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NITRATE CONCENTRATIONS IN GROUND WATER IN THE PALEOVALLEY ALLUVIAL AQUIFERS OF THE NEMAHA NATURAL RESOURCES DISTRICT, NEBRASKA, 1989 and 1994–96

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 98–4106

Prepared in cooperation with the Nemaha Natural Resources District

U.S. DEPARTMENT OF THE INTERIOR
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By A.H. Chen

U.S. Geological Survey

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Lincoln, Nebraska
1998

CONVERSION FACTORS AND VERTICAL DATUM

Multiply	By	To obtain
Length		
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
acre	4,047	square meter
gallon per minute (gal/min)	0.06309	liter per second

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows: °F = (1.8 × °C) + 32

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows: °C = (°F - 32) / 1.8

INTRODUCTION

In the summer of 1989, ground-water samples were collected by the U.S. Geological Survey (USGS) from 80 wells distributed among the four principal aquifer groups in the Nemaha Natural Resources District (NRD). The samples were analyzed for nitrate concentrations and triazine herbicides, and a subset of the samples was selected for major ion and trace element analyses. The results of the 1989 study indicated that ground water from the paleovalley alluvial aquifers contained the largest concentrations of nitrate, with about 33 percent of the samples containing nitrate concentrations more than 5 milligrams per liter (mg/L). This distribution of moderately large nitrate concentrations in ground water likely is due to widespread agricultural activity in the vicinity of the aquifers (Tanner and Steele, 1991).

The results of the 1989 study suggested that ground-water monitoring of nitrate concentrations in the paleovalley alluvial aquifers should continue over time to examine long-term trends. Additionally, the 1989 report indicated that variations in nitrate concentrations could be determined by collecting water samples for nitrate analysis at least semiannually from selected wells in the paleovalley alluvial aquifers.

In 1993 the USGS entered into a cooperative agreement with the Nemaha NRD for the purpose of better characterizing nitrate concentrations in the paleovalley alluvial aquifers of the Nemaha NRD and determining if nitrate concentrations have changed in the aquifers. The specific objectives of this study were to (1) determine if nitrate concentrations in the ground water have changed significantly at the 34 wells in the paleovalley alluvial aquifers from which water samples were collected in 1989; (2) determine nitrate concentrations in ground water in the vicinity of wells sampled in 1989 that showed large nitrate concentrations; and (3) define temporal variations of nitrate concentrations in the paleovalley alluvial aquifers.

This report presents the results of the study. The data-collection procedures and the results for data collected from November 1994 through September 1996 are described. A statistical comparison between the 1989 and 1995 nitrate data is included.

The study area occupies the central part of the Nemaha NRD from the western to the eastern boundary and contains the major paleovalley alluvial aquifers (fig. 1). The paleovalley alluvial aquifers are predominately Pleistocene-age unconsolidated sand and gravel deposits within bedrock valleys (Tanner and Steele, 1991). These aquifers are generally semiconfined to confined and trend east-west. Generally, aquifer deposits are thicker in the western part of the study area and thin toward the east; the saturated thickness of these deposits ranges from 300 feet (ft) in the west to 100 ft or less in the east. Depth to water in the aquifers ranges from about 3 ft to 160 ft in the study area. The aquifers may be hydraulically connected to local shallow aquifers and surface-water systems. Wells in the aquifers generally yield 500 to 1,000 gallons per minute (gal/min) and locally as much as 1,500 gal/min (Tanner and Steele, 1991).

APPROACH

Selection of Wells for Sampling

To determine the changes in nitrate concentrations, if any, that had occurred in the study area between 1989 and 1995, 34 wells in the paleovalley alluvial aquifers from which water samples were collected in the summer of 1989 were resampled during the summer of 1995. Well identification numbers P01 to P34 were assigned to these wells (table 1, fig. 2). However, if irrigation wells sampled in 1989 were unused or abandoned in the 1995 irrigation season, comparable wells located within a 1/2-mile radius and having about the same well depth were substituted for the unused or abandoned ones. Five of the wells sampled in 1989 had nitrate concentrations in excess of 7 mg/L. These five wells (P13, P16, P20, P31, and P32) will be referred to as the original wells. To determine the magnitude of nitrate concentration in ground water in the vicinity of the five original wells, an additional 16 wells, designated as wells P35 to P50, were sampled once during the summer of 1995. Data from 15 of the 16 additional wells were used to determine the magnitude of nitrate concentrations near the five original wells. The 15 wells were in groups of three wells within about a 3-mile radius of each of the five original wells. Because well P44 was found to be more than 3 miles from well P20, it was excluded. To define temporal variations in concentrations of nitrate, four municipal wells (P04, P07, P31, and P40) and one domestic well (P42) were selected for bimonthly sampling from November 1994 to September 1996 (table 2).

