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Chapter 7. Nitrogen in Groundwater Associated with Agricultural Systems

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Chapter 7. Nitrogen in Groundwater Associated with Agricultural Systems

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1. INTRODUCTION

Nitrogen, particularly in the form of nitrate, is the most common contaminant in aquifer systems (Freeze and Cherry, 1979). Hallberg (1989) points to agriculture as the most substantial anthropogenic source of nitrate, and Keeney (1986) suggests that this is caused by the intensive and extensive land-use activities associated with crops and animal production. The discussion of the occurrence of nitrogen in groundwater beneath agricultural systems is presented by examining the factors influencing aquifer vulnerability to nitrogen contamination, and by characterizing the geographic distribution of groundwater contamination by nitrogen. Factors that influence aquifer vulnerability are presented in the context of exposure to nitrogen sources from general agricultural systems and hydrologic conditions that facilitate transfer of those sources to groundwater. This analysis focuses on the occurrence of nitrate in the United States because data are readily available on many variables needed for such an analysis. Data from the US Geological Survey National Water Quality Assessment Program (NAWQA, Gilliom et al., 1995); the Census of Agriculture; the National Resources Inventory; and the State Soils Geographic Database [STATSGO (US Department of Agriculture, 1994)] provide an unique opportunity to directly relate nitrogen in groundwater to agricultural systems at a national or continental scale. Results of international research and monitoring are introduced to compare the occurrence of nitrogen in similar agricultural and hydrologic systems supported by literature and data available from the United Nations Food and Agriculture Organization (FAO).

1.1. Groundwater and Well Water

Selection of groundwater chemistry information is critical to understanding whether the aquifer is contaminated or whether wells used for drinking water have intercepted some contaminated ground or surface water adjacent to the well.

Some excellent studies have provided information about nitrate concentrations in wells used for private and community drinking water (Exner and Spalding, 1985; LeMasters and Doyle, 1989; Kross et al., 1990; Monsanto Company, 1990; US Environmental Protection Agency, 1990; Richards et al., 1996). These studies provide valuable human-health information but less information about the general condition of aquifers that form the groundwater resource. Other regional, national, and statewide studies of the quality of groundwater resources have included assessments of ambient conditions in aquifers (Burkart and Kolpin, 1993; Kolpin et al., 1996; Mueller and Helsel, 1996; Nolan and Stoner, 2000).

Aquifers are subsurface materials that store and transmit groundwater from recharge areas to discharge areas. Recharge areas often cover large parts of the landscape, whereas discharge areas generally are relatively small, such as surface water bodies and withdrawal wells. Aquifers and individual wells can be contaminated by substantially different processes. Aquifers can be contaminated by agricultural-chemical use over large parts of recharge areas. Properly constructed wells down gradient from recharge areas can withdraw water with dissolved contaminants derived from those areas. Agricultural chemicals can contaminate improperly constructed wells without appreciably affecting the aquifer. This contamination can occur when chemicals present near a well move from the surface down the outside of the well casing or laterally into the well through hydrologic units that are not isolated during well construction. The following discussion will only include processes by which aquifers can be impacted by nitrogen derived from agricultural systems and leached to aquifers in recharge areas.

1.2. Forms of Nitrogen in Groundwater

The forms of nitrogen generally measured in groundwater include nitrate (NO_3^-), nitrite (NO_2^-), and ammonia (NH_3^+) ions. Most analyses combine NO_3^- and NO_2^- and investigators report this as NO_3^- because NO_2^- occurs in substantially smaller concentrations in groundwater than NO_3^-. Nitrite also is an intermediate product of both nitrification and denitrification, that is, relatively unstable (Keeney, 1986), which helps explain its limited occurrence in groundwater. Nitrification is an oxidizing process and denitrification a reducing process with respect to NO_3^-, but both are biologically mediated. Organic nitrogen is rarely measured and not well known in groundwater (Korom, 1992). A generally accepted hypothesis is that measurable NH_3^+ and organic nitrogen rarely occur in groundwater because the required biological activity to produce them is minimal in groundwater systems. Nolan and Stoner (2000) reported that nitrate was detected more than 13 times as often as NH_3^+ and organic nitrogen in shallow groundwater of major aquifers of the United States, based on a detection threshold of 0.2 mg/L as nitrogen. In fact, concentrations of ammonia in groundwater rarely exceeded 0.1 mg/L, indicating chemical instability. This chapter will deal dominantly with nitrate (reported as nitrate + nitrite) with reference to NH_3^+ occurrence where limited information is available.

1.3. Nitrate Contamination Levels

Contamination is the occurrence of NO_3^- that exceeds a generally accepted concentration attributable to natural conditions. The authors are not aware of studies to examine minimum natural thresholds of NH_3^+, perhaps because its occurrence is too infrequent and concentrations are comparatively small. Nitrate is the most common contaminant in aquifers (Freeze and Cherry, 1979) and has been the most frequently mentioned groundwater contaminant associated with human activities throughout the world for several decades. The large number of NO_3^- measurements may be due to the establishment of international standards for drinking water for this ion and its wide distribution in the environment (Feth, 1966). The concentrations of nitrate in waters unaffected by human activities were shown to be less than 10 mg/L of NO_3^- by Feth (1966). A wide range of natural or background concentrations in groundwater has been reported for specific geographic locations from as small as 0.2 mg/L NO_3^- in Ohio (Baker et al., 1989) to as much as 100 mg/L NO_3^- in the Sahel of Africa (Edmunds and Gaye, 1997). Nitrogenous minerals have been reported in geologic materials that could provide natural sources of nitrate to groundwater in the northern Great Plains of the United States (Ferguson et al., 1972; Boyce et al., 1976) and in the San Joaquin Valley, California (Strathouse et al., 1980), for example. Extensive analysis of historical data from the United States for the *National Water Summary* by Madison and Brunett (1985) concluded that concentrations in excess of 3 mg/L may be indicative of human inputs. A more recent analysis of US Geological Survey national data from shallow groundwater (<30 m) beneath forest and rangeland concluded that 2.0 mg/L is a probable threshold for background concentration of NO_3^- (Mueller and Helsel, 1996).

1.4. Temporal Factors in Nitrate Contamination

Little monitoring data exists to interpret temporal trends of nitrate in groundwater because few monitoring programs have been designed to look at the quality of groundwater over time. Some examples have documented increased nitrate concentrations that relate to increased use of fertilizer and irrigation in the Snake River Plain of Idaho and the San Joaquin Valley of California (Fuhrer et al., 1999). Studies in the San Joaquin Valley showed that from the 1950s through 1980, the use of nitrogen fertilizer increased from 51,756 to 338,230 metric tons per year. This was accompanied by an increase of nitrate concentrations in groundwater from less than 2 to about 5 mg/L for the same period of time.

