Decadal-Scale Changes of Nitrate in Ground Water of the United States, 1988–2004

Michael G. Rupert* USGS

This study evaluated decadal-scale changes of nitrate concentrations in ground water samples collected by the USGS National Water-Quality Assessment Program from 495 wells in 24 well networks across the USA in predominantly agricultural areas. Each well network was sampled once during 1988–1995 and resampled once during 2000–2004. Statistical tests of decadal-scale changes of nitrate concentrations in water from all 495 wells combined indicate there is a significant increase in nitrate concentrations in the data set as a whole. Eight out of the 24 well networks, or about 33%, had significant changes of nitrate concentrations. Of the eight well networks with significant decadal-scale changes of nitrate, all except one, the Willamette Valley of Oregon, had increasing nitrate concentrations. Median nitrate concentrations of three of those eight well networks increased above the USEPA maximum contaminant level of 10 mg L^{-1}. Nitrate in water from wells with reduced conditions had significantly smaller decadal-scale changes in nitrate concentrations than oxidized and mixed waters. A subset of wells had data on ground water recharge date; nitrate concentrations increased in response to the increase of N fertilizer use since about 1950. Determining ground water recharge dates is an important component of a ground water trends investigation because recharge dates provide a link between changes in ground water quality and changes in land-use practices.

Nitrate (nitrite plus nitrate as nitrogen, $NO_2 + NO_3$–N) is the most common chemical contaminant in the world's ground water aquifers (Spalding and Exner, 1993). The USEPA (2002) has established a maximum contaminant level of 10 mg L^{-1} nitrate as N because of concerns that ingestion of nitrate in drinking water by infants can cause low oxygen levels in their blood. High concentrations of nitrate in drinking water also may be implicated with a high incidence of non-Hodgkin's lymphoma (Weisenburger, 1991, p. 309). Recent studies indicate possible adverse effects at nitrate levels less than the maximum contaminant level (Brender et al., 2004a; Brender et al., 2004b; DeRoos et al., 2003). Long-term exposure to nitrate at concentrations of 2 to 4 mg L^{-1} in community water supplies has possible links to bladder and ovarian cancer (Weyer et al., 2001) and non-Hodgkins lymphoma (Ward et al.,1996).

The largest source of anthropogenic N is fertilizer. Other major sources include animal and human waste, N oxides from utilities and automobiles, and leguminous crops that fix atmospheric N_2 in the soil (Vitousek et al., 1997; Fields, 2004). Before the World War I, the primary sources of supplemental N for crops were animal manure, mineral sources such as potassium nitrate, and crop rotation with legume crops such as alfalfa (*Medicago sativa* L.). Synthetic fertilizers were first produced after World War I, when facilities that had produced ammonia and synthetic nitrates for explosives were converted to the production of N-based fertilizers (Thomson, 2005). Inorganic N fertilizer production was small until after World War II, when the production rates increased dramatically. Nationally, use of N fertilizer has increased rapidly from 1950 through about 1980 and then increased at a slower rate since about 1980.

Numerous studies have documented elevated nitrate concentrations in ground water in many parts of the globe, but only a few studies have determined if nitrate concentrations in ground water are increasing or decreasing with time. Reynolds-Vargas et al. (2006) found that nitrate concentrations of the western Central Valley of Costa Rica increased during a 17-yr time period due to inadequate waste disposal and fertilization of coffee crops. Wassenaar et al. (2006) observed increasing nitrate concentrations in young ground water (<5 yr) of the transboundary Abbotsford–Sumas aquifer of Canada. Broers and van der Grift (2004) reported no temporal trends of nitrate concentrations in the Dutch province of Noord-Brabant, the Netherlands, probably due to nitrate reduction by oxidation of pyrite and organic matter. Rosen (1999) and Close et al. (2001) did not observe any significant trends of nitrate concentrations of ground water in New Zealand, but

Copyright © 2008 by the American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America. All rights reserved. No part of this periodical may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher.

Published in J. Environ. Qual. 37:S-240–S-248 (2008).
doi:10.2134/jeq2007.0055
Received 30 Jan. 2007.
*Corresponding author (mgrupert@usgs.gov).
© ASA, CSSA, SSSA
677 S. Segoe Rd., Madison, WI 53711 USA

M.G. Rupert, U.S. Geological Survey, 201 East 9th St., Pueblo, CO 81003.

Abbreviations: LOWESS, locally weighted scatterplot smoothing; NAWQA, U.S. Geological Survey National Water-Quality Assessment Program; USEPA, U.S. Environmental Protection Agency; USGS, U.S. Geological Survey.

they noted long-term records are hard to come by and are nonexistent in some parts of the country. Ball and MacDonald (2001) reported increasing concentrations of nitrate concentrations in ground water in Scotland. Knapp (2005) reported that increasing concentrations of nitrate in ground water in the UK has resulted in the need to treat or blend water from public supply wells, and in some cases to take them out of service. Bolger and Stevens (1999) did not observe clearly identifiable trends of nitrate concentrations of ground water in Australia, but they noted a very scattered approach to data collection made analysis of nitrate trends difficult. Drake and Bauder (2005) reported increasing nitrate concentrations from 1971 through 2003 near Helena, MT, and attributed the increasing nitrate concentrations to increased urbanization and increasing subsurface disposal of domestic wastewater. Brendle (1997) compared nitrate concentrations sampled during 1984 and 1996 in the alluvial aquifer of the Upper Black Squirrel Creek Basin of east-central Colorado and identified one area where the nitrate concentrations did not change, and another area where nitrate concentrations increased. Brendle (1997) did not identify the source of the increasing nitrate. Rosen (2003) and Shipley and Rosen (2005) observed increasing nitrate concentrations in ground water in Carson Valley, NV, from 1985 through 2001, and attributed the increasing nitrate to the increase of subsurface domestic wastewater disposal in the area. Parliman (2002) evaluated trends of nitrate concentrations in ground water from 25 ground water quality management areas distributed across Idaho, and identified areas with increasing and decreasing concentrations of nitrate from 1961 through 2001.

To date, there has been no comprehensive study to determine if nitrate concentrations in ground water of the United States have increased or decreased with time. Previous studies in the United States have focused on small, localized areas. To fill this void, this study evaluated the changes (trends) of nitrate concentrations in ground water in agricultural areas in the United States at the national scale.

U.S. Geological Survey National Water-Quality Assessment Program

The study described in this paper evaluates ground water monitoring data collected by the U.S. Geological Survey's National Water-Quality Assessment Program (NAWQA; http://water.usgs.gov/nawqa; verified 9 Aug. 2007) between 1988 and 2004 to determine if nitrate concentrations in ground water of selected areas in the United States have increased or decreased. Between 1988 and 2001, NAWQA completed ground water, surface water, and aquatic assessments in 51 study units across the United States. During 2000, NAWQA began revisiting many of those study units to determine if ground water quality, surface water quality, and aquatic ecology have changed over time. This paper describes an interim evaluation of nitrate data collected as of 30 Sept. 2004. Refer to Rosen et al. (2008) of this issue for more details on the NAWQA ground water monitoring design.