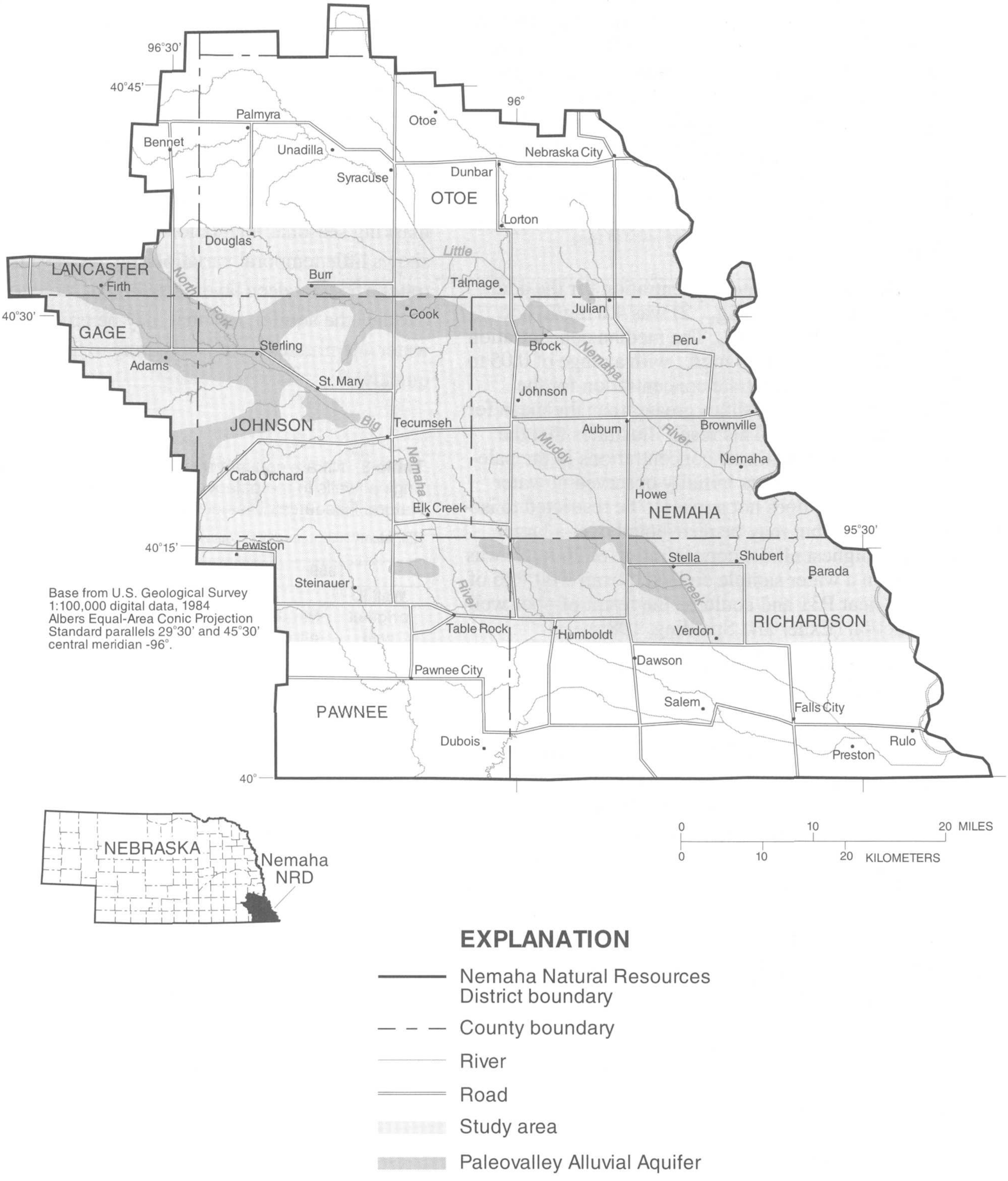

Figure 1. Location of study area (modified from Tanner and Steele, 1991).

Table 1. Well data, field measurements, and nitrate concentrations for 50 wells in the paleovalley alluvial aquifers, Nemaha Natural Resources District, Nebraska, 1995

[ID, identification number; Water use: I, irrigation; M, municipal, D, domestic; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter]

