Nutrients in Shallow Ground Waters Beneath Relatively Undeveloped Areas in the Conterminous United States

By Bernard T. Nolan and Kerie J. Hitt

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 02–4289

NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

Denver, Colorado
2003

U.S. DEPARTMENT OF THE INTERIOR
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FOREWORD

The U.S. Geological Survey (USGS) is committed to serve the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life, and facilitates effective management of water, biological, energy, and mineral resources. (http://www.usgs.gov/). Information on the quality of the Nation's water resources is of critical interest to the USGS because it is so integrally linked to the long-term availability of water that is clean and safe for drinking and recreation and that is suitable for industry, irrigation, and habitat for fish and wildlife. Escalating population growth and increasing demands for the multiple water uses make water availability, now measured in terms of quantity *and* quality, even more critical to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. (http://water.usgs.gov/nawqa). Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. NAWQA results can contribute to informed decisions that result in practical and effective water-resource management and strategies that protect and restore water quality.

Since 1991, the NAWQA Program has implemented interdisciplinary assessments in more than 50 of the Nation's most important river basins and aquifers, referred to as Study Units. (http://water.usgs.gov/nawqa/nawqamap.html). Collectively, these Study Units account for more than 60 percent of the overall water use and population served by public water supply, and are representative of the Nation's major hydrologic landscapes, priority ecological resources, and agricultural, urban, and natural sources of contamination.

Each assessment is guided by a nationally consistent study design and methods of sampling and analysis. The assessments thereby build local knowledge about water-quality issues and trends in a particular stream or aquifer while providing an understanding of how and why water quality varies regionally and nationally. The consistent, multi-scale approach helps to determine if certain types of water-quality issues are isolated or pervasive, and allows direct comparisons of how human activities and natural processes affect water quality and ecological health in the Nation's diverse geographic and environmental settings. Comprehensive assessments on pesticides, nutrients, volatile organic compounds, trace metals, and aquatic ecology are developed at the national scale through comparative analysis of the Study-Unit findings. (http://water.usgs.gov/nawqa/natsyn.html).

The USGS places high value on the communication and dissemination of credible, timely, and relevant science so that the most recent and available knowledge about water resources can be applied in management and policy decisions. We hope this NAWQA publication will provide you the needed insights and information to meet your needs, and thereby foster increased awareness and involvement in the protection and restoration of our Nation's waters.

The NAWQA Program recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for a fully integrated understanding of watersheds and for cost-effective management, regulation, and conservation of our Nation's water resources. The Program, therefore, depends extensively on the advice, cooperation, and information from other Federal, State, interstate, Tribal, and local agencies, non-government organizations, industry, academia, and other stakeholder groups. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch
Associate Director for Water

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
meter (m)	3.281	foot
hectare (ha)	2.471	acre
liter (L)	61.02	cubic inch
milligram (mg)	0.00003527	ounce, avoirdupois
gram (g)	0.03527	ounce, avoirdupois
kilogram (kg)	2.205	pound avoirdupois

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Abstract

Nutrient concentrations in shallow (well depth of 30 meters or less) ground waters of relatively undeveloped areas were evaluated to determine background conditions relative to agricultural and urban land uses. Lands comprising 67 percent or greater forest or range, 10 percent or less agricultural land, and 10 percent or less urban land were used to represent relatively undeveloped areas. Data subsets from the U.S. Geological Survey's National Water-Quality Assessment Program (81 wells) and retrospective studies (320 wells) yielded 75th percentile nitrate concentrations of 0.51 and 1.1 milligrams per liter, respectively, in shallow ground water beneath relatively undeveloped areas. The value of 1.1 milligrams per liter is a reasonable upper bound estimate of relative background concentration of nitrate in shallow ground waters in the United States and incorporates effects of nominal nitrogen load to susceptible aquifers. Relative background concentration of nitrate is variable and depends in part on land use, rock type, and climate. Median nitrate concentration was significantly greater in ground water beneath rangeland (1.20 milligrams per liter) than beneath forest land (0.06 milligram per liter). Median nitrate concentration in ground water beneath rangeland was 1.4–2.7 milligrams per liter in susceptible aquifers, which consist of coarse-textured deposits or fractured rock. Increased relative background concentration of nitrate in rangeland areas likely results from evaporative concentration of nominal nitrogen load associated with natural organic and inorganic sources in hydrogeologically susceptible settings.

INTRODUCTION

Nutrient concentration in shallow ground water (from wells 30 meters deep or less) beneath relatively undeveloped land was evaluated to enable meaningful assessment of anthropogenic effects on ground-water quality. Previous studies of nutrients in watersheds have emphasized anthropogenic sources such as inorganic fertilizer, animal manure, and airborne nitrogen compounds emitted by utilities and automobiles (Nolan and others, 1997; Nolan and Stoner, 2000; Puckett, 1995; Smith and others, 1997). Nitrate is of particular concern because it is common in ground water, can persist for years, and at high concentration has been linked to adverse health effects (Centers for Disease Control and Prevention, 1996; Fan and Steinberg, 1996; Ward and others, 1996). Nitrate also is derived from natural sources, including native organic matter and selected minerals. Measuring nitrate and other nutrients in ground water from reference areas unaffected by agriculture, cities, and other human influences would yield natural background levels against which elevated nitrate concentration could be compared to assess the degree of human influence. Most watersheds in the United States, however, have been affected by human activity to some degree.

In this study, data collected or compiled for the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program were analyzed to infer relative background concentrations of nutrients in shallow, recently recharged ground water. Shallow ground water was analyzed because it is most likely to show recent land-use effects when compared with deeper, older ground water. Shallow ground water is used for drinking-water purposes in many areas and has been the focus of recent studies of aquifer vulnerability (Nolan and others, 1997; Nolan, 2001). Separation of natural and anthropogenic concentrations of nitrate to determine the level of human influence would enhance the usefulness of aquifer vulnerability assessments.

Because all ground waters sampled for the NAWQA Program likely are influenced by humans to some degree, the term "relative background" is used in this report to indicate nutrient concentrations in ground waters that are relatively unaffected by agricultural and urban lands. This definition is distinct from "baseline," which represents "the concentration found at a particular time (for example, the onset) during a study or monitoring program" (Rice, 1999). Ground-water data analyzed in this study were collected over a large time interval (1970–98). The term relative background also is distinct from "background," which is the concentration that results from natural processes. Relative background as defined in this report represents predominantly background concentration plus an extraneous component from low-level influence of human activities. An example of the latter is atmospheric nitrogen (N) from combustion of fossil fuels such as coal and oil.

Relative background concentration in shallow, recently recharged ground water indicates mostly natural processes and is expected to occur before overlying land use shifts from predominantly forest land or rangeland to agricultural or urban land. Deep (greater than 30 meters) ground-water samples were excluded from analysis because (1) they typically are older and not directly comparable to vulnerability assessments of shallow, recently recharged ground water; and (2) effects of natural sources of N on nitrate concentration in deeper, older ground water are difficult to assess because of anoxic conditions. Nitrate concentration in paleorecharge can be estimated by measuring excess N_2 gas to determine denitrification progress (McMahon and Böhlke, 2001), but such determinations were beyond the scope of this study.

National patterns of relative background concentration of nitrate were analyzed using historical (retrospective) data to help separate natural and anthropogenic effects for different land uses and geologic settings in the United States. Retrospective data were included to augment sample size because the NAWQA Program collects samples from very few wells in undeveloped areas. Natural sources of N vary spatially, as do other factors that combine to affect ground-water quality. In certain localized settings, natural geologic sources can contribute large amounts of nitrate to ground water (Hendry and others, 1984). Other factors affecting nitrate concentration in ground water include land-use practices, climate, biogeochemical conditions in the aquifer, and aquifer susceptibility characteristics such as soil type and the presence or absence of rock fractures.

Previous Studies

Previous investigators attempted to define background concentration of nitrate in ground water by evaluating data in relation to human influences. Madison and Brunett (1985) evaluated data for human influences and arbitrarily defined nitrate concentration exceeding 3 milligrams per liter (mg/L) "as indicating possible human inputs." Nitrate concentration less than 0.2 mg/L was associated with natural background levels, and concentrations of 0.21–3.0 mg/L were considered transitional. The nitrate data spanned a period of 25 years and represented about 87,000 wells in the USGS National Water-Data Storage and Retrieval System.

Mueller and Helsel (1996) analyzed nitrate data from wells less than 30 meters deep in forest and pasture areas to derive a background nitrate concentration of 2 mg/L. The historical nitrate data were from a retrospective data set representing more than 10,000 wells sampled during 1970–92 and compiled from a variety of sources by the USGS (Mueller and others, 1995).