The complexities in the distribution of nitrate even in relatively simple hydrogeologic settings can confound interpretations of how groundwater nitrate relates to agricultural practices at the land surface. Recently, accurate methods of determining absolute groundwater dates for recharge as long ago as the 1940s have improved our understanding of groundwater contamination relative to the history of agricultural practices. Small atmospheric concentrations of man-made chlorofluorocarbons (CFCs) have been increasing steadily for more than 50 years in the United States, and have been used to estimate the age of the groundwater within 2 years under

ideal conditions (Plummer et al., 1993). They can be used to resolve recharge dates less than 10 years old, a fact needed to assess water-quality conditions in relatively shallow aquifers (Busenberg and Plummer, 1992; Dunkle et al., 1993; Reilly et al., 1994; Cook et al., 1995; Boehlke and Denver, 1996; Oster et al., 1996; Tesoriero et al., 2000). Application of age-dating technology to aquifers under irrigated cropland showed larger nitrate concentrations, many greater than 10 mg/L, with younger groundwater that was consistent with the history of increased fertilizer and irrigation applications starting about 30 years ago (Stoner et al., 1997). Groundwater older than 36 years was sampled from deeper parts of this unconfined sand and gravel aquifer. This deeper water had significantly lower nitrate concentrations. Other studies have linked nitrate contamination to agricultural practices using tritium dating methods having less accurate resolution of age dating (Hinkle, 1997; Savoca et al., 2000; Burow et al., 1998). Many of these studies incorporated analysis of the groundwater flow system, and possible effects of denitrification support interpretations based on tritium measures of residence time.

2. GROUNDWATER VULNERABILITY TO NITROGEN

The principles upon which groundwater vulnerability may be estimated include both specific vulnerability to sources of nitrogen from agricultural systems and intrinsic features of hydrologic susceptibility (Water Science and Technology Board, 1993; Zaporozec, 1994). Specific vulnerability to agricultural systems is a function of contaminant factors such as the quantity, rate, timing, and methods of nitrogen application, irrigation, and other agricultural management characteristics. Intrinsic susceptibility is a function of hydrogeologic factors such as proximity of an aquifer to the land surface, hydrologic properties of soil, and the amount, timing, and location of aquifer recharge. Understanding the juxtaposition of both specific vulnerability and intrinsic susceptibility is necessary to adequately define groundwater vulnerability.

2.1. Specific Vulnerability Factors and Processes Associated with Agricultural Systems

Manure and inorganic fertilizer are the principal sources of agricultural nitrogen that are easiest to document and compare globally. Mobile nitrogen, generally in the form of NO_3^-, can also be generated *in situ* by mineralization of soil-organic matter, crop residues, legume fixation, and redeposition of ammonia from nearby sources such as manure and crop loss during senescence (Schepers and Mosier, 1991). However, defining the distribution of these *in situ* sources is beyond the scope of this chapter. A substantial factor that has allowed the growth of the world production of food and fiber has been the expanded use of inorganic nitrogen fertilizer for crop production.

Rates of nitrogen fertilizer use and changes by world regions (FAO, 2000) are shown in Figure 1. The most outstanding feature in these data is the dramatic

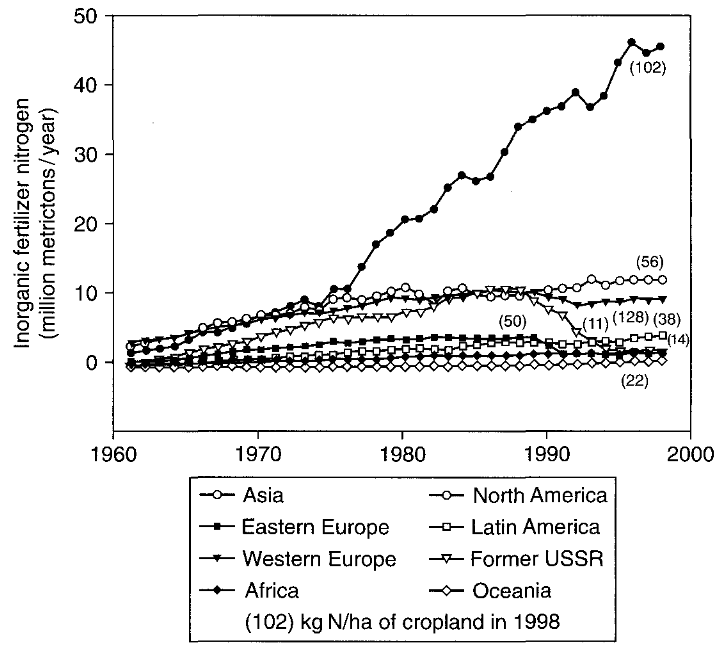

Figure 1. Use of inorganic nitrogen fertilizer by region since 1960.

increase of fertilizer in Asia since the 1970s, although Western Europe currently uses the largest unit-area amount on cropland. Both the American continents continue to increase their use of inorganic nitrogen fertilizer, although at rates less than those prior to the 1980s. Also interesting are declines seen in Europe (both Western and Eastern), and the former USSR since 1989. These trends may be useful to project long-term changes in nitrogen contamination of groundwater throughout the world. Estimates of nitrogen available from livestock manure (Figure 2) show a different global distribution from that of inorganic fertilizer. The estimates were based on FAO statistics (2000) on the number of animals in several categories and the estimated amount excreted by each animal (Lander et al., 1998). The ratio of source-load of manure-N can be classified into two quite different systems (Figure 2). In North America, Asia, Western and Eastern Europe, approximately twice as much nitrogen comes from inorganic fertilizer compared to manure. In the remaining regions, the ratio is inverted with more than twice the nitrogen from manure except in the former USSR (only 1.7). The trend of increasing the concentration of livestock production in the United States (US Department of Commerce, 1997) is also the concentration of the manure generated by livestock. Concentration of manure production is accompanied by a proportionate concentration of nitrogen sources available for leaching to groundwater. The concentration and storage of

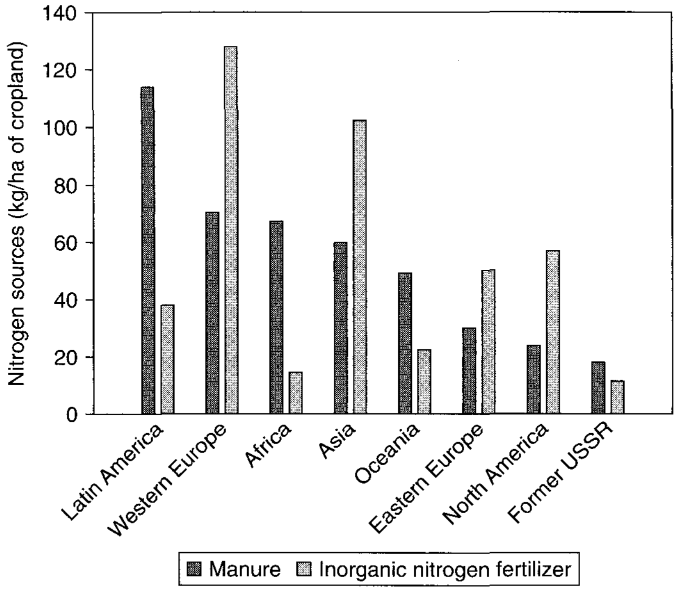

Figure 2. Nitrogen available from animal manure during 1999 by world regions.

