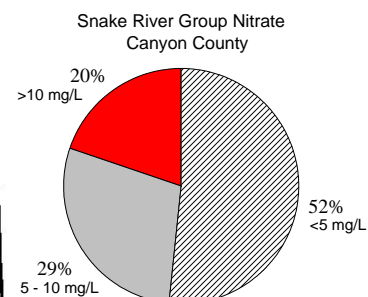
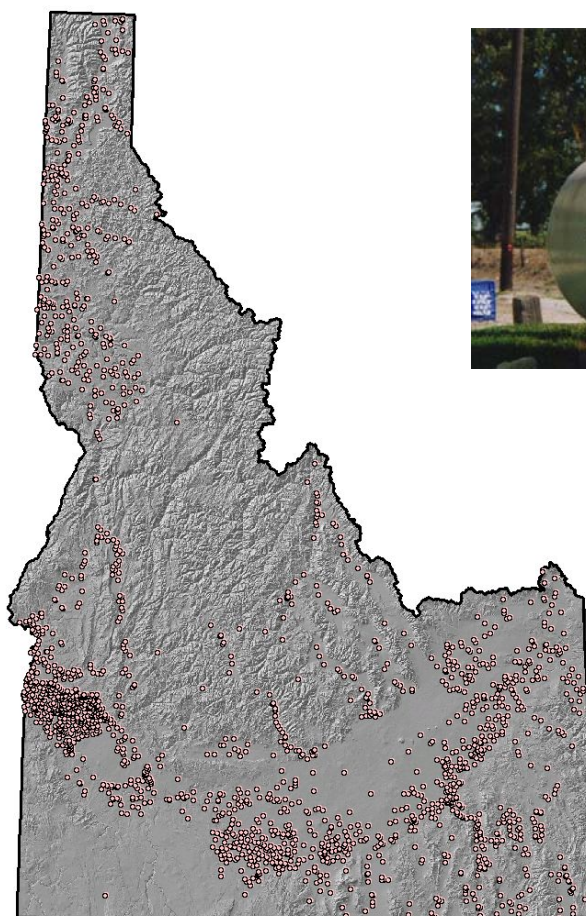
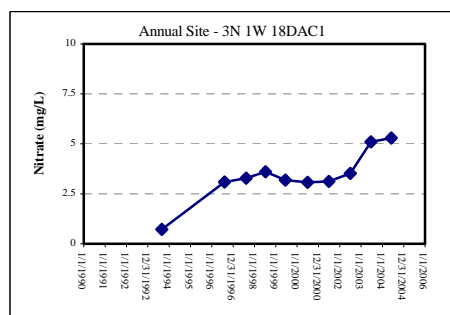


# Nitrate Overview for the Statewide Ambient Ground Water Quality Monitoring Program, 1990 – 2003

Prepared by:

Kenneth W. Neely

Technical Hydrogeologist



Idaho Department of Water Resources  
Ground Water Quality Technical Brief

January 7, 2005

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By

Kenneth W. Neely

Idaho Department of Water Resources

322 East Front Street

P.O. Box 83720

Boise, Idaho 83720-0098

208-287-4852

[ken.neely@idwr.idaho.gov](mailto:ken.neely@idwr.idaho.gov)

[www.idwr.idaho.gov](http://www.idwr.idaho.gov)

January 2005



# Idaho Department of Water Resources

## Ground Water Quality Technical Brief

### *Nitrate Overview for the Statewide Ambient Ground Water Quality Monitoring Program, 1990 - 2003*

December 21, 2004

By Kenneth Neely

#### Introduction

The Idaho Statewide Ambient Ground Water Quality Monitoring Program (Statewide Program) began in 1990 as an effort to study the state's ground water quality and to provide valuable information to Idaho citizens (Figure 1). This Technical Brief summarizes occurrences and trends of nitrate in ground water as observed from more than a decade of collecting data through the Statewide Program. From 1991<sup>1</sup> through 2003, 5,150 nitrate samples from 1,868 Statewide Program wells and springs were analyzed by the U.S. Geological Survey (USGS) Laboratory. Nitrate and other data have been used to characterize the ground water quality in Idaho, to analyze for trends, and to identify the areas where ground water quality problems exist or may be emerging.



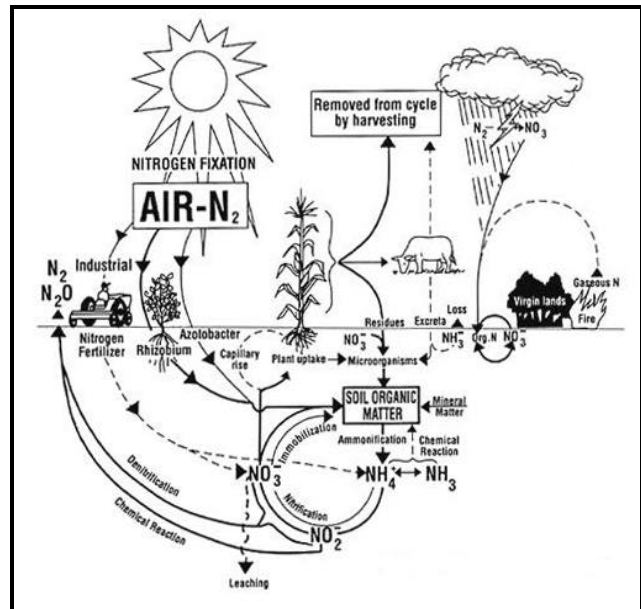
**Figure 1.** Almost everyone appreciates the Idaho Statewide Ambient Ground Water Quality Monitoring Program, which began in 1990.

#### Nitrate Attributes

Nitrate is a negatively charged inorganic ion consisting of one part nitrogen and three parts oxygen ( $\text{NO}_3^-$ ). Nitrate is part of a complex cycle where

<sup>1</sup>1990 is considered a pilot year for the Statewide Program, and the data are not used for analyses in this report unless a site from 1990 was selected for sampling in a later year.

