Chapter 6: Results

This chapter contains six sections. Section 6.1 reports the results of statewide analyses of nitrate concentrations in Texas groundwater as reported in the TWDB groundwater data system. Maps and histograms in this section show the variation of the estimated probability of nitrate detection by location, discretized into 7.5' quadrangles in the horizontal dimensions only. In addition, graphs present variations in nitrate detection frequency with depth and with time throughout the state.

Section 6.2 shows much the same information for five aquifers selected for additional study. Variations in nitrate detection frequency in two dimensions, with depth, and through time are presented. In addition, the behavior of nitrate in the different aquifers is compared.

Section 6.3 shows the results of the attempt to correlate indicator variables to the variations in nitrate detection rates. Regression results for both statewide and single-aquifer data are presented.

Section 6.4 compares the nitrate detection rates calculated from the TWDB data with an independent set of nitrate measurements collected by the Water Utilities Division of the Texas Natural Resource Conservation Commission as part of their Primary Drinking Water Standards enforcement program.

Section 6.5 presents the results of a comparison of the occurrence of nitrate and herbicides as reported in the US Geological Survey's reconnaissance of groundwater in the mid-continental United States.

Section 6.6 presents a brief summary of the results.

Note that all nitrate concentrations in this chapter are given in equivalent units of elemental Nitrogen (nitrate-N). The Primary Drinking Water Standards define the maximum contaminant level (MCL) as 10 mg/l nitrate-N. The equivalent concentration in nitrate-NO3 is 44.3 mg/l.

6.1 STATEWIDE RESULTS

Table 6.1 shows the total number of nitrate measurements in the base data set (46,507 nitrate measurement records) that exceed four threshold concentrations. The thresholds are 10 mg/l (the MCL), 5 mg/l (half the MCL, and a trigger level for increased monitoring), 1 mg/l (selected to indicate human influence on groundwater, as described in Section 4.1), and 0.1 mg/l (the detection limit selected for this study, as described in Section 3.1). The table also lists the estimated probability of exceeding these thresholds in a measurement selected at random from a well in the State, and the upper and lower bounds on the probability estimate (90% two-sided confidence limits). These probability estimates are based on the assumption (described in Section 4.4.1) that the nitrate measurements compose a sample generated through a Bernoulli Process, resulting in a binomial distribution of threshold exceedences. The exceedence probability estimates are calculated by dividing the number of measurements exceeding the threshold by the total number of measurements. The upper and lower bounds on the estimates are calculated using the method described in Sections 4.4.1 and 5.5.1. Because the number of measurements used to calculate these estimates is large, the upper and lower bounds are close to the estimates. This is not the case when estimates are based on smaller numbers, such as those associated with a single 7.5' quadrangle.

Table 6.1 Nitrate Exceedences in Texas (46,507 Measurements)

Threshold (mg/l)	**Exceedences**	**Exceedence Probability**	**Lower Bound**	**Upper Bound**
0.1	29,643	0.6374	0.6337	0.6411
1	20,312	0.4368	0.4329	0.4405
5	7,411	0.1594	0.1566	0.1622
10	4,166	0.0896	0.0874	0.0917

Of the 4,407 7.5' quadrangles that make up the map of Texas used in this study, nitrate measurements are reported in 3554. Exceedence probabilities were estimated for these quadrangles at the four concentration thresholds by the same method as those in Table 6.1. Figures 6.2, 6.4, 6.6, and 6.8 show the spatial distribution of the resulting exceedence probabilities across Texas. An exceedence probability estimate was included in the statewide maps if twelve or more nitrate measurements are recorded for the quadrangle. As shown in Section 4.4.1, this means that for a 50% exceedence probability, the upper and lower limits of the two-sided 90% confidence interval of the probability estimate are 0.25 and 0.75, respectively. In somewhat less abstract terms, if a cell has an 50% exceedence probability estimated from twelve measurements, that cell's true exceedence probability is greater than 25% and less than 75% in nine cases out of ten. Cells with either more measurements or exceedence probabilities closer to zero or one will have narrower confidence intervals.

Histograms of the probability estimates for the quadrangles are presented in Figures 6.1, 6.3, 6.5, and 6.7. Each histogram displays two sets of bars. The taller bars show the number of quadrangles falling in the indicated probability range when all 3554 quads with measurements are counted. This would include, for example, a quad with only one measurement (which must have an estimated exceedence probability of 1 or 0). The shorter bars show quads falling in the indicated probability range from which at least twelve measurements have been collected.

Exceedences of Detection Limit. Figures 6.1 and 6.2 show estimates of the nitrate detection (i.e., measurement in excess of 0.1 mg/l) probability in the 7.5' quadrangles.

At the detection limit of 0.1 mg/l, nitrate is safely within the range of background concentrations. Nearly a third of the quadrangles with measurements (1160 out of 3554 quads) have never reported a concentration at or below this limit and in more than a third (1320 quads), fewer than one measurement in ten has fallen at or below the detection limit.

The map in Figure 6.2 shows that, although detectable levels of nitrate are found throughout the State, measurements below the detection limit are much more common in eastern Texas. Of the 1158 mapped quadrangles, only one west of the 100th meridian (the eastern boundary of the panhandle) has a detection rate below 20%.

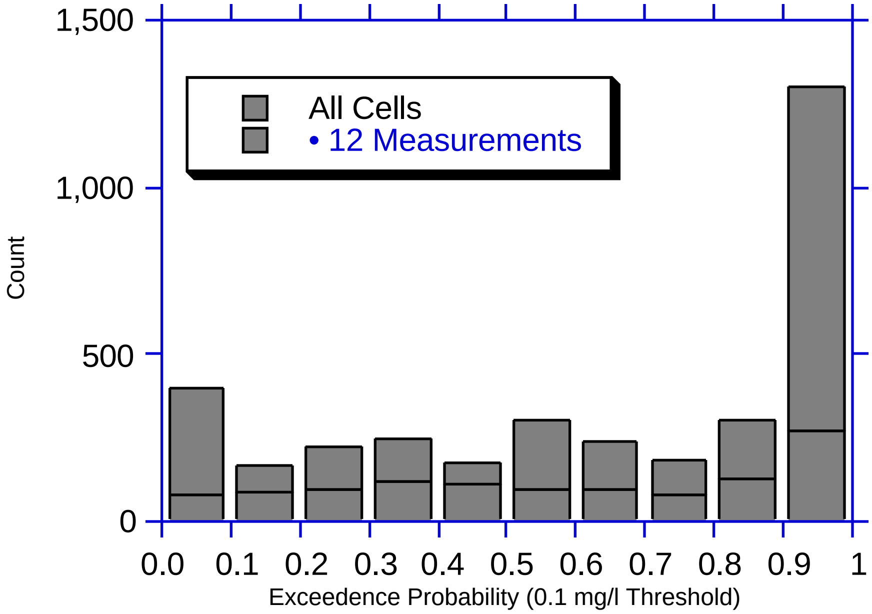


Figure 6.1 Nitrate Detection Histogram

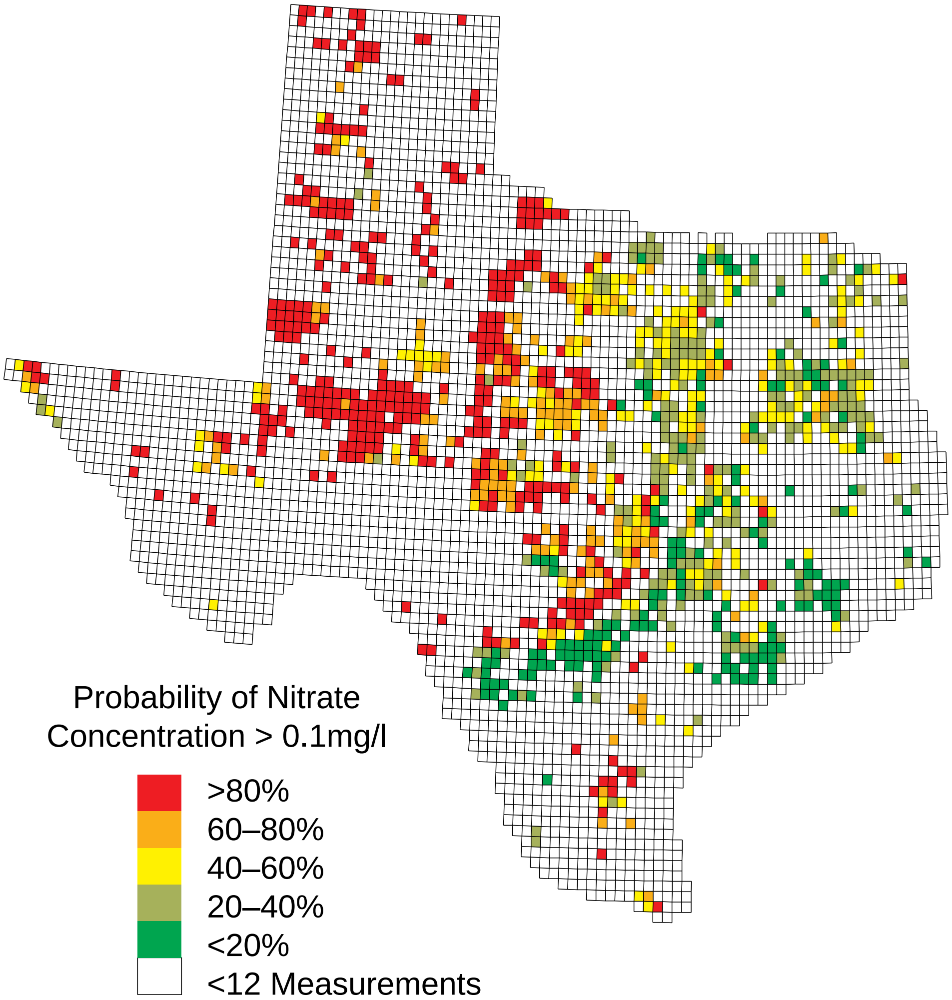


Figure 6.2 Spatial Distribution of Nitrate Detection Probabilities (Binomial Estimate)

Exceedences of 1.0 mg/l Threshold. Figures 6.3 and 6.4 show exceedence probabilities at the 1 mg/l level.

At 1 mg/l, the nitrate concentration is in an ambiguous range. Although this is considerably higher than the normal background level, concentrations of up to 3 mg/l in groundwater are frequently attributed to natural sources (Madison and Brunett 1985). At 1 mg/l, however, it is reasonable to be suspicious of human influences.

Because there are fewer exceedences of the 1 mg/l concentration threshold than of the detection limit, there are more quadrangles with near-zero exceedence probabilities. Figure 6.4 shows an increase in exceedence probability from east to west similar to that seen in the 0.1 mg/l map, but regions of high exceedence probability are more local and less regional in scope. The difference between the Carrizo-Wilcox Aquifer and the adjacent Balcones Fault Zone of the Edwards Aquifer (see Section 6.2) is quite apparent, for example. This result is similar to observations by Baker et al (1994), who noted that "River valley aquifers, sandy soils with high water tables, karst areas, and reef structures with surficial expressions are all reflected in county maps" developed as part of a voluntary well testing program.

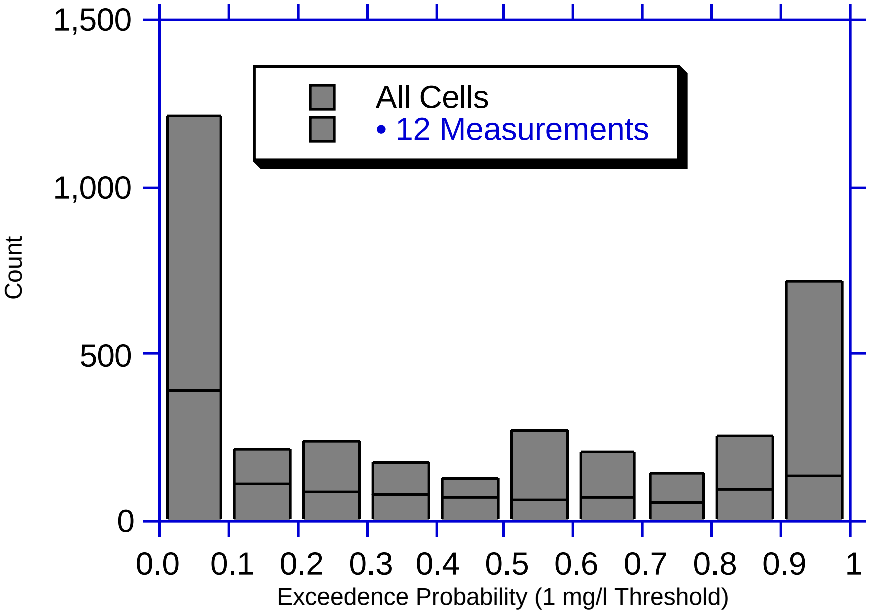


Figure 6.3 Nitrate 1 mg/l Exceedence Histogram

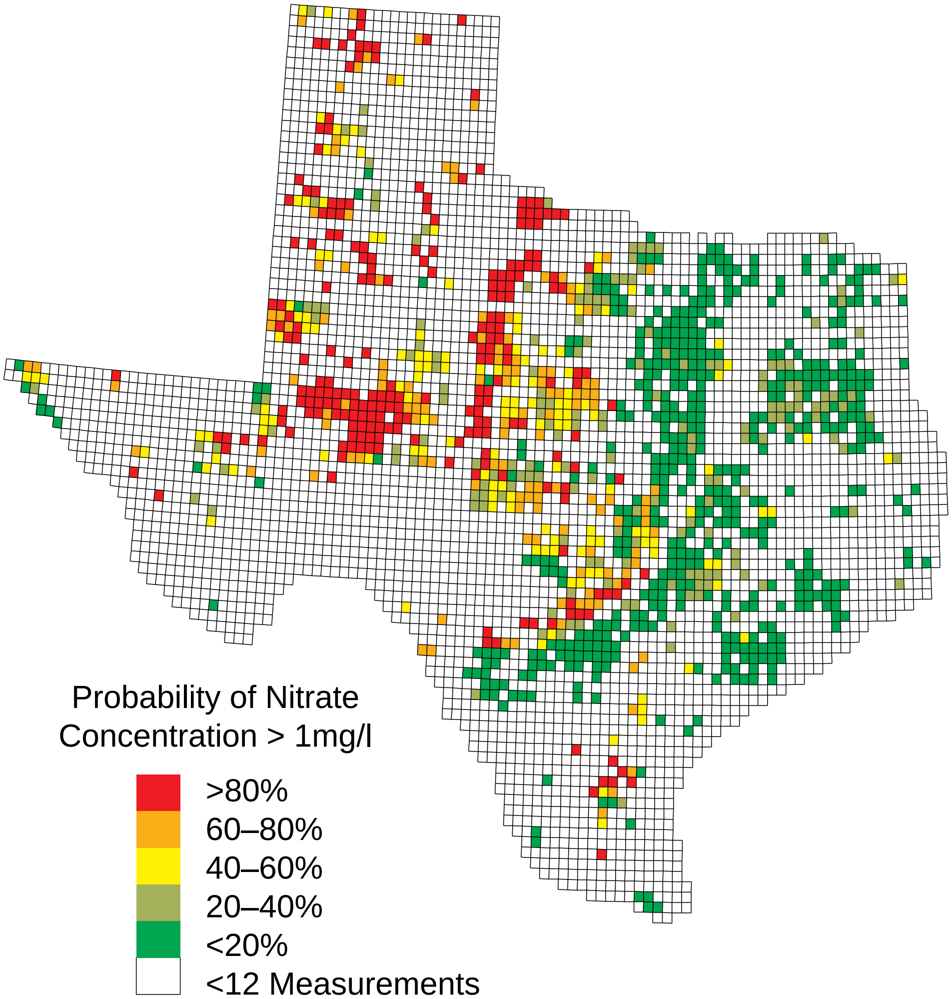


Figure 6.4 Spatial Distribution of 1 mg/l Exceedence Probabilities (Binomial Estimate)

Exceedences of 5 mg/l Threshold. Figures 6.5 and 6.6 show exceedence probabilities at the 5 mg/l threshold.

Nitrate concentrations at or above 5 mg/l due to natural sources are not unheard of, but are very uncommon. Consistent measurements of nitrate above this level clearly indicate either an extraordinarily strong natural source, or the influence of human activities. Also, this concentration is one-half of the MCL for nitrate and, although not considered high enough to endanger human health, it does trigger a switch from annual to quarterly monitoring for nitrate in public water supplies using groundwater (40 CFR 141).

Of the 1158 cells mapped, 1124 have an estimated exceedence probability of 0.0 at the 5 mg/l threshold—in only 34 of these quads has a concentration above this level been measured. The east-to-west trend of increasing exceedence probability seen in the previous maps has been replaced by a group of cells in the western part of north-central Texas, and a scattering of isolated cells mostly in the western part of the State.

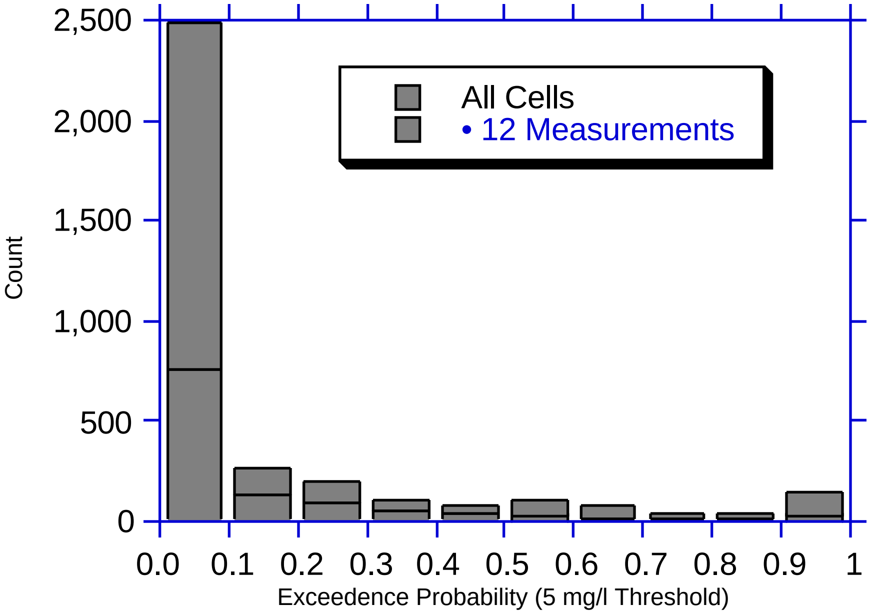


Figure 6.5 Nitrate 5 mg/l Exceedence Histogram

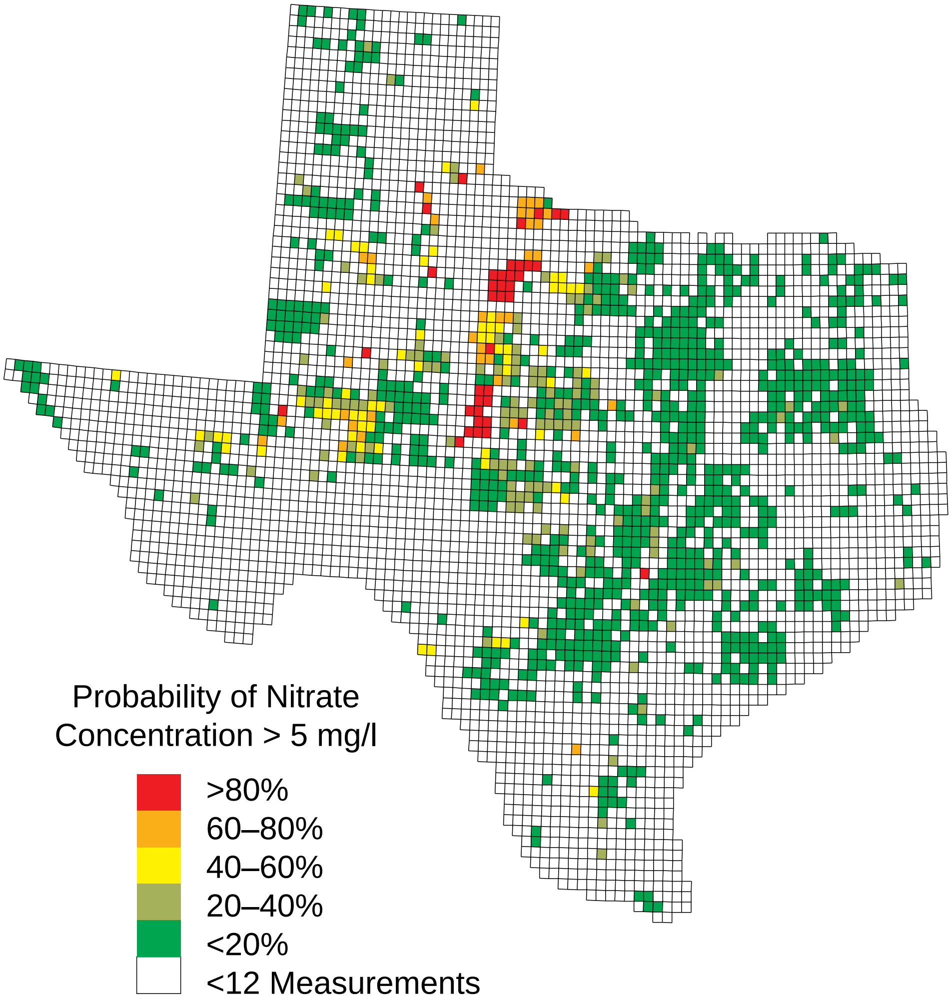


Figure 6.6 Spatial Distribution of 5 mg/l Exceedence Probabilities (Binomial Estimate)

Exceedences of 10 mg/l Threshold. Figures 6.7 and 6.8 show exceedence probabilities at the 10 mg/l level.

