

## ACKNOWLEDGEMENTS

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CHAPTER  
**ONE**

## CHAPTER 1 INTRODUCTION

On December 16, 1974, Congress passed the Safe Drinking Water Act to assure protection of the Nation's drinking water supplies and public health. The Act, otherwise known as Public Law 93-523, led to the promulgation of the National Interim Primary Drinking Water Regulations by the Environmental Protection Agency on December 24, 1975. The federal regulation which sets forth maximum contaminant levels (MCL) for inorganic constituents, turbidity, coliform organisms, pesticides, and radionuclides, based on the 1962 U.S. Public Health Service Standards (USPHSS), was established to protect public health to the maximum extent feasible. It is also the intent of the Act that the States and public water systems take primary control of drinking water programs and that State and federal agencies cooperate in implementing the standards as well as protecting underground sources of drinking water.

One of the inorganic contaminants of major concern in water supply is nitrate. Although it is beneficial to the life processes of all plants and animals, nitrate is equally deleterious to public health and the environment. Nitrate, which may be found in both surface and groundwaters, is not considered a significant health hazard in surface water, since it is readily assimilated by aquatic plants and animals. In groundwater, however, nitrate can accumulate to a hazardous level due to reduced biological activity in the hydrogeologic system.

The major health hazard associated with high nitrate level in drinking water is infantile methemoglobinemia, a blood disorder which impedes the oxygen carrying capacity of hemoglobin. Methemoglobin prevents oxygen transport by the blood and may lead to suffocation. Cyanosis, the blue coloration of the skin, is the first clinically detectable sign of the blood disorder and generally occurs when ten percent of the hemoglobin is in the methemoglobin form. Children over three months and adults, however, suffer no ill effects from ingestion of high nitrate water, since they have a lower pH in their upper gastrointestinal tract which inhibits bacterial conversion of nitrate to nitrite.

Recognizing (1) the need to comply with PL 93-523 and the National Interim Primary Drinking Water Regulations, and (2) the health hazard associated with high nitrate concentration in drinking water, the Arizona Department of Health Services (ADHS) proposed an investigative study of the nitrate concentrations in waters throughout the State. The study was also intended to aid the ADHS in implementing the regulations and identifying methods of nitrate removal to cost effectively comply with the maximum contaminant level for nitrate.

### Governmental Requirements

The primary purpose of the Safe Drinking Water Act, as stated in 1974, is to assure "that water supply systems serving the public meet minimum national standards for protection of public health". The Act, which is an amendment to

the Public Health Services Act, authorized the Environmental Protection Agency to establish Federal standards for the protection of water supplies from all harmful contaminants and define which standards would be applicable to all public water systems. It is also the intent of the Act that each State have primary control of the drinking water program and that federal assistance be provided for its implementation.

One of the primary objectives of PL 93-523 is the establishment of a joint Federal-State program to protect underground sources of drinking water. Specifically, Section 1424(e) of the Act prohibits federal funding of projects which may contaminate groundwater sources, while Section 1421 sets forth guidelines for establishing State programs to protect sole source aquifers. Compliance with this objective would eliminate groundwater pollution by source control, and thus would provide means of protecting underground water supplies in Arizona.

Pertinent regulations concerning nitrate levels in drinking water are embodied in both the National Interim Primary Drinking Water Standards established by EPA in 1975 and in the Drinking Water Regulations recently adopted by the Arizona Department of Health Services.

National Interim Primary Drinking Water Standards. Due to the nature of health hazards associated with nitrate in drinking water, the Environmental Protection Agency set forth separate regulations for compliance. A larger number of water systems were required to meet the nitrate standard compared to other inorganic contaminant requirements. The maximum contaminant level (MCL) set forth for nitrate is 10 mg/l as nitrogen; applicable to water systems which may be used either continuously or intermittently. While the maximum concentration levels for all other inorganic contaminants were set to prevent chronic problems, the MCL for nitrate was set to prevent acute health problems, particularly among infants.

State Drinking Water Regulations. It is the intent of the Safe Drinking Water Act that the States take the lead in adopting standards, reviewing compliance strategies, and bringing enforcement actions where necessary. In compliance with the intent of the Act, the Arizona Department of Health Services adopted the "Drinking Water Regulations for the State of Arizona" on May 26, 1978. The MCL for nitrate of 10 mg/l set forth by EPA as the national standard was also adopted by ADHS.

In order to comply with the standard for nitrate, all "water systems" using groundwater as defined by ADHS are required to have the water analyzed by June 24, 1979, and at three-year intervals thereafter. Systems using surface water, subsequent to a water analysis by June 24, 1978, must provide yearly analyses.

If the MCL for nitrate is exceeded, an additional sample must be taken within 24 hours after determination. If the average of the two samples exceeds the MCL, the water supplier must notify the ADHS by telephone if possible. Written notification must be sent to the ADHS within three days, transmitting the following information:

1. The nature of the violation.
2. The steps and schedule taken to correct the violation.

3. A copy of any public notification.
4. Any other information pertinent to violation or correction thereof.

When the MCL for nitrate is exceeded, public notification must be given in a form dependent on the type of water system provided.

Notification by the water purveyor of a community water system shall include a written notice in the first set of water bills issued after the MCL for nitrate is exceeded. The public notice shall be repeated not less than once every three months as long as such non-compliance continues. If the water system issues water bills less frequently than quarterly, or does not issue water bills, the notice shall be made or supplemented by another form of direct mail. If the failure to comply with the maximum contaminant level is not corrected promptly after discovery, the water supplier must give, in addition to notice by direct mail, other general public notice of failure to comply in a manner determined by the ADHS based on the nature of the failure. The additional notice may be through newspaper publication, press release, or other appropriate means. Notification by the supplier of water of a non-community water system, however, shall be given through conspicuous posting in a location where it can be seen by consumers, in addition to other means prescribed by ADHS.

Notification by the supplier of water of a semi-public water system shall include a written notice in the first set of water bills of the water system issued after the MCL is exceeded, and repeated not less than once every three months as long as such failure continues. If the water supplier issues water bills less frequently than quarterly, or does not issue water bills, the notice shall be made or supplemented in another appropriate form such as direct mail or posting in a conspicuous location.

Notices to the public must be (1) easy to understand, (2) contain all facts relating to the problem, including preventive measures that should be taken by the public, and (3) bilingual in areas designated by ADHS. If a source of water is determined unsafe by ADHS, it shall be made unavailable for use by the water supplier until its safety has been re-established by the ADHS.

#### Authorization and Scope of Work

By an agreement dated May 11, 1978, the ADHS engaged the firm of Brown and Caldwell to conduct an investigative study of (1) nitrate concentrations in water supply sources, (2) alternative treatment methods available to meet the standards, and (3) economic impacts that would result from implementation of each of these treatment or removal systems.

The study is intended to provide the ADHS with (1) a detailed account of the occurrence of nitrate concentrations in drinking water sources in Arizona, (2) a list of known violations of the interim primary standards, and (3) a guide in determining the feasibility of treatment methods for nitrate removal and/or methods of complying with the MCL for nitrate.

## Project Objectives and Goals

The objective of this study, in keeping with the intent of the Safe Drinking Water Act, is to ensure the safety of drinking water supplies throughout the State of Arizona. Accomplishment of the objectives of the Act requires an assessment of public health hazards associated with high nitrate levels in drinking water, identification of the major sources of nitrate contamination, and an evaluation of removal processes. To properly address these major concerns, the investigative study included the following elements:

1. Description of natural and man-made sources of nitrate in drinking water.
2. Identification of the geologic and geographic locations of nitrate occurrences in Arizona drinking water sources.
3. Evaluation of the nitrate situation and the characteristics and magnitude of the problem.
4. Evaluation of the available methods of nitrate removal.
5. Development of capital and operation and maintenance costs for nitrate removal from water supplies.
6. Evaluation of the economic impact of viable nitrate removal methods.
7. Compilation of a list of manufacturers and suppliers of process equipment and package units capable of removing or reducing the nitrate level in drinking water sources.

CHAPTER  
**TWO**

## CHAPTER 2

### NITROGEN: AN OVERVIEW

Nitrogen is an essential element of the earth's life layer and is necessary in the life processes of all plants and animals. Despite its nutritional value, however, nitrogenous compounds such as nitrate may also exert deleterious effects on public health and the aquatic environment. Increasing concern over the safety of drinking water has focused attention on the behavior of nitrogen in the environment, since it is an active element of the dynamic interrelationship between man and the soil-water-plant system. An understanding of the behavior and movement of nitrogen in the environment is therefore essential in evaluating its beneficial and deleterious effects and in implementing control measures to protect and maintain the integrity of water resources. The following section presents an overview of the nitrogen cycle, its interaction with the environment, and its significance in water quality management.

#### THE NITROGEN CYCLE

Nitrogen exists in several chemical forms due to (1) the capability of elemental nitrogen (N) to assume an array of valence states, ranging from ammonium at minus 3 to nitrate with a plus 5 valence, and (2) the effect of living organisms on nitrogen transformations. In water quality management, the principal compounds of concern are nitrogen gas ( $N_2$ ), ammonium/ammonia ( $NH_4^+ / NH_3$ ), nitrite ( $NO_2^-$ ), nitrate ( $NO_3^-$ ), and organic nitrogen. The relationships and biochemical transformations which occur in nature between these various compounds are complex and can best be illustrated in a cyclic system, as shown in Fig. 2-1. The atmosphere serves as a reservoir from which nitrogen is transferred to the soil-water system for assimilation and conversion by plants to organic nitrogen forms such as protein. Animals and humans may then ingest the plants, which provide proteins essential in their life cycles. The biological decomposition of nitrogenous organic waste and dead organic matter ultimately completes the cycle by transforming nitrate to nitrogen gas, which is then diffused back to the atmosphere.

Although the nitrogen cycle is in a continuous state of flux in the receiving environment, some accumulation of nitrogen compounds occurs in portions of the cyclic system due to the variable rates of the many transformation reactions. Characteristic of all biological and chemical reactions, the rates of nitrogen exchange are dependent on several dynamic factors. In terms of transformation reactions, nitrate is an active element of the nitrogen cycle with direct pathways to both the atmospheric nitrogen pool and the nitrogen pool in living matter, as shown in Fig. 2-1. Nitrate also serves as the only common point for the nitrification, denitrification, and fertilization pathways. To facilitate understanding the dynamic features of the nitrogen cycle, nitrogenous compounds can be grouped into active and storage pools or compartments. As identified in Fig. 2-1, the three major nitrogen pools are atmospheric nitrogen, fixed nitrogen, and nitrogen in living matter.

## Nitrogen Fixation

Atmospheric nitrogen, which constitutes approximately 78 percent of the air by volume, is the primary source of supply for the active nitrogen pools.<sup>1</sup> Although there is an estimated 35,000 tons of free nitrogen in the atmosphere above one acre of land, higher plants, animals, and humans are incapable of utilizing the nitrogen supply without an intermediate step referred to as fixation. Nitrogen fixation is the transformation process by which free nitrogen gas is combined chemically with other elements.<sup>2</sup> As shown in Fig. 2-1, there are three nitrogen fixation pathways: bacterial and algal fixation, industrial fixation, and atmospheric fixation.

A number of soil and aquatic microorganisms are capable of directly utilizing molecular nitrogen from the atmosphere for synthesis of proteins. This biological fixation process accounts for most of the natural transformation of free nitrogen gas to compounds which can be used by other plants and animals in their life processes.

Industrial fixation processes include production of nitrogen fertilizers and incidental generation of nitrogen oxides from the oxidation of nitrogen during fossil fuel combustion. In fertilizer production, fixed nitrogen compounds such as ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), and urea ( $\text{NH}_4\text{-CO-NH}_2$ ), are produced by combining  $\text{N}_2$  and  $\text{H}_2$  at extreme high temperature and pressure. Industrial fixation also occurs when  $\text{N}_2$  and  $\text{O}_2$  combine at high temperature during combustion of fossil fuels in power generation plants and internal combustion engines. These fixed nitrogen compounds, though initially released to the atmosphere, are eventually returned to the soil-water system through precipitation.<sup>3</sup>

Minor amounts of nitrogen gas are also transferred to the fixed nitrogen pool by atmospheric fixation. During electrical storms, the high temperatures and pressures created by the arc combine to produce nitrogen products similar to fossil fuel combustion. In summary, these natural and man-caused fixation processes are the primary pathways which provide the transformation of free nitrogen gas to combined nitrogen useable in the life processes of plants and animals.

## Transformations Within the Fixed Nitrogen Pool

In terms of water quality management and pollution control, the biological transformations of the fixed nitrogen pool are the most significant aspects of the nitrogen cycle. Enrichment or degradation of both surface and groundwater sources are dependent upon the dynamic interaction of the various nitrogen compounds with the soil-water-plant system. The complexity is further enhanced by the fact that all the physical, chemical, and biological processes are occurring simultaneously. The two nitrogen pathways of most significance to this study are nitrification, which produces nitrate, and denitrification, which controls nitrate accumulation.

Nitrification. Nitrification is the two-step biological process in which ammonium is converted to nitrate. The process involves two highly specialized groups of nitrifying bacteria which utilize the nitrogenous compounds as an energy

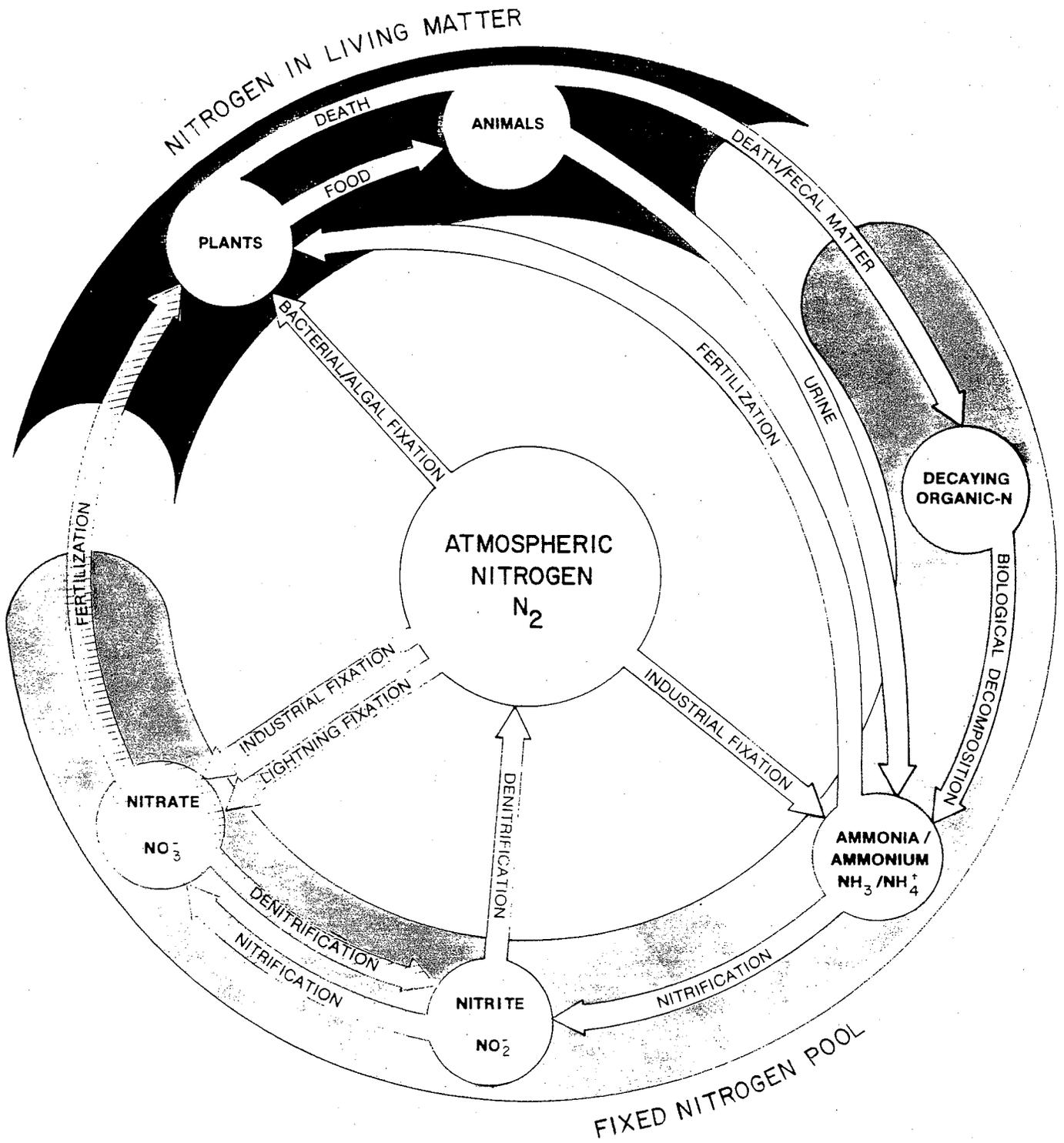


Fig. 2-1 The Nitrogen Cycle

source. Bacteria of the genus Nitrosomonas are capable of sustaining growth only when oxidizing ammonium to nitrite under aerobic conditions, while the genus Nitrobacter converts nitrite to nitrate under similar aerobic conditions and uses this reaction as the sole energy source for growth. In addition to nitrogen fixation from the atmosphere, biological nitrification is also a primary pathway which leads to the occurrence of nitrate in the soil and aquatic environments. Nitrifying bacteria are common inhabitants of the soil-water system and are responsible for the rapid and complete transformation of ammonium to nitrate under suitable environmental conditions. Nitrate, rather than ammonium, is the preferred source of nitrogen for most plants, and is therefore readily absorbed by plant roots in the soil for conversion to proteins in plant tissue.<sup>4</sup>

Denitrification. The process of denitrification, which represents the alternate pathway within the fixed nitrogen pool for nitrate not assimilated in plant systems, is the only biochemical process which returns fixed nitrogen to the atmospheric pool as free nitrogen. Unlike the nitrification process, denitrification is performed by a variety of bacteria genera, including Psuedomonas, Micrococcus, and Bacillus.<sup>5</sup> These microorganisms are not entirely dependent upon denitrification to sustain growth and thus require specific environmental conditions to perform the transformation. When both oxygen and nitrate are present, denitrifiers preferentially use oxygen. Since conversion of nitrate to nitrogen gas is an energy consuming process rather than energy yielding as in nitrification, some form of decomposable organic carbon must be present for utilization by denitrifiers as an energy source. Denitrification of nitrate to nitrogen gas therefore occurs only in the absence of oxygen and in the presence of an adequate organic carbon source. Denitrifying bacteria, like nitrifiers, are common microorganisms in the soil-water systems, and under proper environmental conditions rapidly convert nitrate to elemental nitrogen gas. The highly specific environmental conditions required by denitrifiers is generally the limiting factor in the denitrification process.<sup>6</sup>

Decomposition. Degradation of organic nitrogen compounds from the living matter pool releases fixed nitrogen in the ammonium form to complete the nitrogen cycle, as shown in Fig. 2-1. The biochemical reactions transforming organic nitrogen to inorganic ammonium involve numerous types of bacteria. The process of decomposition also includes bacterial mineralization of soil organic matter which has been deposited in the soil system. As noted, nitrogen compounds are returned to the atmospheric pool only through denitrification, while organic nitrogen is recycled only to the fixed nitrogen pool. Converted organic nitrogen may volatilize to the atmosphere as ammonia gas ( $\text{NH}_3$ ), but is ultimately returned to the fixed nitrogen pool by precipitation without passing through the atmospheric pool.

### Nitrogen Budget

Based on the mass balance for the total nitrogen system, the number of fixation processes appear to exceed available denitrification pathways for the return of free nitrogen to the atmosphere. Since the development of industrial and chemical fixation processes (which yield nitrogen fertilizers), transformation rates within the nitrogen cycle have been altered.

An estimate of the total annual nitrogen budget for the United States land area in 1970 is presented in Table 2-1. Although the balance of nitrogen input to nitrogen return indicates an estimate net annual retention in the soil-water system of eight percent, the significance of this accumulation is difficult to assess. Some of the nations' agricultural land, particularly in arid climates as in Arizona, lack nutrient input from the natural pathways of the nitrogen cycle. In most cases, supplemental nitrogen is added to soil-water systems with limited natural capability to accommodate nitrogen input in excess of crop nutrient requirements. With regard to water quality management and the implications of this phenomenon, it is apparent that proper management and control of supplemental nitrogen input is required to maintain a balanced nitrogen budget and prevent accumulation of nitrogenous compounds to a hazardous level in the soil-water system.

### INTERACTION OF NITROGEN WITH THE SOIL-WATER SYSTEM

The complex transformation and accumulation of nitrogen in the environment requires an understanding of the interactions of the components of the nitrogen cycle with the environment. In recent years, several investigations and national conferences have focused attention on the subject of nitrogenous compound transport through soil-water systems.<sup>7,8,9</sup>

**Table 2-1. Estimated Nitrogen Budget For Total Land Area of United States<sup>a,b</sup>**

	Relative percentage of total annual input
Annual input to the fixed nitrogen pool	
Biological fixation	23
Industrial fixation	36
Mineralization of soil organic nitrogen	15
Rainfall <sup>c</sup>	26
Total annual input	100
Annual return to the atmospheric nitrogen pool	
Denitrification from water system	24
Denitrification from soil system	42
Volatile ammonia release <sup>c</sup>	26
Total annual return	92
Net annual accumulation in soil-water system	8

<sup>a</sup> Source: adapted from Accumulation of Nitrate by the National Academy of Sciences, 1972.

<sup>b</sup> Relative percentages are based on 1970 nitrogen estimates.

<sup>c</sup> Represents transfer from ammonium,  $NH_4$ , to gaseous ammonia,  $NH_3$ , with no net change in fixed nitrogen pool.

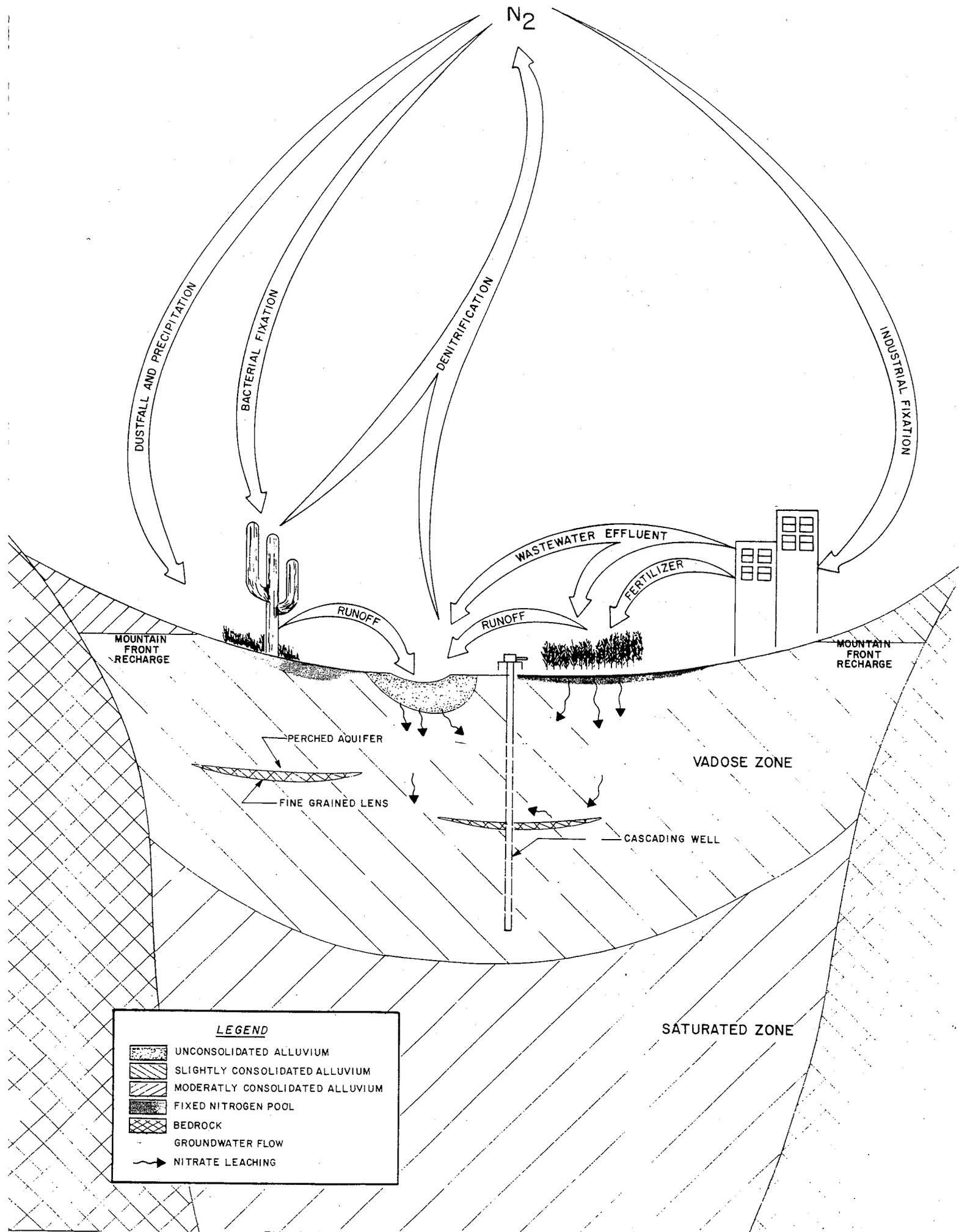


Fig. 2-2 Nitrogen Pathways in Typical Alluvial Basins

The inorganic compounds which make up the fixed nitrogen pool are all soluble in water. Water acts as the solvent, transporter, and storage reservoir for fixed nitrogenous compounds. Hence, the movement of nitrate through the soil-water system is dependent upon the hydrologic features of a localized environment. Surface runoff transports soluble compounds and soil sediment along with pesticides and other contaminants in surface water. Infiltration, however, transports only soluble compounds with recharge water to groundwater, since most insoluble contaminants are either filtered or complexed by soil particles. Nitrogen transport in the soil-water system is therefore influenced by components of the hydrologic cycle.

