Table 5. Gray matrix summary for upper aquifer (plain region) of the Tangshan study unit, People's Republic of China, May 1996 data

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (39 total)	0	10	8	21
Median classification	4.19			

Table 6. Gray matrix summary for upper aquifer (plain region) of the Tangshan study unit, People's Republic of China, May 1996 data, without coliform analysis

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (38 total)	2	11	10	15
Median classification	3.68			

Table 7. Gray matrix summary for upper aquifer (plain region) of the Tangshan study unit, People's Republic of China, September 1996 data

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (39 total)	1	10	15	13
Median classification	3.65			

Table 8. Gray matrix summary for lower aquifer (plain region) of the Tangshan study unit, People's Republic of China, May 1996 data

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (45 total)	10	15	14	6
Median classification	2.71			

Table 9. Gray matrix summary for lower aquifer (plain region) of the Tangshan study unit, People's Republic of China, September 1996 data

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (45 total)	6	20	17	2
Median classification	2.8			

Table 10. Gray matrix summary for aquifer of the mountain region of the Tangshan study unit, People's Republic of China, May 1996 data

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (18 total)	6	9	2	1
Median classification	2.085			

Table 11. Gray matrix summary for aquifer of the mountain region of the Tangshan study unit, People's Republic of China, September 1996 data

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (18 total)	4	10	4	0
Median classification	2.17			

Table 12. Gray matrix summary for aquifer of the coastal region of the Tangshan study unit, People's Republic of China, May 1996 data

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (9 total)	0	2	7	0
Median classification	3.4			

Table 13. Gray matrix summary for aquifer of the coastal region of the Tangshan study unit, People's Republic of China, September 1996 data

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (9 total)	0	5	4	0
Median classification	2.98			

Table 14. Gray matrix summary for aquifer of the Delmarva Peninsula study unit, United States

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (103 total)	38	29	5	31
Median classification	2.22			

Table 15. Gray matrix summary for upper aquifer of the western region of the San Joaquin Valley study unit, California, United States

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (25 total)	4	3	9	9
Median classification	3.65			

Table 16. Gray matrix summary for lower aquifer of the western region of the San Joaquin Valley study unit, California, United States

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (25 total)	1	8	12	4
Median classification	3.37			

Table 17. Gray matrix summary for upper aquifer of the southern region of the San Joaquin Valley study unit, California, United States

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (43 total)	16	16	6	5
Median classification	2.14			

Table 18. Gray matrix summary for lower aquifer of the southern region of the San Joaquin Valley study unit, California, United States

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (14 total)	8	5	0	1
Median classification	1.875			

Table 19. Gray matrix summary for the unassigned aquifer of the southern region of the San Joaquin Valley study unit, California, United States

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (8 total)	4	2	2	0
Median classification	1.675			

Table 20. Gray matrix summary for the eastern aquifer of the San Joaquin Valley study unit, California, United States

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (63 total)	39	16	8	0
Median classification	1.91			

the higher scores (class 3 or higher) of the 16 wells of the lower aquifer in the western San Joaquin Valley. Water quality of the unassigned aquifer of the southern San Joaquin Valley is similar to that of the lower aquifer of the southern San Joaquin Valley. A total of 8 out of 63 wells of the eastern San Joaquin Valley were in class 3 or higher (table 20). Water-quality constituents contributing to the class 3 scores are varied, but include total dissolved solids, nitrate, chloride, and sulfate. Total dissolved solids of the eastern San Joaquin Valley aquifer are lower than those of the western San Joaquin Valley; therefore, the gray matrix scores are correspondingly lower.

Gray matrix summaries of the Sacramento Valley show a marked difference between the subunit survey and the rice land-use survey (tables 21 and 22). The wells of the southeastern Sacramento Valley generally have good water quality. Only 3 wells out of 31 were in class 3 or higher. In contrast, 13 out of 28 wells of the rice land-use survey were in class 3 or higher. The water-quality constituents that contribute to the higher scores of the wells of the rice land-use survey are total dissolved solids, chloride, sulfate, total hardness, nitrite (in three wells), iron, and manganese. Nitrate is not a problem for the ground water of the rice land-use region.

Table 21. Gray matrix summary for aquifer of the Sacramento subunit area of the Sacramento Valley study unit, California, United States

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (31 total)	21	7	1	2
Median classification	1.72			

Table 22. Gray matrix summary for the aquifer of the rice land-use study area of the Sacramento Valley study unit, California, United States

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0to 4.0	4.0 to 5.0
Number of wells (28 total)	3	12	7	6
Median classification	2.72			

Boxplots showing the results of the gray matrix rankings for all study units are shown in figure 30. The highest median ranking is for the wells of the upper aquifer of the plain region of the Tangshan study unit. The median is slightly less when recalculated without the coliform data. Coliform data were available only for the upper aquifer of the plain region of the Tangshan study unit and were not available for any other subunit, including those of the United States. The gray matrix rankings of the upper aquifer of the Tangshan plain region are similar to those of the western part of the San Joaquin Valley with respect to the median ranking and range of ranking, which suggests some similar or common water-quality problems, such as total dissolved solids and the oxidation potential of the water (elevated concentrations of iron and manganese). The wells of the eastern San Joaquin Valley have a much lower ranking because of the dilute nature of that water. The ground water of the eastern San Joaquin Valley is of better quality with respect to total dissolved solids, but its water quality has been degraded because of pesticides, especially DBCP (Domagalski and Dubrovsky, 1991, 1992).

The wells of the Delmarva Peninsula have the greatest range in gray scores. The median gray ranking is below those of the plain and coastal regions of the Tangshan study unit and also below that of the western San Joaquin Valley. Low total dissolved solids contribute to lower gray rankings for the Delmarva Peninsula whereas nitrate, iron, and manganese contribute to higher gray rankings. The wells of the Sacramento subunit survey provide a good representation of the quality of ground water actually used for consumption in that part of the Sacramento Valley. The gray matrix ranking for the Sacramento subunit indicates a very good water quality, and tests for pesticides and volatile organic chemicals showed that organic chemicals are either absent from the water or present only in extremely low concentrations. In contrast, the wells of the Sacramento rice land-use study rank much higher in the gray ranking because of higher concentrations of total dissolved solids and concentrations of iron and manganese, related to the oxidation–reduction potential of the water. This ranking suggests that the rice land use is affecting the quality of the shallow ground-water resource.

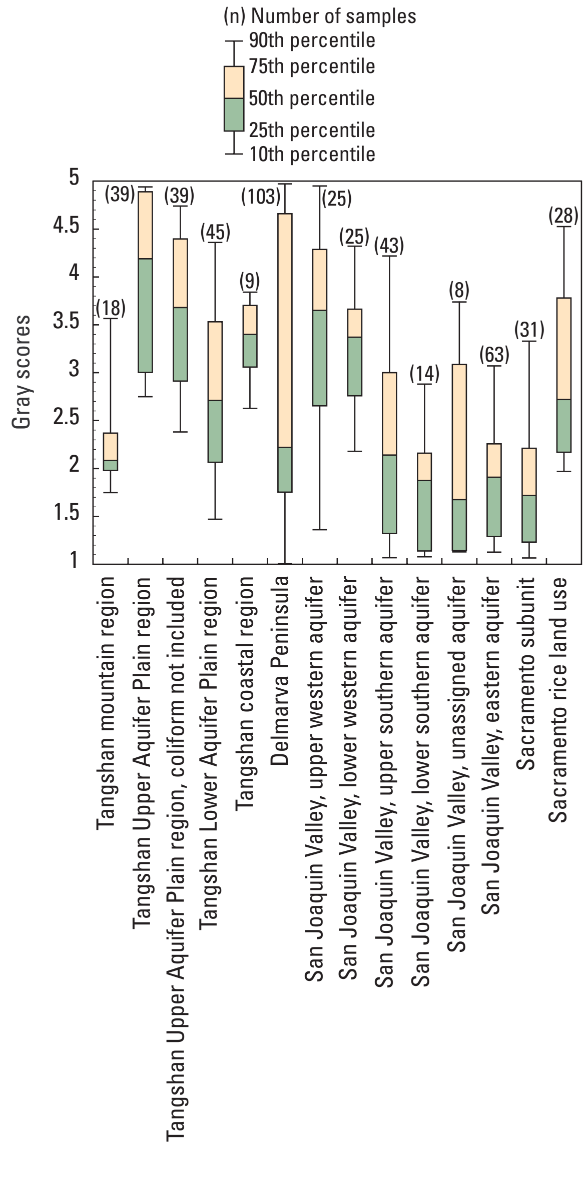

Figure 30. Boxplots of gray scores (gray matrix calculations) for study-unit wells in the People's Republic of China and the United States.