manure also increases nitrogen losses to the atmosphere (Lander et al., 1998). This nitrogen loss to the atmosphere will not likely reduce the nonpoint source-load of nitrogen because the deficit will be made up with inorganic fertilizer applications. In addition, up to 75% of locally derived atmospheric NH_3^+ and NH_4^+ may be redeposited within 400km (Ferm, 1998). If the trend of increasing size of livestock operations is global, there may be an accompanying trend of increasing nitrogen contamination of groundwater from both point sources of manure storage systems and nonpoint sources of manure disposal on fields near large livestock facilities. The processes in agricultural systems that generate nitrate support both plant growth and water contamination. These processes act on both imported sources and nitrate generated *in situ*. Fertilizer and manure are the primary imported sources (Power and Schepers, 1989) and organic-matter mineralization and fixation are the principal processes generating nitrate within the soil (Schepers and Mosier, 1991). Crop uptake and microbial assimilation are the dominant processes that immobilize nitrate in the unsaturated zone. Immobilization by soil microorganisms may be offset by the opposing process of mineralization, both of which generally occur continuously (Keeney, 1986). During periods when neither crops nor soil microorganisms are active, available nitrate will leach through highly permeable soils to the water table when water from precipitation or irrigation exceeds evaporation. In many systems, imported nitrogen sources are added to the nitrogen pool at

precisely these vulnerable periods in spring and fall. The barren-ground periods before crop canopies develop and the time after harvest are also periods of substantial rainfall in many temperate climates. This rainfall provides the recharge water to leach nitrate.

Denitrification is the dominant process that can reduce nitrate in saturated materials beneath agricultural systems. This microbially mediated process occurs most readily above 10°C (Firestone, 1982) and generally requires both reduced oxygen levels (Meisinger and Randall, 1991) and readily available carbon (Parkin, 1987) or other electron donors. Denitrification is an active process in saturated soils with organic carbon and microbial activity that consume dissolved oxygen (Meisinger and Randall, 1991). Rates vary widely in aquifers because many good aquifers have large hydraulic conductivities which often preclude the presence of carbon sources for the depletion of oxygen or support of denitrification. Examples in unconsolidated sand aquifers have shown that denitrification is more likely to reduce nitrate concentrations with increased depth (Komor and Anderson, 1993) and remove as much as 50% of the nitrate leached below the root zone (Puckett et al., 1999). However, the latter study showed that the aquifer received about three times as much nitrogen as would be expected under background conditions.

An analysis of nitrate behavior in shallow groundwater of southeastern United States (Nolan, 1999) reported inverse relations between nitrate concentrations and dissolved oxygen on one hand and dissolved organic carbon, iron, manganese, and ammonia in groundwater on the other. In contrast, denitrification does not occur throughout southeastern United States aquifers as evident by low nitrate concentrations with higher concentrations of dissolved oxygen, some of which were in karst areas. Yusop et al. (1984) showed that denitrification was not a prominent process affecting water quality beneath sandy materials in Belgium. Substantial differences in subsurface denitrification rates were related to slope position in aeolian deposits (Geyer et al., 1992).

2.2. Specific Vulnerability in the United States

A convenient way of defining specific vulnerability to agricultural nitrogen sources and management is to use clusters of relatively homogeneous agricultural systems (Figure 3). The diverse agricultural systems in the United States were classified using cluster analysis (Sommer and Hines, 1991). The analysis included 19 farm enterprise variables, five resource variables, and three farm–nonfarm interaction variables. The analysis measured differences among counties across all 27 variables, grouped counties with the greatest similarities, and produced 12 clusters of US agricultural systems that have analogs on other continents. A further generalization of these clusters to a total of nine agricultural systems was made by combining clusters of "part-time cattle" and "sheep, cattle, and other livestock" into a general "livestock" category. "Fruit, other crops, and vegetables" and "nursery products" were placed in a horticulture category. The resulting pattern of systems for the United States is illustrated in Figure 3. These clusters also make a convenient

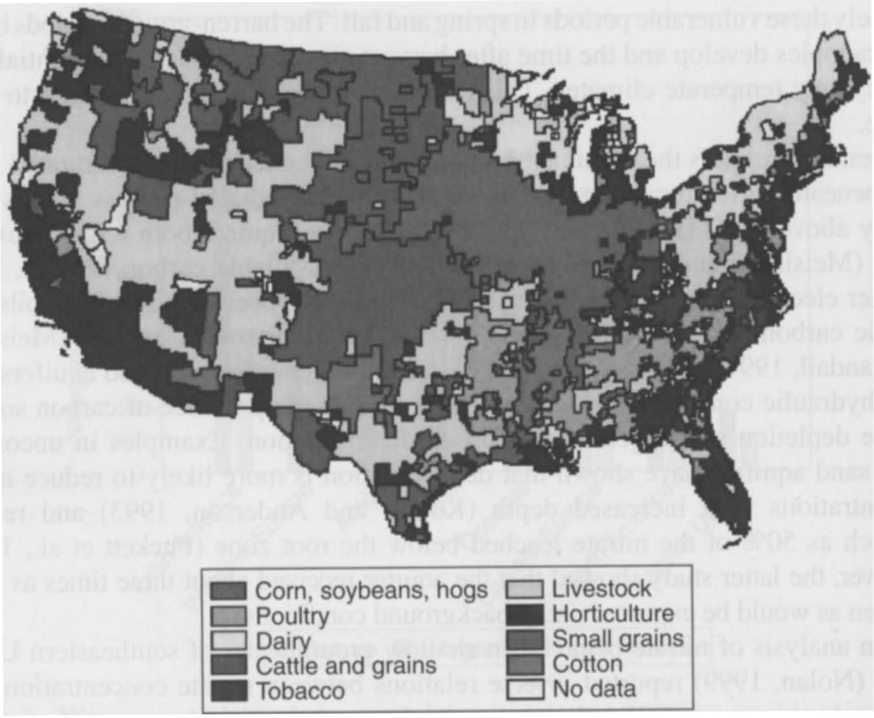

Figure 3. Agricultural systems in the conterminous United States (modified from Sommer and Hines, 1991).

framework in which groundwater measurements can be summarized and related to relatively homogeneous agricultural systems.