Well ID	Well depth (feet)	Water use	Sample date	Field measurements: Specific conductance (µS/cm)	Field measurements: pH (standard units)	Field measurements: Oxygen, dissolved (mg/L)	Nitrate, dissolved (mg/L as N)
P01	214	I	7-20-95	725	7.2	0.1	0.05
P02	325	I	7-28-95	1,090	7.4	.1	.09
P03	320	I	7-28-95	635	7.6	1.9	1.7
P04	111	M	7-20-95	538	7.6	8.6	6.9
P05	68	D	8-29-95	376	7.1	8.1	3.7
P06	150	M	7-20-95	577	7.2	7.0	7.9
P07	175	M	7-20-95	473	7.4	7.9	4.9
P08	142	I	8-31-95	516	7.4	8.0	3.8
P09	58	I	8-04-95	589	6.9	.2	.23
P10	170	I	9-05-95	816	7.1	.3	.23
P11	54	I	8-04-95	543	7.3	.2	.71
P12	59	I	7-24-95	569	7.1	.5	1.2
P13	156	I	7-26-95	802	7.7	.6	3.3
P14	140	I	7-31-95	910	7.3	1.6	.43
P15	301	I	7-20-95	608	7.4	1.5	.54
P16	77	M	7-24-95	366	7.3	7.7	8.2
P17	246	I	7-26-95	408	7.4	4.4	5.6
P18	170	I	7-20-95	669	7.3	1.4	1.2
P19	130	I	7-28-95	490	7.7	7.4	1.2
P20	112	I	7-20-95	505	6.8	4.3	12
P21	190	I	7-28-95	493	7.3	7.1	2.8
P22	150	I	7-28-95	501	7.4	6.3	.71
P23	100	I	8-29-95	737	7.1	1.2	1.1
P24	150	M	7-20-95	689	7.3	4.0	1.6
P25	110	D	7-20-95	461	7.8	1.6	.05
P26	140	D	9-06-95	863	7.4	.1	.05
P27	190	I	7-25-95	627	7.9	7.7	3.2
P28	32	D	8-04-95	364	7.7	5.6	7.0
P29	120	D	9-06-95	593	7.2	0.5	0.9
P30	145	M	7-28-95	572	7.7	2.7	1.2
P31	124	M	7-25-95	643	7.9	8.2	8.7
P32	157	I	8-23-95	635	7.1	6.3	3.5
P33	146	I	8-23-95	460	7.6	7.4	8.8
P34	153	M	7-26-95	664	7.9	.1	.31
P35	190	I	8-29-95	528	7.4	1.0	2.2
P36	150	I	7-26-95	733	7.8	.9	3.4
P37	169	I	7-24-95	636	7.7	3.1	4.0
P38	120	I	7-20-95	743	7.8	.3	.16
P39	110	D	7-31-95	560	7.6	.4	7.9
P40	54	M	7-24-95	560	7.7	2.6	3.3
P41	140	I	7-20-95	502	6.8	5.0	5.8
P42	110	D	7-24-95	411	7.5	7.1	3.8
P43	200	D	7-24-95	393	7.5	2.3	5.5
P44	90	D	7-31-95	493	6.8	2.0	17
P45	120	D	7-25-95	892	7.6	.1	.27
P46	40	D	7-25-95	1,430	7.1	6.1	26
P47	145	M	7-25-95	633	7.6	7.5	9.9
P48	160	D	9-06-95	568	6.9	9.5	21
P49	78	D	8-23-95	477	7.1	8.1	12
P50	65	D	8-04-95	408	8.4	4.6	7.9

