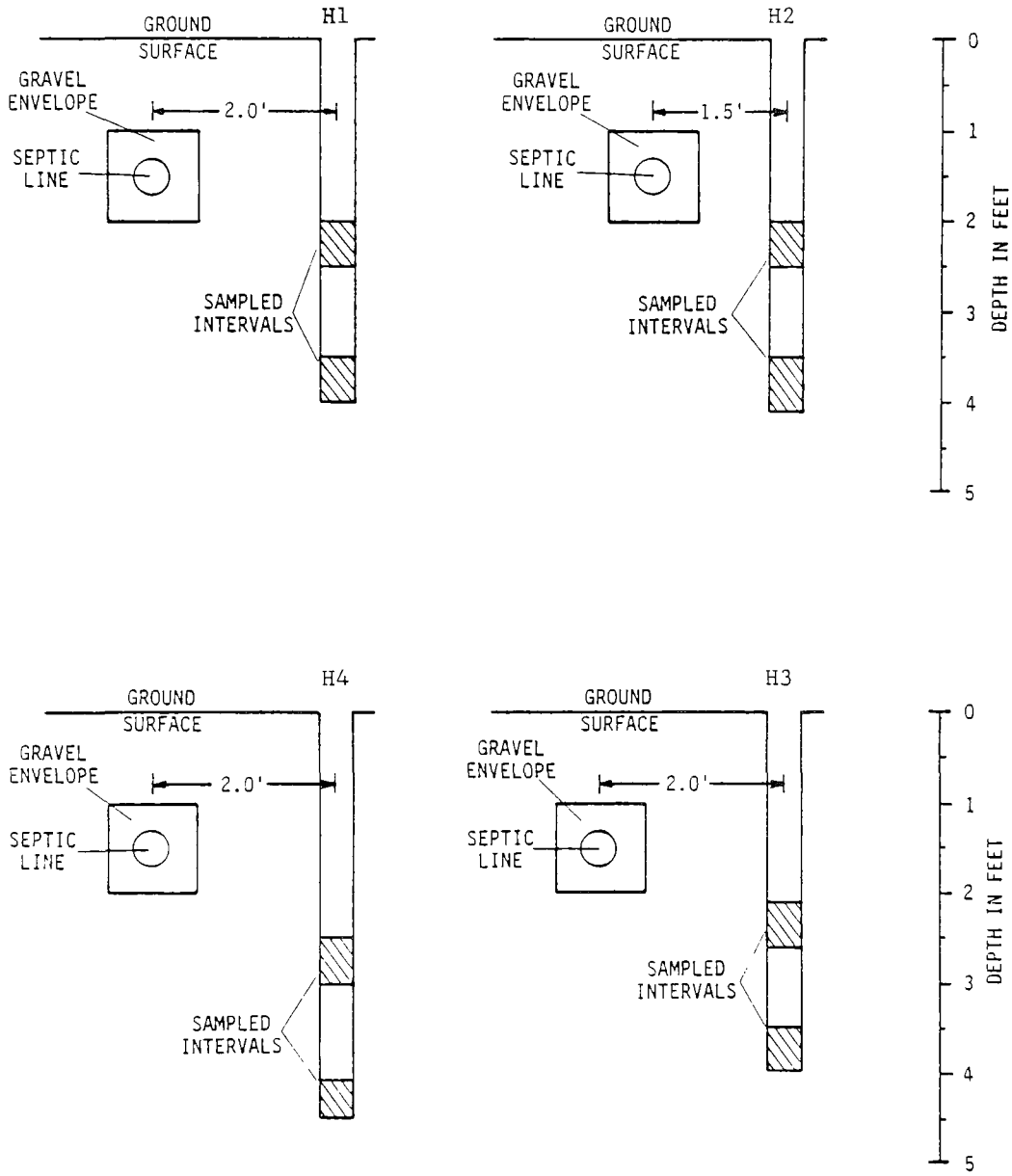

Figure B-3. Depth Intervals Sampled in Holes H1-H4, TAMU Experimental Septic Tank Dump Field.

The positions of the sampling holes and cross sections showing the depth intervals sampled are shown in Figure B-4 and B-5, respectively.

TAMPA, FLORIDA, SEPTIC TANK SITE

A plan of the Tampa septic tank site showing the locations of the sampling holes is presented in Figure B-6. The site is owned by a private homeowner. The septic tank handles the wastewater load of about seven people. Disposal of the tank effluent is to the ground via a recharge pit. This occupies the area marked "Input" on Figure B-6.

Soil samples were collected at discrete depth intervals from auger holes at the six locations indicated in Figure B-6. The maximum depth sampled was 11.5 feet. A total of 64 soil samples were acquired.

Water samples were collected from auger holes H3, H4, H5, and H6. When these holes encountered the water table, the samples were collected using a small peristaltic pump. In addition, samples of lake water and water from a well located about 275 feet up-gradient (southeast) from the recharge pit were collected The ground-water gradient is to the northwest, toward the lake.

INDIAN HILLS, COLORADO, SEPTIC TANK SITE

The Indian Hills site was visited twice, once for water samples and a second time for a suite of soil samples. Indian Hills is an old mountain community (development) about 20 miles southwest of Denver that has been occupied since early in the century. Although a public water supply system has been instituted in recent years, most residences are on individual water wells and septic tank systems. The aquifer supplying the

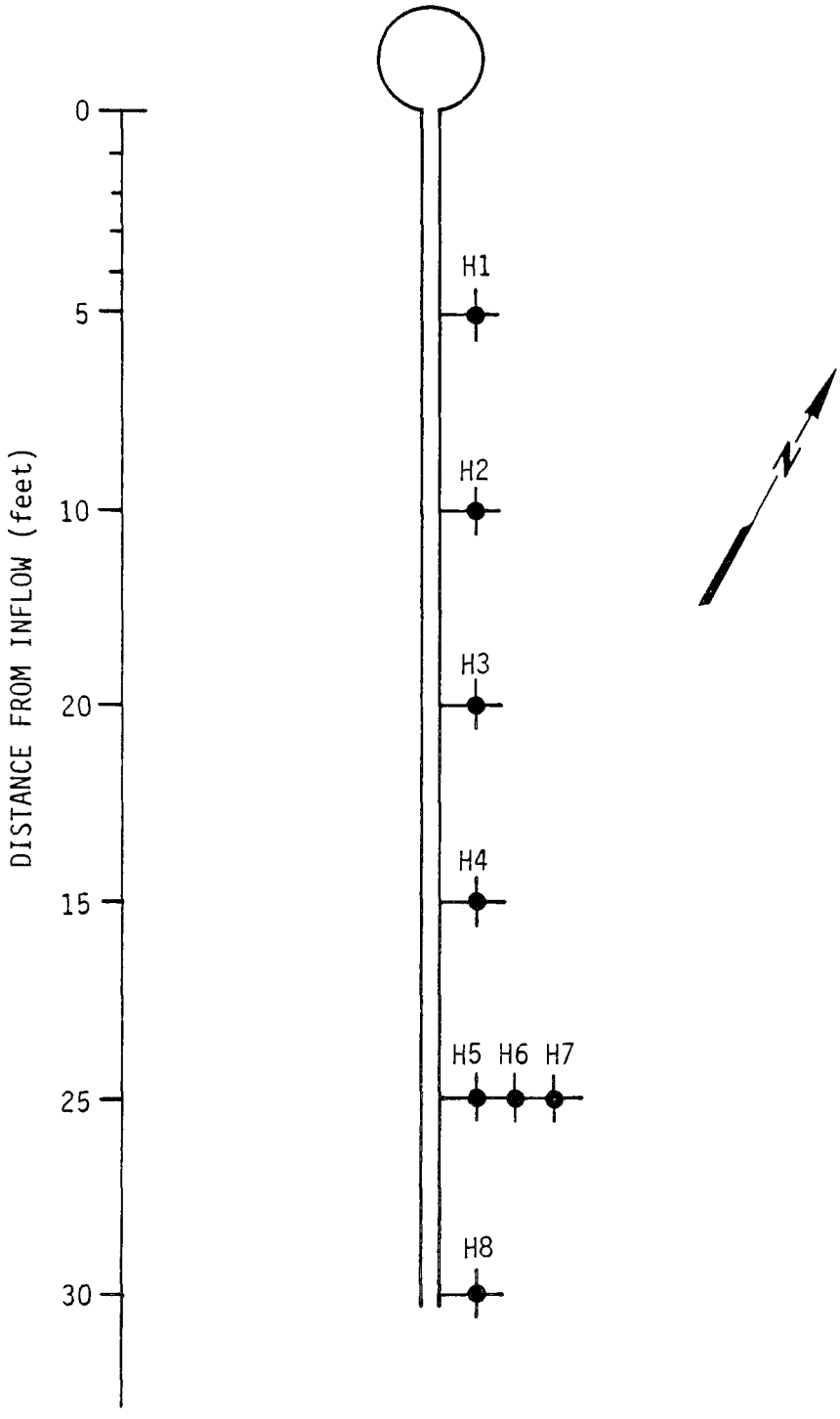

Figure B-4. Locations of Soil Sampling Holes, Rockdale, Texas, Septic Tank Site.

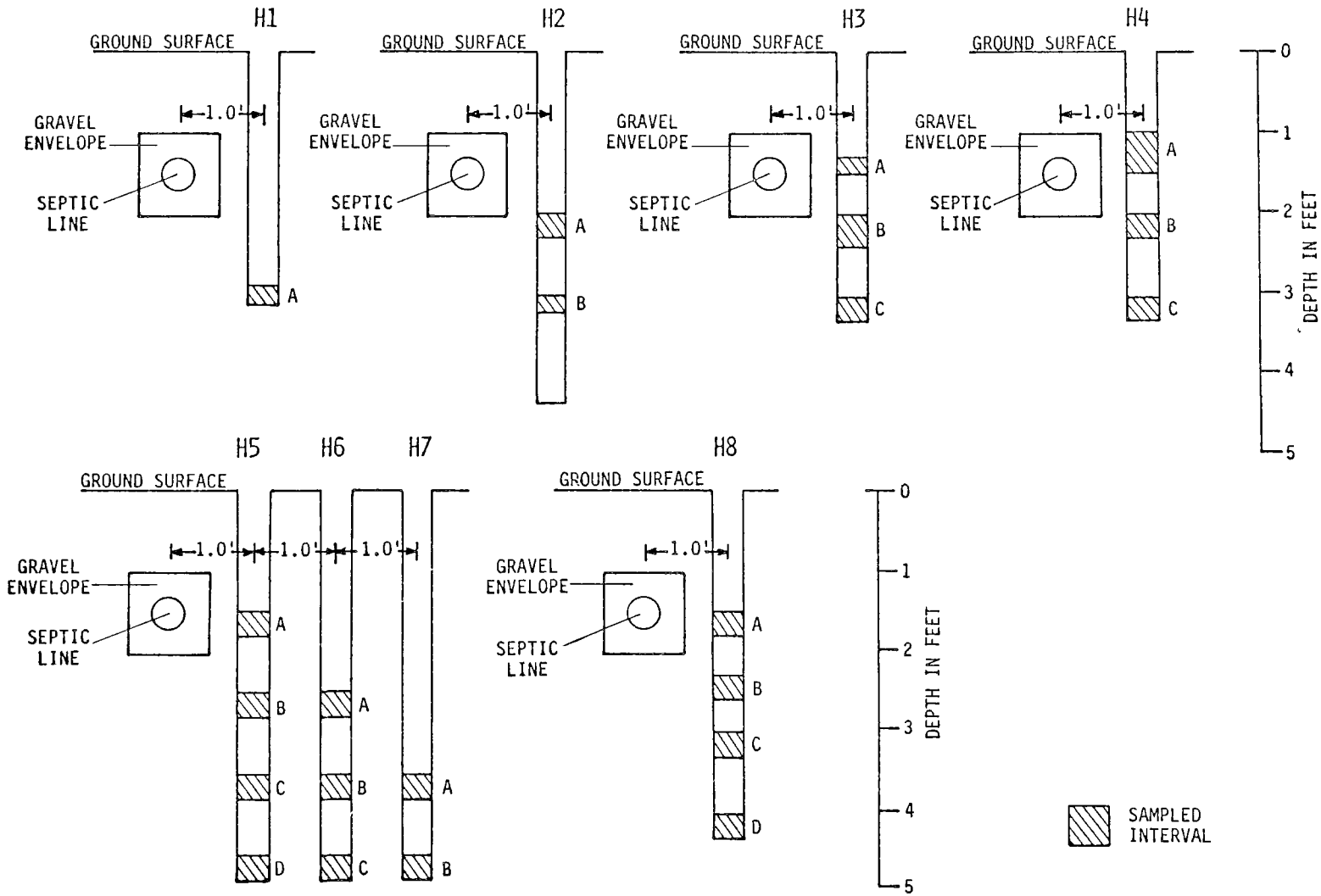

Figure B-5. Depth Intervals Sampled at Rockdale, Texas, Septic Tank Site.

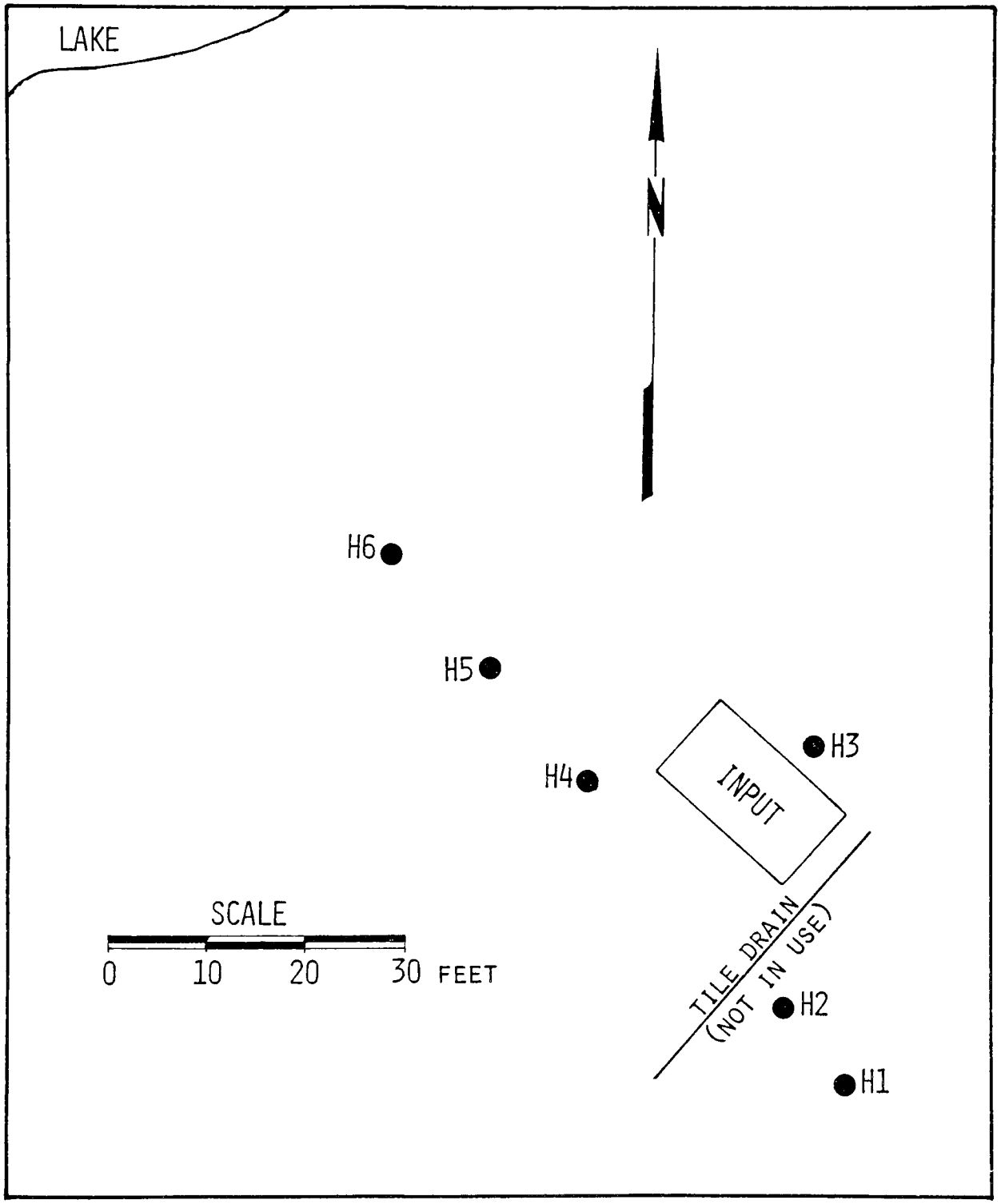

Figure B-6. Plan of the Tampa, Florida, Septic Tank Site Showing Locations of Sampling Holes.

domestic water supplies is a typical aquifer in crystalline rock terrain. The porosity is fracture porosity, and the water is at shallow depths. The community is now apparently recycling part of the water inadvertently through the septic tanks and wells, with resulting high levels of nitrate. The Jefferson County Health Department is aware of the situation and is monitoring the water quality in wells and regulating septic tank design. An intensive study has been conducted in cooperation with the U.S.G.S.