### Nitrogen in Surface Water

Surface runoff along with subsurface interflow, precipitation, dustfall, and direct discharge are the primary mechanisms responsible for the transport of nitrogen to surface waters. As previously discussed, photosynthetic blue-green algae and certain bacterial species in the aquatic environment can also directly fix nitrogen for the atmosphere. Within the surface water system, nitrification, assimilation, denitrification, and ammonia volatilization can occur, as illustrated in Fig. 2-1. Nitrification is most active in the upper layers of the water profile where oxygen supply is most abundant. Denitrification, which produces free nitrogen gas, occurs in the lower water layers and bottom sediments where the absence of oxygen or anoxic conditions are prevalent and sufficient organic material is available. Once converted to the ammonium and nitrate forms, nitrogen is actively assimilated by algae and aquatic plants.

One of the most significant effects of nitrogen in surface waters is its stimulating influence on biological flora. The enrichment of surface waters with potassium, phosphorous, nitrogen, and other nutrients which leads to increased plant and algae growth is referred to as eutrophication. Although eutrophication has beneficial effects in receiving waters by increasing biological productivity, it is undesirable in most locations. Excessive input of nutrients has often resulted in nuisance conditions such as algae blooms and dense growth of aquatic plants. These conditions have resulted in depletion of dissolved oxygen levels, interference with recreational uses, taste and odor problems, and increased water treatment costs.<sup>9</sup> Although high nitrate levels affect the beneficial uses of surface waters, these concentrations are generally below hazardous levels due to rapid assimilation of nitrate associated with high plant growth.

### Nitrogen in Groundwater

The interaction of nitrogen with the soil-water-plant system is pertinent to Arizona due to the importance of groundwater resources. Regulations and control measures relative to disposal of pollutants on land require an understanding of the interaction of nitrogen with the groundwater system. Several environmental components that collectively determine the pollutant potential of nitrogenous compounds on groundwater are graphically illustrated in Fig. 2-2 for an alluvial basin typical of central and southern Arizona. The nitrogen transformation processes between atmospheric and fixed nitrogen pools and hydrogeologic mechanisms which control the movement of nitrogenous compounds are also indicated. In a hydrogeologic context, nitrogen interacts with three distinct zones while moving through the soil profile: the surface zone, the vadose or unsaturated zone, and the aquifer or saturated zone.

The surface zone, which ranges from the air-soil interface to a depth immediately beyond the influence of plant roots, is the most active zone in terms of nitrogen reactions. Fixed nitrogen inputs to the soil surface are generally a result of mineralization of stored organic nitrogen, precipitation, dustfall, natural and man-caused runoff, fertilization, disposal of man and animal waste products, and biological fixation. More than 90 percent of the total nitrogen in the soil system is generally organic, either as living organisms or residual humus. In predominantly arid climates, however, the organic fraction varies widely due to the coarse texture, high temperature, and low moisture content of the soils.<sup>10,11</sup> These conditions allow rapid and complete biological conversion of organic nitrogen to ammonium. Fixed nitrogen present in the surface zone can undergo transformation by ammonia volatilization, immobilization, nitrification, denitrification, and assimilation.<sup>12</sup> A brief explanation of these processes in relation to the soil-water-plant system and their relative significance to nitrate occurrence in groundwater is presented below.

1. Ammonia Volatilization. Non-biological volatilization occurs when ammonium is converted to ammonia gas. The equilibrium relationship between ammonium and ammonia is pH dependent whereby, at pH 7 and below the predominant form is ammonium ion. As pH increases above 7, the equilibrium shifts toward volatile ammonia gas. In the surface zone, alkaline top soils and other factors may cause localized changes to liberate ammonia gas to the atmosphere. Since the volatilization process requires extended air-soil or air-water contact, reaction potential decreases with increasing depth in the soil profile. As shown in Table 2-1, ammonia volatilization does not represent a net decrease in fixed nitrogen; it does, however, release fixed ammonium from a local environment.
2. Immobilization. Geochemical reactions may immobilize ammonium by binding positively charged ions to soil particles carrying a negative charge.<sup>13</sup> Fixation and adsorption to clay particles and organic soil material greatly impedes the mobility of ammonium past the surface zone. Only following prolonged applications of high ammonia solutions will the ammonium adsorption capacity of most soils be exceeded, allowing ammonium to percolate with recharge water to greater depths. This mechanism benefits agricultural activity by holding ammonium close to the soil surface to allow nutrient adsorption into the plant system. Immobilization to adsorption, however, does not permanently remove ammonium from the soil-water system. Replacement by other positively charged ions or conversion by nitrifying organisms are two mechanisms that could remove ammonium adsorbed in soil particles.

Incorporation of ammonium into bacterial cells also serves to immobilize nitrogen in the surface zone, while eventual death of the microorganisms returns nitrogen to the soil.

3. Nitrification. Where diffused oxygen is available, ammonium is rapidly converted to nitrate by nitrifying soil organisms. This reaction is usually the most predominant within the surface zone due to the relative abundance of Nitrosomonas and Nitrobacteria.<sup>13</sup> Nitrification is important in terms of nitrogen mobility in the soil system because it converts ammonium, a nitrogen form not readily subject to leaching, to nitrate, which moves freely with precolating water. The negative charge associated with nitrate is not amenable to the adsorption reactions which affect ammonium mobility. For this reason, nitrification is of great significance to water quality management and nitrate occurrence in groundwater.

Enhancement of nitrification is commonly undertaken in controlled soil systems by utilizing a wet-dry application technique. When the surface zone is saturated with applied water, nitrification is inhibited due to deficient oxygen levels, causing ammonium to build up in a shallow soil layer. During the drying cycle, the soil surface is aerated and provided with an adequate oxygen supply to promote nitrification. Subsequent to conversion to the more mobile form, nitrogen as nitrate can be assimilated by plants, undergo denitrification, or be transported downward with recharging water from the next wetting cycle. This phenomenon is of particular interest when ephemeral streams are used as a waste discharge point.

4. Denitrification. In order for denitrification of nitrate to free nitrogen gas to occur, an anaerobic soil layer and decomposable organic matter must be present within the surface soil.<sup>13</sup> The typical distribution of organic matter in soils is such that high concentrations occur at or near the surface and decline progressively with depth. Several investigations have indicated that denitrification is predominant near the soil surface in spite of its proximity to the atmosphere and that living plants also stimulate denitrification. Both nitrification and denitrification can occur in the same soil profile in irrigated crop lands because of the presence of anaerobic pockets in an essentially aerobic soil. Soil that is completely anaerobic, as caused by the wetting cycle of a controlled system, however, inhibits denitrification unless nitrate is adequately present in the applied water.<sup>5</sup> Denitrification, aside from removal in crops during harvesting, is the only means of completely removing nitrogen from the soil-water-plant system.

5. Assimilation. Incorporation of ammonium and nitrate into the tissue of plants as nutrient substrate is an essential and effective method of reducing nitrogen content in the surface zone. The amount of total nitrogen in the soil that is assimilated by the roots of growing plants is dependent upon the nature of the plant, depth and distribution of rooting, rate of moisture recharge through the zone, nitrogen loading rates, and other factors.<sup>5</sup> In the surface zone, plant assimilation is an important management parameter when applying agricultural fertilizer or in land applications of nitrogen wastes.

Based on the preceding discussion, it is evident that within the surface zone, complex interrelationships exist between the soil-water-plant system and the nitrogen cycle. It can also be noted that the basic processes described are important in retaining nitrogen compounds within a soil layer. A supplemental fixed nitrogen input in excess of the amount that can be accommodated by the five nitrogen pathways would result in nitrogen accumulation within the surface zone. Once nitrogen is transferred with percolating water beyond the effective depth of plant roots, its potential as a nutrient source is reduced. With increasing depth, nitrate becomes a potential groundwater pollutant due to diminishing microbial activity.

In considering nitrate as a pollutant, it is important to recognize that transport through the vadose zone, as shown in Fig. 2-2, is largely a function of the mass flow of recharge. In unsaturated soil, water moves only in this film over the surfaces of soil particles, proceeding slowly as it is impeded by porosity changes in the soil. In time, water fills the micropores of the soil particles, resulting in a soil moisture content referred to as field capacity. Field capacity is defined as the moisture content of soil drained of all residual water by gravity. When additional water is applied beyond the field capacity, the large pores between soil particles fill and localized saturated soil conditions occur within the vadose zone.<sup>13</sup> Water movement through the vadose zone results from natural conditions as in the case of surface runoff recharge along mountain fronts or from incidental recharge, as in irrigation of agricultural land. Under these types of conditions, large volumes of recharge result in relatively rapid water movement through the vadose zone.

Although highly dependent upon hydrogeologic conditions and the lateral dispersion within the vadose zone, transmit time to the groundwater aquifer may also be significantly reduced. Transmit time under conditions of high recharge may be realized within a period of days, weeks, or months. In contrast, low volume recharge rates through the vadose zone may require a transit time of years, decades, or even centuries to reach the main water table.<sup>14</sup> The hydrogeology shown in Fig. 2-2 has been simplified from actual conditions and is presented for the purpose of describing the significant aspects of nitrogen behavior relative to groundwater pollution.

The potential of nitrate pollution depends primarily on the large lateral dispersion conditions which act to dilute both the recharge rate and nitrate concentration. Within the vadose zone, geophysical processes influence the mobility and transport of nitrate ions, while geochemical processes have little or no effect. In the saturated zone, polluted recharge water moves through the aquifer as a discrete body and is not subject to dilution with uncontaminated water of the main aquifer. The aquifer system acts as a repository for past recharge events, accumulating recharge inputs over long periods of time. Recharge water generally originates as a saturated mound, as shown in Fig. 2-2, with its subsurface movement determined by a complex combination of factors, including frequency of recharge inputs, natural hydraulic gradient, subsurface geology, and hydrodynamic pumping patterns.<sup>15</sup> With increasing depth, the recharge mound continues to disperse laterally, making shallow wells the most significant sources of high nitrate waters.

## SIGNIFICANCE OF NITRATE IN WATER QUALITY MANAGEMENT

The preceding section has presented an overview of the complex chemistry of nitrogen, its interaction with the receiving environment, and its impact on water quality. Although nitrogen is an essential element in the life processes of all plants and animals, it can be equally deleterious to public health and the environment when present in certain forms and concentrations. Specifically, nitrate is the most important nitrogen form of concern as a public health hazard in water supplies.

### Health Aspects

High nitrate concentrations in drinking water were initially considered a major health hazard in 1940, when identified as the cause of infantile methemoglobinemia. Subsequent to extended investigations in areas where the problem has been most acute, it has been concluded that nitrate levels in drinking waters should be limited. In 1962, the US Public Health Service recommended that nitrate concentrations in public water supplies should not exceed 10 mg/l as nitrogen.

Infantile methemoglobinemia is a blood disorder which impedes the oxygen carrying capacity of hemoglobin and may lead to suffocation. When high nitrate water is ingested by infants, it is converted to nitrite in the upper gastrointestinal tract. The nitrite then passes into the blood, where it reacts with hemoglobin ( $Fe^{++}$ ) to form methemoglobin ( $Fe^{+++}$ ). Methemoglobin which is incapable of carrying oxygen prevents the blood from transporting oxygen, thereby leading to suffocation.

Cyanosis, the blue coloration of the skin, is the first clinically detectable sign of methemoglobinemia and occurs when ten percent of the hemoglobin is in the methemoglobin form. Infants afflicted with methemoglobinemia and showing cyanosis are commonly referred to as "blue babies". Adults and children over three months, however, suffer no ill effects from ingestion of high nitrate water, since they have a lower pH in their upper gastrointestinal tract which inhibits bacterial conversion of nitrate to nitrite.

## Water Quality Control Aspects

Based on the preceding discussion of the interaction of nitrogen with the soil-water system and the major pathways of nitrogen conversion and transportation within the environment, the following salient points were observed relative to water quality control and resource management:

1. Nitrification readily transforms nitrogen compounds to nitrate in the soil-water system.
2. Nitrate is a preferred plant nutrient, rapidly assimilated by plants and microorganisms in both the soil and aquatic environment.
3. Although nitrate affects the beneficial use of surface waters, high concentrations and associated health hazards seldom occur because of rapid assimilation by aquatic plants.
4. Nitrate is a mobile nitrogen form in the soil system which moves freely with percolating water.
5. Movement of nitrate in the soil system is directly related to the mass flow of recharge.
6. Percolation beyond the surface zone limits the availability and effectiveness of nitrogen removal pathways.
7. Within the effective depth of the plant root system, nitrate can be readily removed by assimilation. Beyond this depth, however, nitrate accumulation may occur in the soil-water system due to the limited methods of nitrate removal and reduced biological activity.

It is apparent from the preceding observations that nitrate, as a public health hazard, is most significant in groundwater where high concentrations can occur. Nitrate as an important parameter in water quality management, therefore, should be properly controlled in accordance with the regulations set forth in the Safe Water Drinking Act of 1974.

CHAPTER  
**THREE**

## CHAPTER 3

### EVALUATION OF EXISTING CONDITIONS

An understanding of the pertinent environmental characteristics of the study area is essential to: (1) adequately identify and evaluate potential sources of nitrogen, (2) properly assess nitrate occurrences in present water resources and associated impacts on present and future conditions, and (3) comply with Public Law 93-523. Based on the preceding chapter, it is apparent that the deposition and accumulation of nitrate in water resources is a function of the chemistry of nitrogen and its interrelationships with the soil-water-plant system. Nitrogenous compounds may enter the soil-water-plant system from both natural and man-caused sources and can be a potential water quality and public health hazard, depending upon the surrounding elements of the environment. Presented in this chapter is a description of study area characteristics relative to major sources of nitrogenous compounds and an evaluation of nitrate occurrences in water supply systems throughout the study area.

#### STUDY AREA CHARACTERISTICS

Within the boundaries of the State of Arizona, large contrasts in environmental conditions exist. Accordingly, both physical and socio-economic environments vary widely throughout the study area. One of the primary reasons for the vast differences in land forms, climate, and vegetation is the considerable range in land elevation.<sup>1</sup> These physical variations, which are commonly found in the Southwest and may occur over relatively short distances, influence to some extent the behavior and transformation of nitrogen and the occurrence of nitrate in water supplies in various parts of the state.

Recognizing the need for areawide planning and the variations in environmental characteristics, the State established the six planning districts shown in Fig. 3-1 to provide a common geographic basis for all environmental planning programs. Each planning district is comprised of one or more counties and has responsibility for the development of an areawide management plan to protect and enhance the quality of the environment. The on-going areawide waste management planning effort under Section 208 of PL 92-500 which includes development of water resource-related programs is of particular significance to this study.

Based on the discussion presented in Chapter 2, it was determined that certain environmental elements influence the chemistry of nitrogen in the soil-water system more than others. Therefore, only those characteristics of the study area that impact the behavior of nitrogen and the occurrence of nitrate in drinking water supplies are presented in the following sections.

## Physiographic Features

Physiographic features of the study area influence the suitability of water resources as future sources for municipal water supply. Geographical features of the area also directly influence population distribution and the extent of areal development.

The state is characterized by two major physiographic provinces separated by a transitional province. As shown in Fig. 3-2, the Plateau Uplands Province, Central Highlands Province, and Basin and Range Lowlands Province occupy 40, 15, and 45 percent of the state's area, respectively. Since each province has varying physiographic characteristics, both water resources and areal development are controlled by different environmental conditions.<sup>1</sup>

Plateau Uplands Province. The Plateau Uplands is characterized by flat-topped mesas, buttes, and deep canyon formations, including the spectacular Grand Canyon. Most of the province lies about 5,000 feet and can be classified as high desert, high plateaus, and timber-covered mountain ranges. Underlying the entire province are extensive, consolidated sedimentary rock formations. Various agents of erosion have transformed these rocks into steep-walled canyons and high isolated mesas. Isolated alluvial deposits occur mostly as border strips along steep stream channels.<sup>1</sup>

Extreme contrasts in terrain have created diverse water resource conditions. The Little Colorado River, which flows into the Colorado River in the upper reaches of the Grand Canyon, drains much of the central portions of the province. Many of the water courses are intermittent and receive flow only in response to precipitation.

In 1974, about ten percent of the state's total population was located in the Uplands area due to rugged physiographic features which have prevented urbanized development. As such, most of the province still lies in its natural state.

Central Highlands Province. The Central Highlands Province serves as a transitional zone which separates the Uplands and Lowlands provinces. The province is characterized as a mountainous area fractured by relatively small, shallow valleys which are not interconnected.

Although areal development is present only in localized areas, about 50 percent of the streamflow produced within the state originates from the Central Province. All major water supply reservoirs in the study area, excluding those on the Colorado River, receive surface inflow from streams in the province. The highland areas of the province account for approximately 30 percent of the drainage area for the Salt and Verde rivers, while producing over 60 percent of the combined streamflow. Reservoir systems located on the Salt and Verde rivers represent the major source of surface water supply for metropolitan areas in Maricopa County.<sup>1</sup>

Basin and Range Lowlands Province. Physiographic features common to the Basin and Range Province include isolated mountain ranges and broad alluvial valleys. The basic geologic features of the Lowland Province were formed by several stages of erosions and deposition of sediment. Consolidated sediment, characterized as "older alluvium", composes the largest volume of valley fill. A

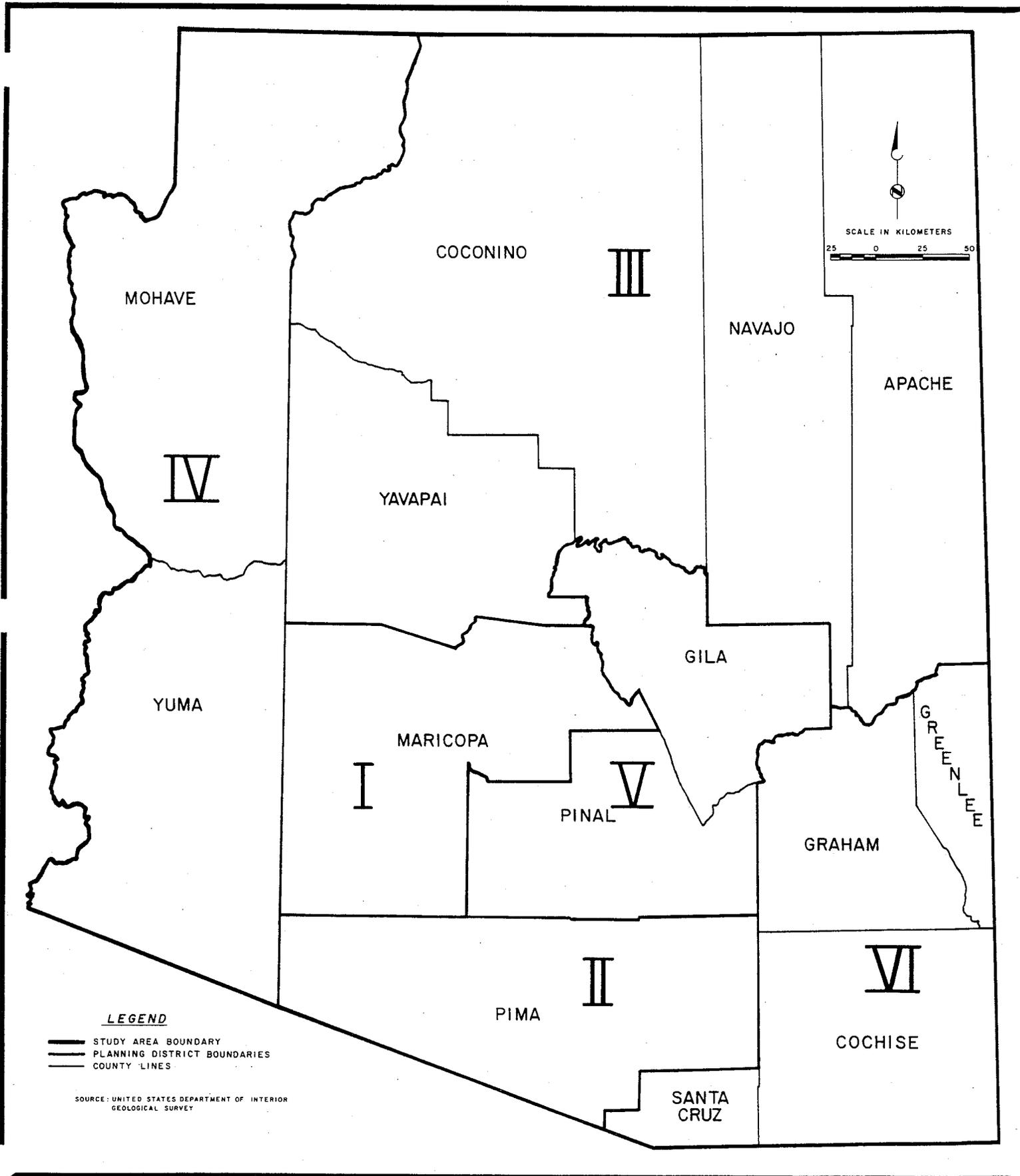
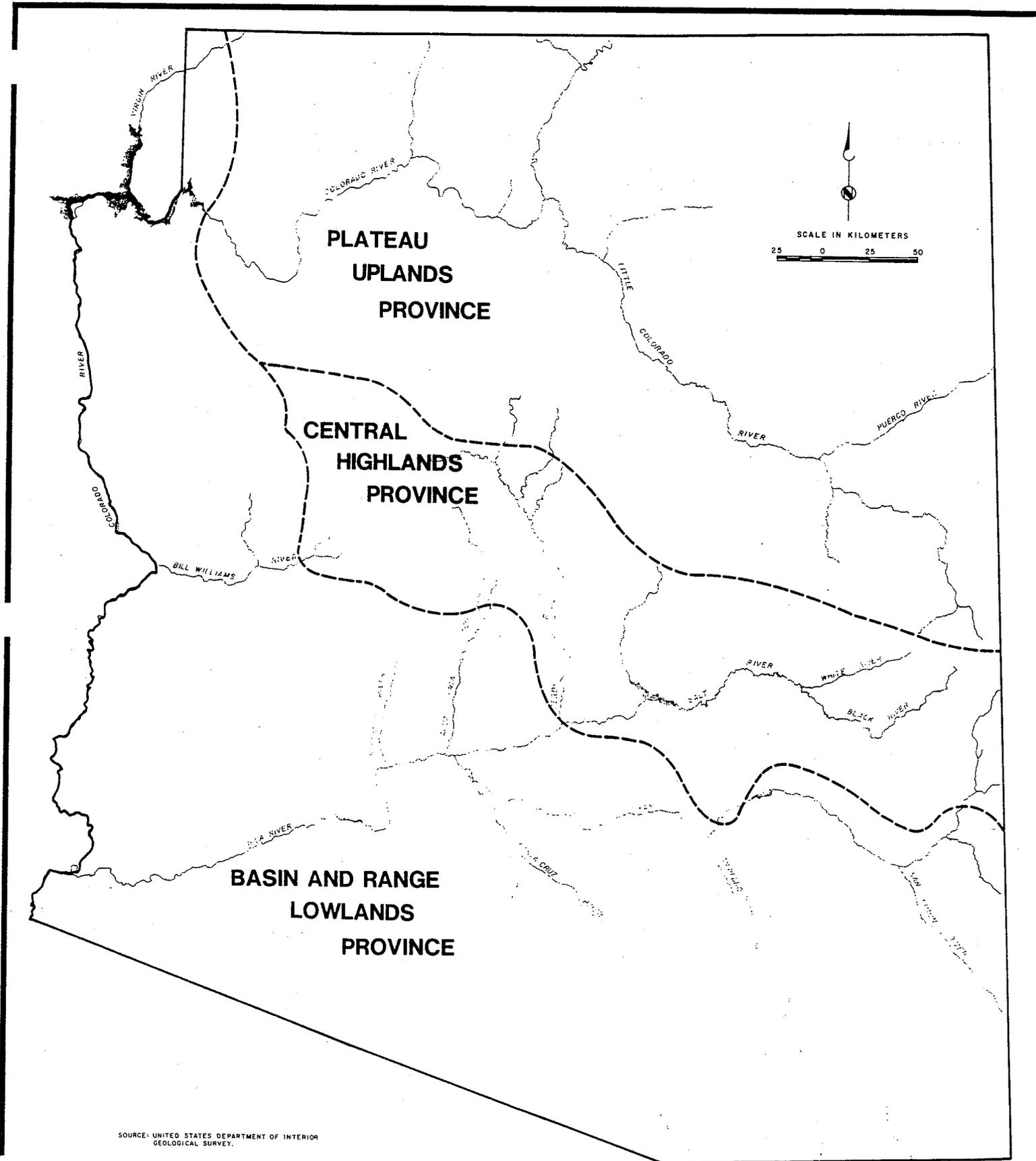


Fig. 3-1 Study Area Boundary



**Fig. 3-2 Major Physiographic Provinces**

slightly less consolidated alluvium consisting of gravel, sand, and silt from the overlying deposits characterized as "younger" alluvium. Loosely consolidated sediment representing the most recent alluvial deposition occupies the present stream courses which cut into the valley floors.

Major groundwater supplies are present in extensive alluvium deposits of the Basin and Range Province which may extend to a combined depth of several thousand feet. Groundwater reservoirs range from shallow localized basins within confining strata to major aquifer systems of great depth in the consolidated older alluvium.