At 10 mg/l, nitrate is considered a human health hazard, and public water suppliers are required to notify the public and take action to reduce the nitrate concentrations when they exceed this level. Concentrations at this level are very rarely due to natural sources. The vast majority of cells with measurements (2708 of 3554) have never had a measurement exceeding this limit.

The map of 10 mg/l exceedence probabilities in figure 6.8 shows only a few quads where this high level of nitrate concentration is found often. Although nearly one in twelve measurements listed in the base data set (4,166 of 46,507) exceeds 10 mg/l, these elevated nitrate levels are very unevenly distributed in space. The only region where exceedences are found consistently, rather than in isolated quads, is in western north-central Texas in an area roughly co-incident with the extent of the Seymour Aquifer (see Section 6.2).

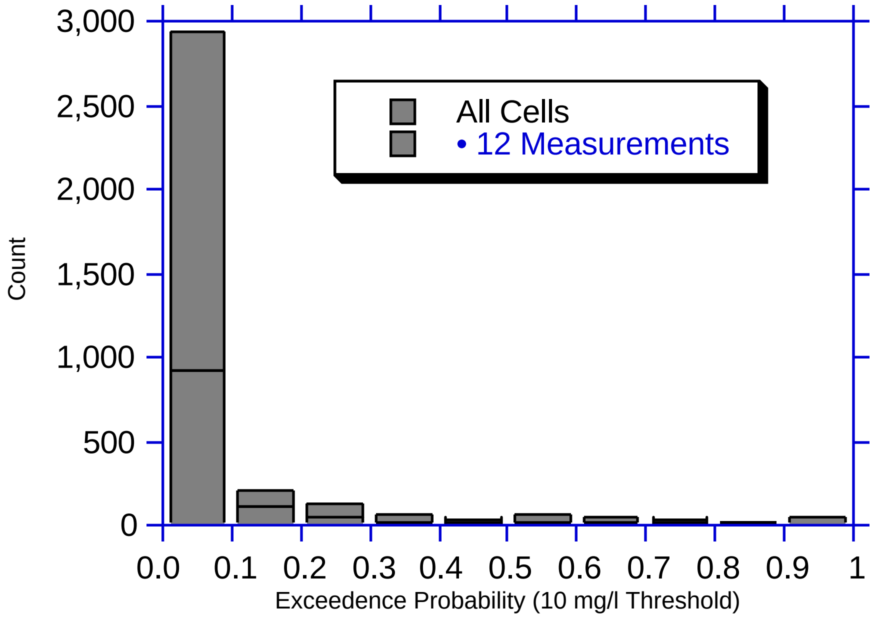


Figure 6.7 Nitrate 10 mg/l Exceedence Histogram

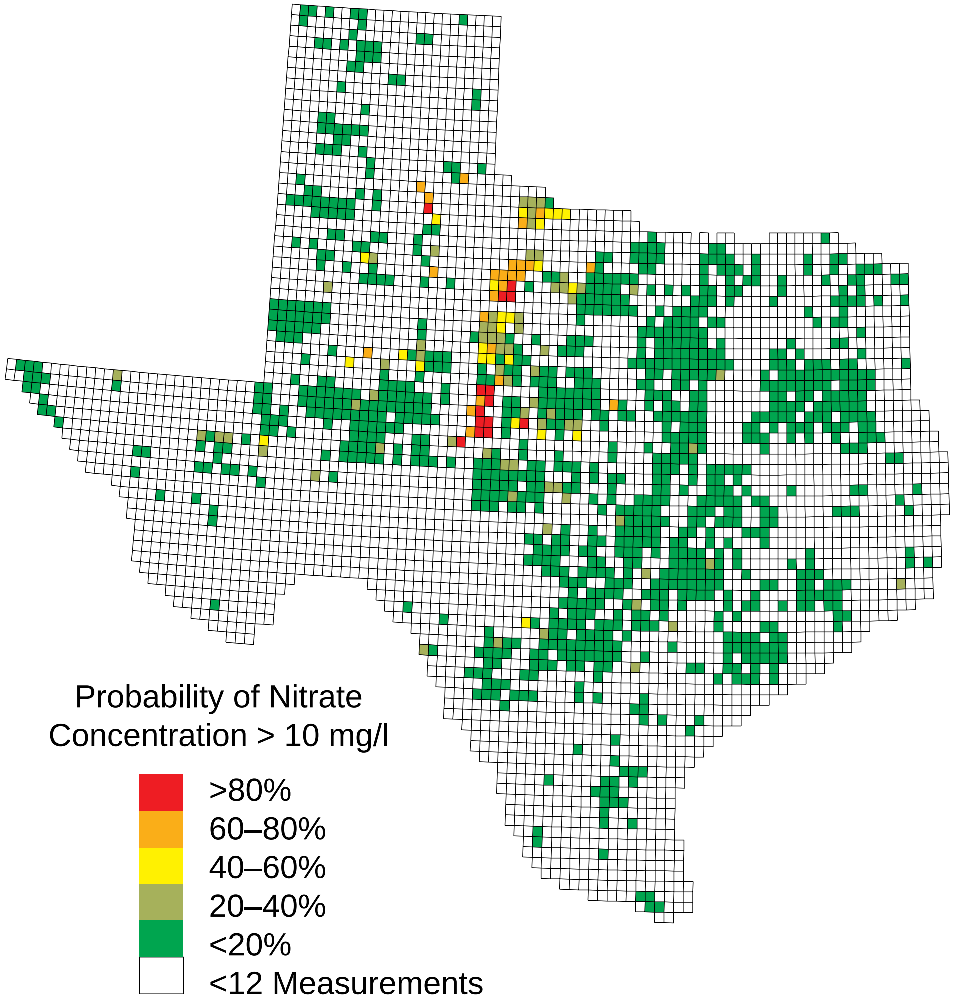


Figure 6.8 Spatial Distribution of 10 mg/l Exceedence Probabilities (Binomial Estimate)

Upper Bound Exceedence Estimates. The exceedence probabilities shown in Figures 6.1–6.8 are all the best estimates of discrete probabilities, calculated by simple division of number of exceedences by number of measurements at four thresholds. Figure 6.9 presents the 95% upper confidence limit on the binomial estimate of the 1 mg/l exceedence probability. By combining the estimated exceedence probability with a measure of the confidence in that estimate, this map presents a conservative estimate of the probability of nitrate contamination in the quadrangles. A cell has an 95% upper confidence limit value of 0.95, for example, if 100 measurements have been taken and 91 have exceeded the threshold, or if 1 measurement has been taken and that measurement did not exceed the threshold. A quad can have a low exceedence probability only if many measurements have been taken and few exceedences have been found.

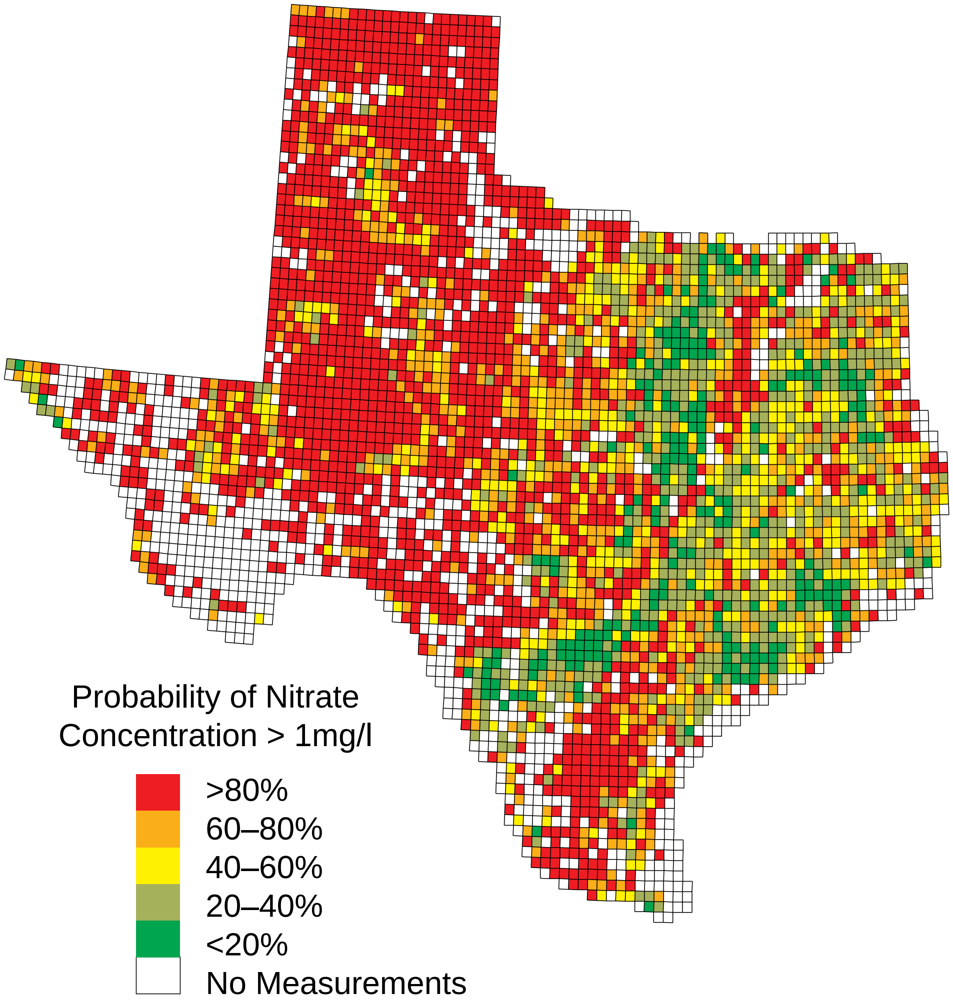


Figure 6.9 Spatial Distribution of Upper 95% Confidence Limit on 1 mg/l Exceedence Probabilities (Binomial Estimate)

Lognormal Exceedence Estimates. In addition to the discrete exceedence probabilities calculated by the binomial estimation method, parameters were calculated for the best-fitting lognormal distribution for each quadrangle with twelve or more measurements. Figure 6.10 shows the spatial distribution of the lognormal estimates of the 1 mg/l exceedence probabilities for quads with at least twelve measurements and one detection of nitrate.

To compare the lognormal distribution to the discrete probabilities, Figure 6.11 shows paired-value plots of the lognormal and discrete exceedence probability estimates at the detection limit, 1, 5, and 10 mg/l threshold concentrations. A point on one of the four graphs is located at coordinates equal to the binomial and lognormal exceedence probability estimates for one quadrangle. A point falls on the diagonal line if the two estimates are identical, above the line if the lognormal estimate is larger, and below the line if the binomial estimate is larger. In comparison to the binomial estimates, the lognormal estimates tend to be higher at the detection limit, 5 and 10 mg/l thresholds, and lower at the 1 mg/l threshold. At the higher concentration thresholds, the lognormal distribution tends to over-predict exceedences with low probabilities, and under-predict exceedences at high probabilities. One possible explanation of the differences in the predictions is that the true probability distributions have longer tails (i.e., more probability distributed to extreme high and low values) than the lognormal distribution allows.

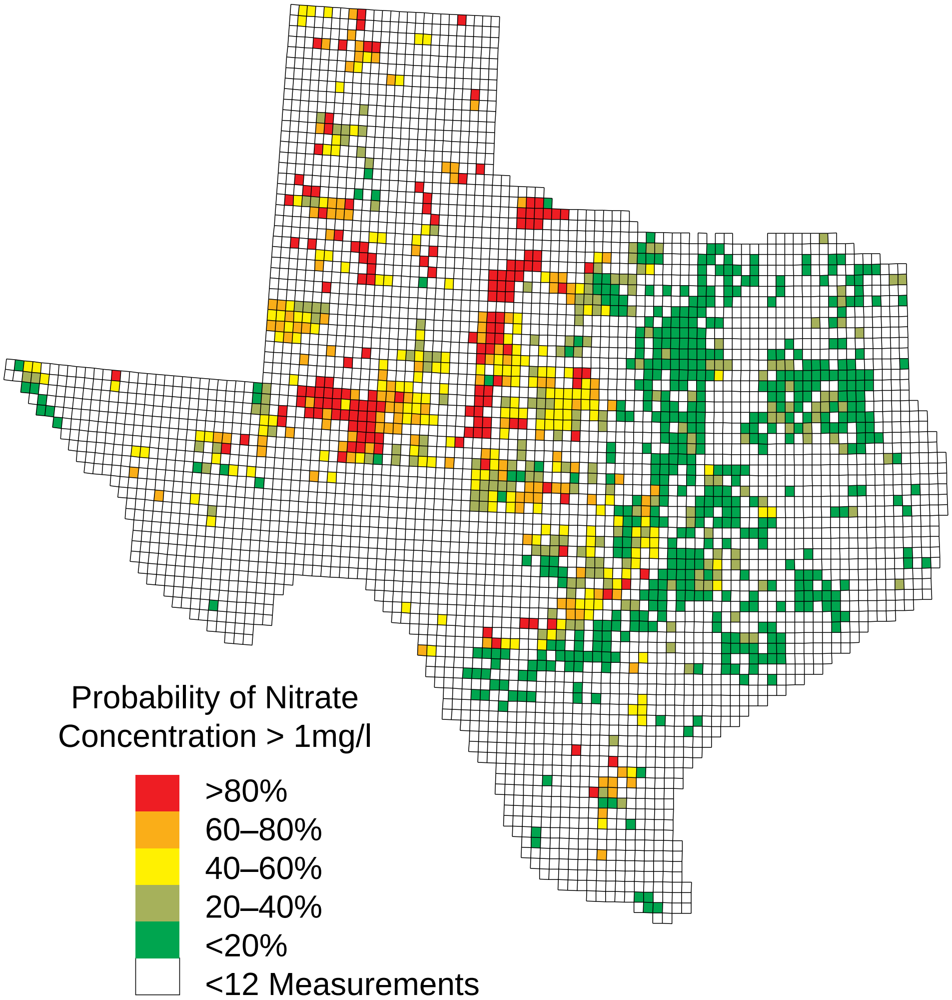
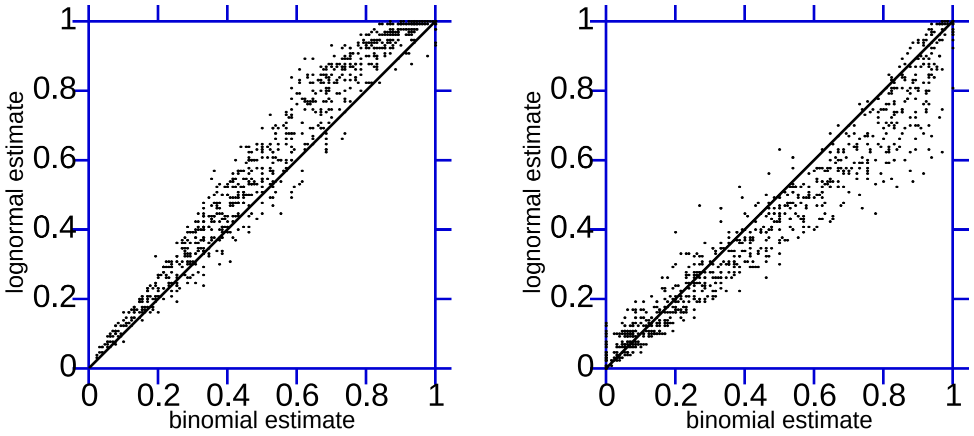


Figure 6.10 Spatial Distribution of 1 mg/l Exceedence Probabilities (Lognormal Estimate)

a) Detection Limit Exceedence Probabilities

b) 1mg/l Exceedence Probabilities



c) 5 mg/l Exceedence Probabilities

d) 10 mg/l Exceedence Probabilities

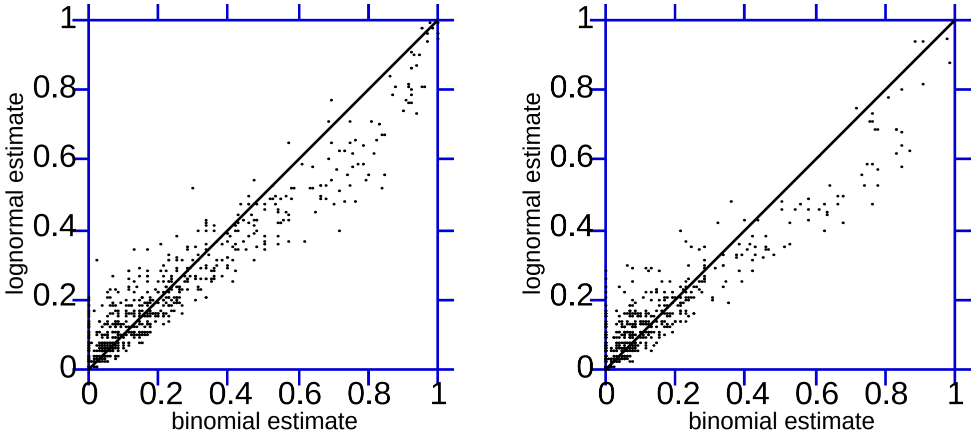


Figure 6.11 Comparison of Discrete and Lognormal Exceedence Probability Estimates

A numerical analysis of the differences between the discrete and lognormal estimates of exceedence probabilities confirms what a visual inspection of the paired-value plots in Figure 6.11 suggests. At all four threshold values, the hypothesis that the two estimates consistently differ can be confirmed with greater than 99.9% confidence using the sign test (Helsel and Hirsch 1992). The more commonly used paired-t test is inappropriate here because the differences between the two estimates are not normally distributed (tested with Probability Plot Correlation Coefficient test). The results of these tests are listed in Tables 6.2 and 6.3.

Table 6.2 Probability Plot Correlation Coefficient Test Results

Threshold	**PPCC**	**α_{PPCC}**
0.1 mg/l	0.988	<0.1
1.0 mg/l	0.963	<0.005
5.0 mg/l	0.948	<0.005
10.0 mg/l	0.913	<0.005

The entry "PPPC" in Table 6.2 is the correlation coefficient between the probability plotting position values (using Blom's Formula) for the binomial and lognormal estimates of the exceedence probabilities for the listed thresholds in the 1134 quadrangles with at least 12 nitrate measurements and at least one nitrate detection. The entry "α_{PPCC}" is the significance level of the test—the probability that the differences between the two estimates are normally distributed. The significance levels are expressed as upper bounds because the PPCC table in Helsel and Hirsch only has exact values for up to 100 pairs.