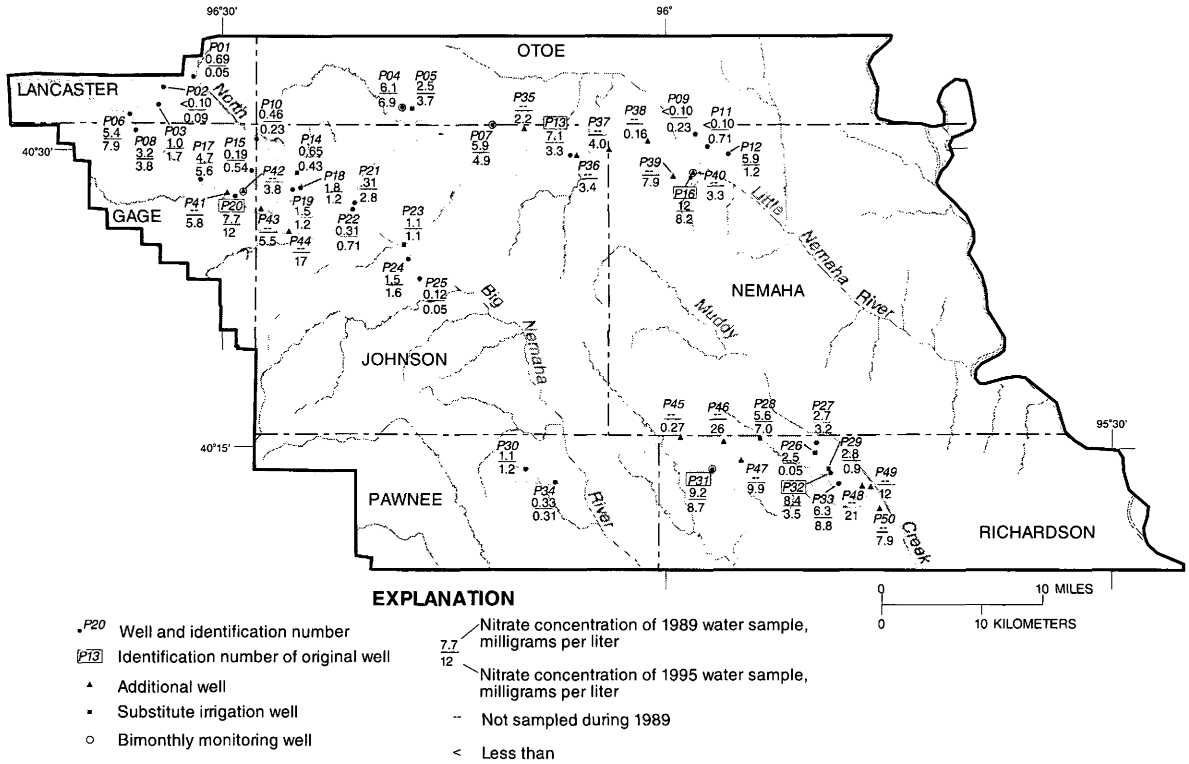

Figure 2. Nitrate concentrations in water from sampled wells in the paleovalley alluvial aquifers, Nemaha Natural Resources District, Nebraska, 1989 and 1995.

Sample Collection and Chemical Analyses

Water samples were collected and analyzed following standard protocols. Water samples were collected from the wells after field measurements of specific conductance, pH (negative log of hydrogen ion concentration), dissolved oxygen, and temperature had stabilized. General sample collection, treatment, preservation and storage, and shipping procedures used during this study are described by Koplin and Burkart (1991). The samples were shipped to the USGS National Water-Quality Laboratory (NWQL) in Arvada, Colorado. Analyses for concentrations of nitrite plus nitrate were done using standard methods (Fishman and Friedman, 1989). Because concentrations of nitrite in oxygenated freshwater are generally negligible compared to nitrate (National Research Council, 1978, p. 118), nitrite plus nitrate concentrations are referred to as nitrate concentrations in this report.

Ten percent of the samples were collected as duplicates for field quality assurance (QA) to verify the precision of the sampling and analytical methods. Duplicate samples were collected in separate containers immediately following collection of the regular sample. The QA program at the NWQL includes participation in USGS and U.S. Environmental Protection Agency interlaboratory evaluations, and submission of blind standard-reference water samples into the NWQL sample stream (Friedman and Fishman, 1982; Jones, 1987). In general, little analytical variation was found when comparing 15 pairs of the original sample results with the duplicate sample results. These sample pairs showed an average 1.5 percent variation and range was 0 to 8.7 percent difference in nitrate concentrations.

Table 2. Bimonthly field measurements and nitrate concentrations in five wells in the paleovalley alluvial aquifers, Nemaha Natural Resources District, Nebraska, 1994–96

[ID, identification number; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; —, no data]

			Field measurements			Nitrate
Well ID	Well depth (feet)	Sample date	Specific conductance (µS/cm)	pH (standard units)	Oxygen, dissolved (mg/L)	Nitrate as nitrogen, dissolved (mg/L)
P04	111	11-28-94	508	7.4	5.9	5.8
		01-24-95	546	7.4	8.6	7.1
		03-28-95	545	7.3	7.8	7.3
		05-31-95	530	7.4	9.5	6.8
		07-20-95	538	7.6	8.6	6.9
		09-26-95	529	7.4	8.5	6.3
		11-28-95	542	7.4	8.3	7.4
		01-30-96	545	7.3	8.4	7.0
		03-26-96	545	7.3	8.2	7.7
		05-21-96	544	7.2	8.3	7.4
		07-22-96	540	7.0	8.9	7.5
		09-09-96	541	7.1	8.9	8.0
P07	175	11-28-94	487	7.4	6.6	4.0
		01-24-95	488	7.3	6.9	4.4
		03-28-95	526	7.3	3.6	2.2
		05-31-95	487	7.3	7.7	4.6
		07-20-95	473	7.4	7.9	4.9
		09-26-95	478	7.2	8.3	4.9
		11-28-95	475	7.2	9.0	4.8
		01-30-96	473	7.1	8.2	4.7
		03-26-96	484	7.3	7.3	4.5
		05-21-96	504	7.0	5.7	3.4
		07-22-96	470	6.7	8.5	4.5
		09-09-96	471	6.9	8.3	4.8
P31	124	11-28-94	617	7.5	8.6	9.0
		01-24-95	598	7.5	9.0	5.4
		03-28-95	640	7.4	8.9	8.4
		05-31-95	622	7.2	8.0	8.7
		07-25-95	643	7.9	8.2	8.7
		09-26-95	640	7.4	8.1	8.3
		11-28-95	642	7.3	8.7	9.4
		01-30-96	643	7.3	9.4	9.3
		03-26-96	646	7.2	9.7	11
		05-21-96	634	7.1	11	9.9
		07-22-96	639	6.9	10	10
		09-09-96	637	7.1	10	11

Table 2. Bimonthly field measurements and nitrate concentrations in five wells in the paleovalley alluvial aquifers, Nemaha Natural Resources District, Nebraska, 1994–96 —Continued