The dependability and suitability of groundwater resources in the Lowland Province have significantly influenced population distribution and extent of areal development within the entire study area. The Basin and Range Province contains approximately 80 percent of the total population and over 90 percent of the cultivated land used for agricultural purposes.<sup>1</sup> The physiographic features common to alluvial valleys in arid climates, as well as availability of groundwater and large acreages of relatively level land, have historically attracted both agricultural activities and urbanization. Groundwater resources in the alluvial-filled basins of the study area therefore are most significant with regard to water quality and resource management.

#### Water Resources

Water resources important to the growth and development of the state include both surface and underground supplies. As mentioned previously, groundwater has been the most reliable source of water supply in the study area and consequently has accounted for about 60 percent of the state's annual water use. Surface water, though unavailable in most areas, accounts for the remaining 40 percent of state withdrawals.<sup>1</sup>

Surface water supplies historically have been developed in response to immediate agricultural and domestic needs. Subsequent depletion of surface water supplies and inhabitation of areas devoid of surface water led to the development of groundwater resources as a source of water supply in many communities. In areas with surface water resources, groundwater is often a vital supplement which assures continuous supply in times of low surface flow.

In order to delineate major surface water drainage and groundwater areas with similar conditions, the three provinces were further subdivided into hydrologically continuous basins, as shown in Fig. 3-3. These designated basins have been used by the Arizona Water Commission as the basis for developing a water resource and use inventory of surface and groundwater to provide background information in the development of water resource management programs throughout the state.

The breakdown of estimated water withdrawal by planning districts and major water uses shown in Tables 3-1 and 3-2, respectively, indicate significant spatial variations in water withdrawal through the state. Planning District I, comprised

of Maricopa County, accounts for 41 percent of the total state withdrawal of ground-water, while Planning District IV accounts for 59 percent of the state's diversion and use of surface water due to its proximity to the Colorado River. The largest single water user in the study area is irrigated agriculture, while remaining water useage is equally distributed between public supply and industry.<sup>1</sup>

**Table 3-1. Estimated Annual Water Withdrawals by Planning District** <sup>a,b</sup>

Planning district/county	Groundwater pumpage	Surface water diversion	Total withdrawal
Planning District I Maricopa County	2,049	941	2,990
Planning District II Pima County	412	0	412
Planning District III Apache County	11	13	24
Coconino County	6	15	21
Navajo County	40	16	56
Yavapai County	23	24	47
Subtotal	80	68	148
Planning District IV Mohave County	34	52	86
Yuma County <sup>c</sup>	541	1,878	2,419
Subtotal	575	1,930	2,505
Planning District V Gila County	16	5	21
Pinal County	1,115	197	1,312
Subtotal	1,131	202	1,333
Planning District VI Cochise County	506	17	523
Graham County	168	113	281
Greenlee County	27	23	50
Santa Cruz County	19	0	19
Subtotal	720	153	873
State total	4,967	3,294	8,261

<sup>a</sup> Source: Arizona State Water Plan, Phase 1, July 1975.

<sup>b</sup> Withdrawal shown in thousands of acre-feet for normalized 1970 conditions. Values shown are based on the location of the water use.

<sup>c</sup> Groundwater pumpage includes approximately 361,000 acre-feet pumped for drainage purposes only.

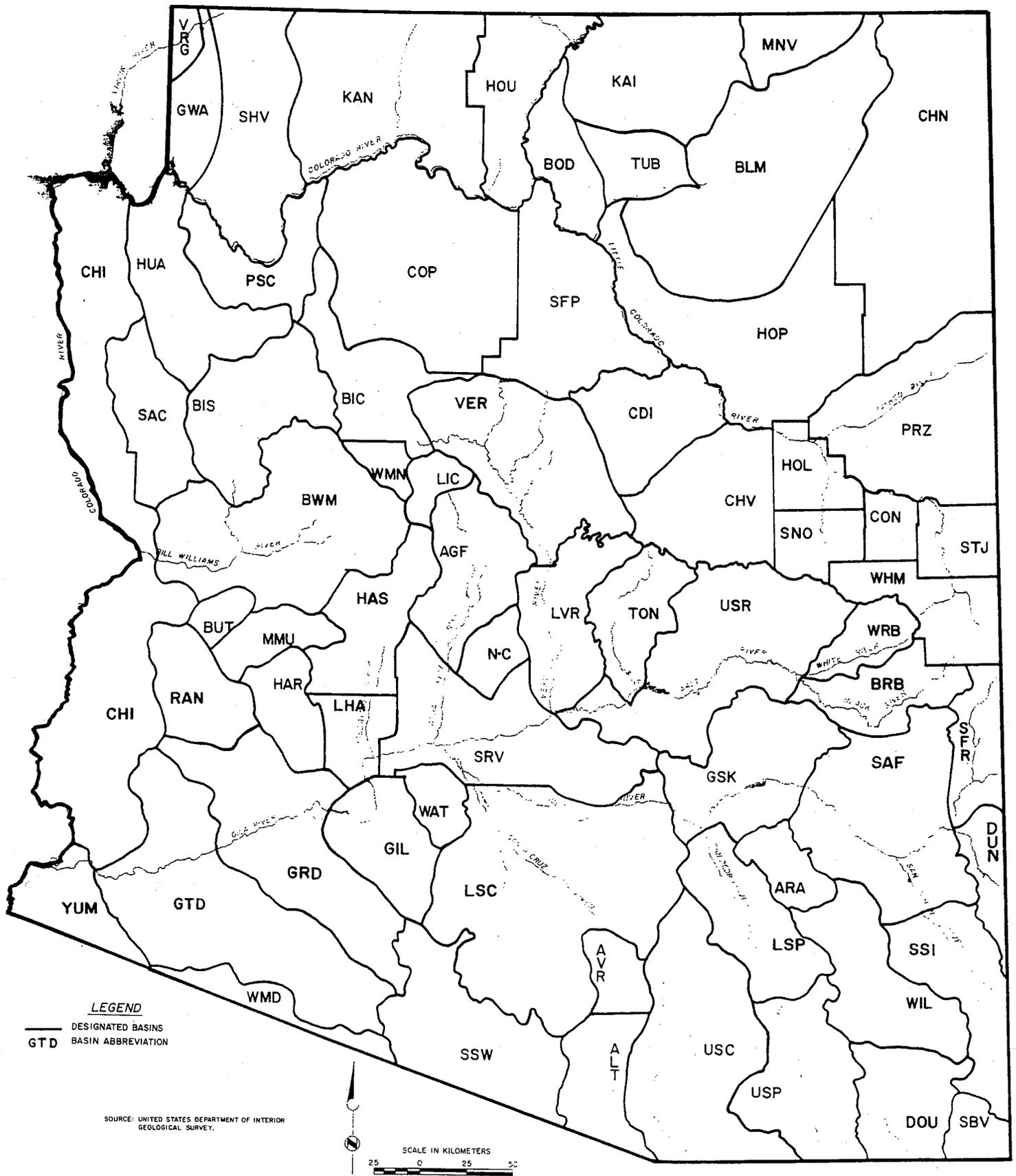


Fig. 3-3 Designated Basins

**Table 3-2. Major Water Uses<sup>a</sup>**

Water use	Source of withdrawal <sup>c</sup>		
	Groundwater	Surface water	Total withdrawal
Agriculture	52.5	34.4	86.9
Public supply <sup>c</sup>	3.1	1.6	4.7
Industry	2.3	1.8	4.1
Drainage <sup>d</sup>	4.3	--	4.3
Sum of water uses	62.2	37.8	100.0%

<sup>a</sup> Source: USGS, Annual Summary of Groundwater Conditions in Arizona, 1975.

<sup>b</sup> Values presented as percent of total state withdrawal. Total withdrawal in 1975 was estimated to be 9.0 million acre-feet.

<sup>c</sup> Includes water use for both domestic and livestock purposes.

<sup>d</sup> Represents groundwater pumpage for drainage purposes only.

Although surface water accounts for almost 90 percent of the state's renewable water supply, downstream appropriation and upstream diversion almost equal present surface supply. Surface water flow available for future development is minor in all areas except the Colorado River mainstem.<sup>1</sup> Groundwater resources in Arizona are non-renewable and exhibit a definite life based on the rate of overdraft and available volume in subsurface storage. Excessive groundwater depletion has led to the designation of critical groundwater areas in some parts of the state whereby future development of irrigated land is prohibited.

Development of groundwater resources as future water supplies is largely dependent upon the availability and suitability of the water, which in turn is a function of potential well yields and water quality. The recently completed Arizona State Water Plan identified groundwater regions within the state with potential suitability for domestic, municipal, industrial, and agricultural supply. Based on the State Plan, it was determined that a major portion of the state, including virtually all of the Upland and Central provinces, has no potential groundwater resources for domestic or municipal supply. Most of the areas identified as having known potential groundwater resources to meet community needs are situated in the alluvial basins of the Basin and Range Province. The availability of water is and will be one of the major factors that will influence land use and population distribution in Arizona.

### Geology and Soils

Geology and soil characteristics, as discussed in Chapter 2, are significant elements of the environment which directly influence the movement of recharge water. The transit time of water movement through the surface and vadose zone, depending upon the mass flow of recharge and hydrogeologic characteristics, can range from days to centuries. Thus the geologic formations of an area relevant to groundwater systems are an important consideration in determining the water quality impact of surface nitrogen sources.

In arid environments, alluvial landforms are the dominant class of groundwater reservoirs. Both upward and downward flow of groundwater is controlled by the physical properties of the geologic strata. The rate of groundwater recharge is a function of the permeability of the alluvial deposit. In general, the permeability is dependent upon the porosity and the degree of consolidation of the alluvial sediment. The amount of void space in a unit volume of rock is referred to as porosity, which is a measure of the volume of water storage in a geologic unit. Consolidation as it applies to permeability is a measure of the degree of interconnection between pore spaces. Porous rocks comprised of interbedded gravels, sands, and silts with little or no consolidation have high permeability and allow relatively free movement of water.

The nature and condition of sediment deposition resulting from the fluvial formation of alluvial basins determines the permeability of each alluvial strata. In the vertical direction, strata variations can often occur over short distances and permeability may change considerably. Although interbedding of the rock units is a geologic complexity with numerous variations, distinct textural compositions associated with different strata can be identified. Present stream courses which have been cut through older alluvium consist of coarse-grained sediment and occur throughout the state, as shown in Fig. 3-4. Fine-grained rock units, imbedded within the older alluvium, are usually found in the central part of alluvial basins. These layers of fine-grained material were formed by ancient deposition, accumulation, and evaporation associated with playas and are referred to as playa formations.<sup>2</sup> Extensive evaporite deposits are contained in these formations which, together with other precipitated salines, could include natural accumulations of nitrate salts.<sup>3</sup>

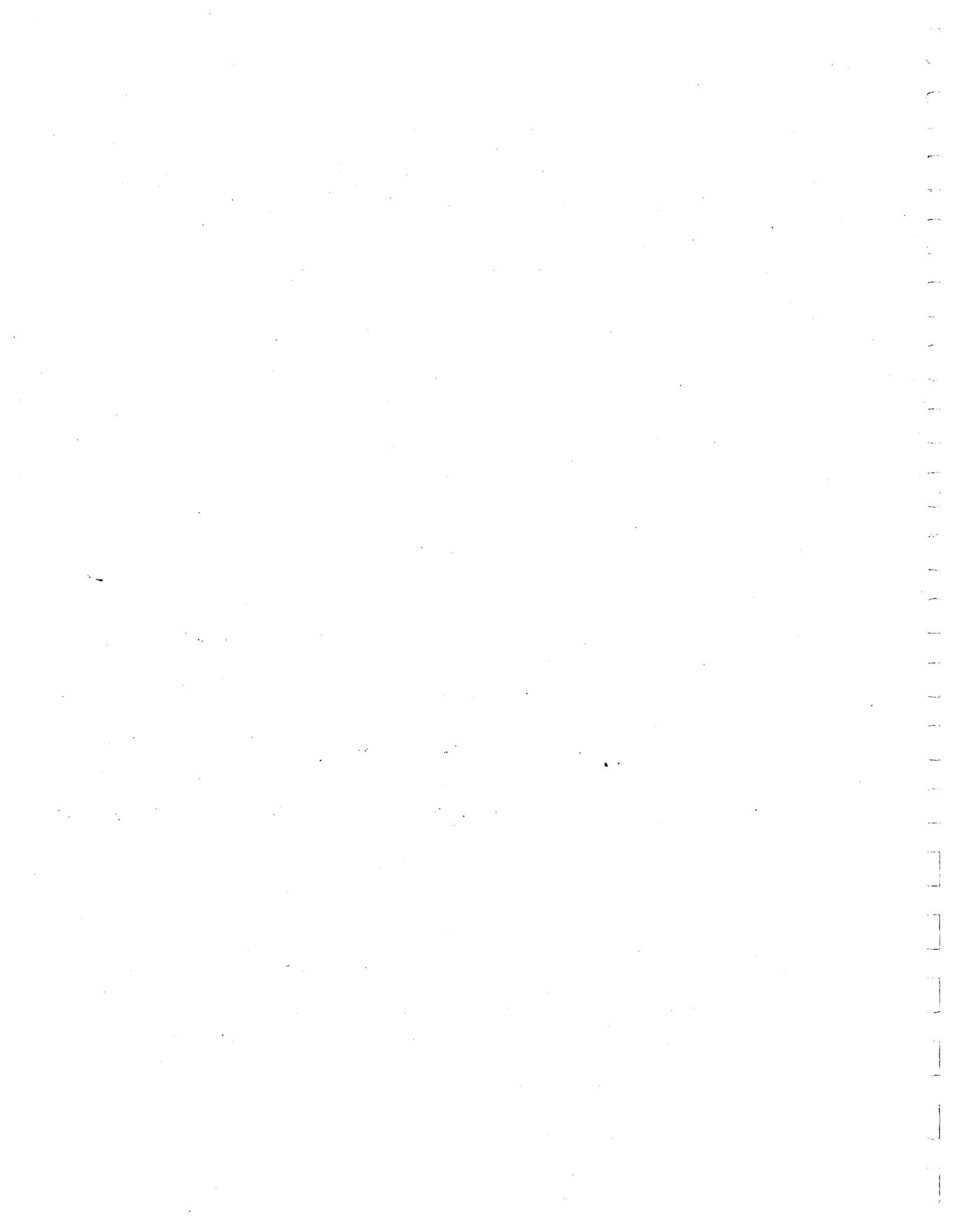
The textural changes in the rock units directly influence the hydraulic dispersion of recharge water. Recharge flow through coarse textured alluvium follows a near vertical path, while flow through finer-grained strata or lenses of lesser permeability undergoes greater lateral dispersion, resulting in a more horizontal flow path. With greater lateral dispersion, the transit time of recharge flow through the unsaturated or vadose zone is significantly increased. Coarse-textured alluvium, as found in most desert stream courses, therefore allows the most rapid rate of groundwater recharge.

Irregularities in the formation of rock units, such as joints, fractures, and faults, may act as a direct conduit for recharge flow through the vadose zone. Land subsidence due to excessive lowering of the water table from the heavy pumpage can create cracks and fissures which in turn could reduce the effective transit of recharge water from the land surface to the aquifer.

### Hydrogeology

Depth to groundwater is another important consideration in evaluating the impact of recharge flow on groundwater quality. Through greater depth of heterogeneous, stratified material in the vadose zone of the alluvial deposits, recharge of flow follows a more complex flow pattern resulting in greater lateral dispersion of both recharge flow and soluble contaminants. A horizontal flow path of contaminated recharge water contacts a larger surface area of the unsaturated zone effectively reducing the contaminant concentration in the aquifer. Although greater depth of the vadose zone can result in a significant lag period, contaminant attenuation may not necessarily occur if dispersion and subsequent dilution are absent.<sup>4</sup> A sudden increase in nitrate concentration in a production well could occur in response to a considerably long transit time of percolating water from a past recharge event.<sup>5</sup>





Many of the groundwater tables within the study area, particularly the Salt River Valley and Upper and Lower Santa Cruz basins, are located at a depth of 400 to 500 feet. Based on current information, the water table elevation is expected to continue to decline due to overdraft conditions. Several other natural and man-caused hydrogeologic conditions, however, affect the recharge of groundwater aquifers and water quality.

A hydrogeologic condition common to localized areas with high infiltration and recharge is groundwater mounding. When surface infiltration exceeds the recharge rate through the soil profile, a subsurface mound may form as previously shown in Fig. 2-2. The mound effect establishes a horizontal hydraulic gradient causing water to flow radially from the mound's center and is most significant when associated with contamination of perched water tables.

The occurrence of perched water tables in the state's alluvial basins has been established in previous studies.<sup>7,8</sup> As shown in Fig. 2-2, perched water develops when there are discontinuities in soil permeability. Clay, silt, or other fine-grained lenses can impede recharge flow and establish a separate saturated zone above the main aquifer. Attenuation mechanisms are significantly limited when contaminated recharge flow is isolated in a perched water table. Thus, perched water drawn to the surface by a shallow pumping well without the benefit of vadose zone attenuation can have significantly higher levels of nitrate than the main groundwater body. Although perched water is a common natural phenomenon in areas of high recharge such as stream courses, storm water is not directly associated with hazardous levels of nitrate. Perched water caused by recharge incidental to man's activity, such as percolating wastewater effluent, represents the conditions of greatest concern.

Perched aquifers also allow greater lateral dispersion at shallower depths. As the surface area of the perched saturated zone increases, a more direct flow path to the underlying aquifer or the land surface can occur by contact with a cascading well. As illustrated in Fig. 2-2, cascading wells short circuit the flow path through the vadose zone. In an investigation of the Cortaro area in the Upper Santa Cruz Basin, highest nitrate levels were observed in wells with cascading water.<sup>7</sup>

Alteration of the natural hydraulic gradient in an unconfined aquifer by heavy well pumpage is another hydrogeologic condition that can effect the quality of groundwater. In the study area, localized water table drawdown can be dramatic. For example, heavy pumpage in two distinct areas in the Salt River Valley effectively separated a large aquifer system into east and west sub-basins. Under such conditions, a hydraulic gradient is formed establishing the pumping site as a convergence point for groundwater movement over a large area. By forming a flow pattern radially toward the lowpoint, this collection mechanism results in additional pathways for contaminant recharge to reach the pumping wells. Recharge water occurring downgradient of the wells under natural conditions can be drawn toward the pumping site under the influence of the modified flow patterns. A variety of other groundwater pollution geometries resulting from hydrologic modification can also significantly effect groundwater quality, depending upon the local hydrogeologic framework.<sup>4</sup>

## SOURCES OF NITROGEN

The release of nitrogenous compounds to the receiving environment may be natural or man-caused. Most significant surface discharges are related to urban, industrial, and agricultural activities and have been thoroughly documented with regard to form and quantity of nitrogen released. In contrast, nitrogen from natural sources is more difficult to identify and quantify due to physical constraints in monitoring natural nitrogen levels. The interaction of both natural and man-caused sources of nitrogen with the receiving environment can have a significant impact on water quality. Depending upon the specific character of the affected environment, nitrogen can be either a serious public health hazard or incorporated by the soil-water-plant system with little or no effect on water quality.

In a hydrologic context, sources of nitrogen can be further classified as a point, line, or diffuse source. These classifications primarily relate to the recharge conditions by which contaminants enter the groundwater-soil system. A point source exhibits stationary properties with recharge occurring directly below the source. A line source such as an alluvial stream course occurs when percolation is more predominant in length rather than the width of the effective surface area. Recharge from large areas such as irrigated lands is described as a diffuse source. These classifications of nitrogen inputs to the soil-water system, along with the volume of recharge flow, are essential in evaluating groundwater quality impacts of natural and man-caused nitrogen sources.

### Natural Sources of Nitrogen

Natural sources of nitrogen include precipitation, dustfall, non-urban runoff, biological fixation, and geologic deposits. Since accurate estimates of nitrogen levels from these sources are currently not available, their relative impact on nitrate concentrations in water supply can only be based on speculation. The following section presents an evaluation of nitrate occurrences with emphasis on the impact of natural sources on a groundwater system.

Precipitation and Dustfall. Precipitation and dustfall represent diffuse sources which return nitrogen in ammonia and nitrate form to the land surface. Increases in nitrogen levels from these sources are influenced by man's activity. The combustion of fossil fuels and the application of liquid ammonia fertilizers with subsequent ammonia volatilization can substantially increase nitrogen concentrations in both rainfall and dustfall.<sup>9</sup> Although these sources have not been thoroughly investigated in the study area, their effect as nitrogen sources appears to be of greater significance in the biostimulation of surface waters than as health hazards in groundwater supplies.

Non-Urban Runoff. The forms and quantities of nitrogen in non-urban runoff from non-fertilized land is dependent upon the content and erosive characteristics of the surface top soil. In alluvial basins, surface runoff generally follows and infiltrates normally dry-stream courses, as illustrated in Fig. 2-2. Although the concentrating effect of this occurrence is unknown, it is apparent that the soil characteristics common to arid climates would limit the contribution of nitrate to groundwater.

Biological Fixation. As previously discussed in Chapter 2, biological fixation may add nitrogen to both soil and surface water environments. In the soil, nitrogen is fixed in proportion to the nutrient requirements of plants and generally does not accumulate to a hazardous level. Nitrogen fixation by blue-green algae represents a significant input to surface waters in terms of biostimulation, but it exhibits little potential as a nitrate health hazard.

Geological Deposits. Nitrate in geologic strata may be of particular importance in the study area. The occurrence of natural nitrate deposits in semi-arid and desert environments has been reported in several investigations, including a USGS study which reported nitrate deposits in 23 states. Specific conditions of nitrogen and water availability, deposition, and concentration were theorized to have culminated in the formation of natural nitrate deposits. The natural accumulation of nitrate in climates similar to the arid regions in central and southern Arizona was further related to evaporite deposits in playa formations.<sup>3</sup>

A recent investigation of groundwater quality in the Salt River Valley indicated that nitrate levels in specific areas within the basin may be of natural origin. Based on a historical review of groundwater quality records, it was determined that high nitrate levels were present prior to extensive agricultural and urban development. High nitrate levels have also been observed in groundwater from fine-grained strata at depths up to 1,000 feet.<sup>10</sup> As discussed previously, natural nitrate occurrences are associated with fine-grained strata due to evaporite accumulation during the formation of playas in alluvial valleys. High nitrate levels at extreme depths in an aquifer may also be an indicator which could substantiate the natural occurrence of nitrate. The characteristics common to certain high nitrate groundwater areas in the Salt River Valley are consistent with these conditions which support the occurrence of natural nitrate deposits.

The water quality hazard of natural nitrate deposits could be further enhanced by hydrologic modification of natural groundwater flow patterns. By altering the natural hydraulic gradient due to large-scale well pumpage, nitrate along with other deposited salts could be transported toward the pumping site. An extensive groundwater depression could therefore cause a concentrating effect by drawing naturally occurring nitrate salts into the pumpage site.

Geologic deposits appear to be most significant of the natural sources discussed with respect to the occurrence of nitrate in groundwater sources in the study area. Nitrogen from precipitation, dustfall, non-urban runoff, and biological fixation is not amenable to environmental mechanisms capable of accumulating nitrate to health hazard levels. Although investigations have not fully documented the occurrence of nitrate deposits in the fine-grained units of the alluvial basins, it is possible that evaporation of nitrate-bearing waters in an arid climate could have resulted in substantial accumulation of nitrate similar to other common salts found in groundwater. Further investigation, however, is necessary to substantiate the occurrence and define the extent of nitrate from this natural source.

## Man-Caused Sources of Nitrogen

Sources of nitrogen that are related to man's activities include municipal and industrial wastewater effluents, subsurface drainage from agricultural land, leachates from septic tanks and sanitary landfills, and runoff from animal feedlots and urban areas. In contrast to most natural occurrences, these sources are generally associated with higher nitrogen concentrations.

Wastewater Effluent. Municipal wastewater effluent discharges are concentrated sources of nitrogen usually regarded as point sources. The nitrogen content of raw municipal wastewater ranges generally from 20 to 85 mg/l as total -N, and is comprised of about 60 percent ammonia and 40 percent organic nitrogen. The largest nitrogen input in wastewater is noncarbonaceous matter in human excrement, which contains hydrolyzed proteins and ammonium. Fresh wastewater generally contains less than one percent of the total nitrogen in the nitrate form. In most cases, nitrification of ammonium in wastewater is inhibited by the relatively slow biological growth rate of Nitrosomonas.<sup>9</sup>

Unless specifically designed to remove nitrogen, conventional secondary wastewater treatment plants do not significantly reduce the nitrogen waste load. Primary and secondary treatment remove approximately 5 to 10 percent, and 10 to 20 percent, respectively, of the total nitrogen load. Although most organic nitrogen is oxidized to ammonium, conventional treatment processes do not provide an environment suitable for the growth of both groups of bacteria needed for complete nitrification and denitrification. The predominant form of nitrogen in secondary effluent therefore is ammonium, or ammonia.<sup>9</sup> As previously discussed, nitrification usually proceeds rapidly once discharged to the receiving environment.

Effluent disposal to stream courses in arid climates is best described in a line source of nitrogen. In Arizona, the majority of wastewater effluent from communities is discharged to ephemeral waterways. With additional flow occurring only in response to precipitation, effluent often constitutes the entire surface flow for most of the year. As previously described, normally dry stream courses are highly permeable and provide the most rapid recharge path to the saturated zone. In the case of effluent discharge from the City of Tucson to the ephemeral Santa Cruz River, surface flow downstream of the plant eventually disappears due to rapid infiltration and evaporation. Depending upon the sewerage service area population, wastewater effluent can represent a significant source of recharge.