Table 6.3 Sign Test Results

Threshold	**n**	+	**Z**
0.1 mg/l	1004	101	-25.3
1.0 mg/l	1053	626	+6.1
5.0 mg/l	918	343	-7.6
10.0 mg/l	800	236	-11.5

The entry "n" in Table 6.3 is the number of quadrangles (out of the 1134 with both lognormal and binomial exceedence probability estimates) with different values for the two exceedence probability estimates. The entry "+" is the number of quads (out of n) in which the binomial estimate is greater than the lognormal estimate. The entry "Z" is the normal variate corresponding to the probability that the binomial estimates are consistently greater than the lognormal estimates of the exceedence probability. The normal variates are calculated by using the large-sample approximation of the sign test, as given in Helsel and Hirsch.

So far, the variation of nitrate concentration of nitrate exceedence probabilities has been limited to the two horizontal dimensions. Two more dimensions, depth and time, have yet to be considered.

Influence of Well Depth. Figure 6.12 shows the variation of the four exceedence probabilities with depth over the State. The graph was prepared by calculating the estimated probability of detecting nitrate at the threshold level (number of exceedences divided by number of measurements) for all wells at least as deep as the value shown on the horizontal axis. The values shown intersecting the left vertical axis are equal to the exceedence probabilities calculated for the 46,507 measurements in the base data set. Values were calculated at ten-foot intervals of depth. The markers on the lines of the graph are present to help distinguish the lines, not to indicate points at which values were estimated.

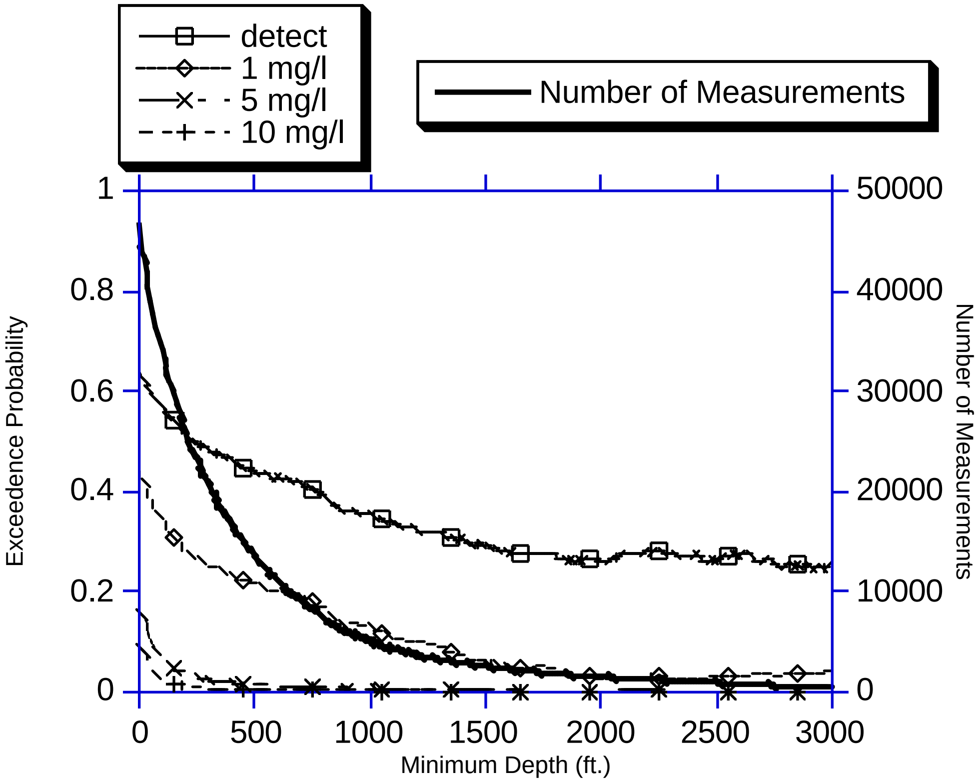


Figure 6.12 Variation of Exceedence Probabilities with Depth

A decrease in the likelihood of detecting nitrate at any threshold level is clearly visible as shallower wells are excluded from the calculation of the exceedence probabilities. This decrease is most pronounced as the shallowest wells are excluded, especially at the higher concentration thresholds. Of 4,166 measurements in exceedence of the MCL, 3,834 (about 92%) were taken from wells less than 200 feet deep.

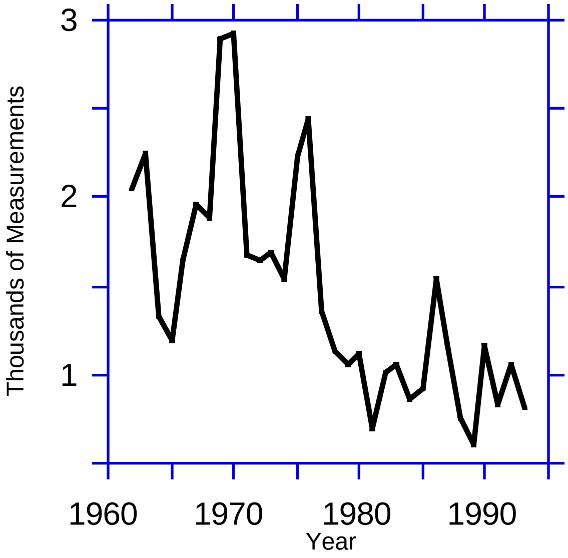


Figure 6.13 Measurements by Year in Base Data Set

Trends through Time. Figure 6.13 shows the number of measurements listed in the base data set for each year from 1962 to 1993. Figure 6.14 shows the variation of the four exceedence probabilities with the year in which the nitrate measurements were taken. In this graph, a marker is plotted for each exceedence probability calculated for the measurements collected in each year.

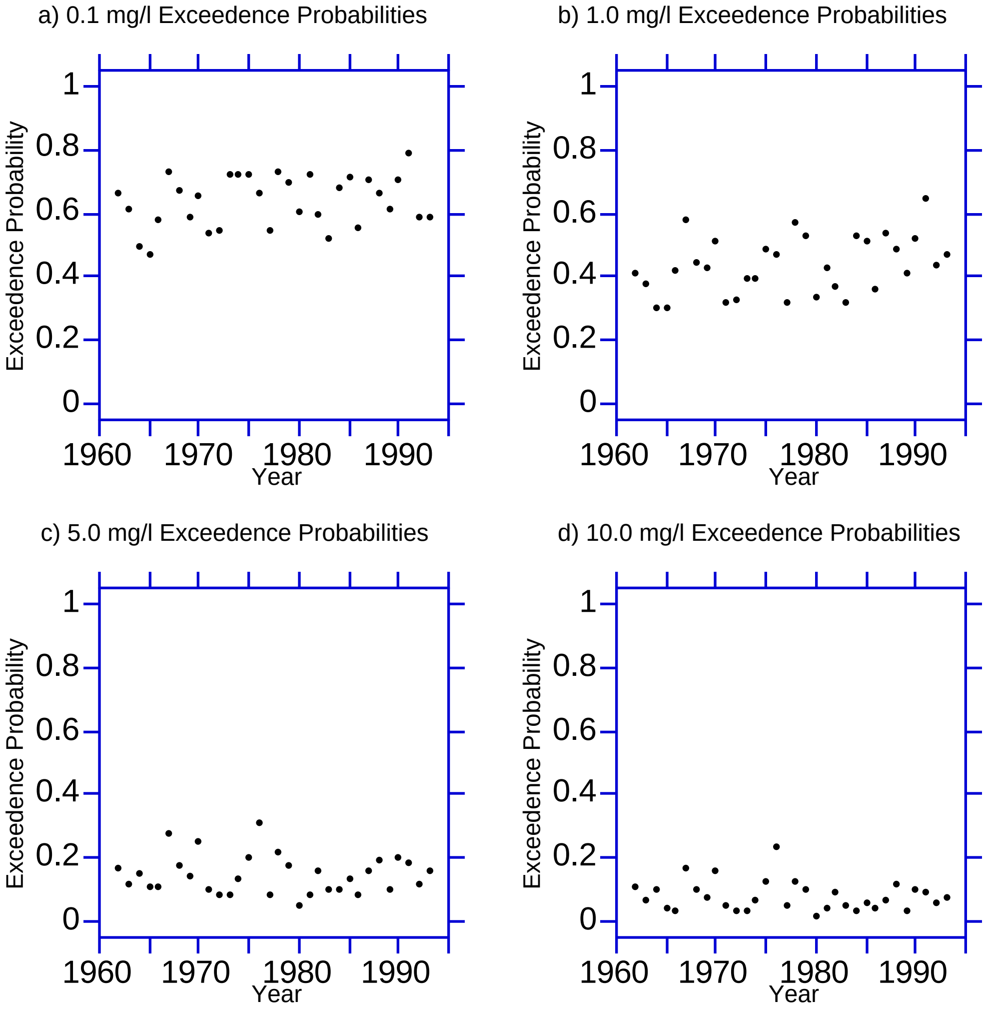


Figure 6.14 Variation of Exceedence Probabilities Over Time

In general, the variability from one year to the next (possibly reflecting changes in sampling locations) is much greater than any trend through time. Linear regression of exceedence probabilities against time confirms this for the detection limit and the 5 and 10 mg/l thresholds. The regression results for the four threshold concentrations are summarized in Table 6.4. The fitted line is measured is considered statistically significant if its t statistic is greater than 2, indicating a probability of less than 5% that the slope does not differ from zero. By this measure, only the fitted line for the 1 mg/l threshold is significant. The slope of 0.003, indicates that the likelihood that a nitrate measurement selected at random from anywhere in the state will exceed 1 mg/l has increased by about three-tenths of a percent each year over the last 30 years. The data and the regression line for this threshold are shown in Figure 6.15.

Table 6.4 Regression Results For Threshold Exceedences through Time

Threshold	Slope	t
0.1 mg/l	0.002	1.33
1.0 mg/l	0.003	2.07
5.0 mg/l	-0.0005	0.42
10.0 mg/l	-0.0008	0.83

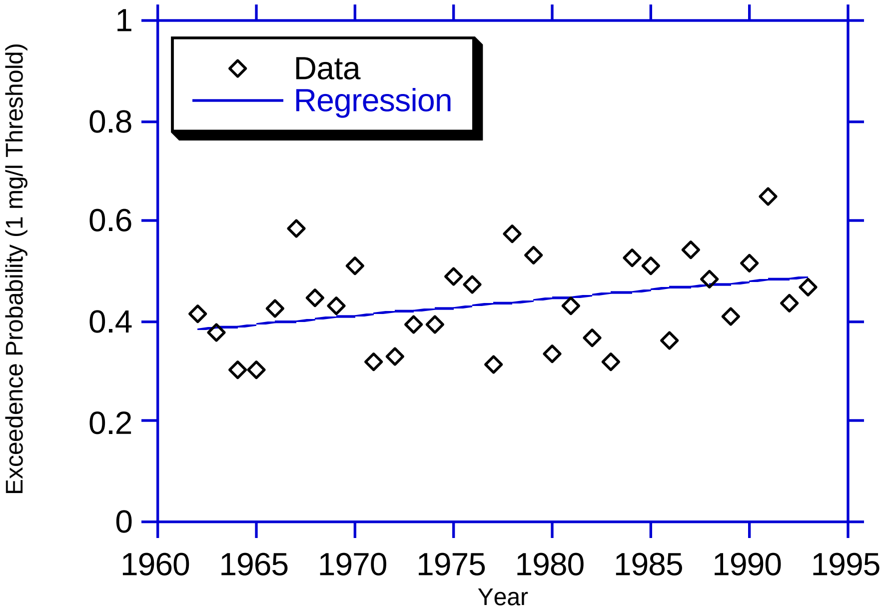


Figure 6.15 Regression of 1 mg/l Exceedence Probability Against Time

Examination of groundwater nitrate measurements statewide shows that there is considerable spatial variation in the likelihood of detecting nitrate at any threshold level. At lower concentrations, there is a general trend of increasing exceedence probability from southeast to northwest, which becomes more localized as the threshold increases. In general, deep wells are less likely to yield high concentrations of nitrate than shallow wells. Although trends in nitrate detection through time are not strong, a significant increase with time in the likelihood of detecting nitrate at the 1 mg/l level has been found. Since increases through time, especially on a as short a time scale as thirty years, are suggestive of human influence, this tends to confirm the usefulness of the 1 mg/l threshold as an indicator of susceptibility of groundwater to human activities.

6.2 SELECTED AQUIFERS

This section reports nitrate detections in wells associated with the five aquifers selected for special study. Figure 6.16 shows the locations of the five selected aquifers on a map of Texas. The map was created by color-coding 7.5' quadrangles by the aquifer associated with wells in that quadrangle. A quadrangle was colored yellow, for example, if it contains a well associated with the Hueco-Mesilla Bolson Aquifer in the study's table of wells. Because the horizontal extent of the Carrizo-Wilcox Aquifer and the Balcones Fault Zone of the Edwards Aquifer overlap, the seven quads that contain wells in both of these aquifers were colored black. The selection of wells to associate with the aquifers is described in Section 3.2.3, which also includes a map of the TWDB's location of the aquifers' boundaries (Figure 3.5).

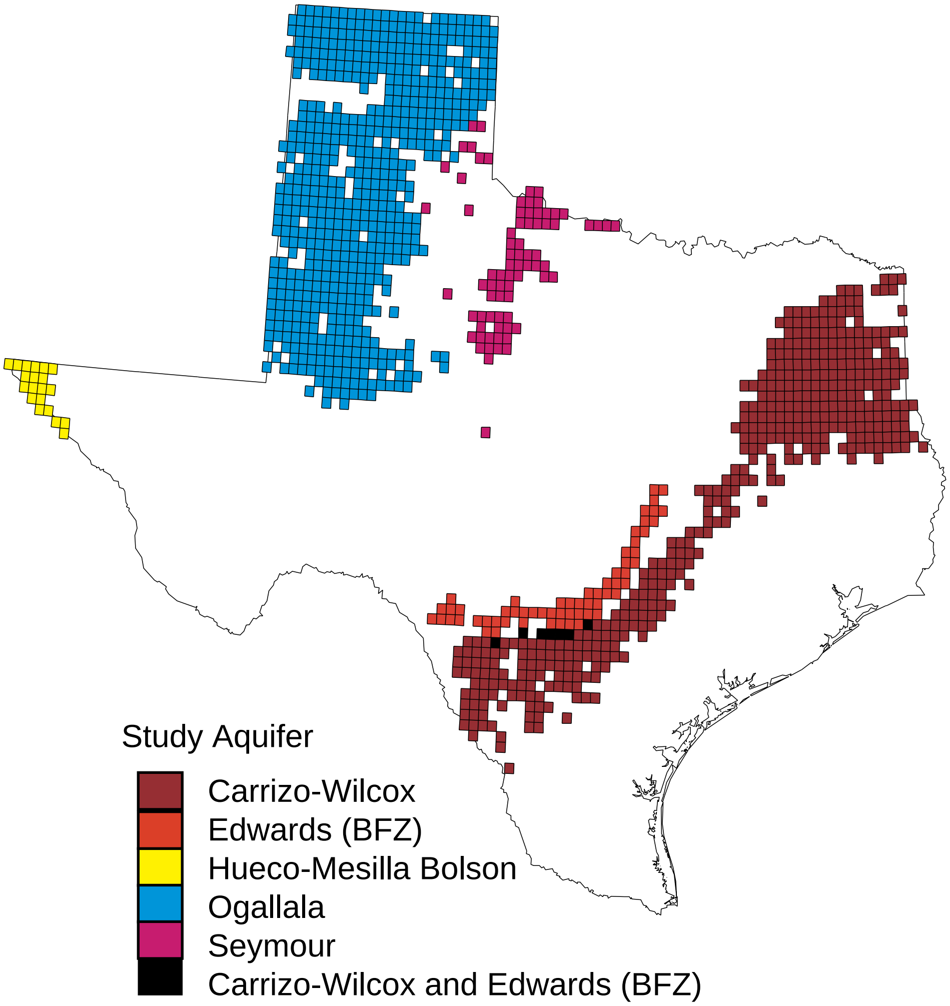


Figure 6.16 7.5' Quadrangles Associated with Study Aquifers

Table 6.5 duplicates Table 3.6, listing the number of wells and measurements associated with each aquifer, and also includes the number of 7.5' quadrangles shown for the aquifer in Figure 6.15. Note that "Edwards (BFZ)" refers to the Balcones Fault Zone of the Edwards Aquifer.

Table 6.5 Wells and Measurements in Selected Aquifers

Aquifer	**Wells**	**Measurements**	**Quadrangles**
Carrizo-Wilcox	2292	4597	433
Edwards (BFZ)	412	1691	67
Hueco-Mesilla Bolson	404	1908	20
Ogallala	3483	4430	588
Seymour	1993	2526	76

Sections 6.2.1 through 6.2.5 describe the results of a variety of analyses of nitrate measurements in each of the five study aquifers. For each aquifer, a table of exceedence probabilities, a map of the spatial distribution of the exceedence probabilities, and charts of variation of exceedence probabilities are presented. This is essentially the same information, presented in the same manner, as was given for the State as a whole in Section 6.1.

Section 6.2.6 presents summary information for all five aquifers and compares the results among them.

6.2.1 Carrizo-Wilcox Aquifer

Table 6.6 Nitrate Exceedences in the Carrizo-Wilcox Aquifer
(4597 Measurements)

Threshold (mg/l)	Exceedences	Exceedence Probability	Lower Bound	Upper Bound
0.1	1124	0.2445	0.2341	0.2552
1	327	0.0711	0.0650	0.0777
5	113	0.0245	0.0209	0.0286
10	63	0.0137	0.0110	0.0169

Of the five study aquifers, the Carrizo-Wilcox is the least contaminated by nitrate. Fewer than 25% of the measurements listed in the database show even a detectable level of nitrate. The nitrate detections occur without much coherent spatial pattern within the aquifer (Figure 6.17), or with much variation with depth (Figure 6.18), although 81 of the 113 nitrate measurements exceeding 5 mg/l came from wells less than 200 feet deep. It may be significant that the quads with the highest 1 mg/l exceedence probabilities are on the western edge of the aquifer, which the TWDB identifies as an outcrop zone.

As with the State as a whole, there is more variability from year to year in nitrate detection rate than discernible trend through time (Figure 6.19). Regression of detection rates against time showed no significant trends at any threshold level.