Boxplots of nitrate concentrations for ground water in all study units are shown in figure 31. The boxplot representing the upper aquifer wells in the Tangshan plain region has the greatest range in nitrate concentrations and the highest concentration of all regions of the Tangshan study unit and all study units of the United States, but it does not have the highest median concentration. In fact, the median concentration of the Tangshan upper plain region is less than that of the mountain aquifer and the lower plain zone region. Over 25 percent of the wells sampled in the upper plain zone exceeded the Chinese standard for nitrate. Over 10 percent of the wells of the mountain region (mountain aquifer) and the lower aquifer (lower plain region) exceeded this standard. Only the wells of the coastal zone of the Tangshan study unit (coastal aquifer) have low nitrate concentrations. The wells sampled in the study units of the United States generally have a lower range of nitrate concentrations than wells in the plain region of the People's Republic of China. Ten percent of the wells of the lower aquifer in the southern San Joaquin Valley exceed the Chinese standard.

Figure 31 shows that nearly 25 percent of the wells of the Delmarva Peninsula and nearly 25 percent of the upper aquifer wells in the western San Joaquin Valley are close to or exceed the American standard (U.S. Environmental Protection Agency) for nitrate. Close to 25 percent of the samples collected in the eastern San Joaquin Valley also exceed the American nitrate standard. Relatively few samples of the ground water collected in the United States, from these studies, exceed the Chinese drinking-water standard for nitrate.

As indicated by the gray matrix rankings, total dissolved solids is a problem for ground water in the People's Republic of China and for some parts of the study units in the United States. Boxplots of total dissolved solids data in ground water for all of the study units are shown in figure 32. At least 25 percent of the wells sampled in the Tangshan upper plain region exceed the Chinese standard for total dissolved solids and about 50 percent of these same wells exceed the secondary standard of the EPA. The higher median concentrations of the upper aquifer relative to those of the lower aquifer, mountain aquifer, and coastal aquifer of the Tangshan study unit suggest that agricultural and other land-use activities have contributed to the total dissolved solids content of ground water. Because the aquifer mineralogy is the same for the upper and lower zones, the higher total dissolved solids concentrations cannot be explained on the basis of natural water–rock interactions.

Ground water of the western San Joaquin Valley also has high total dissolved solids. Although some of the high dissolved solids can be attributed to natural processes, such as higher total dissolved solids content of the recharge water, some can also be attributed to agricultural activities, which have greatly affected the total dissolved solids content of the ground water in the western San Joaquin Valley. The western San Joaquin Valley has a long history of irrigation. Irrigation is required for successful agriculture in the San Joaquin Valley because little or no rain falls during the growing season. The soils of the western San Joaquin Valley tend to be poorly drained. Irrigation of crops and poor drainage in a semiarid environment lead to a high rate of evaporation of the irrigation water. Subsequent recharge can increase the salt loading to the aquifer and thereby increase the degradation of water quality with respect to total dissolved solids. In contrast, irrigation is not used as much in the Delmarva Peninsula, and rain or infiltration of stream water provides more recharge to the aquifers. As mentioned previously, the median concentration of total dissolved solids in the water samples of the Sacramento rice land-use study exceeds that

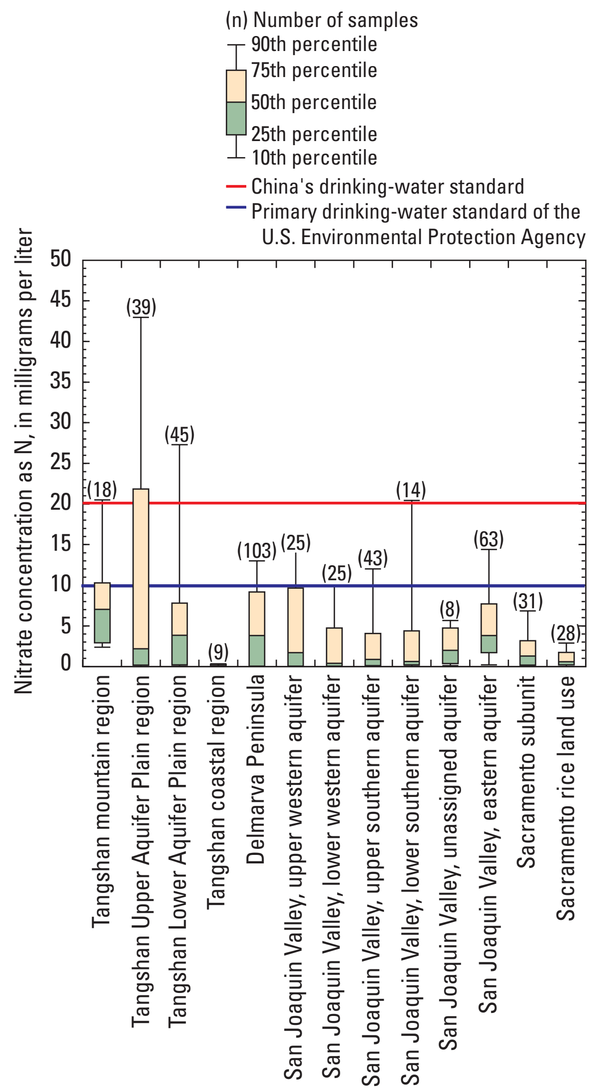

Figure 31. Boxplots of nitrate concentrations in ground water for various zones within study units or for an entire study unit in the People's Republic of China and the United States. N, nitrogen.

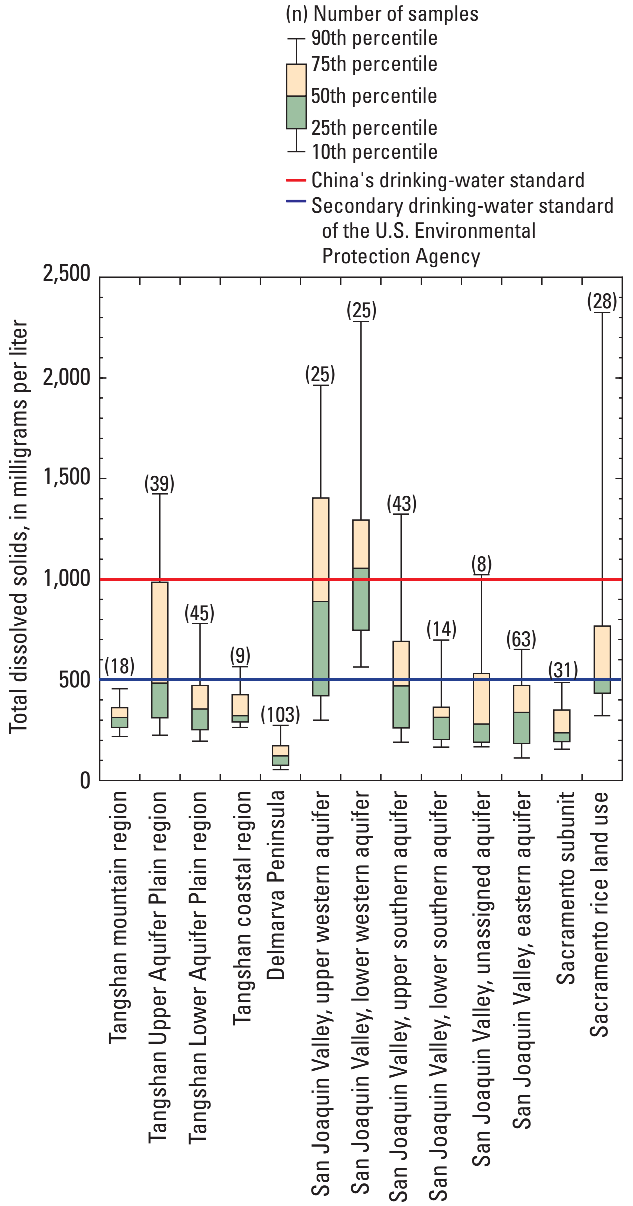

Figure 32. Boxplots of total dissolved solids concentrations in ground water for various zones within study units or for an entire study unit in the People's Republic of China and the United States.

of the total dissolved solids of water samples collected in the Sacramento subunit survey. At least 50 percent of the samples of the rice land-use study exceed the secondary standard for total dissolved solids of the EPA. The high total dissolved solids of the Tangshan aquifer cannot be explained by evaporative concentration of irrigation water because of a different climate. It also cannot be explained on the basis of water–rock interactions because the aquifer mineralogy does not contain salt deposits. The higher total dissolved solids may be attributed to a longer history of agricultural production in the Tangshan region relative to the San Joaquin Valley and other study units of the United States, or to the greater amount of animal and sewage wastes disposed on land within the Tangshan study unit.

Results of the gray matrix rankings indicate that iron concentrations are a water quality problem for some study units. Boxplots of iron concentrations for all study units are shown in figure 25. Iron concentrations that exceed the Chinese standard (0.3 mg/L) are present throughout the Tangshan study unit. The mountain region has the lowest relative iron concentration. Apparently, iron dissolves throughout the upper and lower parts of the plain and coastal aquifers in response to decreasing concentrations of dissolved oxygen. The only study unit in the United States with comparable iron concentrations is the Delmarva Peninsula.