During the first visit, a total of six water samples were collected from water wells having the highest nitrate concentrations. Most of these were collected from outside lawn spigots after letting them run for 5 to 15 minutes.

During the second trip to Indian Hills, a likely candidate septic field was selected for soil sampling. A plan of the site is shown in Figure B-7. The log of the hole showing the sampled intervals is shown in Figure B-8. No previous work has been done specifically at this site. A more ideal sample point would have been within the septic field, but the Jefferson County Health Department advised against this, due to the fact that the investigation might "put someone in violation of county regulations" by penetrating an engineered septic field structure. Five soil samples were collected.

PUEBLO, COLORADO, SEPTIC TANK

This site is located in a rural area about 10 miles north of Pueblo, Colorado. No known previous studies have been made at the site, which is located on the alluvial bottomlands of Fountain Creek.

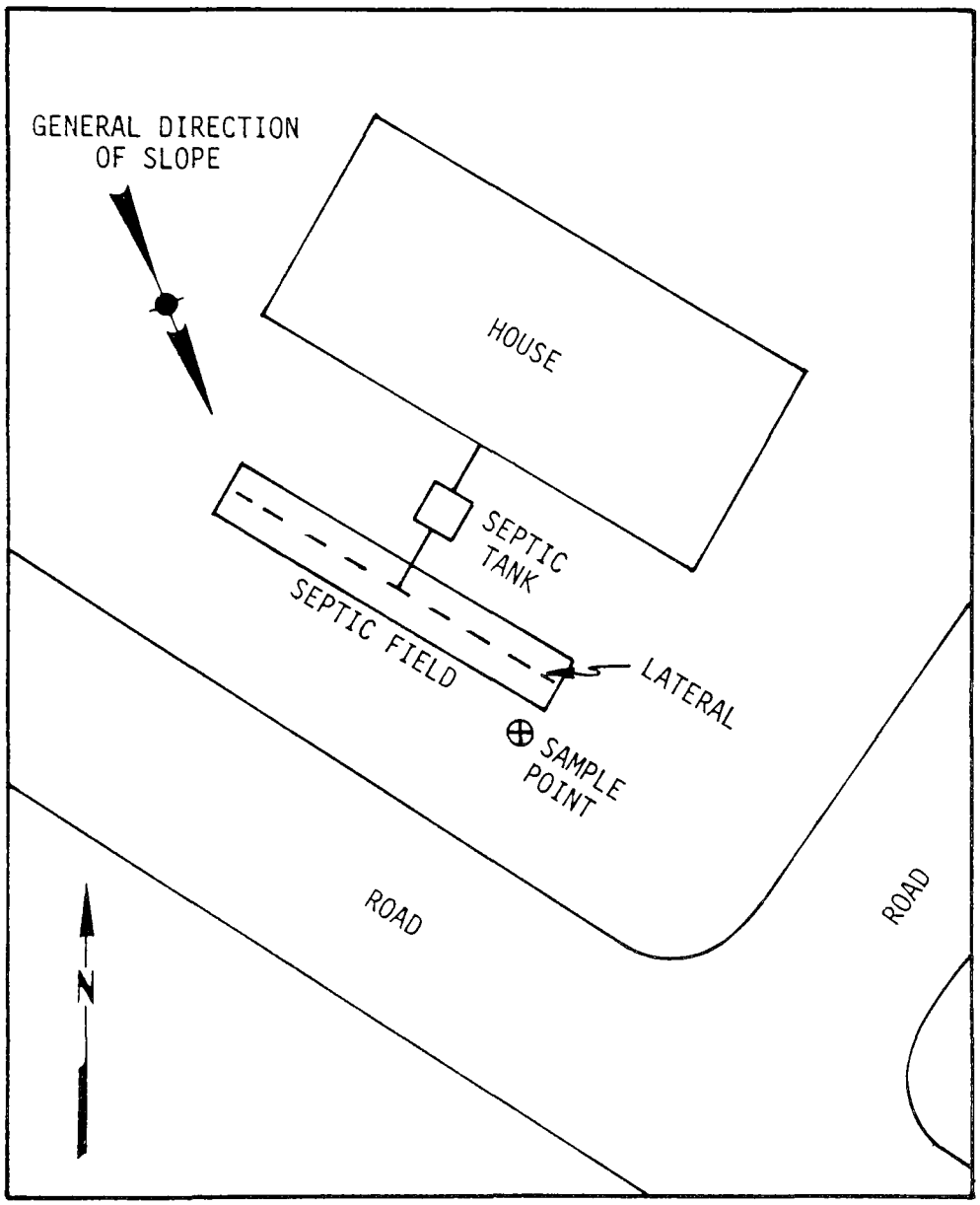

Figure B-7. Plan of the Indian Hills, Colorado, Septic Tank Site (not to scale).

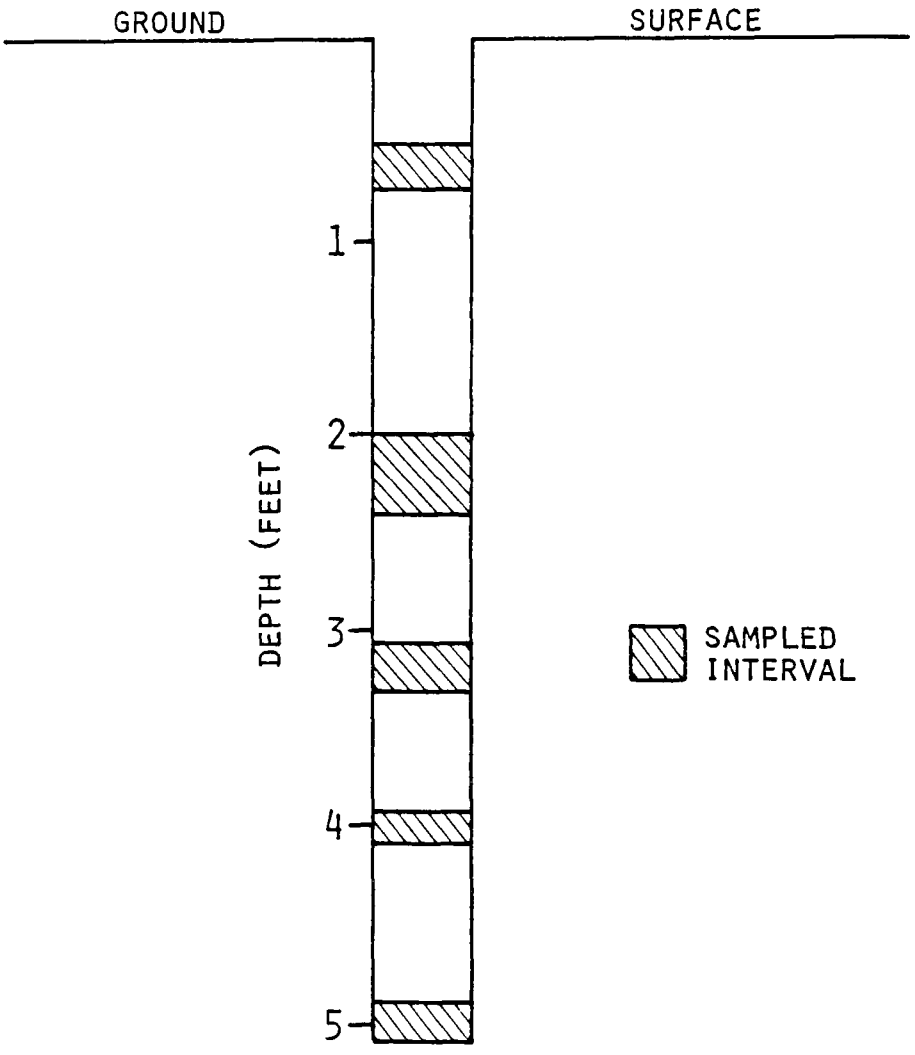

Figure B-8. Depth Intervals Sampled at the Indian Hills, Colorado, Septic Tank Site.

A plan of the sample site is shown in Figure B-9. The sewage disposal system at the site consists of three parts: a "grease trap", a septic tank, and a cesspool with laterals. The samples were collected near one of the laterals leading away from the cesspool. A simplified sample log showing the depths at which samples were collected is shown in Figure B-10. The soil was moist and appeared to have been exposed to effluent, although no odor was detected.

A total of 10 soil samples were collected from the sample hole. In addition, a water sample was collected from the water well, which is located about 50 feet from the septic tank. This well is a shallow well (about 30 feet deep) in the Fountain Creek alluvium.

HOUGHTON LAKE, MICHIGAN, SEPTIC TANK SITES

Houghton Lake is located in the north-central part of Michigan's Lower Penninsula. The area surrounding the lake is a popular resort community. Nearly all of the 27 mile shoreline is developed. Permanent residences are interspersed with summer homes and cottages. Until recently, all of the residences were serviced by individual water wells and septic tank systems.

In 1971, Michigan State University and the State of Michigan Department of Natural Resources began an intensive study of the deteriorating water quality in Houghton Lake. This study identified septic tank disposal systems as a primary source of excess nutrient loading in the lake. Construction of a centralized sewage collection and treatment facility has been underway for several years. At present about 75 percent of the immediate shoreline community is connected to this system.

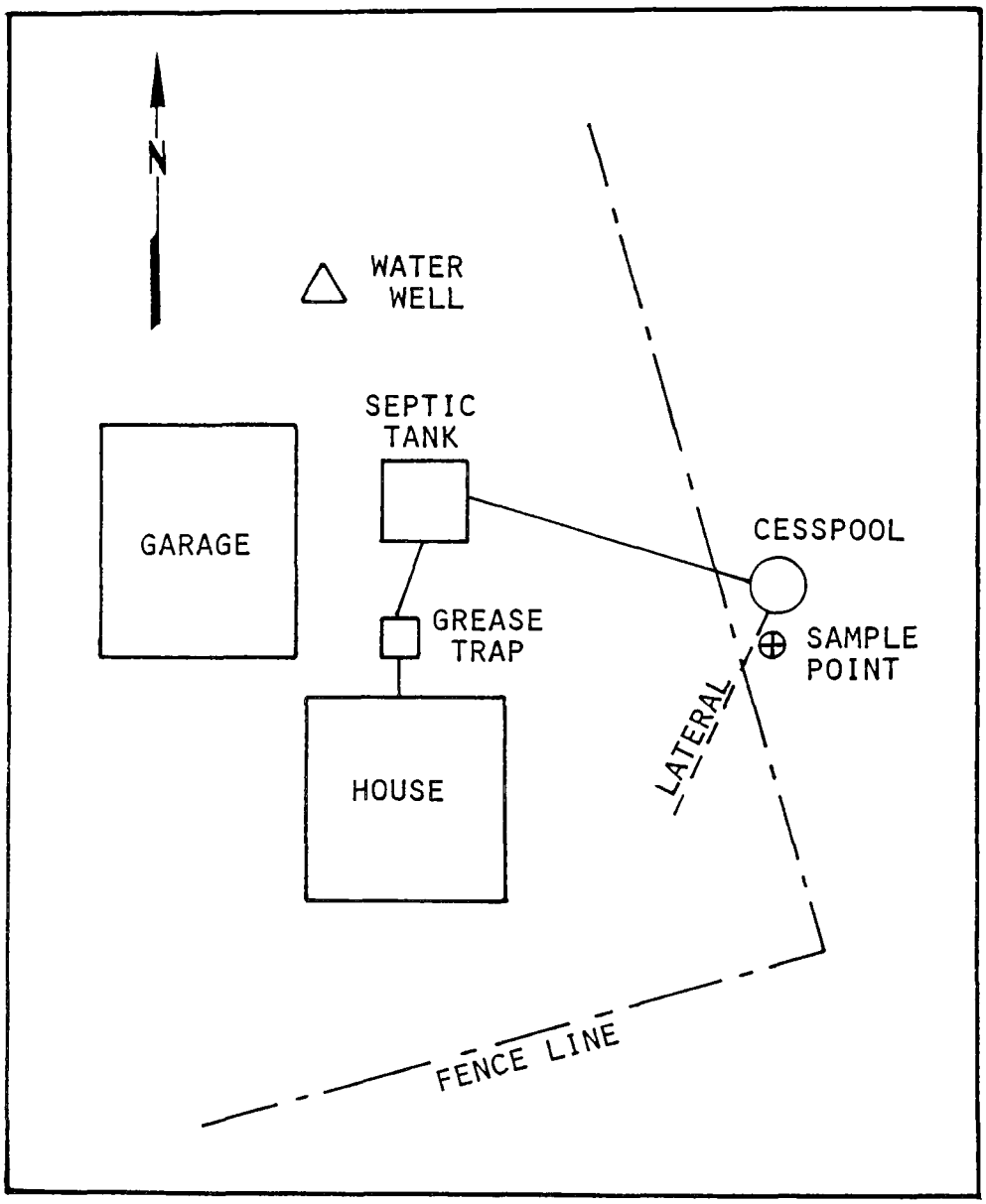

Figure B-9. Plan of the Pueblo, Colorado, Septic Tank Site (not to scale).

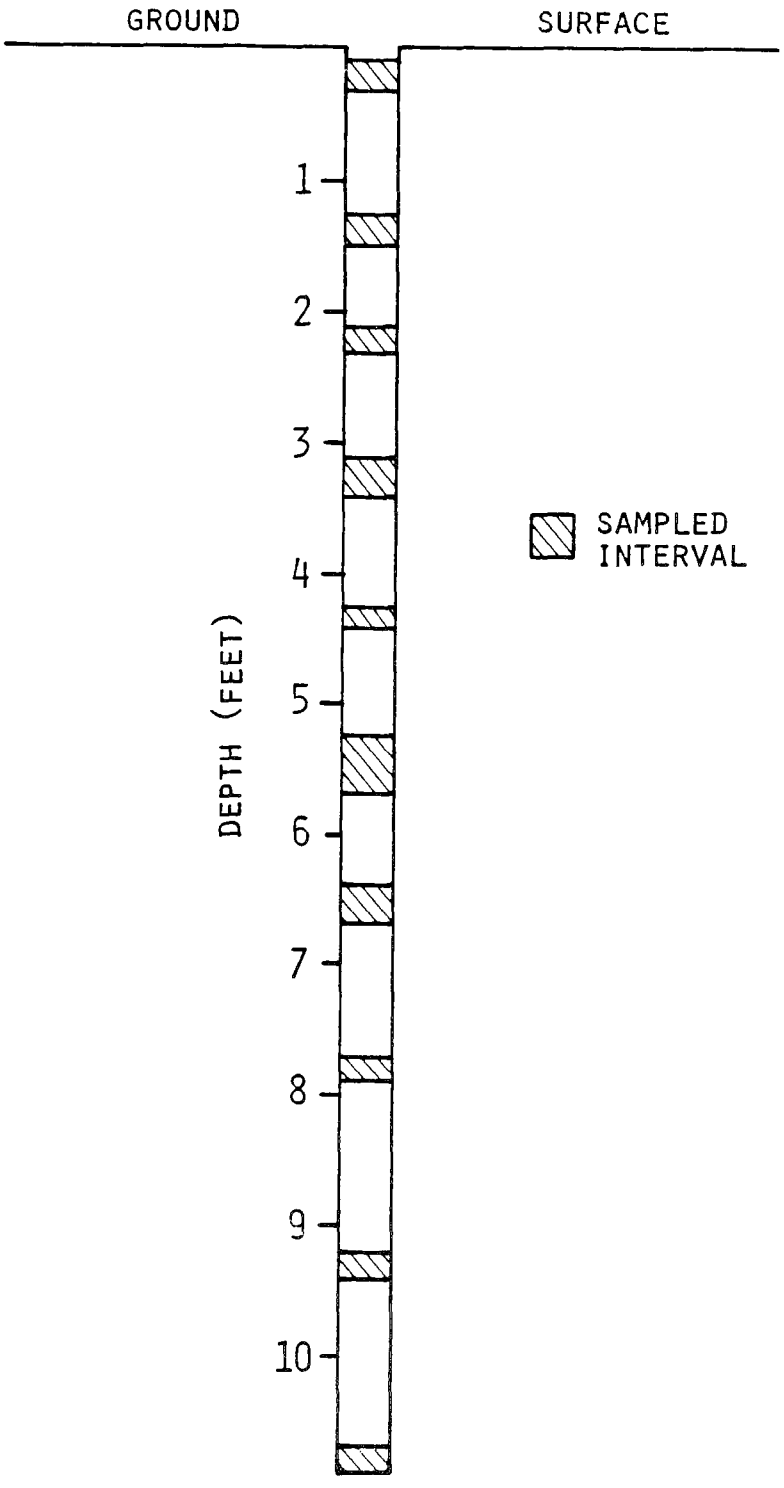

Figure B-10. Depth Intervals Sampled at the Pueblo, Colorado, Septic Tank Site.