The overall objective of this study was to evaluate the changes (trends) of nitrate concentrations in ground water sampled from 14 selected study units in the United States through investigation of water quality and ancillary data at the national scale.

Materials and Methods

In several resampled well networks, not all 30 wells could be resampled because some wells were destroyed or the well ownership changed. Well networks with fewer than 10 wells sampled on a decadal-scale time period were eliminated from this analysis to allow for valid statistical comparisons between well networks. Emphasis was on trends in agricultural areas. Data analysis focused on nitrite + nitrate as N (nitrate). The full-scale implementation of the program began in 1991, but a pilot project in the Delmarva Peninsula of Delaware, Maryland, and Virginia was initiated during the late 1980s; this study included ground water monitoring data collected in the Delmarva Peninsula during 1988 and 1990 because the data were collected using similar sampling and laboratory methods as the NAWQA data collected after 1991.

Ground Water Quality Data

All ground water quality data evaluated by this study were analyzed by the USGS National Water Quality Laboratory using standard methods (Fishman, 1993). Ground water quality data were retrieved from the USGS NAWQA Data Warehouse (http://infotrek.er.usgs.gov/traverse/f?p=NAWQA:HOME:3476068124949793; verified 16 Aug. 2007), which is a database housing all water quality data and selected ancillary data collected in association with the NAWQA program. Data were retrieved during October 2004 for calendar years 1988 through 2004. The data were sorted by well network, and sampling events on decadal-scale time periods were identified. In most cases, the month of sample collection during the first decadal-scale sampling event was within plus or minus 3 mo of the month of sample collection during the second decadal-scale sampling event to minimize potential seasonal differences. The interval between sampling events ranged from 7 to 13 yr, and the average interval between sampling events was 8 yr (Table 1). Fourteen study units had sufficient decadal-scale nitrate data for evaluation by this study (Fig. 1, Table 1).

Ancillary Data

Ancillary data used by this study include data on aquifer lithology, fertilizer use, ground water age, manure production, and well properties. Refer to Rosen and Lapham (2008) for more details on the ancillary data used by this study.

Statistical Methods

The Kruskal–Wallis and Wilcoxon rank–sum nonparametric statistical tests (Ott, 1993) were used to determine whether there were statistically significant differences in nitrate concentrations among samples from wells in various groups, as, for example, those with oxidized conditions or reduced conditions. The Sign test and Wilcoxon signed-rank tests (Helsel and Hirsch, 1992) were used to determine if there was a statistically significant change in nitrate concentrations in paired samples collected from individual wells between the decadal-scale sampling events. The

Table 1. Nitrate concentrations in ground water in selected well networks measured during the first and second decadal-scale sampling events, 1988–2004. See Fig. 1 for locations.

NAWQA Study unit†	Type of well network‡	Well network name used by NAWQA§	Well network identifier used in Fig. 3	No. of wells sampled during both sampling events	Year of first sampling event	Median nitrate conc. from first sampling event	Year of second sampling event	Median nitrate conc. from second sampling event	No. of years between each decadal-scale sampling event	Median difference of nitrate conc. from first sampling event to second sampling event	Sign test *p* value of difference between first and second sampling events	Wilcoxon signed-rank test *p* value of difference between first and second sampling events
Apalachicola–Chattahoochee–Flint Basin (acfb)	**LUS**	**acfbluscr3**	**A**	**18**	**1993**	**1.35**	**2002**	**1.86**	**9**	**0.25**	**0.031¶**	**0.053¶**
Apalachicola–Chattahoochee–Flint Basin (acfb)	**MAS**	**acfbsus1**	**B**	**20**	**1995**	**1.93**	**2002**	**2.56**	**7**	**0.31**	**0.12**	**0.067¶**
Central Columbia Plateau (ccpt)	LUS	ccptlusag2b	C	18	1994	9.70	2002	11.43	8	−1.35	0.24	0.27
Central Columbia Plateau (ccpt)	LUS	ccptlusor1b	D	20	1994	5.65	2002	6.92	8	−0.08	1.00	0.71
Central Columbia Plateau (ccpt)	MAS	ccptsus1b	E	30	1994	0.92	2002	1.99	8	0.02	0.44	0.39
Delmarva Peninsula (dlmv)	LUS	dlmvluscr1	F	12	1988	4.65	2001	6.78	13	−0.08	0.77	0.70
Delmarva Peninsula (dlmv)	**MAS**	**dlmvsus1**	**G**	**12**	**1988**	**8.60**	**2001**	**11.68**	**13**	**3.40**	**0.039¶**	**0.006¶**
Georgia–Florida Coastal Plain (gafl)	LUS	gaflluscr1	H	20	1994	6.25	2002	7.55	8	0.84	0.26	0.13
Nevada Basin and Range (nvbr)	MAS	nvbrsus2	I	16	1995	0.89	2003	0.93	8	0.03	1.00	0.65
Potomac River Basin (poto)	LUS	potolusag1	J	24	1993	4.30	2002	5.38	9	−0.09	0.31	0.15
Rio Grande Valley (riog)	LUS	riogluscr1	K	33	1993	3.00	2000	3.10	7	0.00	1.00	0.89
San Joaquin–Tulare Basins (sanj)	**LUS**	**sanjluscr1a**	**L**	**18**	**1995**	**5.45**	**2002**	**7.04**	**7**	**1.00**	**0.24**	**0.078¶**
San Joaquin–Tulare Basins (sanj)	LUS	sanjlusor1a	M	17	1993	4.60	2001	3.79	8	0.07	0.63	0.98
San Joaquin–Tulare Basins (sanj)	LUS	sanjlusor2a	N	19	1994	9.90	2001	10.80	7	0.62	0.36	0.36
San Joaquin–Tulare Basins (sanj)	MAS	sanjsus1	O	25	1995	3.40	2002	5.40	7	0.45	0.52	0.24
South Platte River Basin (splt)	**LUS**	**spltluscr1**	**P**	**29**	**1994**	**9.20**	**2002**	**10.32**	**8**	**2.03**	**0.026¶**	**0.013¶**
Trinity River Basin (trin)	MAS	trinsus3	Q	16	1994	0.05	2002	0.05	8	0.00	0.73	0.89
Upper Snake River Basin (usnk)	**LUS**	**usnkluscr2&3**	**R**	**13**	**1994**	**1.70**	**2002**	**1.89**	**8**	**0.13**	**0.092¶**	**0.013¶**
Upper Snake River Basin (usnk)	MAS	usnksus1	S	21	1994	1.50	2003	1.43	9	0.04	0.66	0.69
Upper Snake River Basin (usnk)	MAS	usnksus2	T	19	1995	0.63	2004	0.65	9	0.06	0.36	0.41
White River Basin (whit)	LUS	whitluscr1	U	20	1994	0.05	2002	0.05	8	0.00	0.51	0.52
Willamette Basin (eill)	**LUS**	**willlusag3**	**V**	**24**	**1993**	**0.29**	**2002**	**0.14**	**9**	**−0.03**	**0.24**	**0.035¶**
Western Lake Michigan Drainage (wmic)	**LUS**	**wmiclusag2**	**W**	**26**	**1994**	**7.20**	**2002**	**11.29**	**8**	**0.84**	**0.42**	**0.088¶**
Western Lake Michigan Drainage (wmic)	MAS	wmicsus1	X	25	1995	0.05	2002	0.05	7	0.00	0.75	0.39

