

# Seasonal and Long-Term Changes in Nitrate-Nitrogen Content of Well Water in Oklahoma

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## ABSTRACT

To ensure that  $\text{NO}_3\text{-N}$  concentrations in groundwater do not exceed the maximum contaminant level (MCL;  $10 \text{ mg L}^{-1}$ ), drinking water supplies are continuously sampled and analyzed. Water sampling and analytical methods have changed during the past 40 yr, and failure to apply the errors associated with those methods places researchers at risk of reporting invalid  $\text{NO}_3\text{-N}$  changes. The objectives of this research were to compare analytical procedures, seasonal samplings, and storage methods for well water  $\text{NO}_3\text{-N}$  analyses using historical and recent well water data, to identify where changes in  $\text{NO}_3\text{-N}$  concentration have taken place and possible reasons for the changes; and to determine if age of water, well depth, and  $\text{NO}_3\text{-N}$  concentration are related. Benchmark  $\text{NO}_3\text{-N}$  analyses were obtained for 46 water wells which were then sampled each season (fall, winter, spring, and summer) over a 2-yr period. For each sampling, four samples were taken from each well; two were frozen immediately (common today) and two were stored at ambient temperature (benchmark procedure). Nitrate-N was determined on subsamples from all four samples using phenoldisulfonic acid (benchmark procedure) and automated Cd reduction (common today). This work suggests that a minimum difference of  $6.15 \text{ mg NO}_3\text{-N L}^{-1}$  is required before declaring significant differences between historical and current well water  $\text{NO}_3\text{-N}$  levels.

INTEREST in nitrate-N contamination of groundwater is attributable to possible health risks (methemoglobinemia) associated with consumption of water containing high  $\text{NO}_3\text{-N}$  by infants under 3 mo of age. This concern prompted the USEPA to set the maximum contaminant level (MCL) or public health standard for  $\text{NO}_3\text{-N}$  in drinking water at  $10 \text{ mg L}^{-1}$ . To ensure that  $\text{NO}_3\text{-N}$  concentrations in groundwater do not exceed the MCL, possible sources of pollution are continuously scrutinized.

Groundwater can be contaminated by both point and nonpoint sources of pollution. Some point sources include livestock feedlots, improper well construction and locations, and domestic septic disposal systems. Agricultural chemicals, particularly N fertilizers, are commonly cited as major contributors to nonpoint pollution. However, historical data collected in the early 1950s report a number of wells having  $\text{NO}_3\text{-N}$  concentrations in excess of  $10 \text{ mg L}^{-1}$ . This was at a time when fertilizer use was uncommon (Johnson et al., 1995), suggesting that sources other than N fertilizers were responsible for the high  $\text{NO}_3\text{-N}$  levels. This may also be true in current well samplings having high  $\text{NO}_3\text{-N}$  concentrations. Determination of well water age aids in determining whether  $\text{NO}_3\text{-N}$  concentrations are due to leaching of fertilizers applied in recent years or whether they are remnants from a prefertilizer era.

Because most  $\text{NO}_3\text{-N}$  sources are at the soil surface, shallow aquifers should logically be more susceptible to contamination than deeper ones; however, many factors exist that affect  $\text{NO}_3\text{-N}$  movement in soils. Nitrate-N contamination of deeper groundwater can occur where a hydraulic connection and a hydraulic gradient exist between shallow and deep aquifers (Fedkiw, 1991). This results in recharge of the deeper aquifer with  $\text{NO}_3\text{-N}$  rich water from the shallower aquifer. High capacity pumping of deep wells can also draw water downward from overlying aquifers, thus resulting in contamination of the deeper wells. Migration of water through the unsaturated zone of many soils can be quite slow, resulting in inputs of N requiring many years to reach the groundwater reservoir. Therefore, N sources present at one time, although now obliterated, could still result in  $\text{NO}_3\text{-N}$  contamination of deep wells.

Many hydrogeologic and source-related factors exist that control the amount, position, and timing of  $\text{NO}_3\text{-N}$  concentration in groundwater. Complex interactions of those factors make it difficult to draw general inferences about the potential for  $\text{NO}_3\text{-N}$  contamination of groundwater in a particular region. The direct approach to determine where  $\text{NO}_3\text{-N}$  contamination exists is sampling and analysis of well water. Fedkiw (1991) noted that  $\text{NO}_3\text{-N}$  sample variances within and between wells in the same locale and between years or seasons is very large. In Minnesota, Anderson (1989) found that  $\text{NO}_3\text{-N}$  concentrations ranged from  $4.06$  to  $16.3 \text{ mg L}^{-1}$  within the same well during the year. This clearly identifies a weakness associated with seasonal sampling and indicates that one sample is insufficient to provide conclusive evidence of groundwater quality and that recurrent monitoring of water wells is necessary. Anderson (1989) also found that seasonal fluctuations in mean concentrations during the 1982 through 1984 period were greater than the apparent historical increase in  $\text{NO}_3\text{-N}$  concentration. This generated doubt as to whether or not a real increase had taken place or whether errors stemming from seasonal variation obscured the long-term concentration changes.