Clark and others (2000) evaluated nutrient concentrations, including nitrate, in 85 streams draining relatively undeveloped basins of the United States to determine regional background values. The median flow-weighted concentration of nitrate for all basins was 0.087 mg/L. The maximum flow-weighted concentration, 0.77 mg/L, was in the South Fork of the Potomac River in West Virginia. In general, higher flow-weighted nitrate concentration occurred in the northeastern United States and corresponded to higher nitrate concentration in atmospheric deposition.

Rice (1999) described methods for determining baseline concentrations of trace elements in streambed-sediment samples. Baseline was defined as the concentration found at a particular time during a given study or monitoring program. Baseline is distinct from background, which is the concentration that results from natural processes. The most reliable method of determining baseline trace-element concentration involved creating an indicator site group comprising land uses not associated with urban settings.

Ground water in areas relatively unaffected by human activity is expected to have a mostly natural concentration of nitrate. Nitrate concentration from natural sources can be high in localized settings with substantial sources of N and favorable weathering characteristics. Oxidation of exchangeable ammonium in weathered till in southern Alberta, Canada, resulted in mean nitrate concentration of 100 mg/L as N in ground water (Hendry and others, 1984). In contrast, nonweathered till and bedrock resulted in mean nitrate concentrations of 0.5 and less than 0.2 mg/L, respectively, in ground water. Soils in the area have low organic matter content (less than 2.0 percent), and the weathered and nonweathered till both contain numerous shale and sandstone fragments derived from the local bedrock. The authors hypothesized that historically the water table was lower (near the contact between the weathered and nonweathered till) compared to current levels (about 2 meters below land surface). During the historical warm, dry period, exchangeable ammonium in the weathered till above the water table was oxidized to nitrate. The water table rose after the warm, dry period ended and anaerobic conditions occurred in much of the saturated, weathered till. However, high nitrate concentration persists in isolated zones of the weathered till where ground-water conditions are comparatively aerobic. Denitrification is limited in these zones, based on analysis of N isotope ratios.

Native fixed ammonium and organic N likely contributed large amounts of nitrate to soil derived from loess deposits in southwestern and central Nebraska (Boyce and others, 1976). Nitrate concentration as high as 87 milligrams per kilogram (mg/kg) as N (dry weight basis) was observed in soil samples from native range in the region, which retains little moisture because of limited precipitation and high evapotranspiration. In contrast, soil samples representing irrigated corn had lower nitrate concentration, indicating that leaching and(or) denitrification of nitrate had occurred. Irrigation water had leached nitrate from the soil profile. Additionally, nitrate is largely missing from rough, broken land in the region where water infiltration from runoff is more prevalent, suggesting removal from soil by leaching.

The goal of this study was to characterize nutrient concentration in areas largely unaffected by human activity, with emphasis on nitrate. The objectives of the study were:

- To calculate relative background concentrations of nutrients in shallow, recently recharged ground water beneath areas relatively unaffected by agricultural and urban land uses; and
- To compare relative background nitrate concentration for different land uses and geologic settings.

Purpose and Scope

The purpose of the report is to describe nutrient concentration in shallow ground water (wells 30 meters deep or less) beneath relatively undeveloped areas to determine background conditions relative to agricultural and urban lands. The report emphasizes nitrate because it is the predominant nutrient present in ground waters sampled as part of NAWQA land-use studies. Separation of natural and anthropogenic nitrate concentration will permit water-resource managers to assess effects of agricultural and urban land use on ground-water quality. The report also describes variations in nitrate concentration in shallow ground water caused by differences in land cover in relatively undeveloped areas.

Data from shallow ground water beneath relatively undeveloped areas throughout the conterminous United States were analyzed. A retrospective data set consisting of more than 10,000 observations was included to supplement the NAWQA data set, which currently contains 81 wells in relatively undeveloped areas. Including retrospective data in the analysis increased spatial data coverage and revealed regional patterns of nitrate concentration at the national scale.

STUDY METHODS

This study used nutrient data from two sources: (1) 1,880 wells sampled during 1993–98 in 46 NAWQA study units as part of ground-water land-use studies; and (2) a retrospective data set consisting of 10,404 wells sampled during 1970–92. NAWQA land-use studies employ monitoring networks to evaluate the quality of recently recharged ground water (generally less than 10 years old) in areas representing the intersection of a selected land use and an aquifer of interest. Wells in land-use studies typically are installed by the USGS for monitoring purposes, and public-supply wells are avoided because of uncertainties in the location of the recharge area and probable mixing of young and old ground waters due to large pumping volumes. Land-use studies follow well-design and construction criteria to ensure that water-quality samples represent the selected aquifer (Lapham and others, 1995; Lapham and others, 1997). Well locations are selected randomly (Scott, 1990) to ensure that sampling networks represent the environmental setting.

The NAWQA land-use studies comprise 1,170 wells in 49 agricultural areas, 636 wells in 26 urban areas, and 74 wells in 7 relatively undeveloped areas.

Springs and agricultural drains were excluded because of uncertainties in the source of water and contributing land-use area. To preclude bias by wells that were sampled several times, only one sample per well was used in statistical analysis.

Wells were sampled by study-unit personnel using procedures described by Koterba and others (1995). Nutrient analyses reported here consist of dissolved concentrations of ammonia, nitrite, nitrite plus nitrate, and orthophosphate. Concentrations of nitrogen species are based on elemental N (for example, NO_2^- as N), and orthophosphate concentration is based on elemental phosphorus. Nutrient samples were analyzed by the USGS National Water-Quality Laboratory using procedures described in Fishman (1993) and in Patton and Truitt (1992).

The retrospective data set is a compilation of historical water-quality and ancillary data collected during 1970–92 before NAWQA study units began sampling (Mueller and others, 1995). The retrospective data set includes data representing NAWQA study units that began in 1991, plus supplemental data from the NAWQA Delmarva pilot study and selected components of the USGS Toxic Substances Hydrology Program (Kansas, Long Island, Midcontinent, and Nebraska). Data sources were the USGS National Water Information System and the U.S. Environmental Protection Agency (USEPA) national database, STORET. Ancillary data include well depth, land use, and estimated N load. The retrospective data set has three qualities that enhance its usefulness in studies of national scope. More than 10,000 carefully selected observations are available at the national scale, yielding adequate spatial coverage of varying regions, land uses, and aquifers. Wells clustered in small geographical areas are excluded, eliminating spatial bias that can confound large-scale statistical analyses. Finally, nutrient concentrations determined by a variety of laboratory analytical methods (for example, nitrate as N, nitrate as NO_3^-) were aggregated into common constituent groups (for example, nitrate as N) using conversion factors to permit meaningful comparisons among sites (Mueller and others, 1995).

Average land use was determined for relatively undeveloped networks sampled by the NAWQA Program to develop criteria for use in screening the overall NAWQA and retrospective data sets. The objective was to produce data subsets indicative of relative background conditions with respect to agricultural and urban areas. At the time of the study (2001), the NAWQA Program had sampled only seven ground-water networks in relatively undeveloped lands, each containing 1–40 wells.

Anderson land-use data (Anderson and others, 1976) were compiled as weighted averages within 500-meter circular areas surrounding wells in the NAWQA and retrospective data sets. The 500-meter radius represents an appropriate recharge area for shallow, low-volume wells pumping recently recharged ground water. Mean land-use percentages were calculated for each type of network (agricultural, urban, relatively undeveloped) to assess differences among types of land-use studies. Anderson data representing agricultural (cropland-pasture; orchards, groves, vineyards, nurseries, and ornamental horticultural areas; confined feeding operations; other agricultural land), urban (new residential; residential; commercial and services; industrial; transportation, communication, and services; industrial and commercial complexes; mixed urban; other urban land), forest (deciduous forest, evergreen forest, mixed forest), and range (herbaceous rangeland, shrub-brushland, mixed rangeland) lands were used to characterize the land-use studies. Although the Anderson land-use data were collected in the 1970's, their use in this study is appropriate because the majority of water-quality observations encompass the same time period.

To preclude bias introduced by network size (number of wells), mean land-use percentages first were calculated for each network using all wells in the network. Group means representing agricultural, urban, and relatively undeveloped areas then were calculated using the network means as input. The smallest sampling network in undeveloped lands, with only one well in a swampy area, was excluded from these calculations.