† NAWQA, U.S. Geological Survey National Water-Quality Assessment Program.

‡ LUS, NAWQA Land-Use Study designed to assess ground water quality at intermediate scales in selected land use and hydrogeologic conditions; MAS, NAWQA Major Aquifer Study (formerly known as Study Unit Survey [sus]) designed to sample wells widely distributed across the study unit to broadly characterize ground water quality at large regional scales.

§ The first four letters in the name indicate the study unit, the next three letters indicate if the network is a lus or mas (sus), and the remaining letters are unique identifiers.

¶ Significant at the 90% confidence level or greater.

Wilcoxon signed-rank test is similar to the Sign test, but provides more information because it takes into account the relative magnitude of the difference between sampling events. All four nonparametric tests calculate a p value; if the resulting p value is <0.1, the data sets are "significantly" different at the 90% confidence level or greater. The Locally Weighted Scatterplot Smoothing method (LOWESS) (Helsel and Hirsch, 1992) was used to show the central tendency of data in x–y scatter plots.

Ground Water Age Dating

The ground water recharge date (year of ground water recharge) was determined for water from a subset of wells examined by this study (Table 2). Most recharge dates were determined using chlorofluorocarbons (Busenberg and Plummer, 1992; Plummer et al., 1993), but the recharge date of water from 10 wells from the Central Columbia Plateau and 24 wells from the Delmarva Peninsula was determined using sulfur hexafluoride (Busenberg and Plummer, 2000). The recharge date, when based on measurement of the concentration of chlorofluorocarbons or sulfur hexafluoride in water, is based on the time elapsed since isolation of the newly recharged water from the atmosphere.

Quality Assurance and Quality Control of Nitrate Data

Quality assurance/quality control data were examined to determine if nitrate concentrations measured during the first decadal-scale sampling event (1988–1995) can be compared to nitrate concentrations measured during the second decadal-scale sampling event (2000–2004). Laboratory methods and their laboratory reporting levels were examined to ensure they have not significantly changed from 1988 through 2004. Blind spike data collected and analyzed by the USGS Inorganic Blind Sample Program were reviewed to ensure the National Water Quality Laboratory was reporting unbiased nitrate concentrations.

Laboratory Reporting Levels

From 1988 through 1990, the minimum laboratory reporting level for nitrate was 0.1 mg L^{-1}. From 1991 through 2004, the minimum laboratory reporting level was decreased to 0.05 mg L^{-1}. Because the nitrate data were reported at two different minimum laboratory reporting levels, the data had to be adjusted before trends analysis. Only two well networks located in the Delmarva Peninsula were sampled before 1991. Nitrate data from 13 wells in the Delmarva Peninsula were reported as nondetections at 0.1 mg L^{-1}. To make all nitrate data in the data set comparable, data from these wells were deleted from this trends analysis. Nitrate concentrations in water from all remaining wells in the Delmarva Peninsula sampled from 1988 through 1990 were detections at concentrations much larger than 0.1 mg L^{-1}, so they were used in this trends analysis. This procedure maintained the greatest number of analyses and provides the greatest statistical strength in subsequent statistical tests. Debrewer et al. (2008) also evaluated nitrate trends in the Delmarva Peninsula, but did not delete the wells with nondetections at 0.1 mg L^{-1} because the analysis was local in nature and did not need to censor the data for national consistency as this study did.

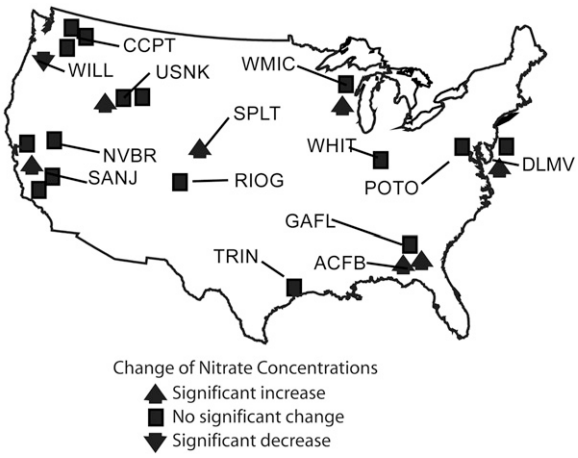

Fig. 1. Locations of U.S. Geological Survey National Water-Quality Assessment Program study units and well networks with and without significant decadal-scale trends of nitrate concentrations. Significant increases or decreases in nitrate concentration were determined using statistical tests at the 90% confidence level (ACFB, Apalachicola–Chattahoochee–Flint Basin; CCPT, Central Columbia Plateau; DLMV, Delmarva Peninsula; GAFL, Georgia–Florida Coastal Plain; NVBR, Nevada Basin and Range; POTO, Potomac River Basin; RIOG, Rio Grande Valley; SANJ, San Joaquin–Tulare Basins, SPLT, South Platte River Basin; TRIN, Trinity River Basin; USNK, Upper Snake River Basin; WHIT, White River Basin; WILL, Willamette Basin; WMIC, Western Lake Michigan Drainage).

Table 2. Summary of ground water recharge age data.