Methods used to analyze groundwater samples for  $\text{NO}_3\text{-N}$  can also be a source of error when comparing historical data. Since the 1950s, several analytical methods have been used to determine  $\text{NO}_3\text{-N}$  in groundwater. Each method has its own inherent random and bias errors. Direct numerical comparisons between data analyzed using two different procedures (without assessing their proper errors) could be inaccurate. Research studies have reported increases in groundwater  $\text{NO}_3\text{-N}$  concentrations spanning time periods of up to 30 yr without addressing the effects of changing analytical methods on those estimates.

Another possible source of error when comparing

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historical data is storage of the sample. Current protocol requires that water samples being analyzed for  $\text{NO}_3\text{-N}$  be cooled at 4 to 10°C for transport or analyzed immediately in the field (Scalf et al., 1981). Recommended maximal holding time for samples is 48 h. This protocol is intended to minimize any biological transformations that may take place. Data compiled years ago that provide the benchmark levels for historical comparisons may include samples taken without observing those guidelines. Unless the statistical parameters associated with an independent estimate are adequately assessed, researchers are at risk of making invalid conclusions about changes in  $\text{NO}_3\text{-N}$  concentrations.

The primary objectives of this research were to use historical and recent data from north-central Oklahoma to compare analytical procedures, seasonal samplings, and storage methods for well water  $\text{NO}_3\text{-N}$  analyses and to identify where changes have taken place. Additional objectives were to estimate the approximate age of water from selected wells using tritium/helium-3 groundwater dating techniques to determine if age of water, well depth, and  $\text{NO}_3\text{-N}$  concentration are related and to identify possible reasons for changes in well water  $\text{NO}_3\text{-N}$ .

## MATERIALS AND METHODS

Seventy-five water wells in Garfield, Grant, and Kingfisher counties in north-central Oklahoma were selected for comprehensive sampling. Those wells were chosen because  $\text{NO}_3\text{-N}$  data collected from 1953 through 1972 were available to serve as benchmark levels (Bingham and Bergman, 1980; Dover, 1953; unpublished records from the files of the U.S. Geol. Survey office in Oklahoma City, OK). The major groundwater basins underlying these counties are alluvium and terrace deposits. The deposits are found along rivers and streams as unconfined aquifers and consist of interfingerings of sand, sandy clay, clay, and gravel. Water quality is affected by nearby streams; however, overall water quality is good and the water can be used for domestic, irrigation, industrial, and municipal purposes. Average annual precipitation for this area ranges from 711 to 864 mm, whereas the average annual evaporation potential ranges from 1500 to 1600 mm. This relationship results in evapotranspiration removing about 80% of Oklahoma's water from availability for use (Oklahoma Water Resour. Board, 1984, p. 18–31). These counties also have substantial agricultural activity associated with continuous wheat production and N fertilization.

Tax records obtained from the three counties were used to determine current ownership of the property on which each well was located. The owners were contacted and informed about the proposed experiment. Due to changes since the original data were compiled, several wells no longer existed. In many cases, verification of well authenticity was also difficult. The wells sampled during the benchmark period were identified by legal description only. This indicated a 0.65 to 2.59 km<sup>2</sup> area on which the well was located. Many of these areas of land contained numerous water wells. Several cooperators were able to verify the source of earlier samplings based on personal knowledge, family records, or inquiries of previous land owners. Information regarding the age of particular wells made proper well selection possible at most locations. Consequently, the number of wells to be sampled was reduced to 46; and permission was obtained from the well owners or operators to begin sampling in the fall of 1993. The well sites

represented an array of soil types and land uses. Wells had an average total depth of 14.6 m and an average depth to water of 6.4 m and included both dug and drilled wells. Water samples were obtained each season (fall, winter, spring, and summer) from September 1993 through July 1995.