The geographic distribution of imported nitrogen sources for 1997, the latest Census of Agriculture year, was summarized by agricultural systems as shown in Figure 4. Inorganic fertilizer estimates were provided by David Lorenz, US Geological Survey (written communication) and are estimated sales of all forms of fertilizer by county. Manure data were estimated using data on livestock numbers from the Census of Agriculture (US Department of Commerce, 1997) and general estimates of the nitrogen content of manure (Lander et al., 1998) from each class of animals. Both inorganic fertilizer and manure estimates were normalized by county area, and counties were aggregated by agricultural systems mapped in Figure 3. A recent analysis of the groundwater risk of nitrate contamination (Nolan et al., 1997) used fertilizer, manure, and wet atmospheric deposition of nitrogen to define risk groups. This analysis of shallow (<30 m) wells showed that counties with well drained soils and sources of nitrogen larger than 21 kg/ha had a significantly larger concentration of nitrate and frequency of concentrations exceeding 10 mg/L than counties with less than 21 kg/ha nitrogen sources. When manure and fertilizer nitrogen are aggregated into agricultural systems (Figure 4), only two systems had

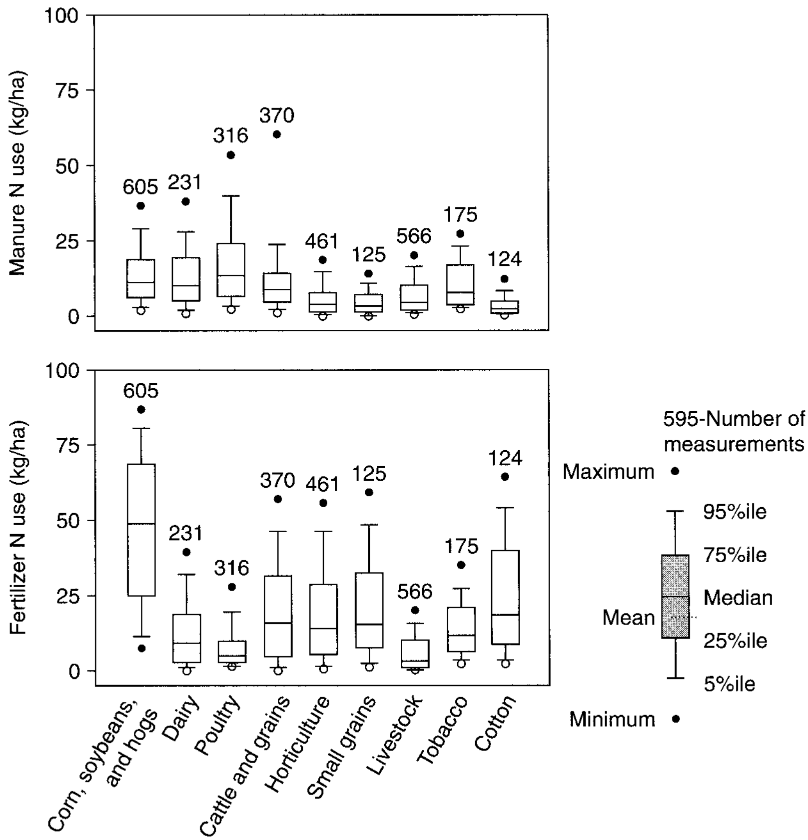

Figure 4. Sources of nitrogen in agricultural systems of the conterminous United States during 1997.

median values that exceed the high risk criteria used by Nolan et al. (1997); corn, soybeans, and hogs (59.7 kg/ha); and cattle and grains (24.41 kg/ha). However, cotton (20.6 kg/ha) and dairy (19.5 kg/ha) had median values close to this threshold.

2.3. Agricultural Management Factors Contributing to Specific Vulnerability

The presence of cropland may be a good indicator of groundwater vulnerability to nitrate contamination. Cropland management incorporates imported nitrogen sources and the agricultural practices that mobilize nitrogen in soil-organic matter during critical periods with reduced plant cover. Row-crop agricultural systems constitute the largest and most extensively managed land-use in the United States. More than 177 million ha in the 48 contiguous states are used for crops

(US Department of Commerce, 1997) such as corn, cotton, soybeans, and wheat. Similarly, large fractions of other continents are used to produce major row crops. Keeney (1986) states that these systems provide vast areas of nonpoint sources of nitrogen. In addition to the external nitrogen inputs needed to sustain row-crop production, tillage and other management activities promote the mineralization of soil-organic matter and crop residue into nitrate providing an *in situ* source (Schepers and Mosier, 1991). These crops are generally managed by various types of soil tillage and weed control that leave the land bare of vegetation for extended periods during the year. In many climates, this bare period coincides with substantial rainfall or snow melt that can enhance leaching of nitrate to groundwater. The bare-ground periods immediately before plant emergence and after harvest coincide with periods of no crop uptake. However, active microbial communities continue converting organic matter to nitrate during warm parts of these periods. Where climate and soil conditions allow multiple crops, leaching potential is not likely reduced if the imported nitrogen exceeds the demands of these additional crops.

Irrigation can contribute substantially to groundwater contamination because it increases the potential for recharge and nitrate leaching. The US counties (Figure 5) where more than 50% of the cropland is irrigated are concentrated in several areas that are vulnerable to nitrate contamination. Larger concentrations of nitrate and

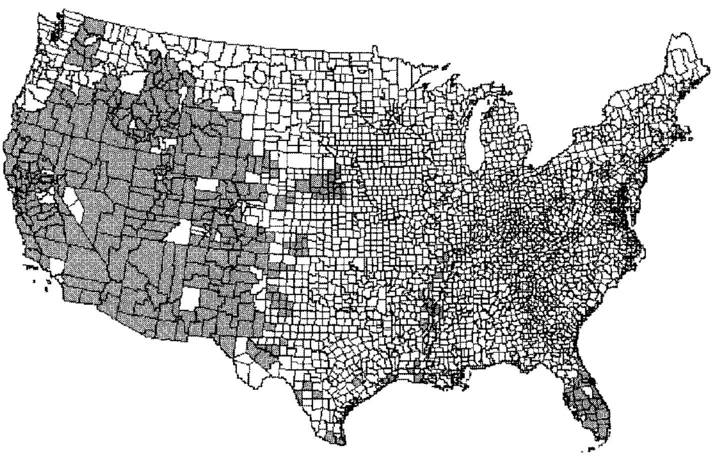

Figure 5. Counties in the conterminous United States in which at least 50% of the cropland is irrigated.

greater frequency of excess nitrate occur in groundwater in these areas than in areas without irrigation (Spalding and Exner, 1993; Eckhoff and Bergman, 1995; Hamilton and Helsel, 1995; Bhatt, 1997; Waddell et al., 2000). Irrigation using groundwater is most practical in areas where aquifers are very near the land surface. The additional recharge afforded by irrigation in excess of crop needs facilitates

leaching of nitrate to groundwater. In some irrigation systems, leaching is intentionally encouraged to remove soluble salts imported with irrigation waters (Power and Schepers, 1989). Other irrigated systems are located where permeable soils require frequent application of nutrients because of the high rates of leaching. Consequently, irrigation in many areas represents multiple contributions to vulnerability by providing both the water and additional nitrogen sources to increase leaching to groundwater. Irrigation is frequently used on crops with large N-fertilizer demand such as corn, potatoes, and vegetables, further compounding the vulnerability of groundwater under irrigation.