Study unit	No. of wells	Age dating tracer used	Ages determined during which decadal-scale sampling event	Reference
Apalachicola–Chattahoochee–Flint Basin (ACFB)	8	chlorofluorocarbons	second	Elizabeth Frick, USGS, personal communication, 2006
Central Columbia Plateau (CCPT)	10	sulfur hexafluoride	second	Lonna Frans, USGS, personal communication, 2006
Delmarva Peninsula (DLMV)	24	sulfur hexafluoride	second	Linda Debrewer, USGS, personal communication, 2006
Rio Grande Valley (RIOG)	33	chlorofluorocarbons	second	Michael G. Rupert, USGS, unpublished data, 2006
San Joaquin–Tulare Basins (SANJ)	2	chlorofluorocarbons	first	Karen Burow, USGS, personal communication, 2006
Upper Snake River Basin (USNK)	5	chlorofluorocarbons	first	Plummer et al., 2000
Western Lake Michigan Drainage (WMIC)	24	chlorofluorocarbons	first	David Saad, USGS, personal communication, 2006

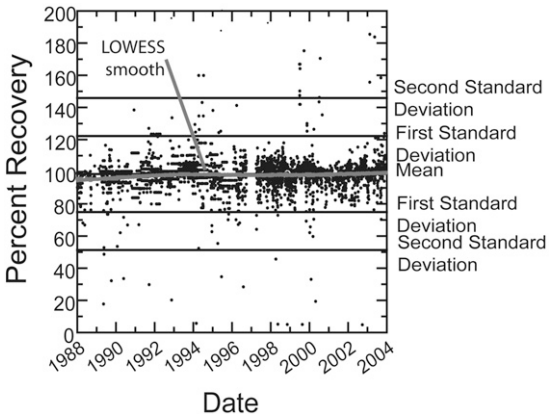

Fig. 2. Percentage recovery of nitrate blind reference samples, 1988–2004. Data collected by the U.S. Geological Survey Inorganic Blind Sample Program (USGS, 1997).

Spike Recovery Data

Since 1981, the USGS has operated an independent quality assurance project called the Inorganic Blind Sample Program (USGS, 1997). The purpose of the Inorganic Blind Sample Program is to monitor and evaluate the quality of laboratory analytical results through the use of double blind quality control reference samples. The blind reference samples submitted by the Inorganic Blind Sample Program to the National Water Quality Laboratory indicate that there is no significant long-term bias in nitrate concentrations reported by the National Water Quality Laboratory, and that nitrate data reported by the National Water Quality Laboratory are suitable for analysis of trends of nitrate in ground water because there is little likelihood that bias will affect trends (Fig. 2). From 1988 through 2004, the Inorganic Blind Sample Program submitted 3779 double blind reference samples to the National Water Quality Laboratory; the concentrations ranged from 0.036 to 3.7 mg L^{-1}. Mean analyte recovery from 1988 through 2004 was 98.57%, and median analyte recovery for the same period was 98.47%, indicating a small negative bias in nitrate concentrations. The LOWESS smooth in Fig. 2 shows there is a slightly larger negative bias for data analyzed between about 1988 and 1992, but it is only 1 or 2% below the overall mean. Only 1.9% of the data lie outside two standard deviations, indicating that very few outliers exist and the laboratory method is performing very well throughout the period of record.

Identification of Oxidized and Reduced Conditions

The oxidation–reduction (redox) state of ground water is an important geochemical control on the presence of nitrate in ground water because reduced conditions promote denitrification. Denitrification takes place when *oxygen* (which is a more favorable electron acceptor) is depleted, and *bacteria* must use nitrate to respire *organic matter*. Denitrification transforms nitrate in ground water to N_2 gas, thus eliminating nitrate from ground water (Chapelle, 1993). For nitrate trends investigations, redox is an important factor because denitrification may obscure any simple relation between changes in nitrate loading at the land surface and concentrations of nitrate in ground water.

A method similar to that described by Paschke et al. (2007) was used to classify ground water as either oxidized, reduced, or a mixture of oxidized and reduced based on concentrations of dissolved oxygen (0.5 mg L^{-1}), nitrate (0.5 mg L^{-1}), Mn (50 μg L^{-1}), Fe (100 μg L^{-1}), and sulfate (4 mg L^{-1}). These concentrations follow those presented by Chappelle et al. (1995) for dissolved oxygen and nitrate, the Geological Survey of Sweden (www.internat.naturvardsverket.se/index.php3?main=/documents/legal/assess/assedoc/gndwdoc/redox.htm; verified 16 Aug. 2007) for Mn and Fe, and Chappelle et al. (2002) for sulfate. As an example, ground water was assigned an oxidized classification if dissolved oxygen and nitrate concentrations were >0.5 mg L^{-1}, Mn concentrations ≤50 μg L^{-1}, Fe concentrations ≤100 μg L^{-1}, and sulfate concentrations >4 mg L^{-1}. Ground water was assigned a reduced classification if dissolved oxygen and nitrate concentrations were ≤0.5 mg L^{-1}, Mn concentrations were >50 μg L^{-1}, Fe concentrations were >100 μg L^{-1}, and sulfate concentrations were >4 mg L^{-1}. For the purposes of this study, the oxidized and nitrate reduction classification of Paschke et al. (2007) were combined into one "oxidized" classification, and the Mn and/or Fe reduction with high sulfate and the Mn and/or Fe reduction with low sulfate classifications were combined into one "reduced" classification. Mixtures of reduced and oxidized water are common, and typically occur when waters of different types are mixed within the well bore during pumping.

Results and Discussion

Twenty-four well networks in 14 NAWQA study units had sufficient nitrate data for evaluating decadal-scale changes in nitrate concentrations (Fig. 1, Table 1). The well networks are widely distributed across the United States, allowing for correlations with a wide range of hydrogeologic and land-use conditions. The median nitrate concentrations of all 495 wells combined increased from 3.2 to 3.4 mg L^{-1}, and mean nitrate concentrations increased from 5.7 to 6.4 mg L^{-1} during the decadal-scale time period. This difference in mean and median concentrations is larger than the variability of nitrate concentrations measured in 388 replicate samples collected from 1992 to 2001 by the NAWQA program and reported by Mueller and Titus (2005), indicating that the increase in nitrate concentrations is not an artifact of statistical variability or noise. The Sign and Wilcoxon signed-rank test results on all 495 wells combined had p values of 0.001, indicating that there is a significant increase in nitrate concentrations in the data set as a whole. Sign test and Wilcoxon signed-rank test results on each individual well network indicate that 8 out of 24 well networks (about 33%) had significant differences of nitrate concentrations at the 90% confidence level ($p < 0.1$) (Table 1). Of the eight well networks with significant changes of nitrate, all except one in the Willamette Valley of Oregon had increasing nitrate concentrations; the Willamette Basin had decreasing nitrate concentrations (Fig. 3). Of the seven well networks with significant increases of nitrate concentrations, median nitrate concentrations in three networks increased above the USEPA (2002) maximum contaminant level of 10 mg L^{-1} (Table 1). About 67% of the well networks did not have a significant change in nitrate concentrations.