			Field measurements			Nitrate
Well ID	Well depth (feet)	Sample date	Specific conductance (µS/cm)	pH (standard units)	Oxygen, dissolved (mg/L)	Nitrate as nitrogen, dissolved (mg/L)
P40	54	11-28-94	322	. 7.1	8.3	6.1
		01-24-95	581	7.4	3.0	3.5
		03-28-95	574	7.4	1.7	3.2
		05-31-95	310	7.0	8.8	5.9
		07-24-95	560	7.7	2.6	3.3
		09-26-95	318	7.8	8.4	5.3
		11-28-95	323	7.8	8.4	6.5
		01-30-96	366	6.8	8.6	3.7
		03-26-96	326	6.8	8.9	6.2
		05-21-96	326	6.5	9.4	5.6
		07-22-96	325	6.4	9.1	6.6
		09-09-96	323	6.5	9.3	7.1
P42	110	11-29-94	410	7.2	7.0	3.6
		01-24-95	411	7.0	6.9	3.6
		03-28-95	409	7.1	6.6	3.7
		05-31-95	408	7.5	--	4.0
		07-24-95	411	7.5	7.1	3.8
		09-26-95	405	6.9	7.2	3.7
		11-28-95	409	7.0	7.0	3.8
		01-30-96	407	6.7	7.7	4.1
		03-26-96	405	7.0	7.4	4.2
		05-21-96	408	6.7	7.0	4.2
		07-22-96	408	6.6	7.3	4.0
		09-09-96	406	6.5	7.4	4.3

NITRATE CONCENTRATIONS AND DISTRIBUTION, 1994-96

Nitrate concentrations and field measurements collected during the summer of 1995 for the 50 wells are listed in table 1. Nitrate concentrations for the study area ranged from 0.05 to 26 mg/L and had a median of 3.3 mg/L. The areal distribution of nitrate concentrations in ground-water samples is shown in figure 2. About 10 percent of the water samples had nitrate concentrations larger than 10 mg/L (wells P20, P44, P46, P48, and P49), and about 34 percent had nitrate concentrations larger than 5 mg/L. Most of these wells are located in the northeastern part of Gage County and the northwestern parts of Johnson and Richardson Counties (fig. 2).

Nitrate concentrations in water samples collected in 1995 for the original five wells that had nitrate concentrations larger than 7 mg/L in 1989 and the additional 15 wells within a 3-mile radius of that original five wells are presented in table 3 and figure 2. Nitrate concentrations in water samples from four of the five wells (P13, P16, P31, and P32) with concentrations larger than 7 mg/L in 1989 decreased in 1995. However, three of the original five wells continued to have concentrations above 7 mg/L: P16 (8.2), P20 (12), and P31 (8.7).

The median nitrate concentration for the additional 15 wells (table 3, fig. 2) was 4.8 mg/L, and range was 0.16 to 26 mg/L. The median concentration for the 34 wells was 1.40 mg/L, with a range of 0.05 to 12 mg/L. The mean nitrate concentration for the 15 wells was about 3.4 times greater than the mean for the 34 wells in 1995. This result illustrates that the extent of the higher nitrate concentrations in the paleovalley alluvial aquifers initially observed in water samples in 1989 does not appear to be restricted to isolated locations but may be distributed over a larger area. The highest nitrate concentration of 26 mg/L was detected in a water sample collected from well P46 of Group 4 near P31 and could be the result of poor well construction (Exner and Spalding, 1985).

A temporal plot of nitrate concentrations in water samples collected bimonthly from November 1994 to September 1996 for five selected wells in the paleovalley alluvial aquifers (fig. 3) was used to identify temporal variations in nitrate concentrations. This plot indicates possible seasonal effects on nitrate concentrations in the shallow ground water. Seasonal variations in nitrate concentrations were most apparent at well P40, which is 54 ft deep (fig. 3). However, systematic variations were not very definitive at relatively deep wells— wells P04 (111 ft deep, P07 (175 ft deep), P31 (124 ft deep), and P42 (110 ft deep). Nitrate concentrations in well P40 were highly variable showing two high levels and two low levels annually. Examination of the 1995 data (fig. 3) shows that in general, the highest concentrations tended to occur in early summer and late fall for well P40, while the lowest concentrations tended to occur between winter and early spring and mid-summer. This fluctuation of nitrate concentration likely is due to variations in the nitrate supply through fertilizer application and the available water at or near land surface.The fall increases in nitrate concentrations observed suggest that shallow ground water is influenced by nitrate leaching from upgradient cultivated and irrigated fields. On the other hand, seasonal variations in nitrate concentrations at the four relatively deep wells were not noticeable (fig. 3). It is most likely these wells were in the semiconfined or confined aquifers in the area; the material overlying the aquifers may be semipermeable or impermeable so that downward movement of water and nitrates was somewhat inhibited. Under such conditions, the downward movement of water and nitrates to these aquifers takes longer than weeks or months (perhaps years), and this may be masking seasonal fluctuations. Well P42, for example, shows little temporal variation (fig. 3), because it penetrates a 55-foot deep layer of sediment, rich in clay, that overlies the aquifer, and that may be preventing the water and nitrates from percolating to the ground water quickly.