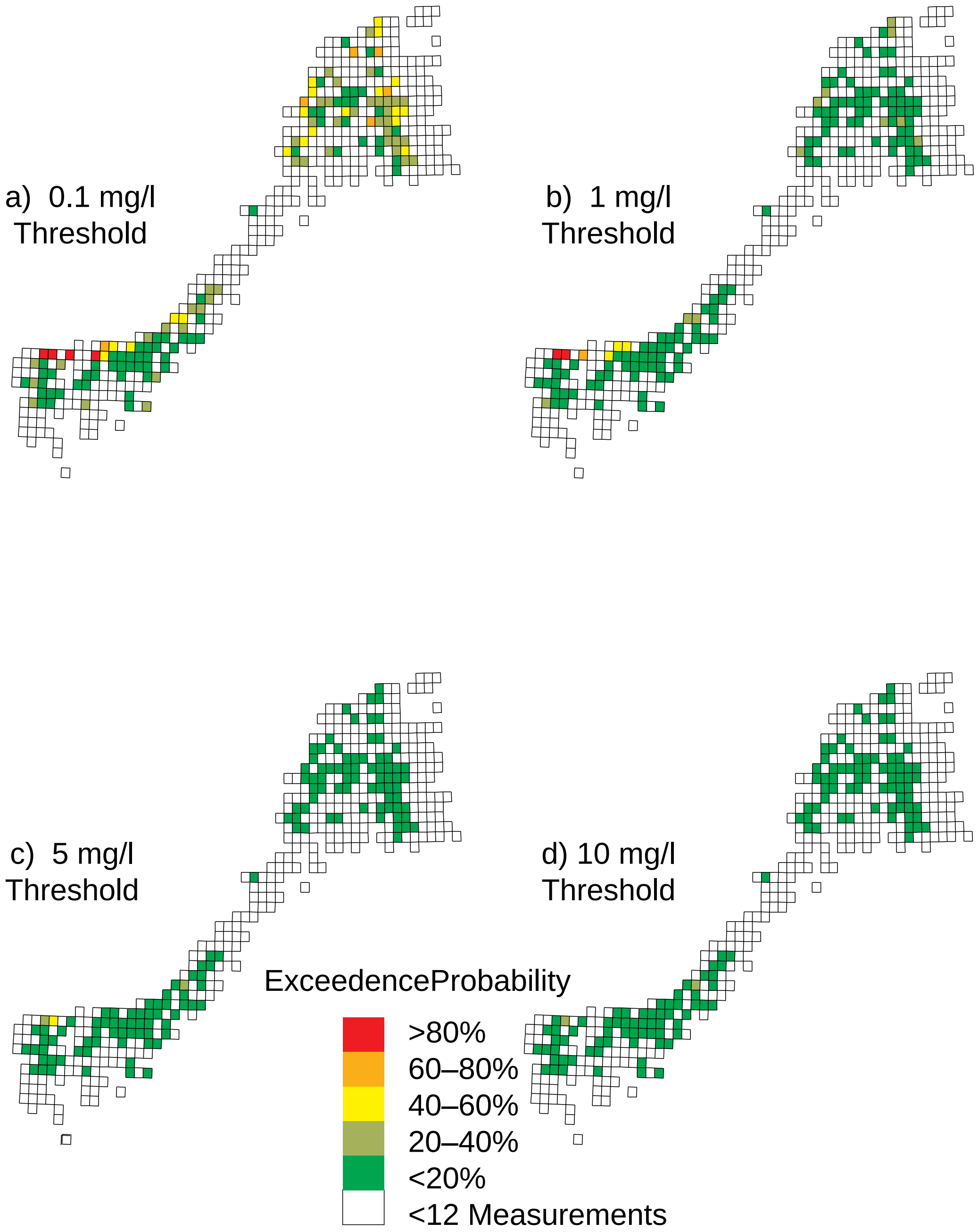


Figure 6.17 Estimated Nitrate Exceedence Probabilities by Quadrangle in the Carrizo-Wilcox Aquifer

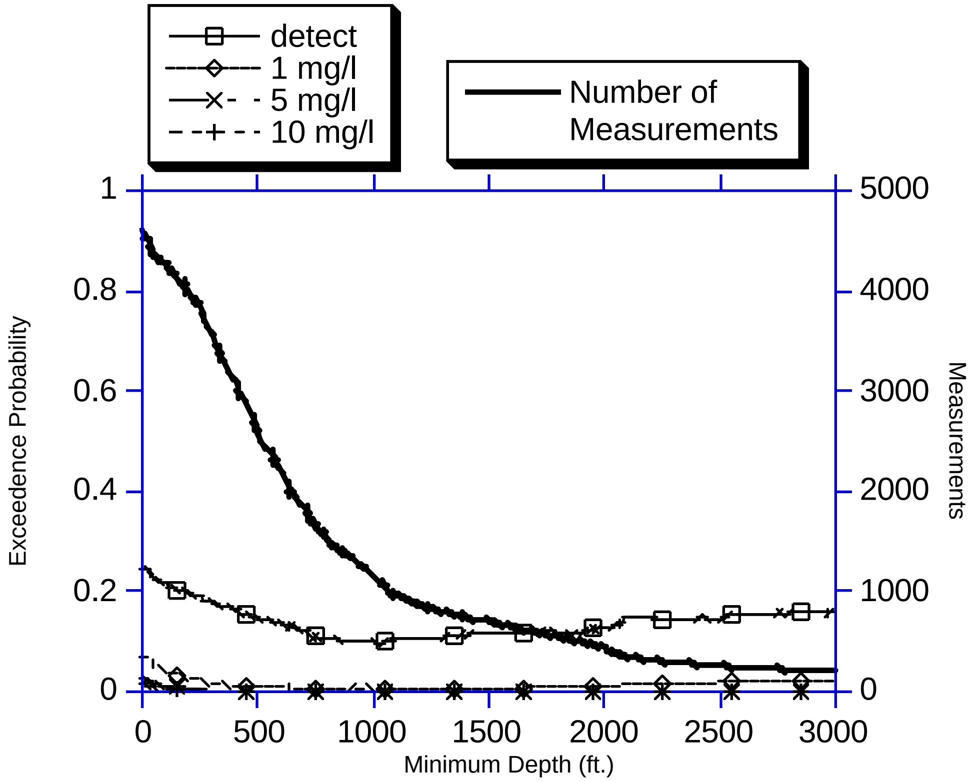


Figure 6.18 Variation of Exceedence Probabilities with Depth in the Carrizo-Wilcox Aquifer

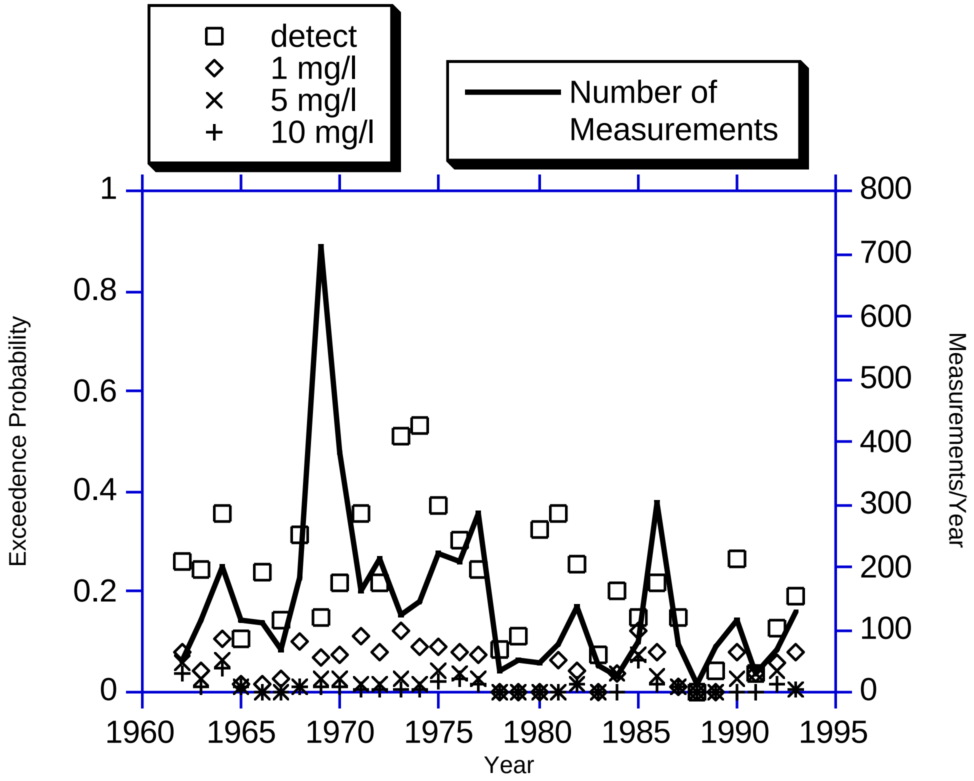


Figure 6.19 Variation of Exceedence Probabilities Over Time in the Carrizo-Wilcox Aquifer

6.2.2 Edwards Aquifer (Balcones Fault Zone)

Table 6.7 Nitrate Exceedences in the Balcones Fault Zone of the Edwards Aquifer (1691 Measurements)

Threshold (mg/l)	Exceedences	Exceedence Probability	Lower Bound	Upper Bound
0.1	1581	0.9350	0.9243	0.9445
1	1248	0.7380	0.7199	0.7556
5	13	0.0076	0.0046	0.0122
10	4	0.0024	0.0008	0.0054

Although the likelihood of *detecting* nitrate is lowest in the Carrizo-Wilcox aquifer, the likelihood of a measurement exceeding 5 mg/l is lowest in the Balcones Fault Zone of the Edwards aquifer. The map of the spatial distributions of exceedence probabilities (Figure 6.20) shows no obvious patterns in detections, but reveals a dramatic shift from high to low probabilities between the 1 mg/l and 5 mg/l thresholds. The same shift is visible when exceedence probabilities are plotted against well depth and time.

Figure 6.21 shows a slight decrease in the likelihood of detecting nitrate as deeper wells are examined, but the trend is not clear until a depth of 1,000 feet is reached. A sharp drop in nitrate detections is associated with the deepest wells (<1700 ft.), but since this is a very small number of wells, the significance of this decrease is unclear.

No significant trends through time are seen in detection rates at any threshold level. Figure 6.22 shows detection probabilities consistently close to 90%, and exceedence probabilities at the 5 and 10 mg/l level consistently close to zero. The 1 mg/l exceedence probability shows considerable variation but no consistent trend through time.

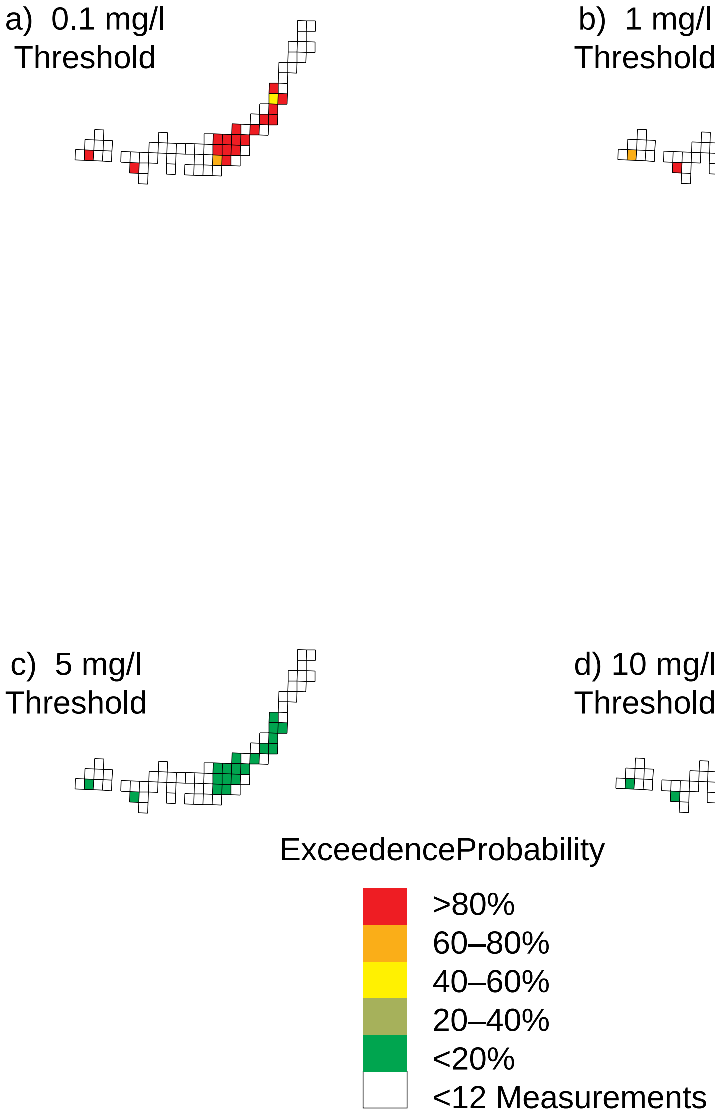


Figure 6.20 Estimated Nitrate Exceedence Probabilities by Quadrangle in the Balcones Fault Zone of the Edwards Aquifer

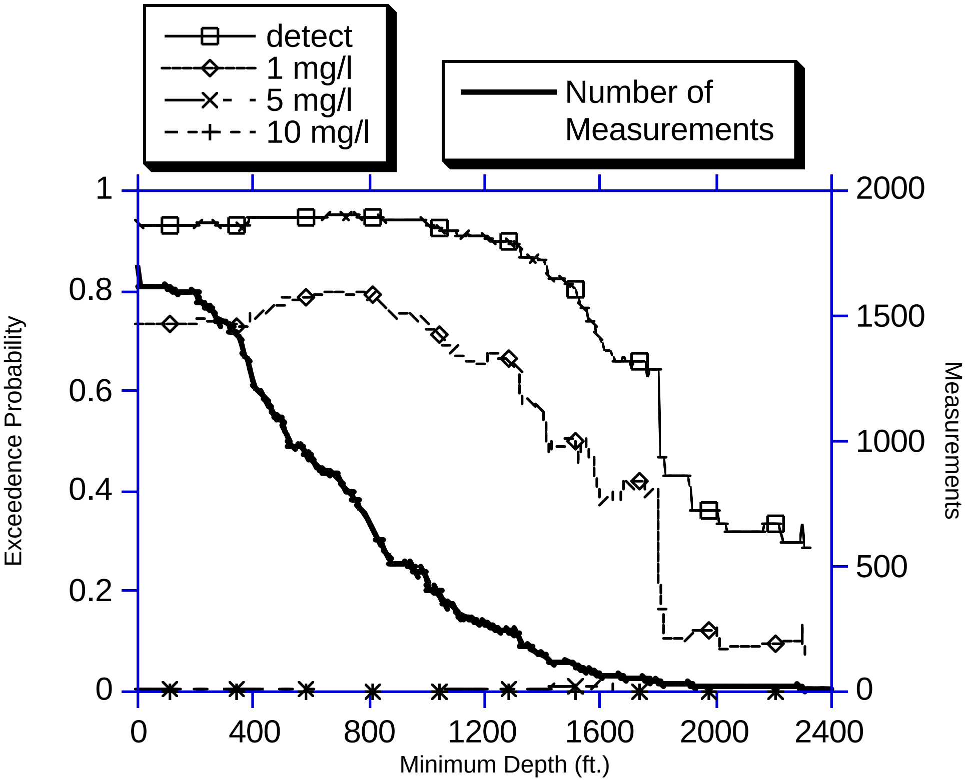


Figure 6.21 Variation of Exceedence Probabilities with Depth in the Balcones Fault Zone of the Edwards Aquifer

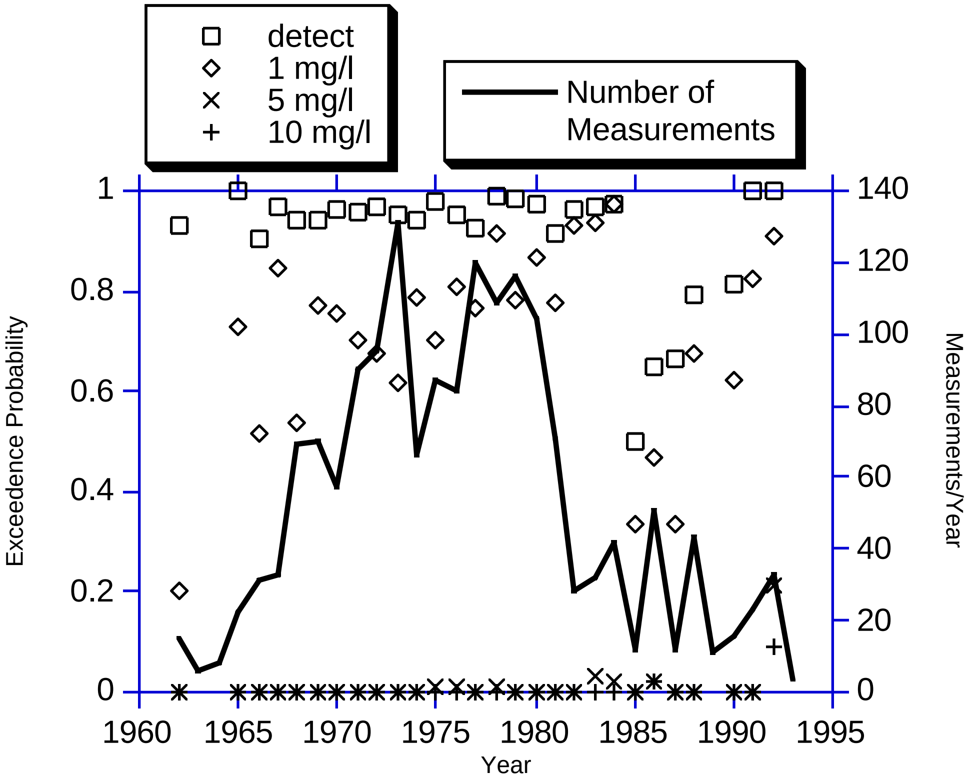


Figure 6.22 Variation of Exceedence Probabilities over Time in the Balcones Fault Zone of the Edwards Aquifer

6.2.3 Hueco-Mesilla Bolson Aquifer

Table 6.8 Nitrate Exceedences in the Hueco-Mesilla Bolson Aquifer (1908 Measurements)

Threshold (mg/l)	**Exceedences**	**Exceedence Probability**	**Lower Bound**	**Upper Bound**
0.1	1506	0.7893	0.7734	0.8046
1	869	0.4554	0.4365	0.4745
5	63	0.0330	0.0266	0.0406
10	18	0.0094	0.0061	0.0139

Because the extent of the Hueco-Mesilla Bolson Aquifer is small, the exceedence probabilities shown in Figure 6.23 have no discernible spatial pattern. As in the Edwards, detections of nitrate and exceedences of the 1 mg/l threshold are quite common, but measurements exceeding the 5 and 10 mg/l thresholds are rare. Figure 6.24 shows very little variation in exceedence probabilities with depth, the least in the five study aquifers.

Few nitrate measurements from the Hueco-Mesilla Bolson appear in the database prior to 1980, making trends through time difficult to detect. Figure6.25 might be interpreted to indicate increased exceedences of the 5 mg/l, but regression of the exceedence probabilities against time shows no statistically significant trends in exceedences of any of the threshold levels.

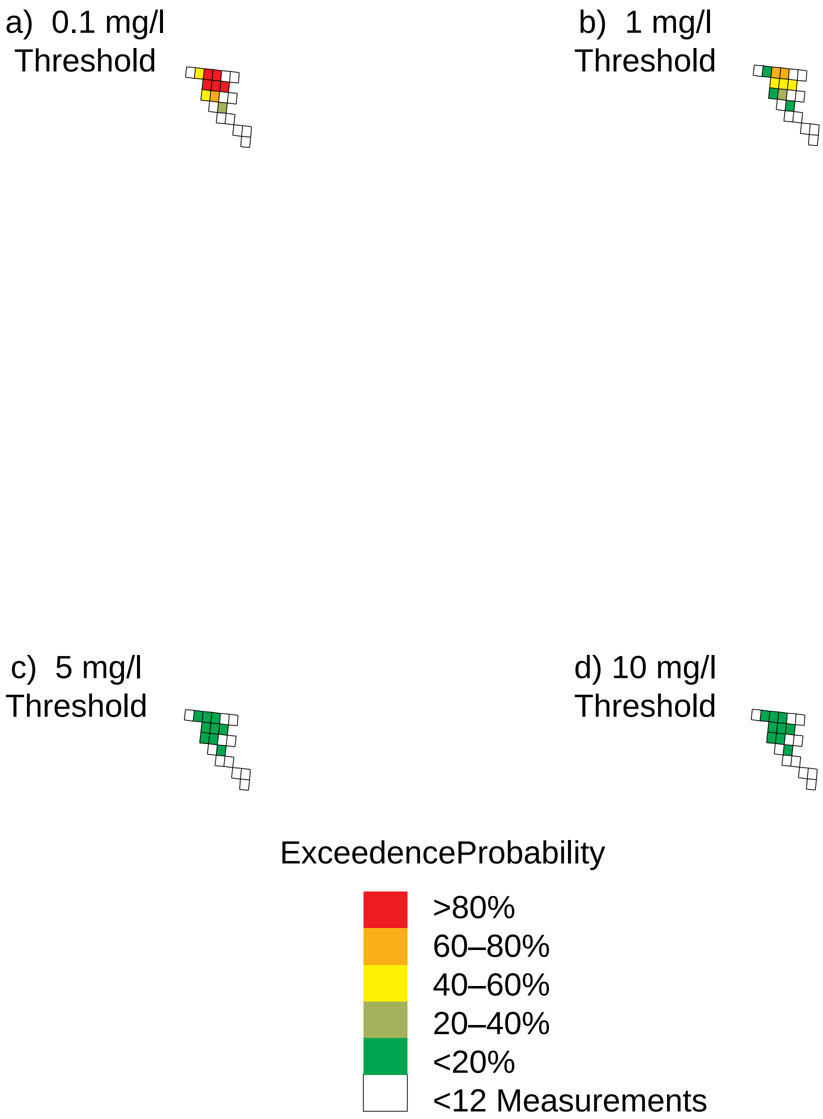


Figure 6.23 Estimated Nitrate Exceedence Probabilities by Quadrangle in the Hueco-Mesilla Bolson Aquifer