The NAWQA and retrospective data sets then were screened on the basis of predominant land use in relatively undeveloped networks to increase the number of available wells for determining relative background concentrations of nutrients. Screening criteria for selection of relatively undeveloped sites were 67 percent or greater forest or range, 10 percent or less agricultural land, and 10 percent or less urban land. Screening the NAWQA and retrospective data sets produced two data subsets representing 81 and 320 sites, respectively (fig. 1). These subsets were designated the "NAWQA subset" and "retrospective subset," respectively. Medians and other percentiles of nutrient concentration in ground water were calculated for the data subsets to estimate relative background concentration of nitrate. Medians were used as a measure of central tendency for chemical concentrations because they are resistant to effects of outliers typical of highly skewed data. Analysis of variance (ANOVA) and Tukey's tests on the ranks were used to determine whether nitrate concentration differed significantly among selected land uses. Censored data were set to half the laboratory reporting level before calculating percentiles.

Regarding the NAWQA data set (1,880 wells in agricultural, urban, and relatively undeveloped areas), only wells 30 meters deep or less and completed in unconfined aquifers were considered. Deeper, anoxic ground water was excluded because the objective was to determine relative background concentration of nitrate for comparison with vulnerability maps representing shallow, recently recharged ground water. Aquifer type was not available in the retrospective data set so only land-use percentages and well depth were used as screening criteria.

The subset of NAWQA sites meeting relative background criteria was small (81 wells) and not amenable to analysis of national patterns. Accordingly, variation in relative background concentration of nitrate was assessed using the 320 retrospective sites that met undeveloped land-use criteria (fig. 1) by comparing different land uses (forest and range) using the Wilcoxon rank-sum test. The 1987 N load representing forest and rangeland areas was compared using the same test. Nitrogen load was compiled as described in Nolan and others (1997), and comprises fertilizer, manure, and atmospheric sources (referred to as "total N" in this report). Because N load is seldom uniform over large

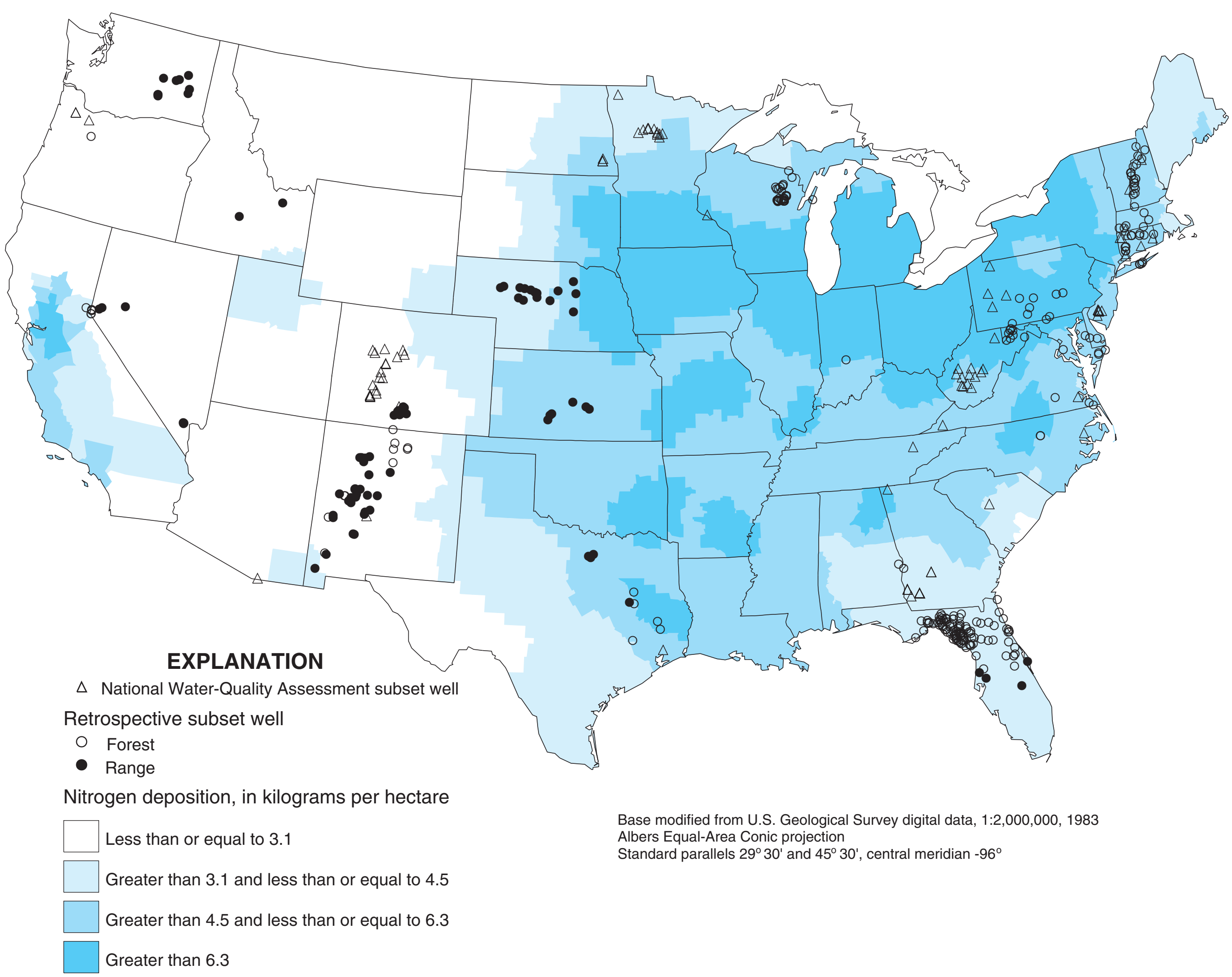

Figure 1. Locations of ground-water sites in the National Water-Quality Assessment Program and retrospective data subsets, and their relation to atmospheric deposition of nitrogen in 1987.

areas, county N load was weighted by land use within 500 meters of sampled wells. Fertilizer N was allocated equally to selected agricultural and urban lands to indicate farm and nonfarm uses. Fertilizer N was allocated to cropland-pasture; orchards, groves, vineyards, nurseries, and ornamental horticultural areas; new residential; residential; commercial and services; transportation, communication, and services; mixed urban; and other urban land. Manure N was allocated to cropland-pasture and confined feeding operations, and atmospheric N was assumed independent of land use within 500 meters of sampled wells. Manure N was not allocated to rangeland because it was assumed that dispersed manure from free-ranging cattle would be a minor source compared with confined feedlots and manure recovered and spread on cropland. An exception is areas around stock wells where cattle congregate. Water samples from stock wells had the highest median nitrate concentration (2.90 mg/L) of any water use compiled in the retrospective subset (fig. 2). Stock wells were excluded from the NAWQA and retrospective subsets because they reflect more concentrated sources of manure on rangeland. Median nitrate concentration also is high in irrigation well samples (2.05 mg/L), but only six samples in the retrospective subset had this water use. Irrigation water quality could indicate fertilizer or manure sources of N, mobilization of nitrate from natural sources of N, or the combined effect of these factors.

Precipitation and potential evapotranspiration data were obtained (David M. Wolock, U.S. Geological Survey, unpub. data, September 2001) using the Parameter-elevation Regressions on Independent Slopes Model (PRISM) (see <http://ocs.oce.orst.edu/prism/prism_new.html>) and compiled in a geographic information system to assess climate differences for wells in forest and rangeland. PRISM is a regression model that incorporates effects of terrain (land elevation and orientation) on climate predictions (Daly and others, 1994).