To obtain a representative groundwater sample, the sample should be taken directly from the aquifer. However, 37 of the 46 wells contained in-place, semipermanent, mounted pumps that limited the options available for sampling. Those wells were pumped for a period of time adequate to remove several bore volumes of water from the well so that samples collected reasonably represented that of the aquifer (Scalf et al., 1981). Of the remaining wells, six were collected via windmills, and three were collected using a teflon bailer. The bailer was rinsed in the field with deionized water following each use (Davis et al., 1993). All samples were handled using established sampling protocol (Barcelona et al., 1987). Each season, four samples were collected from each well in 250-mL plastic bottles; two were stored by freezing the samples immediately using an ice chest containing dry ice, and two were stored at ambient temperatures for 1 to 2 d until analyses were performed. Frozen samples were thawed to room temperature before analyses.

Frozen and nonfrozen samples were analyzed using the phenoldisulfonic acid method (Bremner, 1965; Chapman and Pratt, 1961) and by a "Lachat-Quickchem" automated flow injection system that employs Cd reduction of  $\text{NO}_3\text{-N}$  to  $\text{NO}_2\text{-N}$  and measurement of  $\text{NO}_2\text{-N}$  by the Griess-Ilosvay method (Henriksen and Selmer-Olsen, 1970; Jackson et al., 1975; Keeney and Nelson, 1982). Phenoldisulfonic acid was the method of choice when most of the benchmark data were analyzed. This colorimetric procedure is tedious, time consuming, and is subject to several interferences. Cadmium reduction is currently used by many industrial and public laboratories.

Statistical analyses of data were performed using procedures outlined by SAS (1990). A split-plot in space and time ANOVA model was used to assess the effects of sampling times (4 seasons  $\times$  2 yr), methods of storage (frozen vs. nonfrozen), methods of analysis (phenoldisulfonic acid vs. Cd reduction), and their interactions.

Ten water wells were selected from the 46 and sampled in January 1996 for age determination using tritium/helium-3 groundwater dating techniques (Solomon et al., 1992). Only 10 were selected due to the restrictive cost of analyses. These 10 wells were categorized into one of four groups, i.e., (i) wells <12 m deep with  $\text{NO}_3\text{-N}$  concentrations >15 mg L<sup>-1</sup>, (ii) wells <12 m deep with  $\text{NO}_3\text{-N}$  concentrations <15 mg L<sup>-1</sup>, (iii) wells >12 m deep with  $\text{NO}_3\text{-N}$  concentrations >15 mg L<sup>-1</sup> with high  $\text{NO}_3\text{-N}$ , and (iv) wells >12 m deep with  $\text{NO}_3\text{-N}$  concentrations <15 mg L<sup>-1</sup>. Two samples were collected from each of the 10 wells on the same date. One sample was analyzed for helium-3, and the other for tritium. The helium-3 sample was collected using an apparatus that consisted of a 46-cm long piece of 6.35-mm copper tubing capped on each end by a piece of tygon tubing. The copper tube was held in a vertical position with the lower tygon tube attached to the well discharge via an air-tight connection. The upper tygon tube remained open to allow water to flow through the copper tube. When no air bubbles were observed in either tygon tube, they were closed using pinch clamps. The ends of the copper tube were then crimped using refrigerator clamps, trapping the water sample within the copper tubing. The tygon tubes were removed, and the ends of the copper tubing were capped. Caution was taken during this step to avoid trapping air bubbles in the copper tube and contaminating the sample. The tritium sample was collected in a 500-mL glass bottle with a polypropylene cap leaving no airspace within the bottle. The

samples were forwarded to the University of Rochester, Rochester, NY, for analyses and age estimation by the Department of Earth and Environmental Sciences.

## RESULTS AND DISCUSSION

Highly significant sampling time by method of analysis and sampling time by storage interactions were observed (Table 1). These interactions among sampling time, storage, and method of analysis restrict the reliability with which individuals can make direct numerical comparisons between different sets of  $\text{NO}_3\text{-N}$  data. The overlapping errors associated with combining interdependent variables implied that the benchmark data would have had a different statistical error associated with it than data collected from the same wells in the last 2 yr.

A standard deviation estimate for the benchmark data was derived using the MSE from an ANOVA of  $\text{NO}_3\text{-N}$  values obtained from the nonfrozen samples analyzed using phenoldisulfonic acid. A similar estimate was made for the frozen samples analyzed using Cd reduction.