Global examples of irrigation impacts on groundwater are sufficient to indicate that irrigation is a universal contributor to nitrate contamination. The distribution of irrigated cropland in regions of the world (Figure 6) may indicate that

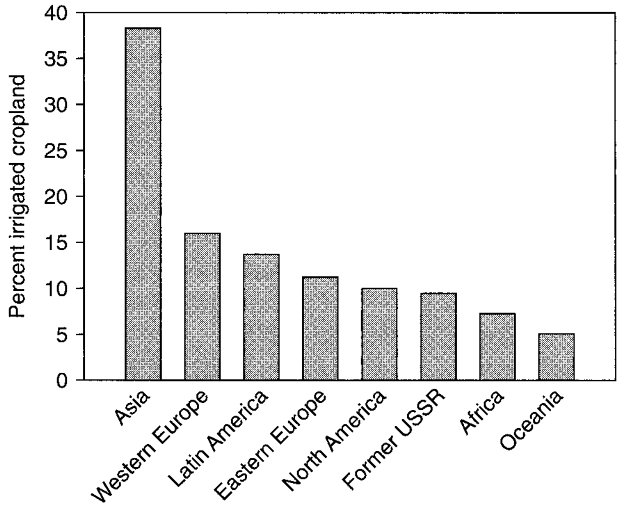

Figure 6. Percent of irrigated cropland in principal regions of the world.

Asia will be a region to experience its greatest impact. Unfortunately, few studies from Asia have been able to distinguish the impact of irrigation from those resulting from multiple cropping or large nitrogen sources. Several investigations have examined nitrate leaching under various agricultural systems in the Great Plains of North America. Hamilton and Helsel (1995) found median concentrations of nitrate in Nebraska under irrigated corn to be slightly less than 10 mg/L. Irrigation water that contains more than 20 mg/L nitrate in this same region results in the addition of 60 kg/ha nitrogen under a common irrigation schedule (Power and Schepers, 1989). In South Dakota, 38% of groundwater samples exceeded 10 mg/L nitrate under irrigated wheat and corn (Bhatt, 1997). In Montana, Eckhoff and Bergman (1995) found nitrate in excess of 5 mg/L to be common under irrigated safflower or sugar

beets and more than 10 mg/L under irrigated small grains. Substantial nitrate leaching was also documented under irrigation where feedlot manure was the source of nitrogen in Canada (Chang and Entz, 1996). Groundwater beneath an irrigated horticultural crop system in Spain (Guimera, 1998) was found to contain as much as 160 mg/L nitrate-N in a setting where irrigation withdrawals cause recirculation of nitrate-loaded water. Irrigated horticultural systems in Chile (Schalscha et al., 1979) were reported to produce concentrations of 20–35 mg/L nitrate in water below the root zone and 9–14 mg/L in shallow wells. Irrigated systems for a variety of cropping systems in India (Khurshid and Khan, 1982) commonly produced more than 10 mg/L nitrate in groundwater, and several areas commonly had in excess of 20 mg/L to as much as 500 mg/L nitrate.

2.4. Intrinsic Susceptibility of Groundwater

Three classes of shallow aquifers in the United States were mapped to show the extent of aquifers most susceptible to agricultural nitrogen contamination. Some shallow aquifer classes that may have similar susceptibility to agricultural nitrogen such as noncarbonate fractured rocks could not be as consistently mapped with the confidence of these classes. Shallow aquifers have been identified as particularly susceptible because large-scale surface activities, such as agriculture, often occur immediately above recharge areas. The proximity of these shallow aquifers to the surface facilitates direct transport of contaminants from surface activities to groundwater. In many agricultural systems, these activities are carried out in soils that are the unsaturated materials immediately above the water table or the top of the groundwater flow system. Such close proximity is commonly associated with shallow carbonate, unconsolidated sand and gravel, and alluvial aquifers.

Carbonate aquifers are bedrock aquifers most commonly formed in limestone, dolomite, and chalk. Karst features, such as solution-enlarged fractures, sink holes, and caves, form in these rocks at land surface and in the subsurface. Boundaries of this class of aquifers (Figure 7) were adapted from carbonate-rock aquifers shown on the Principal Aquifers map of the United States (US Geological Survey, 2000). Water levels in these aquifers may be deep, even though they are commonly unconfined in the outcrop and subcrop areas shown. Where carbonate aquifers are near the land surface they are particularly susceptible to nitrate contamination because of the direct and effective recharge flow-paths from thin soil cover to and through the aquifers via solution features. Geographically diverse examples exist of nitrate contamination associated with a variety of agricultural systems operating over these aquifers. Foster et al. (1982) report some of the most severe nitrate contamination associated with arable land in an eastern England karst region. Nitrate-sensitive areas are also related to arable land over the Great Oolite aquifer of the United Kingdom (Evans et al., 1993). About 18% of the grazing and pasture in the Appalachian region of the United States is underlain by extensive carbonate aquifers where Boyer and Pasquarell (1996) found a strong relationship between nitrate concentration and agricultural land.

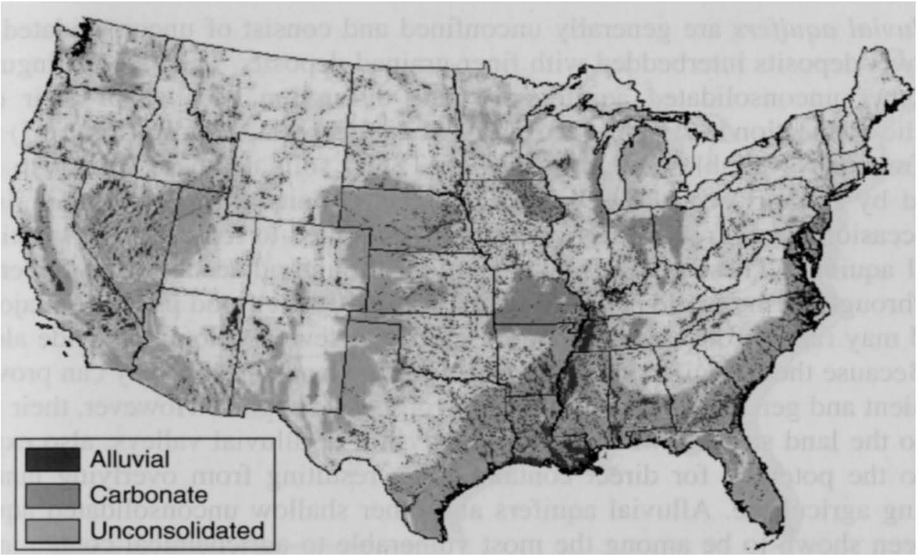

Figure 7. Location of shallow aquifer types in the conterminous United States.