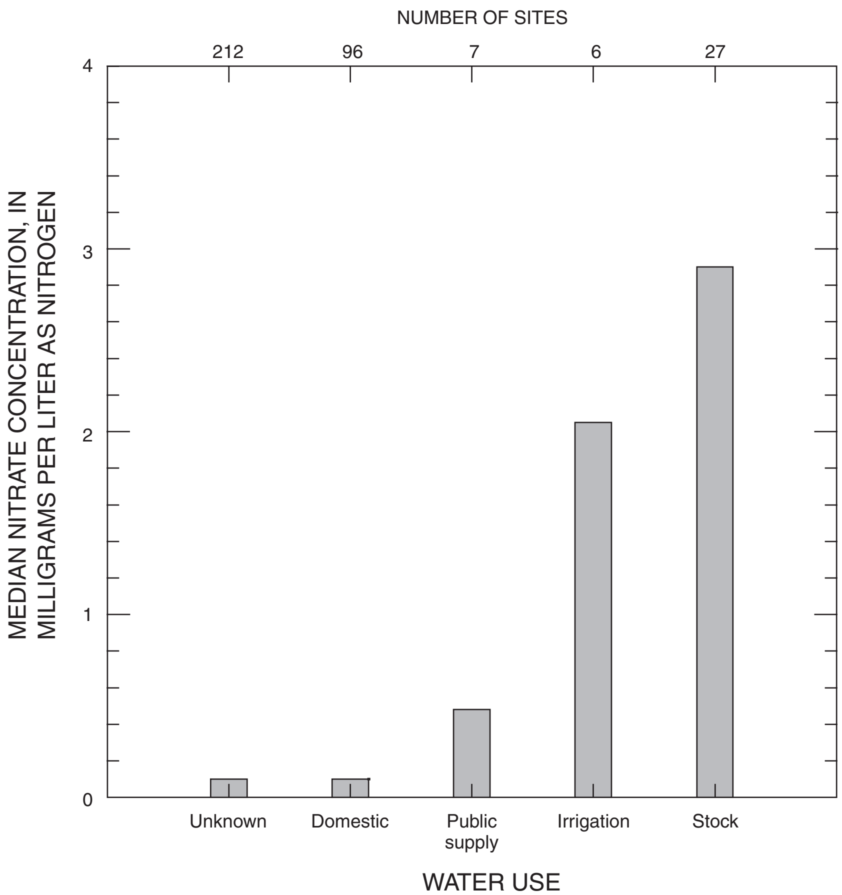

Figure 2. Relation between median nitrate concentration in ground water and water use for sites in the retrospective subset.

NUTRIENT CONCENTRATIONS IN GROUND WATER

Nutrient data from NAWQA studies were analyzed by land use to determine typical concentrations in ground water beneath agricultural, urban, and relatively undeveloped areas. The objective was to verify that nutrient concentrations are substantially lower in ground water beneath undeveloped land—compared with agricultural and urban lands—before determining land-use characteristics of undeveloped land. Median concentrations of ammonia, nitrite, and orthophosphate were about equal to or less than their respective detection limits, and differences in concentrations of these nutrients between land-use groupings statistically were insignificant (attained significance level, p, equals 0.438–0.949) (table 1). From this point on, nitrite plus nitrate is referred to as "nitrate" in this paper because nitrite concentration in NAWQA ground-water samples typically is negligible.

In contrast to the other nutrients, median nitrate concentration in ground water was significantly different (p equals 0.004) in agricultural (2.8 mg/L), urban (1.45 mg/L), and relatively undeveloped areas (0.06 mg/L). Tukey's test indicated that nitrate concentration in the relatively undeveloped areas was significantly lower than in agricultural and urban areas at the 0.05 level (fig. 3). Box plots labeled with different letters (for example, "A" and "B" for urban and undeveloped land uses) in figure 3 indicate that differences in nitrate concentration were statistically significant. The whiskers on the box plots extend to values within 1.5 times the interquartile range (75th percentile minus 25th percentile). Values outside this distance are outliers.

Median orthophosphate concentration is low (0.01 mg/L or less) for all three types of land-use studies (table 1). Phosphorus solubility and mobility in ground water are limited, and source strength is low for phosphorus compared with nitrogen. Estimated N loadings from animal manure and inorganic fertilizer are 3–5 times estimated phosphorus loading (Puckett, 1995).

LAND USE IN RELATIVELY UNDEVELOPED AREAS

Median nitrate concentration in ground-water samples from relatively undeveloped areas (0.06 mg/L) is only slightly greater than the method detection limit, suggesting that these areas are minimally affected by human activity. Land-use characteristics of relatively undeveloped land were evaluated for screening the overall NAWQA data sets, to identify additional wells for determining relative background concentrations of nutrients. Among NAWQA land-use studies, the relatively undeveloped areas had the smallest mean percentages of agricultural and urban lands (about 8 and 4 percent, respectively) and a high percentage of forest land (just over two-thirds or 69 percent), indicating minimal human influence (table 2). Mean percentage of rangeland was about 4 percent in the relatively undeveloped areas. All wells completed in unconfined aquifers of the relatively undeveloped areas were less than 30 meters deep, and median well depth was about 6 meters.

Although rangeland was not studied by NAWQA study units starting in 1991 and 1994, it could indicate relative background conditions for

Table 1. Median concentrations of nutrients in samples from National Water-Quality Assessment Program land-use studies of shallow, recently recharged ground water

[<, less than; MDL, method detection limit; mg/L, milligrams per liter; N, nitrogen; p-value, attained significance level; P, phosphorus]

Nutrient	MDL (mg/L)	Predominant land use			Land-use comparison p-value
		Agriculture	Urban	Undeveloped	
Ammonia as N (mg/L)	0.01–0.02[a]	0.02	0.03	0.03	0.586
Nitrite as N (mg/L)	0.01	<0.01	<0.01	<0.01	0.438
Nitrite plus nitrate as N (mg/L)	0.05	2.80	1.45	0.06	0.004
Orthophosphate as P (mg/L)	0.01	0.01	<0.01	0.01	0.949

[a]Ammonia method has multiple detection limits.

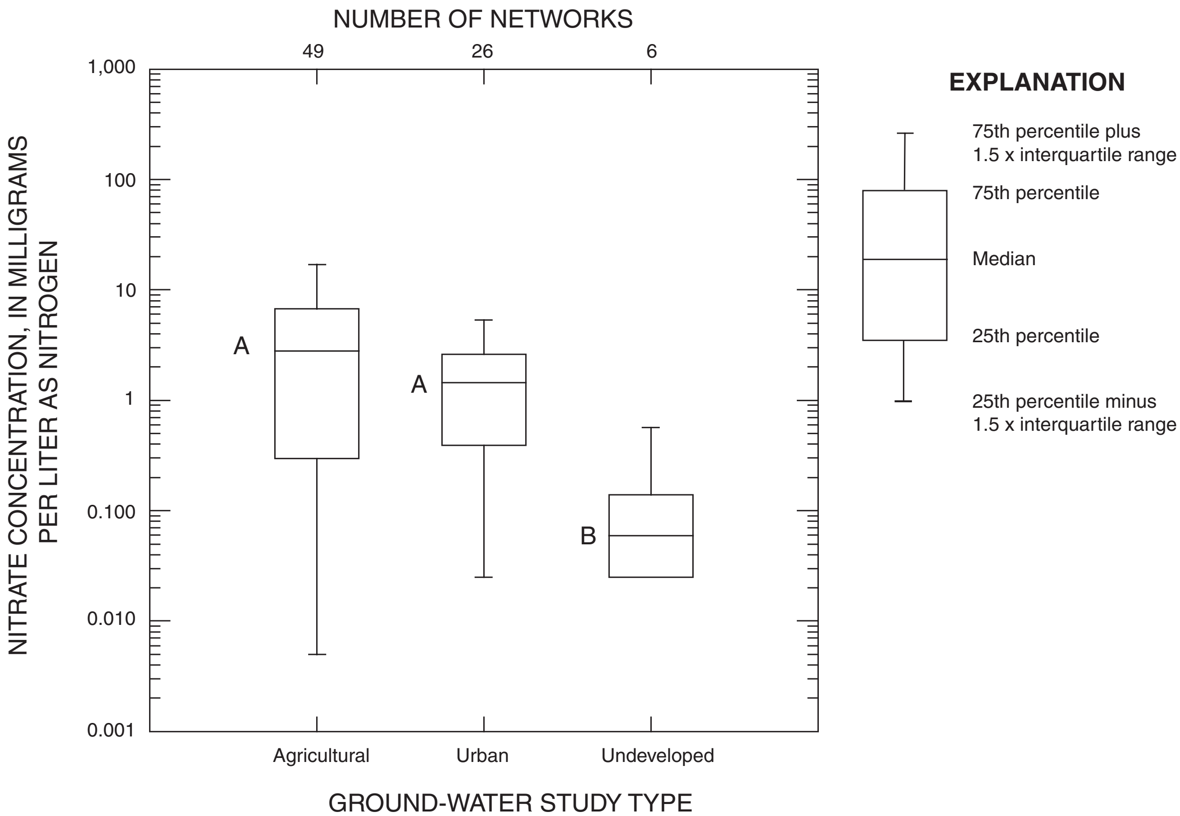

Figure 3. Relation between nitrate concentration in ground water and type of land-use study for National Water-Quality Assessment Program data collected during 1993–98. Box plots labeled with different letters ("A" and "B") indicate statistically significant differences in nitrate concentration.

nitrate in reference to agricultural and urban land use. For this reason, a two-thirds land-cover threshold—used here to indicate predominant land use near a well—was applied to both forest land and rangeland. Relative background criteria were defined as 67 percent or greater forest land or rangeland, 10 percent or less agricultural land, and 10 percent or less urban land. These land-use characteristics were used to indicate water-quality conditions in areas that presently are minimally affected by human activity.