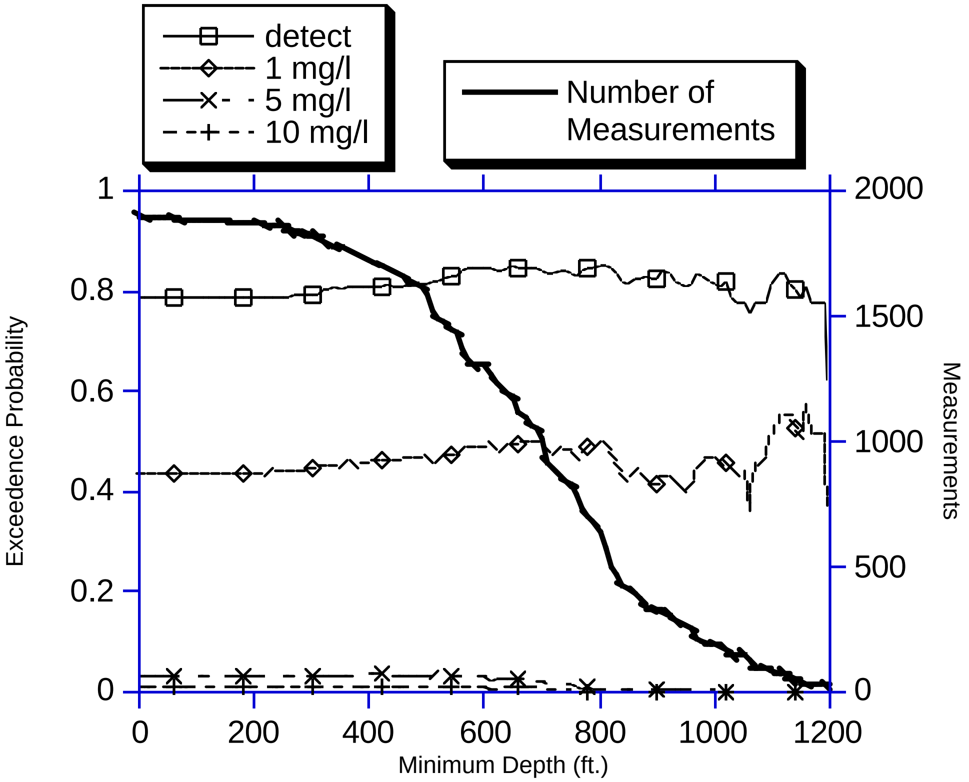


Figure 6.24 Variation of Exceedence Probabilities with Depth in the Hueco-Mesilla Bolson Aquifer

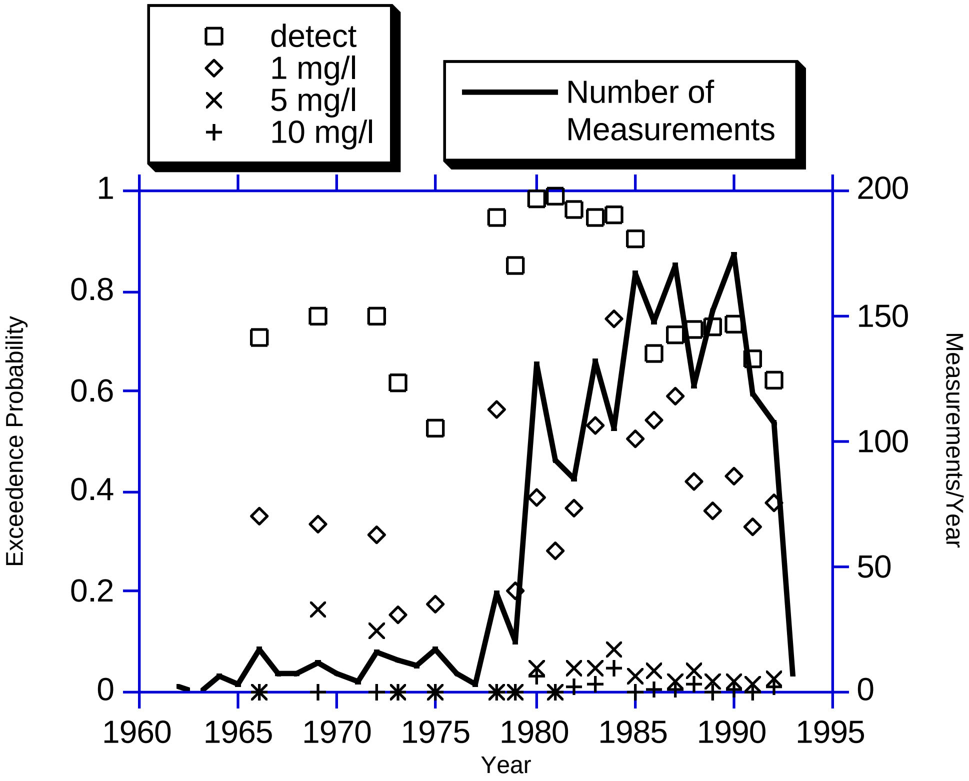


Figure 6.25 Variation of Exceedence Probabilities over Time in the Hueco-Mesilla Bolson Aquifer

6.2.4 Ogallala Aquifer

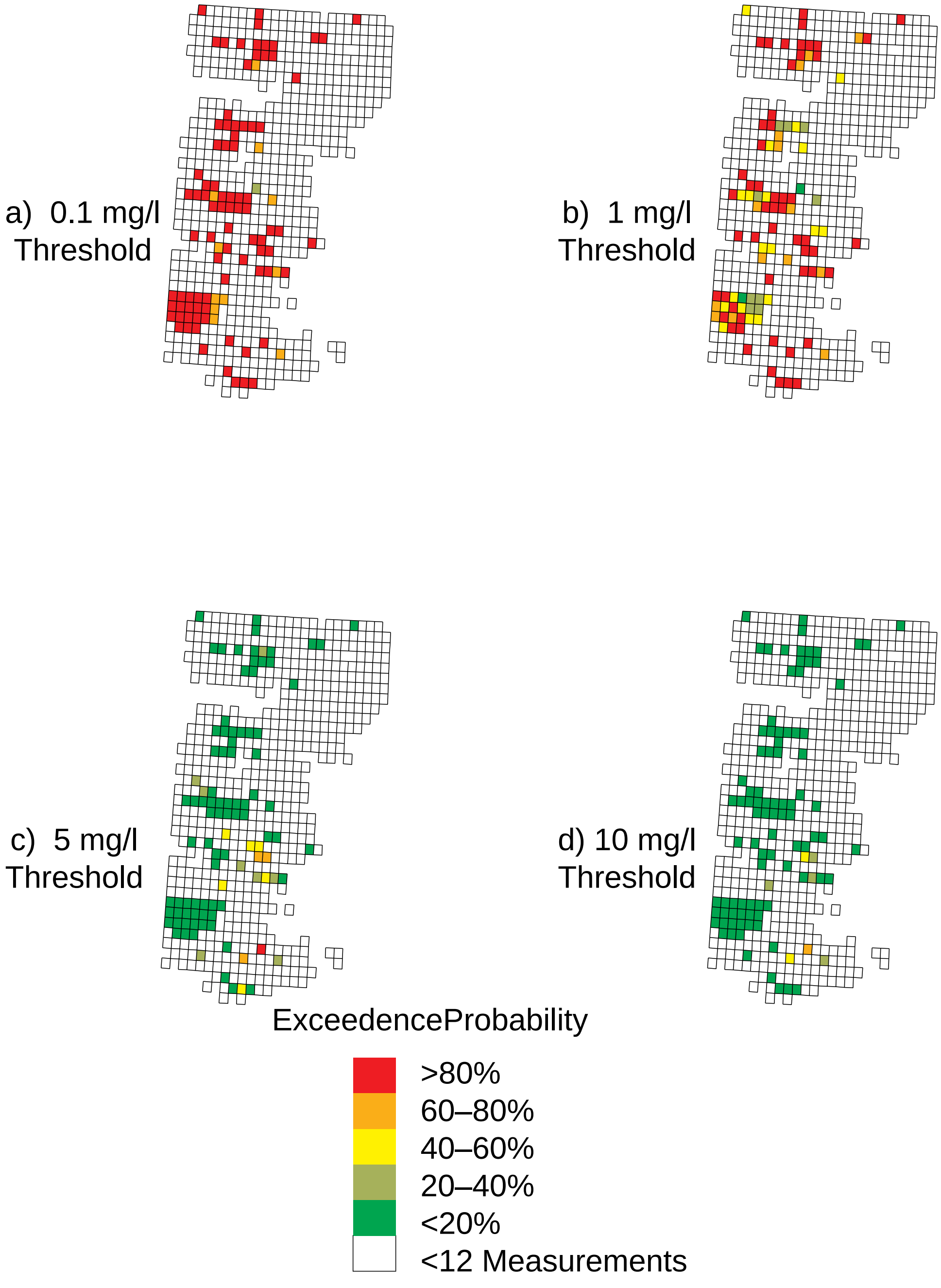
Table 6.9 Nitrate Exceedences in the Ogallala Aquifer (4430 Measurements)

Threshold (mg/l)	Exceedences	Exceedence Probability	Lower Bound	Upper Bound
0.1	4164	0.94	0.9337	0.9458
1	3235	0.7302	0.7191	0.7412
5	549	0.1239	0.1159	0.1323
10	219	0.049436	0.0441	0.0551

As in the Edwards and Hueco-Mesilla Bolson aquifers, nitrate measurements taken from the Ogallala Aquifer are very likely to exceed 1 mg/l, but much less likely to exceed 5 mg/l.

Of the five study aquifers, the Ogallala is the largest. The Texas portion of the aquifer provides water over most of the panhandle, and the aquifer extends northward through the mid-central U.S. In spite of its size, which would easily allow for trends or division into sub-regions, the map in Figure 6.26 shows variations in exceedence probabilities with no clear pattern visible. Detection rates vary, especially at the 1 mg/l threshold, but without exhibiting trend or regionalization.

Only one quad with twelve measurements or more shows a 5 mg/l exceedence probability greater than 80%. This quad was examined in more detail to see if the high rate was due to the influence of a single poorly constructed well. In fact, the 29 measurements taken in that quadrangle (number 2835, between 101_ 37' 30" and 101_ 45' west longitude and 32_ 22' 30" and 32_ 30' north latitude) come from 27 different wells. These are mostly shallow wells—none is


a) 0.1 mg/l Threshold

b) 1 mg/l Threshold

c) 5 mg/l Threshold

d) 10 mg/l Threshold

Figure 6.26 Estimated Nitrate Exceedence Probabilities by Quadrangle in the Ogallala Aquifer

deeper than 100 feet—providing water for domestic use. The region is in Martin and Howard Counties, northwest of Big Spring, in a lightly populated area containing a number of small oil fields. Apart from the shallowness of the wells, no obvious cause for the high incidence of exceedences suggests itself.

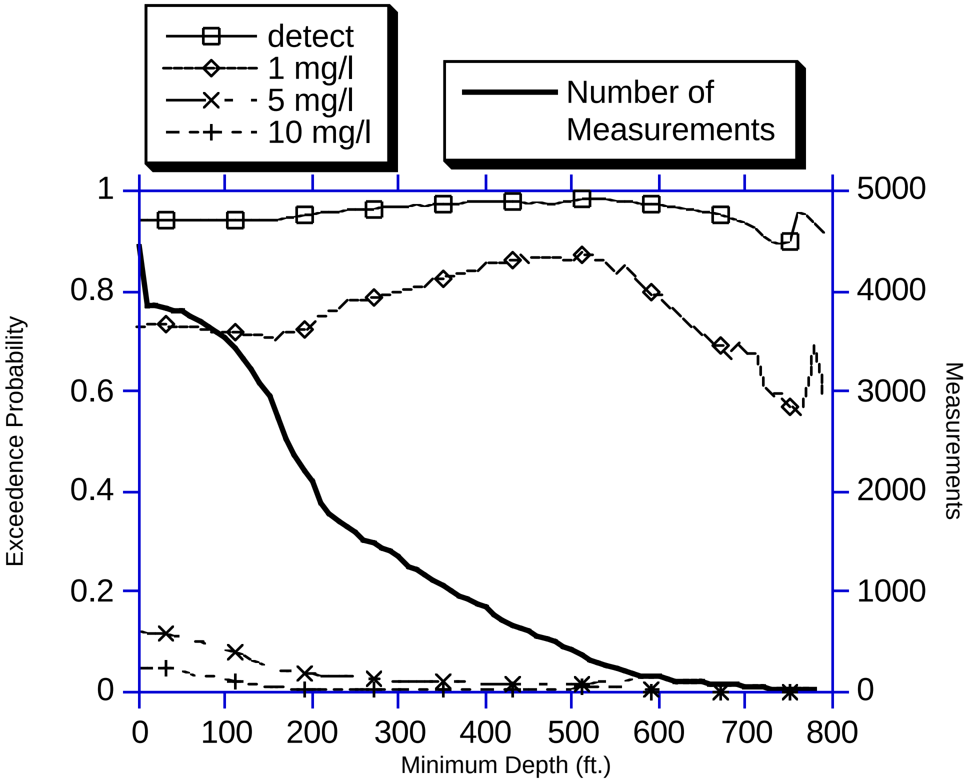


Figure 6.27 Variation of Exceedence Probabilities with Depth in the Ogallala Aquifer

Detection rates show little variation with depth in the Ogallala. Exceedences of the higher thresholds (5 and 10 mg/l) are noticeably lower in wells more than 200 feet deep, but no consistent trend with well depth is apparent in exceedences of the lower thresholds.

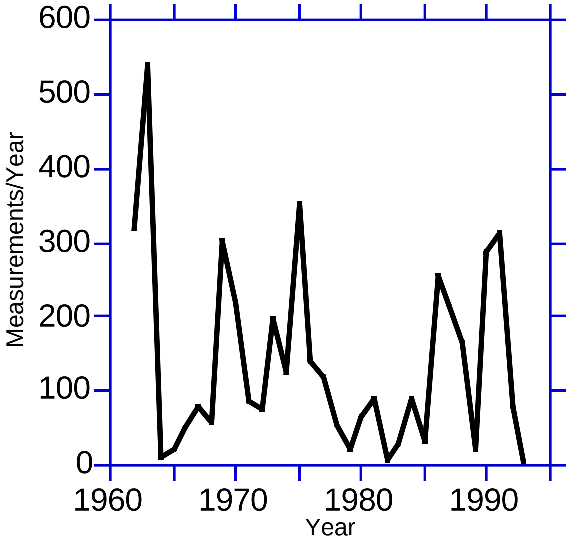
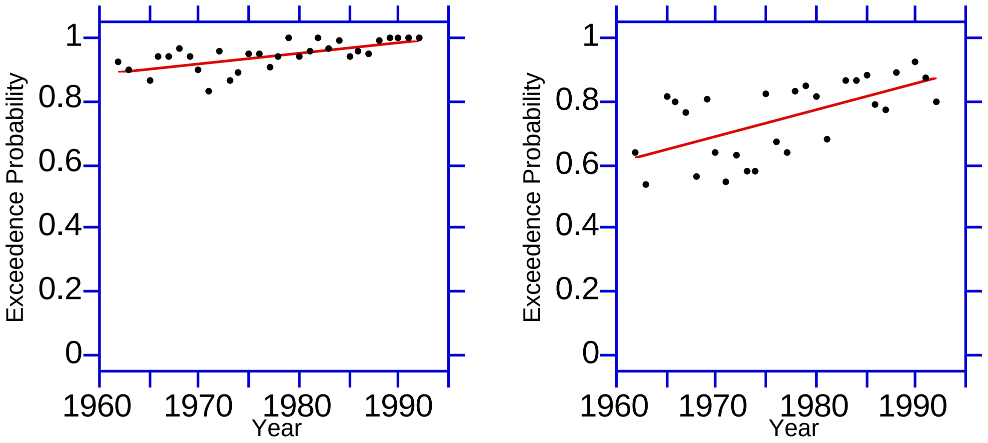


Figure 6.28 Measurements by Year in Ogallala Aquifer

Figure 6.28 shows the number of nitrate measurements per year listed in the data set for the Ogallala Aquifer. Figure 6.29 shows the variation of the four exceedence probabilities calculated for the same years. Statistically significant trends through time can be seen in three of the four exceedence probabilities. Regressions of exceedence probabilities at the detection level, 1 and 5 mg/l have t values greater than 2.0, indicating a 95% or higher probability of a consistent linear trend. Regression results are summarized in Table 6.4 (years with fewer than 12 listed measurements were excluded from the regressions). Regression lines are shown in Figure 6.29 for the three thresholds with significant trends. Probabilities of exceeding the detection limit and the 1 mg/l threshold have grown by about 0.3% per year over the period from 1962–1993, and the probability of exceeding the 5 mg/l threshold has grown by about 0.8% over the same period.

a) 0.1 mg/l Exceedence Probabilities b) 1.0 mg/l Exceedence Probabilities



c) 5.0 mg/l Exceedence Probabilities d) 10.0 mg/l Exceedence Probabilities

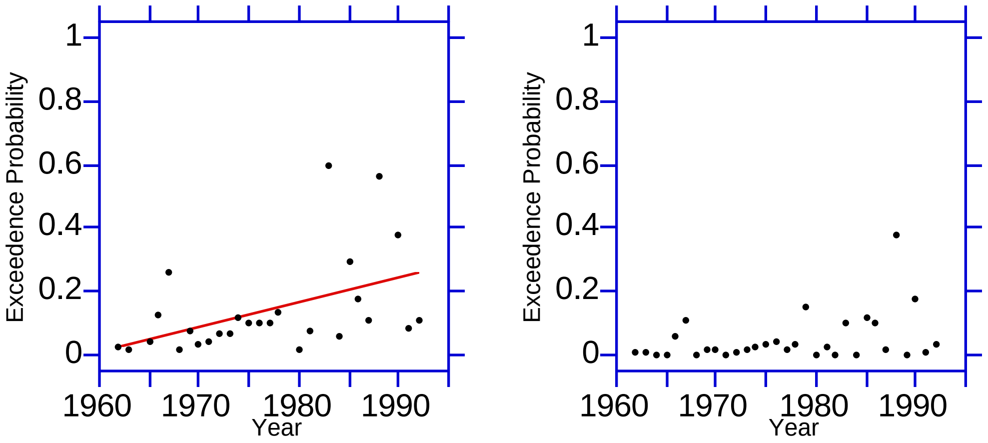


Figure 6.29 Variation of Exceedence Probabilities in the Ogallala Aquifer Over Time

Table 6.10 Regression Results For Threshold Exceedences through Time in the Ogallala Aquifer

Threshold	**Slope**	**t**
0.1 mg/l	0.003	4.94
1.0 mg/l	0.003	3.88
5.0 mg/l	0.008	2.67
10.0 mg/l	0.003	1.95

The increases in exceedence probabilities in the Ogallala point to the possibility of an accumulation of nitrates in the aquifer, which would almost certainly be due to human influences. Although the regressions for the State as a whole were barely statistically significant, the regressions in the Ogallala show an unmistakable trend through time. This may be the most convincing evidence of vulnerability revealed in this study.

6.2.5 Seymour Aquifer

Table 6.11 Nitrate Exceedences in the Seymour Aquifer(2526 Measurements)

Threshold (mg/l)	Exceedences	Exceedence Probability	Lower Bound	Upper Bound
0.1	2420	0.958	0.9508	0.9644
1	2368	0.9374	0.9289	0.9452
5	2073	0.8207	0.8076	0.8331
10	1435	0.568092	0.5517	0.5844

Of the five study aquifers, the Seymour is obviously the most highly contaminated by nitrates. Every quadrangle with twelve or more measurements from this aquifer has an estimated exceedence probability greater than 60% at the 1 mg/l threshold, and only two have exceedence probabilities below 80%. Figure 6.30 shows a slight tendency toward lower exceedence probabilities in the southern part of the aquifer at the higher thresholds, but given the small extent of the aquifer, it is unclear whether this is a significant trend.

Trends of exceedence probabilities with depth and with time in the aquifer are difficult to interpret. Figure 6.31 seems to indicate that shallower wells in the Seymour are less likely to have elevated nitrate levels than deeper wells, but given that in the study database only four wells tapping the Seymour are as deep as 150 feet, there is little room for variation with depth.