Chemical Signatures of Ground Water Affected by Agriculture

The water quality of the aquifers in the Tangshan study unit has been affected by agricultural activities, which have resulted in a redistribution of major ions, in addition to elevated nitrate concentrations, for the agriculturally affected waters relative to natural ground water (fig. 13). The trilinear graph shows that the water becomes more enriched in calcium and sulfate as nitrate concentrations increase. This enrichment can probably be attributed to the application of other chemicals in the applied fertilizers. Agricultural chemicals (fig. 15) also affected the natural ion chemistry of the Delmarva Peninsula as indicated by association with higher nitrate concentrations. Hamilton showed that the ground water that is affected by agricultural activities in the Delmarva Peninsula has significantly higher levels of calcium, magnesium, potassium, and chloride, in addition to nitrate (Hamilton and others, 1993). Because of the evaporative concentration of irrigation water prior to recharge, agriculture signatures of the western and southern San Joaquin Valley ground water, when arranged according to ranges in nitrate concentration, are not as evident as the signatures of Tangshan and the Delmarva Peninsula. There is no clear distinction of signatures for anions, but there appear to be slightly greater proportions of calcium and magnesium in agriculturally affected ground water (figs. 16 and 17). The agricultural signature of ground water of the eastern San Joaquin Valley is represented by slightly elevated chloride and sulfate (fig. 18). As mentioned previously, one signature of agriculturally affected ground water in the Sacramento Valley is elevated total dissolved solids. The increase in total dissolved solids is caused mainly by evaporative concentration, especially during the rice-growing season, as evidenced in the trilinear plot for the wells of the Sacramento rice land-use study (fig. 20). The cation chemistry tends to shift from a calcium–magnesium water to a water with sodium as the most abundant cation. The shift probably results from precipitation of carbonate minerals such as calcite or aragonite.

The effects of agricultural land-use on major element chemistry can be further assessed by comparing the range in concentrations of individual water-quality constituents in ground water that have low nitrate concentrations with those that have high nitrate concentrations. Boxplots of calcium and sulfate concentrations in Tangshan study unit ground water with low nitrate (less than 0.5 mg/L as N) and high nitrate in ground water are shown in figures 33 and 34. The median calcium and sulfate concentrations in low nitrate wells are lower than those in high nitrate wells. The difference in medians for calcium was statistically significant at $p = 0.0032$ whereas the difference for sulfate was significant at $p = 0.0013$ using the nonparametric Mann–Whitney test. Evidence of geochemical processes that affect nitrate concentration can be seen by comparing the pH of ground water in samples from low and high nitrate wells (fig. 35). The difference in medians is statistically significant ($p = 0.0004$) by the Mann–Whitney test. It would be expected that iron concentrations might be higher in wells with low nitrate because of the oxidation state of the water. That is the case for the wells of the Tangshan study unit (fig. 36). The difference in medians is significant ($p = 0.003$) by

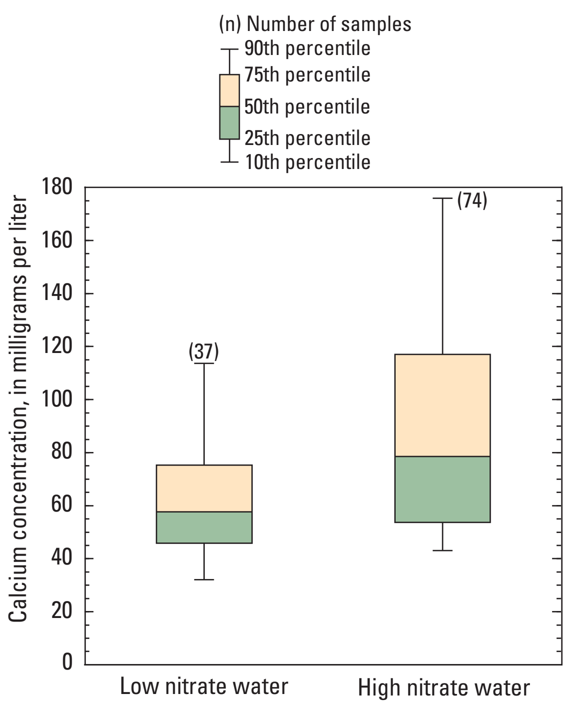

Figure 33. Boxplots of calcium concentrations in wells with low and high nitrate in the Tangshan study unit, People's Republic of China.

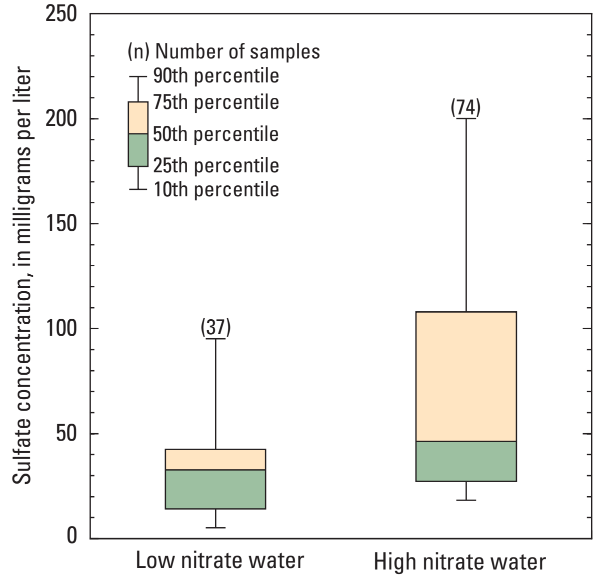

Figure 34. Boxplots of sulfate concentrations in wells with low and high nitrate in the Tangshan study unit, People's Republic of China.

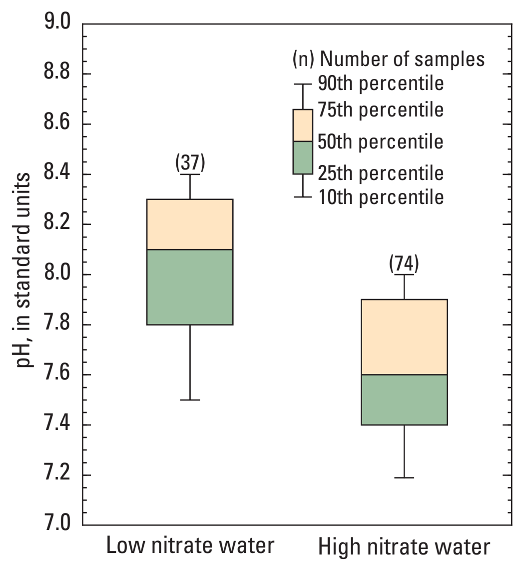

Figure 35. Boxplots of pH in wells with low and high nitrate in the Tangshan study unit, People's Republic of China.

the Mann–Whitney test (fig. 36). It is possible that iron dissolution and nitrate reduction may be partially linked by geochemical processes in the Tangshan aquifer. No other water-quality constituents, such as chloride, sodium, potassium, and magnesium, had statistically different concentrations in ground water of high or low nitrate in the Tangshan study unit.

Agriculture is most likely to affect the major element chemistry of ground water when concentrations of the major elements in natural ground water are very low, as in the case of the Delmarva Peninsula. Hamilton

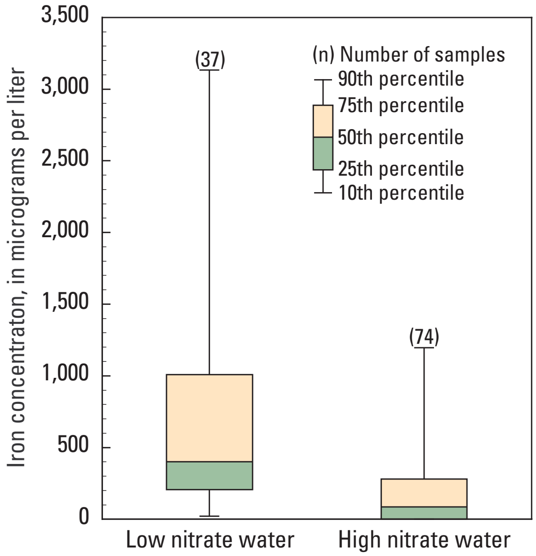

Figure 36. Boxplots of iron concentrations in wells with low and high nitrate in the Tangshan study unit, People's Republic of China.

and others (1993) found that the concentrations of calcium, magnesium, potassium, and chloride were higher in waters affected by nitrate contamination relative to natural ground water. Those authors attributed the changes to the application of various fertilizers. Evaporative processes that occur after irrigation and prior to recharge affect the ground water of the Central Valley of California. Furthermore, it is more difficult to see changes in the major element chemistry of ground water in that region that can be attributed to fertilizer application.

Principal Component Analysis

Principal component analysis is a statistical technique that can help explain variation in large data sets of multiple components, such as the water chemistry of the study units. Principal component analysis will allow for the grouping of variables that may help to explain a process that is controlling the particular grouping observed. The following constituents were selected to represent the variables for principal component analysis for this study: total dissolved solids, sodium, potassium, calcium, magnesium, chloride, sulfate, fluoride, bicarbonate, nitrate, and iron. These constituents were measured in the ground water of all study units. Principal component analysis may provide reasons for the variation observed for these constituents. Principal component analysis requires a normally distributed data set. The water chemistry data from these study units are generally not normally distributed. Therefore, a log transform was applied to all data to approximate normality. Results of principal component analysis for the various study units are shown in tables 23 through 28. The first two principal components are shown for each study unit because subsequent ones could not be attributed to any geochemical or anthropogenic process. The first two principal components explain between just under 60 percent to close to 70 percent of the variation with this set of water-quality data.