Soil samples were collected adjacent to two active septic tank/tile field systems in the Houghton Lake area. A combined total of 19 soil samples were collected from these two sites.

Site A is located about one-fourth mile from the lake in the community of Houghton Lake Heights. A plan of the site is shown in Figure B-11. The system serves a single family residence and has been in operation for about six years. Soil samples were collected at several depth intervals from a hole at the low end of the drain field. The depth intervals sampled are indicated in Figure B-12. In addition, a single near-surface sample was obtained right at the edge of the drain field (see Figure B-11).

Site B is located about one-half mile from the lake on a glacial moraine. The site is about 135 feet above the level of the lake. The water table is fairly deep (>20') and the soils are composed of sand and gravel. The septic tank system at Site B serves a nursing home with about 25 to 30 occupants. The system consists of three tanks in series. The tank effluent is discharged to two drain fields. The system is overloaded and effluent was observed seeping from the ground at one of the tile fields. A plan of the site is shown in Figure B-13.

One of the tile fields at this site is functioning properly. A suite of soil samples was obtained from a point immediately downslope from this field. This sample point is designated B-1 in Figure B-13. The depth intervals sampled at this point are shown in Figure B-12. Sampling was only carried out to a depth of 3.2 feet because a dense gravel layer was encountered.

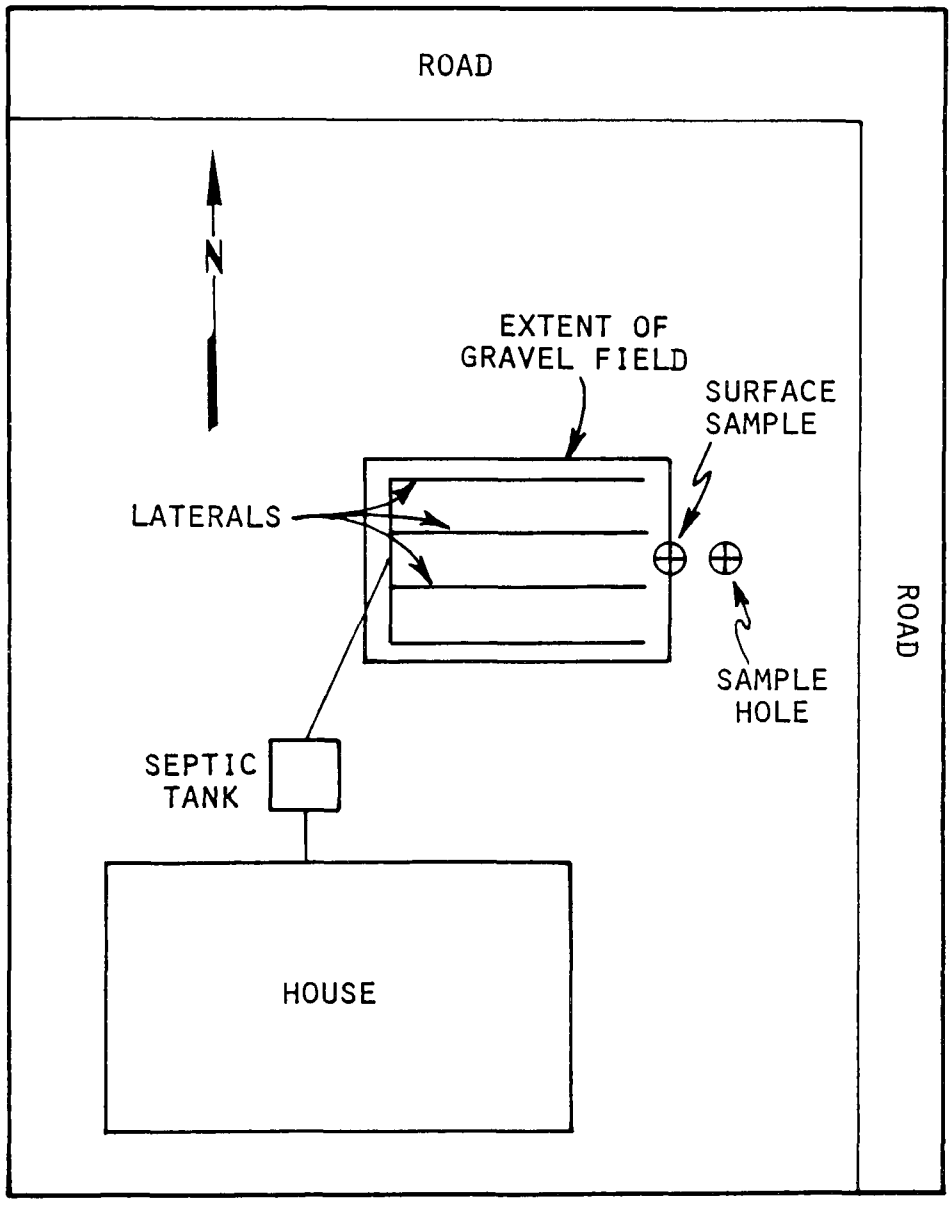

Figure B-11. Plan of Houghton Lake, Michigan, Septic Tank Site A (not to scale)

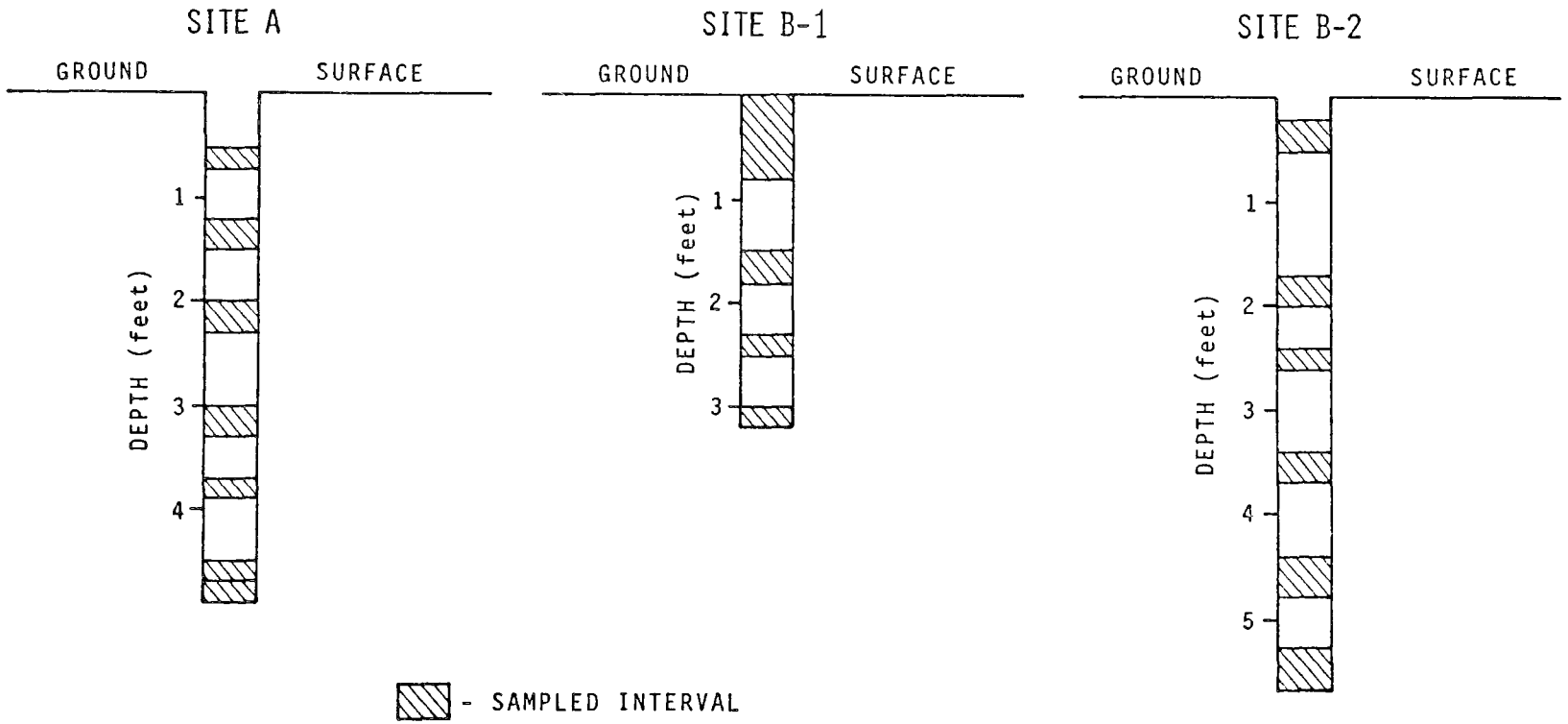

Figure B-12. Depth Intervals Sampled at the Houghton Lake, Michigan Septic Tank Sites.

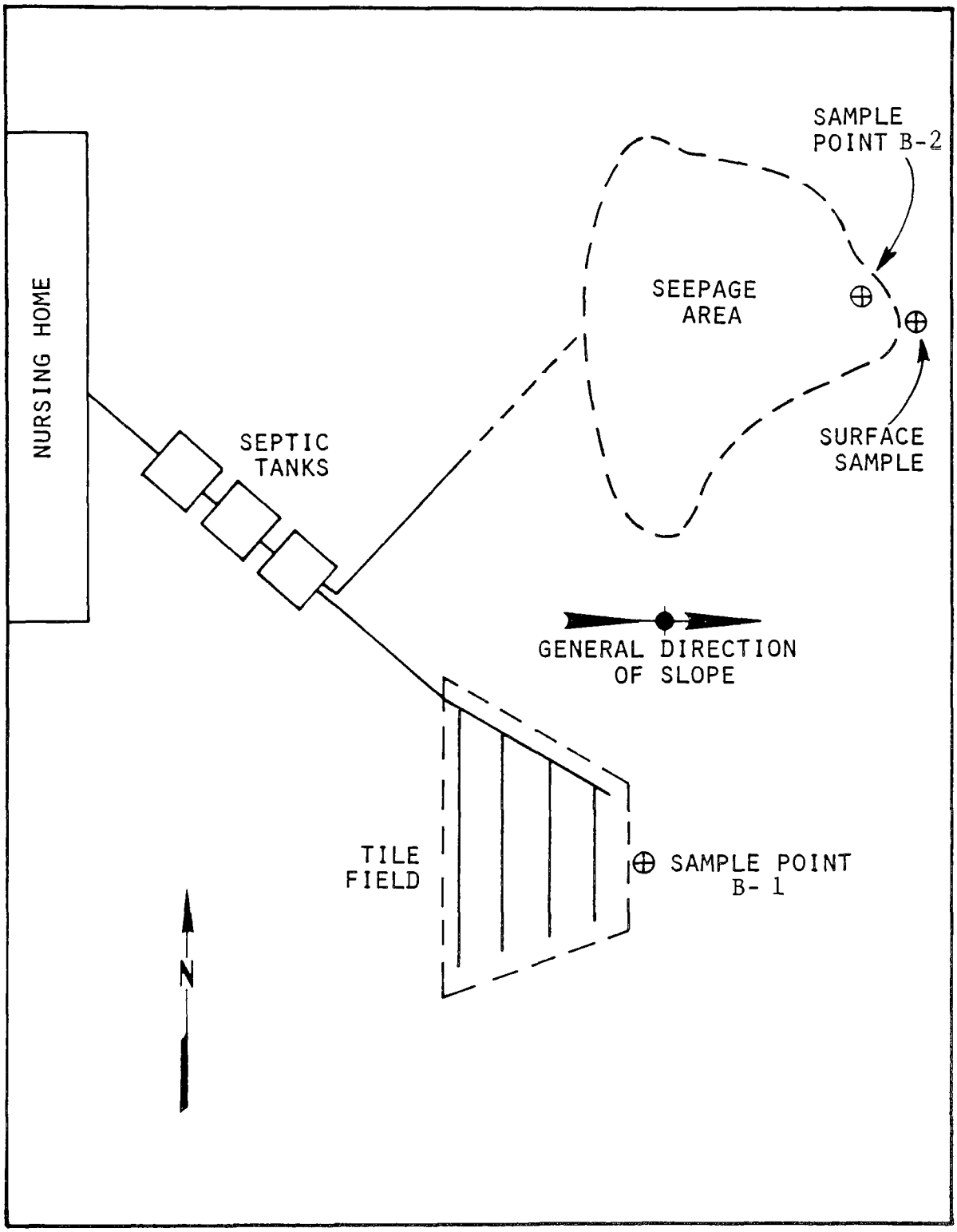

Figure B-13. Plan of Houghton Lake, Michigan, Septic Tank Site B (not to scale).

The other tile field at the nursing home site is overloaded. The exact location of the tile field was not delineated because of the heavily overgrown, spongy nature of the soil. Effluent was observed seeping from the soil surface and flowing for a distance of about 10 feet down the side of the moraine. Samples were acquired from a point immediately downslope from the point where the effluent reentered the soil. This sample point is designated B-2 in Figure B-13. The sampled intervals for Point B-2 are also indicated in Figure B-12.

It was obvious that during periods of heavy use and/or rainfall, the area of seepage to the surface is much greater than that observed on the sampling data. A near-surface (0.2-0.6 feet) sample was, therefore, taken at a point about five feet downslope from Point B-2. This sample point is also indicated in Figure B-13.

CITY OF TAMPA, FLORIDA, SPRAY IRRIGATION SITE

A plan of the Tampa Fowler Avenue Spray Irrigation Site, showing the locations of the monitoring wells that were sampled, is presented in Figure B-14. Duplicate samples were obtained from each of the 11 wells. The wells range from 38 to 103 feet in depth. The wells were pumped for about five minutes prior to collecting the water samples. Ten ml of 1N H_2SO_4 were added to each sample as a preservative. The samples were stored at 4°C prior to shipment (14 days). They were frozen upon receipt in Austin.

Soil samples were obtained at three locations in Spray Lot 7, adjacent to wells 1B and 1C (see Figure B-14). Spray Lots 6 and 7 have been in operation since September of 1973.

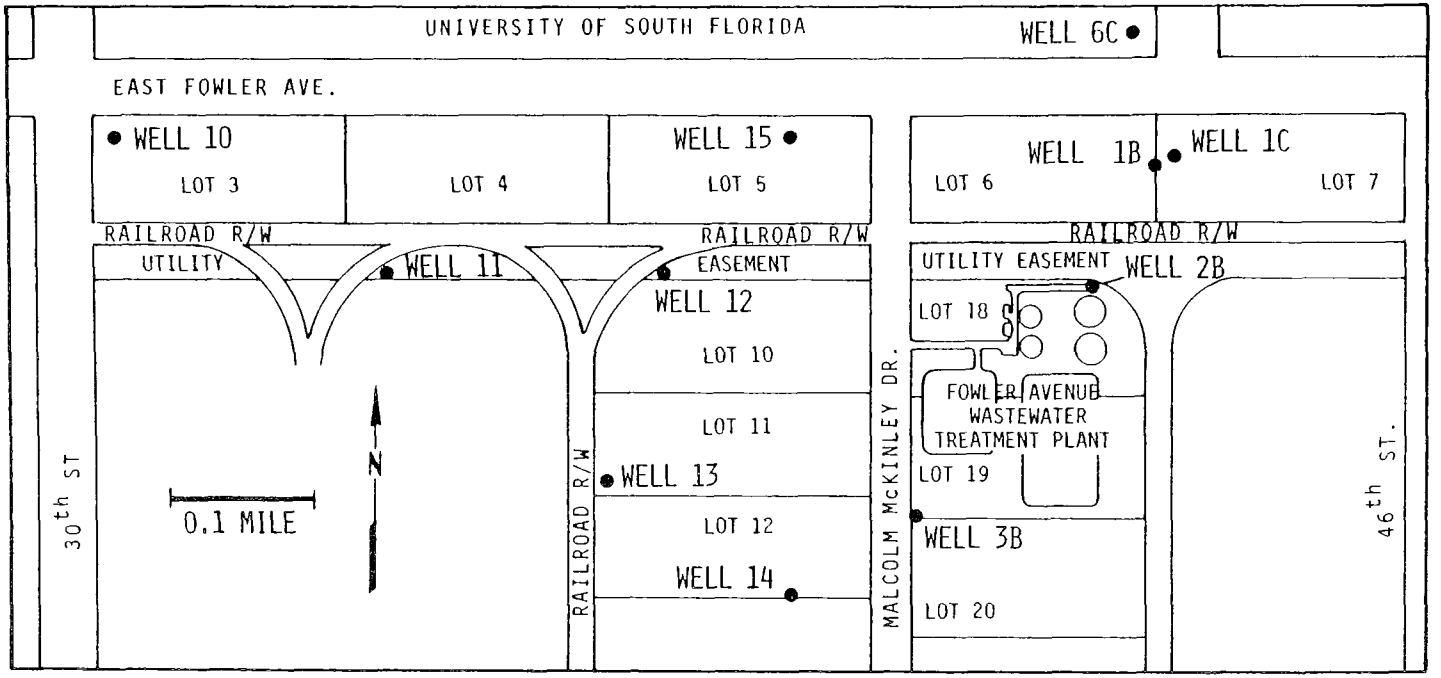

Figure B-14. Plan of Tampa, Florida, Wastewater Spray Irrigation Site.