Once discharged, nitrogenous compounds in wastewater effluent undergo the transformations described in Chapter 2. An investigation of nitrogen transformations in the Santa Cruz stream course indicated that nitrification is related to both flow distance and physical characteristics of the stream course. Nitrate concentrations in the effluent from the City of Tucson treatment plant increased with flow distance, while total nitrogen and ammonium concentrations decreased. The rate of nitrification was also found to increase with greater flow surface area due to enhanced oxygen transfer. Although not directly measured, the loss of both total nitrogen and ammonium in the surface flow can be attributed to denitrification, ammonia volatilization, ammonium fixation, and nitrate leaching.<sup>11</sup> Several investigations have also related the discharge of effluent from the City of Tucson treatment plant to the occurrence of high nitrate levels in groundwater downgradient of the treatment plant.<sup>7,11,12</sup>

A phenomenon which could better define the hazard associated with nitrate in wastewater discharged to ephemeral stream courses is the effect of the diurnal flow characteristics of wastewater effluent. In the Santa Cruz River, for example, where no stream flow exists during most of the year, a significant variation in the distance of the wetted front from the source occurs due to the diurnal flow variation in wastewater discharge. Flow distance during peak discharge has extended 25 miles downstream, while the wetted distance during low flow has been limited by infiltration and evaporation to about 11 miles.<sup>11</sup> As previously discussed, the wet-dry cycle in a controlled land application system enhances nitrification. This same effect can be observed in the 14-mile distance of the Santa Cruz River that undergoes both wetting and drying on a daily basis. Increased nitrification during the drying period could allow larger amounts of nitrate to be transported downward through infiltration of effluent during subsequent peak flow periods.

Irrigated Agriculture. Agricultural return flow from chemically fertilized cropland represents another major source of nitrogen. Surface runoff and infiltration of agriculture irrigation waters are primarily diffuse or nonpoint pollution sources to both surface and groundwater resources. As previously described, application of fertilizers and irrigation water in excessive amounts can result in the occurrence of significant nitrate levels in recharge water percolating to the saturated zone. The amount of excess nitrate, however, varies for each crop and soil condition and is dependent on the interrelationship of the soil-water-plant system. In addition to the biochemical processes within the surface zone, nutrient uptake rates of crops during the growing season, fertilizer application techniques, and other farming practices ultimately determine the availability of excess nitrate for transport with surface runoff or infiltration.

In western farming, the "leaching fraction" plays a significant role in irrigation practices. "Leaching fraction" is described as the amount of water applied in excess of crop evapotranspiration demands to maintain soil salinity at tolerant levels for crop growth. In the study area, high levels of dissolved salts are frequently encountered in groundwater used for irrigation, thus requiring a high leaching fraction to provide adequate soil conditions for crop production. This practice, which has been addressed in numerous studies and publications, thus results in larger subsurface return flows percolating through the vadose zone.<sup>7, 14, 15</sup>

In Arizona, the agricultural land under irrigation is most predominant in the Basin and Range Lowland Province. Due to the relative scarcity and high cost of irrigation water, there are generally no significant surface tailwater or return flows. Subsurface return flow, however, is commonly estimated to be 30 to 50 percent of the applied irrigation water. In 1976, more than 100,000 tons of commercial fertilizer as N were purchased in the state.<sup>13</sup> For these reasons, irrigated agriculture recharge flow has been considered as a major potential source of nitrate in groundwater.

Land Application of Effluent. Application of municipal wastewater effluent to crop and non-crop land has become of increasing interest to communities as an alternative means of supplementing increasing water supply demand. Treatment technologies are not available whereby land treatment systems can be utilized for beneficial reuse and recovery of wastewater and nutrient content. The nutrient requirements for optimum crop production and the large nitrogenous waste loads, however, may often be imbalanced.<sup>15</sup> As previously discussed, nitrogen in excess of uptake mechanisms is a potential water quality hazard in groundwater.

Within the Salt River Valley and Upper Santa Cruz designated basins, the use of effluent for irrigation has occurred for several years. Due to economic reasons, effluent has been applied in volumes in excess of both water consumption and nutrient requirements. These applications of wastewater effluent have been related to high nitrate levels in isolated areas of both basins.<sup>7,12</sup>

Controlled land treatment systems have been characterized into three principal processes: slow rate, rapid infiltration, and overland flow. Each process varies in terms of hydraulic and nitrogen application rates, need for vegetation, pre-application treatment, and final disposal of applied wastewater. The three processes are basically tailored for application in areas with differing site characteristics. When nitrogen management is factored into the design, controlled land treatment systems do not present potential nitrate hazards.<sup>15</sup>

Septic Tanks. Individual treatment systems such as septic tanks can also be a significant source of nitrogen. In a properly operating septic tank system, the total nitrogen present in the domestic waste is converted to nitrate in the soil adsorption leach field. Depending upon the characteristics and design of the leach field, nitrate may or may not be recharged with percolating water. Nitrate levels in the recharge flow may be minimized if the leach field conditions promote denitrification or if nitrate is readily available to plant systems overlying the disposal field. If site characteristics or faulty design preclude these conditions, however, nitrate may be recharged to the vadose zone.

Individual septic tanks are considered point sources, while large unsewered areas using septic tanks are considered a diffuse source. Although associated with a relatively small mass flow of recharge, septic tank failures have been a commonly reported cause of high nitrate levels in groundwater.<sup>7,8</sup> High nitrate levels detected in groundwater samples adjacent to the Santa Cruz River in the Tucson area were linked to two separate clusters of septic tanks. Effective operation of septic tank systems where soil conditions, topography, and groundwater conditions are such that these systems can be expected to perform adequately is important in preventing impairment of groundwater quality.

Sanitary Landfills. Although sanitary landfills are not directly associated with any hydrologic components, solid waste contains several inorganic, organic, and microbiological contaminants. Depending upon the nature of the waste, climate, and modifications produced by chemical, physical, and biological processes, sanitary landfills may represent a potential point source of nitrogen in groundwater.

Organic nitrogen and ammonium are generally the dominant forms of nitrogen produced in landfills. Under aerobic conditions, however, nitrification is likely to occur. Pollutant transport through a landfill site is usually in the form of a leachate. In most cases, leachate production is derived from an external water source. Precipitation, flood waters, groundwater mounds, and perched watertables may penetrate a disposal site and introduce the needed moisture for leachate production. Sanitary landfills located along stream courses in the study area are subject to all these water sources.

Animal Feedlots. Subsurface drainage and surface runoff from animal feedlots constitutes a significant point source of nitrogen. The trend toward confinement of large numbers of animals on small land areas has increased the amount of feedlot waste at localized sites. Ammonium and organic nitrogen concentrations in feedlot runoff have been detected as high as 300 and 600 mg/l, respectively.<sup>9</sup>

Feedlots containing more than 1,000 cattle or equivalent animals units are required to obtain a NPDES permit for waste discharge. Operations within the state, Maricopa, Pinal, and Pima counties are the most active agencies in regulating livestock.

Most feedlots operate oxidation ponds to treat feedlot wastes. Under normal operating conditions, treatment ponds and lagoons do not allow nitrate leaching due to a dense anaerobic bottom layer. A high potential for nitrate leaching exists, however, if the lagoon is drained and the soil bottom is allowed to dry. Nitrification can then produce high levels of nitrate in the aerated soil which subsequently may be leached through the lagoon bottom when treatment operation is again initiated.

Urban Runoff. Urban runoff can contribute nitrogen as a diffuse source following precipitation events. Composition of urban runoff is highly variable and is dependent upon factors such as land use characteristics, frequency and intensity of precipitation, and drainage and collection patterns. In arid climates, extended periods of no rainfall allow contaminants to accumulate, subsequently resulting in high contaminant concentrations in runoff from initial rainstorm events. Annual nitrate loadings for selected urban watersheds in the Tucson region have been estimated to range from 0.10 to 10.0 pounds/acre.<sup>16</sup> Stormwater tributary to high recharge areas such as arroyos and dry stream courses can represent a significant nitrate hazard to groundwater.

## EXISTING NITRATE LEVELS AND OCCURRENCES

An understanding of the chemistry and behavior of nitrogen in the environment and a review of available water quality data are the preliminary steps in identifying existing levels and evaluating the occurrences of nitrate in Arizona drinking water supply sources. The preceding sections have presented an overview of the transformation cycle of nitrogen in the soil-water-plant system, including an evaluation of the environmental characteristics of the state relevant to the occurrence of nitrate in water supplies. Based on the analysis of the nitrogen cycle, it was determined that nitrate accumulation in water supply sources is a significant health hazard of increasing concern that is more predominant in groundwater than surface water sources. To that end, the following evaluation has been directed primarily toward nitrate occurrences in groundwater sources.

A two-step procedure was undertaken to compile and evaluate available water quality data for the state's water resources. Because of (1) the dynamic effect of environmental elements on nitrogen transformation, (2) the site specificity of nitrate accumulation, (3) the limitations of available data, and (4) the large expanse and distinct variation in environmental characteristics in the study area, the evaluation process has been limited to an overview of the general magnitude and characteristics of the nitrate situation in the state's existing water resources. The investigative process was undertaken in two phases, as follows:

Phase I- Preliminary Data Search and Analysis. A data search was conducted to compile surface and groundwater quality data for the state's water supply sources. Surface water quality data was limited to relatively recent analyses, while the last 10 years of available data was reviewed for groundwater quality. Data from surface water quality stations, partial-record stations, and miscellaneous sites designated by the United States Geological Survey were examined for nitrate concentrations exceeding 10 mg/l as N. Townships with one or more active wells which had exceeded the MCL for nitrate were recorded as groundwater areas with potentially high levels of nitrate.

Phase II- Identification of Potential Problem Areas. Based on the above findings, a listing was compiled of water supply systems that are located in or adjacent to the defined areas of potential high nitrate levels. Systems with insufficient water quality data were also included in the assessment where warranted. The listing was developed based on the water supply systems registered in the ADHS Directory of Public Water Suppliers. The compilation of state water supply systems was then investigated for nitrate violations as recorded in the ADHS water quality file.

### Sources of Data

Data reviewed to identify areas of potential high nitrate levels was based on an extensive list of references. The United States Geological Survey (USGS) water quality data file and a report published by the Department of Agricultural Chemistry and Soils of the University of Arizona were the two major references utilized in the analysis. Supplemental data was also obtained from Water Quality Management basin plans, ADHS reports, Arizona Water Commission bulletins and maps, and 208 Area-wide Waste Management Plan draft reports. Appendix B to this report provides a complete list of references and sources of information and data.

### Limitations of Data

Collection and subsequent interpretation of data are the bases of any assessment of a water quality problem or condition. The reliability and validity of the data partially dictates the validity and usefulness of the resultant findings. Proper cognizance of the limitations of data and reporting techniques therefore facilitates the conduct of the evaluations process and the development of resultant findings and recommendations.

The reliability and limitations of data identified during the investigative process are primarily related to groundwater quality analyses. Single water quality samples are of primary concern, since data analysis or interpretation is restricted.

In an alluvial aquifer, the vertical distribution of nitrate is not uniform, since there is little vertical mixing. Since water from each recharge event often retains a general chemical identity, vertical stratification may exist with high nitrate concentrations isolated in the aquifer under varying conditions. Water quality data from a system of wells perforated at specific depth zones would be required to best define the vertical and horizontal distribution of nitrate within an aquifer. Since this type of sampling and reporting system is not usually available due to economic factors, adjacent production wells of different depths could be used to approximate vertical distribution of chemical constituents.

Available data on nitrate levels in groundwater were primarily obtained from production wells with a wide variation in flowrate. There are two major limitations to using only production wells as sampling points. First, since most production wells are designed to pump a maximum amount of water, the perforated zone usually has a large vertical contact area with the aquifer. If a production well produces high nitrate water, the depth or depths in the aquifer at which high levels of nitrate occur is difficult to determine. Second, the composition of the pumped water may vary significantly from the time of initial testing of a new or deepened well until a stable cone of depression is formed. Initially the well may pump a vertically composited sample. As the cone of depression forms, water initially in the upper portion of the aquifer is drawn deeper, which subsequently constitutes a larger percentage of the water pumped to the surface. Water quality data from a production well therefore only represents the condition at a localized site in the aquifer at a given time.

In summary, limitations of data must be recognized when interpreting chemical analyses to quantify constituent levels in production wells. Although the vertical distribution of nitrate concentration is difficult to determine, general observations can be made with regard to the occurrence of nitrate in groundwater. By reviewing historical water quality records for production wells, trends can be identified. Monitoring of production wells also appears to be the most economical and practical method of correlating nitrogen sources with nitrate levels in groundwater.

#### Analysis of Available Water Quality Data

In surface water, nitrate concentrations exceeding the MCL were found to occur only in agricultural return drains and in stream channels where wastewater effluent has been the major source of flow. These surface waters, however, would not be considered as sources for drinking water supply. Analysis of available data indicated that none of the existing surface drinking water supplies contain nitrate greater than 10 mg/l  $\text{NO}_3\text{-N}$ . As previously discussed, the nitrogen transformation mechanisms common to surface waters generally prohibit nitrate accumulation to hazardous levels. Based on the analysis of data, it is apparent that reported nitrate concentrations in the surface water sources of Arizona are consistent with the generally observed occurrence of nitrate in surface waters.

Nitrate levels greater than the MCL have been reported for a number of groundwater sources in the state. Analysis of historical data indicated that high nitrate levels in groundwater have existed in some areas of the state since the 1920's,<sup>10</sup> while recent investigations indicate a fluctuating trend in nitrate concentrations in the unconfined aquifers. Based on available data, groundwater areas with potentially high nitrate levels are shown in Fig. 3-5. Except for a few isolated occurrences, all groundwater areas identified as high in  $\text{NO}_3\text{-N}$  concentration are contained within the Basin and Range Lowlands Province.

The highest number and most frequent occurrence of nitrate levels exceeding the MCL were reported for wells located in the Salt River Valley, Upper Santa Cruz, and Lower Santa Cruz basins. Areas with high nitrate concentrations within these basins are generally located along recent alluvial stream courses which include the Santa Cruz, Lower Salt, Agua Fria, Hassayampa, and Gila rivers. Scattered high nitrate areas have also been reported to occur in the San Pedro, San Simon, and upper Little Colorado River basins. Analysis of the areal distribution pattern indicated that most groundwater areas identified with potential high nitrate levels are located within alluvial basins which are subject to urban and agricultural activities.

Within the designated groundwater basins shown in Fig. 3-5, more than 150 water supply systems registered with ADHS were identified as having groundwater supplies with potential high nitrate levels. Most of these systems, as shown in Table 3-3, are located in the Salt River Valley, Lower Santa Cruz, and Upper Santa Cruz basins. Following a review of the ADHS water quality data files, only the fifteen water systems listed in Table 3-4 have reported nitrate violations. Relatively frequent violations have been reported for the City of Glendale and northwestern Phoenix, while the remaining water systems have only single nitrate violations currently on file. Several of the water supply systems located in potentially high nitrate groundwater areas, however, have not reported any current violations of the MCL for nitrate.

Nitrate occurrences in the groundwater areas shown in Fig. 3-5 have been associated with both man-caused and natural nitrogen sources and are useful in assessing the impact of land sources of nitrogen. Analysis of nitrate levels in groundwater from the Salt River Valley and Upper Santa Cruz basins has shown increasing nitrate levels in some specific areas, while decreasing levels have been observed in other areas. Natural nitrate deposits, nitrate recharge from wastewater effluent discharge and irrigation, and large-scale pumping are the likely causes for the varying trends in nitrate levels.

Nitrate concentrations in excess of the MCL have been reportedly common in the West Basin of the Salt River Valley, which includes the communities of northwest Phoenix, Glendale, Goodyear, Avondale, and Buckeye.<sup>10</sup> Both gradual and relatively sudden increases in nitrate levels have been observed in these areas.

Decreasing nitrate levels have also occurred in some groundwater areas of the Salt River Valley, as well as the Upper Santa Cruz Basin. The reductions in nitrate levels have been noted primarily in areas where (1) effluent irrigation has been discontinued, (2) large-scale pumping had withdrawn nitrate-laden groundwater, and (3) dilution or replacement with less concentrated recharge had occurred. Although the mechanism for the above occurrences is not presently well established, it is apparent that the hydrogeologic characteristics of alluvial deposits could possibly allow these rapid changes to occur.

In the Santa Cruz and Salt-Gila river basins, wastewater effluent has been discharged to ephemeral stream channels or used for irrigation for many years. As previously described, these sources of nitrogen are associated with substantial recharge flows and thus have high nitrate contamination potential. As shown in Fig. 3-6, major point sources of wastewater effluent and irrigated lands in the state are located within the groundwater areas designated as having high nitrate potential. The effect of these sources on groundwater quality can be estimated based on the significant correlation of the location of groundwater areas within the major alluvial valleys. In order to further illustrate the potential impact of point and diffuse sources of wastewater effluent, the location of high well production areas throughout the state is indicated in Fig. 3-7 relative to the location of these nitrogen sources. As indicated, high production wells are generally located in areas with hydrogeologic conditions conducive to rapid infiltration rates such as alluvial stream courses. In planning future groundwater sources for drinking water supply, the location of these nitrogen sources is therefore an important consideration.

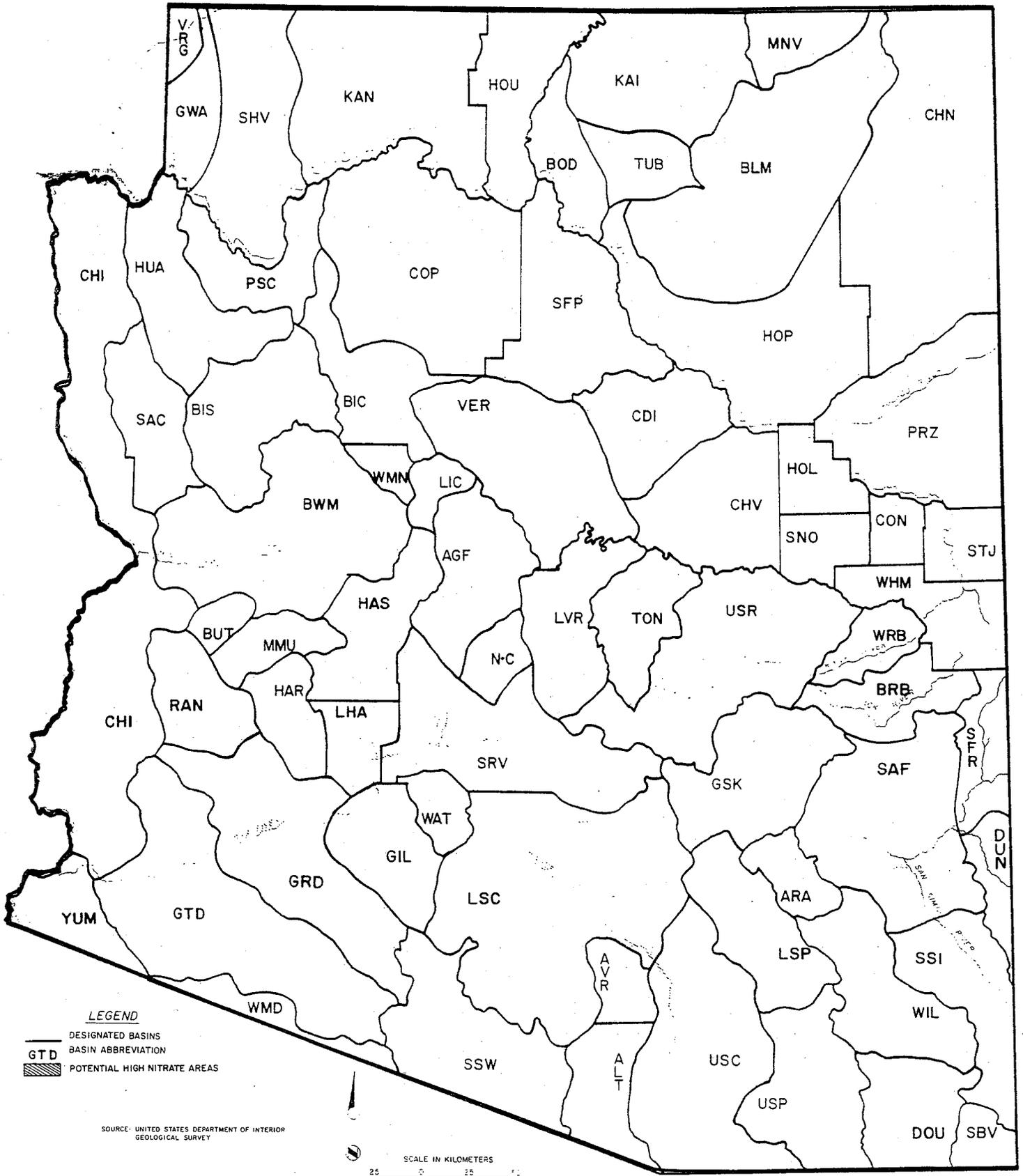
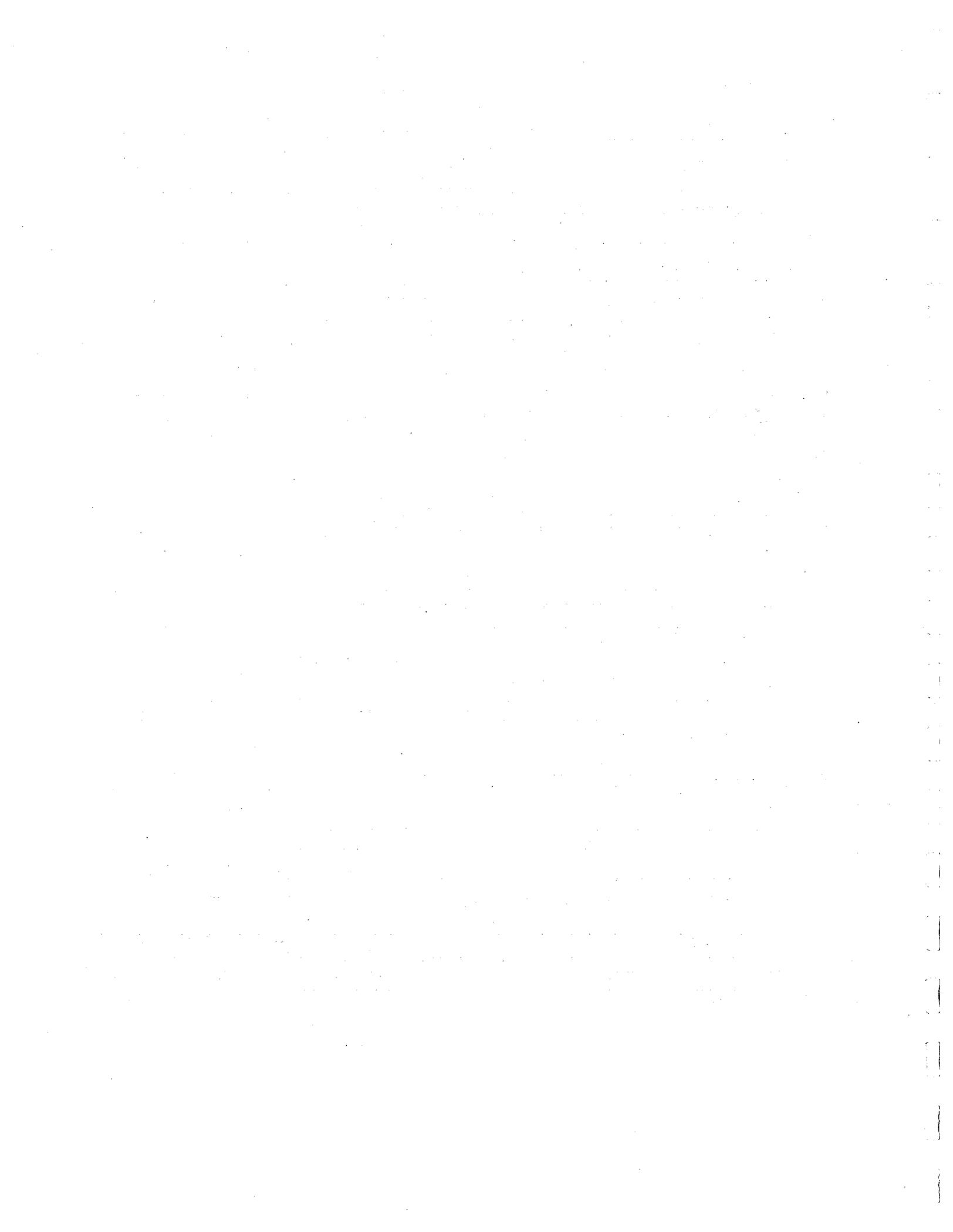