The first principal component is probably a general indication of the water chemistry that is attributed to recharge processes. The sign of the loadings is the same (tables 23 to 28) and of generally similar magnitude for major constituents of the ground water, such as total dissolved solids, magnesium, calcium, potassium, chloride, and sulfate. Two important points in interpreting the results of principal component analysis are the absolute values of the loadings and the positive or negative value of the results relative to one another. For example, all of the results for principal component 1 of the Tangshan study unit have the same sign, indicating that those water-quality constituents are affected by a similar process such as dissolution of minerals, which provides magnesium, calcium, sodium, chloride, and sulfate to the ground water. The second principal component shows that nitrate and iron concentrations are related but in opposite ways because of the change in sign, which is an indication of redox processes. As nitrate concentrations increase, iron concentrations tend to decrease, and as iron concentrations tend to increase, nitrate concentrations decrease.

Principal component analysis can be obtained for each well under investigation. The individual variable range for the principal component 2 of the Tangshan study unit is shown on the geomorphology map in figure 37. The figure shows where the state of ground water is mainly under reducing or oxidizing conditions. The range of principal component 2 values is also shown for the Delmarva Peninsula in figure 38. Like the map of the Tangshan study unit, this map shows the locations where the state of ground water is under reducing conditions and where nitrate reduction may be removing some of the nitrate from the ground water.

The eastern San Joaquin Valley was the only location for this study that does not show an indication of iron dissolution or nitrate reduction. The lack of these two types of redox processes indicates that the ground water in this region is oxidizing, the iron concentrations are low, and the nitrate reduction is not an important process because nitrate reduction to nitrogen gas does not occur to a large extent. In the eastern San Joaquin Valley, the oxidizing condition is consistent with the sandy or coarse-grained texture of the aquifer materials, which allows for greater diffusion of oxygen to the ground water.

Table 23. Results of principal component analyses of chemical data from the Tangshan study unit, People's Republic of China

[N, nitrogen; —, loadings have absolute values of less than 0.30]

Water quality constituent	Principal component 1	Principal component 2
Total dissolved solids	–0.424	—
Magnesium	–0.368	—
Calcium	–0.361	—
Sodium	–0.325	—
Potassium	—	—
Chloride	–0.36	—
Sulfate	–0.351	—
Fluoride	—	–0.494
Nitrate as N	—	0.581
Bicarbonate	—	–0.305
Iron	—	–0.36
Percent variation explained	47.5	20.4
Cumulative percent variation explained	47.5	67.9

Table 24. Results of principal component analyses of chemical data from the Delmarva Peninsula study unit, United States

[N, nitrogen; —, loadings have absolute values of less than 0.30]

Water quality constituent	Principal component 1	Principal component 2
Total dissolved solids	0.421	—
Magnesium	0.387	—
Calcium	0.382	—
Sodium	—	–0.341
Potassium	0.365	—
Chloride	0.405	—
Sulfate	0.303	—
Fluoride	—	—
Nitrate as N	—	0.488
Bicarbonate	—	–0.401
Iron	—	–0.516
Percent variation explained	39.9	23.7
Cumulative percent variation explained	39.9	63.6

Table 25. Results of principal component analyses of chemical data from the western region of the San Joaquin Valley study unit, California, United States

[N, nitrogen; —, loadings have absolute values of less than 0.30]

Water quality constituent	Principal component 1	Principal component 2
Total dissolved solids	–0.429	—
Magnesium	–0.4	—
Calcium	–0.425	—
Sodium	–0.334	–0.456
Potassium	—	—
Chloride	–0.383	—
Sulfate	—	—
Fluoride	—	—
Nitrate as N	—	0.424
Bicarbonate	—	—
Iron	—	–0.528
Percent variation explained	42.0	15.8
Cumulative percent variation explained	42.0	57.8

Table 26. Results of principal component analyses of chemical data from the southern region of the San Joaquin Valley study unit, California, United States

[N, nitrogen; —, loadings have absolute values of less than 0.30]

Water quality constituent	Principal component 1	Principal component 2
Total dissolved solids	0.42	—
Magnesium	0.356	—
Calcium	0.383	—
Sodium	0.302	0.456
Potassium	0.348	—
Chloride	0.325	—
Sulfate	0.375	—
Fluoride	—	0.359
Nitrate as N	—	–0.353
Bicarbonate	—	—
Iron	—	0.42
Percent variation explained	42.5	21.5
Cumulative percent variation explained	42.5	64.0

Table 27. Results of principal component analyses of chemical data from the eastern region of the San Joaquin Valley study unit, California, United States

[N, nitrogen; —, loadings have absolute values of less than 0.30]

Water quality constituent	Principal component 1	Principal component 2
Total dissolved solids	–0.431	—
Magnesium	–0.308	–0.417
Calcium	–0.397	—
Sodium	–0.324	0.399
Potassium	—	–0.343
Chloride	–0.342	—
Sulfate	–0.371	—
Fluoride	—	0.584
Nitrate as N	—	—
Bicarbonate	–0.352	—
Iron	—	—
Percent variation explained	44.5	17.3
Cumulative percent variation explained	44.5	61.8

Table 28. Results of principal component analyses of chemical data from the Sacramento Valley study unit, California, United States

[N, nitrogen; —, loadings have absolute values of less than 0.30]

Water quality constituent	Principal component 1	Principal component 2
Total dissolved solids	0.427	—
Magnesium	0.376	—
Calcium	0.36	—
Sodium	0.368	—
Potassium	—	—
Chloride	0.264	—
Sulfate	0.402	—
Fluoride	0.154	—
Nitrate as N	—	–0.682
Bicarbonate	0.359	—
Iron	—	0.566
Percent variation explained	48.2	14.1
Cumulative percent variation explained	48.2	62.3

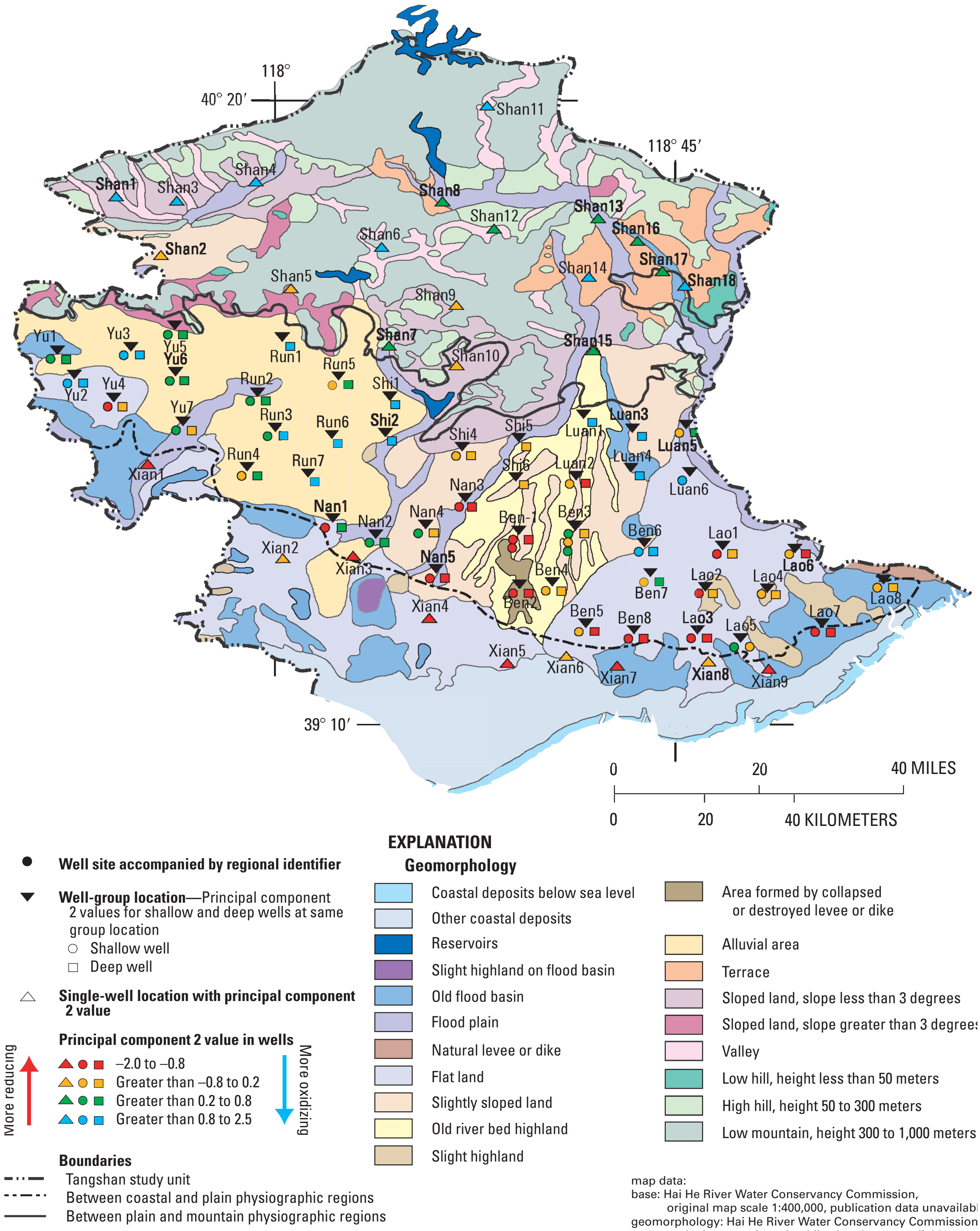

Figure 37. Geomorphology and range of principal component 2 values for wells of the Tangshan study unit, People's Republic of China.