RELATIVE BACKGROUND CONCENTRATIONS OF NUTRIENTS IN GROUND WATER

Land-use characteristics of all shallow wells in both the NAWQA and retrospective data sets were compared with relative background criteria (67 percent or greater forest land or rangeland, 10 percent or less agricultural land, and 10 percent or less urban land) to identify additional wells for calculating percentiles of relative background concentration. The NAWQA data set yielded a subset of 81 sites relatively unaffected by agricultural and urban lands. Median nitrate concentration associated with ground-water samples in the NAWQA subset was 0.11 mg/L (table 3), which reflects mainly forest land; only 15 sites had 67 percent or greater of rangeland within 500 meters of sampled wells. Median concentrations of ammonia and orthophosphate in ground-water samples from this data subset were 0.04 and 0.01 mg/L, respectively. These concentrations were similar or equal to those of the relatively undeveloped NAWQA land-use studies, which had median ammonia and orthophosphate concentrations of 0.03 and 0.01 mg/L, respectively (table 1).

In contrast, 320 sites in the retrospective data set met relative background land-use criteria. Median nitrate concentration associated with ground-water samples in the retrospective subset was 0.10 mg/L (table 3), about the same as that obtained with the NAWQA subset (0.11 mg/L). The 75th percentile nitrate concentration (1.1 mg/L), however, is more than twice that of the NAWQA subset (0.51 mg/L). This difference might reflect the influence of rangeland sites in the retrospective subset. More than one-third (110) of the sites in the retrospective subset had 67 percent or greater rangeland within 500 meters of sampled wells.

The 75th percentile (1.1 mg/L) associated with the retrospective subset is a reasonable upper-bound estimate of relative background concentration of nitrate in shallow, recently recharged ground waters of the United States. This value is conservative; three-fourths of the retrospective subset samples had lower nitrate concentration. The 75th percentile value incorporates the influences of nominal N loads and hydrogeologic factors. These factors cause the relative background concentration of nitrate to vary considerably, as discussed in the next section.

The relative background concentration of nitrate (1.1 mg/L) is less than the background concentration (2 mg/L) in ground water reported by Mueller and Helsel (1996). The 1.1-mg/L value, however, agrees with the transitional concentration range (0.21–3.0 mg/L) reported by Madison and Brunett (1985). Nitrate concentration less than 0.2 mg/L was associated with natural background levels, and concentration greater than 3 mg/L indicated potential human influence (Madison and Brunett, 1985). The concept of relative background as used in this report is consistent with that of transitional concentration, which indicates natural background concentration plus some extraneous component.

The 75th percentile relative background concentration of nitrate (1.1 mg/L) is comparable to the 25th percentile concentration of nitrate (0.52 mg/L) in shallow, recently recharged ground water beneath agricultural and urban lands sampled by NAWQA study units that began in 1991 and 1994. The 25th percentile concentration in agricultural and urban areas is an alternative estimate of relative background—three-fourths of ground-water samples from these areas had nitrate concentration greater than 0.52 mg/L. The 0.52-mg/L value is within the transitional range (0.21–3.0 mg/L) reported by Madison and Brunett (1985). The remaining samples with nitrate concentration of 0.52 mg/L or less are presumed relatively unaffected by agricultural and urban land use.

Table 2. Mean percentage of selected land uses within 500 meters of sampled wells, and median well depth associated with National Water-Quality Assessment Program land-use studies of shallow, recently recharged ground water

Ground-water study type	Number of networks	Mean percent land use				Median well depth[a] (meters)
		Agriculture	Urban	Forest	Range	
Agricultural	49	86.5	2.0	5.7	2.8	9.8
Urban	26	7.3	83.5	5.2	1.7	8.2
Undeveloped	6	7.5	3.6	69.4	3.5	5.8

[a]Unconfined aquifers only.

Table 3. Relative background concentration of nitrate in ground water from shallow wells in predominantly undeveloped areas for the National Water-Quality Assessment Program and retrospective subsets

[mg/L, milligrams per liter]

Data set	Predominant land use	Number of wells	Nitrate concentration percentile (mg/L)		
			25th	50th	75th
NAWQA (1993–98)	Forest/range	81	<0.05	0.11	0.51
Retrospective (1970–92)	Forest/range	320	0.05	0.10	1.10
	Forest	235	0.05	0.06	0.43
	Range	85	0.13	1.20	2.30

Median concentrations of ammonia and orthophosphate were 0.02 and 0.01 mg/L, respectively, for ground-water samples from the retrospective subset; however, these statistics are based on 78 observations or less, compared with 320 nitrate values. Nitrate is emphasized in the remainder of this paper because it is the predominant nutrient in ground-water samples collected for the NAWQA land-use studies, and because comparatively few samples in the retrospective subset had ammonia and orthophosphate data.

VARIABILITY OF RELATIVE BACKGROUND CONCENTRATION OF NITRATE IN GROUND WATER

To explore the effect of land use on nitrate concentration in shallow ground water beneath relatively undeveloped areas, data in the retrospective subset were stratified by predominant land use, forest or range. Median nitrate concentration in shallow ground water beneath forested areas and rangeland was 0.06 mg/L and 1.20 mg/L, respectively (table 3). A Wilcoxon rank-sum test indicated that this difference was highly significant (p less than 0.001). Although natural sources of N accumulate in forested land, conversion of ammonium to nitrate (a two-step process called nitrification) requires aerobic conditions (Speiran, 1996). Reducing conditions in forested areas comprising portions of Virginia, West Virginia, Maryland, and Pennsylvania likely inhibit conversion of ammonium derived from organic N to nitrate (Ator and Denis, 1997). The spatial distribution of wells in the retrospective subset relative to forest land and rangeland is shown in figure 4.

The difference in nitrate concentration in ground water beneath forest and rangeland also could be influenced by differences in N loading, natural sources of N, or other factors such as climate. To assess differences in N load, total N within 500 meters of wells in the retrospective subset was stratified by predominant land use (forest or range). Nitrogen load estimates used in this study, however, do not explain the higher nitrate concentration found in ground water beneath rangeland. Median total N load was estimated as 4.5 kilograms per hectare (kg/ha) in forested areas but only 1.9 kg/ha in rangeland areas (Wilcoxon rank-sum p is less than 0.0001) (fig. 5). These N loads are dominated by atmospheric inputs; median N loads from atmospheric sources were estimated as 4.0 and 1.9 kg/ha, respectively, for forest and rangeland. The forested sites primarily are in the eastern United States and coincide with areas of high estimated N load by atmospheric deposition (fig. 1).

The median total N loads reflect the weighting method used to allocate N sources in this study. Neither fertilizer N nor manure N was allocated to rangeland; fertilizer N was allocated to selected agricultural and urban land, and manure N to cropland-pasture and confined feeding operations. Manure N was not allocated to rangeland because it was assumed that manure amounts from free-ranging cattle would be negligible compared with amounts in confined feedlots and manure recovered and spread on cropland.

Nitrate concentration in shallow ground water beneath rangeland might be derived from natural geologic sources such as exchangeable ammonium in till or loess deposits, or, if derived from sources at the land surface, then nitrate concentration likely is affected by hydrogeologic factors such as rock fractures. Rangeland sites in the retrospective subset were stratified by surficial geology to test the potential effect of geology on nitrate concentration in shallow ground water. The analysis used only those surficial geology units with five or more rangeland observations in the retrospective subset (table 4). The source of the surficial geology data was a 1:7,500,000-scale map published as part of the USGS National Atlas map series (Hunt, 1979). Median nitrate concentration and median total N load for the seven surficial geology groups with five or more sites classified as rangeland are shown in figure 6. Of these, five units had median nitrate concentration greater than 1 mg/L (about the 75th percentile for the retrospective subset): flood plain and alluvium gravel terraces (1.4 mg/L), basalt (1.5 mg/L), sand sheets (1.7 mg/L), Wisconsinan loess (1.7 mg/L), and fan gravels (2.7 mg/L). Median total N load was low (1.6–3.8 kg/ha) for these five groups and was dominated by atmospheric inputs.