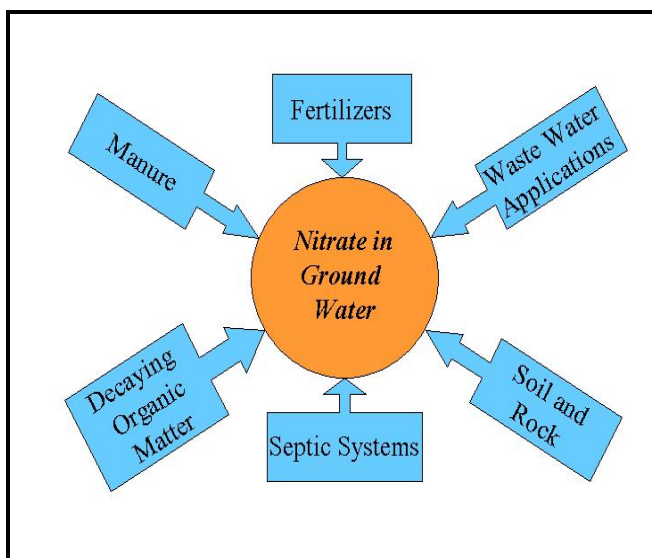
nitrogen ions are released, change ionic forms, travel through air, soil, and water, and are used by plants, animals, and humans (Figure 2). The nitrogen cycle also includes atmospheric nitrogen ( $\text{N}_2$ ), ammonia ( $\text{NH}_3$ ), the ammonium ion ( $\text{NH}_4^+$ ), and nitrite ( $\text{NO}_2^-$ ) (Brown and Johnson, 1991). Nitrate is a conservative (i.e., does not break down rapidly) and mobile constituent in water.



**Figure 2.** The nitrogen cycle (Brown and Johnson, 1991).

Nitrate sources can be natural or anthropogenic (related to human activities), and can have both inorganic and organic origins. Anthropogenic sources include fertilizers, manure, septic systems, decaying organic matter, and waste water (Figure 3). The greatest use of nitrates is for fertilizers (USEPA, 2004a). Since elevated nitrate levels do not often occur naturally in ground water, the concentrations in ground water above background levels are almost always the result of land surface activities. IDWR considers nitrate levels over two milligrams per Liter (mg/L) to be an indication of land surface impacts to the ground water quality.





**Figure 3.** Nitrate sources that may impact ground water quality.

### Nitrate Drinking Water Standard

The nitrate standard of 10 mg/L (measured as total N) in drinking water was first established by the United States Public Health Service in 1962 (Jasa and others, 1998), based on a study of infants with methemoglobinemia. In 1974, the Safe Drinking Water Act was passed by Congress to protect U.S. citizens from harmful constituents in their drinking water, and it authorized the U.S. Environmental Protection Agency (EPA) to set health-based standards. The EPA established a Maximum Contaminant Level (MCL) of 10 mg/L for nitrate (Total N). In 1997, the Idaho Department of Environmental Quality (IDEQ) promulgated Ground Water Quality Rules, which were adopted by the Idaho State Legislature (IDEQ, 1997). The rules include a standard for nitrate of 10 mg/L.

### Nitrate and Human Health

Nitrate in drinking water can have serious and even deadly effects on infants from birth to six months old. Concentrations over 10 mg/L can cause methemoglobinemia, which is also known as blue baby syndrome (McCasland and others, 1998).

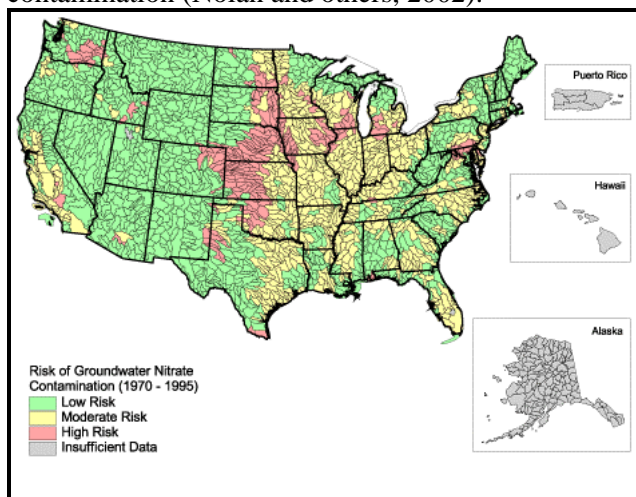
Nitrate may have a relationship with non-Hodgkin's lymphoma (Ward and others, 1996). A University of Iowa study found an association between relatively low levels of nitrate in water and bladder cancer in almost 22,000 women age 55 to 69 (Weyer and others, 2001). The study also found a positive association between nitrate and ovarian cancer and inverse associations

between nitrate and uterine and rectal cancers (Weyer and others, 2001).

High nitrate levels in drinking water may be associated with risk of stomach cancer (Morales-Suarez-Varela and others, 1996). The Wisconsin Department of Natural Resources (2003) reported that "some scientific studies have found evidence suggesting that women who drink nitrate-contaminated water during pregnancy are more likely to have babies with birth defects" and that "people who have heart or lung disease, certain inherited enzyme defects, or cancer may be more sensitive to the toxic effects of nitrate than others". A possible relationship between high nitrate levels and miscarriage was noted from a study in Indiana (Morbidity and Mortality Weekly Report, 1995).

### Nitrate in U.S. Groundwater – Nationwide, Western U.S., and Idaho

Nitrate levels are highest in the Midwest where ground water is relatively close to the land surface, and where nitrogen fertilizers have been applied to agriculture lands for decades. The U.S. EPA (2004b) ranked the middle part of the United States as having "high" and "moderate" risk for ground water contamination by nitrate (Figure 4). The USGS also examined nitrogen input and aquifer vulnerability on a national scale, and showed that the Midwest, as well as smaller areas in the east and west, ranked high in both categories, (Nolan and others, 2002; USGS, 2001). Using a logistic model, the USGS found that areas with high nitrogen loading and well-drained soils overlying unconsolidated sand and gravels had greater risks of nitrate contamination (Nolan and others, 2002).



**Figure 4.** Nitrate risk to ground water in the U.S. USEPA, 2004b).

Nolan and others (2002) categorized some large areas in Washington, Oregon, Idaho, Arizona, and California as “high risk” for ground water contamination by nitrate because of high nitrogen input and, in some cases, high aquifer vulnerability. Ryker and Jones (1996) noted that land use, fertilizer input, and water usage were all important factors with respect to the potential for nitrate contamination in the ground water of the Central Columbia Plateau.