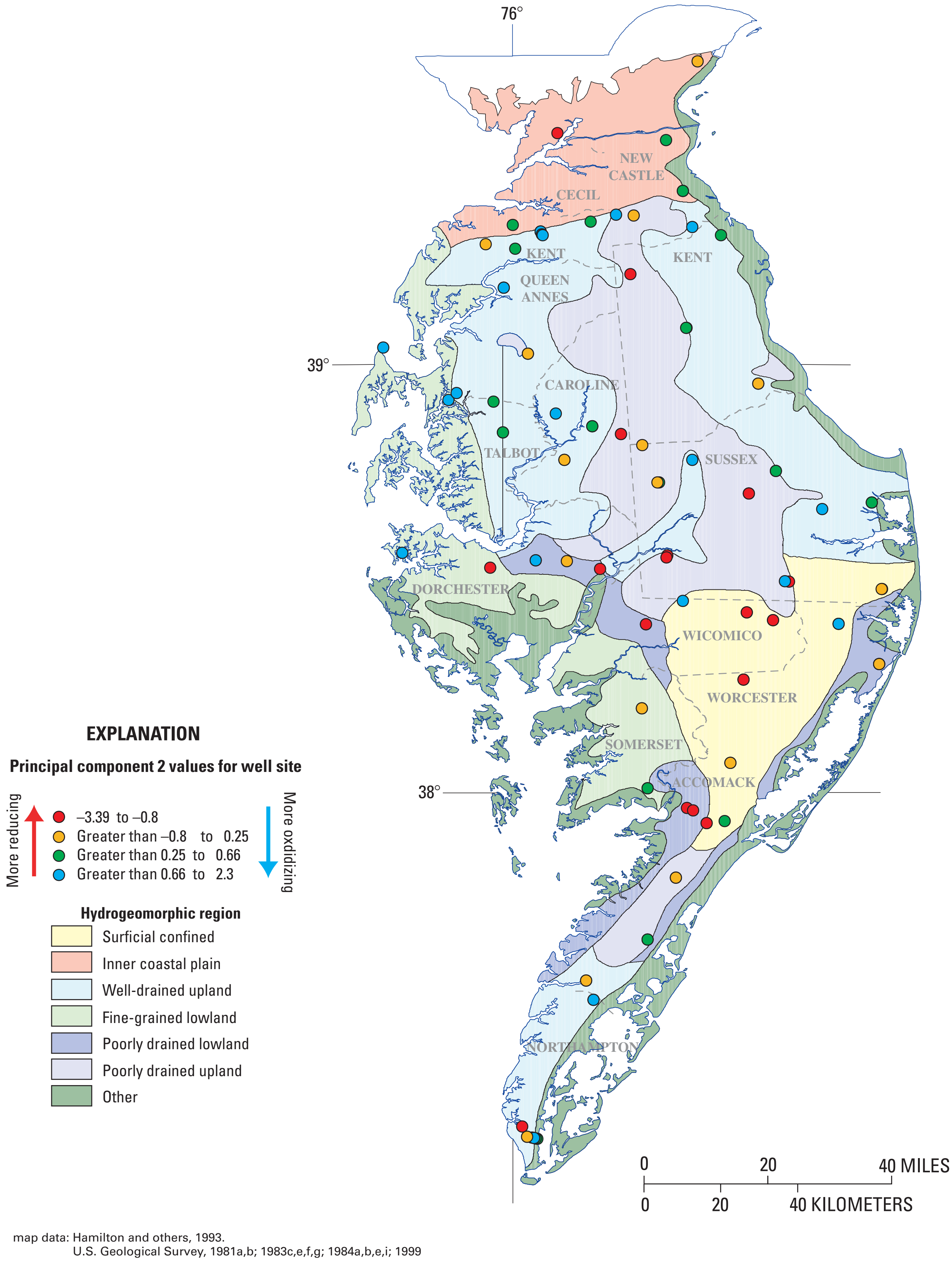

Figure 38. Range of principal component 2 values for wells of the Delmarva Peninsula study unit, United States.

NITRATE AND DETECTION FREQUENCY OF PESTICIDES IN GROUND WATER

Comparison of Nitrate Use in Study Units

Nitrogen use data for each county in the study units were available for comparison of application amounts per given area. In each case, the most recent year of available nitrogen use data was used where a complete set of data was available.

A comparison of nitrate usage for counties within the four study units is shown in table 29. Data for study units of the United States were obtained from Battaglin and Goolsby (1995). Their data are based on documented sales, in each county, of fertilizers that are used primarily for agriculture. Therefore, the authors of this report assumed that all of the fertilizer that was purchased was used. The Hai He River Water Conservancy Commission obtained data for the Tangshan study unit through a similar process. On table 29, we see that nitrogen applications for some counties of the Central Valley of California are higher than those for the Delmarva Peninsula, but overall, the use is similar per unit area for the study units of the United States. The nitrogen usage in the counties of the Tangshan study unit is considerably higher than that of the study units of the United States by as much as a factor of 10, in some cases. Therefore, higher use of nitrogen fertilizer in this agricultural region of the People's Republic of China is one possible explanation for the higher nitrate concentrations and for other agricultural contaminants found in the ground water of the Tangshan study unit.

In contrast to nitrogen fertilizer, counties in the United States have a higher use or generation of manure than counties in the People's Republic of China. The usage or generation of manure within the study units is shown in table 30. Data for the study units of the United States were obtained from Puckett and others (1998). Puckett and others (1998) based their estimates on the animal census of each county. Through a similar process, the Hai He River Basin's Water Conservancy Commission obtained data for the counties of the Tangshan study unit. This generation of manure can be attributed to larger animal production facilities in the United States, especially cattle production. Manure is not necessarily used as an agricultural additive in the United States, but the generation of manure at animal operation centers represents a potential point source of nitrogen and other contaminants to ground water.

The amount of nitrogen in manure varies depending on the animal source. The nitrogen contents assumed for calculating possible nitrate effects from various animals are shown in table 31. The principal elements in manure are carbon, oxygen, and hydrogen. In all cases, nitrogen is a minor component of manure. The highest N content, 0.11 percent, is for broiler or other meat-type chickens, and the lowest, 0.028 percent, is for hogs, pigs, horses, and ponies. Although the N content in manure is relatively low, nitrate formed from the oxidation of manure can migrate to ground water. Six wells in the People's Republic of China were sampled for nitrogen isotopes and oxygen isotopes in nitrate. Two of the wells (Shan15 and BenS3) had a clear signature of nitrogen from fertilizer because the values for $\delta^{15}N$ were close to 5 per mill (fig. 39). Two wells showed a mixed source of the nitrate because the

Table 29. Comparison of nitrate use in counties within study units in the People's Republic of China and the United States

[km^2, square kilometer; Mg, megagram]

Tangshan study-unit counties	Nitrogen use, 1996 (Mg/km^2)	Delmarva study-unit counties	Nitrogen use, 1991 (Mg/km^2)	Sacramento Valley study-unit counties	Nitrogen use, 1987 (Mg/km^2)	San Joaquin Valley study-unit counties	Nitrogen use, 1987 (Mg/km^2)
Laoting	59.1	Kent	5.3	Butte	2.4	Fresno	4.0
Zunhua	48.4	New Castle	3.0	Colusa	4.1	Kern	2.3
Fengnan	50.4	Sussex	3.1	Glenn	3.1	Kings	6.3
Fengrun	44.1	Caroline	4.9	Placer	0.2	Madera	2.4
TangHai	56.5	Cecil	2.7	Sacramento	2.5	Merced	4.8
Luannan	49.3	Dorchester	2.4	Solano	2.6	San Joaquin	7.4
Yutian	33.1	Kent	5.8	Sutter	7.9	Stanislaus	4.6
Qianxi	40.5	Queen Annes	5.2	Tehama	0.4	Tulare	2.9
Tangshan	36.0	Somerset	2.0	Yolo	4.8		
Luan Xian	28.5	Talbot	4.9	Yuba	2.2		
Qian'an	23.7	Wicomico	2.2				
		Worcester	2.0				
		Accomack	1.7				
		Northampton	2.9				