Fig. 3-5 Potential High Nitrate Areas





**Table 3-3. Water Systems Investigated for Nitrate Concentration Levels (continued)**

Water supply system	County	Water system number	Designated basin
	Maricopa		
City of Tempe		07-100	SRV
Tobin Water Company		07-074	SRV
City of Tolleson		07-101	SRV
Valencia Water Company		07-078	SRV
Valley Utilities		07-079	SRV
West End Water Company		07-080	SRV
West Phoenix Water Company		07-081	SRV
Westward Hills Water Company		07-083	SRV
White Tanks Water Company		07-084	SRV
Wittman Water Company		07-086	SRV
Wranglers Roust Water Company		07-087	SRV
Youngtown		07-103	SRV
	Mohave		
Chloride Water Corporation		08-005	SAC
	Pima		
None		18-700	LSC
None		20-489	USC
Abram Ranch		20-513	USC
Acacia Gardens Mobile Home Park		20-509	USC
Acorn Water Company		10-006	USC
Action Sand and Gravel		20-526	USC
Adobe Manor Trailer Lodge		20-002	USC
Ajo Improvement Company		10-001	ALT
Aqua Linda Homeowners Water Association		10-135	USC
Arizona Maintenance Company		10-094	USC
Arizona Water Company, Ajo System		10-003	GRD
Carolanne Drive Homeowners		20-529	USC
Central Water Company		10-009	AVR
Community Water Company of Green Valley		10-004	USC
Cortaro Acres Homeowners Association		10-134	USC
Cortaro Water Users Association Oshrin		10-143	LSC
Cortaro Water Users Association Price		10-146	LSC
Cortaro Water Users Association Puerta del Norte		10-072	LSC
Cortaro Water Users Association Marana		10-150	LSC
Cortaro Water Users Association		10-151	LSC
Dateland Water Company		10-040	USC
Despoblado Water Company		10-044	USC
Dewey Water Company		10-035	USC
Duke Water Company		10-045	USC
E and T Water Company		10-046	USC
Farmers Investment Company		10-048	USC
Flowing Wells Irrigation District		10-051	USC
Frichs Foothills Ranch Apartments		10-121	USC
Halcyon Acres Water Users		10-057	USC
Honea Water Company, System 1		10-137	LSC
Honea Water Company, System 2		10-059	LSC
Hub Water Company		10-060	USC
I.M. Water Company Hunter Estates		10-131	USC
I.M. Water Company Palo Verde		10-136	USC
K & V Water Company		10-133	USC
Las Quintas Serenas Water Company		10-064	USC
Lazy C Water Company		10-065	USC
Logan Hills Water Company		10-067	USC
Lyn Lee Water Company		10-007	LSC

**Table 3-3. Water Systems Investigated for Nitrate Concentration Levels (continued)**

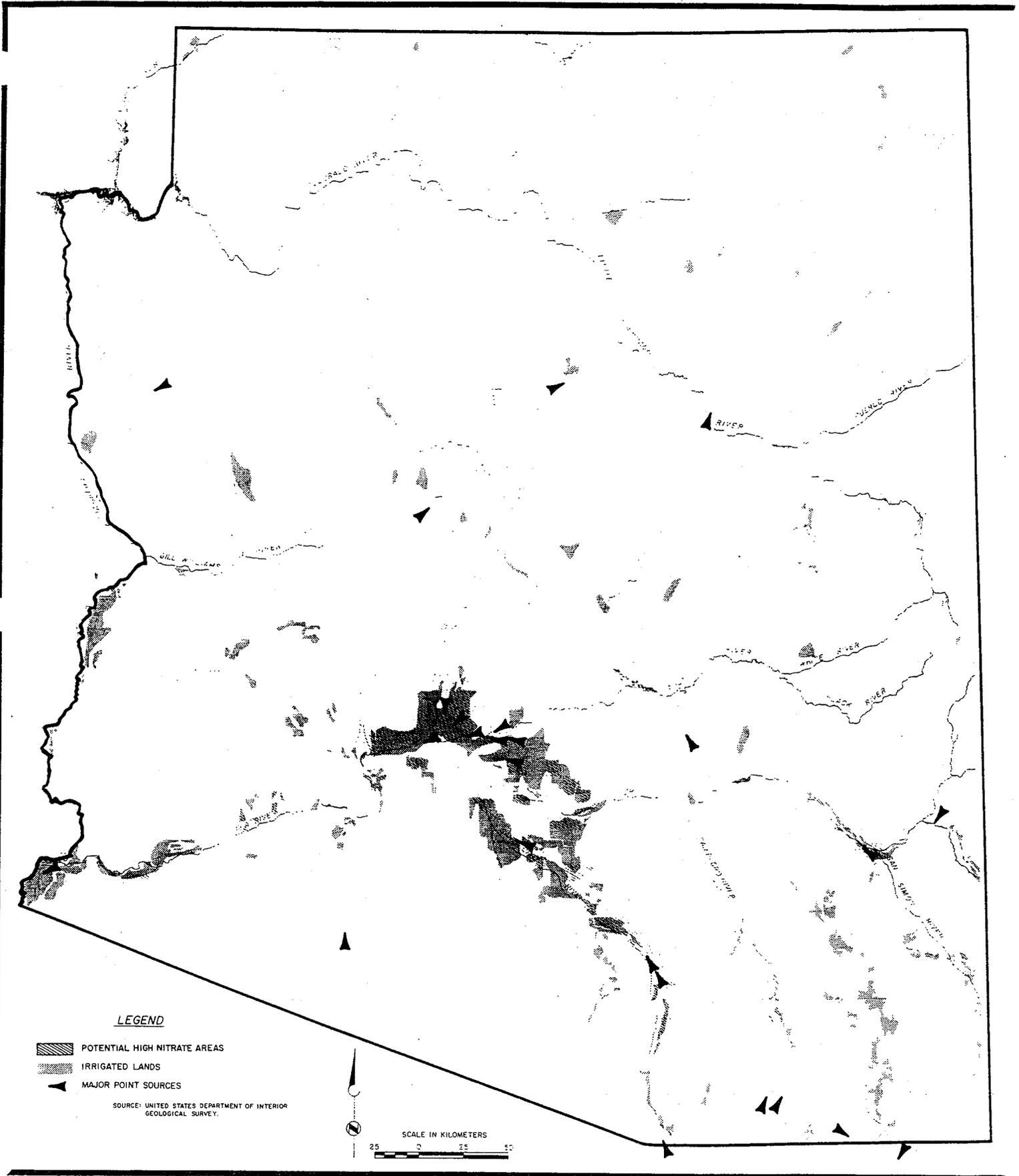
Water supply system	County	Water system number	Designated basin
	Pima		
Marana Water Company, Avra Ranchettes		10-070	LSC
Marana Water Company, El Tirador		10-139	LSC
Marana Water Company, Happy Acres		10-138	LSC
Mesa del Oro Water Company		10-073	LSC
Mesaland Water Co-op		10-074	USC
Metropolitan Water Company, Number 15		10-148	USC
Metropolitan Water Company, Number 1		10-147	USC
Metropolitan Water Company, Number 2		10-078	USC
Metropolitan Water Company, Number 3		10-085	USC
Metropolitan Water Company, Number 4		10-086	USC
Metropolitan Water Company, Number 5		10-076	USC
Metropolitan Water Company, Number 6		10-083	USC
Metropolitan Water Company, Number 8		10-079	USC
Metropolitan Water Company, Number 12		10-087	USC
Metropolitan Water Company, Number 13		10-091	USC
Metropolitan Water Company, Number 14		10-145	USC
Metropolitan Water Company, Number 7		10-084	USC
New Pueblo Development Incorporated		10-141	USC
Picture Rocks Water Company		10-092	LSC
Ray Water Company, Lansing Strave		10-095	USC
Ray Water Company, Sunhaven		10-096	USC
Rillito Water Users Association		10-098	LSC
Rincon Creek Ranch Water Company		10-099	USC
Rocking K Ranch		10-127	USC
Sahuarita Village Water Company		10-123	USC
Sandario Water Company		10-093	AVR
Silver Shadows Water Company, Number 2		10-106	USC
Silver Shadows Water Company, Number 3		10-107	USC
Silver Shadows Water Company, Number 4		10-108	USC
Silver Shadows Water Company, Number 1		10-105	USC
Stiller Water Company		10-109	LSC
Summit Subdivision		20-178	USC
Tanque Verde Water Company		10-110	USC
City of Tucson		10-112	USC
Village Water Company		10-115	LSC
	Pinal		
Antle Company		11-002	LSC
Arizona Water Company, Arizona City		11-008	LSC
Arizona Water Company, Casa Grande		11-009	LSC
Arizona Water Company, Coolidge		11-014	LSC
Arizona Water Company, Valley Farms		11-016	LSC
Bogle Farms		11-099	LSC
Bogle Farms, Maricopa Farm		11-098	LSC
Case Grande West Water Company		11-024	LSC
Desert Carmel Service Company		11-027	LSC
City of Eloy		11-030	LSC
Evergreen Air Station		11-034	LSC
Florence Town		11-017	LSC
Lake in the Desert Water Company		11-058	LSC
Maricopa Coop Water Company		11-054	LSC
Maricopa Mountain Water Company		11-322	LSC
Maricopa Water Company, Incorporated		11-036	LSC
Mohawk Water Company		11-328	LSC
Papago Butte Irrigation District Number 4		11-097	LSC
Ranchelle Water Company		11-028	LSC
South Mountain Water Company		11-061	LSC

**Table 3-3. Water Systems Investigated for Nitrate Concentration Levels (continued)**

Water supply system	County	Water system number	Designated basin
Citizens Utility Company, Rio Rico	Santa Cruz	12-011	USC
Antelope Water Company	Yuma	14-001	GTD
Arizona Public Service		14-312	YUM
Del Sur Improvement District		14-025	YUM
Green Acres Water Company		14-065	YUM
Jones Subdivision Co-op		14-070	YUM
Mohawk Valley Water Company		14-031	GTD
Texas Hill Farms, Incorporated, Number 4		14-420	YUM
Wellton Community Water Company		14-022	GTD
Yuma City Loma Vista		14-033	YUM
City of Yuma		14-024	YUM

**Table 3-4. Water Supply Systems with Known Nitrate Violations as of October, 1978**

County	Water supply system	Highest level NO <sub>3</sub> -N, mg/l
Pinal	Arizona Water Company, Arizona City	14.0
Pinal	Arizona Water Company, Casa Grande	17.3
Pima	Cortaro Water Users Association, Puerta del Norte	22.2
Pima	Frichs Foothills Ranch Apartments	13.6
Maricopa	City of Glendale	24.0
Pima	Honea Water Company, System number 1	11.1
Pima	Lyn Lee Water Company	12.9
Pima	Marana Water Company, El Tirador	11.6
Pinal	Mohawk Water Company	17.6
Maricopa	City of Phoenix	34.2
Maricopa	City of Scottsdale	>10.0
Maricopa	Sun City Water Company	11.8
Maricopa	City of Tempe	12.9
Pima	City of Tucson	12.9
Pima	Village Water Company	16.2



**Fig. 3-6 Correlation of Potential High Nitrate Areas and Major Nitrogen Sources**



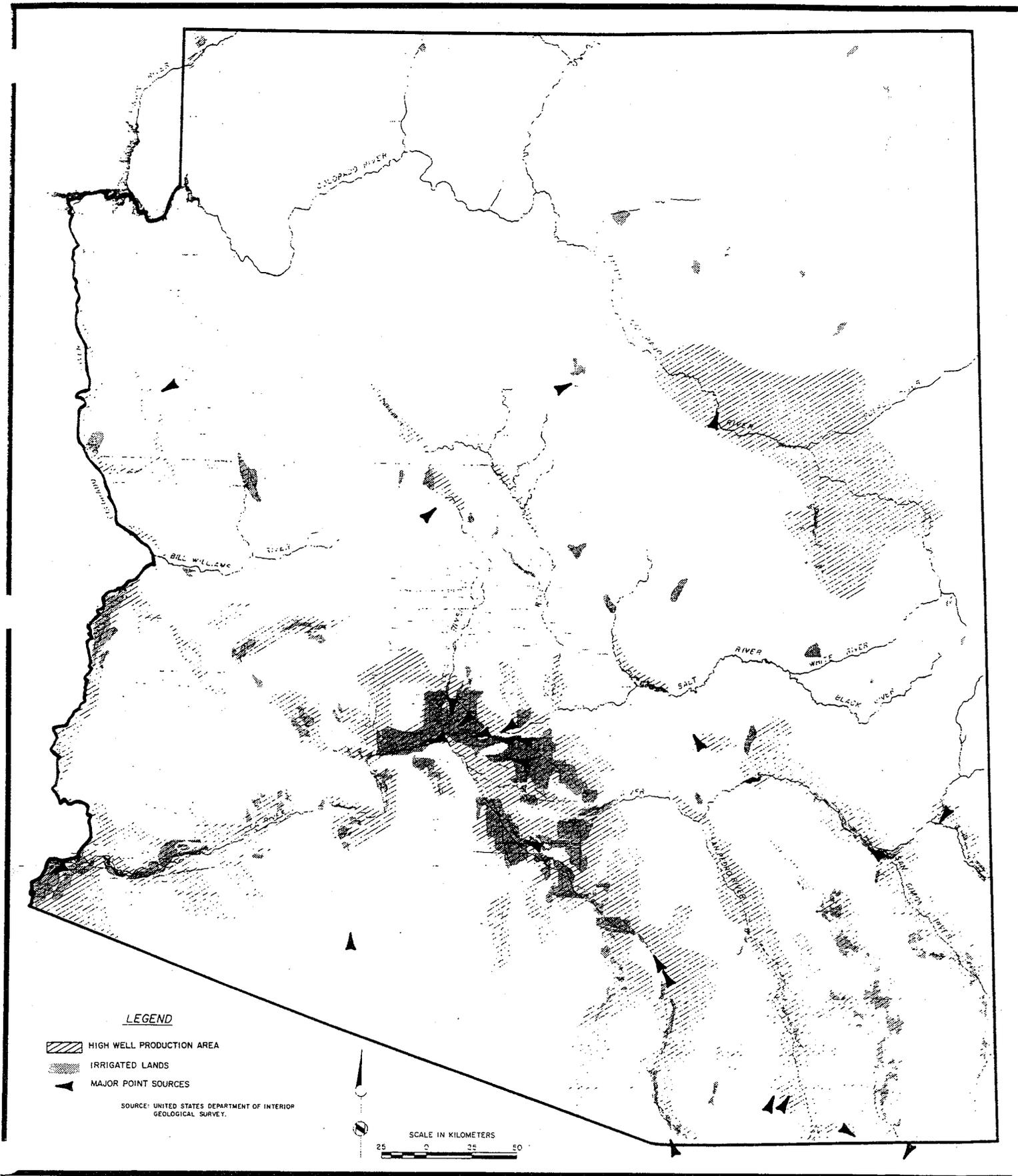


Fig. 3-7 Correlation of High Permeable Soils and Major Nitrogen Sources



## SUMMARY OF ANALYSES

The primary objective of the preceding section was to develop an inventory of study area characteristics and the sources of nitrogen which, depending upon the particular groundwater system, are of major importance in the control of groundwater degradation due to nitrate accumulation. It is apparent from the evaluation of existing conditions that factors such as water resource development and use, geology, hydrology, population, land use, and population sources vary throughout the study area and that no single factor can explain the occurrence of nitrate in the state's groundwater resources. In several instances, specific nitrogen sources and site-specific characteristics have been reported as the cause of high nitrate levels in groundwater, while in other cases the probable sources or causes of high nitrate are only speculative. The general trend and areal distribution of nitrate has been evaluated in order to identify groundwater areas with potential high nitrate levels or which warrant further investigation.

The following salient observations summarize existing conditions relative to the occurrence of nitrate in groundwater resources in the state:

1. Nitrate levels in excess of the MCL are most prevalent in the Salt River Valley, Upper Santa Cruz, and Lower Santa Cruz basins. Most frequent violations within these basins have been reported for the northwestern Phoenix and Glendale areas.
2. Based on preliminary findings of a recent investigation<sup>10</sup> of groundwater quality in the Salt River Valley, natural nitrate deposits appear as the probable cause for the high nitrate levels in groundwater of the Salt River Valley west basin.
3. Occurrences of high nitrate concentrations in most areas identified in Fig. 3-5 appear to be associated with man-caused sources of nitrogen, the most significant of which is discharge of wastewater effluent to ephemeral stream courses and irrigation with wastewater effluent.
4. Within the potential high nitrate areas shown in Fig. 3-5, nitrate levels have been reported to change with time. These changes are reflective of both land surface discharge activities and hydrologic modifications due to well pumpage.
5. Based on the direct correlation of land surface nitrogen sources and reported high nitrate occurrences, source control measures appear as an effective means of reducing the health hazards associated with high nitrate concentrations.



CHAPTER  
**FOUR**



## CHAPTER 4 NITRATE CONTROL TECHNIQUES

The quality of water supply can be regulated through application of both management and treatment process techniques. Water resource management primarily involves non-structural techniques to regulate and control the quality of water supply sources, while treatment techniques rely on the operation of treatment facilities to produce the required quality of water supply. The use of both techniques may be necessary for optimum management of water quality and compliance with current water quality standards. The least cost combination of management and treatment modes is dependent upon a number of site-specific factors; therefore, they must be balanced to meet the needs of a given locality. The nature of the water quality hazard, the type and relative abundance of water supply, environmental concerns, legal and institutional constraints, and social elements all influence the feasibility of water quality management alternatives as well as treatment/removal techniques.

The accumulation of nitrate in water supply has been identified as a potential water quality and public health hazard. Nitrate accumulation is most significant in groundwater which, in most cases, can be related to land surface sources of nitrogen. In the preceding chapter, groundwater areas throughout the state with potential for high nitrate concentration levels were identified. Communities with groundwater supplies exceeding the MCL for nitrate that do not qualify for exemption or variances, as established by ADHS, will therefore have to evaluate alternative measures to comply with the drinking water regulations set forth in Public Law 93-523. This chapter presents a description of resource management techniques and treatment technologies which can be implemented to control or reduce nitrate concentration levels in water supply.

### ALTERNATIVE WATER RESOURCE MANAGEMENT TECHNIQUES

Where primary and secondary drinking water regulations are exceeded, provision of a water treatment facility may not be the best apparent and cost-effective approach to improve water supply quality or provide the best water quality. This situation may be of particular importance to small water utilities serving communities of a thousand consumers or less due to the apparent lack of information on applicable treatment technology.<sup>1</sup> Because of the natural quality of groundwater and the mechanisms which contribute to its degradation, it is generally more appropriate to first consider management techniques such as pollutant source control and water supply blending as alternative solutions to water quality problems. A brief description of applicable management options that could be feasibly employed to reduce the frequency of occurrence and limit the concentration of nitrate and other impurities in water supply is presented in the following section.

## Alternate Water Supplies

The use of alternate water supply to improve water quality essentially involves changing from an existing source of supply to one of higher quality that would comply with the standards. This method includes a wide range of possible options, some of which are specifically applicable to the control of nitrate accumulation and the quality of water resources in the state. In general, the quality of water supply could be improved either by developing available surface water sources or another groundwater aquifer of higher quality to replace existing sources of poor quality. It is apparent, however, that the use of alternate water supplies on a large scale will be influenced by the nature of present and future water supplies and uses and the economics of changing water sources.

In Arizona, where there is limitation in water resources and the emphasis is toward more efficient use of available water, alternate sources of supply are extremely limited. As the state approaches full development of its surface water supplies, it is evident that groundwater will serve as the principal source of water supply in the future. Legal constraints, however, would severely restrict the feasibility of transferring groundwater from one basin to another, since percolating groundwater is considered to be a property right and current land owners have the legal rights as appropriators of the underlying groundwater. Substitution of an alternate groundwater supply of acceptable quality would require acquisition by sale of the overlying property and thus reassignment of the groundwater rights. The allowable pumpage amount and export water volume, however, would be subject to further legal constraints, therefore making alternate water supply difficult at best to implement on a large scale.

On a smaller scale where a single groundwater aquifer is involved, there are several more plausible alternate source options. Since nitrate accumulation occurs most often in direct relation to land surface sources of nitrogen, higher quality water could be attained by relocating municipal or domestic wells within the basin. By evaluating the location of significant nitrogen sources and existing hydrogeologic characteristics of the aquifer, well sites may be located where nitrate accumulation is minimal or sufficiently diluted by favorable groundwater conditions. As an example, relocation of wells upstream of the major sources of nitrogen, such as the discharge point of wastewater effluent, could result in a source of higher quality water. As discussed previously, however, heavy well pumpage can cause dramatic hydrologic modification, thereby causing the pumping site to be the convergence point of groundwater and contaminant recharge movement over a large area. Groundwater movement in the west basin of the Salt River Valley, for example, is predominantly controlled by a large well pumpage drawdown in the proximity of Luke Air Force Base. Based on a recent USGS report on groundwater conditions in the western portion of the Salt River Valley, it is apparent that groundwater over a 500-square mile area converges toward the large drawdown area.<sup>2</sup> In this regard, knowledge of the hydrogeologic conditions and location of major nitrogen sources can facilitate the proper operation of a well system to minimize the influence of groundwater pumpage, thereby enhancing the quality of the water supply.

In addition to areal location, an alternate source of water supply of better quality could be attained by simply deepening or upgrading existing wells, thus extracting groundwater from a different zone within the aquifer. Nitrate contamination has been reported most often in shallow wells where high nitrate recharge experiences short transit times through the vadose zone prior to being returned to the land surface. Generally, dilution and mixing within the aquifer is such that groundwater from the deeper zones of the aquifer is protected at least by long transit times from contaminated recharge. Under certain conditions, deepening the well intake can result in a significant reduction in the concentration level of nitrate in water supply. Sealing of the well intake at the shallower depths would also prevent contamination from high nitrate recharge percolating from a land surface source.

In all cases, the use of alternate sources of water to enhance the quality of community water supply is subject to site-specific conditions and overall economic feasibility. The availability and value of a groundwater resource for all types of water uses is a function of (1) location with respect to its final useage, (2) depth to ensure sufficient well production, and (3) water quality. Any one of these factors may render a potential groundwater source unsuitable when the cost for development is compared with other alternative water quality management options.

#### Water Importation

Augmentation of water supply from relatively distant sources is another management technique to improve water quality. Diversion and importation of surface water such as the proposed Central Arizona Project (CAP) could potentially be utilized to enhance the quality of water as well as supplement the quantity of supply. With the established appropriations of Colorado River water and the costs associated with transmission and treatment, development constraints to divert supplemental water supply to communities in need could preclude water importation as a feasible option for water quality enhancement.

#### Water Supply Blending

Water supply blending is an accomplished technique used in larger water collection, storage, and distribution systems to control and improve water quality. This management technique is primarily dictated by internal control of the system to achieve a uniform quality of water supply. Since nitrate contamination in groundwater is most often a localized occurrence impacting only a specific well site, provisions within the system to allow dilution with higher quality groundwater could effectively reduce nitrate concentration. Effective use of this management technique is dependent upon the components, configuration, and size of the water supply system. For larger communities which rely on multiple groundwater wells and storage facilities the blending of water from a high nitrate area could be implemented by simple alteration of systems operation. In rural areas where communities utilize a less extensive supply system or are dependent on a single domestic well, system flexibility to adequately dilute contaminated water may be severely limited. In this respect, the economic feasibility of water supply blending is primarily contingent upon enhancing water quality through internal system modification without resulting in large capital expenditures.

## Source Control

Prevention of water resource contamination by source control is well recognized as a sound water quality management practice. Containment or removal of pollutants at the source prior to contact with water resources can result in economic savings as well as minimizing public health hazards. By limiting the types and concentrations of pollutants that must be removed from raw water supply, more efficient and less complex treatment techniques can be implemented.

In groundwater systems, the natural dynamics are such that source control is an extremely important consideration in the management of water quality. Since (1) the large aquifer storage volume to groundwater recharge ratio results in long residence periods, (2) few pollutant removal pathways exist in the saturated zone, and (3) dilution and groundwater mixing is relatively limited, groundwater systems act as repository for past recharge events. Pollutants which are capable of migrating with recharge flow through the vadose zone and are not effectively removed by the attenuating properties of the soil system are collected and accumulated in the groundwater for long periods of time.

Successful implementation of source control to mitigate a pollution problem depends on identifying and analyzing all possible sources and then formulating feasible control measures for the more significant sources. Both structural and non-structural methods have shown to be effective on point, line, and diffuse pollution sources. The degree of difficulty and management complexity of implementing source control measures, however, generally increases significantly from point to diffuse sources.

Preceding chapters have described the interaction of nitrate with the groundwater system and identified significant nitrogen sources within the state which appeared to be directly correlated with high nitrate occurrences. Source control measures oriented toward these nitrogen sources would provide an effective means of reducing the potential for nitrate accumulation in groundwater resources throughout the state.

Agricultural and Soil Management. Irrigated agriculture has been identified as a major source of groundwater degradation.<sup>3,4,5,6</sup> In agricultural areas, nitrate accumulation in groundwater has been principally attributed to excessive application of nitrogen fertilizer beyond economic crop response and the rate of irrigation water applied to the crop. The basic management objective, therefore, is to increase the efficiency of nitrogen fertilizer use such that the fraction of nitrogen loss through nitrate leaching is minimized while maintaining economically favorable crop yields. In most cases, high crop yields and protection of groundwater quality can both be achieved through sound agricultural management.<sup>7</sup>

Reducing the contribution of nitrogen fertilizer to nitrate leaching can be accomplished by numerous agricultural management methods. Presented below is a brief description of several of the methods that are currently recognized as effective agricultural practices which assist in mitigating the accumulation of nitrate in groundwater.

1. Soil testing and plant analysis- by determining both the amount of available plant nutrients that are present in the soil and the nutrient uptake requirements of specific crops, supplemental nutrient needs can be more accurately estimated.

If fertilizer is applied at rates determined by these methods, crops will receive proper nutrient amounts at the least cost and nutrient losses to leaching will be minimized.