The sample collected at Location A consists of a single 1.25 inch diameter core. The core sample extends from the surface to a depth of 10 feet. Those collected at Location B consist of both core and augered samples. The core extends to a maximum depth of 20 feet. Augered samples were collected from discrete intervals to a depth of about 7 feet.

Samples collected at Location C consist of two cores and a suite of auger samples. One core extends to a depth of 20 feet, and the other to a depth of 1.9 feet. The augered samples were collected from discrete intervals to a depth of 8 feet. A total of 21 discrete augered samples were collected from the three locations.

TALLAHASSEE, FLORIDA, SPRAY IRRIGATION SITE

The Tallahassee spray irrigation site is located adjacent to the Thomas P. Smith Wastewater Renovation Plant. Figure B-15 is a plan of the plant and spray fields, showing the locations of the three soil sample holes and four of the six wells that were sampled. These four wells are maintained by the City of Tallahassee. The average depth is about 40 feet. The two other wells that were sampled are maintained by the U.S. Geological Survey. They are located about 0.1 and 0.5 miles south (down-gradient) of the irrigation fields. Well No. 17 is 152 feet deep and Well No. 21 is 247 feet deep. Water levels vary over the region and during the year from about 15 feet to 35 feet below land surface.

The four city wells are completed in sand overlying the St. Marks Limestone (Floridan Aquifer). The two U.S.G.S. wells are cased through the surficial sand deposits and are open to the limestone of the Floridan Aquifer. The sand and the underlying Floridan Aquifer are hydraulically connected.

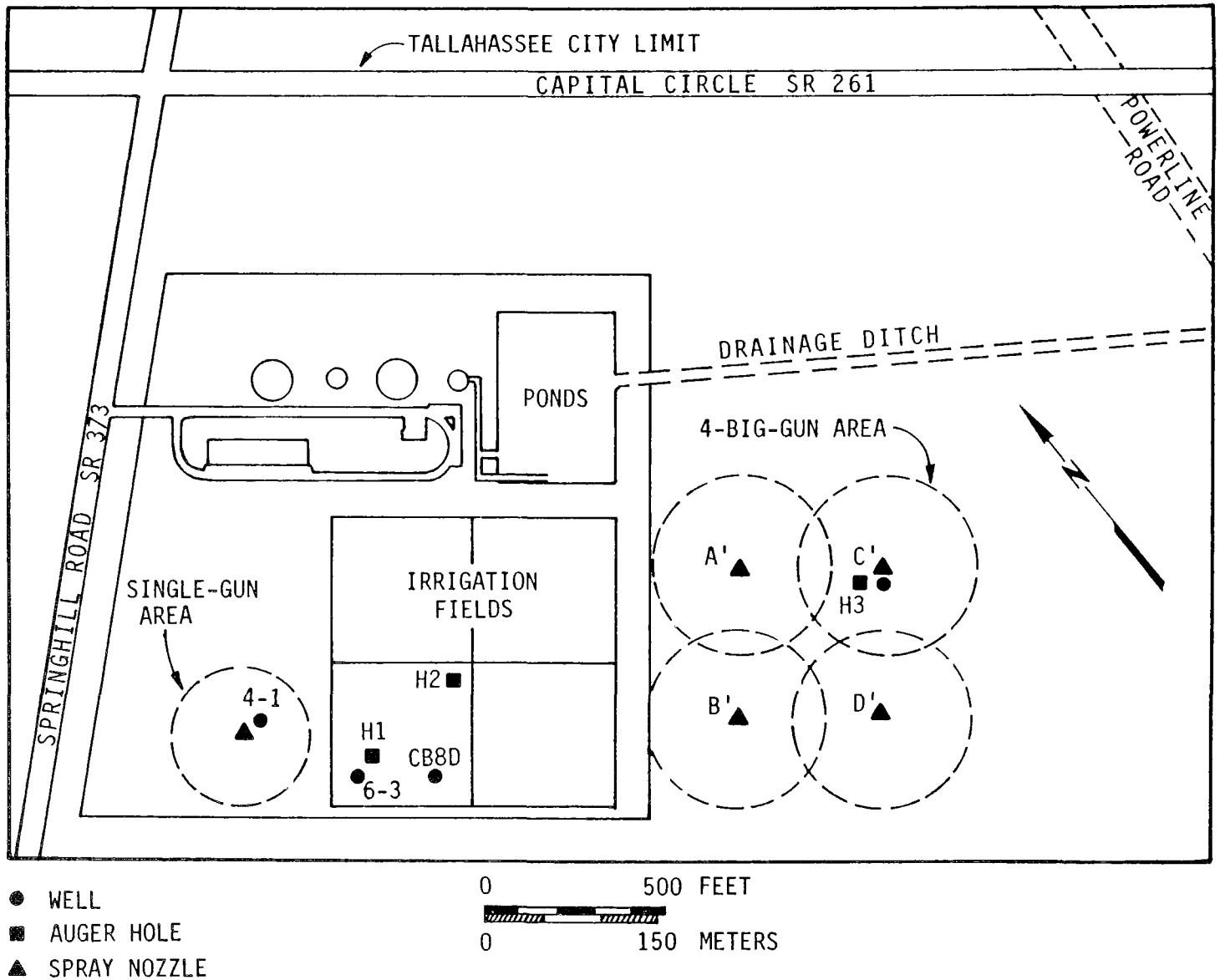

Figure B-15. Plan of Tallahassee, Florida, Spray Irrigation Site Showing Locations of Sampled Wells and Auger Holes.

Samples from the six wells were obtained by pumping the wells for about five minutes, or until the water level dropped below the pump. Two one-quart samples were then collected. Ten ml of 1N H_2SO_4 were added to the samples collected from Wells 4-2, 6-3, and 17. No preservative was added to the samples collected from Wells CB8D, 4-1, and 21. These samples were placed in a freezer within one hour of the time they were collected, and had frozen within five hours.

The soil samples were collected using a 4 inch diameter soil auger. The samples were taken from measured depth increments and were sealed in plastic bags. They were put on dry ice within three hours of the time they were collected. The locations of the three soil sampling holes are shown in Figure B-15. The depth intervals sampled in each hole are shown in Figure B-16. A total of 19 soil samples were collected.

ABILENE, TEXAS, LAND APPLICATION SITE

The Abilene wastewater irrigation farm is located in Jones and Shackleford Counties, Texas, about eight miles northeast of the city off State Route 351. A map of the site is presented in Figure B-17. The treatment plant, immediately adjacent to the farm, handles an average wastewater flow of slightly more than ten million gallons per day. After receiving secondary treatment, the water is stored in several large holding ponds. The water is delivered to the fields via ditches. Irrigation is by flooding (overland flow and/or ridge and furrow). When no irrigation is required, the water is discharged from the ponds to the Deadman Creek drainage system, a part of the Brazos River Basin. The irrigation schedule is determined by the farmers who lease the land from the city.

A total of 16 soil samples were acquired from two locations at the farm. The samples are from specific depth intervals from the surface to a maximum depth of about seven feet. The sampling

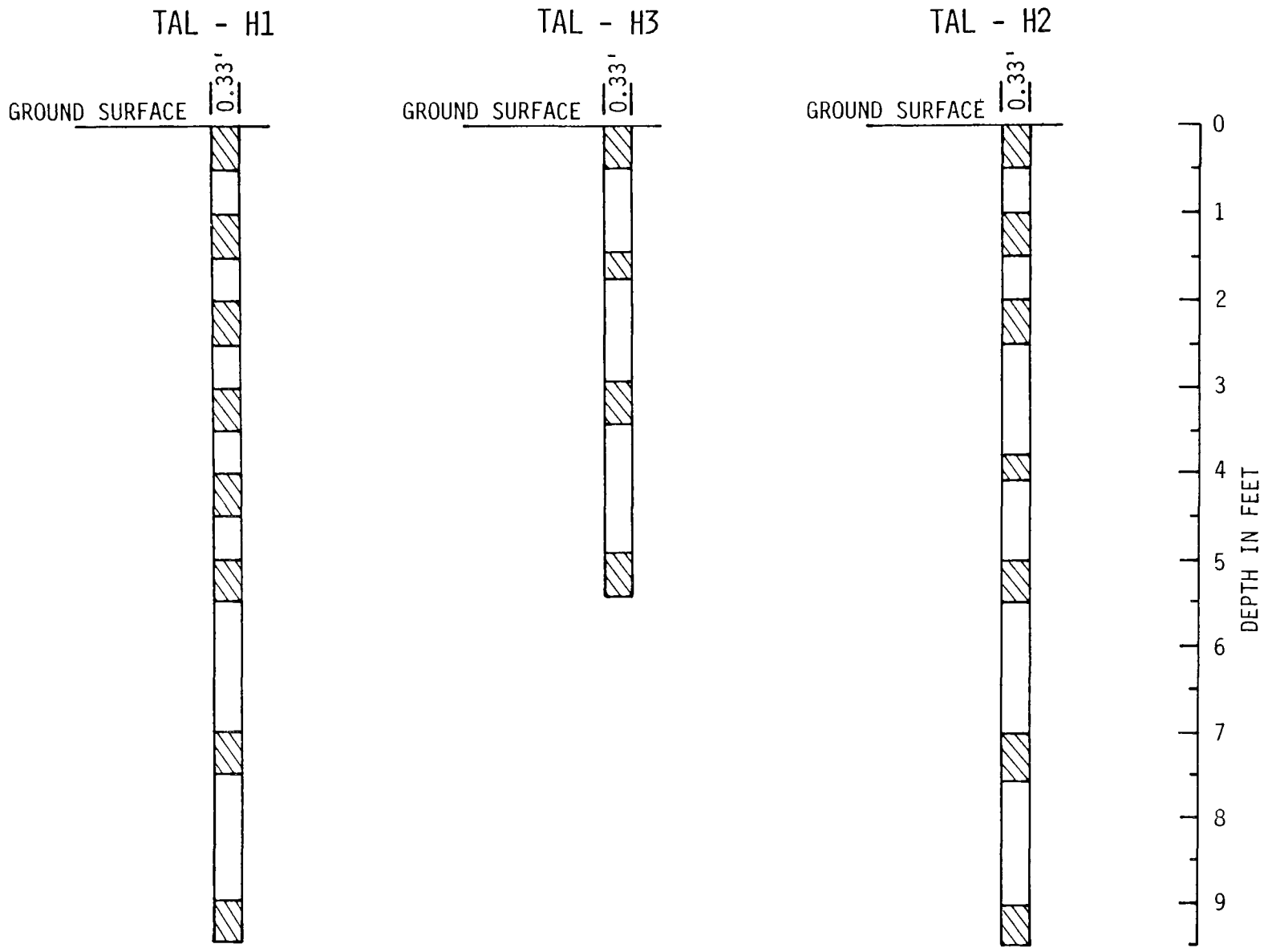

Figure B-16. Depth Intervals Sampled at the Tallahassee, Florida, Wastewater Spray Irrigation Site.

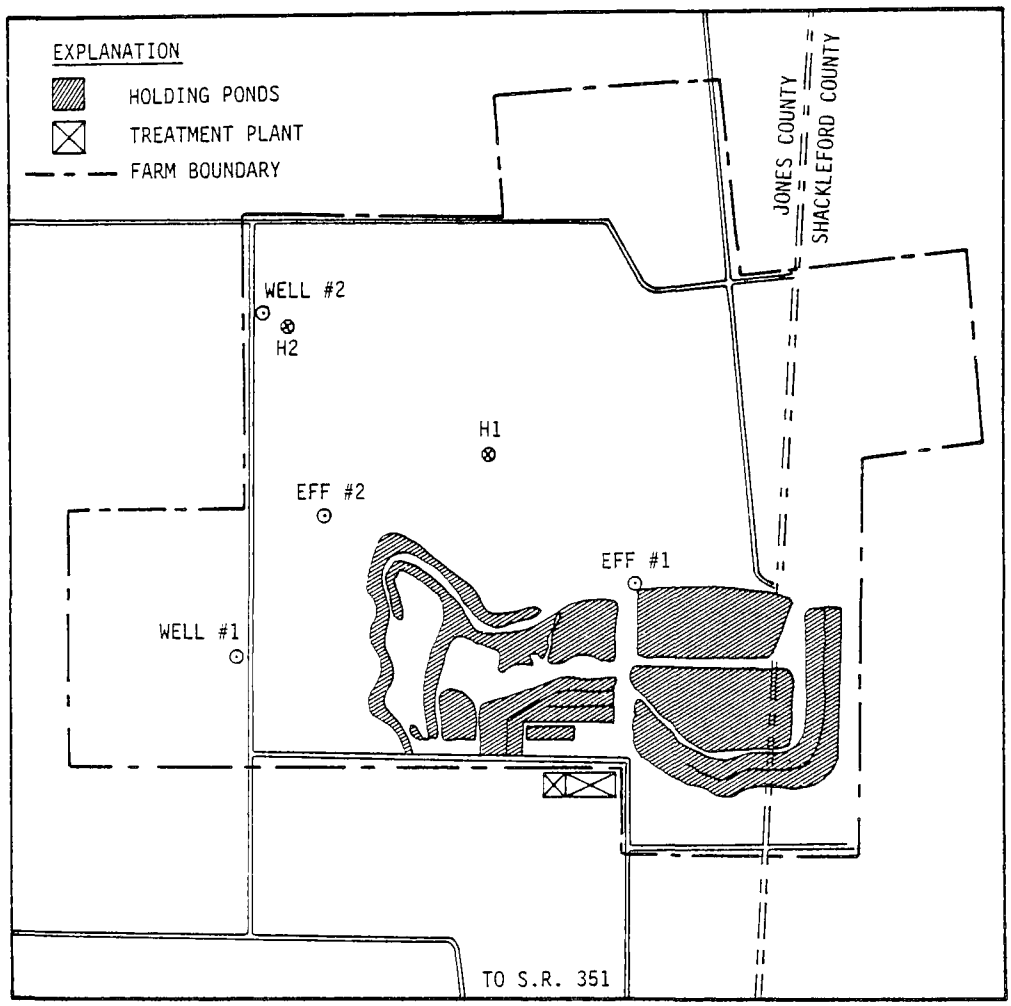

Figure B-17. Plan of the Abilene Municipal Wastewater Land Application Site, Showing Sampling Locations.

locations, designated H1 and H2, are indicated in Figure B-17. The depth intervals sampled from each site are shown in Figure B-18.

Six water samples were obtained at the Abilene site. Two of the samples are from wells located within the irrigated area. The wells are shallow (about 25 and 50 feet). One is not in use. The other is used for watering a lawn and small vegetable garden. Both are completed in a sand and gravel bed.

Two of the water samples are of the irrigation water (treated effluent). These samples were taken from ditches delivering water to the fields. The last two water samples were obtained from soil sampling hole H1. Water was encountered in H1 at a depth of 5.2 feet. The hole was extended to 6.3 feet and a sample of water was collected. The hole was then bailed out four times, over a period of about 30 minutes, and another sample was acquired. The locations from which the water samples were obtained are shown in Figure B-17.

SAN ANGELO, TEXAS, LAND APPLICATION SITE

The San Angelo wastewater irrigation farm is located about five miles east of the city off Texas Farm/Market Road 380. A map of the site is presented in Figure B-19. At present, wastewater receives primary treatment only. The plant is currently being expanded to provide secondary treatment. The method of irrigation is flooding.

Soil samples were collected at four locations on the farm. These are indicated in Figure B-19. At two of the sampling locations (H1 and H3) surface samples were collected. Samples were collected from discrete depth intervals at the other two locations (H2 and H4) to a maximum depth of 6.4 feet. The depth intervals sampled at these two sites are shown in Figure B-20. The total number of samples collected was 15.