Table 30. Usage or generation of manure in counties within study units in the People's Republic of China and the United States

[km^2, square kilometer; Mg, megagram]

Tangshan study-unit counties	Total manure, 1996 (Mg/km^2)	Delmarva study-unit counties	Total manure, 1992 (Mg/km^2)	Sacramento Valley study-unit counties	Total manure, 1992 (Mg/km^2)	San Joaquin Valley study-unit counties	Total manure, 1992 (Mg/km^2)
Laoting	1,225.8	Kent	1,604.1	Butte	801.6	Fresno	3,575.8
Zunhua	1,831.1	New Castle	540.6	Colusa	495.2	Kern	1,266.7
Fengnan	1,623.7	Sussex	8,973.5	Glenn	2,905.6	Kings	7,990.9
Fengrun	3,133.5	Caroline	5,052.0	Placer	626.3	Madera	2,837.5
TangHai	158.5	Cecil	2,141.1	Sacramento	5,399.1	Merced	10,601.4
Luannan	1,753.0	Dorchester	2,023.7	Solano	2,498.6	San Joaquin	8,727.9
Yutian	1,165.1	Kent	2,873.8	Shasta	596.5	Stanislaus	13,824.5
Qianxi	1,806.1	Queen Annes	2,123.9	Sutter	992.4	Tulare	7,434.1
Tangshan	4,461.0	Somerset	6,212.5	Tehama	1,430.9		
Luan Xian	4,240.2	Talbot	1,741.1	Yolo	1,163.6		
Qian'an	3,066.1	Wicomico	8,042.8	Yuba	3,375.4		
		Worchester	5,922.9				
		Accomack	1,437.8				
		Northampton	18.5				

Table 31. Nitrogen content of manure from various animals (Puckett and others, 1998)

[kg, kilogram; N, nitrogen; Mg, megagram]

Animal	(N content of manure in kg of N)/(Mg of manure)
Beef cows	0.315
Milk cows	0.4
Heifers and calves	0.31
Steers	0.315
Hogs and pigs	0.28
Sheep and lambs	0.45
Horses and ponies	0.28
Chickens (more than 3 months old)	0.83
Chickens (less than 3 months old)	0.62
Broilers and other meat-type chickens	1.1
Turkeys	0.74

$\delta^{15}N$ values were close to 10. Finally, two wells had relatively high enrichment in $\delta^{15}N$, which is assumed to be from manure or sewage. Although an isotropic signature from two of the sampled wells indicated a source of nitrate from animal waste, this signature could also have come from sources of nitrate from human wastes or sewage. In the People's Republic of China, sewage inputs to ground water are a possibility because not all rural areas have adequate wastewater treatment.

Physical and Chemical Factors Related to the Detection Frequency of Nitrate

Nitrate concentrations versus well depths for the Tangshan study unit are shown in figure 40. These results are consistent with the isotope dating results; nitrate concentrations also are above those expected for natural ground water are present to a depth of 130 to 140 m. Below that depth, nitrate concentrations tend to be below detection limits. Nitrate concentrations in older water, therefore, range from low to undetectable, and the higher concentrations are a result of a

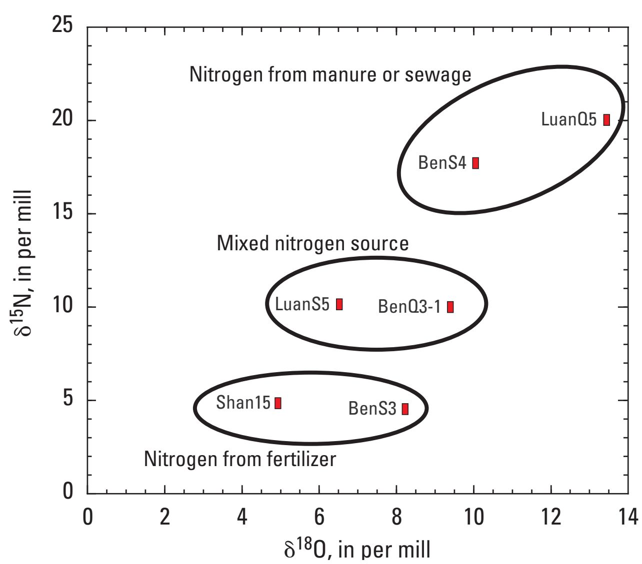

Figure 39. $\delta^{15}N$ and $\delta^{18}O$ in nitrate for select wells of the Tangshan study unit, People's Republic of China. N, nitrogen; O, oxygen; δ, delta.

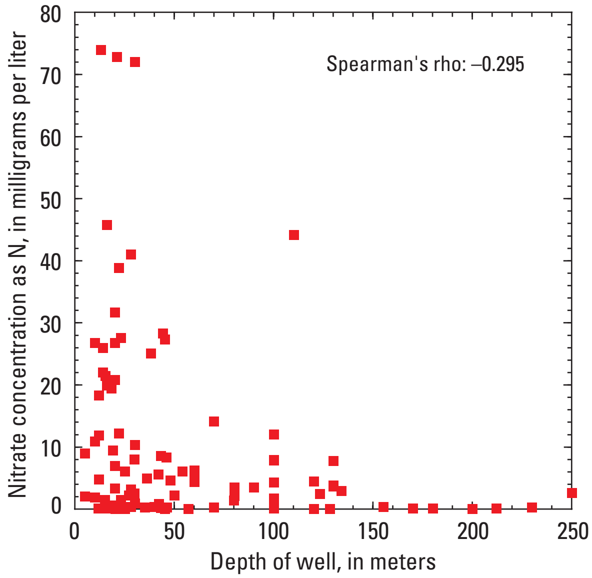

Figure 40. Nitrate concentration versus well depth for wells of the Tangshan study unit, People's Republic of China. N, nitrogen.

combination of land use practices, hydrology, and geochemical processes. No linear relation of nitrate and well depth is apparent (fig. 40). The Spearman's rho (ρ) or Spearman's rank correlation, a nonparametric test, was used to determine whether a consistently decreasing trend of nitrate concentration correlated with well depth. A nonparametric test was required because the data were not normally distributed. Spearman's rho is a test of the correlation between ranks of two variables, in this case nitrate concentrations and well depths. Values of ρ will be between –1 and 1. A negative value implies an inverse relation whereas a positive value indicates a positive relation. A value near zero indicates no correlation between the two variables. An absolute value of 1 implies a strong monotonic relation for the two variables. The value of ρ for the two variables (well depth and nitrate concentration) was –0.295, indicating a weak relation between well depth and nitrate concentration. Nitrate concentrations versus depth to water are shown in figure 41. The value of ρ for this pair of variables is 0.05, which indicates no relation between depth to water and nitrate concentration. It was not possible to plot nitrate concentration against the depth to the top of the screened intervals of individual wells because location of well screens is not known for the wells of the Tangshan study unit. The absence of a strong relation between nitrate concentrations and well depth is not unusual. The value of ρ for nitrate and well depth of the Delmarva Peninsula is –0.152, and the value for the wells of the San Joaquin Valley is –0.302. Similar results were obtained in an analysis of the eastern San Joaquin Valley by Burow and others (1998). Burow's team suggested that factors other than well depth, such as soil and sediment texture, may be more important in the distribution of nitrate in ground water of the eastern San Joaquin Valley.

Nitrate concentrations versus iron concentrations for the wells of the Tangshan study unit are shown in figure 42. As expected, most of the wells with higher nitrate concentrations also have low iron concentrations, but some have relatively high iron concentrations. In those wells, nitrate reduction is apparently not sufficient to reduce nitrate to relatively low levels. Those wells may be affected by a combination of nitrogen from fertilizer and sewage or manure. The value of ρ for the combination of nitrate and iron concentrations in the Tangshan study unit is –0.382, which suggests a weak monotonic relation between the two variables.

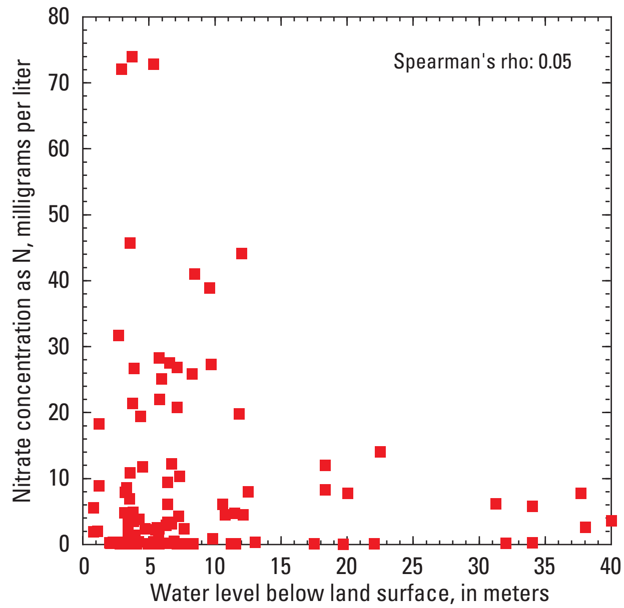

Figure 41. Nitrate concentration versus water level below land surface for wells of the Tangshan study unit, People's Republic of China. N, nitrogen.