2. Control of the rate and time of application- close control of the amount of fertilizer used and application timing are considered to be the two most important factors in limiting nitrate leaching. Recent investigations have concluded that optimum nitrogen application rates should be limited to the amount of nutrient uptake within a 2- to 3-week period, and that application should be as near the time of plant use as possible.<sup>6</sup> Avoidance of applications prior to expected high precipitation or irrigation periods was also recommended to limit the availability of nitrogen when percolation rates are excessive. Irrigation efficiencies commonly are set to allow 30 to 50 percent of the applied water to percolate below the root zone to prevent salt buildup.
3. Fertilizing operations- the method of fertilizer application and placement relative to the crop root system and soil moisture has also proven to be an effective management technique.<sup>7</sup> When supplemental nutrients are applied proportional to actual crop needs, proper application and placement is important to ensure nutrient accessibility; that is, minimize reliance on movement of required nutrients through the soil-water-plant system.
4. Fertilizer types- the use of fertilizers which maintain applied nitrogen in the  $\text{NH}_4$  form is another technique to minimize nitrate leaching. As discussed previously, nitrogen in the  $\text{NH}_4$  form is relatively immobile in the soil-water system, whereas nitrate moves more freely with percolating soil-water. Chemical inhibitors have been developed that can be incorporated with nitrogen fertilizer to delay nitrification or transformation from ammonium to nitrate. One such inhibitor was reported to effectively maintain fall-and winter-applied nitrogen in the  $\text{NH}_4$  nitrogen form for a substantial period.<sup>6</sup> By incorporating the chemical inhibitor with the nitrogen fertilizer, considerable reduction in nitrate leaching was accomplished. If slow-releasing nutrients are not adequately assimilated by the crop during the growing season, however, high nitrate levels may appear in the soil during non-crop periods when potential for nitrate leaching is enhanced.
5. Irrigation efficiency- improved irrigation efficiency can result in decreased percolation return flows, thereby limiting the transport of nitrate beyond the root zone. The regulation of applied irrigation water is dictated by several other factors such as the method used for application, salt buildup, and the availability and cost of water; however, the impact of irrigation practices on groundwater quality should be recognized when evaluating soil conditions and selecting crop types.

It is evident that the control of nutrient losses due to leaching is dependent upon a number of interrelated factors associated with the soil-water-plant system. Furthermore, successful implementation of the various agricultural management techniques is directly related to optimizing both the nitrogen and water balance for the system. This is most apparent in areas which utilize wastewater effluent as the source of irrigation water. As mentioned previously, favorable economics have generally resulted in the application of effluent in amounts exceeding both water consumption and nutrient requirements. In a recent study<sup>8</sup> conducted by EPA, the environmental changes resulting from long-term land application of municipal wastewater effluent at locations in California and Texas were investigated. At both sites where effluent had been applied to cropland for several years, underlying groundwater was detected to contain nitrate levels exceeding the MCL. Since effluent had been applied on lands during periods when growing crops were either absent or required little supplementary nutrients, it was reported that the cause of nitrate accumulation was the imbalance between effluent-nitrogen loading rates and crop uptake. The study recommended that effluent storage facilities be utilized to provide better operational flexibility and more effective balance of water and nitrogen within the soil-water-plant system.

The potential impact of wastewater effluent irrigation on groundwater quality is presented in Table 4-1. Irrigation with typical municipal wastewater effluent at two application rates is compared with well-water irrigation in terms of both water and nitrogen balance on the system. Although five acre-feet per year is an average irrigation rate for cotton crops in central and southern Arizona, application rates of up to ten acre-feet per year have been used in farming operations located near wastewater treatment facilities.<sup>9</sup> Based on the assumptions listed in Table 4-1, it was estimated that the soil moisture surplus available for groundwater recharge when the higher irrigation rate is applied would be 2.8 times the amount resulting from the lower application rate. As also indicated, the estimated depth of percolation resulting from an irrigation rate of ten acre-feet per year would be about 65 feet per year. With respect to the nitrogen balance, a considerable difference in the amount of nitrogen exceeding crop needs and system losses is apparent between well and effluent irrigation practices. Excess nitrate from well irrigation with fertilization was estimated to range from 5 to 56 pounds per acre, while a range of 138 to 281 and 340 to 626 pounds per acre of excess nitrate was estimated for the low and high rate effluent irrigation practices, respectively.

By combining the water and nitrogen mass balances, it can be noted that the nitrate concentration in percolate resulting from the well irrigation practice with proper fertilizer application was estimated to be within the MCL for nitrate (10 mg/l  $\text{NO}_3\text{-N}$ ), while the nitrate concentration from both effluent irrigation practices would significantly exceed the standard. Nevertheless, the dynamics of the soil-water-plant system discussed herein and illustrated in Table 4-1 have been simplified based on certain assumptions and are presented only for the purpose of illustrating the importance of maintaining a reasonably balanced nitrogen and water budget in agricultural management practices.

**Table 4-1. Potential Impact of Wastewater Effluent Irrigation<sup>a</sup>**

Annual mass balance	Water source for crop irrigation <sup>b</sup>		
	Wastewater effluent		Groundwater
<b>Water<sup>c</sup></b>			
Irrigation rate	5.0	10.0	5.0
Precipitation	0.9	0.9	0.9
Consumptive use <sup>d</sup>	3.0	3.0	3.0
Soil moisture storage <sup>e</sup>	0.5	0.5	0.5
Change in soil moisture storage <sup>f</sup>	0	0	0
Soil moisture surplus available for percolation <sup>g</sup>	2.9	7.9	2.9
Percolation depth <sup>h</sup> , feet per year	24.2	65.8	24.2
<b>Nitrogen<sup>i</sup></b>			
Nitrogen applied in fertilizer <sup>j</sup>	-----	-----	145
Nitrogen applied in effluent <sup>k</sup>	410	815	-----
Plant assimilation <sup>l</sup>	67	67	67
Estimated nitrogen losses, denitrification/volatilization/surface runoff, <sup>d</sup> 15 to 50 percent	62-205	122-408	22-73
Estimated nitrate excess	138-281	340-626	5-56
Potential nitrate concentration in percolate <sup>n</sup> , NO <sub>3</sub> -N mg/l	18-36	16-29	1-7

<sup>a</sup> Developed from Evaluation of Groundwater Monitoring Plan (WETS) by Wilson, Martin and Lonergan, University of Arizona, 1977.

<sup>b</sup> Based on a typical cotton farming operation on sandy loam soil; fields are double-cropped and irrigated on a 12 month-basis. Effluent irrigation method assumes no chemical nitrogen supplements; well irrigation method assumes standard fertilizer application.

<sup>c</sup> Values shown in acre-feet per year unless otherwise noted.

<sup>d</sup> Represents water loss by surface evaporation and plant uptake.

<sup>e</sup> Average soil moisture storage within root zone; assumes 1.8 inches of available water per foot and a rooting depth of 3.33 feet.

<sup>f</sup> Assumes no apparent change in soil moisture due to 12 month irrigation operation.

<sup>g</sup> Assumes "worst condition" of no surface runoff; all surplus soil moisture represents deep percolation.

<sup>h</sup> Based on relationship  $d/D = A_s (P_{fc} - P_{wp})$  where:

  d = water applied

  D = depth of water penetration in soil profile

  A<sub>s</sub> = apparent specific gravity (A<sub>s</sub>=1.5)

  P<sub>fc</sub> = soil water holding percentage at field capacity.

  P<sub>wp</sub> = soil water holding percentage at wilting point, (P<sub>fc</sub>-P<sub>wp</sub>) assumed to be 8 percent.

<sup>i</sup> Values shown in pounds per acre of total nitrogen unless otherwise noted; nitrogen balance assumes "best condition" of no soil mineralization release of available nitrogen.

<sup>j</sup> Source: Ibach, D.B., Fertilizer Use in the United States by Crops and Areas - 1964 Estimates, U.S. Department of Agriculture, Economics Report No. 408.

<sup>k</sup> Based on total nitrogen content in wastewater effluent of 30 mg/l.

<sup>l</sup> Source: EPA, Process Design Manual for Land Treatment of Municipal Wastewater, 1977.

<sup>m</sup> Residual soil nitrogen assumed to be in nitrate form.

<sup>n</sup> Represents nitrate excess in soil moisture surplus.

Wastewater Management. Wastewater effluent is a major point or line source of nitrogen, depending on the method of discharge and conditions present in the receiving environment. As mentioned previously, conventional secondary wastewater treatment does not significantly reduce the nitrogen waste load contained in municipal wastewater. The combined removal of total nitrogen in a conventional primary-secondary facility is generally less than 30 percent, as shown in Table 4-2. Effective control of nitrogen in wastewater, therefore, requires the use of advanced wastewater treatment processes. The four major treatment processes which are currently being applied in full-scale facilities for nitrogen removal are ammonia stripping, selective ion exchange, biological nitrification-denitrification, and breakpoint chlorination. Because the ammonia/ammonium ion is the predominant form of nitrogen in secondary wastewater effluent, nitrogen removal processes have been primarily designed to remove the  $\text{NH}_3/\text{NH}_4$  form. Nitrification usually proceeds rapidly once wastewater effluent is discharged to the receiving environment; therefore, removal of ammonia/ammonium at the wastewater treatment facility is an effective source control measure to mitigate the accumulation of nitrate in groundwater. To date, the use of these removal processes has generally been limited to situations where surface water quality is endangered by oxygen deficiencies and eutrophic conditions due to discharge of high ammonium effluent. The cost associated with advanced wastewater treatment for nutrient removal, however, has generally precluded its wide-scale use.

Recently, land treatment techniques which involve use of the soil-water-plant system have received greater emphasis as a nutrient removal method. The reclamation and reuse requirements set forth in P.L. 92-500 and 95-217 also emphasize land treatment as the preferred wastewater management technology. Based on nitrogen management and sound engineering practice, land treatment can be a reliable wastewater management technique for the control of nitrate.

Several other wastewater techniques can be employed to effectively remove nitrogen from wastewater, as shown in Table 4-2. Most notably, the use of selective ion exchange, oxidation ponds, and algae stripping can significantly remove nitrogen in wastewater. Based on the wide range of total nitrogen removal efficiency of each method, it is apparent that site-specific variables will dictate the best apparent and reliable wastewater management technique for the effective removal of nitrogen.

#### ALTERNATIVE TREATMENT TECHNIQUES

In the event that management techniques such as those described in the foregoing section do not allow compliance with the drinking water standards, alternative treatment techniques to remove excess nitrate in the water supply will need to be evaluated. Since the standard for nitrate applies to both community and non-community systems, applicable treatment technology would therefore be required to serve both small, rural water systems as well as large, well-developed water supply systems. To date, however, there is a lack of information regarding water treatment techniques specifically designed for the removal of nitrate.

The most common water treatment technologies used for the removal of inorganic chemicals are conventional chemical coagulation and water softening processes. These processes, however, are not effective for the removal of nitrate due to its ionic form and chemical oxidation state. Demineralization processes, commonly used

**Table 4-2. Effect of Various Treatment Processes on Nitrogen Compounds**<sup>a</sup>

Treatment process	Effect on constituent			Removal of total nitrogen entering process, percent <sup>b</sup>
	Organic N	NH <sub>3</sub> /NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	
Conventional treatment process				
Primary	10-20% removed	no effect	no effect	5-10
Secondary	10-25% removed <sup>c</sup> urea ▶NH <sub>3</sub> /NH <sub>4</sub> <sup>+</sup>	10% removed	nil	10-20
Advanced wastewater treatment processes				
Filtration <sup>d</sup>	30-95% removed	nil	nil	20-40
Carbon sorption	30-50% removed	nil	nil	10-20
Electrodialysis	100% of suspend organic N removed	40% removed	40% removed	35-45
Reverse osmosis	100% N suspend organic N removed	85% removed	85% removed	80-90
Chemical coagulation <sup>d</sup>	50-70% removed	nil	nil	20-30
Land application				
Irrigation	▶NH <sub>3</sub> /NH <sub>4</sub> <sup>+</sup>	▶NO <sub>3</sub> <sup>-</sup>	▶plant N	40-90
Infiltration/percolation	▶NH <sub>3</sub> /NH <sub>4</sub> <sup>+</sup>	▶plant N ▶NO <sub>3</sub> <sup>-</sup>	▶N <sub>2</sub>	0-50
Major nitrogen removal processes				
Nitrification	limited effect	▶NO <sub>3</sub> <sup>-</sup>	no effect	5-10
Denitrification	no effect	no effect	80-98% removed	70-95
Breakpoint chlorination	uncertain	90-100% removed	no effect	80-95
Selective ion exchange for ammonium	some removal, uncertain	90-97% removed	no effect	80-95
Ammonia stripping	no effect	60-95% removed	no effect	50-90
Other nitrogen removal processes				
Selective ion exchange for nitrate	nil	nil	75-90% removed	70-90
Oxidation ponds	partial transformation to NH <sub>3</sub> /NH <sub>4</sub> <sup>+</sup>	partial removal by stripping	partial removal by nitrification-denitrification	20-90
Algae stripping	partial transformation to NH <sub>3</sub> /NH <sub>4</sub> <sup>+</sup>	▶cells	▶cells	50-80
Bacterial assimilation	no effect	40-70% removed	limited effect	30-70

<sup>a</sup> Source: Environmental Protection Agency, Process Design Manual for Nitrogen Control, 1975.

<sup>b</sup> Will depend on the fraction of influent nitrogen for which the process is effective, which may depend on other processes in the treatment plant.

<sup>c</sup> Soluble organic nitrogen, in the form of urea and amino acids, is substantially reduced by secondary treatment.

<sup>d</sup> May be used to remove particulate organic carbon in plants where ammonia or nitrate are removed by other processes.

in industrial water treatment and brackish water desalting applications, appear to be the most applicable treatment techniques. Although ion exchange, reverse osmosis, and electrodialysis are proven technologies in the demineralization, dealkalization, and softening of numerous industrial process streams and treatment of brackish water, only one full-scale nitrate removal facility is currently in service. A continuous ion exchange system was installed to treat groundwater containing 20 to 30 mg/l  $\text{NO}_3$  as N; however, several site-specific conditions and system operational features have limited the development of standard operation and cost data. Due to the lack of operating experience from proven, full-scale nitrate removal facilities as well as documentation of the demonstrated suitability of alternate treatment techniques, several other alternative treatment technologies have been evaluated to determine the feasibility of their use in various applications related to nitrate reduction/removal in drinking water supply. The following section presents a description of treatment techniques which under certain conditions may be cost effective or have present or future application to comply with water quality objectives established by the NIPDWR for nitrate.

### Chemical Reduction

Investigations have been undertaken to develop a chemical denitrification system which would reduce nitrate in solution to a gaseous nitrogen form, preferably  $\text{N}_2$ .<sup>10</sup> Denitrification was described in Chapter 2 as the only biochemical process which returns fixed nitrogen to the atmospheric nitrogen pool. In natural systems, the denitrification process is performed by various bacteria under specific environmental conditions. The chemical reduction process, however, employs the use of chemical reducing agents to denitrify nitrate to nontoxic, gaseous nitrogen end products, which then can be stripped from solution. Nitrate reduction using ferrous iron reducing agents was determined to be the most economically feasible method. The denitrification reaction is quite complex, however, and produces a voluminous amount of chemical sludge. Under optimum conditions, the ferrous iron reduction yielded a 70 percent removal efficiency of nitrate, but the chemical dosage required to complete the reduction of nitrate to gaseous nitrogen limited the practical application of this treatment technique. An eight-to-one iron-to-nitrate ratio was necessary to perform the chemical reduction reaction. If the nitrate level in water supply is 20 mg/l  $\text{NO}_3$  as N, over 800 mg/l of iron sulfate, ( $\text{FeSO}_4$ ) which is the least expensive form of ferrous iron, would be required to attain the 10 mg/l nitrate standard. Based on this chemical relationship, the incremental increase in sulfate concentration would greatly exceed the recommended sulfate limit of 250 mg/l.

From these studies, it is apparent that a chemical denitrification system is presently not a practical or economical treatment technique for water supply. Although the denitrification process is an effective biological method of nitrate control in the natural environment, additional research and investigation would be required before the chemical reduction method could be considered viable for application in water treatment.

### Biological Denitrification

Biological denitrification has also been identified as a technique for nitrate removal in water supply. The process consists of (1) an anaerobic filter bed where denitrifying bacteria would biologically reduce nitrate to nitrogen gas, (2)

an aeration basin to replenish the dissolved oxygen level in the feed water, (3) a conventional slow-rate sand filter to remove biological solids sloughed from the anaerobic filter, and (4) disinfection of the feed water by chlorination. Similar to the natural nitrification-denitrification process, an organic energy source is required for the biological reaction to occur. In nitrification-denitrification facilities for nitrogen control in wastewater treatment, methanol is generally used as the source of energy due to its low cost. Sugar, acetic acid, acetone, and ethanol, however, are also suitable. Nitrate removal efficiencies of about 90 percent could be expected from a properly designed biological denitrification facility.

Although the biological denitrification technique is readily available and has been utilized in many wastewater treatment installations, there are several undesirable features that constrain its potential use in water supply treatment. First, groundwater usually has extremely low background organic levels; thus, use of a biological system which requires the addition of organics to the water supply during the treatment phase does not appear attractive. Second, the influence of flow and temperature changes to the stability of a biological process and the variations in feed water quality would increase the potential for system upsets and process failures. Finally, the production of a biological sludge would result in additional solids handling and disposal requirements. For these reasons, biological denitrification has not been considered to be practical and effective for use in water supply treatment.

### Distillation

Saline and highly mineralized or brackish waters have been effectively converted to potable water supply by the process of distillation. This treatment technique is generally considered to be the most highly developed and economical method for desalination of seawater.<sup>12</sup> In distillation and other evaporation processes, pure water vapor is produced along with a liquid residue containing the dissolved salts originally present in the raw water supply. The vapors are condensed as potable water and collected as a separate stream in the treatment system, while the liquid residue, consisting of a highly concentrated brine stream, is collected for waste disposal. Distillation plants having capacities up to several million gallons per day are currently in operation and have proven their reliability to produce a potable water supply.

Although distillation is a feasible and proven technique, its practical application on water with relatively dilute total dissolved solids (TDS) concentration or solely for the removal of nitrate is uncertain. The distillation process lacks specificity for nitrate; however, its overall salt removal capability is an attractive consideration for use on highly mineralized groundwaters which also contain excessive levels of nitrate. Because of the high energy requirements associated with all treatment technologies utilizing phase-change separation, distillation processes appear to be more suitable for applications involving higher concentrations of TDS, such as seawater, or large capacity installations for treatment of high nitrate occurrences. In fact, distillation plants have been most economically viable for relatively large-scale seawater desalting operations. Furthermore, the complex technology inherent in distillation plants would most likely preclude its use as a practical means for removal of nitrate.

## Ion Exchange

An ion exchange system employs the use of resins to replace certain ions in the feed with ions fixed to the resin matrix. Exchange resins are generally insoluble solids comprised of fixed cations or anions capable of exchanging with oppositely-charged, mobile ions in the bulk solution. The exchange rates and overall system efficiency is dependent upon the chemical equilibrium relationships established between the ion exchange resin and the bulk solution. Based on laboratory data from research studies,<sup>13,14</sup> nitrate removal by ion exchange with synthetic, organic, anion-exchange resins appears to be a feasible technique for use in water treatment.

A synthetic ion exchange resin consists of a polymer framework with acidic or basic groups bonded to the framework. Both functional groups are charged and must be associated with a charged counter-ion, which is only weakly associated with the functional groups and therefore may be exchanged for ions in the bulk solution passing through an ion exchange bed. Resins are currently available with varying degrees of exchange selectivity of preference for ions in the bulk solution. This phenomena is a function of the ionic concentration of the feed water and the relative affinity of a resin for a particular ion in the solution.

A study was recently conducted on various strong-base and weak-base exchange resins to determine nitrate selectivity.<sup>13</sup> For all commercially available synthetic resins, the exchange order for common water anions was determined to be in the following preferential order: (1) sulfate, (2) nitrate, (3) chloride, (4) bicarbonate. The investigation concluded that sulfate is always preferred over nitrate, and since nitrate is preferentially removed before chloride, sodium chloride (NaCl) can be used as the regenerant for the sulfate-nitrate removal system. The use of a single-bed ion exchange system was also recommended as an effective means of nitrate removal from water supply.

There are three types of a single-bed ion exchange system which can be applied for nitrate removal: cocurrent fixed bed, countercurrent fixed bed, and continuous countercurrent. Factors which influence the selection of the most cost-effective type of ion exchange system for a particular application include flow rates, contaminant loads, operation and maintenance constraints, and waste disposal options. These systems allow the use of ion exchange processes over a wide range of nitrate removal applications, particularly with respect to the required treatment flow volume.

The cocurrent system is the most common type of ion exchange system used in small-scale water softening and demineralization facilities. In the cocurrent system, the feed water and regeneration flow are applied to the same direction through a fixed bed contact column. This system generally involves relatively little basic equipment which can be easily operated and maintained with only periodic attention. For applications where flow volumes and contaminant loads are relatively low (less than 1000 gpm and 250 mg/l of TDS), cocurrent ion exchange can be effectively and economically applied for nitrate removal. This ion exchange system would also be appropriate for small water systems or individual home installations because of its low operation and maintenance requirements. An inexpensive source of NaCl regenerant should be provided, since cocurrent systems require greater amounts of regenerant chemicals than the other two systems.

As compared to the above system, countercurrent ion exchange systems utilize a more efficient method of regeneration and consequently employ more equipment and automated controls. In countercurrent systems, feedwater is applied in the opposite direction of the regeneration flow. This ion exchange scheme can accommodate higher flow volumes and contaminant loads than cocurrent systems due to the mode of operation and increased regeneration efficiency. Because more equipment is required, countercurrent systems involve higher capital expenditures as well as operation and maintenance costs. The quality of treated water is generally consistent over the entire exchange cycle with minimal contaminant leakage through the resin bed.

In the continuous countercurrent system, resin is moved around a single loop of connected vessels, while both the feedwater and regeneration solution flow in the opposite direction. Unlike the two fixed bed systems, feedwater and resin regeneration occur continuously within the vessel loop. The continuous ion exchange system has several advantages in large-scale operations over the conventional fixed bed systems. Since the resin is continuously regenerated, the system provides a more consistent flow; thus, large tanks to store water for use during the conventional regeneration cycle are not necessary and the resin utilization is maximized. The continuous system also requires a smaller resin inventory, and unlike the conventional system, the resin bed exhaustion can be adjusted to maintain the effluent quality at a specified nitrate concentration level. The waste brine stream is also produced continuously rather than in slug loads, which is characteristic of fixed bed systems, thus improving disposal operations. The continuous system does, however, require complex automated valving and process control system, which could limit its practical application in small-scale systems. Nitrate removal by the continuous countercurrent mode of ion exchange is most appropriate in application for larger communities with relatively high water demand.

In any event, a case-by-case technical evaluation of the different types of ion exchange is necessary to determine the most effective ion exchange process. Based on review and evaluation of available information and literature, the following observations can be made regarding the use of ion exchange (IE) for nitrate removal:

1. IE exhibits selectivity toward nitrate removal, although sulfate is the most preferred water anion.
2. IE removal system does not reduce the influent TDS level; rather, it exchanges specific ions while maintaining the same ionic concentration as the feedwater.
3. IE is a proven treatment technology which can be readily adapted for nitrate removal applications.
4. The anionic composition of the raw water supply will effect the operational characteristics of an IE treatment system. Waters containing high levels of sulfate or nitrate will result in relatively short exchange cycles, frequent regeneration cycles, and in increased demand for regeneration chemicals.

5. Due to the nature of IE removal mechanisms, the concentration of nitrate in the effluent following breakthrough will be several times greater than the influent nitrate level.
6. The most cost-effective IE system requires the operation of the exchange cycle until just prior to nitrate breakthrough rather than to total ion-exchange capacity of the resin bed, which occurs more rapidly.
7. Rapid, accurate nitrate monitoring is required to optimize removal efficiency and aid in process control.
8. IE systems can accommodate a wide range of treatment flow rates by utilizing the different types of systems as well as by varying the size and number of main exchange vessels and resin capacity.
9. A concentrated waste brine stream, typically less than 5 percent of the throughput volume, is produced during the regeneration and rinse cycles. A means of disposal for the waste stream would therefore be required.

#### Reverse Osmosis

Reverse osmosis utilizes a membrane separation technique to reject inorganic ions, turbidity, organic material, bacteria, and viruses. Unlike ion exchange, the product water has a considerably reduced TDS level than the influent stream. The semi-permeable membranes used in reverse osmosis act as a filter to retain ions on the brackish water side, while treated water is permitted to pass through the membrane. The removal of inorganic ions by reverse osmosis is directly related to the molecular size, shape, and charge of the ionic constituents. Thus, the percent rejection of a given ion varies with both water and membrane characteristics. Monovalent nitrate ions can be removed by the reverse osmosis process; however, process efficiency has not been established or demonstrated due to the lack of operational data.

The water flux or throughput volume in a reverse osmosis (RO) system is dependent upon the applied water pressure. As the pressure of the feedwater is increased, the flow of water through the membrane also increases. For this reason, system operating pressures between 400 and 800 psi are commonly recommended to provide economical percent recovery rates. In general, removal efficiencies and power consumption remain nearly equal over a wide range of TDS levels. Therefore, the economic incentive is to increase percent recovery, to maximize product flow, and reduce the brine stream volume.<sup>15</sup> As percent recovery is increased, however, the salt concentration in the brine stream also increases and a buildup of salts at the membrane surface occurs. This phenomena is termed concentration polarization and can lead to precipitation of sparingly soluble salts such as  $\text{CaSO}_4$  and  $\text{CaCO}_3$  and permanent membrane fouling. Concentration polarization is minimized by employing the use of multiple membrane stages and setting the percent recovery for a single stage low enough to prevent fouling and clogging at the membrane surface. Each ion in the feedwater must then be rejected at each membrane

stage such that the overall system efficiency is lower than the percent rejection for a single membrane stage. As an example, if an ion has a rejection efficiency of 85 percent per stage, the overall removal efficiency of a three-stage RO system would be between 60 to 70 percent.

Based on current information, it is apparent that RO systems are capable of removing various water impurities, including nitrate; however, there is lack of information regarding specificity of the process to nitrate removal. Furthermore, the majority of water impurities such as organics and colloidal material is not commonly present in groundwater, thereby reducing the economic attractiveness of RO systems.