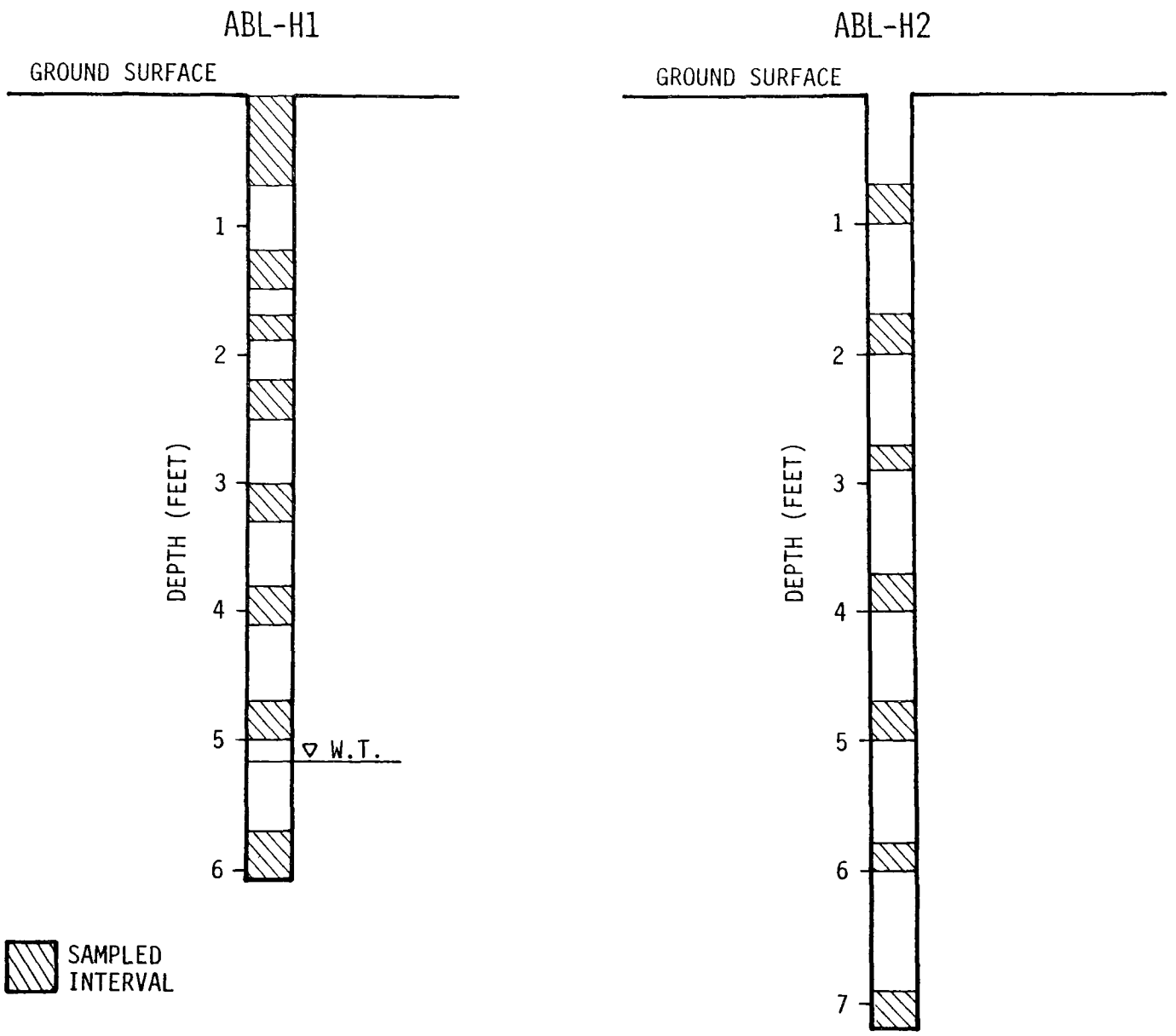

Figure B-18. Depth Intervals Sampled At the Abilene Land Application Site.

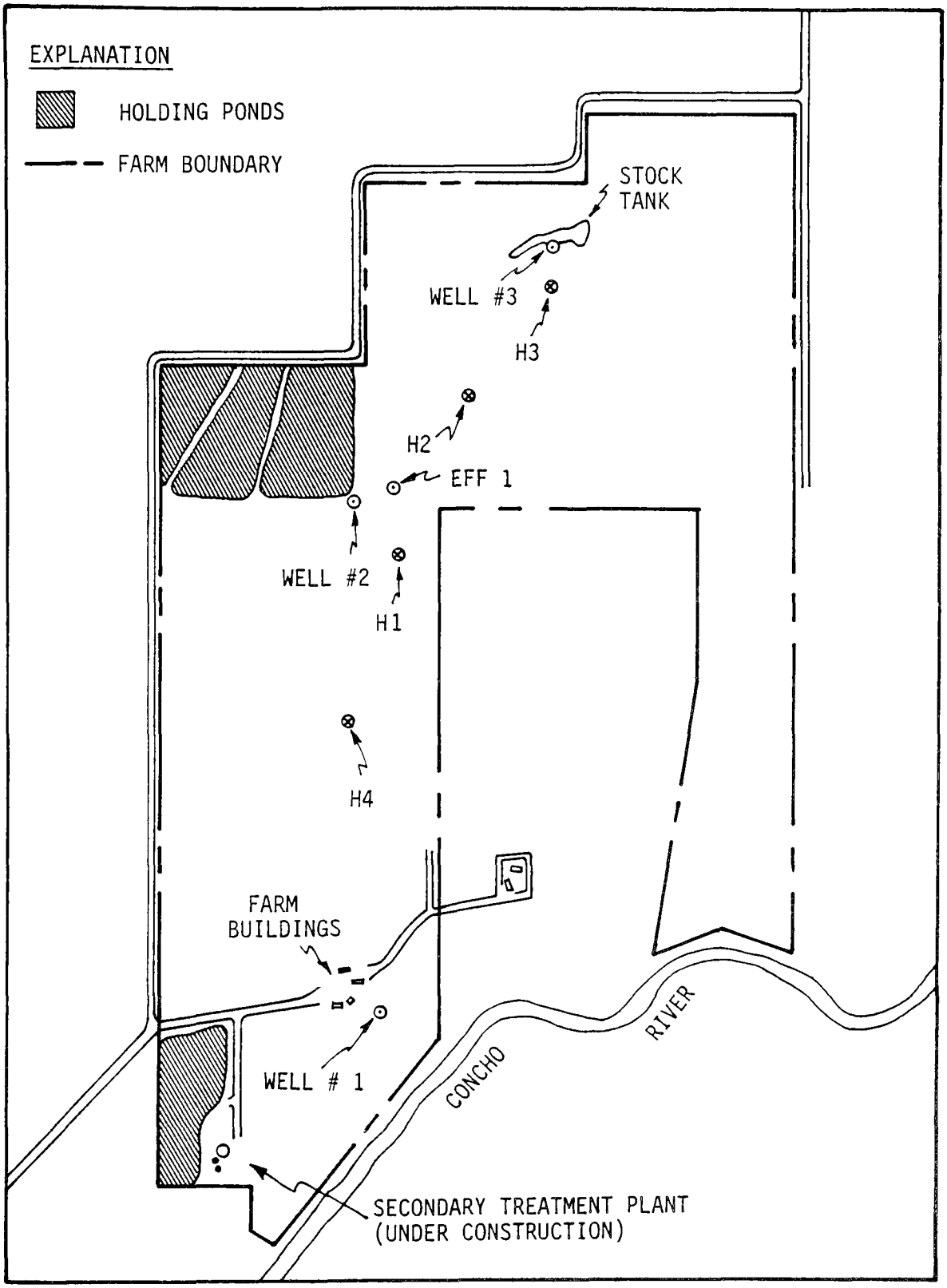

Figure B-19. Plan of the San Angelo, Texas, Municipal Wastewater Land Application Site, Showing Sampling Locations.

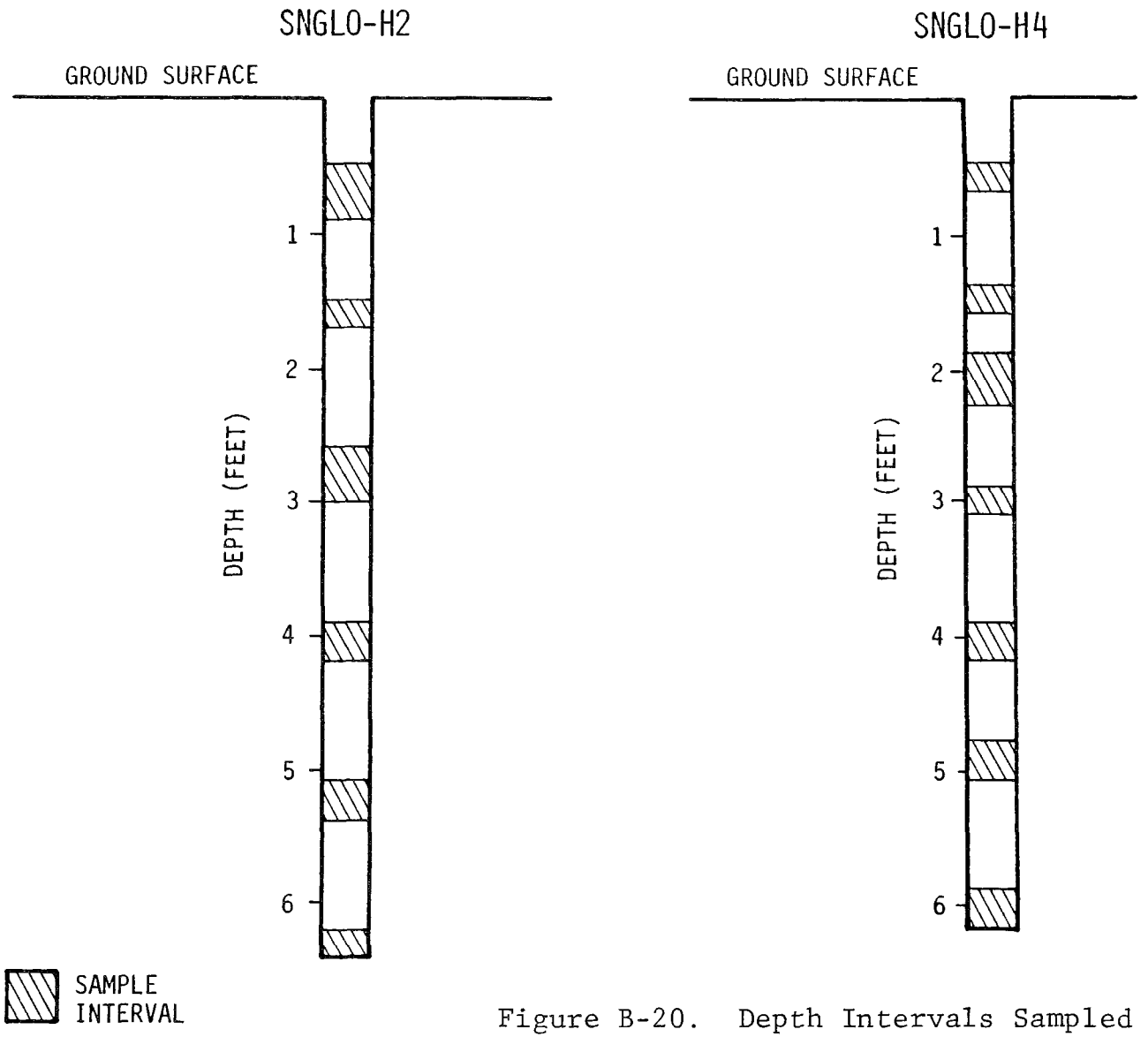

Figure B-20. Depth Intervals Sampled at the San Angelo, Texas, Land Application Site.

Four water samples were collected in San Angelo. Three are well-water samples from wells in the irrigated areas. The fourth is a sample of the irrigation water.

Well No. 1 serves the farm building complex. The well is 78 feet deep. The water level at the time of sampling was about 35 feet below land surface. It is operated with an electric submersible pump. The sample was collected at the well head after pumping for a period of 20 minutes. This well may penetrate more than one water-bearing zone.

Well No. 2 is located adjacent to a small corral and is used to supply a watering trough. It is 48 feet deep. The water level was at 22 feet. The sample was collected in the same manner as at Well No. 1.

Well No. 3 is a shallow well (exact depth unknown) used to maintain a stock watering pond. It is operated by a windmill and pumps nearly continuously at about 4 gpm. The sample was collected from the pipe where the well discharges to the pond.

The sample of irrigation water was collected as the water was being applied to a field. The delivery system is made up of buried 12-inch pipe along the boundaries of the fields. Water is applied directly from the holding ponds. The water sampling locations are indicated in Figure B-19.

MICHIGAN STATE UNIVERSITY WASTEWATER LAND APPLICATION SITE

Michigan State University began its program to investigate the effects of land application of municipal wastewater in 1973. A plan of the irrigation site is shown in Figure B-21. The site was once farmed but has been lying idle for about 15 years. The vegetation cover is mainly old-field vegetation. About one-fifth of the site is comprised of a Beech-Maple woodlot.

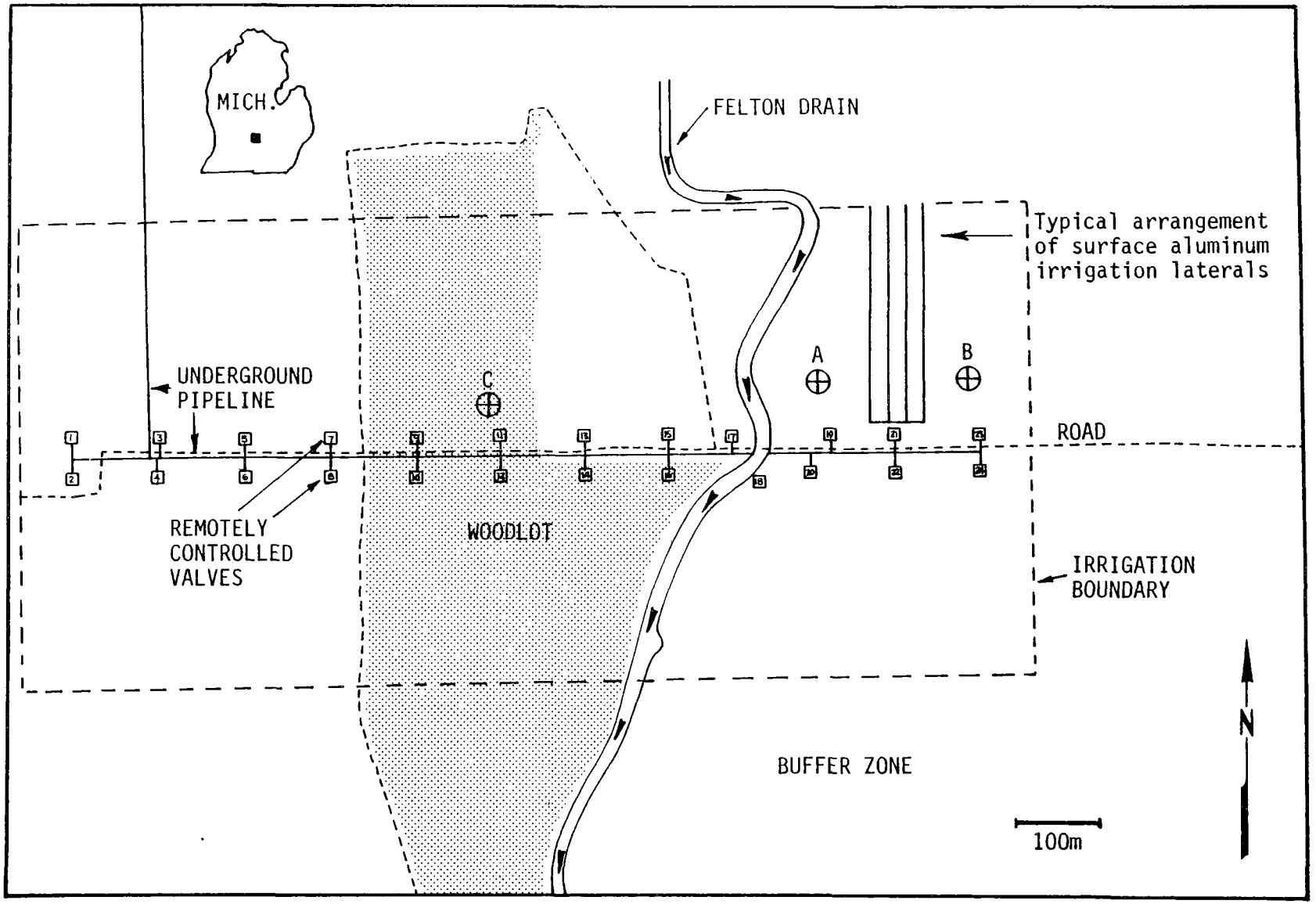

Figure B-21. Plan of the MSU Experimental Wastewater Application Site, Showing Sampling Locations (A,B,C).

Samples were collected from three locations at the MSU spray site (see Figure B-21). Sample Point A is located in an old-field area receiving 4 inches of effluent per week. Sample Point B is located in a control area which receives no effluent. The third soil sampling, Point C, is located in the Beech-Maple woodlot. This area receives 4 inches of effluent per week. The depth intervals sampled at each point are indicated in Figure B-22. Sixteen soil samples were collected in all.

In addition to these soil samples, seven water samples were collected. Five of these are of soil water obtained from lysimeters in the old-field and woodlot areas. The sixth is from a pond located in the woodlot, and the seventh is a sample of ground water. This was obtained from the top of the water table (depth = 5 feet) at sample Point C.

GREELEY, COLORADO, CATTLE FEEDLOT SITE

Soil samples were collected from a feedlot near Greeley, Colorado. No known previous work has been done for this site, with the exception of soil mapping by the Soil Conservation Service. The feedlot is an operation consisting of about 40,000 cattle. Part of the feedlot is on the bottomland of the Cache la Poudre River (a tributary of the South Platte), and part is on an adjoining terrace. Runoff from the feedlot is apparently impounded to prevent it from entering the Cache la Poudre River.