Nonfrozen samples analyzed using phenoldisulfonic acid and the frozen samples analyzed using Cd reduction had standard deviations of  $\pm 2.48$  and  $\pm 3.67$   $\text{mg L}^{-1}$ , respectively. This suggests that a minimum difference of  $6.15$   $\text{mg L}^{-1}$  be used to make direct comparisons between historical (nonfrozen samples analyzed using phenoldisulfonic acid) and current water samples. The standard deviation ( $\pm 2.48$   $\text{mg L}^{-1}$ ) was assigned to benchmark  $\text{NO}_3\text{-N}$  values, and tests on independent means comparing benchmark and current data were performed for each well. Changes in  $\text{NO}_3\text{-N}$  between benchmark and current data are reported in Table 2. Seven of the 46 wells were excluded from all ANOVAs because they were determined to be point-source contaminated; however, changes over time within these wells are included in the discussion.

Direct comparisons of historical vs. current estimates for each well, disregarding the statistical analyses, would have detected increases in 35 of the 46 wells (76%). Using the appropriate statistics, significant increases in well water  $\text{NO}_3\text{-N}$  over time were found in only 18 wells (39%), while 7 (15%) showed decreases and 21 (46%) exhibited no change ( $p < 0.05$ ). The average  $\text{NO}_3\text{-N}$  concentrations for the wells during the past 2 yr (including those determined to be point-source contaminated) ranged from  $0.61$  to  $99.4$   $\text{mg L}^{-1}$  and had a mean of

$14.0$   $\text{mg L}^{-1}$ . Increases in  $\text{NO}_3\text{-N}$  concentration ranged from  $5.67$  to  $96.7$   $\text{mg L}^{-1}$  and had a mean of  $23.1$   $\text{mg L}^{-1}$ . Decreases ranged from  $5.24$  to  $46.4$   $\text{mg L}^{-1}$  and had a mean of  $22.9$   $\text{mg L}^{-1}$ . Assignment of the appropriate standard deviation to benchmark data is crucial when making historical comparisons involving well water  $\text{NO}_3\text{-N}$ , and the chance of incorrectly declaring changes without proper statistical treatment of the data is apparent.

Of the 18 wells that showed historical increases, seven were identified as being likely contaminated by point-source pollution. Wells 13, 14, 24, and 44 were all located on highly vulnerable farmsteads. The soil texture for these sites ranged from a fine sand to a sandy loam, and the average depth to groundwater was  $5.2$  m. All of these wells were located near livestock corrals that

**Table 2. Comparisons of well water  $\text{NO}_3\text{-N}$  between benchmark samples (nonfrozen, phenoldisulfonic acid) and current samples (frozen, Cd reduction) from the same wells.**

Well no.	$\text{NO}_3\text{-N}$		Significance
	Benchmark§	Current¶	
mg L <sup>-1</sup>			
1	20.7	19.3	NS
2	0.77	8.68	NS
3	0.02	11.5	‡
4	42.8	2.50	**
5	0.11	10.3	†
6	0.18	2.78	NS
7	0.02	14.7	‡
8	0.14	11.0	‡
9	6.75	9.20	NS
10	8.78	10.8	NS
11	0.00	0.71	NS
12	0.15	11.0	‡
13	0.31	34.6	‡
14	0.29	15.3	‡
16	11.3	15.1	NS
18	5.85	13.7	‡
19	36.0	11.1	**
20	3.83	11.9	†
21	0.29	4.76	NS
23	2.70	10.4	†
24	1.31	16.6	‡
25	67.5	21.1	**
26	38.3	20.9	**
28	2.25	4.47	NS
29	4.50	6.17	NS
30	3.60	3.51	NS
31	5.85	16.7	‡
32	0.77	3.27	NS
33	2.70	99.4	‡
34	1.91	7.58	†
35	2.00	7.24	NS
36	1.13	4.46	NS
37	1.24	5.38	NS
38	22.5	1.31	**
39	1.40	44.3	‡
41	6.98	15.7	†
42	6.75	1.32	*
43	0.38	1.20	NS
44	2.25	16.8	‡
45	1.76	6.49	NS
46	3.38	4.44	NS
48	0.02	1.35	NS
49	1.91	0.69	NS
50	3.38	92.9	‡
51	13.5	12.7	NS
52	5.85	0.61	*

\*,\*\* Decrease at the 0.05 and 0.01 probability levels, respectively.

†,‡ Increase at the 0.05 and 0.01 probability levels, respectively.

§ Measured and reported from 1953 through 1972.

¶ Determined over eight sampling dates from 1993 through 1995.