Unconsolidated sand and gravel aquifers are found in a variety of depositional environments such as glacial outwash, coastal plain sediments, and aeolian sands. The map of these aquifers (Figure 7) includes the semi-consolidated and unconsolidated aquifers from the Principal Aquifers map of the US National Atlas (US Geological Survey, 2000). In the areas of the United States with continental glacial deposits the map was generated by calculating sand content from sieve variables in STATSGO (US Department of Agriculture, 1994). STATSGO map units in which the dominant soil contained more than 50% sand were interpreted to overlie shallow unconsolidated aquifers. Frequent and high nitrate concentrations have been related to a variety of agricultural systems located over outwash aquifers. These systems include livestock and horticulture (Zebarth et al., 1998) and potatoes (Hill, 1982) in Canada; potatoes and corn in North-central United States (Landon et al., 1995; Prunty and Greenland, 1997); and seed corn and horticulture in southern Michigan (Kehew et al., 1996). Nitrate contamination of coastal unconsolidated aquifers has been well documented along the entire eastern US coastal plain (Weil et al., 1990; Reay et al., 1992; Craig and Weil, 1993; Tyson et al., 1995; Lichtenberg and Shapiro, 1997) as well as in similar aquifers in Spain (Guimera et al., 1995). Aeolian sands such as the Nebraska Sand Hills, Quaternary sands of northern India (Kakar, 1981), and dune deposits in areas bordering the North Sea and northern Atlantic (Andersen and Kristiansen, 1984) are also classified as unconsolidated aquifers. Nitrate contamination appears to be less well documented in aeolian sands, perhaps because these sands form landscapes that are not conducive to substantial agricultural development.

Alluvial aquifers are generally unconfined and consist of unconsolidat and gravel deposits interbedded with finer-grained deposits. They are distin from other unconsolidated aquifers for this discussion because of thei hydraulic connection to streams. This class of aquifers was mapped (Figure 7 flood frequency variables found in the STATSGO soils database similar t mapped by Burkart et al. (1999). STATSGO map units with dominant so were occasionally or frequently flooded were compiled to represent the loc alluvial aquifers. These aquifers are commonly found adjacent to and und rivers throughout the world. They often are limited to the flood plains of ma ers and may range from several hundred meters to several kilometers wide river. Because these aquifers are at or very near the land surface, they can pr convenient and generally plentiful quantity for water supplies. However, the imity to the land surface, which is commonly flat in alluvial valleys, also e them to the potential for direct contamination resulting from overlying la including agriculture. Alluvial aquifers and other shallow unconsolidated a have been shown to be among the most vulnerable to agrichemical contam in the United States (Burkart and Kolpin, 1993). Other studies have show production to be directly related to excess nitrate (Schepers et al., 1991) vial and terrace aquifers of the Great Plains of the UnitedStates. Agricultural contamination of similar aquifers has been reported on other continents in Africa (Adetunji, 1994), Europe (Pekny et al., 1989) and Asia (Kakar, 1981).

2.5. An Example Linking Specific Vulnerability and Intrinsic Susceptibi Factors

A number of vulnerability or risk classification systems based on ove land-use and susceptibility characteristics have been developed for the United Kellogg et al. (1994) used agrichemical sources and soil characteristics to leaching potential. Nolan et al. (1997) used a combination of nitrogen loading, tion density, soil drainage, and land use to classify and map the risk of nitrate c nation of groundwater. The study by Nolan et al. (1997) included water-quality verify that the areas with highest and lowest risks coincided with areas where concentrations and frequency of nitrate exceeding 10 mg/L were also highest a est. Burkart et al. (1999) proposed an overlay method to assess vulnerability of a variety of methods for characterizing groundwater vulnerability to agric contamination.

A geographical information system overlay was used as an example here areas with relative vulnerability to nitrate contamination of groundwater and defi context in which water-quality data can be aggregated. The vulnerability classi (Figure 8) was generated by overlying maps of all three shallow aquifers (Fi areas dominated by soils with permeability greater than 64 mm/h (high-perm soils; Figure 8), and counties with more than 50% irrigated cropland (Figure result is four vulnerability classes that utilize one specific vulnerability factor tion, and two intrinsic susceptibility factors, shallow aquifers and permeable soi

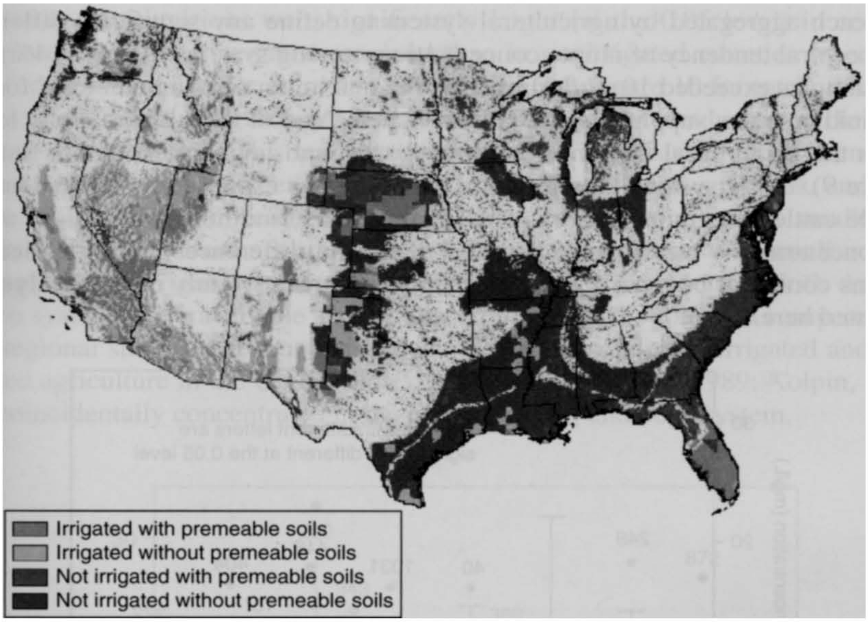

Figure 8. Distribution of irrigation and soil permeability in areas of the conterminous United States underlain by shallow aquifers.

3. DISTRIBUTION OF GROUNDWATER NITROGEN IN SHALLOW AQUIFERS OF THE UNITED STATES

Groundwater quality analyses were aggregated to characterize the distribution of nitrate in agricultural systems and in four classifications of aquifer vulnerability (Figure 8). These data were assembled for a groundwater nutrient retrospective analysis as part of the US Geological Survey NAWQA Program. The database contains historical analyses from more than 10,000 wells representing the groundwater quality in 20 NAWQA study areas and selected regional studies in the 48 conterminous states. These data resulted from a nationally consistent set of selection criteria that produced high quality data on both nitrate and ammonia concentrations.