Idaho ground water studies have been completed by the USGS, IDWR, IDEQ, Idaho State Department of Agriculture, Idaho universities, National Resource Conservation Service, Farm Bureau, and other entities. The results of these studies show that the highest nitrate impacts to ground water have been in southern Idaho. Specifically, nitrate contamination is common in south central Idaho (Cassia, Minidoka, and Twin Falls Counties), in southwestern Idaho (Ada, Canyon, and Owyhee Counties), and in west central Idaho (Washington County).

### **Idaho’s Statewide Program**

The Statewide Program is designed to assess the current condition of ground water quality, to identify potential problem areas, and to detect trends in the major aquifers of Idaho. Since the inception of the Statewide Program in 1990, over 1,900 monitoring sites (existing wells and springs) have been sampled for a wide variety of ground water quality parameters, such as common ions (calcium, magnesium, etc.), trace elements (iron, copper, arsenic, etc.), bacteria, nutrients, radioactivity, volatile organic compounds, and pesticides. Most of the monitoring sites (67%) are used for domestic purposes; other common water uses are irrigation, public supply, stock, commercial, and industrial.

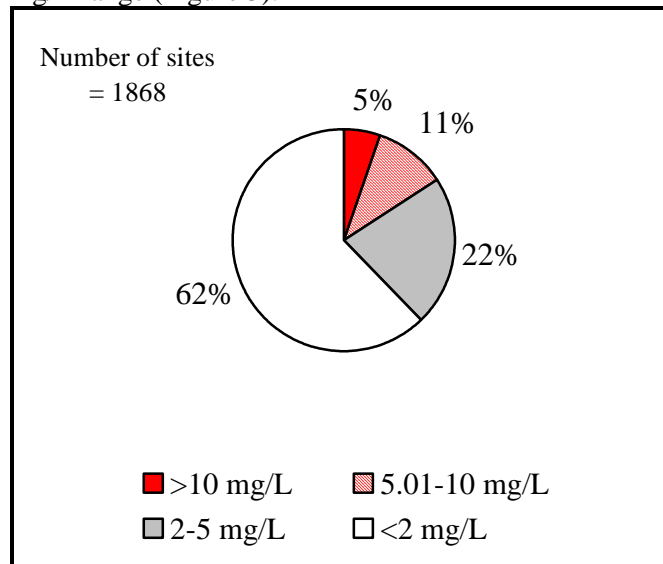
The initial network design called for about 1,600 monitoring sites. Since it was not feasible to sample that many sites each year, it was determined that about 400 monitoring sites would be sampled annually. Sample locations were selected using a stratified random technique. The state was stratified into 20 Hydrogeologic Subareas based on hydrogeology and geomorphology. Potential sample locations were selected randomly in each subarea from the PLSS grid, and monitoring sites were chosen for each selected grid.

From 1991 to 1994, the network was built during a time period called the First Round. Most sites were re-sampled between 1995 and 1998 during the Second

Round. The Third Round encompassed five years (1999-2003) as new sites were added as replacements and to fill in data gaps. Currently, most monitoring sites are scheduled to be sampled once every five years. About 100 sites are sampled annually in order to provide some trend data in a shorter time frame.

### **Statewide Program Nitrate Results**

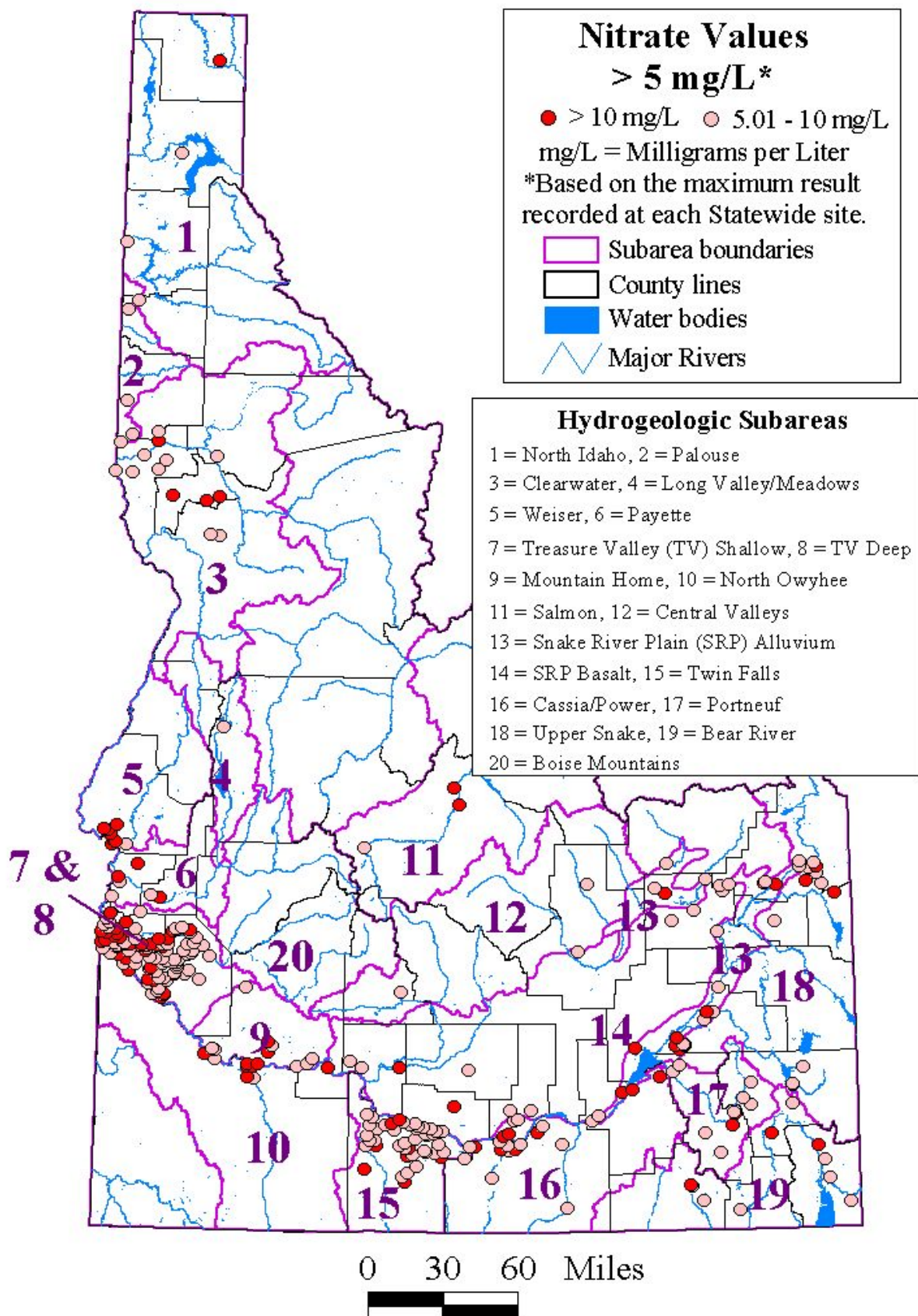
A total of 5,150 individual nitrate results are available for 1,868 Statewide Sites based on sampling from 1991 through 2003. Nitrate concentrations ranged from less than the laboratory minimum reporting level of 0.05 mg/L to 110 mg/L. The MCL for nitrate was exceeded at 96 sites (5 percent), and another 202 sites (11 percent) had at least one nitrate result in the 5.01 to 10 mg/L range (Figure 5).