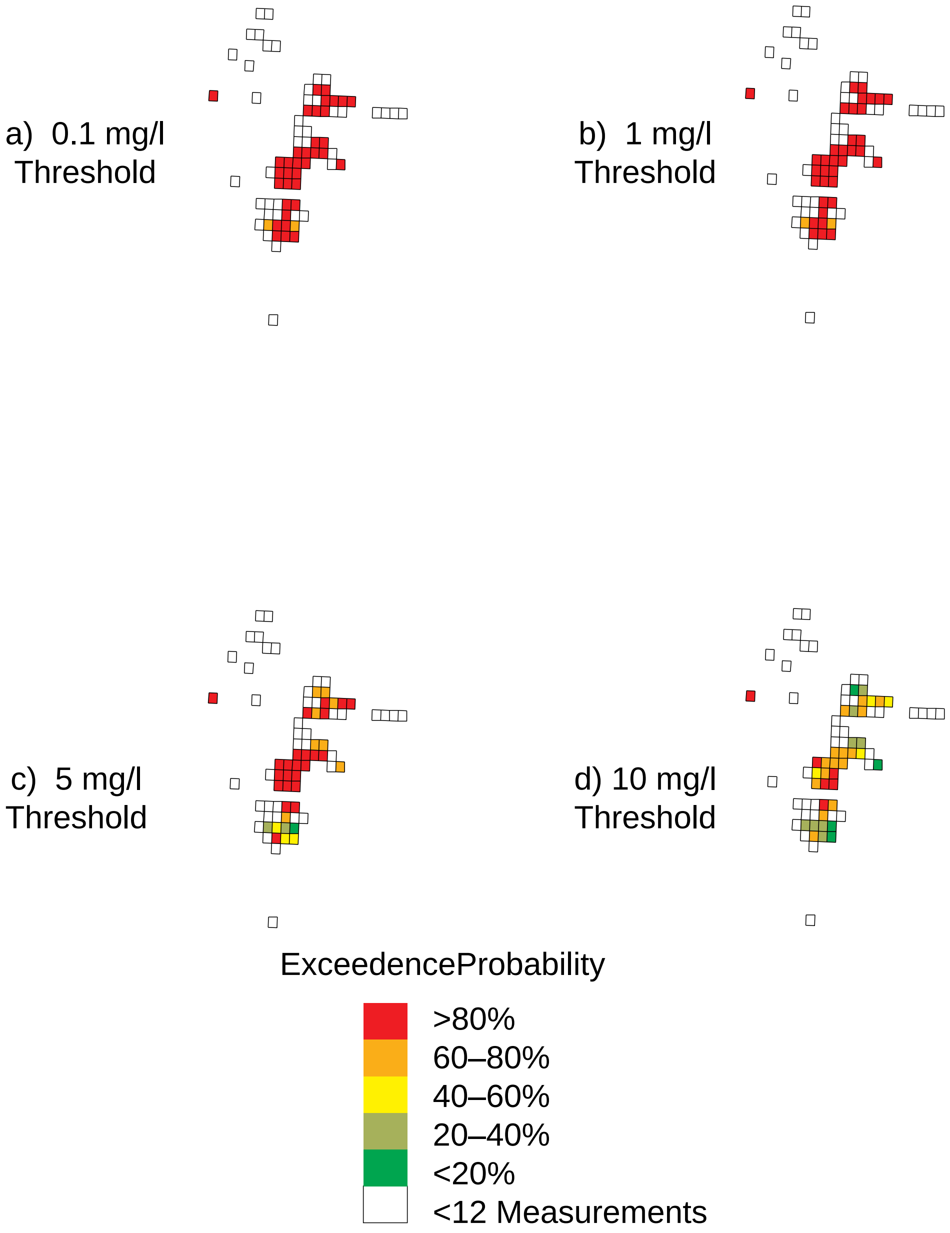


Figure 6.30 Estimated Nitrate Exceedence Probabilities by Quadrangle in the Seymour Aquifer

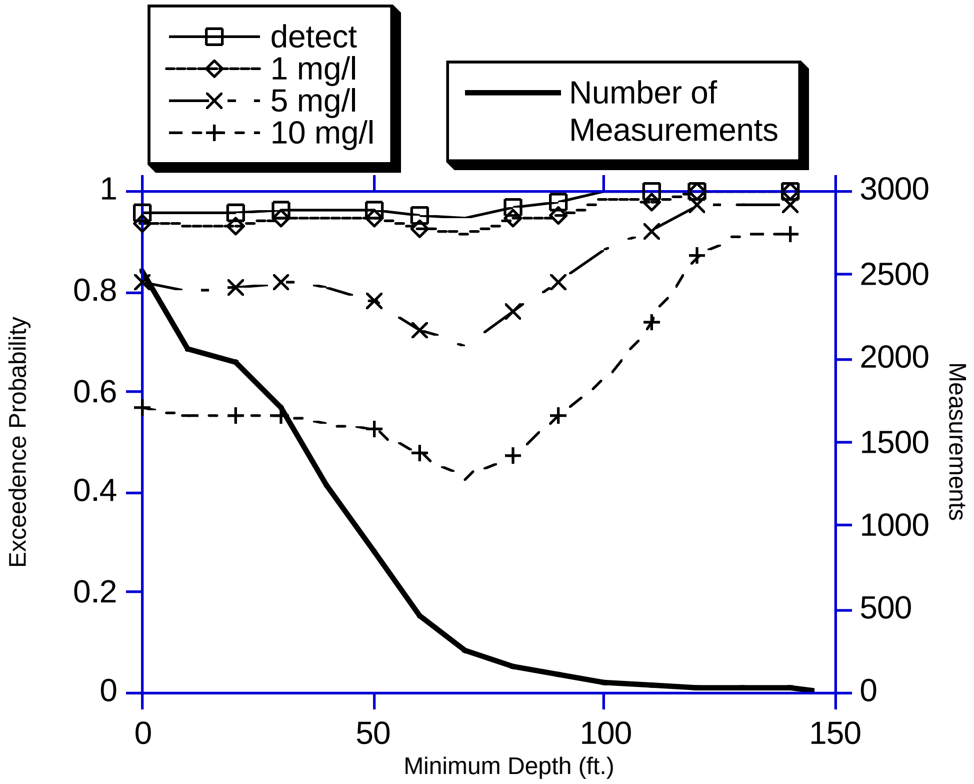


Figure 6.31 Variation of Exceedence Probabilities with Depth in the Seymour Aquifer

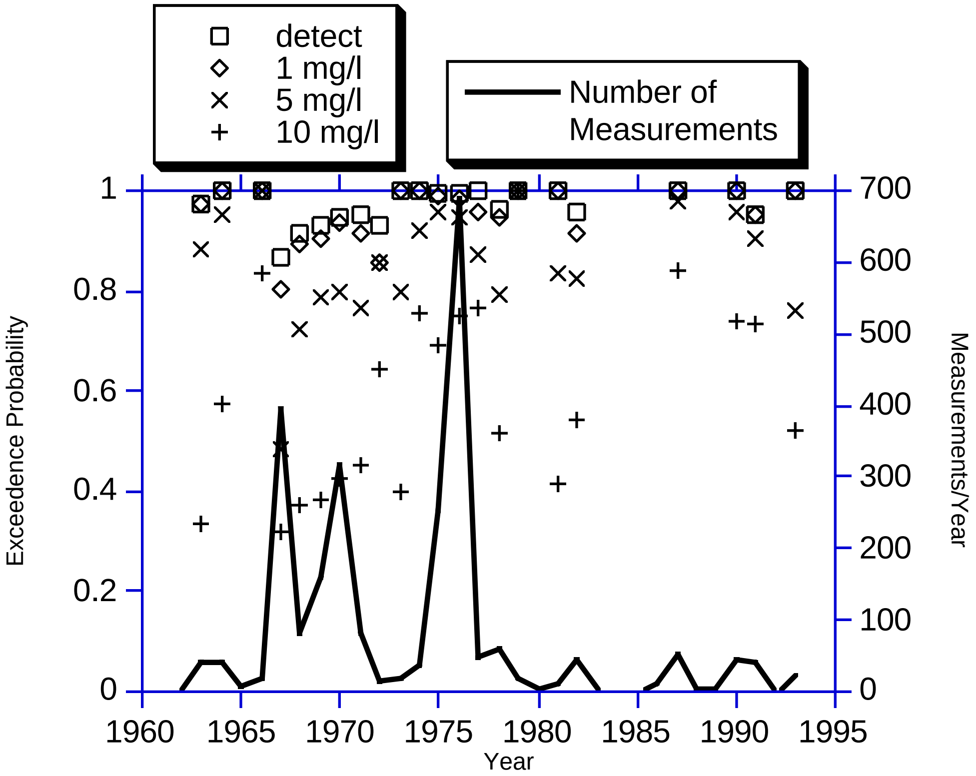


Figure 6.32 Variation of Exceedence Probabilities over Time in the Seymour Aquifer

The sampling history of the Seymour aquifer is very uneven. In only three years, (1967, 1970, and 1976) have more than 100 nitrate measurements from the Seymour been recorded and in 9 years fewer than 12 measurements were recorded; in 1984, none were recorded. Figure 6.32 may show a trend toward increasing likelihood of exceedences of the 10 mg/l threshold, but the t statistic of a regression on this probability against time is 1.95, indicating less than 95% probability that the trend is significant. Given the high incidence of exceedences at all levels, it is safe to say that the Seymour Aquifer is highly vulnerable to nitrate contamination.

6.2.6 Aquifer Summary

Figure 6.33 compares the estimated exceedence probabilities at the four thresholds for the statewide base data set and for each of the five study aquifers. The lines on the figures are provided as a visual aid and do not reflect any prediction for exceedence probabilities at intermediate thresholds. The figure reaffirms the trends discussed in the preceding sections. The Carrizo-Wilcox clearly has the lowest nitrate concentrations of the five aquifers and has lower exceedence probabilities at all thresholds than the state as a whole. The Seymour clearly has the highest concentrations, and higher exceedence probabilities at all thresholds than the state as a whole.

The Edwards (Balcones Fault Zone), the Hueco-Mesilla Bolson, and the Ogallala have intermediate values for exceedence probabilities. In these aquifers nitrate is more likely to be found at the 0.1 and 1.0 mg/l levels than in the state as a whole, but less likely to be found at the 5 and 10 mg/l levels than in the state as a whole. One possible explanation for this variation is that all three aquifers have porous compositions, which makes them very penetrable, and vulnerable to surface influences. At the same time their permeability leads to more mixing than in more tightly formed aquifers, and hence more dilution and fewer detections at high concentrations. The lack of strong trends with depth tends to confirm this possibility.

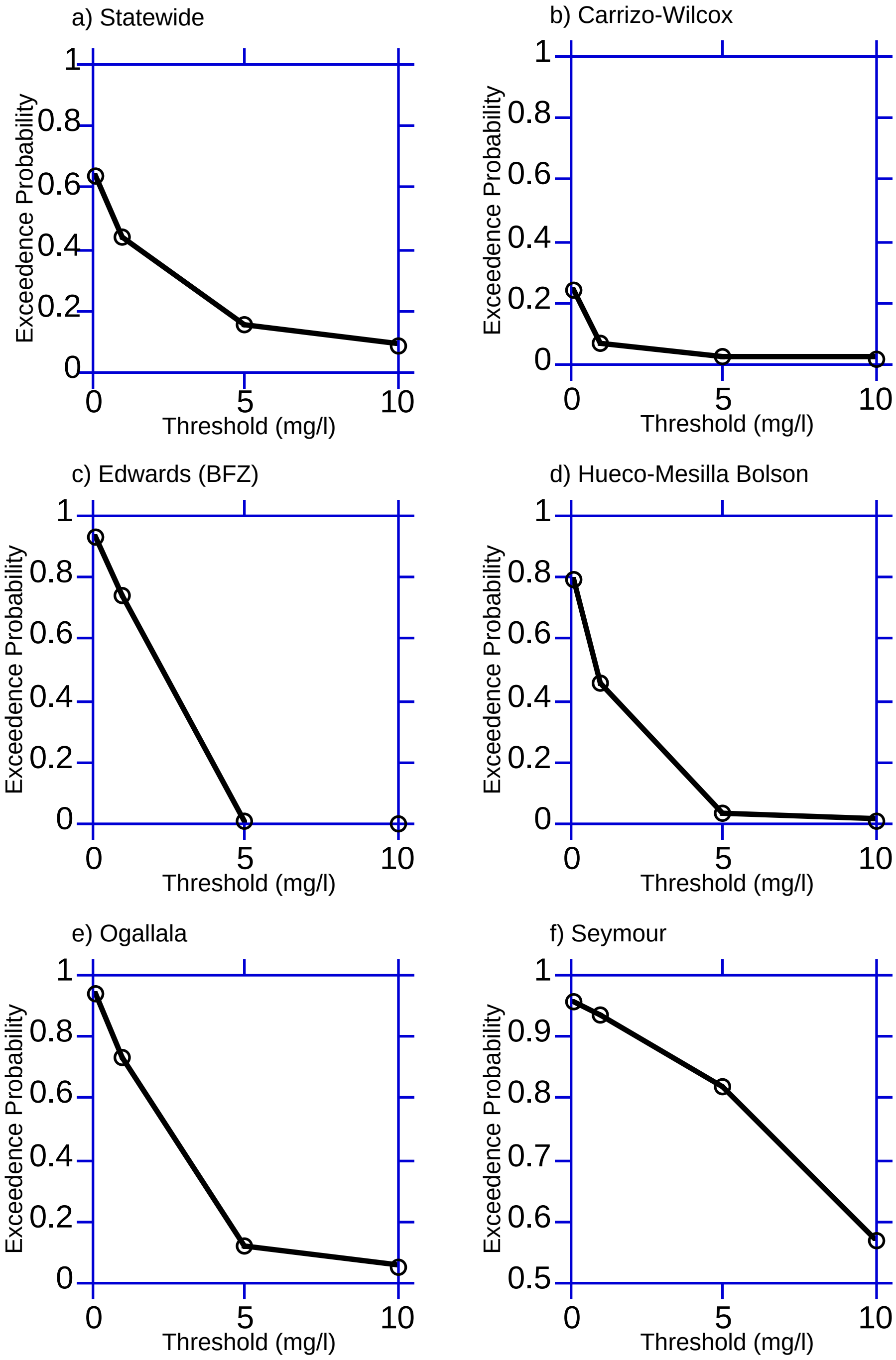
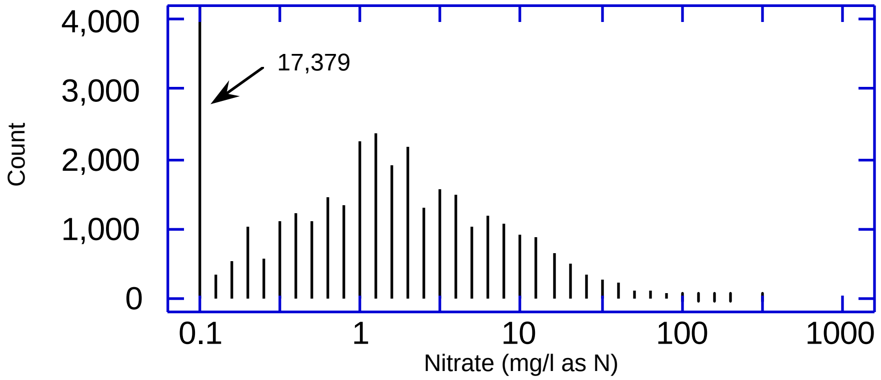


Figure 6.33 Comparison of Exceedence Probabilities Statewide and in Five Study Aquifers

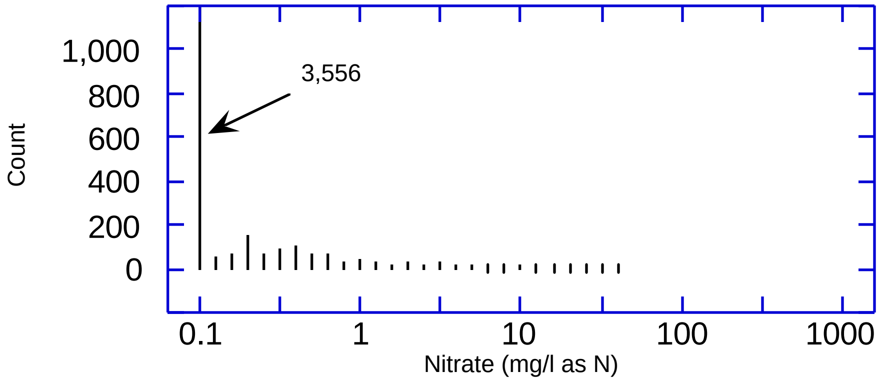
Figure 6.34 summarizes the nitrate measurements statewide and in the five aquifers as histograms. Each histogram approximates the shape of the probability distribution of nitrate concentrations in the corresponding population of water samples. Note that the concentrations are expressed as logarithms. The graphs in Figure 6.33 approximate the inverse of the cumulative probability of nitrate concentrations in the state and the aquifers. The graphs in Figure 6.34 approximate the probability densities of the state and the aquifers. The shapes of the distributions vary considerably from aquifer to aquifer. In general, the tails of the distributions (especially at the low end of the concentration range) are very long, as represented by the high numbers at the detection limit. The Seymour Aquifer comes closest to a lognormal distribution, but is very long in the tails at both ends.