Two sites were selected for sampling at this feedlot. Both are in cattle pens. The first site (A) was chosen in the older part of the feedlot, which has been operating since the 1930's. This site is on a gravel terrace. The log for the sample hole is shown in Figure B-23. A total of 5 soil samples were retained for transport back to Austin. Gravel that could not be penetrated with the soil auger was encountered at a depth of

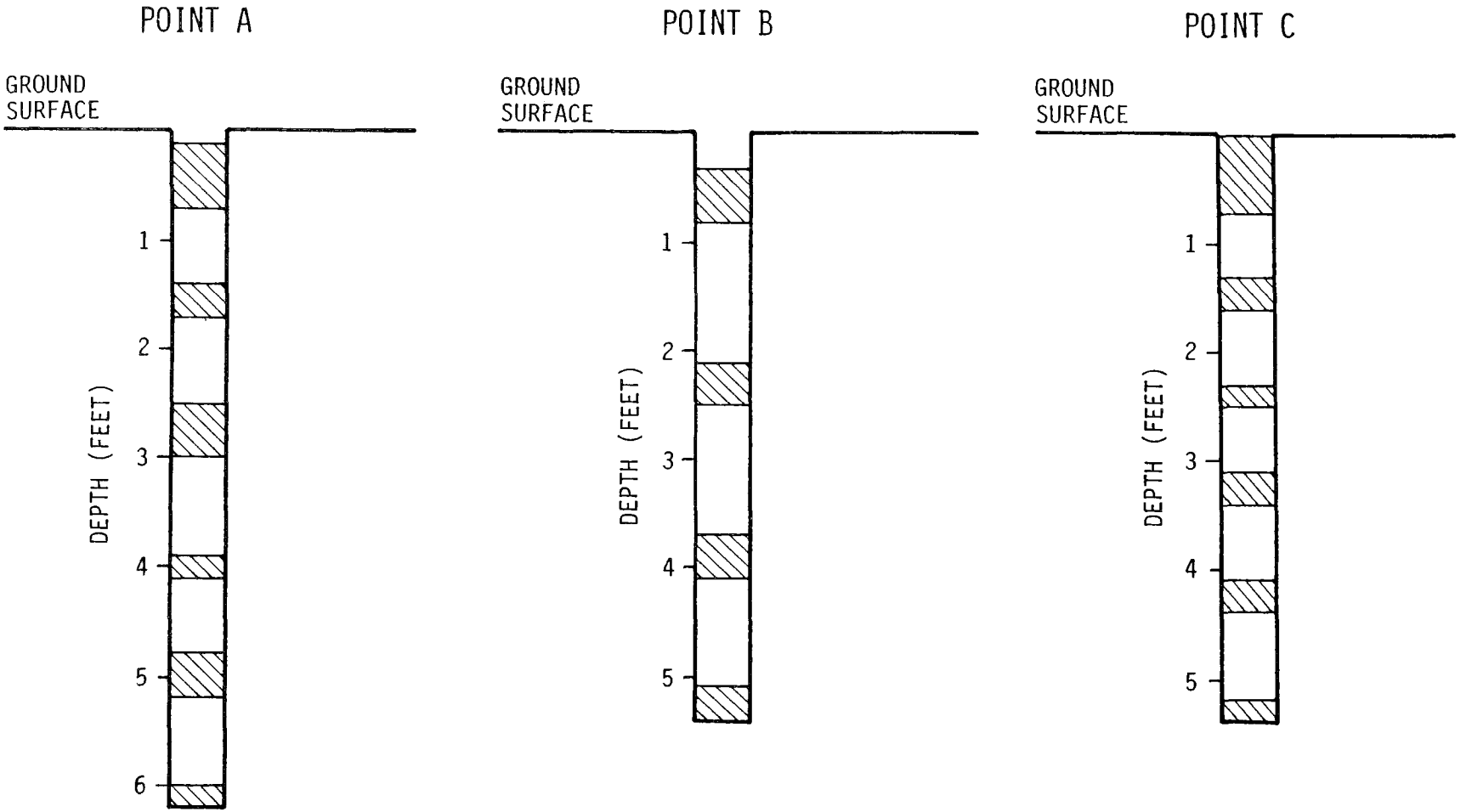

Figure B-22. Depth Intervals Sampled at the MSU Wastewater Land Application Site.

SAMPLED INTERVAL

only two feet, so the sample point was considered only a partial success. A second sample site (B) was therefore chosen on the bottomlands, as a backup. This site has been used as a feedlot for about 12 years. The log of this sample hole is also given in Figure B-23. Seven samples were collected from this hole to a depth of 6 feet.

In addition to these soils samples, one water sample was collected from a shallow well near the feedlot. No data are available for this well, but it is apparently a shallow well in the Cache la Poudre River alluvium. The water has a foul odor and appears to be contaminated, but part of the contamination may be from surface runoff.

DIMMITT, TEXAS, CATTLE FEEDLOT SITE

The Dimmitt Feedlot was selected as the representative feedlot for the North Texas High Plains. Little or no previous work has been done at the site except for soil mapping by the Soil Conservation Service. The site is located in the Ogallalla Formation. The feedlot is built concentrically around one of the "playas" that are typical of the Llano Estacado. Drainage from the feedlot is inward into the central playa lake. The feedlot has been in operation about eleven years. A plan of the site is shown in Figure B-24.

Two sites were selected for soil sampling at the Dimmitt Feed Yard. The first site (A) was selected in a cattle pen in the oldest part of the feedlot. A log of the sample hole is shown in Figure B-25. The hole was augered to a depth of only 48 inches because a hard, impenetrable caliche layer was encountered at that depth.

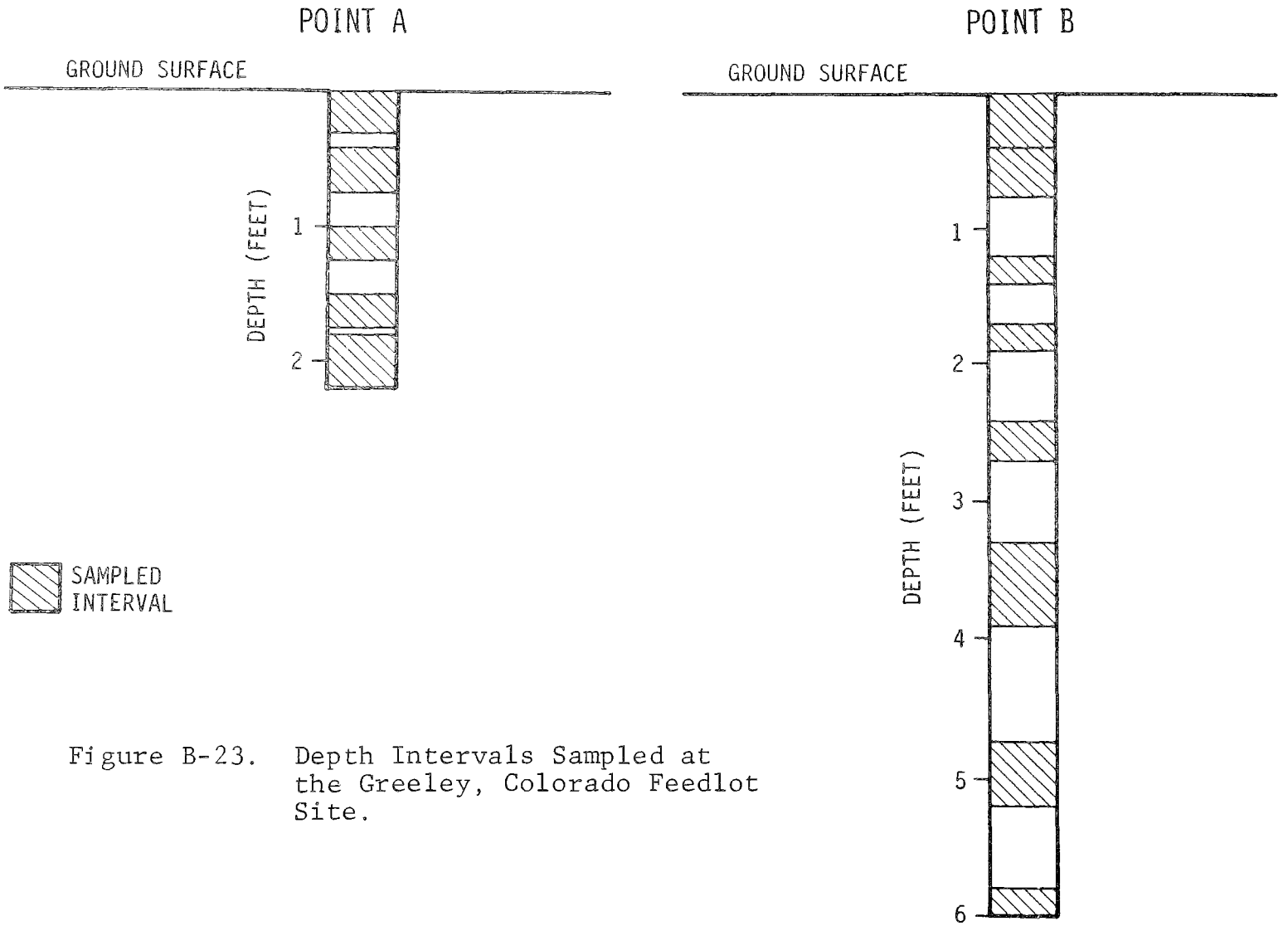

Figure B-23. Depth Intervals Sampled at the Greeley, Colorado Feedlot Site.

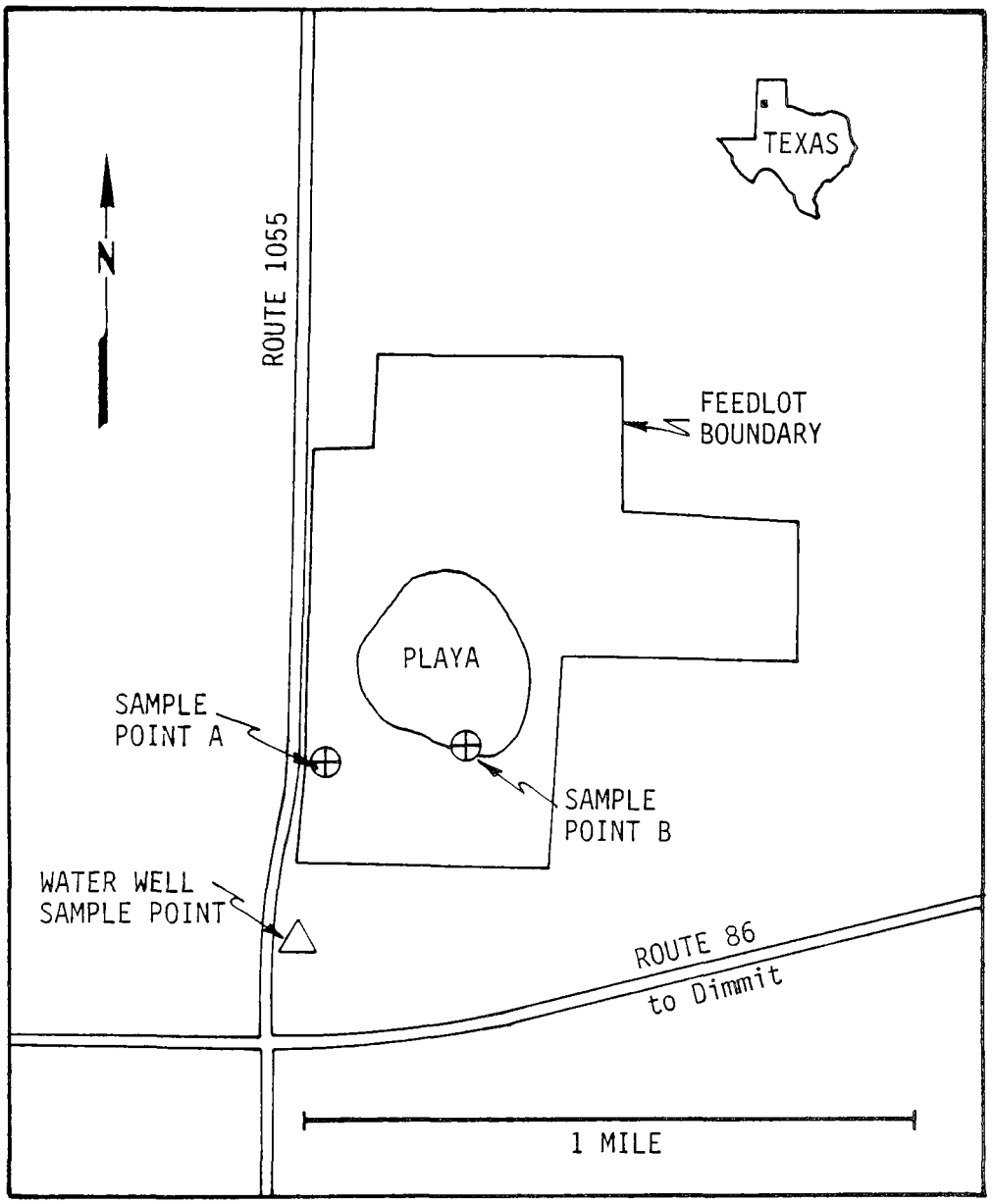

Figure B-24. Plan of the Dimmitt, Texas, Feedlot Site, Showing Sampling Locations.

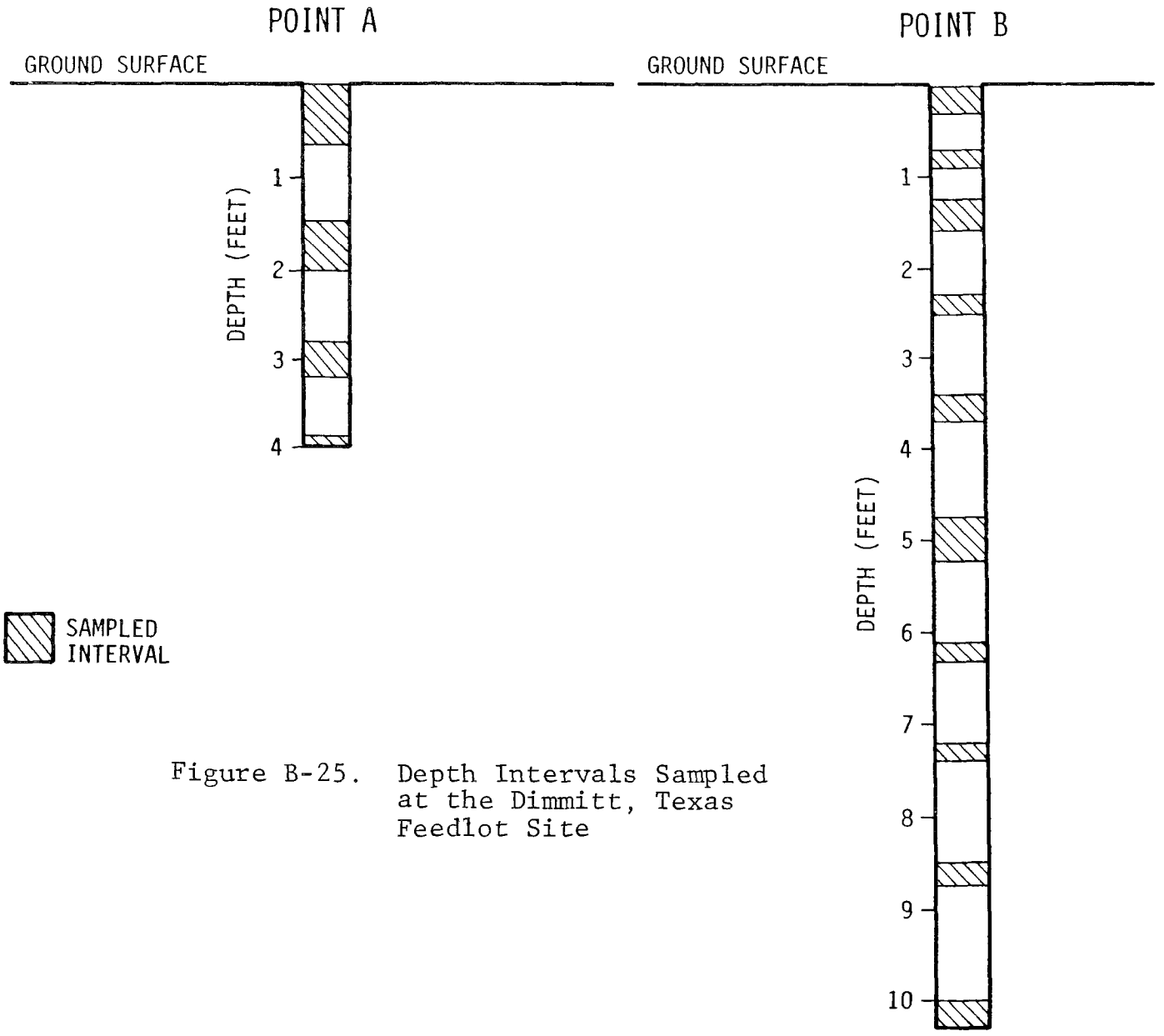

Figure B-25. Depth Intervals Sampled at the Dimmitt, Texas Feedlot Site

Experience at the first sample hole and at the site at Greeley indicated that little precipitation probably infiltrates within the cattle pens. The tightly packed manure mat in the pens appears to act as a virtual pavement, and most precipitation probably goes to surface runoff. Consequently, it was decided to collect a suite of samples at the edge of the playa lake at the Dimmitt site. The log of this sample hole (B) is also shown in Figure B-25. The upper 8 inches at this site is black, spongy, odoriferous washed-in manure. Fourteen samples were collected from these two holes.