The results of this study are similar to most other studies that observed significant trends of nitrate concentrations in ground water (Wassenaar et al., 2006; Ball and MacDonald, 2001; Knapp, 2005; Drake and Bauder, 2005; Rosen, 2003; Shipley and Rosen, 2005); when trends are observed they are usually increasing trends. Well networks in the Central Columbia Plateau did not have significant changes in nitrate concentrations using data analyzed by this study (Table 1). However, Frans (2008) observed a significant downward trend in nitrate concentrations between 1998 and 2002 using only wells that had nitrate concentrations >10 mg L^{-1}. The trends observed in the Upper Snake River Basin of Idaho were similar to that observed by Parliman (2002), who identified some areas with and other areas without increasing trends of nitrate.

Nitrate concentrations tend to decrease as well depth increases. This trend has been observed in other comprehensive nitrate ground water studies in the United States (Mueller and Helsel, 1996; Nolan and Stoner, 2000). The largest changes in nitrate concentrations (±20 mg L^{-1}) occurred in the shallowest portion of the aquifers (<20 m); changes in nitrate concentrations decreased as well depth increased.

The largest changes of nitrate concentrations occurred in alluvial aquifers (Fig. 4). Alluvium with a relatively large percentage of gravel tended to have larger changes in nitrate concentrations than alluvium with sand and alluvium with clay. Some of the smallest changes occurred in basalt aquifers. Although alluvial aquifers had the largest changes, the Kruskal–Wallis test indicated there was no significant difference in median nitrate changes between any aquifer lithologies ($p = 0.4$), only the magnitude of changes was larger.

Correlations of Trends of Nitrate Concentrations in Ground Water with Oxidized–Reduced Conditions

Ground water with reduced conditions had nitrate concentrations that were commonly less than the laboratory reporting level and had very small to no changes in nitrate concentrations (Fig. 5). Ground water with oxidized conditions, and ground water that is a mixture of oxidized and reduced water, was more likely to have large changes of nitrate (Fig. 5). There were no significant differences in change of nitrate concentrations in oxidized and mixed water, but reduced water had significantly ($p < 0.05$) smaller changes in nitrate concentrations than oxidized and mixed water (Fig. 5). These smaller changes of nitrate concentrations in reduced water were also observed by Broers and van der Grift (2004) in the Netherlands, where no temporal trends of nitrate concentrations were observed probably due to nitrate reduction.

Wells with reduced conditions were temporarily deleted from the data set, and the Sign and Wilcoxon signed-rank tests were recalculated to determine if any additional well networks with significant changes in nitrate could be identified. The Sign and Wilcoxon signed-rank test results were the same with or without the reduced-condition wells. Eliminating reduced water from the analysis eliminated the nondetections, which did not affect the results of the nonparametric tests because the tests are performed on ranked data and the nondetections were ranked identically near zero.

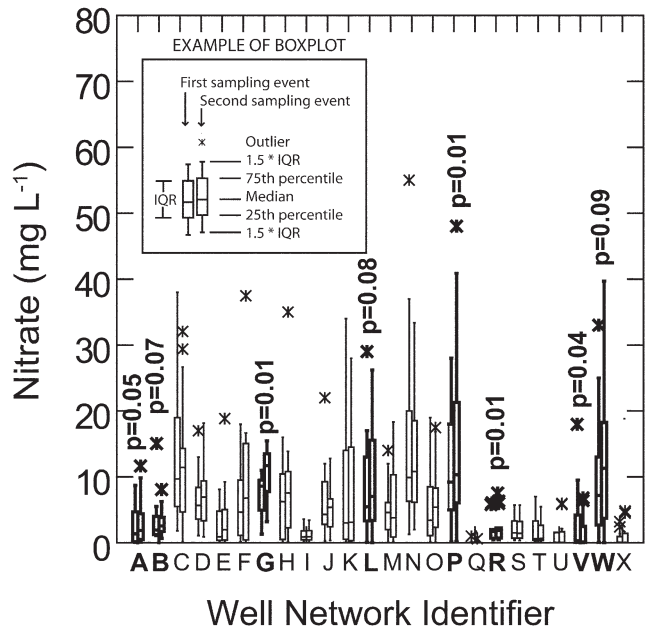

Fig. 3. Nitrate concentrations of water sampled from well networks during the first and second decadal-scale sampling event. For each well network, the left box is for the first sampling event, and the right box is for the second sampling event. The *p* values and bold text denote well networks with significant trends in nitrate concentrations at the 90% confidence level or greater. The *p* values were calculated using the Wilcoxon signed-rank test. See Table 1 for study unit and well network names (IQR; interquartile range).

There were no significant differences in median depths of wells with oxidized and reduced ground water (30 and 26 m, respectively), but median depths of wells with mixtures of oxidized and reduced ground water were significantly shallower (10 m). In this data set, mixed conditions mostly occurred in shallow wells with short screen intervals, indicating that recently recharged oxidized ground water is probably mixing with older reduced ground water in the well bores or that significant reduction is occurring near the water table over short screen intervals.

Oxidized–reduced conditions changed in water from 30 wells (6% of total) between the decadal-scale sampling events. Before sampling, all wells were sufficiently purged at least three well volumes and until field parameters for dissolved oxygen, pH, specific conductance, temperature, and turbidity became constant, so the changes in redox state are believed to be the result of changes in hydrologic conditions and not an artifact of sampling methods. Water from 14 wells changed from oxidized or mixed oxidized and reduced conditions to reduced conditions; nitrate concentrations in water from these wells decreased significantly. Water from 16 wells changed from reduced or mixed oxidized and reduced to oxidized; nitrate concentrations in water from these wells increased significantly. These results imply that changes in the oxidation–reduction conditions of ground water can significantly affect trends of nitrate concentrations in ground water. Water from 5 out of 24 wells in the Willamette Basin changed to reduced conditions between the decadal-scale sampling events, which may partially explain why the Willamette Basin had a significant decrease of nitrate concentrations.

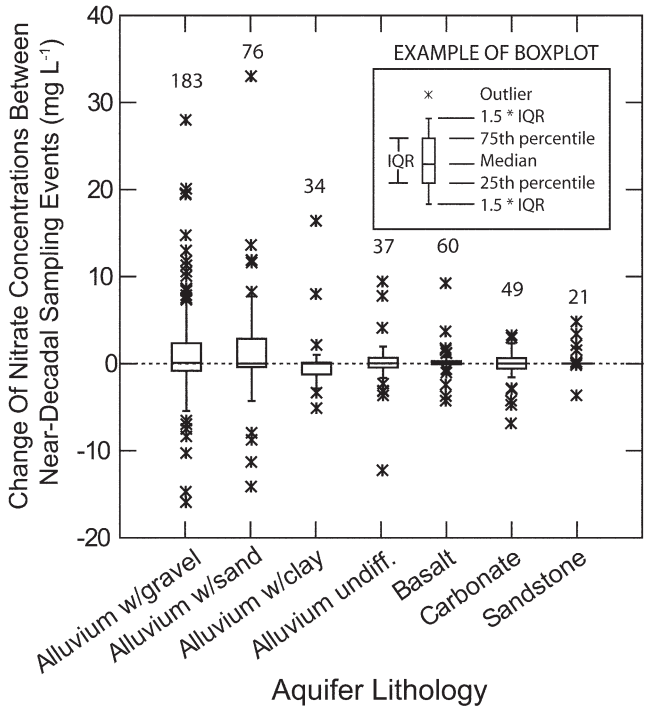

Fig. 4. Change of nitrate concentrations between decadal-scale sampling events in selected aquifer lithologies (IQR; interquartile range).