The analysis presented here included only wells with depths of 30 m or less. It is hypothesized that deeper wells generally yield older water that would be less likely to contain nitrate related to recent land use. This selection of shallow wells resulted in a dataset of 3,125 wells with nitrate analyses in 493 counties. An analysis of a similar subset of these data (Bernard T. Nolan, personal communication) determined that nitrate concentrations from wells deeper than 30 m were significantly smaller than that from shallow wells. These groundwater data were analyzed to determine if there were differences in the nitrate concentrations among the nine agricultural systems shown in Figure 3. The values for both nitrate and ammonia

were each aggregated by agricultural system to define any significant differences in the central tendency of nitrate concentrations among systems. Almost 14% of the total samples exceeded 10 mg/L nitrate-N, the maximum contaminant level for public drinking-water supplies in the United States. Almost 24% of the wells located within the agricultural system of corn, soybeans, and hogs exceeded this standard (Figure 9). Other systems in which this standard was exceeded by more than 10% include cattle and grains, poultry, small grains, dairy, and horticulture. Few ammonia concentrations were greater than 0.1 mg/L and differences among agricultural systems could not be readily distinguished. Consequently, only nitrate analyses are presented here.

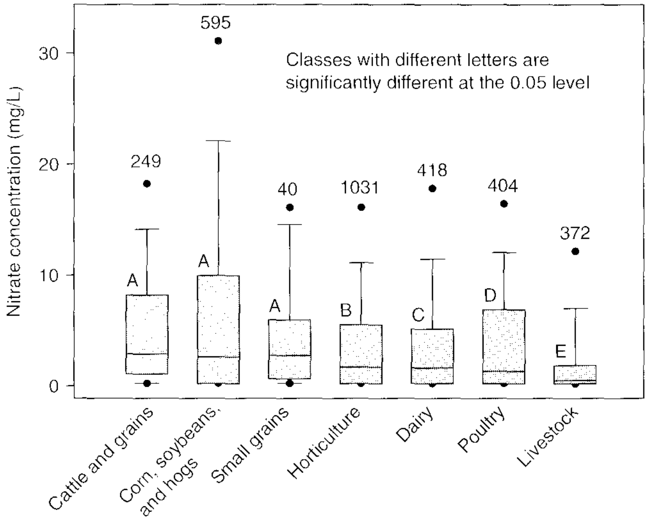

Figure 9. Nitrate concentrations under agricultural systems in the United States.

Nonparametric statistics were used because nitrate concentrations were not assumed to be normally distributed. Results of a Kruskal–Wallis test indicated there were significant differences among the nitrate concentrations associated with agricultural systems at the 0.05 level. Figure 9 shows the distribution of nitrate concentrations among agricultural systems. Results of Tukey's multiple variable comparison test performed on the ranks of nitrate concentrations show that groundwater concentrations in three systems (cattle and grains; corn, soybean, and hogs; and small grains) were significantly larger than all other systems at the 0.05 level. Unfortunately, too few nitrate samples were available to evaluate either tobacco or cotton systems. However, nitrate concentrations among the cattle and grains system; corn, soybean, and hogs system; and small grains system were not significantly different.

Nitrate concentrations were significantly larger (at the 0.05 level) in counties with greater than 50% irrigated cropland than in nonirrigated counties when analyzed for all samples under all systems combined (see Figure 10 for total). This difference was defined using Tukey's multiple comparison test conducted on the ranks of nitrate concentration. This test also confirmed the significance of differences in nitrate concentrations between irrigated and nonirrigated corn, soybeans, and hogs system. The apparent differences between irrigated and nonirrigated small grain systems (Figure 10) were not statistically significant due to the very small number of samples from irrigated areas. No samples of irrigation associated with dairy or tobacco systems were available and too few from poultry or cotton to compare. Two other regional studies that found significant differences between irrigated and nonirrigated agriculture in the United States (Power and Schepers, 1989; Kolpin, 1997) were coincidentally concentrated in the corn, soybean, and hogs system.

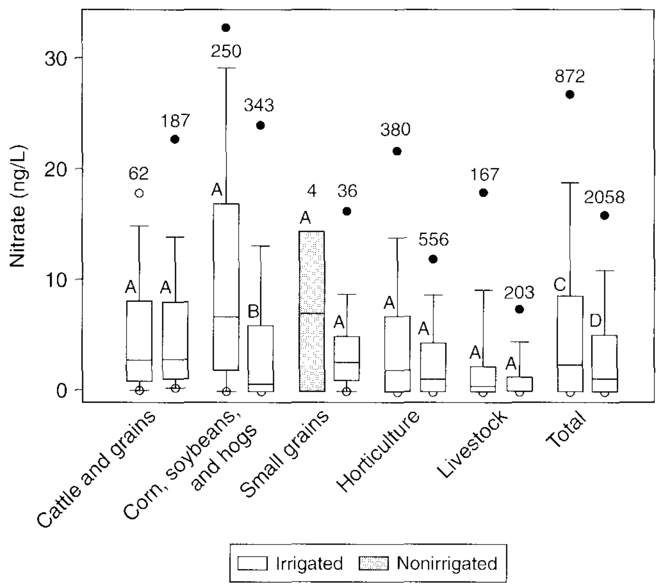

Figure 10. Nitrate concentrations in irrigated and nonirrigated agricultural systems in the United States. Classes with different letters (A, B) are significantly different at the 0.05 level.

Nitrate concentrations were analyzed to show variations among samples drawn from shallow aquifer types; unconsolidated, alluvial, and carbonate (Figure 11). There were significant differences among nitrate concentrations from the three aquifer types at the 0.05 level using Tukey's multiple variable comparison performed on

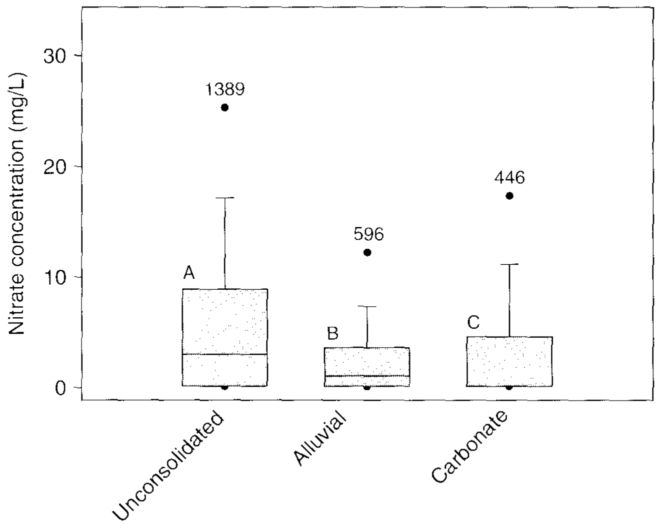

Figure 11. Nitrate concentrations grouped by shallow aquifer types.

nitrate ranks. Unconsolidated aquifers were found to have the largest nitrate concentrations followed by alluvial aquifers and carbonate aquifers (Figure 11). Carbonate aquifers, when close to the land surface, can be directly connected to the surface through karst features such as enlarged fracture systems and sink holes that provide direct recharge paths not available in the other types of aquifers. However, although generally thin, the soils, colluvium, and glacial deposits that overlie these aquifers may provide a sufficient barrier to nitrate leaching to protect many carbonate aquifers. Unconsolidated and alluvial aquifers are both composed of sand and gravel, but may differ in the nature and thickness of overlying materials. The significantly larger nitrate concentrations found in unconsolidated aquifers may result from the overlying soils being developed directly in the sand and/or gravel. Alluvial aquifers, on the other hand, can be buried under varying thicknesses of fine-grained floodplain deposits that are less permeable than sand, contain substantial organic matter fractions, and have low dissolved oxygen, typical of groundwater discharge areas. These differences in overlying materials or terrain and related flow systems are sufficient to reflect significant differences in the nitrate concentrations.