A single water well sample was collected from an irrigation well near the site (Figure B-24). No data were obtained for this well, but the pump size indicated the well is several hundred feet deep.

APPENDIX C

SAMPLE NUMBERING SYSTEM

All samples used in the statistical analysis were assigned a sample code number for identification. The sample numbers consist of several parts separated by hyphens.

The first part of the sample number identifies the location from which the sample was obtained. Location codes are defined in Table C-1.

The second part of the sample number identifies the sampling hole, in the case of soil samples, or the well number, in the case of ground-water samples. For samples collected by Radian in the intensive sampling program, these are related to the holes identified in the various sections of Appendix B.

Soil samples have a third part in their sample identification numbers. This part is a number indicating the level within a particular sampling hole from which the sample was obtained. This number is roughly related to depth: deeper samples have higher numbers. An example of the numbering system follows:

a sample is numbered:

HLMA-H2-3

HLMA indicates that the sample is from Houghton Lake, Michigan, site A. H2 indicates that the sample is from the second sampling

TABLE C-1. LOCATION CODES USED IN SAMPLE IDENTIFICATION NUMBERS

ID Code	Sampling Location
TAMU	Texas A&M University; College Station, Texas
RT	Rockdale, Texas
TAM	Tampa, Florida
IH	Indian Hills, Colorado
PU	Pueblo, Colorado
HLMA	Houghton Lake, Michigan, Site A
HLMB	Houghton Lake, Michigan, Site B
TAL	Tallahassee, Florida
ABL	Abilene, Texas
SNGLO	San Angelo, Texas
MSU	Michigan State University; East Lansing, Michigan
GR	Greeley, Colorado
DI	Dimmitt, Texas
LT	Lockhart-Taylor Area, Texas
GC	Grand Caymen Island (Caribbean)
MCM	Macon County, Missouri
QNY	Queens County, New York
RU	Runnels County, Texas

hole completed at that site, and the "3" indicates that the sample is the third sample collected from the sampling hole H2.

These sample code numbers may be used to relate the basic data given in Appendix D to the sites identified in Section 6 and Appendix B.

APPENDIX D

BASIC DATA

The analytical data upon which this report is based are presented in Tables D-1 and D-2. Table D-1 contains soil sample data, and Table D-2 contains ground-water sample data

TABLE D-1. SOIL SAMPLE DATA

Sample@ Number	Source*	Depth (meters)	NO_3^- Concentration (ppm)	$\delta^{15}N$ (ppt)	Reference†
HLMA-H1-1	ST	0.2	22.1	+10.0	a
HLMA-H2-2	ST	0.4	26.1	+20.5	a
HLMA-H2-3	ST	0.7	46.8	+12.3	a
HLMA-H2-5	ST	1.2	30.8	+ 7.4	a
HLMA-H2-6	ST	1.4	52.3	+13.9	a
HLMA-H2-7	ST	1.5	25.8	+10.5	a
HLMB-H1-1	ST	0.1	71.5	-12.8	a
HLMB-H1-3	ST	0.7	18.1	+ 7.6	a
HLMB-H1-4	ST	0.9	9.4	+ 7.8	a
HLMB-H2-1	ST	0.1	8.1	+ 8.0	a
PU-H1-1	ST	0.1	106.4	-12.7	a
PU-H1-4	ST	1.0	34.9	+12.5	a
PU-H1-7	ST	2.0	30.0	+ 7.3	a
PU-H1-8	ST	2.4	21.0	+ 6.8	a
PU-H1-9	ST	2.8	48.2	+ 6.7	a
PU-H1-10	ST	3.3	18.9	+23.8	a
IH-H1-4	ST	1.2	8.3	-20.0	a
RT-H5-1	ST	0.5	5.0	+17.0	a
RT-H5-2	ST	0.8	1.8	+19.0	a
RT-H8-2	ST	0.7	20.1	+ 7.3	a
RT-H8-3	ST	1.0	8.7	+10.0	a
TAMU-H1-2	ST	1.1	10.9	+13.0	a
TAMU-H2-1	ST	0.7	10.3	+ 7.2	a
TAMU-H4-1	ST	0.8	5.7	+11.0	a
TAMU-H2-3	ST	0.6	15.0	+ 8.0	a

(continued)

TABLE D-1 (continued)

Sample@ Number	Source*	Depth (meters)	NO_3^- Concentration (ppm)	$\delta^{15}N$ (ppt)	Reference†
TAM-H4-1	ST	0.1	18.0	+ 3.9	a
TAM-H4-3	ST	0.4	56.0	- 6.3	a
TAM-H4-4	ST	0.8	23.2	+ 5.8	a
TAM-H4-5	ST	0.9	14.2	+18.8	a
TAM-H4-6	ST	1.1	28.8	- 0.4	a
TAM-H4-7	ST	1.2	10.4	+21.0	a
TAM-H4-8	ST	1.5	19.3	+26.7	a
TAM-H4-9	ST	1.9	31.7	+ 3.8	a
TAM-H5-2	ST	0.4	34.2	+24.6	a
TAM-H5-4	ST	0.7	23.8	+25.9	a
TAM-H5-11	ST	3.0	8.0	+30.3	a
TAM-H4A-1	ST	3.0	102.6	+ 8.6	a
DI-H1-1	AW	0.1	36.2	+ 8.7	a
DI-H1-3	AW	0.9	16.8	- 0.2	a
DI-H2-4	AW	0.7	40.4	- 5.0	a
DI-H2-5	AW	1.1	46.8	+10.5	a
DI-H2-6	AW	1.5	142.9	- 3.9	a
DI-H2-7	AW	1.9	48.8	- 5.7	a
DI-H2-8	AW	2.2	91.9	+23.4	a
DI-H2-9	AW	2.6	100.7	- 5.2	a
GR-H2-2	AW	0.2	30.1	+27.7	a
GR-H2-4	AW	0.4	44.0	+26.4	a
GR-H2-6	AW	0.5	31.5	+13.4	a
GR-H2-8	AW	0.8	47.0	+18.6	a
GR-H2-10	AW	1.1	82.0	+14.2	a
GR-H1-4	AW	0.3	43.8	+ 3.5	a
GR-H1-7	AW	0.6	30.5	-22.0	a

(continued)

TABLE D-1 (continued)

Sample@ Number	Source*	Depth (meters)	NO_3^- Concentration (ppm)	$\delta^{15}N$ (ppt)	Reference†
MSU-H1-1	MWW	0.1	10.4	+ 6.9	a
ABL-H1-4	MWW	0.5	12.6	+16.7	a
ABL-H1-7	MWW	1.2	6.3	+ 3.5	a
SNGLO-H2-1	MWW	0.2	17.1	+ 6.4	a
SNGLO-H2-2	MWW	0.5	16.5	+ 8.5	a
SNGLO-H2-3	MWW	0.9	22.8	+ 0.2	a
SNGLO-H2-4	MWW	1.2	30.8	+10.4	a
SNGLO-H2-6	MWW	1.9	17.0	+ 8.3	a
LT-H1-1	AW	0.3	1116.0	+17.3	b
LT-H2-1	AW	0.3	37.0	+37.6	b
LT-H3-1	AW	0.3	25.0	+17.6	b
RU-HA-1	O	0.6	348.0	+ 4.4	c
RU-HA-2	O	0.9	458.0	+ 3.8	c
RU-HA-3	O	1.2	381.0	+ 4.5	c
RU-HA-4	O	1.5	237.0	+ 3.6	c
RU-HA-5	O	2.1	105.0	+ 2.7	c
RU-HA-6	O	2.4	104.0	+ 2.0	c
RU-HA-7	O	2.7	44.0	+ 2.5	c
RU-HB-1	AW	0.3	42.5	+15.3	c
RU-HB-2	AW	0.9	25.0	+17.9	c
RU-HB-3	AW	1.2	19.0	+11.8	c
RU-HB-4	AW	1.8	43.0	+11.6	c
RU-HB-5	AW	2.3	32.0	+ 7.0	c
RU-HC-1	O	0.3	43.0	+ 3.3	c
RU-HC-2	O	0.9	65.0	+ 3.9	c
RU-HC-3	O	1.5	75.0	+ 5.0	c
RU-HC-4	O	2.1	104.0	+ 3.8	c

(continued)

TABLE D-1 (continued)

Sample@ Number	Source*	Depth (meters)	NO_3^- Concentration (ppm)	$\delta^{15}N$ (ppt)	Reference†
RU-HD-1	AW	0.3	180.0	+13.6	c
RU-HD-2	AW	0.9	1682.0	+16.5	c
RU-HD-3	AW	1.2	1300.0	+15.2	c
RU-HD-4	AW	1.5	429.0	+13.7	c
RU-HD-5	AW	1.8	706.0	+14.1	c
RU-HD-6	AW	3.0	700.0	+14.0	c
RU-HE-1	O	0.6	30.0	+24.6	c
RU-HE-2	O	1.2	126.0	+31.0	c
RU-HE-3	O	2.1	36.0	+19.2	c
RU-HG-1	AW	0.6	135.0	+21.9	c
RU-HH-1	O	0.8	10.0	+12.4	c
RU-HH-2	O	1.4	25.0	+ 7.8	c
RU-HJ-2	AW	0.9	805.0	+ 9.7	c
RU-HK-1	O	0.5	13.0	+ 5.8	c
RU-HK-2	O	1.1	36.0	+ 6.5	c
RU-HK-3	O	1.8	58.0	+ 5.6	c
RU-HK-4	O	2.1	49.0	+ 4.6	c
RU-HK-5	O	2.4	45.0	+ 4.9	c
RU-HL-1	O	0.3	78.0	+ 4.4	c
RU-HL-2	O	0.9	36.0	+ 5.7	c
RU-HL-3	O	1.5	32.0	+ 6.2	c
RU-HM-1	AW	0.9	1032.0	+14.0	c
RU-HN-1	O	0.3	37.0	+ 3.3	c
RU-HN-2	O	0.9	32.0	+ 8.6	c
RU-HN-3	O	1.5	19.0	+ 6.2	c
RU-HO-1	O	0.6	225.0	+ 6.7	c
RU-HO-2	O	0.9	450.0	+ 5.7	c

(continued)

TABLE D-1 (continued)

Sample@ Number	Source*	Depth (meters)	NO_3^- Concentration (ppm)	$\delta^{15}N$ (ppt)	Reference†
RU-HO-3	O	2.1	65.0	+ 6.4	c
RU-HO-4	O	2.7	70.0	+ 6.2	c
RU-HP-1	ST	0.6	33.0	+17.8	c
RU-HP-2	ST	0.9	33.0	+13.0	c
RU-HQ-1	AW	1.5	17.0	+15.9	c
RU-HR-1	O	2.0	10.0	+10.4	c
RU-HS-1	O	0.0	631.0	+ 9.8	c
RU-HT-1	AW	0.9	306.0	+14.6	c
RU-HU-1	ST	0.6	711.0	+10.3	c
RU-HU-2	ST	0.9	523.0	+12.4	c

@Sample numbers are explained in Appendix C.

*Sources: ST = Septic Tank; AW = Animal Waste; MWW = Municipal Wastewater; O = Other.

†References: a = This work; b = Kreitler, unpublished data; c = Kreitler (2).

TABLE D-2. GROUND-WATER SAMPLE DATA

Sample[@] Number	Source*	NO_3^- Concentration (ppm)	$\delta^{15}N$ (ppt)	Reference[†]
IH-W1	ST	108.0	+ 6.0	a
IH-W2	ST	66.0	+ 7.5	a
IH-W4	ST	90.0	+10.0	a
IH-W5	ST	92.0	+ 3.3	a
MSU-W4	MWW	14.0	+ 8.0	a
MSU-W5	MWW	8.0	+26.0	a
LT-W1	AW	16.0	+18.2	b
LT-W2	AW	341.0	+17.2	b
LT-W3	AW	313.0	+17.8	b
LT-W4	AW	200.0	+ 7.3	b
LT-W5	AW	147.0	+18.4	b
LT-W6	AW	226.0	+11.8	b
LT-W7	AW	271.0	+ 9.8	b
LT-W8	AW	12.0	+16.6	b
GC-W1	ST	27.3	+21.7	b
GC-W2	ST	29.0	+14.2	b
GC-W3	ST	12.3	+19.0	b
GC-W4	ST	11.9	+18.0	b
MCM-W1	AW	75.0	+15.9	c
MCM-W2	Aw	62.0	+10.8	c
MCM-W3	AW	105.0	+18.8	c
MCM-W4	ST	260.0	+14.5	c
MCM-W5	AW	330.0	+13.7	c
MCM-W6	AW	60.0	+16.6	c
MCM-W7	AW	95.0	+13.5	c
MCM-W8	AW	145.0	+16.2	c
MCM-W9	AW	215.0	+14.8	c

(continued)

TABLE D-2 (continued)

Sample[@] Number	Source*	NO_3^- Concentration (ppm)	$\delta^{15}N$ (ppt)	Reference[†]
MCM-W10	AW	180.0	+12.2	c
MCM-W11	AW	145.0	+15.2	c
QNY-W1	ST	20.0	+21.3	c
QNY-W2	ST	30.0	+12.1	c
RU-W15	AW	200.0	+ 3.3	c
RU-W16	O	243.0	+ 2.0	c
RU-W18	AW	288.0	+ 6.4	c
RU-W67	O	154.0	+ 7.5	c
RU-W105	O	21.0	+ 7.4	c
RU-W211	O	211.0	+ 7.5	c
RU-W165	O	78.0	- 1.1	c
RU-W-201	O	96.0	+ 2.2	c
RU-W233	O	416.0	+ 7.0	c
RU-W234	O	290.0	+ 3.3	c
RU-W309	O	390.0	+ 4.5	c
RU-W366	O	32.0	+ 2.5	c
RU-W369A	O	257.0	+ 7.0	c
RU-W386	O	366.0	+ 5.8	c
RU-W388	AW	978.0	+10.3	c
RU-W419	O	186.0	+ 5.3	c
RU-W421	O	105.0	+ 8.6	c
RU-W506	O	174.0	+ 5.2	c
RU-W551	O	184.0	+ 6.6	c
RU-W551A	O	470.0	+ 8.3	c
RU-W552	O	94.0	+ 1.2	c
RU-W728	O	61.0	+ 2.7	c
RU-W865A	O	1360.0	+14.1	c
RU-W865B	O	1260.0	+13.0	c

(continued)

TABLE D-2 (continued)

Sample[@] Number	Source*	NO_3^- Concentration (ppm)	$\delta^{15}N$ (ppt)	Reference[†]
RU-W867A	AW	579.0	+10.4	c
RU-W868	O	21.0	+13.1	c
RU-W1002	O	223.0	+ 5.0	c
RU-W1003	O	225.0	+ 6.3	c
RU-W1034	AW	1238.0	+12.0	c
RU-W1004	O	250.0	+10.0	c
RU-W1005	O	75.0	+ 6.8	c

[@]Sample numbers are explained in Appendix C.

*Sources: ST = Septic Tank; AW= Animal Waste; MWW = Municipal Wastewater; O = Other.

[†]References: a = This work; b = Kreitler, unpublished data; c = Kreitler (2).

APPENDIX E

CLIMATE CLASSIFICATIONS

The sites in this study were classified with respect to climate using the Köppen system, as described by Trewartha and others (11). Five great climatic groups are defined under this system as follows:

A -- Tropical Humid Climates: temperature of coolest month over 64.4° (18°C).

B -- Dry Climates: potential evaporation exceeds precipitation.

C -- Humid Mesothermal Climates: temperature of coldest month between 64.4° (18°C) and 26.6°C (-3°C).

D -- Humid Microthermal Climates: temperature of coldest month under 26.6° (-3°C); warmest month over 50° (10°C).

E -- Polar Climates: temperature of warmest month under 50° (10°C).

In addition, a sixth climate group (H) is used to refer to undifferentiated highland climates. The great complexity of mountain climates depends on contrasts in altitude and in exposure to sun and winds. Highland areas are therefore grouped together under a single designation.

The five main climate groups are subdivided into a number of finer classifications by adding a one or two letter qualifying code to the letter designation of a climate group (e.g., Caf). The definitions of the various qualifying codes are given in Table E-1.

TABLE E-1. QUALIFYING CODES OF THE KOPPEN CLIMATE CLASSIFICATION SYSTEM*

Code	Definition
S	Steppe
a	Temperature of the warmest month over 71.6° (22°C).
b	Temperature of the warmest month below 71.6° (22°C).
h	Hot: average annual temperature over 64.4° (18°C).
k	Cold: average annual temperature below 64.4° (18°C).
f	Moist throughout the year: no month with less than 2.4 inches of rain.
w	Dry season in winter, or low sun period: at least one month with less than 2.4 inches of rain.