**Table 1. Split-plot in space and time ANOVA for well water  $\text{NO}_3\text{-N}$ , 1993–1995.**

Source	df	Mean squares	F value	Pr > F
Well	38	618.87	25.66	0.0001
Sampling time	7	10.85	0.45	0.8693
Well × Sampling (a)	202	24.11		
Storage of samples	1	1.18	0.46	0.4987
Sampling × Storage	7	13.89	5.37	0.0001
Well × Storage (Sampling) (b)	240	2.58		
Method of analysis	1	43.74	6.87	0.0090
Sampling × Method	7	81.21	12.76	0.0001
Storage × Method	1	15.33	2.41	0.1212
Sampling × Storage × Method	7	7.18	1.13	0.3436
Error (c)	472	6.36		

were frequently used. These factors made these particular wells prime candidates for point-source animal waste  $\text{NO}_3\text{-N}$  contamination. The water from Well 13 was estimated to have entered the aquifer from 3 to 5 yr ago (Table 3). This supports the hypothesis that recent land management practices can contribute to contamination of recharge water at the ground surface. Water from Well 14 was 18 yr old (Table 3), placing its recharge within a time frame when animal waste could have been a source of  $\text{NO}_3\text{-N}$  contamination. Well 24 contained water that was 15 yr old (Table 3). In addition to being vulnerable to animal waste runoff, the casing of Well 24 was damaged. The length of time this problem existed was unknown; however, this introduced another factor that tends to support point-source contamination at the site.

Wells 33, 39, and 50 were probably contaminated as a result of poor well construction. Well 33 was located near several oil pumping units and drilling rigs. Originally drilled to discover oil, its initial bore size was 20 cm in diameter. When no oil was found, a 13-cm casing was installed to use the site as a water well. The remaining 7 cm was neither packed nor sealed, allowing any surface contamination to have direct access to the groundwater system. This well was also located in the immediate vicinity of an excessively manure-fertilized garden and a septic system, thus indicating that recent point source contamination (not associated with aquifer recharge) may have caused this high  $\text{NO}_3\text{-N}$  level. Well 39 was a large diameter, hand-dug well. This type of well is vulnerable to contamination because of its design and shallow depth to aquifer (5.5 m, Table 3). Well 39 was located at an urban residence and was not associated with any type of agricultural production; however, the water, which was 3 yr old (Table 3), contained the third largest mean  $\text{NO}_3\text{-N}$  concentration of all wells sampled. Well 50 was a 15-m drilled well, but it had only been cased to a depth of 6 m. Well 50 was also located on a down slope gradient from a residence septic system and a corral. Wells 33 and 50 had the largest  $\text{NO}_3\text{-N}$  concentrations of all wells sampled (99 and 93  $\text{mg L}^{-1}$ , respectively) (Table 2). Water samples from Well 33 and Well 50 represented a mixing of old and young waters. Well 33 contained mostly older water, which could have en-

tered the aquifer as long as 100 yr ago. The best estimate of its approximate age was from 50 to 75 yr (Table 3). Since the benchmark  $\text{NO}_3\text{-N}$  concentration for this well was 2.70  $\text{mg L}^{-1}$ , the recently recharged portion of the water probably contained most of the  $\text{NO}_3\text{-N}$  determined. Well 50 provided a sample mixed to the point that an age determination could not be made. Analysis of water from other wells in the vicinity (within 1.60 km) of Well 33 and Well 50 failed to show any signs of contamination (4.75–7.65  $\text{mg L}^{-1}$ ), supporting the conclusion that  $\text{NO}_3\text{-N}$  levels in these wells were due to point sources.

Of the other four wells tested for age (Table 3), Well 1 and Well 11 showed no significant changes, whereas Well 3 and Well 41 showed increases over time ( $p < 0.05$ ; Table 2). Well 1 was a shallow well with a  $\text{NO}_3\text{-N}$  concentration of 19.3  $\text{mg L}^{-1}$  (Table 2). The water in this well was estimated to be about 100 yr old (Table 3); however, pure old water (low or no tritium) is very difficult to age with certainty. Well 11 was also a shallow well, but its concentration and age were 0.71  $\text{mg L}^{-1}$  (Table 2) and 22 yr (Table 3). Well 3, a deep well, and Well 41, a shallow well, contained water that was 10 and 13 yr old, respectively. This lack of relationship between depth and age supports the hypothesis that factors exist which affect the rate of water movement through soils. Because no evidence suggested point-source contamination of these wells, increases were probably due to nonpoint sources.