Nitrate concentrations versus total dissolved solids are plotted in figure 43. The calculation of ρ for this set of two variables is 0.317, which suggests a weak positive monotonic relation between the ranks of the two variables. Although nitrate seems to be weakly related to total dissolved solids, the relation is not statistically significant when compared with other tests. The median of total dissolved solids was tested in wells of low nitrate (less than 0.5 mg/L as N) and in wells of higher nitrate (greater than 0.5 mg/L as N) concentrations. The medians were assessed to be statistically similar ($p = 0.27$) when tested with the nonparametric Mann–Whitney test of medians. The p value associated

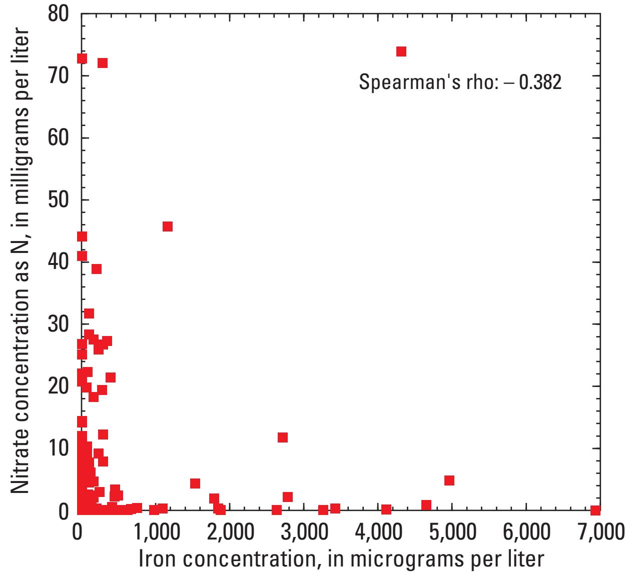

Figure 42. Nitrate concentration versus iron concentration for wells of the Tangshan study unit, People's Republic of China. N, nitrogen.

with an observed value of a test statistic is the smallest level of significance that would have allowed the null hypothesis to be rejected. A value of *p* less than 0.05 suggests that medians are different. Therefore, the relatively high *p* value of 0.27 suggests that the medians are statistically the same. Although nitrate and total dissolved solids are not strongly correlated, the total dissolved solids of the ground water in the plain region of the Tangshan study unit seem to have been affected by agricultural or other land-use practices. As mentioned previously, total dissolved solids (fig. 32) of the upper aquifer of the plain region are higher relative to other

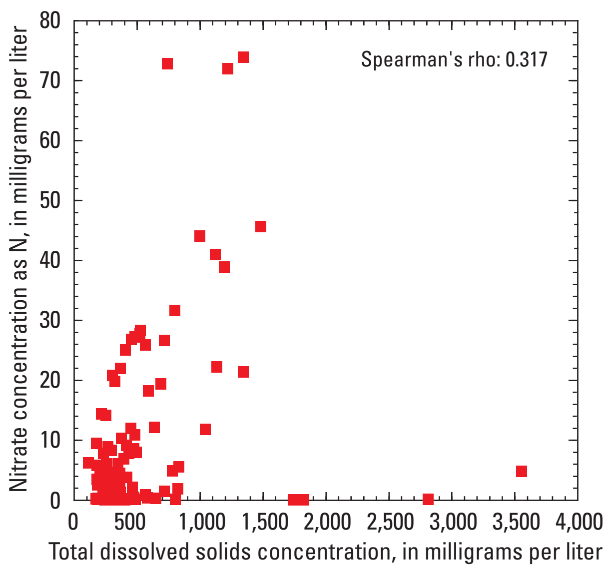

Figure 43. Nitrate concentration versus total dissolved solids concentration for wells of the Tangshan study unit, People's Republic of China. N, nitrogen.

locations of the Tangshan study unit. This difference cannot be explained by water–rock interactions because of similar mineralogy; also, the deeper ground water would be expected to have a higher total dissolved solids content because of the longer time for mineral dissolution and equilibrium to occur.

As part of this project, a collaborative laboratory and field study of ammonia and nitrate transport has been completed by the Hai He River Water Conservancy Commission and Tsinghua University (Xianbi Lue, written commun., 1998). Soil samples from Luannan County were collected for a laboratory scale simulation and a field experiment. The soil type in that part of Luannan County is fine sand with less than 0.02 percent clay content. The results of those studies indicated that, while ammonia nitrogen is strongly adsorbed to soil particles, it is also rapidly oxidized to nitrate and then easily transported to deeper soil horizons. The collaborative team also showed that the use of nitrogen from manure results in a lower amount of nitrate transport. The experimental design also compared different water management scenarios. Nitrate transport was greatest during the rainy or monsoon season, and irrigation during the monsoon season resulted in the highest transport of nitrogen to deeper subsurface horizons.

The locations of wells with corresponding levels of nitrate concentrations for the Tangshan study unit are shown in figure 44. Boxplots of nitrate concentrations of well by name designation in the Tangshan study unit are shown in figure 45. The wells of the Tangshan study unit have a name designation, which indicates a regional location, such as the Shan (mountain), or Xian (coastal) wells, or named as part of governmental entity, such as the Ben, Lao, Luan, Nan, Run, Shi, or Yu designations. The location that tends to have the most dense distribution of wells with high nitrate is in the western part of the study unit, where wells are labeled "Yu," with decreasing concentrations of nitrate extending eastward to the locations where wells are labeled "Run." A few locations in the mountain (Shan) region had samples that exceeded 10 mg/L of nitrate as N and, in some instances, even 20 mg/L. In contrast, wells of the Xian designation always tend to have low nitrate. Another cluster of wells with higher relative nitrate concentrations is the location where wells are labeled as "Luan" or "Ben." The location of the Ben wells is where the variation in concentration is greatest. The median concentration of the Ben wells is relatively low, compared with the Yu wells. This great variation in the nitrate concentrations of the Ben wells, along with the relatively low median concentration in that area, suggests that land-use practices around individual wells may be most responsible for the outlying concentrations. The higher median concentrations of the Yu wells suggest that a combination of land use and hydrologic