Analysis of the four vulnerability classes (Figure 8) shows the cumulative effects of soil permeability and irrigation on the distribution of nitrate concentrations in shallow aquifers (Figure 12). It was hypothesized that vulnerability to nitrate contamination increased when shallow aquifers were overlain by soils with permeability exceeding 64 mm/h. It was further hypothesized that irrigation provided an increase in the potential for nitrate contamination. Four vulnerability

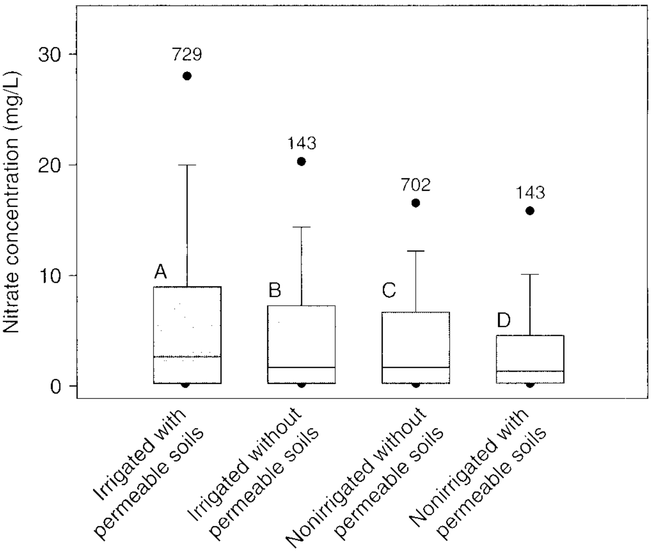

Figure 12. Nitrate concentrations grouped by aquifer vulnerability classes.

classes were defined using permutations of irrigation intensity and presence or absence of high-permeability soils. There were significant differences among samples from all four vulnerability classes at 0.05 level using Tukey's multiple variable comparison applied to ranks of nitrate concentration. Shallow aquifers in highly irrigated areas yielded significantly larger nitrate concentrations than those in nonirrigated areas regardless of overlying soil permeable (>64 mm/h). Since nitrate concentrations in nonirrigated areas with low-permeability soils were significantly larger than in areas with permeable soils is not intuitive. This apparent conflict with the hypothesis that permeable soils are more susceptible to contamination may result from influence of other factors, particularly the combination of agricultural systems associated with irrigation and less permeable soils.

4. CONCLUSIONS

This chapter focused on processes by which aquifers can be affected by nitrogen derived from agricultural systems. The primary form of nitrogen of concern for drinking water, nitrate, is costly to remove in water treatment. Many major aquifers used for urban drinking water are buried deep beneath large population centers. These aquifers are geographically removed from recharge areas near agricultural systems. However, shallow aquifers in urban areas may be contaminated by atmospheric and turf fertilizer sources of nitrogen. Groundwater sources for large municipal water

supplies can be and often are blended with several sources allowing dilution of any nitrate contamination. Most rural drinking-water supplies, however, are served through individual or a limited number of wells that are usually completed in shallow aquifers. These shallow aquifers are commonly recharged beneath agricultural activities. Limited research results have shown that once a shallow aquifer has been contaminated by nitrate, it may take decades for the groundwater quality to improve even after pollution controls have been implemented. Few programs exist that routinely monitor private groundwater systems for contamination from agricultural nitrogen. This makes it difficult for well owners to know trends in nitrate contamination of their aquifer over time. Consequently, local and regional understanding about vulnerable aquifers beneath certain agricultural systems becomes critical information for preventive and effective protection of water supplies, particularly in rural settings.

Two lines of evidence support several factors that contribute to groundwater vulnerability to nitrate contamination in agricultural settings. Research from several regions of the world provides a collection of spatially anecdotal information to hypothesize globally applicable hydrologic and agricultural factors contributing to groundwater vulnerability. Preliminary analysis of a United States dataset compiled by the US Geological Survey NAWQA Program from a variety of sources confirms these hypotheses for most agricultural systems.

Shallow unconfined aquifers have been most susceptible to nitrate contamination associated with agricultural systems. Unconsolidated aquifers and alluvial aquifers are more vulnerable, although shallow carbonate aquifers provide a smaller but substantial contamination risk. In areas dominated by irrigation, shallow aquifers are more vulnerable to nitrate contamination than areas without irrigation. The presence of permeable soils over shallow aquifers compounds the risk of contamination in irrigated areas.

Three agricultural systems (cattle and grains; corn, soybean, and hogs; and small grains) produced significantly larger concentrations of groundwater nitrate than other agricultural systems. However, significant differences of nitrate concentrations among these three systems could not be confirmed. Irrigation, particularly in corn, soybean, and hogs systems was found to have consistently larger groundwater nitrate concentrations in the United States data as well as in studies from outside this country.

Varying time lags exist in shallow groundwater responses to changes in agricultural inputs at the surface. If trends in increased fertilizer use and groundwater nitrate in the United States are repeated in other regions of the world, Asia may experience increasing problems because of recent and substantial increases in fertilizer use in that region. Both the American continents also continue to increase their use of inorganic nitrogen fertilizer, albeit at rates less than those seen prior to the 1980s and those presently seen in Asia. Scientists and policymakers should be interested in learning if there will be a reduction in the trend of increasing concentrations of nitrate in groundwater where fertilizer inputs have been reduced. The most rapid responses may be seen in areas with extensive macropore flow where land-use changes may produce the earliest changes in groundwater quality. It will be

particularly interesting to monitor changes in groundwater nitrate in both Western and Eastern Europe as well as in the former USSR where fertilizer use overall has dropped since the early 1990s. Groundwater nitrate measurements in these regions may provide tests of hypotheses that reduced nitrate contamination will follow reduced inorganic fertilizer inputs. Fertilizer-use trends may be useful to estimate long-term changes in nitrogen contamination of groundwater throughout the world. Use of these trends to strategically locate long-term monitoring will help answer questions about whether and when proportional changes in concentrations of nitrate will follow these changes in fertilizer.

If the trend in concentrated livestock production seen in the United States is global, there may be an accompanying trend of increasing nitrogen contamination locally in groundwater. Concentrated livestock operations provide both point sources of nitrogen in the immediate area of the confinement as well as larger areas of intense nonpoint sources as fields close to facilities become used for manure disposal.

A major contributor to groundwater vulnerability is the distribution of irrigated cropland. Regions were this practice expands, such as in Asia, may experience its greatest impact. More data and research will be needed in Asia to determine if patterns of water-quality degradation in irrigated areas is repeated in this region.

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