The driving force in membrane separation is the applied pressure which influences both the resultant water quality and quantity. Reverse osmosis treatment systems commonly employ staged membrane units to enhance percent recovery as well as allow modular expansion to accommodate increasing treatment capacity needs. In most cases, chemical feed is required to control the pH of the feedwater, minimizing membrane fouling and plugging. In contrast to IE, a less concentrated waste brine stream is produced on a continuous basis, generally comprising 20 to 30 percent of the feedwater. A multi-stage, modular RO treatment configuration would be capable of effective nitrate removal; however, it could be more practically applied where water supply is also high in TDS or has other contaminant problems.

### Electrodialysis

Electrodialysis (ED) is another membrane separation process, which unlike RO systems, has the chemical ions as the mobile species. A direct electric current provides the driving force for the charged ions to migrate through selective, semi-permeable membranes. Ions migrate from diluting channels into concentrating channels under the influence of an applied electric field. An electrodialysis stack or operating unit consists of a negatively-charged cathode plate separated from a positively-charged anode plate by a series of alternating cation and anion permeable membranes. The configuration of the anionic and cationic permeable membranes produces an alternating series of diluting and concentrating channels between the respective membranes. Product water is then collected from the dilution channels, while the brine stream is withdrawn from the concentrating channels.

Typical TDS removal from the feedwater in ED treatment systems ranges from 25 to 60 percent per stage with practical applications of up to six membrane stages per module. The amount and type of water impurity to be removed can be controlled by the amount of electrical current used and the membrane surface area.<sup>16</sup> Detailed process removal data for nitrate removal applications are presently not available; however, existing ED plants having capacities up to about 1 mgd are commonly used to produce potable water supply from brackish water.

Similar to RO, efficiency of ED systems can be affected by fouling of the membranes by sparingly soluble salts. One ED system has been developed to minimize and control scale formation by reversing the DC current direction and thus the flow path of diluting and concentrating channels on a regularly timed cycle.<sup>15</sup> With respect to nitrate removal, ED systems may be more feasible than RO units because they require less energy and typically exhibit lower operating costs within the TDS range most commonly found in groundwater sources.

## VIABLE NITRATE CONTROL TECHNIQUES

The foregoing discussion has presented an overview and description of various management and treatment techniques which could mitigate and control the accumulation of nitrate in water supply. For any particular technique or combination of techniques to be considered viable, conformance with identified constraints must be achieved. Factors such as reliability in meeting water quality standards, compatibility with the existing water supply system, and economic impact must be evaluated to determine the feasibility and applicability of each alternative. Based simply on characteristics of available state water resources and demonstrated technology, it is evident that certain management and treatment process techniques can be eliminated from further consideration.

Source control is obviously the most desirable management technique in preventing groundwater degradation. Any managerial efforts directed toward control of major wastewater and agricultural sources would significantly reduce the frequency of high nitrate occurrences in state groundwater resources. The economic feasibility of nitrogen control from these sources requires evaluation of both present and future impact on groundwater quality as well as adequate protection of drinking water supply.

Water supply blending and deepening of municipal wells appear to offer economical means of reducing the concentration level of nitrate to comply with the drinking water quality standard. In contrast, use of an alternative water resource which requires major diversion and importation of water is limited by legal and economic factors and does not appear presently to be a viable management technique.

The magnitude of the nitrate pollution problem and the limited array of effective management solutions present a significant need for efficient and economic treatment process techniques. Based on the preceding discussion, ion exchange, reverse osmosis, and electro dialysis can be considered as the feasible treatment methods for nitrate removal. Although all three are proven technologies in demineralization, dealkalization, and softening of water supply and numerous industrial process streams, ion exchange is the only treatment technique that has been used to specifically reduce nitrate levels in drinking water. Reverse osmosis and electro dialysis have shown reduction capability between 40 to 90 percent, but lack specificity to nitrate removal and both are more expensive than IE. In certain situations where removal of several water supply contaminants is required, however, these processes may prove to be viable. Because the viability of treatment techniques depends upon process flexibility and reliability, as well as economic feasibility, it is apparent that a more detailed analysis of each of the three treatment systems on a case-by-case basis is necessary prior to any full-scale application.

CHAPTER  
**FIVE**

## CHAPTER 5

### EVALUATION OF AVAILABLE TREATMENT METHODS

In the preceding chapter, available management techniques were described and the current state-of-the-art of nitrate removal techniques was reviewed. Preliminary analysis of available information indicated that ion exchange can be considered as the most viable and practical treatment technology for full-scale application to nitrate removal.

An ion exchange treatment system, operated in any of the three process modes with the appropriate anion-exchange resin, can effectively and consistently reduce nitrate concentration in water supply. Evaluation of its cost effectiveness over a range of varying conditions, however, is limited by the paucity of actual operating data for on-line facilities. Two of the most important variables which affect the performance and efficiency of ion exchange processes are flow volume and the ionic composition of the raw water supply. In most cases, variation in flow volume will only influence the selection of the specific process mode which would provide the most reliable and cost-effective treatment operation. The ionic composition of the raw water supply, however, will significantly affect the performance and efficiency of ion exchange for nitrate removal. To that end, the use of electrodialysis or reverse osmosis should be considered as alternative treatment systems for nitrate removal.

High sulfate levels in the influent, as discussed previously, reduce the resin exchange capacity for nitrate ions and limit the economics and practical use of ion exchange. At a certain concentration level of sulfate, use of either electrodialysis or reverse osmosis may prove to be a more economical and practical removal technique. To date, the breakpoint composition of raw water supply which would influence selection of an alternate treatment process to ion exchange has not been established or defined.

Both water supply demand and composition can be expected to vary among the state's water resources that reportedly contain high nitrate levels. Analysis of water quality of 73 domestic, municipal, and agricultural wells in Maricopa County indicated an average sulfate concentration of 342 mg/l and a standard deviation of 280 mg/l.<sup>1</sup> The deviation from the average is an indication of the wide variation in sulfate concentrations in groundwater sources. It is probable that the breakpoint concentration of sulfate at which electrodialysis or reverse osmosis should be considered is within the range of sulfate concentration commonly found in state groundwater resources. Evaluation of all three viable nitrate removal methods is therefore necessary to determine applicability/suitability and economic impact of each treatment process.

**Table 5-1. Typical Water Compositions<sup>a</sup>**

Parameter	Waters			
	A	B	C	D
Total TDS	202	498	975	995
Ca <sup>+2</sup>	30	80	150	150
Mg <sup>+2</sup>	0	0	0	0
Na <sup>+</sup>	30	80	150	150
Cl <sup>-</sup>	37	143	100	70
SO <sub>4</sub> <sup>-2</sup>	15	60	400	400
CO <sub>3</sub> <sup>-2</sup>	0	0	0	0
HCO <sub>3</sub> <sup>-</sup>	15	60	100	100
NO <sub>3</sub> <sup>-</sup>	75	75	75	125
pH	7.0	7.0	7.0	7.0
Water temperature, °F	70	70	70	70

<sup>a</sup> Chemical constituents shown in mg/l and reported as individual ions.

Although adequate operational data is presently not available, a technical evaluation was undertaken to determine the sensitivity of each viable treatment method to both water composition and flow volume. For purposes of analysis, four water samples with varying quality were established for use in the evaluation. As shown in Table 5-1, total TDS, sulfate, and nitrate concentrations were varied to provide the basis in determining and understanding the tradeoffs between the three viable treatment methods. With the exception of nitrate, Water A contains low levels of all major cations and anions as compared to the other three types, while both TDS and sulfate levels are increased in Waters B and C. The increase in sulfate level should affect nitrate removal by ion exchange but should have limited effect on the performance of electro dialysis and reverse osmosis systems. In Water D, both TDS and sulfate levels are similar to the levels in Water C, except the nitrate level has been increased. Based on a review of water quality data for groundwater sources in central and southern Arizona, the chemical compositions of the waters shown in Table 5-1 can be considered typical of the quality of groundwater with potential high nitrate concentration.

Since the unit cost of treated water primarily varies with (1) the type of treatment process, (2) raw water composition, and (3) system capacity, the economic impact of all three parameters was evaluated. To facilitate the conduct of the evaluation process, a number of equipment manufacturers and distributors were contacted for assistance in the development of process performance and cost data. Appendix C presents the list of manufacturers who provided assistance or contributed information used in the following evaluation process.

### TECHNICAL EVALUATION

The paucity of actual operational data on nitrate removal techniques has constrained the detailed technical evaluation of the three treatment processes: ion exchange, electro dialysis, and reverse osmosis. The following evaluation therefore was based primarily on nitrate removal data provided by equipment manufacturers and general operating experience gained through the application of the three processes in the demineralization of brackish water supplies. A comparison of operational characteristics of each process is summarized in Table 5-2, while the following section presents a description of the estimated performance characteristics.

**Table 5-2. Comparison of Operational Characteristics of Viable Nitrate Removal Processes**

Parameter	Operational characteristics		
	Ion exchange	Reverse osmosis	Electrodialysis
pH	0-14 <sup>a</sup>	2-8 <sup>b</sup>	1-13 <sup>b</sup>
Temperature	0-70 C <sup>a</sup>	0-30 C <sup>b</sup>	0-65 C <sup>b</sup>
Feed pressure	low (60 psi)	high (up to 800 psi)	low (60 psi)
Resin or membrane life	5 years <sup>a</sup>	1-3 years <sup>b</sup>	5 years <sup>b</sup>
Nitrate removal efficiency	up to 100 percent	85 percent at each membrane	35 percent per stage
Nitrate specific	yes	no	no
Pretreatment required	filtration	filtration	filtration
Chemical feed required	yes (for regeneration)	yes (inhibition of membrane fouling)	no
Method of cleaning	backwashing	flushing with detergent solution	polarity reversal, flushing with with strong acid or base solution, disassembly and scrubbing of membranes
Favorable demineralization range, mg/l	1,000	1,500-10,000	1,000-3,000
Potential nitrate concentration in effluent during process upsets	250 percent of influent nitrate level	influent nitrate level	influent nitrate level
Brine waste stream	low volume, highly concentrated (20,000 mg/l)	high volume, brackish (2,500 mg/l)	high volume, brackish (2,500 mg/l)
Effluent nitrate monitoring	required to optimize plant efficiency, monitor product quality	required to monitor product quality	required to monitor product quality
Organic leaching potential	?	?	?
Existing nitrate removal facility	yes (one)	no	no

<sup>a</sup> Based on selective ion exchange resins.

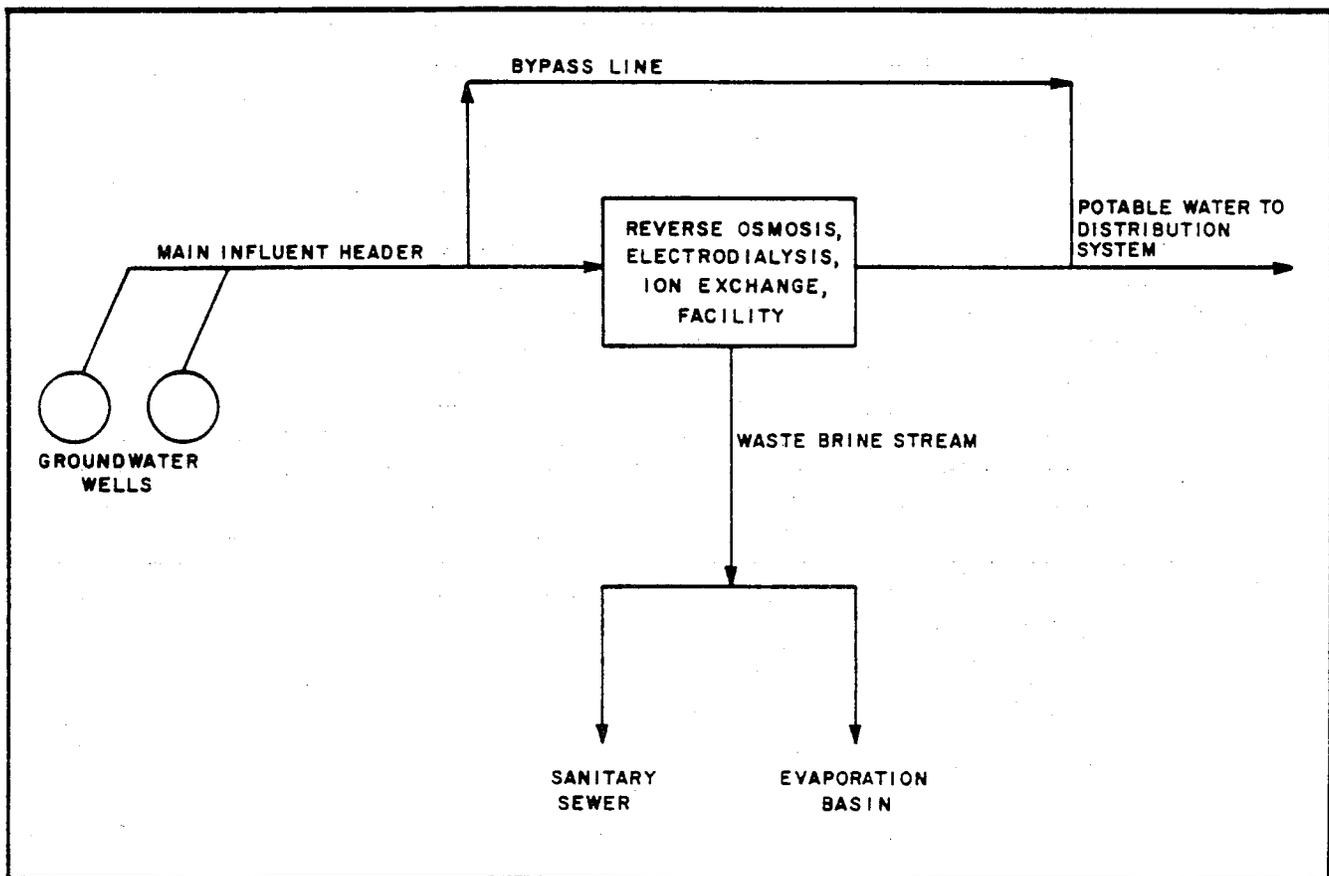
<sup>b</sup> Based on cellulose acetate membranes.

## Nitrate Removal Efficiency

Removal efficiency is one of the principal factors which establishes the viability of a particular treatment method. With respect to nitrate removal, the efficiency of the process dictates the portion of raw feedwater which can bypass the treatment units for blending with the treated water portion, as illustrated in Fig. 5-1. A higher removal efficiency can therefore result in a lower treatment capacity requirement and consequently reduced capital and operation and maintenance costs.

Laboratory tests<sup>2,3,4</sup> have shown that ion exchange is capable of removing nearly all nitrate present in the influent feedwater. Depending on the resin bed depth and loading rate, trace occurrences of nitrate in the effluent can be expected due to bed leakage and re-exchange anions. Proper engineering design and process control, however, will minimize the occurrence of nitrate leakage in treated water.

The theoretical performance efficiency of resins and the expected impact of competing anions on nitrate exchange capacity can be estimated based on chemical mass action analyses.<sup>2</sup> These approximations, however, are based on certain assumptions to simplify the analysis and require field verification during pilot plant testing. Interferences in removal efficiency of ion exchange processes have been observed in waters with moderate amounts of unoxidized iron, silica, and colloidal material.<sup>3</sup>



**Figure 5-1. Schematic Diagram for Nitrate Removal Processes**

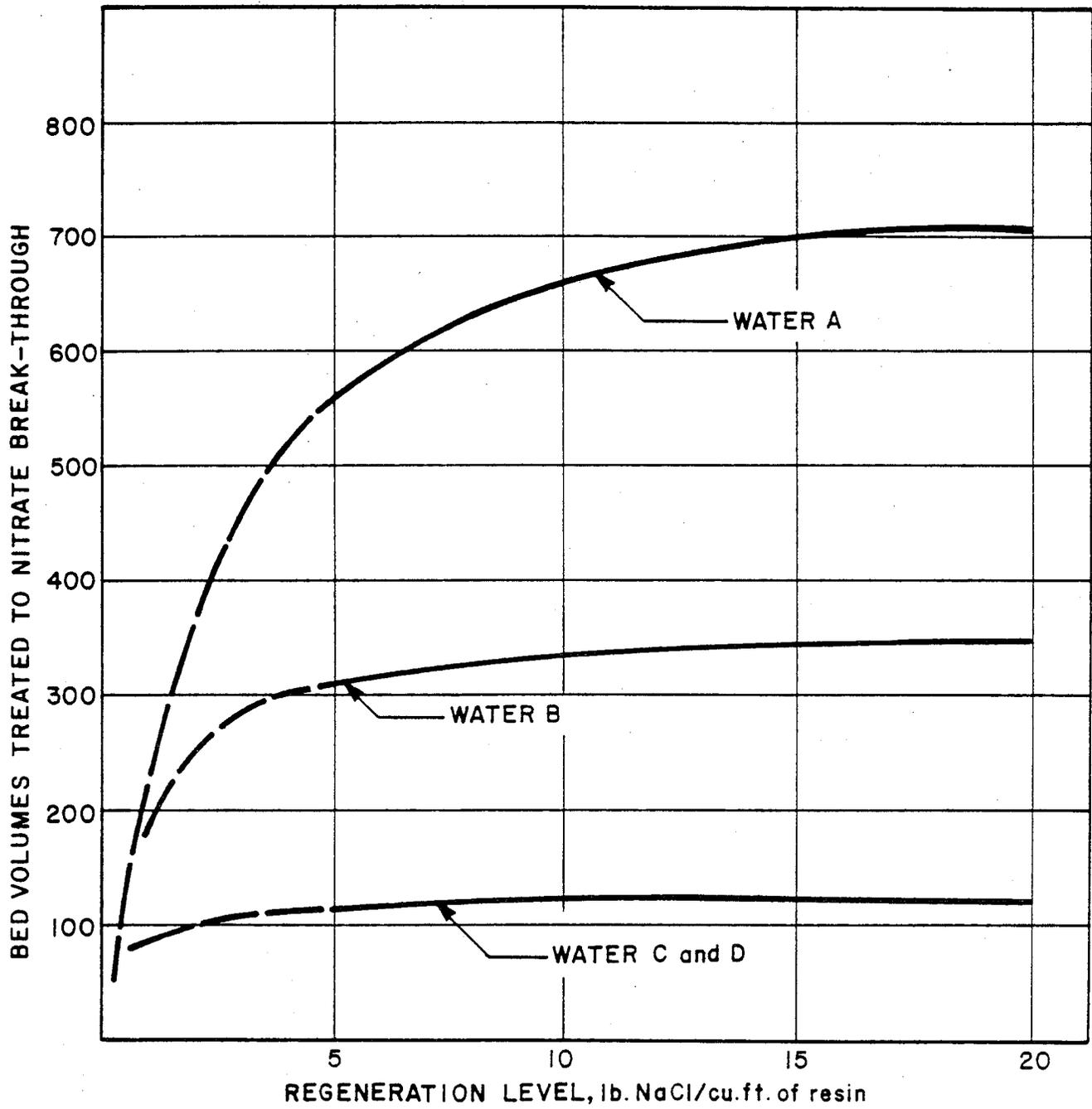


Figure 5-2. Nitrate Removal Versus Regenerant Salt Dosage

A mass action calculation was performed by the Functional Polymer Division of Diamond Shamrock on the four water samples, as shown in Fig. 5-2. As indicated, the nitrate exchange capacity, in terms of bed volumes treated, was estimated as a function of the regeneration level. The impact of total TDS, particularly sulfate, on the efficiency of the ion exchange process is clearly indicated by the difference in bed volumes treated prior to nitrate breakthrough for each water source. The exchange cycle could treat about 650 bed volumes of Water A, 300 of Water B, and 100 of Waters C and D, before regeneration would be required. As indicated, treatment of Water D would consume approximately six times the amount of regenerant salt required for Water A and thus result in increased operation and maintenance cost. Although there is a considerable difference in nitrate concentrations, Waters C and D would have similar exchange characteristics because of the identical high sulfate levels.

The increase in concentration of competing ions from Water A to Water D was also determined to impact the bypass fraction of the flow volume. A bypass fraction of about 55 percent would result in a concentration of 10 mg/l NO<sub>3</sub> as N in the product stream of Waters A, B, and C. Because of the increased nitrate concentration contained in Water D, however, about 75 percent of the flow volume would require nitrate removal to produce the same blended effluent quality. During the study, two equipment manufacturers expressed reservations and technical concerns regarding the feasible application of ion exchange for Waters C and D. Both cited the frequency of regeneration and reduced bypass fractions as the limiting factors and recommended further investigation of alternative treatment techniques. Although commercially available resins have varying nitrate exchange capacities, the reluctance of the manufacturers to utilize ion exchange for Waters C and D appears to be indicative of the breakpoint sulfate level which warrants further consideration of reverse osmosis and electrodialysis. Demonstration/operational studies, however, would be required to verify this finding.

The efficiency of reverse osmosis systems as it applies to nitrate removal is currently uncertain. Removal efficiencies ranging from 60 to 95 percent have been reported by manufacturers of reverse osmosis equipment.<sup>5</sup> In wastewater treatment applications, pilot studies have demonstrated removals between 25 and 80 percent; however, the tests were not conducted specifically for nitrate removal.<sup>6</sup>

Laboratory tests were recently conducted on a groundwater source similar in composition to Water B, as shown in Table 5-1. Although the test results have not been published, it was indicated that the membranes used for the tests were determined to be relatively inefficient in reducing nitrate concentration.<sup>2</sup> For purposes of this analysis, equipment manufacturers estimated the removal efficiency of reverse osmosis to be about 85 percent, with a 25 percent bypass fraction. In any event, it is apparent that detailed information on its performance is necessary before reverse osmosis can be reliably considered for nitrate removal applications. The Charlotte Harbor Water Association in Florida, for example, has received a grant from the EPA to study the removal of various contaminants, including nitrate, from spiked groundwater by low and high pressure reverse osmosis systems. The information and data from this study will be available in the near future to provide a better assessment of the applicability of reverse osmosis to nitrate removal.<sup>7</sup>

To date, there is also a paucity of operating data available on actual nitrate removal using electrodialysis. Although estimates indicate that a removal efficiency of approximately 35 percent per stage could be expected, the use of multiple stack units can result in a higher removal efficiency. Published data for wastewater treatment pilot studies indicates a range of 30 to 50 percent efficiency; however, nitrate was not the primary consideration in the study.<sup>6</sup> Under normal operating conditions, the waste brine stream of both electrodialysis and reverse osmosis systems represents about 15 to 30 percent of the feed volume. The large volume of waste brine and low removal efficiencies of both systems would therefore result in lower percent recoveries than for ion exchange.

### Pretreatment Requirements

All three treatment systems would require some form of pretreatment to protect downstream process equipment from frequent fouling and clogging due to suspended materials. Although groundwater is usually devoid of applicable suspended material, both exchange resins and semi-permeable membranes can be seriously damaged by solids in the feedwater. For small installations, cartridge or package filtration units can be used to pre-treat the feedwater for solids, while pressure or automatic back-wash filters are advisable for larger community systems.

As previously mentioned, unoxidized iron, silica, and colloidal material reduce the nitrate exchange capacity of ion exchange systems. Fouling problems can develop in most anion-exchange resins due to oxidation and precipitation of iron, which deteriorates the granular structure of the resin.<sup>3</sup> Pretreatment by chlorination or aeration will effectively remove excess iron, while silica and colloidal material can be removed by coagulation-sedimentation.

Membrane fouling is a major problem with reverse osmosis systems, since colloidal material, organics, or sparingly soluble salts may deposit on the membrane, thereby decreasing the product water flow rate. Since high nitrate concentrations are generally associated with groundwater, little problem should be expected with organics or colloids. Chemical feed for pH adjustment, however, would be necessary to prevent precipitation of sparingly soluble salts on the membrane. Adjustment of pH of the feed stream will prevent formation of  $\text{CaCO}_3$  and  $\text{Ca}_3(\text{PO}_4)_2$  scales, while sodium hexametaphosphate, a dispersing agent, will inhibit  $\text{CaSO}_4$  scale formation. Although electrodialysis membranes are subject to fouling by charged particles and sparingly soluble salts, several cleaning methods may be employed to clean the membranes without any chemical feed system.

A package electrodialysis plant is currently on the market with a system which periodically reverses the direct current (DC) polarity in the membrane stacks. This process technique disrupts the membrane films to prevent scale formation and membrane fouling, thereby eliminating the need for acid and chemical pretreatment of the feedwater. Use of the DC reversal system in electrodialysis can result in significant reduction in operation and maintenance costs, since the acid-chemical pretreatment section generally requires high maintenance.<sup>8</sup> In any event, adequate pretreatment of feedwater must be considered to eliminate or minimize many of the operational problems and malfunctions that are characteristic of exchange resin or membrane demineralization processes.

## Operation and Maintenance Requirements

In comparison to conventional water treatment plants, labor requirements for all three of the viable treatment processes are minimal. Systems operation can range from manual to fully automatic, depending upon the flowrate and chemical composition of the feedwater. All three process units are purposely designed to maximize on-stream time and minimize operator attendance and maintenance. Process control valves, feedwater flowrate and pressure, effluent monitoring, and on-stream time are typically controlled automatically. Routine maintenance is required for mechanical equipment and cleaning and replacement of resins and membranes. Normal resin and membrane life expectancy, as shown in Table 5-2, is 5 years and 1 to 5 years, respectively. Since reverse osmosis involves a high pressure system, equipment and membrane maintenance are usually greater than those for electrodialysis. Low pressure electrodialysis units can also be installed with plastic piping and valve manifolds, thus eliminating the need for corrosion protection which is required for metal pipes. Unlike ion exchange systems, operation and maintenance requirements of both reverse osmosis and electrodialysis remain relatively constant over a wide range of TDS levels.