**Figure 5.** Percent of Statewide Program sites in four nitrate concentration ranges.

Results indicate that nitrate is present in many aquifers throughout Idaho and higher concentrations are more common in the southern part of the state. Figure 6 shows that clustering of sites with maximum nitrate results over 5 mg/L occurred in several regions of the state such as the southwest (Treasure Valley Shallow, Payette, and Weiser Subareas), south central (Twin Falls and Cassia/Power Subareas), and in the eastern part of the state.

Statistical tests were conducted on the Statewide Program data to check for relationships between the average nitrate values and well depth, water temperature, chloride, hardness, pH, sodium, and



**Figure 6.** Statewide Program sites with nitrate concentrations greater than 5 mg/L.



sulfate. Results from Spearman rho tests (Conover, 1980) indicate all seven variables correlate with nitrate at a greater than 95% Confidence Level (CL) (Table 1). However, the strongest correlations occurred with chloride, hardness, sodium, and sulfate, and all four had positive correlations with nitrate. The other constituents had significant correlations, but much lower correlation coefficients.

**Table 1.** Pearson and Spearman rho test results for nitrate and seven variables<sup>1</sup>.

Nitrate concentrations versus:	Pearson coefficient	Pearson probability	Spearman coefficient
Well Depth	-0.06	0.009	-0.05
Water Temp.	0.06	0.009	0.17
Chloride	0.31	0.000	0.54
Hardness	0.52	0.000	0.57
pH	-0.07	0.004	-0.10
Sodium	0.38	0.000	0.40
Sulfate	0.46	0.000	0.51

<sup>1</sup>Tests are based on the average concentration at each site for nitrate, chloride, hardness, pH, sodium, and sulfate.

### Statewide Nitrate Trends

Trend analyses were accomplished using four approaches:

1. Statewide and Hydrogeologic Subareas.
2. Annual Sites.
3. Nitrate Priority Areas.
4. Summary of Welhan's (2004) kriging study.

### Statewide and Subarea Nitrate Trends

Mann Whitney (Conover, 1980) rank sum tests, which use all of the nitrate data, did not indicate any significant differences in median values between the three rounds at the 95% CL. Wilcoxon signed rank tests (Conover, 1980), which use only paired data (i.e., the wells that were sampled in all three rounds) indicated that the median values for the 2<sup>nd</sup> and 3<sup>rd</sup> Rounds were significantly higher than the median for the 1<sup>st</sup> Round at the 95% CL. However, the actual numerical changes in median values were very small, and thus the efficacy of the tests on a diverse dataset such as this one is questionable.

Nitrate trend analyses were done for all 20 Hydrogeologic Subareas delineated for the Statewide Program. Based on the maximum nitrate value for each site within each round, 10 subareas had increases in the median value from the 1<sup>st</sup> to the 2<sup>nd</sup> Round at the 95%

CL (Table 2). However, only one subarea had an increase from the 2<sup>nd</sup> to the 3<sup>rd</sup> Round. One subarea had a significant decrease from the 2<sup>nd</sup> to the 3<sup>rd</sup> Round.

**Table 2.** Results from Wilcoxon Signed Rank Tests comparing median nitrate values between rounds of sampling for Statewide Hydrogeologic Subareas. A **red** probability value indicates a significant increase at the 95% CL; a **blue** value indicates a significant decrease at the 95% CL.

Subarea	FR-SR <sup>2</sup>	SR-TR <sup>2</sup>	FR-TR <sup>2</sup>
North Idaho	0.07	0.09	0.51
Palouse	<b>0.02</b>	0.25	<b>0.01</b>
Clearwater	<b>0.00</b>	1.00	<b>0.00</b>
Long Valley/Meadows	0.14	0.75	0.59
Weiser	<b>0.03</b>	0.85	0.35
Lower Payette	0.19	0.18	<b>0.04</b>
TV Shallow	<b>0.00</b>	0.12	<b>0.00</b>
TV Deep	0.41	0.42	0.38
Elmore	0.96	0.99	0.94
N. Owyhee	0.86	0.18	0.17
Salmon	0.65	0.68	0.51
Central Valleys	0.56	0.16	0.71
SRP Alluvium	<b>0.04</b>	0.06	0.84
SRP Basalt	<b>0.00</b>	0.83	<b>0.00</b>
Twin Falls	<b>0.04</b>	<b>0.05</b>	<b>0.00</b>
Cassia/Power	<b>0.01</b>	0.57	0.25
Portneuf	<b>0.00</b>	0.09	0.25
Upper Snake	<b>0.05</b>	0.67	0.78
Bear River	0.06	<b>0.01</b>	0.12
Boise Mountains	0.33	0.37	0.79