*Only those codes used in this study are given.

APPENDIX F

SOIL CLASSIFICATIONS

The soils at the various sites were classified according to the regional scheme presented by Trewartha and others (11). Ten basic soil categories are used in this scheme, as shown in Table F-1.

Podzol and tundra soils (Classes 1 and 9) are the typical zonal soils of humid, high-latitude regions. Podzols occur in forested areas, while tundra soils lie in the treeless areas closer to the pole. These soil classes are largely confined to the northern hemisphere. The surface layer of a podzol soil typically is rich in partially decomposed organic material. Below this layer, the A horizon is strongly leached. Material leached from the A horizon accumulates in the B horizon. The C horizon is often composed of sandy glacial drift.

Podzolic soils (Class 2) tend to be similar to the true podzols, but their A horizons are not so heavily leached. Podzolic soils are generally more fertile than the true podzols.

Podzolic-latosolic soils (Class 3) occur in the southeastern United States. The upper horizons are weathered and clay rich. They contain a leached zone as a result of podzolic processes.

Latosolic soils (Class 4) occur in areas of high temperature and precipitation. They are commonly very deeply weathered, and are rich in clay and oxides of iron and aluminum. These commonly occur in a layer of hardpan (laterite).

TABLE F-1. MAJOR CLASSES OF SOILS

	Soil Class	Identifying Number
Soils of the Humid Lands	Podzol Soils	1
	Podzolic Soils	2
	Podzolic-latosolic Soils	3
	Latosolic Soils	4
	Tundra Soils	9
Soils of the Subhumid Lands	Chernozemic Soils	5
	Chernozemic-desertic Soils	6
	Desertic Soils	7
Other Soils	Alluvial Soils	8
	Complex Soils of Areas of High Local Relief	10

Chernozemic soils (Class 5) develop in dryer areas than those above. They typically contain a deep surface layer which is rich in organic materials and nutrients. They are not severely leached.

Chernozemic-desertic soils (Class 6) are transitional between the chernozemic soils and the true desertic soils. They may develop a hardpan, commonly of lime (caliche) due to the low precipitation and high evaporation.

The true Desertic soils (Class 7) are low in organic content and typically contain decomposing rock fragments. Due to the very low rainfall, these soils are frequently immature and horizon differentiation is poor.

Two basically non-zonal categories of soil are the alluvial soils (Class 8) and the soils of areas of high local relief (Class 10).

The characteristics of alluvial soils are highly dependent on the characteristics of the parent alluvium. Little characterization of soils in the areas of high local relief can be made because of the complex influences of slope and local climate.

APPENDIX G

STATISTICAL ANALYSES OF THE ENTIRE DATA BASE

In this and the following appendix, statistical tables which supplement those given in Section 7 are presented. These two appendices are presented for completeness of documentation and for the benefit of those who are interested in further details of the statistical analyses. The discussions in these two appendices are brief, however, since the results are discussed in Section 7.

In this appendix, statistical analyses of the entire data base, including septic tank, feedlot, irrigation, and other sources, are presented. Separate analyses of the four source classes are discussed in the following appendix.

The primary objective is to analyze the relationship between the dependent variable DEL and the various independent variables. Various approaches to multivariate problems of this type exist, such as the following: (1) correlation, partial correlation, and regression, (2) automatic interaction detection, (3) factor analysis, and (4) path analysis.

While all of these approaches have merits, the first was selected for several reasons. This approach requires relatively few *a priori* assumptions and allows one to explore the data freely. Correlations and regression, moreover, allow the analysis of continuous variables as continuous variables, whereas automatic interaction detection involves discrete subdivisions of a data set. Also, the output from the selected method is

relatively easy to interpret, especially compared to results from a factor analysis.

Various data plots, especially plots of regression residuals, were produced to determine whether a nonlinear form of any of the variables should be analyzed. No evidence of nonlinear trends was seen, however.

Some of the tables presented in this and in the following appendix are also presented and discussed in the text. The complete set of statistical correlation tables is included here for the convenience of the reader.

Table G-1 indicates the variables which correlate significantly with DEL, and Table G-2 presents the complete correlation matrix for DEL and the variables which correlate most highly with DEL. Table G-2 indicates the extent to which these independent variables are correlated with each other. Note especially the relatively high correlation between PRECIP and ELEV; these are the two variables with the highest correlations with DEL.

Table G-3 presents the significant correlations of PPM with other variables.

Tables G-4 and G-5 present the correlations and partial correlations of the variables SEPTIC, FEEDL, and IRRIG with DEL. The partial correlation is the correlation of one variable with another given that one or more other variables are fixed. The most important conclusions from these tables are as follows:

(1) The DEL value is higher in the feedlot data than in data from septic tank, irrigation, and other sources as a whole. This is indicated by the positive (although small) correlation between FEEDL and DEL.

(2) The correlation between FEEDL and DEL cannot be "explained" by the influence of other factors; as other variables are fixed, the correlation between FEEDL and DEL changes very little.

(3) The correlations for the septic and irrigation variables also change by a fairly small amount as other variables are fixed.

It should be recalled that the mean values for DEL for the four sources are analyzed in Section 7. The difference between the DEL value for feedlots and for the three other sources as a whole is due primarily to the difference between the DEL values for feedlots as opposed to those in the fourth, or "other" category.

TABLE G-1. VARIABLES WHICH HAVE STATISTICALLY SIGNIFICANT CORRELATIONS WITH DEL

	Correlation with DEL	Level of Significance
TEMP	.13	.10
PRECIP	.29	.01
ELEV	-.31	.01
FEEDL	.19	.05
C AW	.15	.05
C BSK	-.13	.10
C DAF	.18	.05
C H	-.18	.05
SOIL 4	.15	.05
SOIL 5	.27	.01
SOIL 6	-.26	.01
SOIL 10	-.18	.05
HLM B	-.13	.10
IH	-.18	.05
DI	-.19	.05
LOCTAY	.22	.01
GNDCMN	.15	.05
MACON	.15	.05
RUNLS	-.15	.05

TABLE G-2. CORRELATIONS INVOLVING VARIABLES MOST CLOSELY RELATED TO DEL

	DEL	PRECIP	ELEV	SOIL 5	SOIL 6	LOCTAY
DEL	1.	.29	-.31	.27	-.26	.22
PRECIP	.29	1.	-.61	.21	-.69	.08
ELEV	-.31	-.61	1.	-.35	.35	-.21
SOIL 5	.27	.21	-.35	1.	-.58	.58
SOIL 6	-.26	-.69	.35	-.58	1.	-.33
LOCTAY	.22	.08	-.21	.58	-.33	1.

TABLE G-3. VARIABLES WHICH HAVE STATISTICALLY SIGNIFICANT CORRELATIONS WITH PPM

Variable	Correlation with PPM	Level of Significance
TEMP	.17	.05
PRECIP	-.14	.10
LAT	-.13	.10
RADSAM	-.36	.01
SOIL	-.16	.05
SEPTIC	-.25	.01
FEEDL	.29	.01
IRRIG	-.13	.10
C BSK	-.15	.05
C CAF	.25	.01
SOIL 3	-.14	.10
SOIL 6	.23	.01
TAM	.14	.10
RUNLS	.36	.01

TABLE G-4. CORRELATION OF SEPTIC, FEEDL, IRRIG WITH DEL

	Correlation	Partial Correlation*
SEPTIC	.07	-.03
FEEDL	.19**	.15**
IRRIG	-.01	-.02

*The partial correlations were computed with the following variables fixed: PPM, ELEV, SOIL, C AW, SOIL 2, SOIL 3, SOIL 5. These were selected by stepwise regression analysis.

**Statistically significant at the .05 level.

TABLE G-5. CORRELATION OF SEPTIC, FEEDL, IRRIG WITH DEL WITH VARIOUS INDEPENDENT VARIABLES FIXED

	Variables Fixed*							
	NONE	ELEV	SOIL 5 ELEV	C AW SOIL 5 ELEV	SOIL 2 C AW SOIL 5 ELEV	SOIL 3 SOIL 2 C AW SOIL 5 ELEV	PPM SOIL 3 SOIL 2 C AW SOIL 5 ELEV	SOIL PPM SOIL 3 SOIL 2 C AW SOIL 5 ELEV
SEPTIC	.07	.05	.06	.03	.03	-.02	-.01	-.03
FEEDL	.19	.24	.18	.18	.19	.19	.16	.15
IRRG	-.01	-.02	-.00	.01	-.03	-.03	-.01	-.02

*The variables ELEV, SOIL 5, C AW, SOIL 2, SOIL 3, PPM, and SOIL were selected in that order by stepwise regression analysis for inclusion in a model to predict DEL.

APPENDIX H

SEPARATE STATISTICAL ANALYSES FOR THE DIFFERENT SOURCE TYPES

In this and the preceding appendix, statistical tables which supplement those given in Section 7 are presented. In this appendix, the results done separately for the four different source types are given. Some of the correlation tables presented here are also discussed in the text. The complete set is given here, however, for the convenience of the reader.

Tables H-1 through H-4 present the significant correlations of the other variables with DEL. Tables H-5 through H-8 present similar results for the variable PPM.

Tables H-9 through H-13 present the results of multiple regression analyses to develop models to predict DEL. Table H-9 summarizes the results, and Tables H-10 through H-13 present further details, including the forms of all four equations and the analysis of variance tables, not presented in the text.

The primary purpose of this analysis is not to develop equations to be used to estimate DEL, but to investigate the strength of the relationship between DEL and the prediction variables. This point is discussed further below.

The regression models were developed by using stepwise regression analysis. This method adds variables to and deletes variables from a model one at a time until no further significant improvement in the predictive accuracy can be made. The set of

candidate predictor variables included all except the site variables (HLM A, HLM B, etc.), RADSAM, and SEQNCE. Thus, the multiple correlations presented can be thought of as indicating the strength of the relationship between DEL and the set of candidate physical predictor variables.

It is seen (from Table H-9) that the multiple correlations for septic, feedlot, and irrigation sources are all between .54 and .56; thus, only about

$$(.55)^2 = .30$$

or 30% of the total variation in DEL can be explained in terms of the predictor variables used in this study. In the case of other sources, only about 5% can be explained.

TABLE H-1. VARIABLES WHICH HAVE STATISTICALLY SIGNIFICANT CORRELATIONS WITH DEL: SEPTIC TANK SOURCES

Variable	Correlation with DEL	Level of Significance
TEMP	.35	.01
PRECIP	.33	.05
ELEV	-.39	.01
LAT	-.31	.05
RADSAM	-.27	.10
C H	-.32	.05
SOIL 10	-.32	.05
HLM B	-.25	.10
IH	-.32	.05

NOTE: C H, SOIL 10, AND IH occur simultaneously in this data subset and, therefore, are indistinguishable for the purposes of statistics.

TABLE H-2. VARIABLES WHICH HAVE STATISTICALLY SIGNIFICANT CORRELATIONS WITH DEL: FEEDLOT SOURCES

Variable	Correlation with DEL	Level of Significance
PRECIP	.32	.05
ELEV	-.37	.01
SEQNCE	-.30	.05
RADSAM	-.38	.01
C BSK	-.38	.01
C CAF	.25	.10
SOIL 5	.32	.05
SOIL 6	-.32	.05
DI	-.44	.01
LOCTAY	.27	.10

TABLE H-3. VARIABLES WHICH HAVE STATISTICALLY SIGNIFICANT CORRELATIONS WITH DEL: IRRIGATION SOURCES

Variable	Correlation with DEL	Level of Significance
SOIL	-.55	.10

NOTE: This data set included only 10 points, so a correlation of at least .54 was required for significance at the .10 level.

TABLE H-4. VARIABLES WHICH HAVE STATISTICALLY SIGNIFICANT CORRELATIONS WITH DEL: OTHER SOURCES

None at .10 level of significance

NOTE: TEMP, PRECIP, ELEV, LAT are all constants within this data set. Only one climate classification (C CAF), one soil type (SOIL 6), and one geographical location (RUNLS) were represented.

TABLE H-5. VARIABLES WHICH HAVE STATISTICALLY SIGNIFICANT CORRELATIONS WITH PPM: SEPTIC TANK SOURCES

Variable	Correlation with PPM	Level of Significance
SEQNCE	-.26	.10
RADSAM	-.41	.01
SOIL 6	.39	.01
MACON	.23	.10
RUNLS	.64	.01

TABLE H-6. VARIABLES WHICH HAVE STATISTICALLY SIGNIFICANT CORRELATIONS WITH PPM: FEEDLOT SOURCES

Variable	Correlation with PPM	Level of Significance
TEMP	.46	.01
ELEV	-.25	.10
LAT	-.40	.01
SEQNCE	-.38	.01
RADSAM	-.40	.01
C BSK	-.40	.01
C CAF	-.52	.01
DI	-.26	.10
GR	-.26	.10
RUNLS	.62	.01

TABLE H-7. VARIABLES WHICH HAVE STATISTICALLY SIGNIFICANT CORRELATIONS WITH PPM: IRRIGATION SOURCES

Variable	Correlation with PPM	Level of Significance
PRECIP	-.63	.05
SNGLO	.77	.01

TABLE H-8. VARIABLES WHICH HAVE STATISTICALLY SIGNIFICANT CORRELATIONS WITH PPM: OTHER SOURCES

Variable	Correlation with PPM	Level of Significance
D*SOIL	-.34	.01
SOIL	-.33	.01

TABLE H-9. COMPOSITE RELATIONSHIPS BETWEEN DEL AND PREDICTOR VARIABLES

Source	Terms in Model†	Multiple Correlation	Significant at Level	Standard Error
Septic	D*SOIL ELEV SOIL	.56	.01	8.3
Feedlot	ELEV SOIL C BSK SOIL 5	.54	.01	8.3
Irrigation	SOIL	.55	.10*	6.4
Other	PPM SOIL	.23	.25	5.4

† These variables were selected for inclusion in the equations by using the stepwise regression procedure.

*Borderline. The small sample size (10) accounts for the lower level of significance in this case.

TABLE H-10. REGRESSION MODEL FOR DEL: SEPTIC TANK SOURCES

Multiple Correlation: .56 Standard Error: 8.3

Regression Model: DEL = 19.8 + 4.2 (D*SOIL) - .0024 (ELEV) - 11.3 (SOIL)

ANALYSIS OF VARIANCE

Source	Degrees of Freedom	Sum of Squares	Mean Square	F
Regression	3	1542	514	7.46*
Residual	48	3308	69	

*Easily significant at the .01 level.

TABLE H-11. REGRESSION MODEL FOR DEL: FEEDLOT SOURCES

Multiple Correlation: .55 Standard Error: 6.4

Regression Model: DEL = 17.0 - 9.4 (SOIL)

ANALYSIS OF VARIANCE

Source	Degrees of Freedom	Sum of Squares	Mean Square	F
Regression	4	1327	332	4.95*
Residual	47	3152	67	

*Significant at the .01 level.

TABLE H-12. REGRESSION MODEL FOR DEL: IRRIGATION SOURCES

Multiple Correlation: .55 Standard Error: 6.4

Regression Model: DEL = 17.0 - 9.4 (SOIL)

ANALYSIS OF VARIANCE

Source	Degress of Fredom	Sum of Squares	Mean Square	F
Regression	1	141	141	3.45*
Residual	8	327	41	

*Significant at .10 level (borderline).

TABLE H-13. REGRESSION MODEL FOR DEL: OTHER SOURCES

Multiple Correlation: .23 Standard Error: 5.4

Regression Model: DEL = 5.2 + 0.0036 (PPM) + 2.4 (SOIL)

ANALYSIS OF VARIANCE

Source	Degrees of Freedom	Sum of Squares	Mean Square	F
Regression	2	95	47	1.65*
Residual	61	1750	29	

*Significant at .25 level.

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(Please read Instructions on the reverse before completing)

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

This report describes the methods, results, conclusions, and recommendations of an investigation of a technique to identify sources of nitrate in ground water. A discussion of the theoretical basis of the technique is also provided. Over 300 soil and ground water samples were collected for this study. The samples are from numerous sites around the United States, representing a variety of environmental conditions. The nitrate in 66 of these samples was separated from other nitrogen species, converted to N_2 gas, purified, and analyzed to determine the ratio $^{15}N/^{14}N$. These data were combined with the results of analyses performed previously by Jones (1) and Kreitler (2). Standard statistical techniques were used to analyze the observed variations in $\delta^{15}N$ values, with respect to several nitrate sources and various environmental factors. It was found that nitrates from feedlots, barnyards and septic tanks can be distinguished from natural soil nitrates on the basis of their $\delta^{15}N$ values. They cannot, however, be distinguished from each other. Environmental factors contributed to the observed variation in $\delta^{15}N$ values.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Ground Water Waste Disposal Nitrates	Septic Tanks Feedlots Land Application	48 F

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