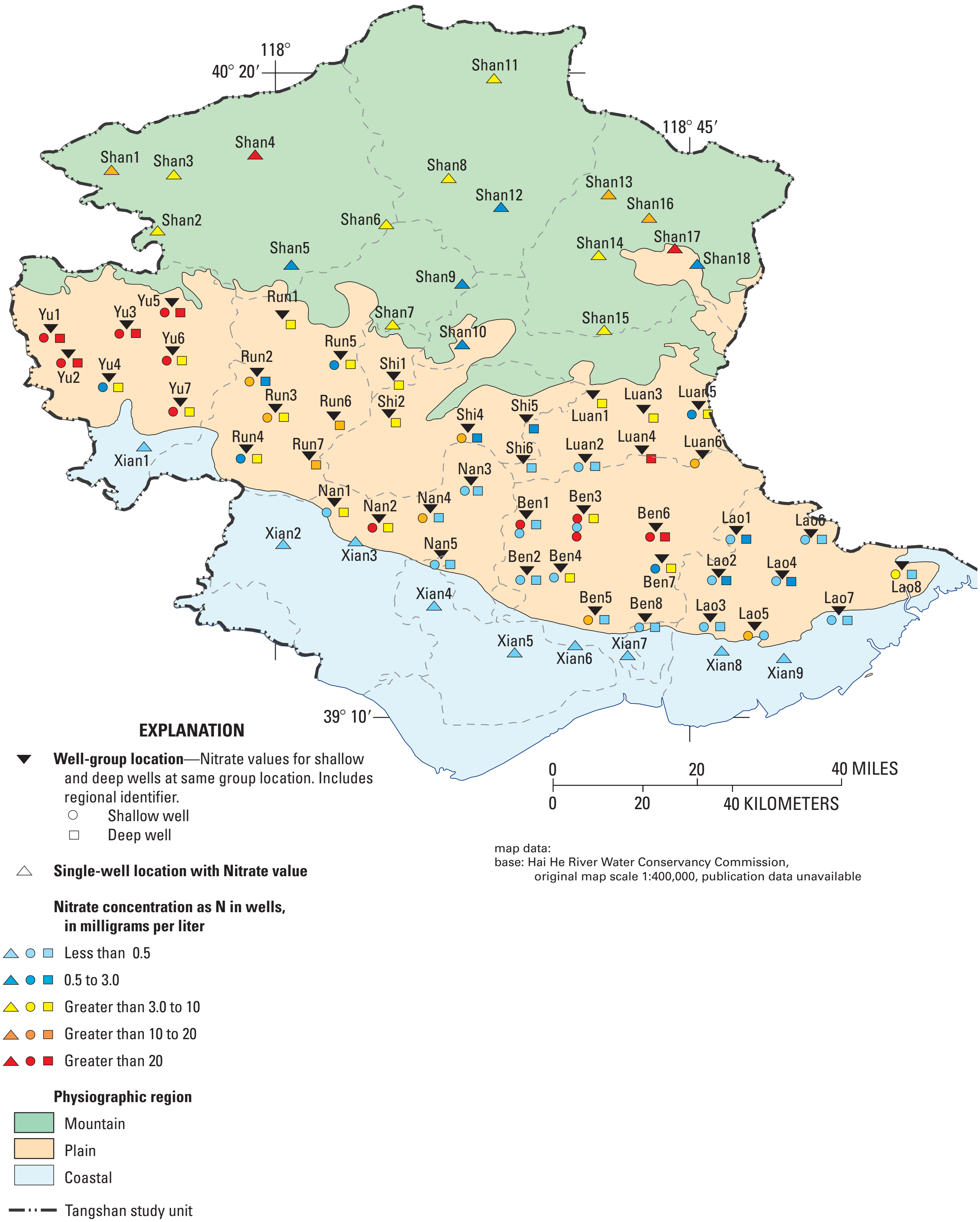

Figure 44. Locations of wells and corresponding levels of nitrate concentrations for the Tangshan study unit, People's Republic of China. Well location Ben3 has three shallow wells (Q1, Q2, and Q3); Ben1 has two shallow wells (Q1 and Q2); all others have either one shallow well or no shallow well. N, nitrogen

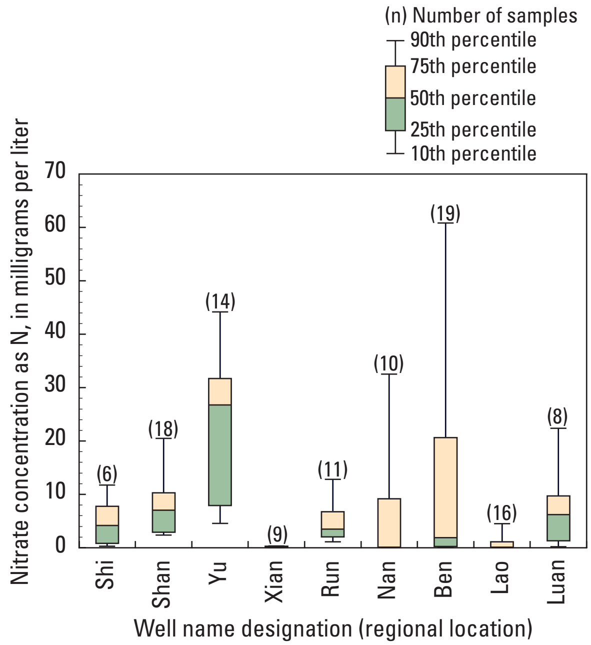

Figure 45. Boxplots of nitrate concentrations by Chinese name designation for wells of the Tangshan study unit, People's Republic of China. N, nitrogen.

factors may be responsible for the high nitrate concentrations of wells in that region. It has already been shown that the ground water in that region has low iron and probably contains dissolved oxygen. Those factors would tend to inhibit the reduction of nitrate.

The distribution of nitrate in ground water may also be due to other important factors, such as well construction techniques, the texture of the unsaturated zone, climate, and ground-water pumpage. Some wells in the Tangshan study unit are perforated from near, or at, ground level, which allows water with high amounts of nitrate that is derived from the soil zone to directly infiltrate the well. Extremely high amounts of ground-water pumpage can result in the drawdown of water levels and the transfer of contaminants to deeper subsurface zones. The ratio of ground-water recharge to ground water use in the People's Republic of China is near 1 or less than 1 depending on the strength of the Asian monsoon. The ratio of the Delmarva Peninsula is not known, but that region does not rely as heavily on irrigation water as do the Tangshan and California study units. In fact, rainfall is normally sufficient in the Delmarva Peninsula to support agriculture. The San Joaquin Valley is highly dependent on irrigation water, and its areas have serious ground-water overdraft problems (Gronberg and others, 1998). Although ground water is used for irrigation in the Sacramento Valley in some areas, irrigation water is normally provided from the Sacramento River. As previously mentioned, some regions of the Tangshan study unit, such as the Yu region, have several ground-water problems, including elevated nitrate, total dissolved solids, and coliform bacteria. These problems indicate either well construction problems or a highly vulnerable aquifer setting, or some combination of factors that is seriously degrading ground-water quality. Because a more detailed description of agricultural land-use management for the Tangshan study unit is beyond the scope of the current study, not all causative factors can be completely addressed here. Dating of the ground water in shallow and deeper zones and more thorough land-use analyses might be addressed in future studies.

Pesticides

Pesticides have been detected in the ground water of all three study units of the United States. Koterba and others (1993) reported on pesticides in the shallow ground water of the Delmarva Peninsula. The most commonly detected pesticides were organonitrogen and other herbicides, which are applied directly to the soil. These herbicides included atrazine, cyanazine, simazine, alachlor, metolachlor, and dicamba. These herbicides were generally present in concentrations below drinking-water standards. The detection frequency of these herbicides was most strongly correlated with corn, soybean, and small grains (winter wheat, barley, hay) grown in well-drained soils. Pesticides in ground water have affected the suitability of the ground water resource in parts of the San Joaquin Valley (Domagalski and Dubrovsky, 1991, 1992; Domagalski, 1997). The types of pesticides that are most frequently detected in the Central Valley of California and the Delmarva Peninsula are herbicides and soil fumigants; insecticides are only rarely detected. Herbicides and soil fumigants have a greater frequency of detection because they are applied directly to the soil and can migrate to ground water after rainfall or irrigation application, unless degradation reactions occur in the soil. Although herbicides or fumigants are frequently detected in ground water, only rarely are their concentrations above drinking-water standards. One exception is for the soil fumigant DBCP. Soil fumigants tend to be used more in the Central Valley of California relative to other agricultural regions of the United States because of the higher amount of fruit production in California. DBCP was used heavily in parts of the eastern San Joaquin Valley where orchards and vineyards are the principal land use (the use of DBCP was stopped in 1977). The EPA drinking-water standard for DBCP is set at 0.2 μg/L.

DBCP was detected in 1,419 of 4,507 wells sampled between 1971 and 1988 with a median concentration near 2.0 μg/L or a factor of 10 greater than the drinking-water standard (Domagalski, 1997). Other factors that contributed to the multiple detections of DBCP were high water solubility, high use in areas with coarse-grained soil texture, and a long environmental half-life.

Few ground-water samples in the Tangshan study unit had been studied previously for the presence of pesticides. As a result, the collaborative team decided to sample wells of transects 1 and 2 (fig. 4) for pesticides. Samples were extracted in the People's Republic of China, and the extracts were returned to the United States for analysis by mass spectrometry. Ground-water extracts were indistinguishable from blank extracts, indicating that pesticides were not present. However, samples were not available for wells of the Yu region, where high nitrate was found. Therefore, although no pesticides have been detected in one part of the study unit, sampling should be completed in other regions. Pesticide applications may not be as high in the People's Republic of China as in the United States. That may be one explanation for the lack of pesticide detections in the ground water of the Tangshan study unit. Another possible explanation is that pesticides are present in the soil horizons, but have not yet been transported to the water table.

SUMMARY AND CONCLUSIONS

A regional assessment of ground-water quality in one region of the People's Republic of China, the Tangshan region, showed that nitrate, total dissolved solids, iron, and other contaminants are affecting the recently recharged ground water. When compared with the ground water in similar agricultural regions of the United States, median nitrate concentrations tended to be similar, but the data from the Tangshan study unit showed a much greater range in concentrations. In the People's Republic of China, the nitrate drinking water standard is set at 20 mg/L as N, whereas in the United States, the nitrate drinking water standard is set at 10 mg/L as N. Many wells in the regions under investigation in the United States exceeded the American (EPA) standard, but only a few wells in the United States exceeded the Chinese standard. The high values of nitrate concentrations in the Tangshan ground water were attributed to larger nitrate applications, to the application of animal wastes and sewage to agricultural land and to land near ground-water wells, to regional hydrology such as soil texture and oxidation–reduction processes, and possibly to well construction techniques. The use of dating techniques, especially the $^3H/^3He$ method, indicated that recently recharged water could be detected to depths as much as 150 m in the Tangshan study unit. The implication for that study unit is that agricultural contaminants could also be detected to those depths and that the drilling of deeper wells may be necessary, in some locations, to provide water of suitable quality. The western part of the San Joaquin Valley was shown to have some similar water quality problems, especially with respect to total dissolved solids. Total dissolved solids of the San Joaquin Valley are elevated mainly because of the evaporation of irrigation water in a semiarid environment. The climate of the Tangshan study unit is less arid than that of the San Joaquin Valley, and so the higher total dissolved solids content may be attributed less to evaporation and more to the longer period that the land has been in agricultural production, and to the greater amounts of land disposal of manure and animal wastes. Pesticides do not seem to be a current problem for this region of the ground-water system in the People's Republic of China, but not all areas were sampled adequately to provide a full assessment.

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