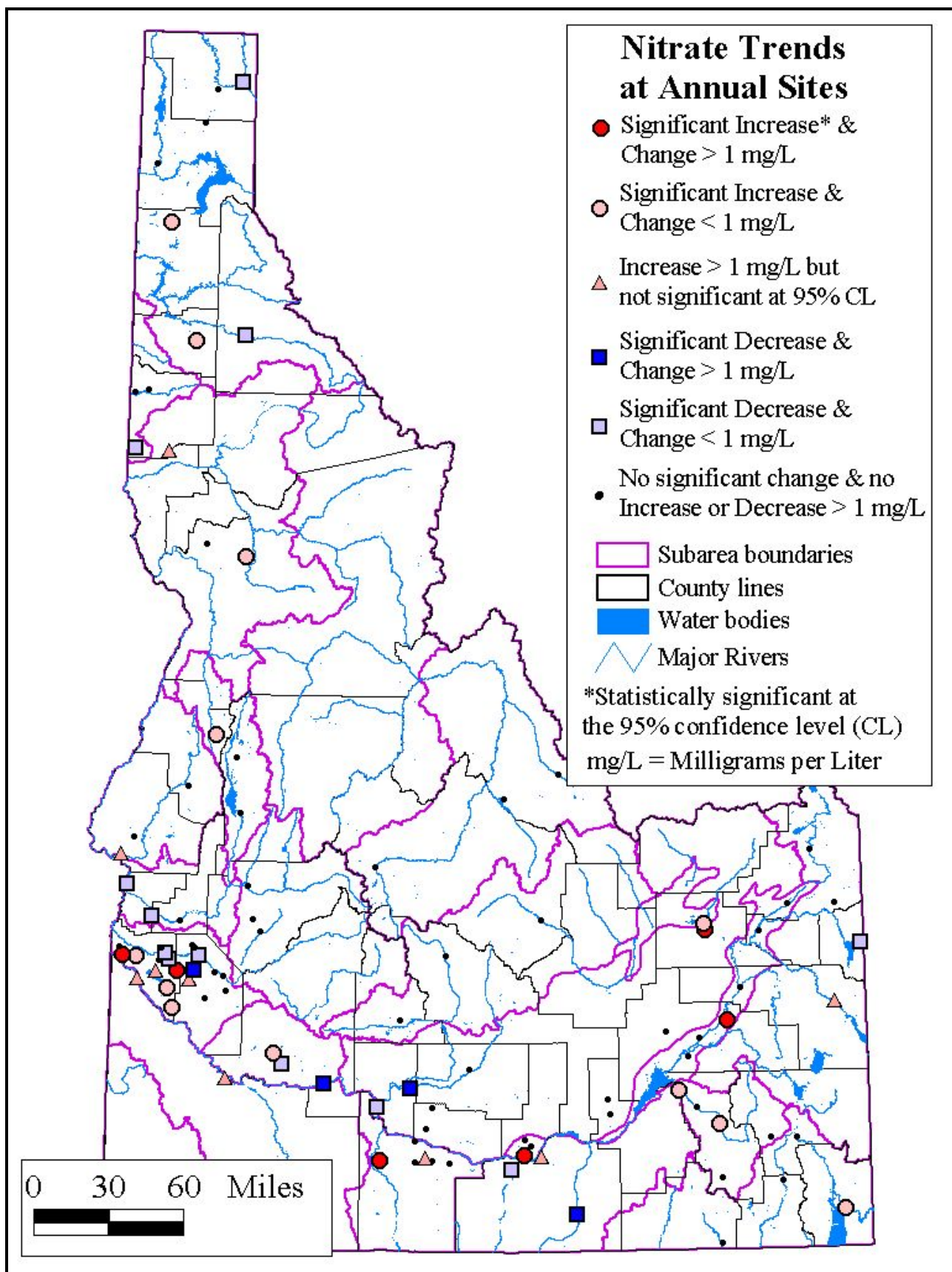
<sup>2</sup>FR = First Round (1991-1994). SR = Second Round (1995-1998). TR = Third Round (1999-2003).

### Nitrate in Annual Sites

In 1995, 100 sites were selected to be sampled annually (sample collection at one site was discontinued in 2000). A total of 1,029 nitrate samples have been analyzed for the Annual Sites through 2004<sup>3</sup>. Most Annual Sites have at least 10 sampling events.

Spearman rho test results indicate that 18 sites had significant increases at the 95% CL, and 16 sites had significant decreases (Figure 7). However, only 6 of the sites with significant increases and four of the sites with significant decreases experienced concentrations changes that were greater than 1 mg/L from the initial value to the most recent nitrate sample result.

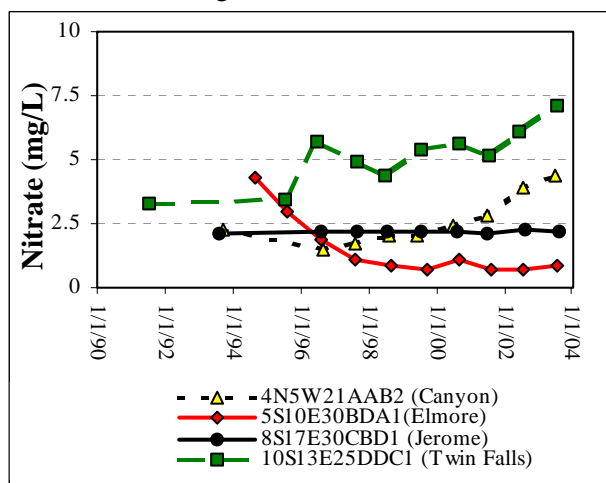
<sup>3</sup>Data from 2004 is provisional and is included only in the analyses of nitrate in Annual Sites for this report.



**Figure 7.** Nitrate trends at Statewide Program Annual Sites.



Nine sites had increases that were greater than 1 mg/L from the initial reading to the reading in 2004, but the trends were not significant at the 95% CL. No other sites than the four previously mentioned had decreases greater than 1 mg/L. Overall, 27 Annual Sites showed evidence of nitrate increases and 16 Annual Sites had nitrate decreases. All seven sites in the west-central and northern parts of the state with significant changes at the 95% CL has less than 1 mg/L change from the initial nitrate value to the nitrate value in 2004. Examples of trends in nitrate concentrations at Annual Sites are shown in Figure 8.