Figure 6.35a summarizes the nitrate measurements in the five study aquifers in a different way, using boxplots. In a boxplot, the box contains the central 50% (between the 25th and 75th percentile) of the values in the plotted group, and the whiskers extend to the lowest and highest values within 1.5 times the width of the box. The Edwards and Seymour Aquifers show the least variation in nitrate concentrations, as illustrated by the narrowness of their boxes. Points farther from the boundaries of the box are plotted as circles or "outside" values (Helsel and Hirsch 1992) The Hueco-Mesilla Bolson has the smallest number of outside values. Note that since more than 75% of the nitrate measurements in the Carrizo-Wilcox (CZWX) are below the detection limit, the width of the box is zero, and there are no whiskers on its plot. As a result, every



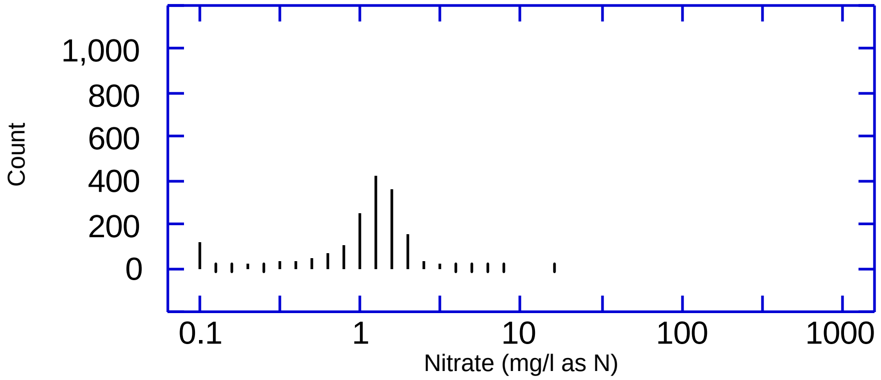
a

) Statewide Nitrate Concentration Histogram



b

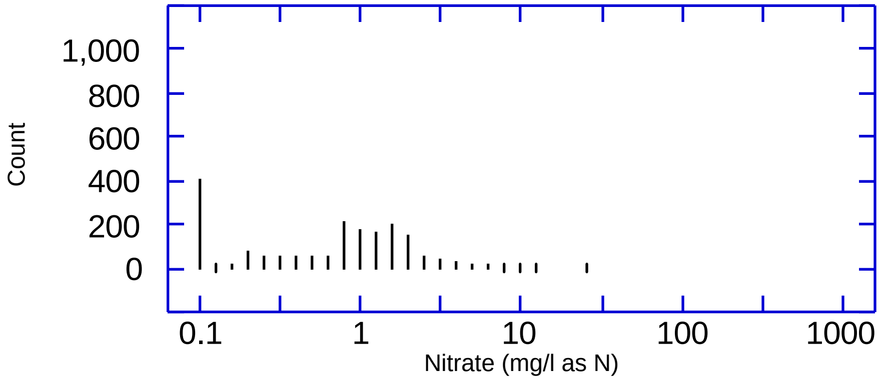
) Carrizo-Wilcox Aquifer Nitrate Concentration Histogram



c

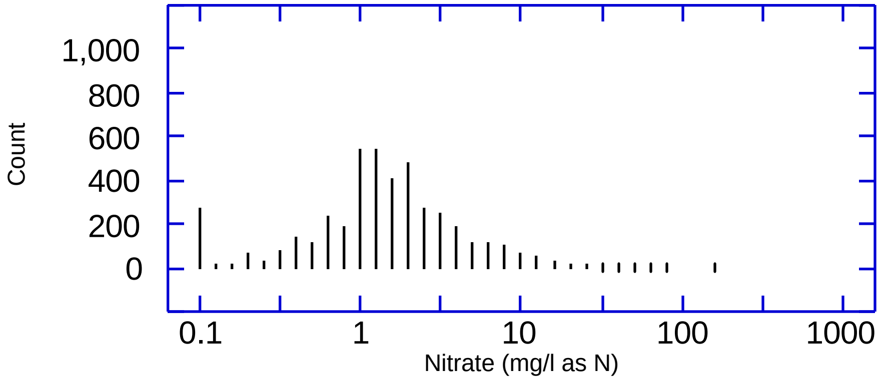
) Edwards Aquifer (Balcones Fault Zone) Nitrate Concentration Histogram

Figure 6.34 Histograms of Nitrate Concentrations in Texas and Five Study Aquifers



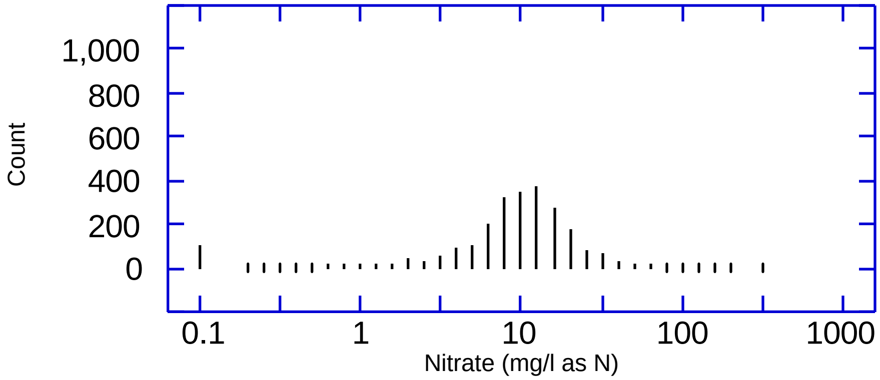
d

) Hueco-Mesilla Bolson Aquifer Nitrate Concentration Histogram



e

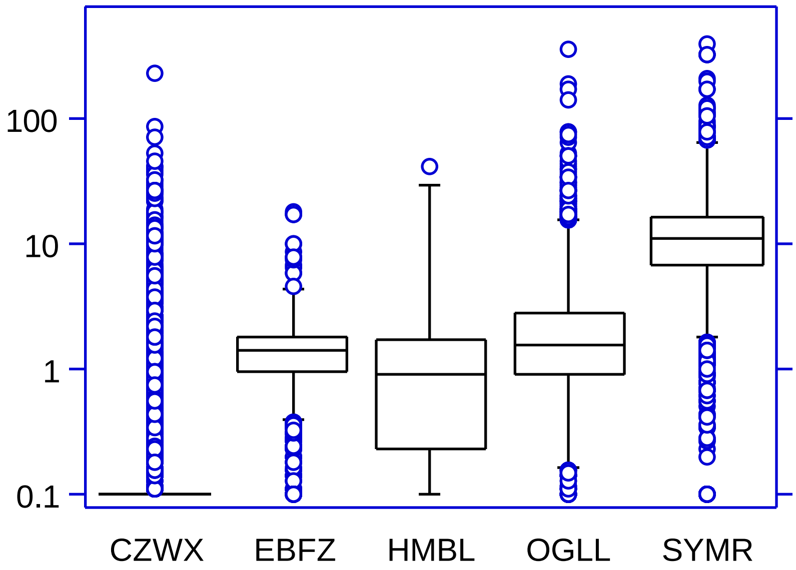
) Ogallala Aquifer Nitrate Concentration Histogram



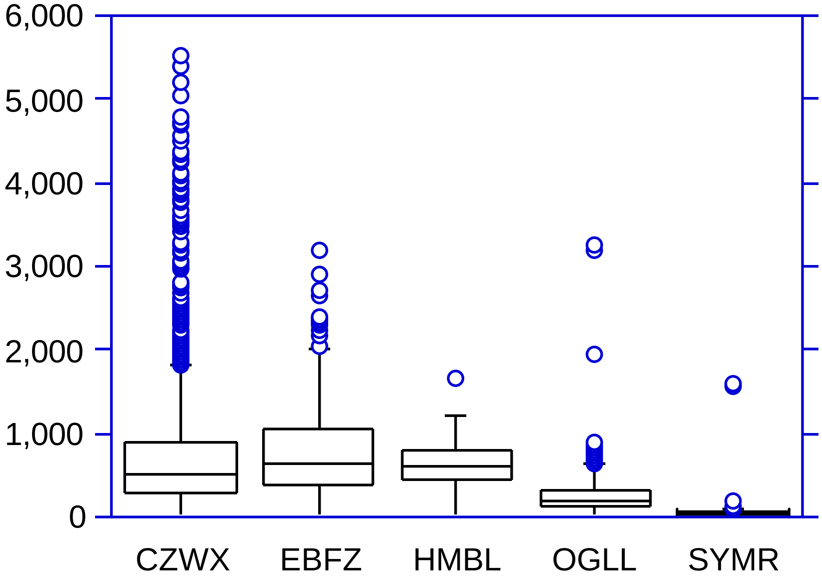
f)

Seymour Aquifer Nitrate Concentration Histogram

Figure 6.34 (Continued) Histograms of Nitrate Concentrations in Texas and Five Study Aquifers



a) Nitrogen Concentration



b) Well Depths

Figure 6.35 Boxplots of Well Depths and Nitrate Concentrations in Five Study Aquifers measurement over 0.1 mg/l is plotted as an outside value. This is another example of the effects of censored data on statistical representations.

In boxplots of normally distributed data, the boxes and whiskers are symmetrical, and roughly one point in 100 is an outside value. Although the plots for the Balcones Fault Zone of the Edwards Aquifer (EBFZ), the Ogallala Aquifer (OGLL), and the Seymour Aquifer (SYMR) are roughly symmetrical, which might indicate lognormal distribution (the plots are on a log scale), they have more outside points than a normal distribution, indicating a tail-heavy distribution. This is similar to the conclusion drawn earlier about the lack of fit of a lognormal distribution to data from single quadrangles.

Another comparison can be made from these data. A second boxplot, Figure6.35b, shows the distribution of well depths in the five aquifers. The two aquifers with the shallowest wells, the Seymour and the Ogallala, are also the ones with the highest nitrate concentrations. This observation tends to confirm the assumption that shallow groundwater is more vulnerable than shallower groundwater. However, the Edwards and Hueco-Mesilla Bolson Aquifers, which have higher detection rates than the Carrizo-Wilcox, also tend to have slightly deeper wells than the Carrizo-Wilcox. The relationship between depth and water quality remains somewhat ambiguous.

6.3 INDICATORS AND REGRESSION

In order to evaluate the predictive capacity of the potential indicator parameters, a series of stepwise multiple linear regression were performed. In each regression, an estimated exceedence probability was taken as the dependent variable, and average precipitation, average soil thickness, average soil organic matter content, and nitrogen fertilizer sale figures were taken as the independent variables. Each of these variables was evaluated on 7.5' quadrangles across the State, as described in Chapter 5. The regressions were performed using STATGRAPHICS, a statistical and graphic data analysis package for personal computer.

In stepwise multiple linear regression, an independent variable is added to the model in the analysis if the additional information it provides is significant at a chosen confidence level. As the model is being constructed, partial F statistics are calculated for each variable not currently in the model, as though each were the next variable to be added. For a confidence level of 95%, a variable can be added to the regression if its F value is greater than 4.0. At the same time, partial F statistics are calculated for each variable already in the model, as though each were the last added to the model. If the F statistic for any variable in the model falls below the selected threshold, it is removed from the model. See Draper and Smith (1981) for a more complete discussion of this method. The F statistics for variables included and not included are combined in a single column in the following tables. The listed values are the partial F statistics for the final selected model for each exceedence probability.

In the first set of regressions, every 7.5' quadrangle with twelve or more measurements was included. These are the 1158 quadrangles that were mapped in Section 6.1. The regressions attempt to fit a model of the form

$$P_t = \beta_0 + \beta_1 T + \beta_2 O + \beta_3 R + \beta_4 N \tag{6-1}$$

where P_t is the exceedence probability in the quadrangle for threshold t, T is the soil thickness, O is the organic content of the soil, R is the average annual precipitation, and N is average annual nitrogen fertilizer sales. The results of the regressions are summarized in Table 6.12.

The purpose of the regression is primarily to identify those parameters with significant correlation to the exceedence probabilities, rather than to create a predictive model. To this end, all the variables are shown in the table, whether or not they were included in the final model.

The models resulting from the first two regressions listed in Table 6.12 include only the soil organic content and average precipitation as independent variables. In both cases, the precipitation is the more influential variable. Precipitation decreases markedly in Texas with distance from the coast, and nitrate detections increase from southeast to northwest. The regression reflects the parallels between these trends. That higher nitrate values are found where there is less precipitation runs somewhat counter to intuition, since higher recharge rates, which are driven by precipitation, are usually associated with greater vulnerability (as in DRASTIC). Possibly, higher precipitation leads to shorter residence time in the aquifers, and lower concentrations as a result. It is less surprising that higher soil organic content is associated with lower nitrate detections, since organic processes may tend to fix nitrate in the soil, preventing it from reaching groundwater.

Table 6.12 Regression Results for Quads with 12 or More Measurements

Threshold	**r^2**	**Indicators**	**Coefficient**	**Partial F**
Detection	0.414	Constant (ß$_0$)	1.201	--
		Thickness (ß$_1$)	--	0.215
		Organic (ß$_2$)	-0.0065	45.31
		Precip. (ß$_3$)	-0.0175	531.98
		Fertilizers (ß$_4$)	--	0.906
1 mg/l	0.398	Constant (ß$_0$)	1.046	--
		Thickness (ß$_1$)	--	3.26
		Organic (ß$_2$)	-0.00534	24.53
		Precip. (ß$_3$)	-0.019712	541.17
		Fertilizers (ß$_4$)	--	2.40
5 mg/l	0.154	Constant (ß$_0$)	0.1530	--
		Thickness (ß$_1$)	0.00369	39.42
		Organic (ß$_2$)	--	0.538
		Precip. (ß$_3$)	-0.00695	125.14
		Fertilizers (ß$_4$)	-0.01510	51.38
10 mg/l	0.079	Constant (ß$_0$)	0.047	--
		Thickness (ß$_1$)	0.00234	27.85
		Organic (ß$_2$)	--	0.105
		Precip. (ß$_3$)	-0.003184	46.29
		Fertilizers (ß$_4$)	0.009497	35.79

The regressions on detection and 1 mg/l exceedences have r^2 statistics of roughly 0.4, meaning that the regression equation predicts about 40% of the deviations from the mean value of the probabilities. That only two variables should predict this much of the variation is surprising. More surprising is the fact that regressions on precipitation alone yield r^2 values of 0.391 and 0.387 for detection and exceedence of 1 mg/l. The predictive capability of the first two regressions rests almost entirely on the inverse correlation between rainfall and nitrate exceedences.

The regressions on the exceedence probabilities of the higher concentrations have little meaning. Combining all available variables to produce an equation with little predictive power, they simply indicate a general lack of significant correlation between the dependent and the independent variables.

The second set of regressions, also fitting the model given in equation 6-1, was run on quadrangles containing twelve or more measurements from wells tapping the five study aquifers. These are the quads presented in the series of maps in Section 6.2. The results for these quads, summarized in Table 6.13, are very similar to those for the state as a whole. The organic material in the soil has

Table 6.13 Regression Results for Quads Associated with Study Aquifers

Threshold	**r^2**	**Indicators**	**Coefficient**	**Partial F**
Detection	0.409	Constant (ß$_0$)	1.289	--
		Thickness (ß$_1$)	--	0.668
		Organic (ß$_2$)	-0.0134	38.57
		Precip. (ß$_3$)	-0.0170	106.71
		Fertilizers (ß$_4$)	--	0.325
1 mg/l	0.387	Constant (ß$_0$)	1.130	--
		Thickness (ß$_1$)	--	0.122
		Organic (ß$_2$)	-0.0107	21.54
		Precip. (ß$_3$)	-0.0192	116.79
		Fertilizers (ß$_4$)	--	0.070
5 mg/l	0.116	Constant (ß$_0$)	0.202	--
		Thickness (ß$_1$)	0.0100	15.62
		Organic (ß$_2$)	-0.0070	11.14
		Precip. (ß$_3$)	-0.0053	11.59
		Fertilizers (ß$_4$)	-0.0254	20.01
10 mg/l	0.085	Constant (ß$_0$)	0.1600	--
		Thickness (ß$_1$)	0.0067	12.29
		Organic (ß$_2$)	-0.0039	6.15
		Precip. (ß$_3$)	-0.0031	7.03
		Fertilizers (ß$_4$)	-0.0192	19.99

more influence, but the equations contain the same independent variables and have roughly the same predictive power.

The third set of regressions, summarized in Table 6.14, is applied to the same quadrangles as the second, but now a series of dummy variables have been added, indicating the aquifer from which water was taken for the measurements and soil thickness and fertilizer sales have been dropped from consideration. The model to be fitted is thus

$$P_t = ß_0 + ß_1 O + ß_2 R + ß_3 C + ß_4 E + ß_5 H + ß_6 G + ß_7 S$$

where O and R have the same meanings as in the equation 6-1, and C, E, H, G, and S are the dummy variables representing the Carrizo-Wilcox, Edwards(BFZ), Hueco-Mesilla Bolson, Ogallala, and Seymour Aquifers, respectively. If the measurements come from the Carrizo-Wilcox Aquifer, for example, the variable C is assigned a value of 1. G is used to represent the Ogallala aquifer because O is already used to represent soil organic content.

The results of the various regressions show that of the parameters tested, the most influential by far in determining the probability of nitrate detection or exceedence of threshold concentration is the aquifer from which the water is collected.

These regression results may be slightly misleading regarding the influence of geologic parameters relative to the other indicators. For example, although precipitation drops out of the regression when the dummy variables for the aquifers are included, this does not mean that it has no influence. The fact that the 1 mg/l exceedence probabilities in the Carrizo-Wilcox and Ogallala Aquifers differ by roughly 67% may be in part due to the difference in average rainfall over

Table 6.14 Regression Results for Quads Associated with Study Aquifers, Including Dummy Variables for Aquifers

Threshold	**r^2**	**Indicators**	**Coefficient**	**Partial F**
Detection	0.809	Constant ($ß_0$)	0.857	--
		Organic ($ß_1$)	--	0.200
		Precip. ($ß_2$)	0.00408	9.14
		CW ($ß_3$)	-0.748	711.40
		ED ($ß_4$)	--	2.118
		HM ($ß_5$)	-0.199	11.37
		OG ($ß_6$)	--	1.913
		SR ($ß_7$)	--	0.125
1 mg/l	0.787	Constant ($ß_0$)	0.736	--
		Organic ($ß_1$)	--	0.0002
		Precip. ($ß_2$)	--	0.879
		CW ($ß_3$)	-0.664	828.9
		ED ($ß_4$)	--	0.052
		HM ($ß_5$)	-0.373	34.33
		OG ($ß_6$)	--	0.052
		SR ($ß_7$)	0.187	29.21
5 mg/l	0.758	Constant ($ß_0$)	0.021	--
		Organic ($ß_1$)	--	0.566
		Precip. ($ß_2$)	--	0.0005
		CW ($ß_3$)	--	0.0004
		ED ($ß_4$)	--	0.0383
		HM ($ß_5$)	--	0.0578
		OG ($ß_6$)	0.094	28.1
		SR ($ß_7$)	0.779	939.9
10 mg/l	0.691	Constant ($ß_0$)	0.011	--
		Organic ($ß_1$)	--	0.004
		Precip. ($ß_2$)	--	0.0007
		CW ($ß_3$)	--	0.0414
		ED ($ß_4$)	--	0.0455
		HM ($ß_5$)	--	0.0013
		OG ($ß_6$)	0.031	4.35
		SR ($ß_7$)	0.545	653.4

in the parts of the state where they are located. Dummy variables for spatially distinct aquifers will subsume a great deal of spatially variable data.

A fourth set of regressions was run for the 1 mg/l threshold exceedence probability on quadrangles within single aquifers. Again, the model to be fit is given in equation 6-1. The results of the regressions are shown in Table 6.15. No model could be fit to the data from the Hueco-Mesilla Bolson Aquifer because the number of quadrangles in that aquifer is too small.

The results of the regressions show that the selected indicators have very little value within the aquifers. No significant correlations were found in the Edwards or Seymour Aquifers, and the regressions in the Carrizo-Wilcox and Ogallala Aquifers have little explanatory power, as indicated by their r^2 values.

The final conclusion to be drawn from the regressions is that a model of exceedence probabilities as good as any that can be drawn from the indicator data included in this study would apply average exceedence probabilities for each aquifer and ignore the other indicators.

Table 6.15 Regression Results for 1 mg/l threshold within Study Aquifers

Aquifer	**r^2**	**Indicators**	**Coefficient**	**Partial F**
Carrizo-Wilcox	0.041	Constant (ß$_0$)	-0.053	--
		Thickness (ß$_1$)	--	0.249
		Organic (ß$_2$)	-0.0060	6.97
		Precip. (ß$_3$)	--	0.719
		Fertilizers (ß$_4$)	--	0.004
Edwards (BFZ)	--	Constant (ß$_0$)	--	--
		Thickness (ß$_1$)	--	0.154
		Organic (ß$_2$)	--	0.223
		Precip. (ß$_3$)	--	0.092
		Fertilizers (ß$_4$)	--	0.250
Ogallala	0.0996	Constant (ß$_0$)	0.964	--
		Thickness (ß$_1$)	--	0.039
		Organic (ß$_2$)	-0.0068	4.84
		Precip. (ß$_3$)	--	0.027
		Fertilizers (ß$_4$)	-0.0201	10.39
Seymour	--	Constant (ß$_0$)	--	--
		Thickness (ß$_1$)	--	0.259
		Organic (ß$_2$)	--	0.187
		Precip. (ß$_3$)	--	0.248
		Fertilizers (ß$_4$)	--	0.264

6.4 COMPARISON WITH WATER UTILITIES DIVISION DATA

The objective of this section is to determine how well the data collected by the TWDB over a period of more than 30 years from wells constructed for many purposes predicts the likelihood of finding nitrate in samples collected in a much shorter period from wells used for public water supply. Nitrate measurements collected by the Water Utilities Division (WUD) of the Texas Natural Resource Conservation Commission as part of its Primary Drinking Water Standards enforcement effort are collected in a database maintained independently of the TWDB Groundwater Data System. Records of nitrate measurements collected between February 1993 and October 1994 were extracted from this database for comparison to the quadrangle exceedence probabilities estimated from the TWDB database.

Of 16,538 measurements recorded in the WUD database, 11,698 were collected from water systems using groundwater exclusively, and could be traced to well locations. 11,614 of these measurements could be identified with quadrangles with at least one measurement included in the analysis of the TWDB data, and 6,992 could be identified with one of the 3,554 quadrangles with 12 or more TWDB measurements (see Section 5.?).

Because the number of measurements in the WUD database is relatively small, only 132 quads have 12 or more measurement records in both databases, limiting the scope of quad-by-quad comparison of exceedence in the two databases. Figure 6.36 shows a scatter plot of this comparison for exceedences of the 0.1 mg/l threshold.