Table 3. Nitrate concentrations within a 3-mile radius of five original wells in the paleovalley alluvial aquifers, Nemaha Natural Resources District, Nebraska, 1989 and 1995

[ID, identification number; concentrations are in milligrams per liter]

1989		1995		
Well ID original well	**Nitrate as nitrogen[1]**	**Well ID additional well**	**Nitrate as nitrogen**	**Well depth (feet)**
		Group 1		
P13	7.1		3.3	156
		P35	2.2	190
		P36	3.4	150
		P37	4.0	169
		Group 2		
P16	12		8.2	77
		P38	.16	120
		P39	7.9	110
		P40	3.3	54
		Group 3		
P20	7.7		12	112
		P41	5.8	140
		P42	3.8	110
		P43	5.5	200
		Group 4		
P31	9.2		8.7	124
		P45	.27	120
		P46	26	40
		P47	9.9	145
		Group 5		
P32	8.4		3.5	157
		P48	21	160
		P49	12	78
		P50	7.9	65

[1]Data from Tanner and Steele (1991).

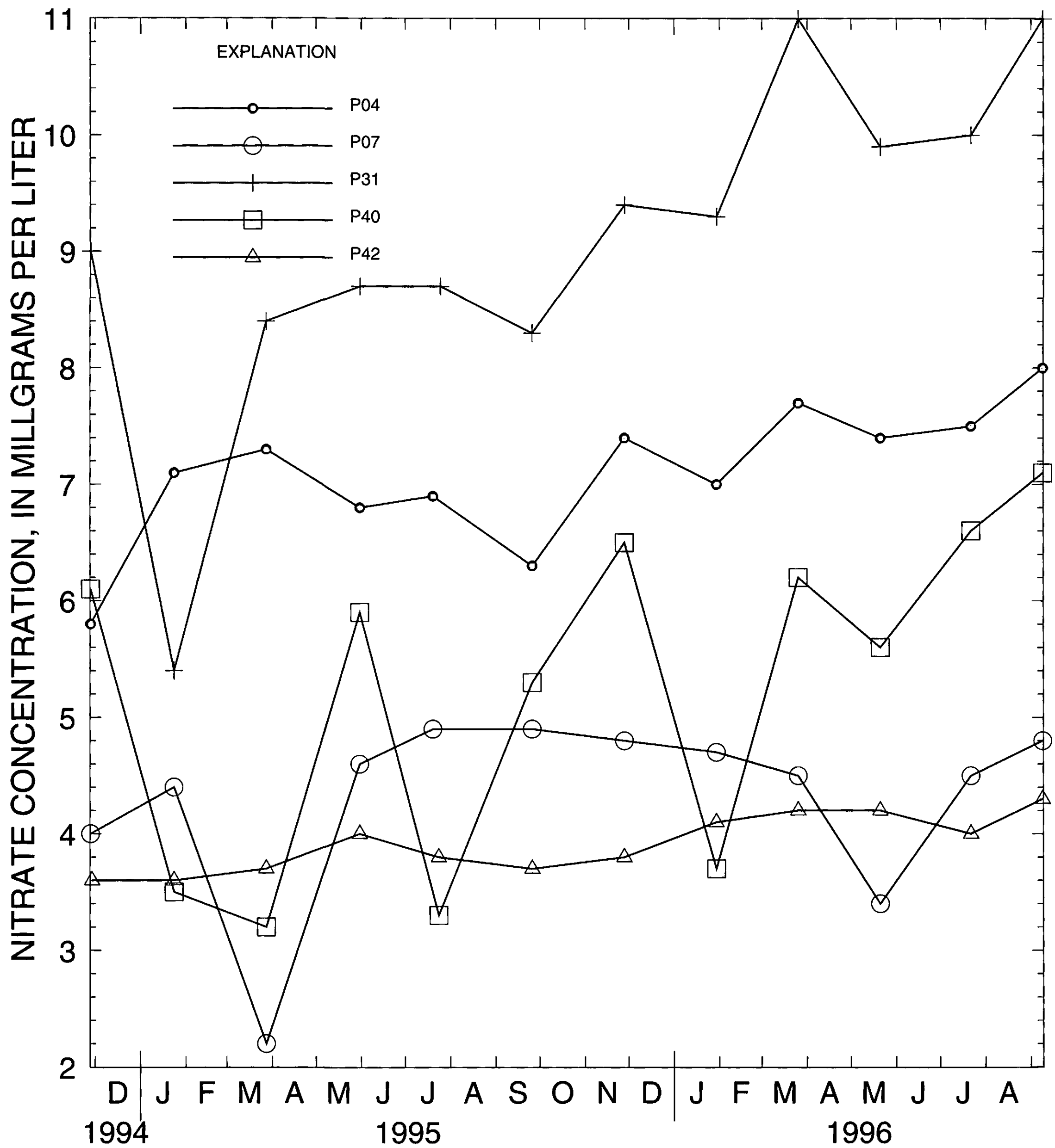

Figure 3. Temporal variations in nitrate concentrations for five selected wells in the paleovalley alluvial aquifers, Nemaha Natural Resources District, Nebraska, 1994–96.