**Figure 8.** Four examples of nitrate trends in Statewide Program Annual Sites.

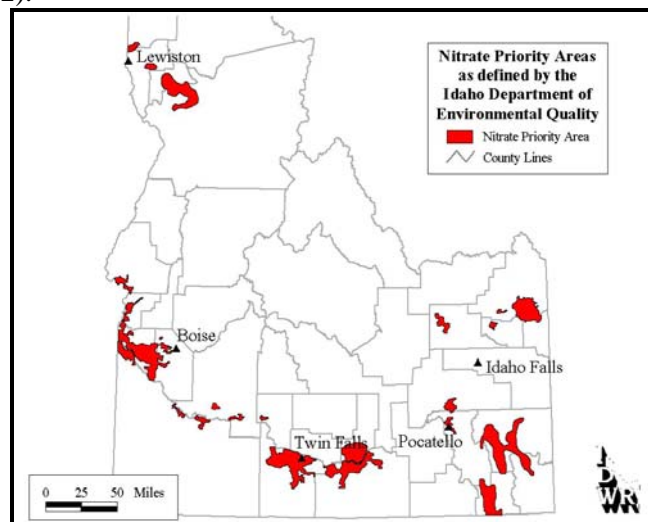
### Trends in Nitrate Priority Areas

Twenty-five Nitrate Priority Areas (NPA) were defined for Idaho by IDEQ based on ground water quality samples collected by state and federal agencies (Figure 9). Nitrate trend analyses were conducted for 13 NPAs; analyses were not conducted for 12 NPAs because they had less than five Statewide Program sites.

Five of the 13 NPAs showed increasing trends that were statistically significant at the 95% CL (Table 3 and Figure 10). These results agreed in part with the results of Parlman (2002) for trend analysis in NPAs, but there were also discrepancies. Agreement was better for the FR to SR analyses between this study and Parlman's than for the FR to the TR. Perhaps this is because at the time of Parlman's report, only two years of sampling (1999 and 2000) were available for the TR.

Only one NPA had a decreasing nitrate trend, and one had an increasing trend from the FR to the SR, but a decreasing trend from the SR to the TR (Table 3).

Figure 11 shows the Lower Boise/Canyon County NPA, which had the most significant increase in nitrate trends of the 13 NPAs analyzed. Median values increased from 4.1, to 5.4, to 6.2 mg/L from the 1<sup>st</sup> to the 3<sup>rd</sup> Round. The changes between rounds were all significant at the 95 percent confidence level (Figure 12).



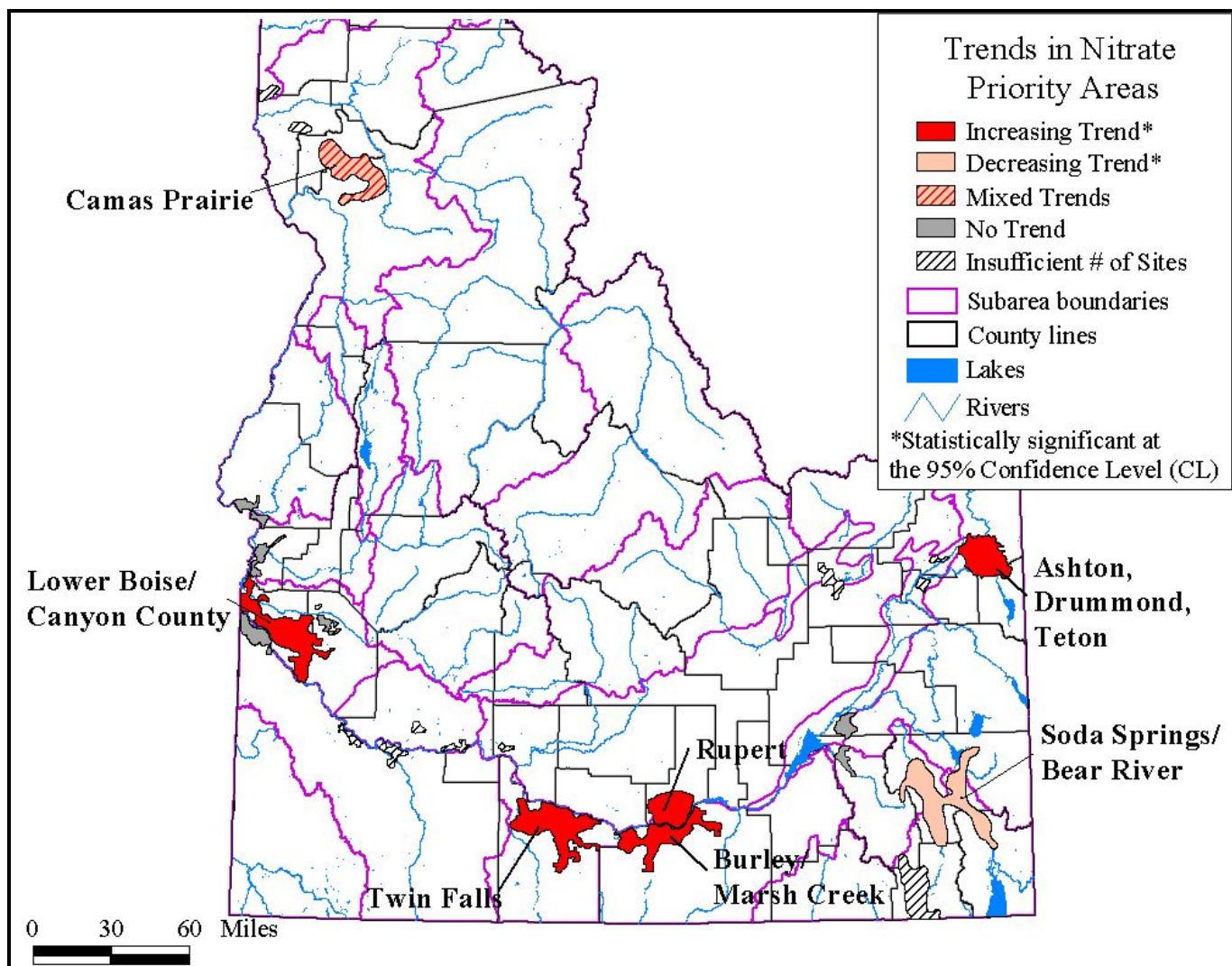
**Figure 9.** Nitrate Priority Areas as designated by IDEQ.

**Table 3.** Results from Wilcoxon Signed Rank Tests comparing median nitrate values between rounds of sampling for NPAs. A **red** probability values indicates a significant increase at the 95% CL; a **blue** value indicates a significant decrease at the 95% CL.