Elevated nitrate concentration (greater than 1 mg/L) associated with four of the groups (flood plain and alluvium gravel terraces, basalt, sand sheets, and fan gravels) likely is attributable to interaction of nominal N load with coarse-textured deposits or rock fractures. The highest median nitrate concentration (2.7 mg/L) occurred in ground water associated with fan gravel deposits (fig. 6). Although median total N load is low (1.9 kg/ha), coarse-grained deposits can readily

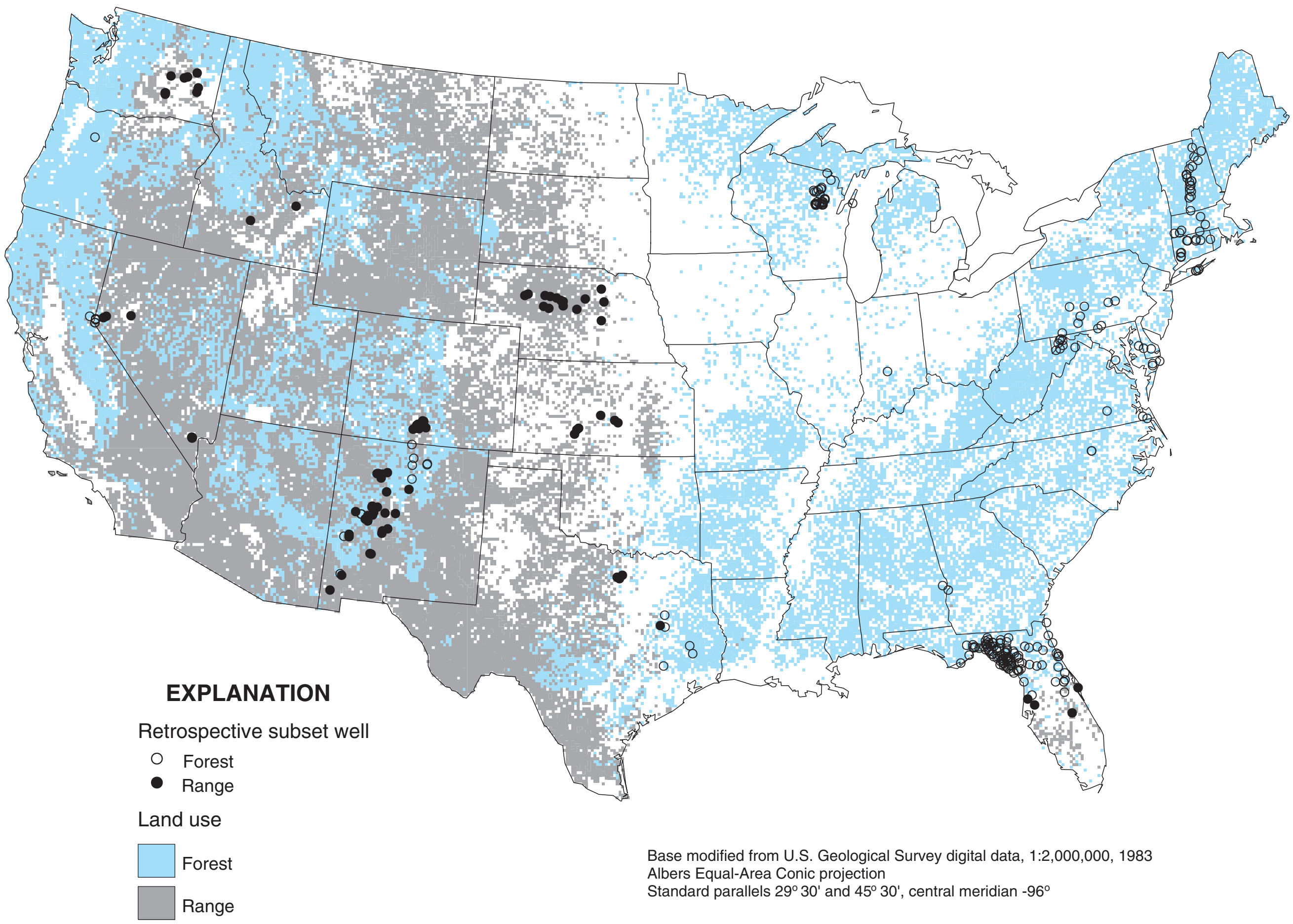

Figure 4. Distribution of sites in the retrospective subset with respect to forest and rangeland.

convey water and chemicals to ground water. In contrast, fine-grained, poorly drained soils commonly are anaerobic, which promotes denitrification. Mueller and others (1995) analyzed retrospective data from shallow wells in agricultural areas and reported that median nitrate concentration in ground water was 4.7 mg/L beneath well-drained soils and 0.17 mg/L beneath poorly drained soils. Nolan and Stoner (2000) reported that comparatively small N load (less than 65 kg/ha) was related to high nitrate concentration in ground waters (4 mg/L or more) of agricultural areas with fractured rock or well-drained soils that facilitate nitrate leaching. Median nitrate concentration in ground water beneath agricultural land generally increased with increasing percentage of well-drained soils. These same processes would tend to increase nitrate concentration in ground water beneath flood plain and alluvium gravel terraces (median nitrate concentration equals 1.4 mg/L). Retrospective subset samples in rangeland associated with fan gravel deposits are located in western New Mexico and southeastern Nevada, and those associated with flood plain and alluvium gravel terraces are located in central Nebraska and western New Mexico (fig. 7). For clarity of presentation, only surficial geology units representing five or more sites and having nitrate concentration generally greater than 1 mg/L are shown in figure 7. Surficial units not shown—gravel, sand, and clay deposited by glacial streams, for example—potentially have high ground-water nitrate concentration in areas with high nitrate loading. Relative background concentration of nitrate in such areas, however, generally was less than 0.4 mg/L, presumably because of minimal anthropogenic and(or) natural sources of N.

High nitrate concentration in basalt aquifers (median nitrate concentration equals 1.5 mg/L) can result from fractures that convey water and chemicals downward through the subsurface. Ground water in the basalt aquifer underlying irrigated agricultural areas of the eastern Snake River Plain, Idaho, contained elevated nitrate concentrations (Rupert, 1997). Within the basalt aquifer, the highest nitrate concentration (75th percentile greater than 5 mg/L) was found where ground water is pumped to the land surface and used for irrigation; irrigation water containing elevated concentrations of major ions and nitrate percolates back to ground water and mixes with native water. Retrospective subset samples in rangeland associated with basalt are located in southeastern Idaho, eastern Washington, and western New Mexico (fig. 7).

High median nitrate concentration associated with sand sheets (1.7 mg/L) seems to reflect the combined effect of coarse-textured soils and nominal N load from natural sources. Retrospective subset samples in rangeland associated with sand sheets are located primarily in northwestern Nebraska (fig. 7) in the sand hills area adjacent to areas with natural sources of nitrate, described by Boyce and others (1976). The sand hills have been grazed by domestic cattle since the area was settled, and bison once were numerous in the area. In a study of the High Plains aquifer (Litke, 2001), historical ground-water samples from the sand hills of Nebraska had a median nitrate concentration of 2.4 mg/L, which is comparable to the value for sand sheets (1.7 mg/L) in the current study. The High Plains study area encompasses most of Nebraska, and portions of Kansas, New Mexico, Oklahoma, South Dakota, Texas, and Wyoming. Background concentration of nitrate in paleorecharge to the High Plains aquifer ranged from 2.3 to 4.1 mg/L (McMahon and Böhlke, 2001). Analysis of nitrogen isotope ($\delta^{15}N$) data indicated that the N source is natural and consistent with a mixture of plant matter, exchangeable ammonium, and animal manure (Peter B. McMahon and Johnkarl Böhlke, U.S. Geological Survey, unpub. data, September 2002).