Surface-applied N fertilizer is commonly cited as the major source of nonpoint  $\text{NO}_3\text{-N}$ . Leaching of excessively-applied N fertilizer provides a source of nonpoint  $\text{NO}_3\text{-N}$  under certain circumstances; however, if leaching was a source of  $\text{NO}_3\text{-N}$  for Well 1 and Well 11, an opposite relationship between age and  $\text{NO}_3\text{-N}$  concentration would be expected. Since fertilizer use was uncommon 100 yr ago, the older water should have minimal  $\text{NO}_3\text{-N}$ , and the younger water should have the greatest concentrations. Likewise, no relationship between  $\text{NO}_3\text{-N}$  and average aquifer depth existed for all wells showing increases (excluding those contaminated by point sources; Fig. 1), or for all wells sampled (excluding those contaminated by point sources) in either the benchmark years or the past 2 yr (Fig. 2). Although leaching of surface-applied N fertilizer may have been the cause of increased  $\text{NO}_3\text{-N}$  for some wells in the study, the lack of relationship between concentration and depth (Fig. 1 and 2) indicate that this cause was not widespread, and nonpoint sources of  $\text{NO}_3\text{-N}$  other than those found at the soil surface must exist.

Of the seven wells showing decreases over time, two have been identified as prior sites of point-source contamination. Well 4 was located on a site used for poultry production when the benchmark data were collected. It has since become a residence well, without poultry, which may explain the decrease in  $\text{NO}_3\text{-N}$  values. Well 38 was a hand-dug well when sampled in the 1950s. Since that time, it has been properly cased and secured, and the concentration of  $\text{NO}_3\text{-N}$  in the water has decreased. Wells 25 and 26 were both located on the same section of land. The land was irrigated cropland overly-

**Table 3. Benchmark and current  $\text{NO}_3\text{-N}$  in well water, type of location, depth to aquifer, and age for 10 wells selected.**

Well no.	$\text{NO}_3\text{-N}$		Type of location	Depth to aquifer	Age§
	Benchmark†	Current‡			
mg L <sup>-1</sup>				m	yr
1	20.7	12.6	farmstead	5.1	≈ 100
3	0.02	8.6	farmstead	5.7	10
11	0.00	1.0	farmstead/corral	3.0	22
13	0.31	49.3	farmstead/corral	4.5	3–5
14	0.29	13.7	farmstead/corral	5.1	18
24	1.31	17.4	farmstead/corral	4.8	15
33	2.70	86.5	rural residence	11.5	50–75
39	1.40	50.4	urban residence	5.5	3
41	6.98	13.1	farmstead	5.4	13
50	3.38	39.0	farmstead/corral	7.9	not determined

† Measured and reported from 1953 through 1972.

‡ Sampled on 15 Jan. 1996.

§ Determined using tritium/helium-3 dating techniques.

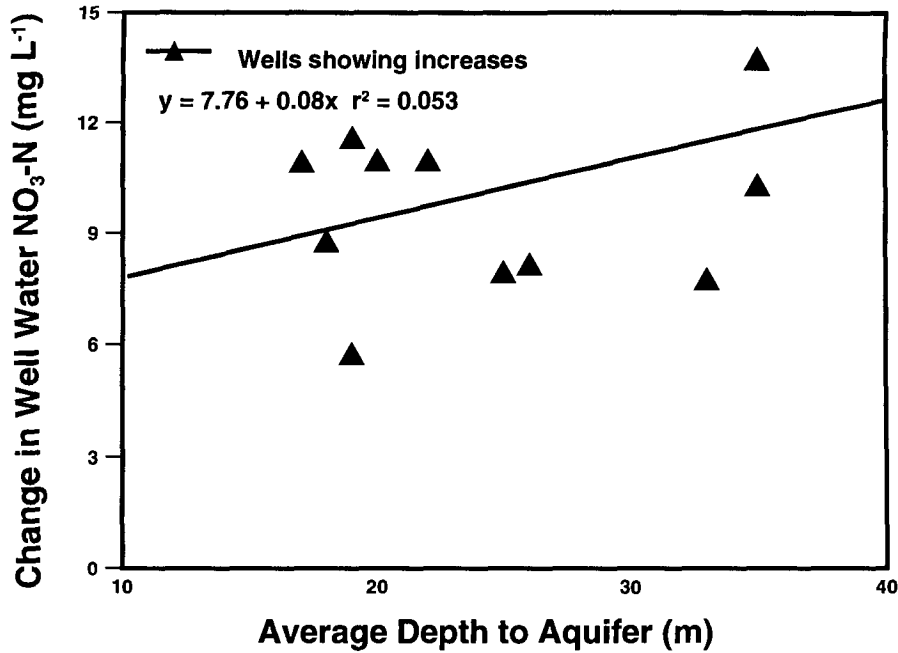


Fig. 1. Linear relationship of changes in NO<sub>3</sub>-N on the average depth to aquifer for water wells showing increases over time (excluding those point-source contaminated).