Correlations of Changes of Nitrate Concentrations in Ground Water with Nitrogen Input and Ground Water Recharge Date

The increase of total fertilizer use in the United States is reflected in nitrate concentrations in ground water (Fig. 6). Water from a subset of wells in the Apalachicola–Chattahoochee–Flint Basin, Central Columbia Plateau, Delmarva Peninsula, Rio Grande Valley, San Joaquin–Tulare Basins, Upper Snake River Basin, and Western Lake Michigan Drainage study units had ground water age estimates, allowing nitrate concentrations to be plotted with the year the ground water was recharged (Fig. 6). The increase of nitrate concentrations roughly mimics the increase in national N fertilizer use; the increase of maximum values of nitrate concentrations compared to total fertilizer use indicates there may have been a minimum 10 or 15 yr time lag. Similar correlations between ground water age and fertilizer use have been observed at more localized scales (Johnston et al., 1998; Katz et al., 2001; Tesoriero et al., 2006). Decadal-scale changes of nitrate concentrations are larger (≤33 mg L^{-1}) in waters younger than 1980 than in waters older than 1980 (<5 mg L^{-1}), indicating that younger water may be more susceptible to changes in N input or irrigation management.

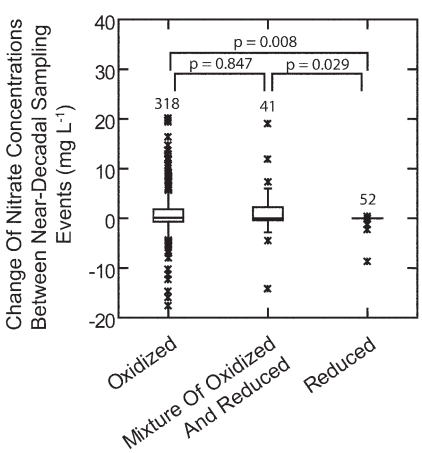

Fig. 5. Decadal-scale change of nitrate concentrations in oxidized, mixed oxidized and reduced, and reduced ground water. The oxidation state was determined using water quality data collected during the second decadal-scale sampling event. The *p* values are from the Wilcoxon Rank Sum test.

Figure 6 indicates that increasing nitrate concentrations are likely the result of increasing fertilizer use when investigated at the national scale. However, Rosen (2003), Drake and Bauder (2005), Shipley and Rosen (2005), and Reynolds-Vargas et al. (2006) attributed increasing nitrate concentrations in ground water to domestic wastewater. Unfortunately, no national-scale data exist on the changes of the number or distribution of domestic septic systems over time, so relations between changes of nitrate concentrations and changes of domestic septic systems could not be investigated.

Ground water recharge date was correlated with depth to top of well screen, total well depth, depth to ground water, and saturated interval (total well depth minus depth to ground water) to determine if these depth variables can be used as a surrogate for ground water recharge date. For instance, the oldest water should have the greatest well depths and the youngest water should have the shallowest well depths. There was no correlation between ground water recharge date and any of the depth variables; these depth variables cannot be used as a surrogate for ground water recharge date in this data set. However, Böhlke (2002), Tesoriero et al. (2006), and Wassenaar et al. (2006) observed correlations between well depth and ground water age. The lack of a correlation in this study might result from lumping data from multiple sites with wide ranges of recharge rates.

Conclusions

Twenty-four well networks in 14 NAWQA study units had sufficient nitrate data for evaluating decadal-scale changes of nitrate concentrations. The Sign and Wilcoxon signed-rank test results on all 495 wells combined had *p* values of 0.001, indicating that there is a significant increase in nitrate concentrations in the data set as a whole. Sign test and Wilcoxon signed-rank test results on each individual well network indicate that 8 of the 24 well networks (about 33%) had significant changes of nitrate concentrations at the 90% confidence level ($p < 0.1$). Of the eight well networks with significant changes of nitrate, all except one in the Willamette River Basin had increasing nitrate concentrations during the decadal-scale time period; the Willamette Basin had decreasing nitrate concentrations. Of the seven well networks with significant increases of nitrate concentrations, median nitrate concentrations in three networks increased above the USEPA maximum contaminant level of 10 mg L^{-1}. Changes

in nitrate concentrations were largest in shallow ground water in alluvial aquifers with a relatively large percentage of gravel.

Ground water was classified as being oxidized, reduced, or a mixture of oxidized and reduced. Oxidized ground water and mixtures of oxidized and reduced ground water had large changes of nitrate. Reduced ground water had nitrate concentrations that were commonly less than the laboratory reporting level and had very small to no changes in nitrate concentrations, probably because the nitrate had been denitrified to N_2 gas. The lack of nitrate trends in reduced waters has also been observed in the Netherlands. Oxidized–reduced conditions changed in water from 30 wells (6% of total) during the decadal-scale time period. Nitrate concentrations decreased significantly in water that changed from oxidized or mixed to reduced. Nitrate concentrations increased significantly in water that changed from reduced or mixed to oxidized. Based on these results, changes in the oxidation–reduction conditions of ground water can significantly affect trends of nitrate concentrations in ground water.

A subset of wells had data on ground water recharge date, which allowed correlations with historic fertilizer use. Fertilizer use in the United States increased dramatically starting about 1950. Nitrate concentrations in ground water increased in response to the increase of N fertilizer use, similar to that observed in other, more localized studies.

There was no correlation between ground water recharge date and depth to top of well screen, total well depth, depth to ground water, and saturated interval, indicating that they cannot be used as a surrogate for ground water recharge date in this data set. Other, more localized studies have observed significant relations between ground water age and well depth; the lack of correlation in this data set may be due to lumping the data from multiple sites with wide ranges of recharge rates.

Probably the most important conclusion from this study, and by other ground water trends investigations, is that ground water recharge ages are an essential component of any ground water trends investigation. Ground water recharge ages provide the ability to correlate changes in land-use practices with changes in ground water quality. Without ground water recharge dates, it is much more difficult to determine why trends in ground water quality were or were not observed even after significant changes in nitrate concentrations are identified.