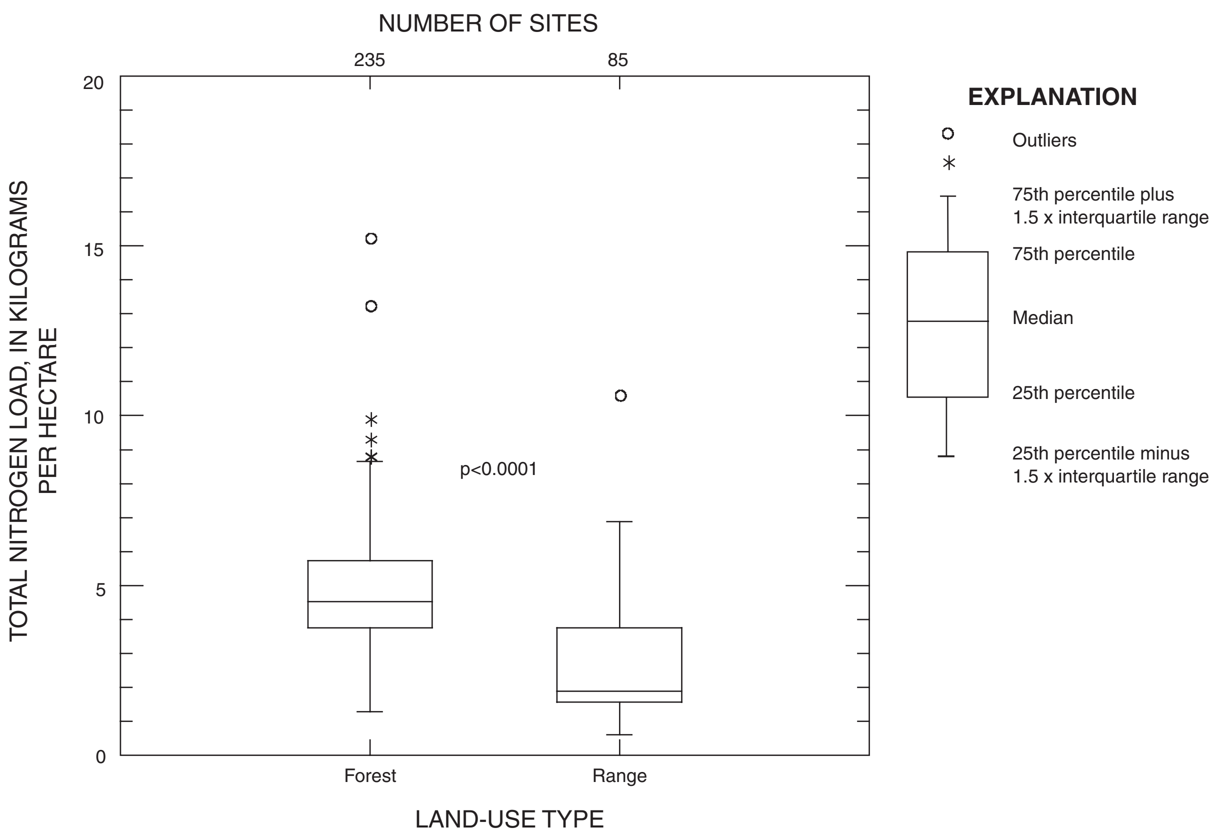

Figure 5. Relation between nitrogen load from fertilizer, manure, and atmospheric deposition and predominant land use for sites in the retrospective subset.

Table 4. Surficial geology units with five or more rangeland observations in the retrospective subset

Term used in figure 6	Corresponding surficial geology unit in Hunt (1979)
Shaley or sandy	Shaley or sandy ground; on mixed sandstone and shale formations; where shaley, contains considerable swelling clay.
Lake deposits	Lake deposits.
Flood plain—alluvium	Flood plain and alluvium gravel terraces.
Basalt	Basalt.
Sand sheets	Sand sheets, mostly with dunes or sand mounds at surface.
Wisconsinan loess	Wisconsinan loess.
Fan gravels	Fan gravels.

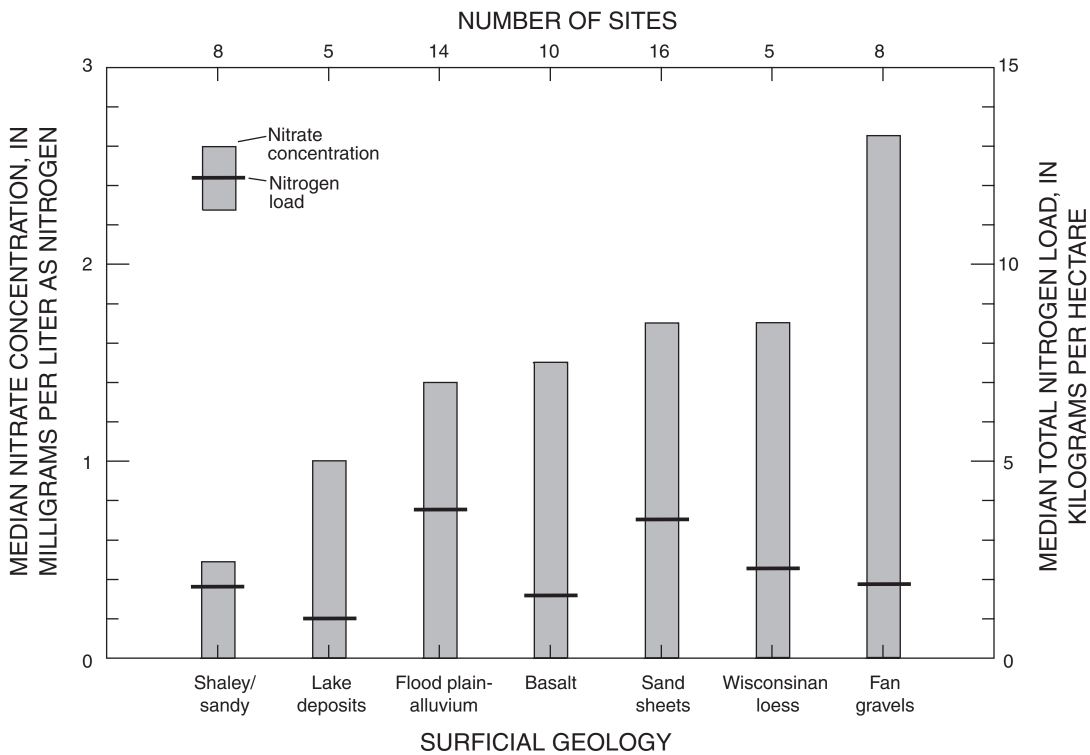

Figure 6. Relation between median nitrate concentration in ground water, surficial geology, and median nitrogen load from fertilizer, manure, and atmospheric deposition for rangeland sites in the retrospective subset. Surficial geology units representing five or more rangeland sites are shown.

Nitrogen from mineral sources is released from sandy soils in some areas. The sand fraction of A and C soil horizons that formed on slate in central California contained 978–1,121 mg/kg of N, much of which was released during a laboratory weathering experiment (Holloway and others, 1998). The N content of the sand about equaled or exceeded that of the silt fraction (950–983 mg/kg N). The soil samples were treated with hydrogen peroxide before measuring N concentration to remove soil organic matter to determine the amount of N contributed by the slate. A mass balance calculated for rock, saprolite, and soil fractions indicated that much of the N is released during transformation of rock to soil in the area.

High median nitrate concentration associated with Wisconsinan loess (1.70 mg/L) is more difficult to explain by leaching because loess deposits commonly are fine grained and might be related to natural geologic sources of N, range animals, or a combination of these factors. Native fixed ammonia and organic matter in deep loess deposits apparently contributed high nitrate concentration to upland soils in south-central Nebraska (Boyce and others, 1976). Strong negative correlation between fixed ammonium and nitrate in soil samples suggested release of ammonium from clay and subsequent nitrification. Nitrate in the soil samples, however, was enriched in $\delta^{15}N$ relative to ammonium, indicating that at least some of the nitrate was derived from an organic source. Retrospective subset samples in rangeland associated with Wisconsinan loess are located in southeastern Washington (fig. 7).

Evaporative processes can cause nitrate concentration as high as 1,900 mg/L (wet basis) in soils of the High Plains (Kevin F. Dennehy, U.S. Geological Survey, unpub. data, January 2001). Soil disturbance followed by irrigation or precipitation can readily transmit nitrate from natural sources to the water table in such areas. Precipitation and potential evapotranspiration (PE) data were compiled for wells in forest and rangeland areas, and PE was subtracted from precipitation to estimate the net downward flux (PMPE) of water. Median PMPE was 35.6 centimeters per year (cm/yr) in forested areas and –27.9 cm/yr in rangeland, indicating potential for upward water movement and evaporative concentration of nitrate in the latter areas (fig. 8). A Wilcoxon rank-sum test indicated that this difference is highly significant (p less than 0.0001).