ing a shallow aquifer, which may explain why the NO<sub>3</sub>-N levels have remained considerably more than 10 mg L<sup>-1</sup>. However, no information was obtainable regarding the history of the area to determine the source of high benchmark levels of NO<sub>3</sub>-N. No historical information was available for Wells 19, 42, and 52. Wells 19, 25, and 26 probably were point-source contaminated, improperly sampled, or inaccurately analyzed as their NO<sub>3</sub>-N concentrations grossly exceeded the average for that time period.

The average NO<sub>3</sub>-N concentration for the wells in this study over the past 2 yr (excluding those that were point-source contaminated) was 8.40 mg L<sup>-1</sup>. The average benchmark NO<sub>3</sub>-N concentration (excluding previously point-source contaminated wells) was 2.90 mg L<sup>-1</sup>. The average time span between benchmark and current sampling dates for all wells was 38 yr. Assuming continuous and constant accumulation, this would represent an average increase of 0.14 mg L<sup>-1</sup> yr<sup>-1</sup>. This figure closely agrees with that of Chen and Druliner

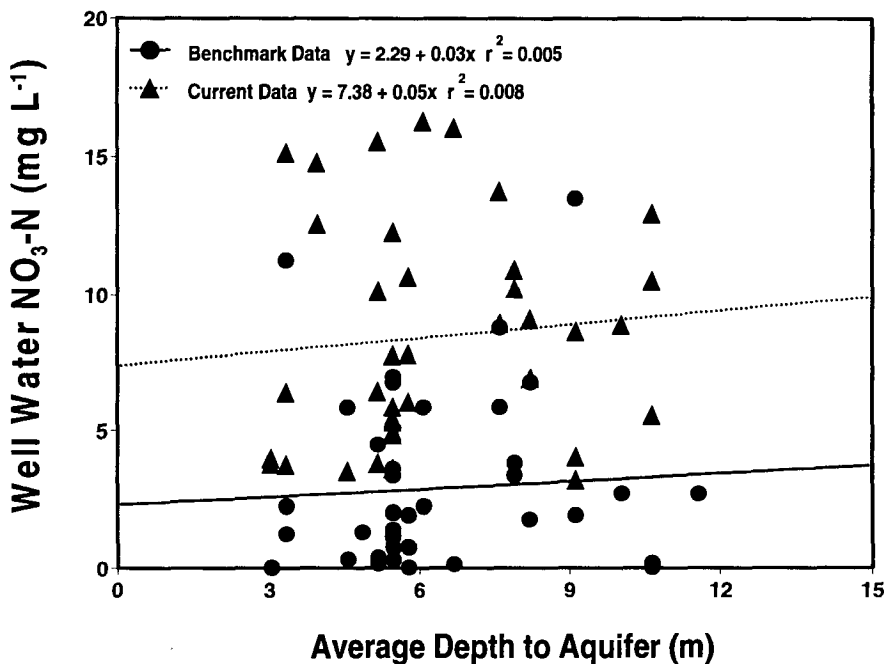


Fig. 2. Linear relationship of NO<sub>3</sub>-N on the average depth to aquifer for benchmark and current data from water wells (excluding those point-source contaminated).

(1988), who found  $\text{NO}_3\text{-N}$  concentrations in Nebraska groundwater to be increasing at a rate of  $0.12 \text{ mg L}^{-1} \text{ yr}^{-1}$ .

## CONCLUSIONS

Significant interactions were detected among seasonal sampling, sample storage, and method of analysis for well water  $\text{NO}_3\text{-N}$ . Consequently, there is considerable risk of drawing incorrect conclusions about  $\text{NO}_3\text{-N}$  changes when making direct numerical comparisons between historical levels (obtained from analyzing nonfrozen samples using phenoldisulfonic acid) and current levels (obtained from analyzing frozen samples using Cd reduction). By estimating the statistical errors associated with independent samples, more reliable determinations about changes in  $\text{NO}_3\text{-N}$  can be made. The standard deviation for historical  $\text{NO}_3\text{-N}$  values (nonfrozen analyzed using phenoldisulfonic acid) used in these experiments was  $\pm 2.48 \text{ mg L}^{-1}$ . The current samples (frozen samples analyzed using Cd reduction) had a standard deviation of  $\pm 3.67 \text{ mg L}^{-1}$ . This suggests that a minimal difference of  $6.15 \text{ mg L}^{-1}$  be used to make direct comparisons between historical (nonfrozen samples analyzed using phenoldisulfonic acid) and current water samples. Increases in well water  $\text{NO}_3\text{-N}$  over time were found in only 18 wells (39%), while 7 (15%) showed decreases and 21 (46%) exhibited no change ( $p < 0.05$ ). No relationship was detected among depth to aquifer, age of water, and well water  $\text{NO}_3\text{-N}$  for the benchmark population, the current population, or the wells which showed increases.