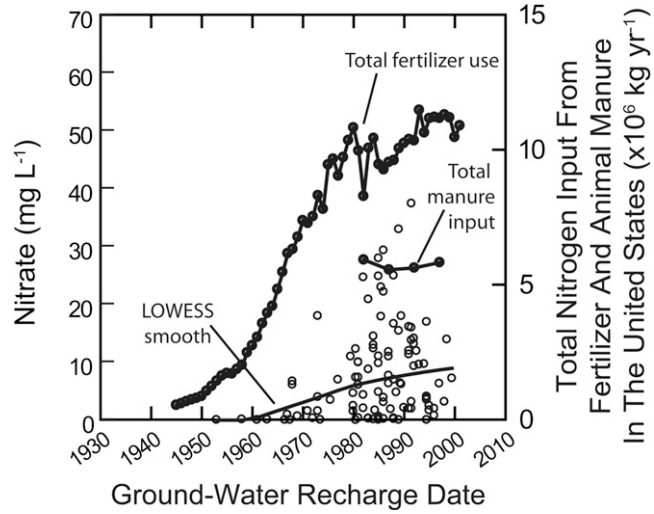

Fig. 6. Nitrate concentrations in ground water, ground water recharge date, total N fertilizer use, and total manure N input in the United States using ground water monitoring data collected in the Apalachicola–Chattahoochee–Flint Basin, Central Columbia Plateau, Delmarva Peninsula, Rio Grande Valley, San Joaquin–Tulare Basins, Upper Snake River Basin, and Western Lake Michigan Drainage study units. [Fertilizer data from Alexander and Smith (1990) and Ruddy et al. (2006); manure data from Ruddy et al. (2006)].

Acknowledgments

Although it is impossible to thank all of the people involved in the USGS NAWQA program, I would like to thank the people directly involved with the NAWQA Ground water Trends Team (alphabetically, Laura Bexfield, Neil Dubrovsky, Steve Grady, Wayne Lapham, Mike Moran, and Michael Rosen) and the people who authored study unit papers published as companion papers in this volume (Karen Burow, Linda Debrewer, Lonna Frans, Betsy Frick, Suzanne Paschke, Sherlyn Priest, David Saad, and Jennifer Shelton) for their advice and assistance. Data analysis would not have been possible without the efforts of the Trends Data Team (Frank Voss, Tom Trombley, David Litke, and Toby Welborn). The efforts of all USGS personnel from the study units who collected and evaluated chemical data used in this analysis also are greatly appreciated, as are the colleague reviews by Neil Dubrovsky, David Mueller, and Larry Puckett.

References

Alexander, R.B., and R.A. Smith. 1990. County level estimates of nitrogen and phosphorus fertilizer use in the United States, 1945 to 1985. U.S. U.S. Geol. Surv. Open-File Rep. 90–130 USGS, Reston, VA.

Ball, D.F., and A.M. MacDonald. 2001. Groundwater nitrate vulnerable zones for Scotland. British Geological Survey Commissioned Rep. CR/01/250. British Geological Survey, Edinburgh, UK.

Böhlke, J.K. 2002. Groundwater recharge and agricultural contamination. Hydrogeol. J. 10:153–179.

Bolger, P., and M. Stevens. 1999. Contamination of Australian groundwater systems with nitrate. Occasional Paper 03/99. Land and Water Resources Res. and Dev. Corp., Canberra, Australia.

Brender, J.D., J.M. Olive, J.M. Felkner, L. Suarez, K. Hendricks, and W. Marckwardt. 2004a. [Abstract] Intake of nitrates and nitrites and birth defects in offspring. Epidemiology 15:S184.

Brender, J.D., J.M. Olive, M. Felkner, L. Suarez, W. Marckwardt, and K.A. Hendricks. 2004b. Dietary nitrites and nitrates, nitrosatable drugs, and neural tube defects. Epidemiology 15:330–336.

Broers, H.P., and B. van der Grift. 2004. Regional monitoring of temporal changes in groundwater quality. J. Hydrol. 296:192–220.

Brendle, D. 1997. Have nitrate concentrations changed in the alluvial aquifer of the Upper Black Squirrel Creek Basin since 1984. U.S. Geol. Surv. Fact Sheet FS-072-97. USGS, Pueblo, CO.

Busenberg, E., and L.N. Plummer. 1992. Use of chlorofluorocarbons (CCl3F and CCl2F2) as hydrologic tracers and age-dating tools: Example–The alluvium and terrace system of central Oklahoma. Water Resour. Res. 28:2257–2284.

Busenberg, E., and L.N. Plummer. 2000. Dating young ground water with sulfur hexafluoride: Natural and anthropogenic sources of sulfur hexafluoride. Water Resour. Res. 36:3011–3030.

Chapelle, F.H. 1993. Ground water microbiology and geochemistry. John Wiley & Sons, New York.

Chappelle, F.H., P.M. Bradley, D.R. Lovley, K. O'Neill, and J.E. Landmeyer. 2002. Rapid evolution of redox processes in a petroleum hydrocarbon-contaminated aquifer. Ground Water 40:353–360.

Chappelle, F.H., P.B. McMahon, N.M. Dubrovsky, R.F. Fujii, E.T. Oaksford, and D.A. Vroblesky. 1995. Deducing the distribution of terminal

electron-accepting processes in hydrologically diverse groundwater systems. Water Resour. Res. 31:359–371.

Close, M.E., M.R. Rosen, and V.R. Smith. 2001. Fate and transport of nitrates and pesticides in New Zealand's aquifers. p. 185–220. *In* M.R. Rosen and P.A. White (ed.) Groundwaters of New Zealand. New Zealand Hydrological Society, Wellington, New Zealand.

Debrewer, L.M., Ator, S.W., and J.M. Denver. 2008. Temporal trends in nitrate and selected pesticides in Mid-Atlantic ground water. J. Environ. Qual. 37:S-296–S-308.

DeRoos, A.J., M.H. Ward, C.F. Lynch, and K.P. Cantor. 2003. Nitrate in public water systems and the risk of colon and rectum cancers. Epidemiology 14:640–649.

Drake, V.M., and J.W. Bauder. 2005. Ground water nitrate-nitrogen trends in relations to urban development, Helena, Montana, 1971–2003. Ground Water Monit. Rem. 25:118–130.

Fields, S. 2004. Global nitrogen: Cycling out of control. Environ. Health Perspect. 112:A557–A563.

Fishman, M.J. (ed.). 1993. Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory: Determination of inorganic and organic constituents in water and fluvial sediments. U.S. Geol. Surv. Open-File Rep. 93-125. USGS, Denver, CO.

Frans, L.M. 2008. Trends of pesticides and nitrate in ground water of the Central Columbia Basin Plateau, Washington, 1993–2003. J. Environ. Qual. 37:S-273–S-280.

Helsel, D.R., and R.M. Hirsch. 1992. Statistical methods in water resources. Elsevier Science Publishing Co., New York.