NPA Name (Rank <sup>1</sup> )	FR-SR <sup>2</sup>	SR-TR <sup>2</sup>	FR-TR
Weiser (1)	0.40	0.13	0.18
Twin Falls (2)	0.09	0.07	<b>0.00</b>
Burley/Marsh Creek (3)	<b>0.01</b>	0.26	0.08
Lower Boise/ Canyon County (4)	<b>0.00</b>	<b>0.01</b>	<b>0.00</b>
Camas Prairie (5)	<b>0.01</b>	<b>0.05</b>	0.09
Fort Hall (7)	0.07	0.23	0.14
Ashton, Drummond, Teton (8)	<b>0.03</b>	0.21	<b>0.04</b>
Rupert (9)	0.03	0.23	0.06
Payette (10)	0.08	0.69	0.14
Homedale/ Marsing (12)	0.24	0.61	0.24
Pocatello (17)	0.08	0.74	0.31
Soda Springs/ Bear River (18)	0.32	<b>0.00</b>	0.09
Boise/Meridian (24)	<b>0.75</b>	0.74	0.87

<sup>1</sup>Rank was assigned by IDEQ.

<sup>2</sup>FR = First Round (1991-1994). SR = Second Round (1995-1998). TR = Third Round (1999-2003).



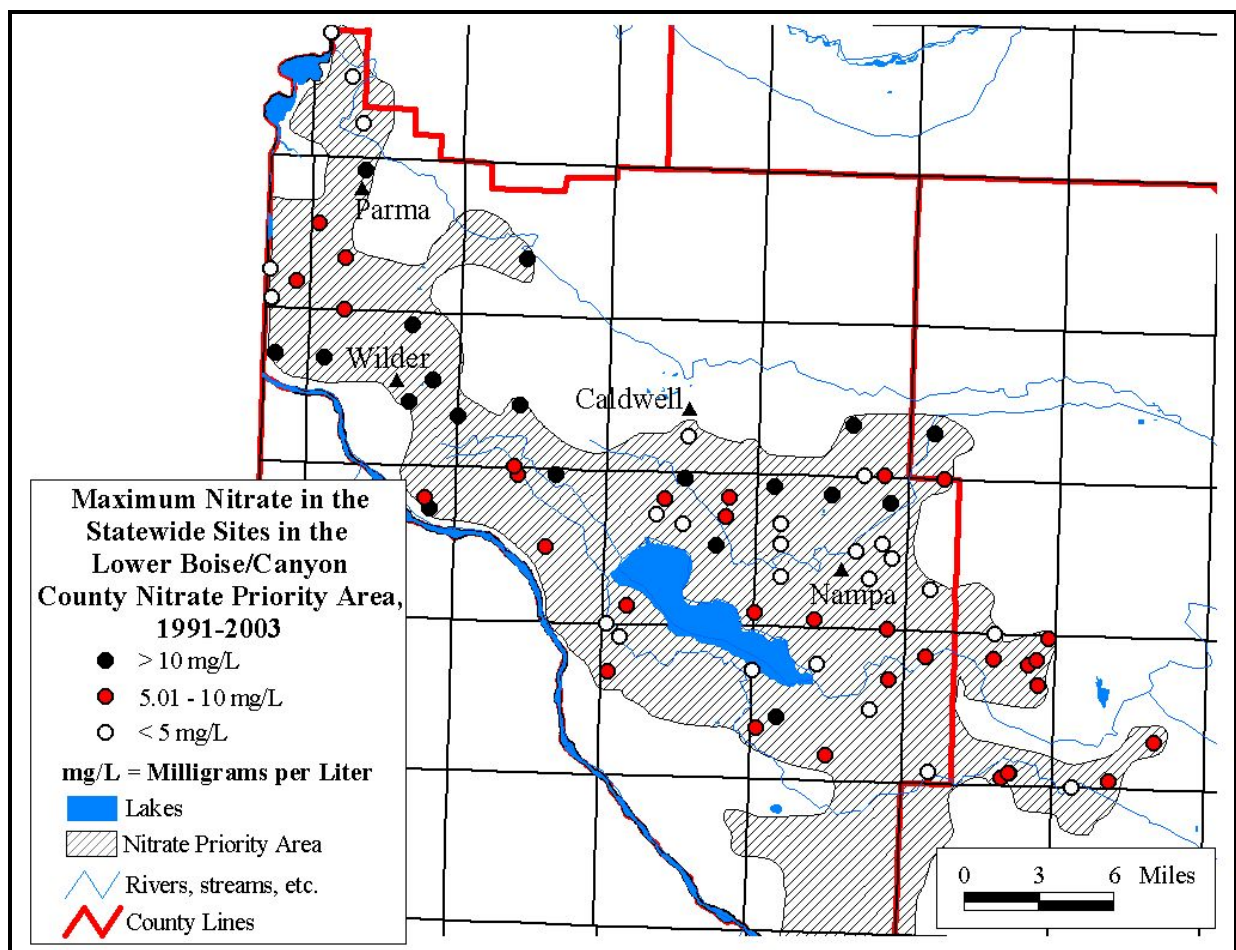
**Figure 10.** Trends in Nitrate Priority Areas based on Statewide Program sites

Twelve of the 27 Annual Sites (44%) that had nitrate increases significant at the 95% CL, or had nitrate changes greater than 1 mg/L from the initial results to the results in 2004, occurred within NPA boundaries, and another four sites (15%) with these magnitudes of increases were within one mile of an NPA boundary. Only five of the 16 Annual Sites (31%) with statistically significant decreasing trends at the 95% CL were inside NPAs. Conversely, 11 of the 16 Annual Sites (69%) with significant decreasing nitrate trends occurred outside the NPAs at distances greater than one mile from the boundaries.