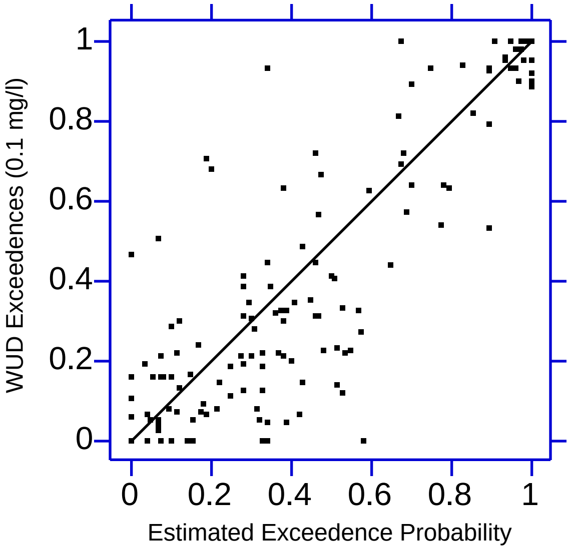


Figure 6.36 Quad-by-Quad Comparison of Estimated 0.1 mg/l Exceedence Probabilities with WUD Nitrate Measurements

To form a comparison based on all the WUD measurements, the data were aggregated by the estimated exceedence probability of the quadrangles in which the water samples were collected. The results of this comparison for the 0.1 mg/l threshold are shown in Figure 6.37. Figure 6.37a shows, for example, that of all the measurements in the WUD database collected from quads with an estimated 0.1 mg/l exceedence probability between 0.9 and 1.0, about 89% had concentrations above the threshold. The figure clearly shows a trend toward higher frequencies of nitrate detection in quads with higher estimated exceedence probabilities. The trend breaks down, however, in quadrangles with the lowest estimated exceedence probabilities. Figure 6.37b makes a similar comparison of aggregated measurements, limited to quads where the exceedence probability estimate is based on 12 or more measurements from the TWDB database. In this comparison, the agreement of estimated exceedence probabilities and exceedences recorded in the WUD database improves, but the same break in the trend at low probabilities can be seen.

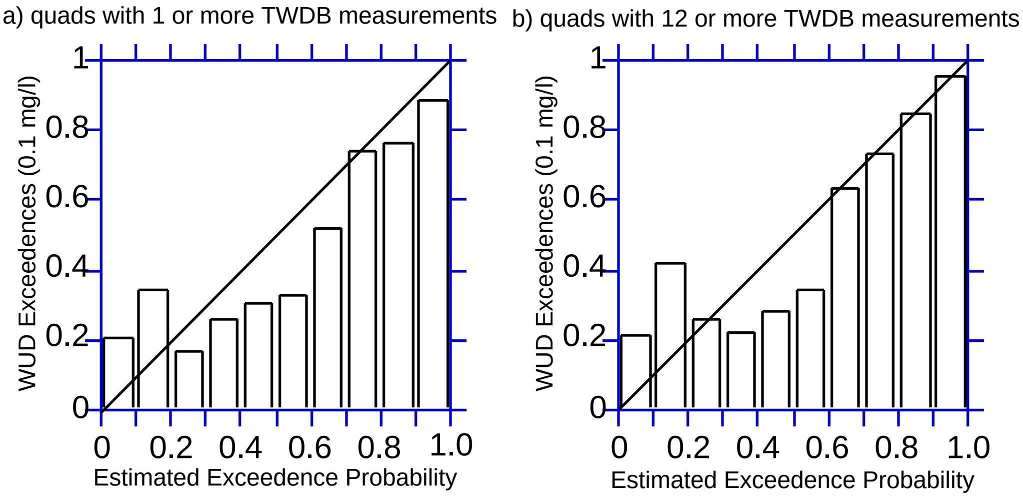


Figure 6.37 Aggregated Comparison of Estimated 0.1 mg/l Exceedence Probabilities with WUD Nitrate Measurements

Taken together, Figures 6.36 and 6.37 suggest that the TWDB data under-predict the WUD measurements about as often as they over-predict. In aggregate, the two data sets agree but there is often a considerable difference in the detection rates within a single quad. The same behavior can be seen in graphs of the same information for higher threshold levels, which are presented on the following pages in Figures 6.38 through 6.43

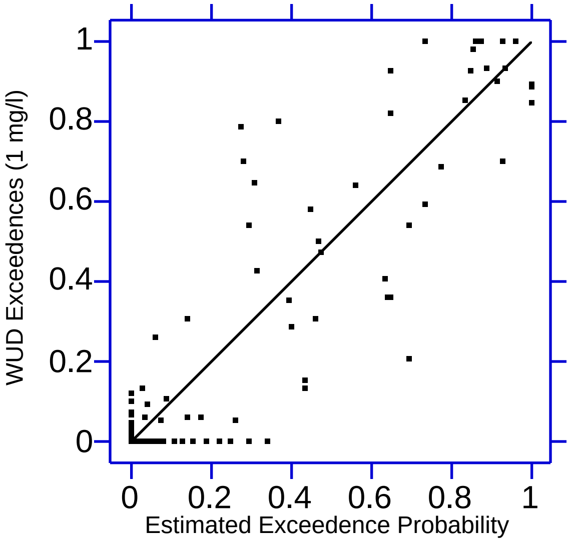


Figure 6.38 Quad-by-Quad Comparison of Estimated 1 mg/l Exceedence Probabilities with WUD Nitrate Measurements

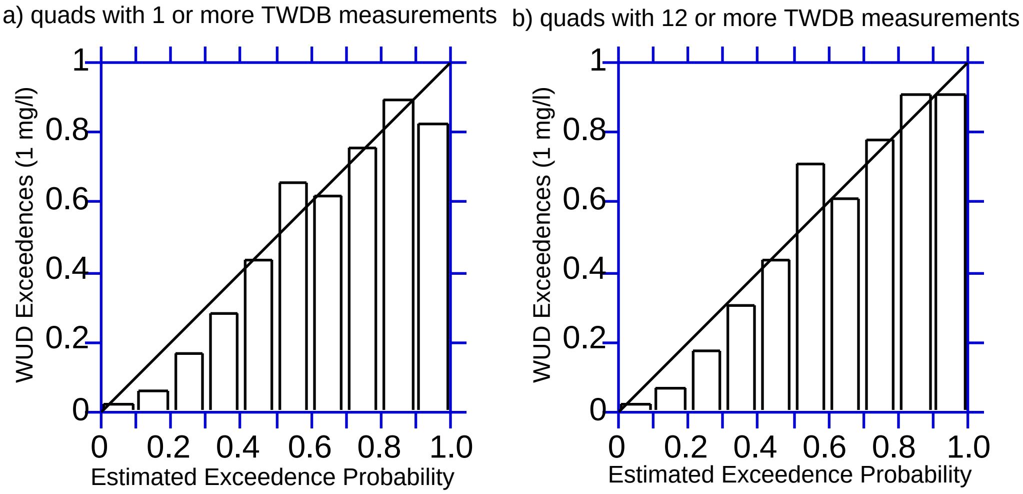


Figure 6.39 Aggregated Comparison of Estimated 1 mg/l Exceedence Probabilities with WUD Nitrate Measurements

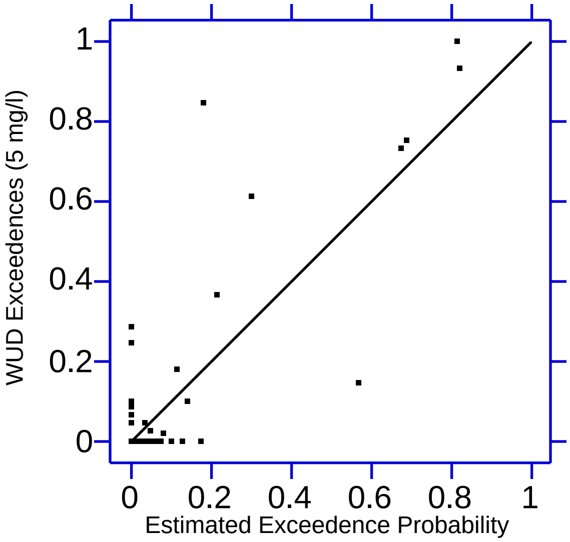


Figure 6.40 Quad-by-Quad Comparison of Estimated 5 mg/l Exceedence Probabilities with WUD Nitrate Measurements

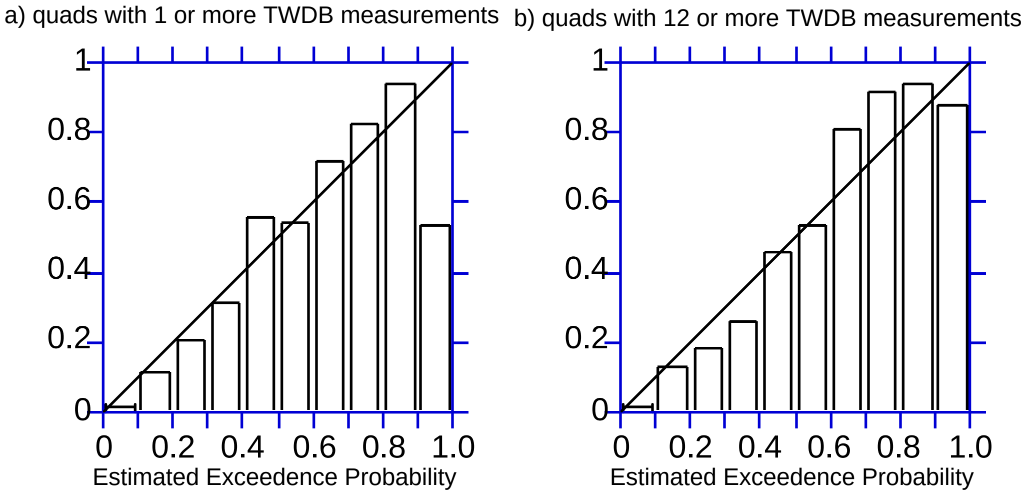


Figure 6.41 Aggregated Comparison of Estimated 5 mg/l Exceedence Probabilities with WUD Nitrate Measurements

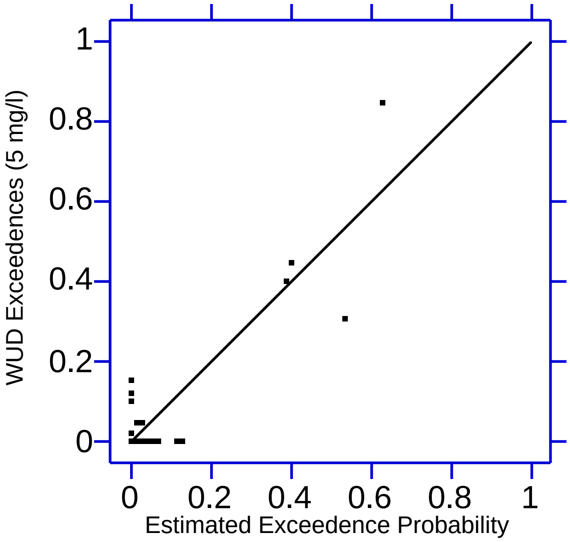


Figure 6.42 Quad-by-Quad Comparison of Estimated 10 mg/l Exceedence Probabilities with WUD Nitrate Measurements

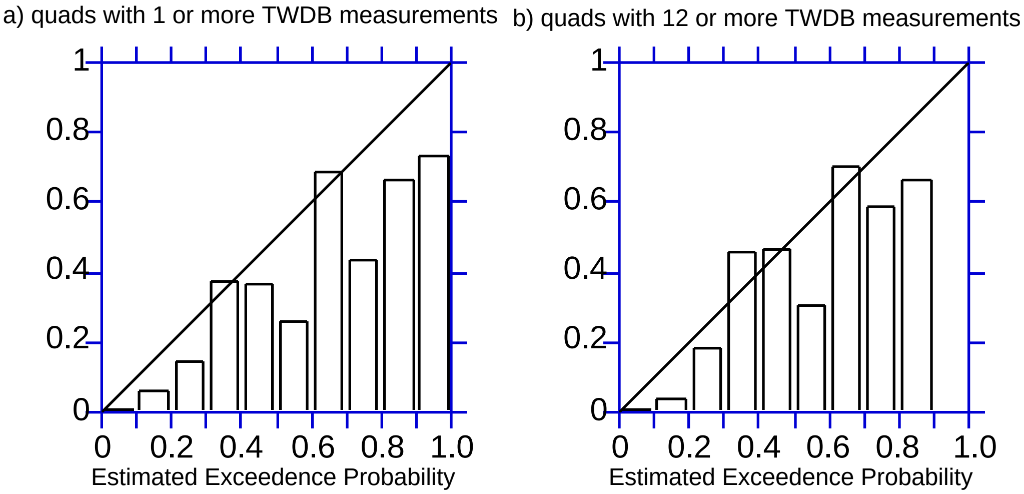


Figure 6.43 Aggregated Comparison of Estimated 10 mg/l Exceedence Probabilities with WUD Nitrate Measurements

One possible interpretation of the higher-than-predicted 0.1 mg/l exceedence rates quads with low exceedence probabilities is that there has been a gradual buildup of nitrate in groundwater systems, and that regions that in were in equilibrium at nitrate concentrations below 0.1 mg/l, are now loaded above that level. If this were the case, however, one would expect to see this pattern repeated at the higher exceedence thresholds, especially at the 1 mg/l level, where the TWDB data shows an increase in the statewide detection rate over time.

The higher-than-predicted 5 mg/l exceedence rates and lower-than-expected 10 mg/l exceedence rates in quads with high exceedence probabilities may be due in part to the influence of drinking water regulations. More frequent sampling is required in systems where the 5 mg/l threshold is exceeded, and water sources with nitrate concentrations in excess to 10 mg/l violate the MCL and are likely to be removed from water supply systems. These factors could lead to over-sampling of water with nitrate above 5 mg/l and under-sampling of water with nitrate below 10 mg/l. No attempt was made to compensate for either of these potential biases.

6.5 NITRATE AND HERBICIDES IN MIDWEST DATA SET

Although nitrate is the only constituent studied in this work, the initial objective was to devise a system for predicting the likelihood of finding man-made agricultural chemicals in groundwater. This section addresses the question of how the occurrence of elevated levels of nitrate relates to the presence of agricultural chemicals. Because of the scarcity of herbicide data from Texas, the comparison is made using data from the herbicide and nitrate reconnaissance carried out in near-surface aquifers of the mid-continental U.S. by Kolpin, Burkart and Thurman (1992).

The report lists results of chemical analyses of 599 water samples collected from 303 wells in the mid-continental states of Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota and Wisconsin. Concentrations are listed for a variety of nutrients, herbicides and herbicide metabolites. Of interest to this work are the measurements of nitrate, seven herbicides (alachlor, atrazine, cyanazine, metolachlor, metribuzin, prometon, and simazine) and two dealkylated atrazine metabolites (deethylatrazine and deisopropylatrazine). The detection limit for nitrate is 0.05 mg/l. The detection limit for the herbicides and atrazine metabolites is 0.05 μg/l.

In general, detectable levels of herbicides are more likely to be found in water samples with elevated nitrate levels. Of 170 samples with nitrate concentrations above 3 mg/l, 84 (49%) had detectable levels of at least one herbicide or metabolite. In contrast, of 429 samples with nitrate concentrations less than or equal to 3 mg/l, 70 (16%) had detectable levels of at least one herbicide or metabolite.

However, it is also true that of 246 samples with no detectable nitrate, 22 (9%) had detectable levels of at least one herbicide or metabolite. The absence of nitrate in a well, apparently, cannot be considered a guarantee that the well is also free of herbicides—a less specific approach to the use nitrate as an indicator of herbicides is called for.

Such an approach might be based on the idea that the same conditions that lead to a high incidence of elevated nitrate levels would also lead to a high incidence of herbicide detections. A simple comparison of nitrate and herbicide concentrations in samples grouped by two geologic parameters tends to confirm this idea.

Burkart and Kolpin (1993a), in their analysis of the midwest data, found that nitrate and herbicide concentrations were higher in samples collected from unconsolidated aquifers than in samples collected from bedrock aquifers. They also found that nitrate and herbicide concentrations tend to decrease as aquifer depth increases. (Aquifer depth is defined as the vertical distance from the land surface to the top of the aquifer material, regardless of whether the material is saturated or not.)

The matrix presented in Figure6.44 shows the number of water quality samples collected from wells falling into each of four categories based on aquifer class (bedrock or unconsolidated) and aquifer depth. The matrix also shows the number of nitrate measurements in excess of two threshold values, and number of herbicide detections in samples from the four categories. The rates of exceedence and rank of the four categories based on those rates are summarized in Table 6.16 .

	Depth ≤ 30 feet	Depth > 30 feet
Bedrock	Measurements: 113	Measurements: 95
	Nitrate > 1 mg/l: 42	Nitrate > 1 mg/l: 13
	Nitrate > 3 mg/l: 30	Nitrate > 3 mg/l: 6
	Herb. Detections: 25	Herb. Detections: 11
Unconsolidated	Measurements: 335	Measurements: 56
	Nitrate > 1 mg/l: 164	Nitrate > 1 mg/l: 26
	Nitrate > 3 mg/l: 120	Nitrate > 3 mg/l: 14
	Herb. Detections: 104	Herb. Detections: 14

Figure 6.44 Herbicide and Nitrate Measurements Grouped by Geologic Parameters

Table 6.16 Aquifer Categories Ranked by Nitrate and Herbicide Detection Rates

	Nitrate Conc. > 1 mg/l		**Nitrate Conc. > 3 mg/l**		**Herbicide Detections**	
Aquifer Category	**rate**	**rank**	**rate**	**rank**	**rate**	**rank**
Deep Bedrock	14%	4	6%	4	12%	4
Shallow Bedrock	37%	3	26%	2	22%	3
Deep Unconsolidated	46%	2	25%	3	25%	2
Shallow Unconsolidated	49%	1	36%	1	31%	1

The results of this simple comparison are consistent with the hypothesis that conditions leading to increased vulnerability to nitrate contamination, as evidenced by high rates of elevated nitrate concentration, also lead to increased vulnerability to herbicides. This observation holds whether the threshold for elevated nitrate is set at 1 mg/l, as in this study, or at 3 mg/l, as Madison and Brunett (1985) suggest.

Although this comparison of nitrate and herbicide detections is far from conclusive, it suggests that an analysis of the occurrence of a widely measured constituent like nitrate can be used to gain insight into the occurrence of less commonly measured constituents like herbicides.

6.6 SUMMARY

The contents of this chapter have demonstrated how groundwater quality data can be regionalized with a GIS and a database management system, how that regionalized data can be analyzed statistically to classify those regions according to estimated probability of detecting excess nitrate, and how other parameters associated with those regions can be compared with the regional exceedence probabilities to form a predictive model. In addition, the regional exceedence probabilities were compared with an independent data set to test their predictive accuracy, and a simple analysis showed a possible connection between nitrate detections and vulnerability to herbicide contamination.

Sections 6.1 and 6.2 demonstrate the partitioning of the subsurface into two types of regions: the two-dimensional grid of 7.5' quadrangles and the geologic regions of the five study aquifers. Water quality measurements are grouped by their association with these regions, and estimates of the probability that excess concentrations of nitrate will be found in the regions are calculated from those groups of measurements. The probability estimates are then used to identify the regions as more or less vulnerable to contamination by nitrate.

Section 6.3 presented the results of an attempt to generalize the results of the quadrangle exceedence probabilities by relating them to indicator variables evaluated on the same quadrangles. The regression results showed significant predictive potential only for average annual precipitation, which was inversely related to the probability of finding high nitrate concentrations, and with association of water quality measurements with specific aquifers. The only parameter associated with a source of nitrate, nitrogen fertilizer sales by county, was found to have no significant value as an indicator of nitrate exceedence probabilities.

In both Sections 6.1 and 6.2, an effort was made to identify the degree to which variations in depth and time, which cannot easily be represented in the two-dimensional domain of a GIS, influence the likelihood of finding nitrate at elevated concentrations.

Section 6.4 compared independent water samples with the nitrate exceedence probabilities presented in section 6.1. While quadrangles with higher predicted exceedences did, in aggregate, have higher frequencies of nitrate detection, there was considerable variation in individual quadrangles between predicted exceedence probabilities and frequencies of exceedence in the independent data set.

Section 6.5 shows by a simple analysis of data from the mid-continental U.S. that regions identified as vulnerable to nitrate contamination may also be vulnerable to contamination by man-made herbicides.