Operation and maintenance of ion exchange units can vary significantly with the ionic composition of the feedwater. For a given flow volume, treatment of Water A as compared to Water D involves a considerable difference in the frequency of regeneration and thus, use of equipment and chemicals. For a given flowrate of 100 gpm, for example, the estimated time for resin bed exhaustion is 64 and 9 hours for Waters A and D, respectively. It is apparent that plant operator attention would be significantly increased with Water D for chemical handling and servicing of equipment. Additional exchange vessels would also be required with Water D to compensate for the regeneration cycle while maintaining continuous operation.

Ideally, nitrate removal processes should be capable of being on-stream for varying periods of time with minimum skilled operator attention. In most cases, groundwater sources in the state currently require only chlorination for disinfection purposes. Thus, increased demand for trained operators, particularly in smaller communities, is a significant element in the decision-making process for selection of nitrate removal methods.

## Process Upsets

With respect to health hazards associated with process malfunctions and upsets, ion exchange exhibits the highest potential due the characteristics of the exchange cycle and the unavailability of adequate process monitoring units.

In a chloride ion exchange system, the effluent nitrate concentration may reach a level several times higher than the influent nitrate level in the event of a process upset. The peak concentration would generally occur after breakthrough, so any process upset that would result in the delay of the regeneration cycle could release a plug load of extremely high nitrate water into the distribution system. The maximum effluent nitrate levels which may be expected in the event of any process upset in both reverse osmosis or electrodialysis systems, however, is the influent nitrate level. For all cases, provision for either effluent wasting or an on-stream nitrate analyzer for continuous process monitoring would be necessary to ensure a fail-safe operation or prevent the release of high nitrate water.

## Process Monitoring

Although electrodialysis and reverse osmosis systems for nitrate removal may not require continuous monitoring of the product water once their efficiencies are proven, ion exchange systems would require a reliable monitoring system and preferably use of an automatic nitrate analyzer. To date, the fastest method of accurate nitrate analysis is by ion chromatography, which requires a 20-minute turn-around time.<sup>2</sup> Although current technology only permits the resin bed to be regenerated on the basis of either cycle time or bed volumes of water treated, the ion exchange process is usually reproducible from cycle to cycle once stable operating conditions have been established. Because of process monitoring limitations, a significant safety factor must be incorporated into the regeneration frequency to assure that nitrate breakthrough does not occur. Current operation for nitrate removal, therefore, does not allow optimum use of the resin exchange capacity. If an automatic nitrate analyzer is developed, the system could be designed to regenerate just prior to nitrate breakthrough and assure optimum utilization of the resin exchange capacity at all times.

## Waste Disposal

All of the viable nitrate removal methods produce a concentrated brine stream, as shown schematically in Fig. 5-1. The percent recovery of product water is a function of several factors, including (1) the type of process used, (2) specific process design factors, (3) chemical composition of feedwater, and (4) type of pretreatment. As shown in Table 5-2, the brine stream from the ion exchange process is characterized by low volume and high concentration, while both reverse osmosis and electrodialysis are typically high in volume and relatively low in concentration. Furthermore, ion exchange systems discharge waste loads in slugs following regeneration, while membrane processes produce a continuous waste stream.

Disposal of brine waste is a site-specific consideration which would result in a significant increase in cost if an environmentally acceptable and inexpensive method is not available. Two alternative disposal methods available in this region are (1) discharge to sanitary sewers, and (2) use of evaporation basins. Storage tanks could be used to regulate discharge of brine solution to the sanitary sewers so as not to cause upsets at the wastewater treatment facility. The concentration of brine from a chloride ion exchange system may be toxic to activated sludge processes if not sufficiently diluted with influent wastewater. Although the waste stream of both reverse osmosis and electrodialysis systems would not present toxic problems to the waste treatment facility, both may contribute significant flow volumes to the treatment plant.

Evaporation basins would be an effective disposal method because of the high net evaporation rates in Arizona. The salt residues in the lined evaporation basin would build up continuously over the life of the plant. The volume of waste brine and physical and environmental characteristics of the site, however, would dictate the required size and proper design of the disposal facility.

## ECONOMIC IMPACT OF THE VIABLE TREATMENT METHODS

Assessment of economic impact and/or comparison of two or more alternative means of performing a given function is generally accomplished by analysis of both capital and operation and maintenance costs based on a given set of conditions. Several limitations, however, presently preclude the development of a detailed economic analysis of the three viable nitrate removal methods. First, actual operational and cost data is not available from pilot or full-scale nitrate removal facilities. Second, site-specific variables play a significant role in determining the feasibility of a process such that generalized cost data may not necessarily apply. Finally, there is a considerable difference between the applicability of the ion exchange process and the demineralization processes to nitrate removal. Although all three processes are capable of removing nitrate, both demineralization processes are also capable of removing a variety of other water impurities. Certain intangible elements, such as varying water qualities, therefore limit the conduct of a detailed economic comparison of the three viable removal methods.

For purposes of this analysis, the economic impact of available nitrate removal methods was evaluated based on published literature and research documents. As mentioned previously, a number of equipment manufacturers were contacted to solicit assistance in estimating both capital and operation and maintenance costs associated with the application of each treatment method. The economic sensitivity of each method was also analyzed with respect to water composition and flow volume to determine any economic breakpoint among the three removal methods. The water composition of the four water sources presented in Table 5-1 and treatment flow rates of 10, 50, 200, 500, and 1500 gpm were utilized as the basis of analyses. Operation and performance data was based on expected removal efficiencies of reverse osmosis and electro dialysis systems and on laboratory research of commercially available anion resins for chloride ion exchange systems.

The major components of the capital cost include cost of site preparation, unit process equipment, shipping, plant piping and valving, plant building, chemical storage, booster pumps, and instrumentation. An allowance of 25 percent of the above components for installation costs and contingencies is also included. Cost elements not included in the capital cost but may be significant in specific cases include land for the treatment site, pretreatment processes, and waste brine stream disposal. Similarly engineering, administrative, legal, and financing costs were not included due to their site specificity. To facilitate the economic analysis, cost estimates and prices of comparable work were obtained from all available sources of information. Amortization of the total capital cost was based on a 20-year period and 7 percent interest rate, with no salvage value. For a common basis of comparison, cost estimates are based on current price levels for equipment, power, chemicals, and labor.

Operation and maintenance includes all costs for labor, power, chemicals, resin or membrane replacement, supplies, and other materials. These costs were also adjusted to reflect current salary rates, equipment, material, and power costs in the state.

Based on the preceding evaluation criteria, the unit cost of treatment for each of the three viable nitrate removal processes was estimated, as shown in Table 5-3 and Fig. 5-3, in terms of total annual cost per 1,000 gallons of product water. Salient observations regarding the economic impact of each removal process include:

**Table 5-3. Economic Comparison of Viable Nitrate Removal Methods** <sup>a,b</sup>

Water type <sup>c</sup>	Flowrate <sup>d</sup> , gpm	Construction cost <sup>e,f</sup>			Operation and maintenance cost <sup>g</sup>			Total cost		
		RO	ED	IE	RO	ED	IE	RO	ED	IE
A	10	1.49	1.50	0.58	0.91	0.65	0.39	2.40	2.15	0.97
	50	-	0.56	-	-	0.51	-	-	1.07	-
	200	0.37	0.29	0.28	0.57	0.42	0.31	0.94	0.71	0.59
	500	0.34	0.32	0.19	0.57	0.42	0.30	0.91	0.74	0.49
	1,500	0.29	-	0.15	0.57	-	0.20	0.86	-	0.35
B	10	1.49	1.50	0.58	0.91	0.65	0.45	2.40	2.15	1.03
	50	-	0.56	-	-	0.51	-	-	1.07	-
	200	0.37	0.29	0.28	0.57	0.42	0.37	0.94	0.71	0.65
	500	0.34	0.32	0.19	0.57	0.42	0.32	0.91	0.74	0.51
	1,500	0.29	-	0.15	0.57	-	0.22	0.86	-	0.37
C	10	1.49	1.50	0.58	1.08	0.65	0.64	2.57	2.15	1.22
	50	-	0.56	-	-	0.51	-	-	1.07	-
	200	0.37	0.29	0.29	0.68	0.42	0.56	1.05	0.71	0.85
	500	0.34	0.32	0.20	0.68	0.42	0.45	1.02	0.74	0.65
	1,500	0.29	-	0.16	0.68	-	0.34	0.97	-	0.50
D	10	1.49	1.50	0.58	1.08	0.65	0.66	2.57	2.15	1.24
	50	-	0.56	-	-	0.51	-	-	1.07	-
	200	0.37	0.29	0.29	0.68	0.42	0.58	1.05	0.71	0.87
	500	0.34	0.32	0.20	0.68	0.42	0.48	1.02	0.74	0.68
	1,500	0.29	-	0.16	0.68	-	0.36	0.97	-	0.52

<sup>a</sup> All costs in dollars per thousand gallons based on current equipment and construction price levels, November 1978. Nitrate removal methods include RO-Reverse osmosis, ED-Electrodialysis, and IE-Ion exchange.

<sup>b</sup> Total cost based on treatment of groundwater to a nitrate concentration level at or below 44 mg/l NO<sub>3</sub> (10 mg/l NO<sub>3</sub>-N); does not include cost for pretreatment processes and waste brine disposal.

<sup>c</sup> Refer to Table 5-1 for chemical composition of water types.

<sup>d</sup> Represents total product flow from nitrate removal facility; service flowrates, blending percentage and percent recovery vary for each removal method.

<sup>e</sup> Construction cost represents the cost of equipment and construction of required facilities for nitrate removal; cost do not include allowance for engineering contingencies and administrative, legal and financial services.

<sup>f</sup> Based on amortization of total construction cost at 7 percent interest rate over 20 year period and influent water volume over one year.

<sup>g</sup> Based on estimated annual operating/maintenance expenses and influent water volume over one year.

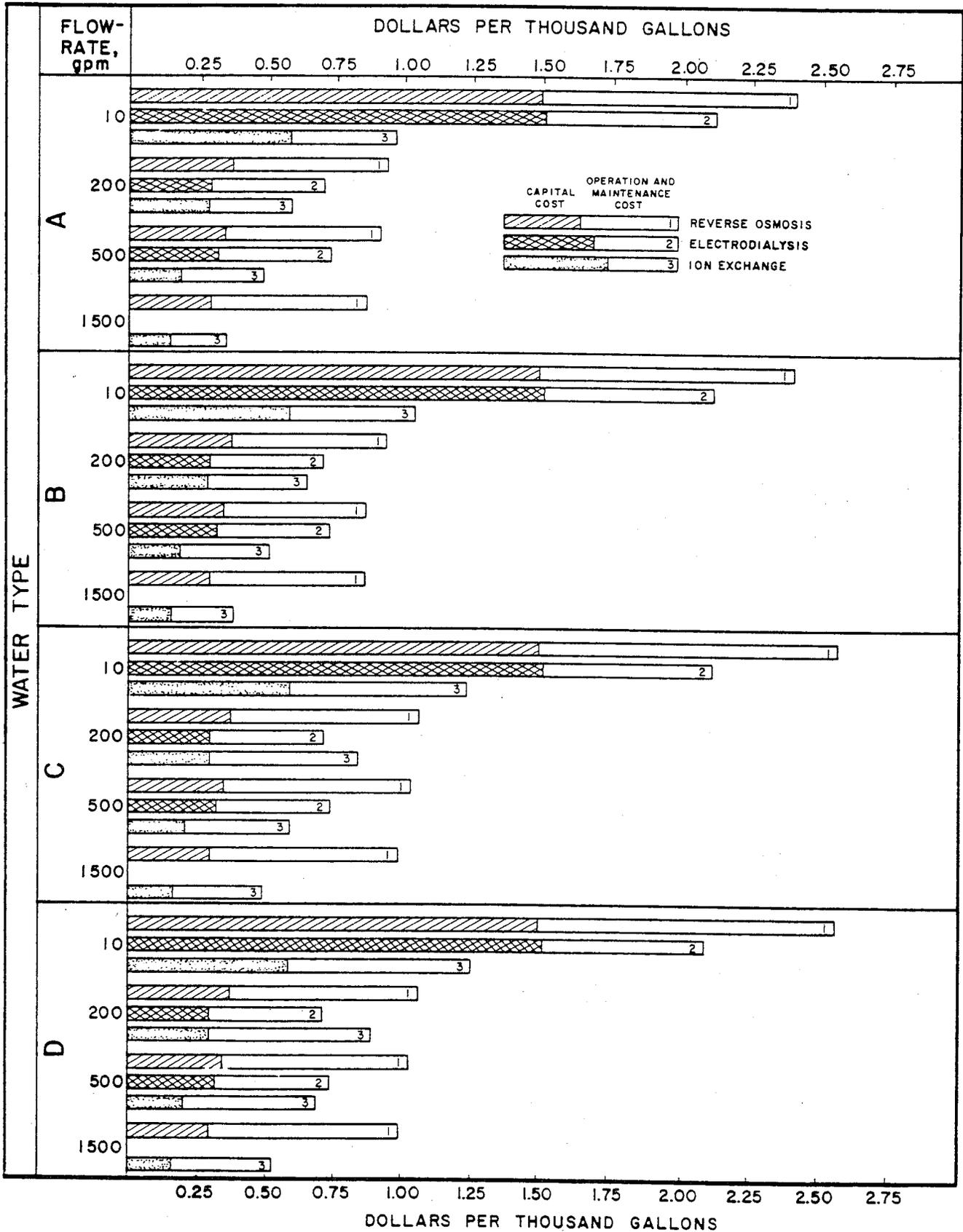


Figure 5-3. Economic Evaluation of Nitrate Removal Methods

1. Total unit cost of each of the three removal methods decreases with flowrate increases. The highest percent reduction in unit cost is apparent as flow rates increase from 10 to 200 gpm. As shown in Table 5-3, total unit cost of treatment of Water B by ion exchange decreases from \$1.03 per 1,000 gallons at 10 gpm to \$0.37 per 1,000 gallons at a flowrate of 1,500 gpm.
2. Total unit cost associated with both reverse osmosis and electrodialysis exhibits little variation with changing water type. In contrast, unit cost of ion exchange varies considerably from Water A to D. The cost difference, however, decreases with increasing flowrate.
3. Ion exchange has the least unit cost for product water in all but two cases. At the 200 gpm flowrate, the operation and maintenance cost of ion exchange was estimated to be higher than that of electrodialysis. It is uncertain if this case can be considered the economic breakpoint among the two treatment methods because of the apparent cost trend at higher flowrates. The relationship, however, illustrates the relative impact of water composition on the cost of treatment by ion exchange systems.
4. Based solely on information at hand and the findings of this economic analysis, it is apparent that reverse osmosis will result in the highest total unit cost for all four water types and the ranges of flowrates considered. In certain cases, cost differences between ion exchange and electrodialysis are too minimal to permit valid selection of the most economical process.

In summary, ion exchange can be considered as the least costly method of nitrate removal. With respect to the four water sources considered during the analysis, no definite economic breakpoint was determined among the viable treatment methods. The minimum unit cost margin in certain cases between ion exchange and electrodialysis could warrant a more detailed analysis of actual operating data when available. The conduct of side-by-side operational/demonstration study is therefore necessary to determine process tradeoffs and establish process design parameters specifically applicable to nitrate removal in water supply.

CHAPTER  
**SIX**

## CHAPTER 6

### SUMMARY OF FINDINGS AND RECOMMENDATIONS

This chapter presents the significant findings of the preceding investigative study of nitrate occurrence in Arizona water supply sources and recommendations based on the results of the study. To facilitate the analysis, the study was divided into two phases: (1) an assessment of nitrate occurrences throughout the state, and (2) an evaluation of available management and treatment methods of nitrate removal. Significant findings of the study include:

1. Nitrate concentrations in excess of the maximum contaminant level of 10 mg/l as N reportedly exist in several groundwater areas and water supply sources in the state.
2. With the exception of few isolated occurrences, all groundwater areas identified as being high in nitrate concentration are located within the alluvial basins of the Basin and Range Lowlands Province.
3. Groundwater sources with high nitrate levels are prevalent in the Salt River Valley, Upper Santa Cruz, and Lower Santa Cruz basins. These basins are also associated with the highest levels of urban and agricultural activities in the state.
4. Specifically, most frequent violations of the MCL for nitrate have been reported for the northwestern Phoenix, Tolleson, and Glendale areas.
5. Available information indicates that high nitrate occurrence in the province is related to both natural and man-caused nitrogen sources. Naturally occurring nitrate deposits have been speculated as the source of high nitrate levels in groundwater areas in the vicinity of the City of Glendale. Discharge of wastewater effluent and irrigated agriculture are the most significant man-caused sources of nitrogen due to their relationship which high recharge flows in areas of rapid infiltration rates such as alluvial stream courses. In specific instances, individual septic tank systems, sanitary landfills, and wastewater lagoons have also caused nitrate leaching and accumulation in groundwater.

6. Although the two most significant man-caused sources of nitrate and the occurrence of high nitrate levels in the state can be reasonably correlated, a more detailed investigation would be warranted to determine the specific and causal relationship between known sources of nitrogen and groundwater contamination.

It is apparent from the assessment of nitrate occurrence and the findings presented above that there is a need to identify effective methods to regulate and control the occurrence of high nitrate levels in Arizona water supplies. One of the primary objectives of PL 93-523, otherwise known as the Safe Water Drinking Act, is the formulation of programs to protect underground sources of drinking water. Compliance with this objective requires protection of groundwater resources primarily by source control measures. In the case of natural nitrate occurrences, however, it is equally necessary to identify alternate water quality management and treatment techniques to regulate and control the quality of water supply. The following section presents the significant findings of the second phase of the investigative study regarding nitrate control techniques:

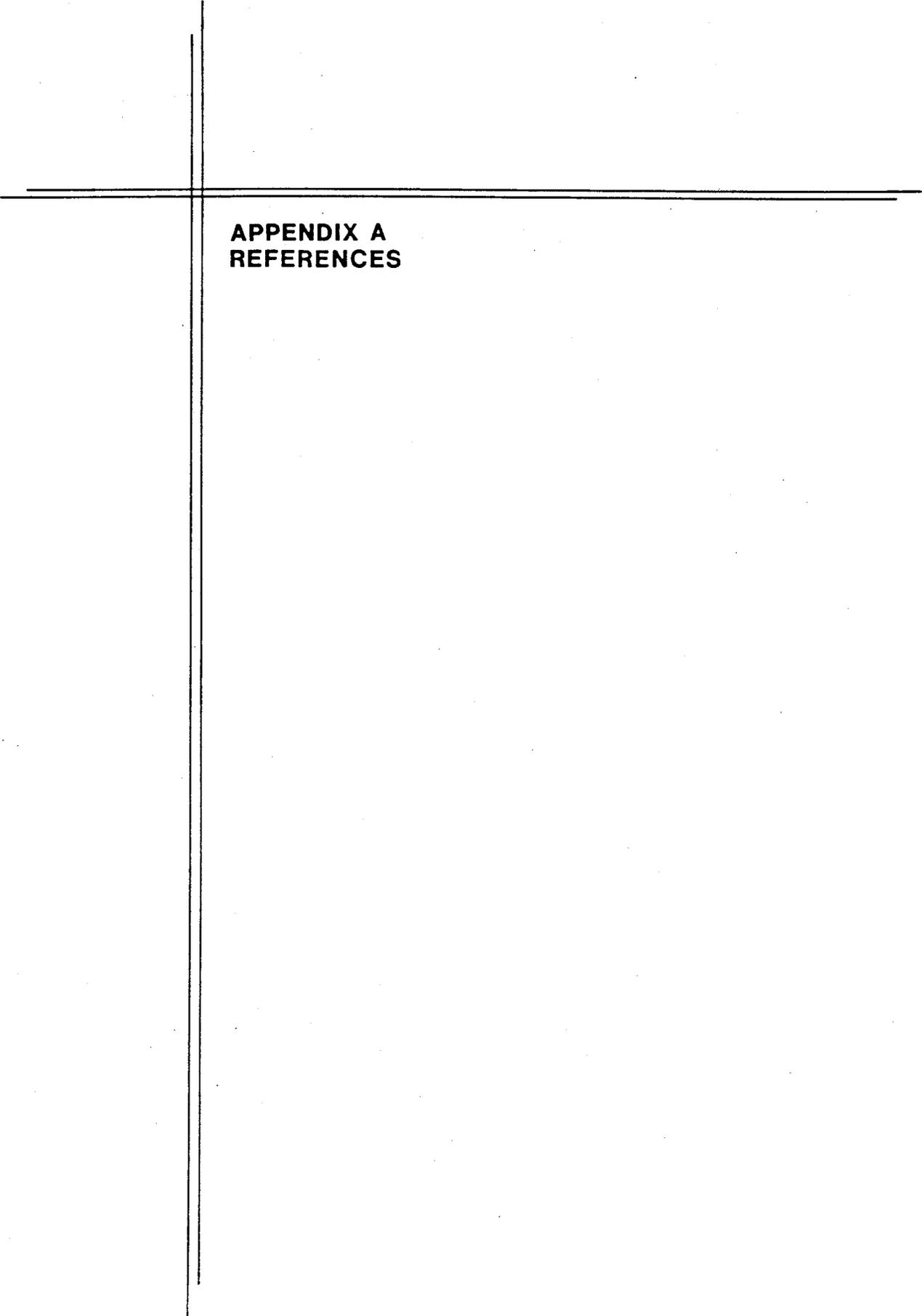
1. Based on the correlation of land surface nitrogen sources and reported nitrate occurrences, source control measures would in most cases provide an effective, long-term solution to the accumulation of nitrate in groundwater sources.
2. Management techniques such as water supply blending and well modification or relocation may be effective control methods; however, these control techniques are site specific and require detailed analysis on a case-by-case basis.
3. Minimal information regarding treatment techniques for nitrate removal is currently available, primarily because of the lack of on-line treatment facilities specifically designed for nitrate removal.
4. Based solely on available information, ion exchange appears to be the most applicable and economical treatment method for nitrate removal, while electrodialysis and reverse osmosis may be feasible alternates under certain conditions. An economic evaluation of the three viable removal methods indicated that ion exchange would result in the lowest total unit treatment cost over a considerable range of water compositions and flow rates.
5. Data pertaining to removal efficiencies, design factors, and operating experience would be required prior to the conduct of any detailed economic evaluation, process selection, or full-scale operation of the three available treatment techniques for nitrate removal.

6. Operating parameters and process instrumentation, which vary for each removal method, significantly affect process efficiency. A proven rapid method of analyzing nitrate is currently not available for application in process control and monitoring. As such, current methods of nitrate analysis do not allow for rapid detection of nitrate breakthrough which is essential for the effective performance of any of the three treatment processes.

Based on the findings of this investigative study and the apparent limitations of available nitrate control/removal methods, it is recommended that the following considerations be implemented to facilitate a more detailed and conclusive evaluation of viable removal methods to regulate and control nitrate occurrence in Arizona water supply sources:

1. Based on the schedule for compliance with PL 93-523, all water supply systems using groundwater as defined by ADHS are required to have chemical analyses performed by June, 1979. Compliance with this requirement will allow review of water quality data and enable the ADHS to further identify nitrate problem areas in the state. It is recommended that an inventory of nitrogen sources be developed and an analysis of their impact on groundwater quality be undertaken for each case where violation of the MCL has been reported. Furthermore, investigation of site-specific conditions pertaining to: (1) hydrogeologic characteristics of the groundwater source, (2) operational characteristics of the water supply system, and (3) historical water quality records be conducted to ascertain the cause of nitrate accumulation to concentrations exceeding the MCL. Proper regulation and control techniques can only be formulated and implemented after a thorough review of existing conditions.
2. It is apparent from the above findings that there exists a definite need for more detailed operational studies in order to fully evaluate the efficiency of the various methods of nitrate removal. Furthermore, without detailed cost data available, there will be limited basis for the State to: (1) review compliance strategies, (2) determine variances and exemptions, and (3) bring enforcement actions where necessary. Recognizing the need to protect public health and that groundwater resources are an essential element to the growth and development of Arizona, it is therefore recommended that a demonstration/operational study of the three most viable treatment methods be undertaken to establish design guidelines and operating parameters applicable to state groundwater resources. Conduct of a side-by-side pilot plant study of ion exchange, reverse osmosis, and electrodialysis systems would provide a basis for evaluating in detail process trade-offs and determining operating parameters and concerns such as energy requirements, methods of disposal for regenerant-brine streams, and process applicability at various treatment flowrates. In summary, this effort would provide a sound basis in the decision-making process and enable the State to take a lead role in implementing the objective set forth by the Safe Water Drinking Act.

# **APPENDICES**



**APPENDIX A  
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## APPENDIX A

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**APPENDIX B  
SOURCES OF WATER SUPPLY  
CHEMICAL QUALITY DATA**



## APPENDIX B

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**APPENDIX C  
PROCESS EQUIPMENT MANUFACTURERS**

## APPENDIX C

### Process Equipment Manufacturers

1. Chemical Separations Corporation  
PO Box 549  
Oak Ridge, Tennessee 37830
2. Diamond Shamrock, Functional Polymers Division  
800 Chestnut Street  
Redwood City, California 94064
3. Ecodyne, Graver Water Division  
2720 US Highway 22  
Union, New Jersey 07083
4. Fluid Engineering Company  
PO Box 35726  
Phoenix, Arizona 85069
5. Ionics  
65 Grove Street  
Watertown, Massachusetts 02172
6. Osmonics  
15404 Industrial Road  
Hopkins, Minnesota 55343
7. Permutit Company, Inc.  
PO Box 355, East 49 Midland Avenue  
Paramus, New Jersey 07562