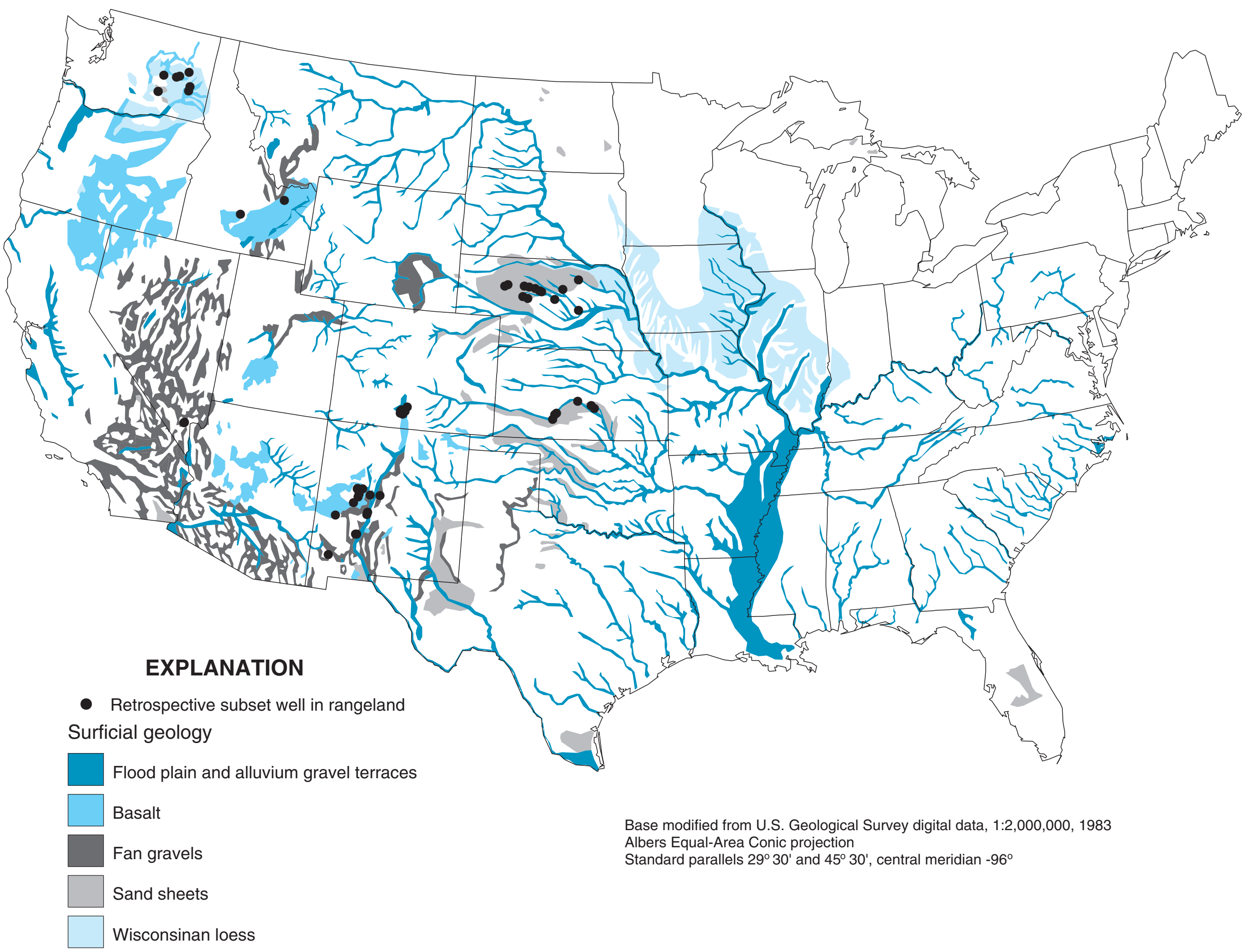

Figure 7. Locations of rangeland sites in the retrospective subset for surficial geology units that had median nitrate concentration greater than 1 milligram per liter. Surficial geology units representing five or more rangeland sites are shown.

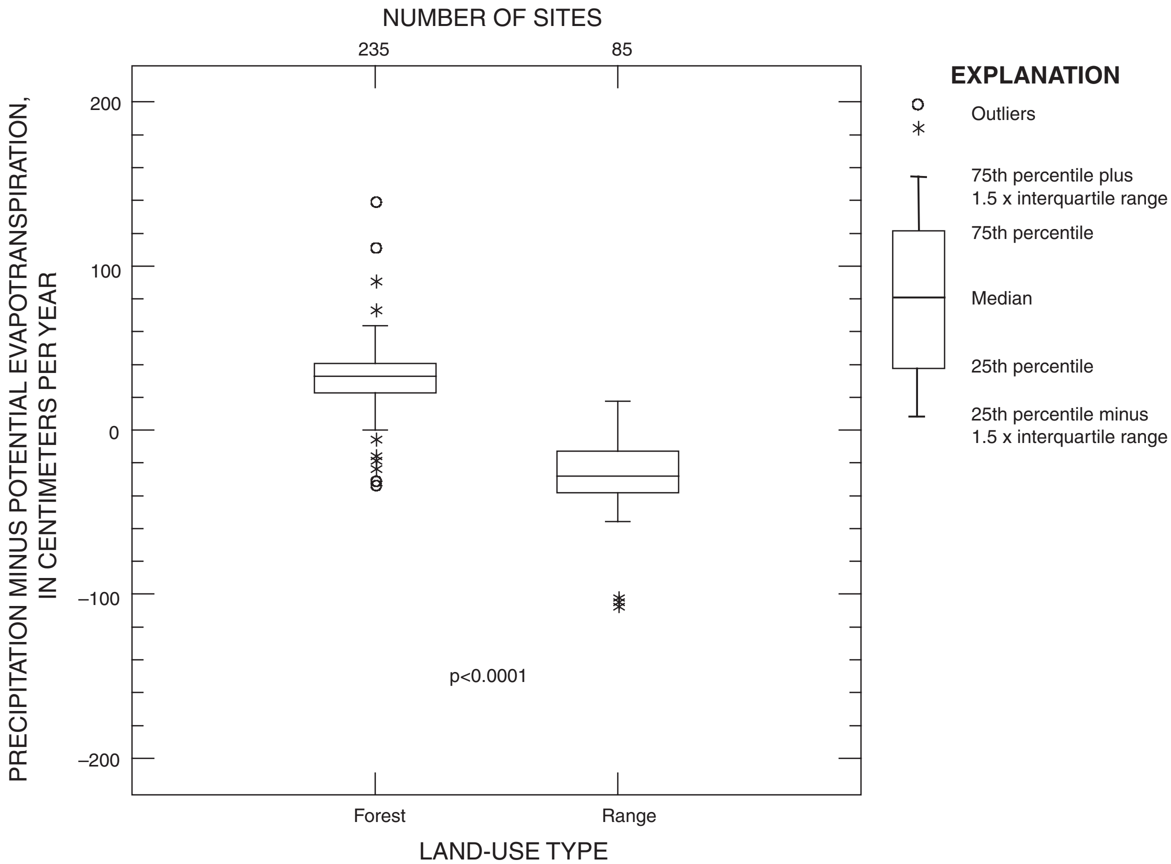

Figure 8. Relation between net downward flux of water and predominant land use for sites in the retrospective subset.

SUMMARY

The 75th percentile value (about 1 mg/L) obtained with the retrospective subset is a reasonable upper bound estimate of relative background concentration of nitrate in shallow, recently recharged ground waters of the conterminous United States. This value incorporates effects of nominal N load from predominantly natural sources in hydrogeologically susceptible areas mostly unaffected by agriculture and urban land. Additionally, the 1-mg/L value agrees with the range of nitrate concentration (0.21–3.0 mg/L) considered transitional between natural background and human-influenced concentrations in a previous study (Madison and Brunett, 1985). Relative background concentration of nitrate is variable, however, and depends in part on land use, hydrogeology, and climate. Study findings indicate the importance of establishing local background conditions. Retrospective data indicate that ground-water samples from rangeland areas had significantly higher relative background concentration of nitrate (median equals 1.2 mg/L) compared with forested areas (median equals 0.06 mg/L). Additionally, median nitrate concentration in ground water beneath rangeland was from 1.4 to 2.7 mg/L in hydrogeologically susceptible aquifers consisting mainly of coarse-textured deposits or fractured rock. Study results suggest that in rangeland areas, nitrate from predominantly natural sources of N is concentrated by evapotranspiration and migrates to shallow ground water through coarse-grained sediments or rock fractures.

The relative background concentration of 1 mg/L is an order of magnitude less than the U.S. Environmental Protection Agency (USEPA) maximum contaminant level (MCL) of 10 mg/L for nitrate and provides a useful basis for assessing anthropogenic effects on shallow ground-water quality, especially when local background data are unavailable. Management for prevention of ground-water contamination is more feasible and much less costly than if MCLs already have been exceeded. Nitrate is a naturally occuring substance. Relative background concentration is particularly useful for nitrate because, compared with synthetic chemicals such as pesticides, mere detection of nitrate does not trigger an immediate water-quality concern. Rather, nitrate concentration greater than about 1 mg/L suggests greater influence by anthropogenic factors and the need for additional monitoring to protect water resources. Relative background concentrations of ammonia (median equals 0.02–0.04 mg/L) and orthophosphate (median equals 0.01 mg/L) were well below levels of environmental concern in this study.

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