Johnston, C.T., P.G. Cook, S.K. Frape, L.N. Plummer, E. Busenberg, and R.J. Blackport. 1998. Ground water age and nitrate distribution within a glacial aquifer beneath a thick unsaturated zone. Ground Water 36:171–180.

Katz, B.G., J.K. Boehlke, and H.D. Hornsby. 2001. Timescales for nitrate contamination of spring waters, northern Florida, USA. Chem. Geol. 179(1–4):167–186.

Knapp, M.F. 2005. Diffuse pollution threats to groundwater: A UK water company perspective. Q. J. Eng. Geol. Hydrogeol. 38:39–51.

Mueller, D.K., and D.R. Helsel. 1996. Nutrients in the Nation's waters: Too much of a good thing? U.S. Geol. Surv. Circ. 1136. USGS, Denver, CO.

Mueller, D.K., and C.J. Titus. 2005. Quality of nutrient data from streams and ground water sampled during water years 1992–2001. U.S. Geol. Surv. Sci. Invest. Rep. 2005–5106. USGS, Denver, CO.

Nolan, B.T., and J.D. Stoner. 2000. Nutrients in groundwaters of the conterminous United States, 1992–1995. Environ. Sci. Technol. 34:1156–1165.

Ott, R.L. 1993. An introduction to statistical methods and data analysis. Duxbury Press, Wadsworth Publishing Co., Belmont, CA.

Parliman, D.J. 2002. Analysis of nitrate (NO_3–N) concentration trends in 25 ground water-quality management areas, Idaho, 1961–2001. U.S. Geol. Surv. Water-Resour. Invest. Rep. 02-4056. USGS, Boise, ID.

Paschke, S.S., L.J. Kauffman, S.M. Eberts, and S.R. Hinkle. 2007. Overview of regional studies of the transport of anthropogenic and natural contaminants to public supply wells. Section 1. *In* S.S. Paschke (ed.) Hydrogeologic settings and ground water flow simulations for regional studies of the transport of anthropogenic and natural contaminants to public-supply wells: Studies begun in 2001. U.S. Geol. Surv. Prof. Pap. 1737-A. USGS, Denver, CO (in press).

Plummer, L.N., R.L. Michel, E.M. Thurman, and P.D. Glynn. 1993. Environmental tracers for age-dating young ground water. p. 255–294. *In* W.M. Alley (ed.) Regional ground water quality. Van Nostrand Reinhold, New York.

Plummer, L.N., M.G. Rupert, E. Busenberg, and P. Schlosser. 2000. Age of irrigation water in ground water from the Eastern Snake River Plain aquifer, south-central Idaho. Ground Water 38:264–283.

Reynolds-Vargas, J., J. Fraile-Merino, and R. Hirata. 2006. Trends in nitrate concentrations and determination of its origin using stable isotopes (O-18 and N-15) in groundwater of the western Central Valley, Costa Rica. Ambio 35:229–236.

Rosen, M.R. 1999. The importance of long-term, seasonal monitoring of groundwater wells in the New Zealand National Groundwater Monitoring Programme (NGMP). J. Hydrol. 38:145–169.

Rosen, M.R. 2003. Trends in nitrate and dissolved-solids concentrations in ground water, Carson Valley, Douglas County, Nevada, 1985–2001. U.S. Geol. Surv. Water-Resour. Invest. Rep. 03-4152. USGS, Carson City, NV.

Rosen, M.R., and W.W. Lapham. 2008. Introduction to the U.S. Geological Survey National Water-Quality Assessment (NAWQA) of ground-water quality trends and comparison to other national programs. J. Environ. Qual. 37:S-190–S198.

Rosen, M.R., Voss, F.D., and J.A. Arufe. 2008. Evaluation of intra-annual variation in U.S. Geological Survey National Water Quality Assessment ground water quality data. J. Environ. Qual. 37:S-199–S-208.

Ruddy, B.C., D.L. Lorenz, and D.K. Mueller. 2006. County-level estimates of nutrient inputs to the land surface of the conterminous United States, 1982–2001. U.S. Geol. Surv. Sci. Invest. Rep. 2006-5012. USGS, Reston, VA.

Shipley, D.O., and M.R. Rosen. 2005. Identification of nitrate and dissolved-solids sources in ground water by GIS analyses. Environ. Practice 7:32–43.

Spalding, R.F., and M.E. Exner. 1993. Occurrence of nitrate in groundwater: A review. J. Environ. Qual. 22:392–402.

Tesoriero, A.J., K.R. Burow, D.A. Saad, E.A. Frick, and L.J. Puckett. 2006. Linking ground water age and chemistry along flow paths to examine the influence of land use practices on water quality. EOS Trans. Am. Geoph. Union 87:1380.

Thomson, G. 2005. How products are made. Available at www.madehow.com/Volume-3/Fertilizer.html (accessed 10 Jan. 2006, 31 Oct. 2006; verified 9 Aug. 2007). Thomson Corp., Farmington Hills, MI.

USEPA. 2002. List of drinking water contaminants and their MCL's. Available at www.epa.gov/safewater/contaminants/index.html (accessed 7 Feb. 2006, 2 May 2007; verified 9 Aug. 2007). USEPA Rep. 816-F-02-013. USEPA, Washington, DC.

USGS. 1997. USGS Inorganic Blind Sample Project monitoring and evaluating laboratory analytical quality. U.S. Geol. Surv. Fact Sheet FS-136-97. USGS, Denver, CO.

Vitousek, P.M., J. Aber, R.W. Howarth, G.E. Likens, P.A. Matson, D.W. Schindler, W.H. Schlesinger, and G.D. Tilman. 1997. Human alteration of the global nitrogen cycle: Causes and consequences. Iss. Ecol. 1:1–17.

Wassenaar, L.I., M.J. Hendry, and N. Harrington. 2006. Decadal geochemical and isotopic trends for nitrate in a transboundary aquifer and implications for agricultural beneficial management practices. Environ. Sci. Technol. 40:4626–4632.

Ward, M.H., S.D. Mark, K.P. Cantor, D.D. Weisenburger, A. Correa-Villaseñor, and S.H. Zahm. 1996. Drinking water nitrate and the risk of non-Hodgkin's lymphoma. Epidemiology 7:465–471.

Weisenburger, D.D. 1991. Potential health consequences of ground water contamination by nitrates in Nebraska. p. 309–315. *In* I. Bogardi et al. (ed.) Nitrate contamination-exposure, consequence, and control. Springer-Verlag, Berlin.

Weyer, P.J., J.R. Cerhan, B.C. Kross, G.R. Hallberg, J. Kantamneni, G. Breuer, M.P. Jones, W. Zheng, and C.F. Lynch. 2001. Municipal drinking water nitrate level and cancer risk in older women: The Iowa women's health study. Epidemiology 11:327–338.