Concentrations of nitrate in three of the five wells that were sampled bimonthly from November 1994 to September 1996—P04, P31, and P40—appeared to be increasing over time, whereas the concentrations of nitrate in the remaining two wells (P07 and P42) showed no apparent increase in concentrations with time (table 2 and fig. 3). Wells P04, P31, and P40, in which nitrate concentrations appear to be increasing, are public supply wells that provide drinking water for the Brock, Burr, and Humboldt communities. Because of the short period of record (2 years) for these wells and the large variation in nitrate concentrations, data are insufficient for the identification of statistically significant trends in nitrate concentrations.

COMPARISONS OF NITRATE CONCENTRATIONS, 1989 AND 1995

Concentrations of nitrate in water samples collected from 34 wells in 1989 and 1995 are shown in table 4 and figure 4. Increases in nitrate concentrations from 0.04 to 3.8 mg/L were observed in samples from 18 of the 34 wells. Decreases in nitrate concentrations from 0.02 to 4.9 mg/L were observed at 15 wells. The nitrate concentration at well P23 remained unchanged. Median nitrate concentrations for water samples collected from 34 wells decreased from 2.15 mg/L in 1989 to 1.40 mg/L in 1995 (table 4).

A paired-statistical comparison of the 34 nitrate concentrations collected in 1989 and in 1995 using the Wilcoxon signed-ranks test (Conover, 1980) showed no significant difference between the two data sets at the 95-percent confidence level. The p-value of the test was 0.78. A p-value is the probability of getting a test statistic equal to or more extreme than the value computed from the same data when the medians of the two populations being tested are the same. That is, the larger the p-value is above 0.05, the greater is the confidence that there is no difference between the medians of the two populations.

SUMMARY AND CONCLUSIONS

Nitrate concentrations in paleovalley alluvial aquifers of the Nemaha Natural Resources District at 50 wells sampled during the summer of 1995 ranged from 0.05 to 26 mg/L. The median concentration was 3.3 mg/L. About 10 percent of the water samples collected in 1995 had nitrate concentrations larger than 10 mg/L and about 34 percent had nitrate concentrations larger than 5 mg/L.

Samples were collected and analyzed for nitrate in 1995 from 15 additional wells, well identification numbers P46-P50, that were within a 3-mile radius of the five wells sampled in 1989 that had nitrate concentrations larger than 7 mg/L. The results of these analyses showed that a median nitrate concentration of 4.8 mg/L was about 3.4 times larger than the median concentration of 1.40 mg/L observed from the 34 wells representing the paleovalley alluvial aquifer in 1995. Thus, the extent of nitrate concentrations in the paleovalley alluvial aquifers does not appear to be restricted to isolated locations, but may be distributed over a larger area.

A plot of nitrate concentrations in water samples collected bimonthly from November 1994 to September 1996 for four municipal wells and one domestic well in the paleovalley alluvial aquifers was used to identify temporal variations in nitrate concentrations. This plot reflects possible seasonal effects on nitrate concentrations in the ground water. Seasonal variations in nitrate concentrations were most apparant in water samples from shallow well P40; however, systematic variations were not definitive at the remaining four relatively deep wells (wells P04, P07, P31, and P42). Downward movement of water and nitrates at the deep wells may be inhibited by semipermeable material overlying the aquifer and, therefore, seasonal fluctuations were masked. Nitrate concentrations in water samples from municipal wells P04, P31, and P40 appeared to be increasing from November 1994 to September 1996.

Table 4. Nitrate concentrations for 34 sampled wells in the paleovalley alluvial aquifers, Nemaha Natural Resources District, Nebraska, 1989 and 1995

[ID, identification; mg/L, milligrams per liter; <, less than]

	Nitrate as nitrogen			
	1989	1995	Change from 1989 to 1995	
Well ID	(mg/L)	(mg/L)	(mg/L)	(percent)
P01	0.69	0.05	-0.64	-93
P02	[1]<.10	.09	.04	80
P03	1.0	1.7	.70	70
P04	6.1	6.9	.80	13
P05	2.5	3.7	1.2	48
P06	5.4	7.9	2.5	46
P07	5.9	4.9	-1.0	-17
P08	3.2	3.8	.60	19
P09	<.10	.23	.18	360
P10	.46	.23	-.23	-50
P11	<.10	.71	.66	1,300
P12	5.9	1.2	-4.7	-80
P13	7.1	3.3	-3.8	-53
[2]P14	.65	.43	-.22	-34
P15	.19	.54	.35	180
P16	12	8.2	-3.8	-32
P17	4.7	5.6	.90	19
P18	1.8	1.2	-.60	-33
P19	1.5	1.2	-.30	-20
P20	7.7	12	3.8	49
P21	.31	2.8	2.5	800
P22	.31	.71	.40	130
[2]P23	1.1	1.1	0	0
P24	1.5	1.6	.10	7
P25	.12	.05	-.07	-58
[2]P26	2.5	.05	-2.45	-98
P27	2.7	3.2	.50	18
[2]P28	5.6	7.0	1.4	25
[2]P29	2.8	.9	-1.9	-68
P30	1.1	1.2	.1	9
P31	9.2	8.7	-.50	-5
P32	8.4	3.5	-4.9	-58
P33	6.3	8.8	2.5	40
P34	.33	.31	-.02	-6
Median	2.15	1.40	-.75	-35

[1]A less-than value is assumed to be 0.05.