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## REFERENCES

- Anderson, H.W., Jr. 1989. Effects of agricultural quality of water in surficial sand-plain aquifers in Douglas, Kandiyohi, Pope, and Sterns counties. U.S. Geol. Survey, St. Paul, MN.
- Barcelona, M., J.F. Keely, W.A. Pettyjohn, and A. Wehrmann. 1987. Handbook: Ground water. p. 107-126. USEPA Rep. 625/6-87/016. USEPA, Office of Res. and Development, U.S. Gov. Print. Office, Washington, DC.
- Bingham, R.H., and D.L. Bergman. 1980. Reconnaissance of the water resources of the Enid quadrangle in north central Oklahoma. Map HA-7. U.S. Geol. Survey, Oklahoma City, OK.
- Bremner, J.M. 1965. Inorganic forms of nitrogen. p. 1179-1237. *In* C.A. Black et al. (ed.) Methods of soil analysis. Part 2. Agron. Monogr. 9. ASA, Madison, WI.
- Chapman, H.D., and P.F. Pratt. 1961. Methods of analysis for soils, plants, and waters. p. 153-157. Univ. of California Div. of Agric. Sci., Riverside, CA.
- Chen, H.H., and A.D. Druliner. 1988. Agricultural chemical contamination of ground water in six areas of the High Plains aquifer, Nebraska. p. 103-106. National water summary, 1986—hydrologic events and ground water quality. U.S. Geol. Survey Water Supply Paper 2325. U.S. Gov. Print. Office, Washington, DC.
- Davis, M., D. Peterson, and E. Giles. 1993. Groundwater bulletin. Dec. issue. Illinois Groundwater Consortium, Carbondale, IL.
- Dover, T.B. 1953. Chemical character of public water supplies in Oklahoma. Bull. 8. Div. of Water Resour., Oklahoma Planning and Resour. Board, U.S. Geol. Survey, Oklahoma City, OK.
- Fedkiw, J. 1991. Nitrate occurrence in U.S. waters (and related questions): A reference summary of published sources from an agricultural perspective. USDA Publ. U.S. Gov. Print. Office, Washington, DC.
- Henriksen, A., and A.R. Selmer-Olsen. 1970. Automatic methods for determining nitrate and nitrite in water and soil extracts. *Analyst* 95:514-518.
- Jackson, W.A., C.E. Frost, and D.M. Hildreth. 1975. Versatile multirange analytical manifold for automated analysis of nitrate-nitrogen. *Soil Sci. Soc. Am. Proc.* 39:592-593.
- Johnson, G.V., W.R. Raun, and E.R. Allen. 1995. Oklahoma soil fertility handbook. 3rd ed. p. 95-98. Oklahoma Plant Food Educational Soc. Dep. of Agron., Oklahoma State Univ., Stillwater, OK.
- Keeney, D.R., and D.W. Nelson. 1982. Nitrogen—inorganic forms. p. 643-698. *In* A.L. Page et al. (ed.) Methods of soil analysis. Part 2. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.
- Oklahoma Water Resources Board. 1984. Oklahoma's water atlas. Publ. 120. Oklahoma Water Resour. Board, Oklahoma City, OK.
- SAS Institute. 1990. SAS/STAT user's guide, release 6.03 ed. SAS Inst., Cary, NC.
- Scalf, M.R., J.F. McNabb, W.J. Dunlap, R.L. Cosby, and J.S. Fryberger. 1981. Manual of ground-water quality sampling procedures. p. 43-82. USEPA Rep. 600/2-81-160. U.S. Gov. Print. Office, Washington, DC.
- Solomon, D.K., R.J. Poreda, S.L. Schiff, and J.A. Cherry. 1992. Tritium and helium 3 as groundwater age tracers in the Borden aquifer. *Water Resour. Res.* 28:741-755.