[2]Samples were obtained from substituted wells in 1995.

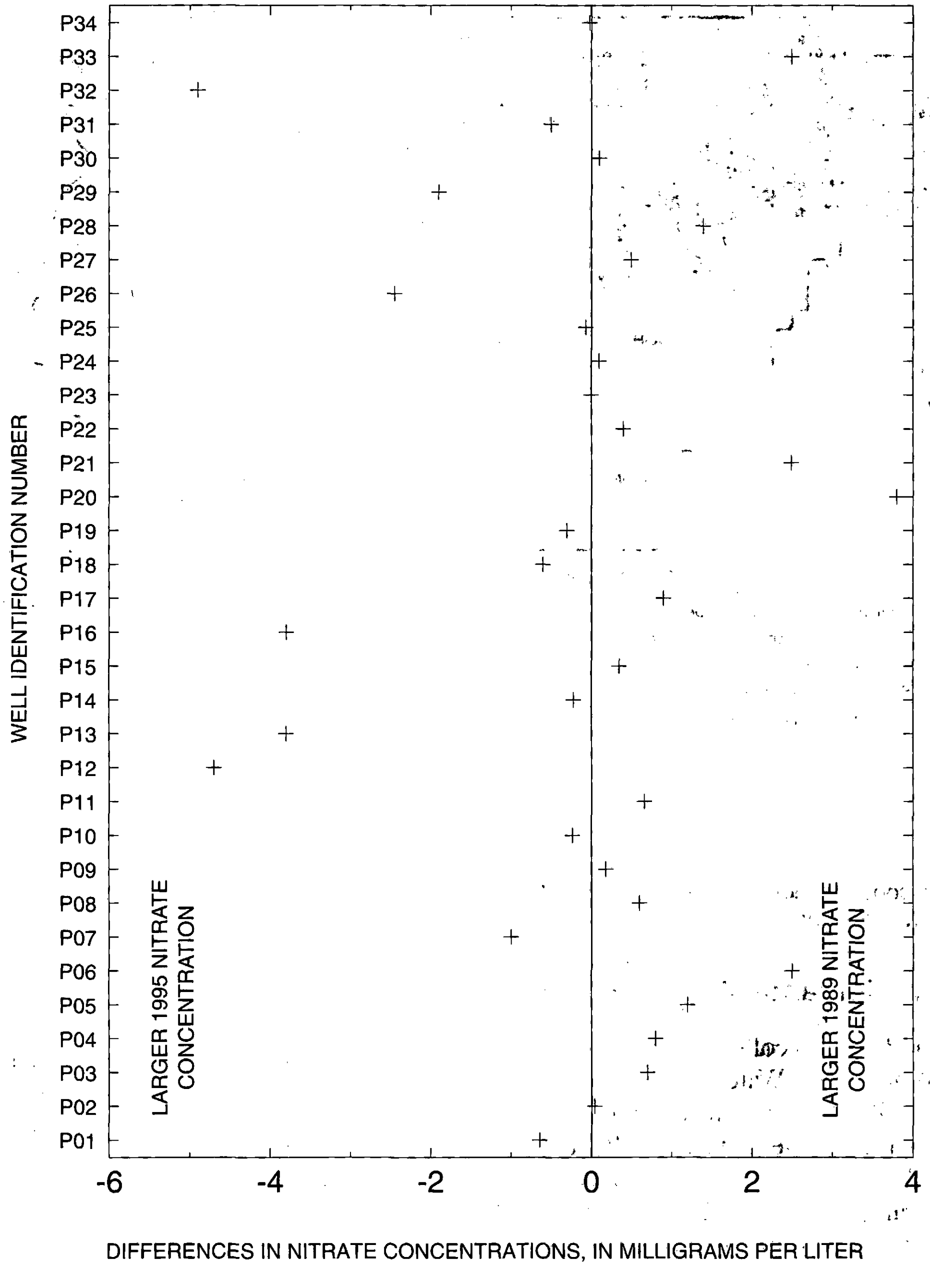

Figure 4. Comparison of 1989 and 1995 nitrate concentrations in water samples from the paleovalley alluvial aquifers, Nemaha Natural Resources District, Nebraska.

Considering results from 34 wells sampled in 1989 and in 1995, the median nitrate concentration decreased from 2.15 mg/L in 1989 to 1.40 mg/L in 1995. Nonetheless, a statistical comparison showed that nitrate concentrations have not changed significantly at the 95-percent confidence level.

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