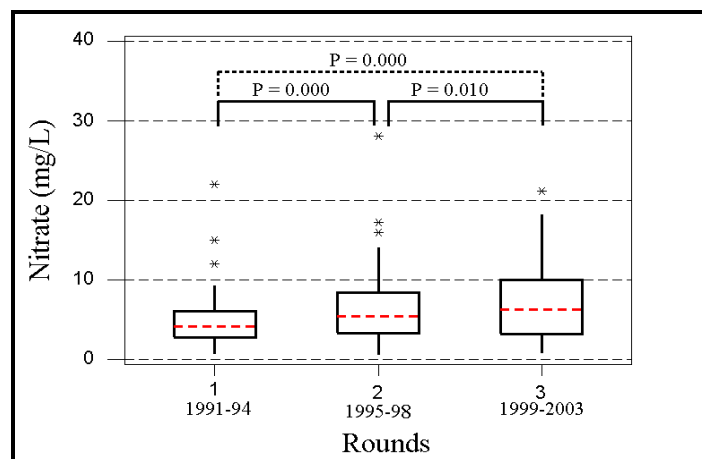
The relationship between NPAs with increasing nitrate trends and the occurrence of Annual Sites with increasing nitrate trends is seen clearly in the Lower Boise/Canyon County, Twin Falls, Rupert, and

Burley/Marsh Creek NPAs (Figure 13). These four NPAs had 10 Annual Sites with increasing nitrate concentrations either inside the boundaries, or within one mile of the boundaries. However, only two Annual Sites with decreasing nitrate trends occurred within these four NPAs.

The relationship between NPAs and nitrate trends at Annual Sites did not occur in eastern Idaho. In this region, there were two large NPAs with statistically significant changes in nitrate; Ashton/Drummond/Teton River had an increasing nitrate trend while Soda Springs/Bear River had a decreasing nitrate trend. However, none of the eight Annual Sites with increasing or decreasing nitrate trends occurred within any of the eight NPAs in this part of the state, included the two NPAs with significant nitrate changes.



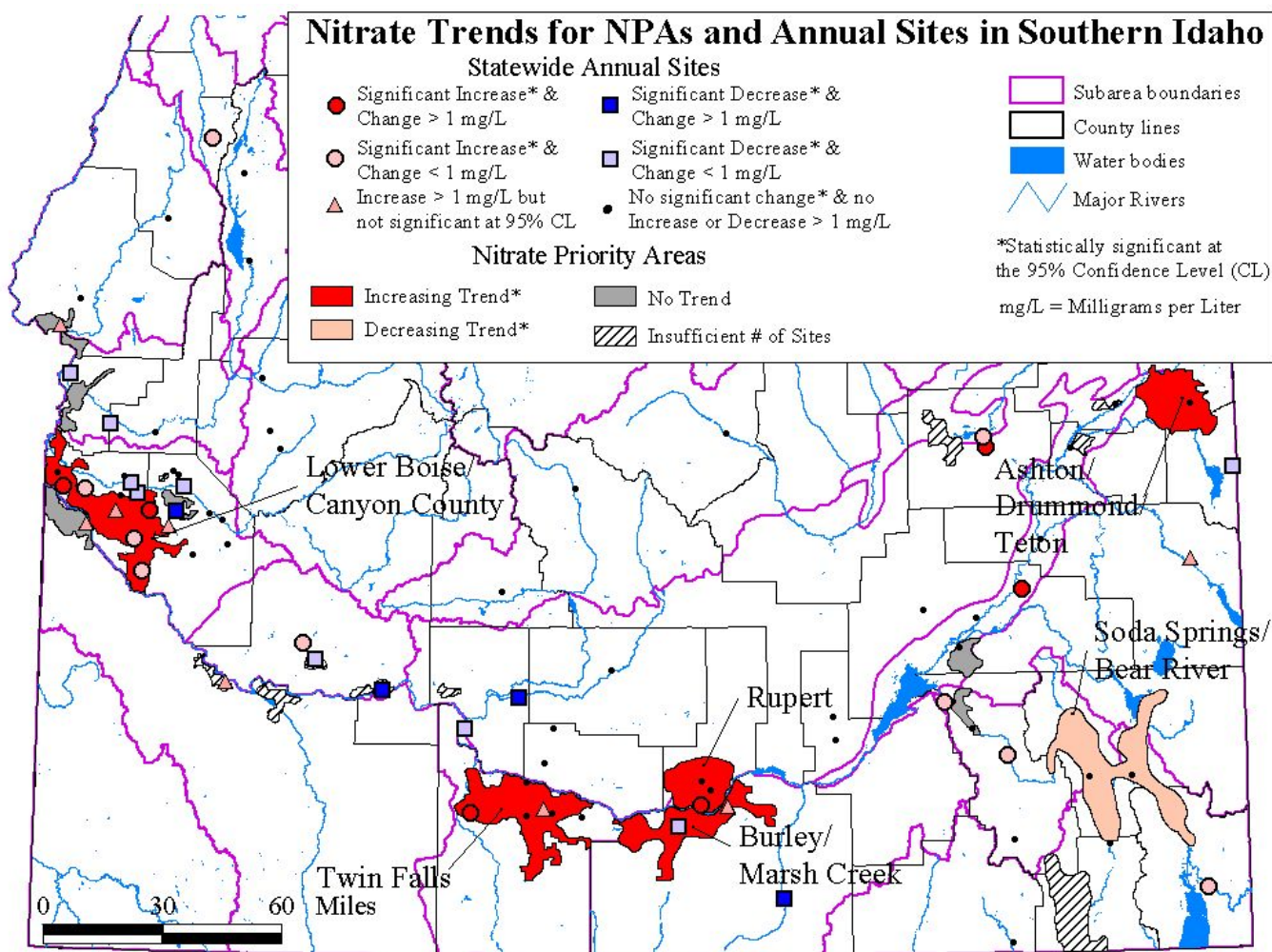
**Figure 11.** Maximum nitrate results for the Statewide Program sites in the Lower Boise/Canyon County NPA.



**Figure 12.** Boxplots<sup>1</sup> showing nitrate changes in the Lower Boise/Canyon County Nitrate Priority Area for Statewide Program Sampling Rounds 1 through 3.

<sup>1</sup>Boxplot explanations: The red dashed line is the median value. The box encompasses 50% of the data from the 25<sup>th</sup> to 75<sup>th</sup> percentiles. The vertical lines are whiskers which extend the data a maximum of two times the box height. The stars are outliers.





**Figure 13.** Nitrate trends for Nitrate Priority Areas and Statewide Program Annual Sites in southern Idaho.

### Kriging Results

Dr. John Welhan, Idaho State University, conducted kriging analyses on select Statewide Program data to determine if spatial and/or temporal trends could be detected. The project's overall goals were: 1) examine the feasibility of kriging for nitrate, arsenic, and pesticides, 2) map spatial and temporal water quality patterns, 3) use geostatistical methods for filtering and synthesizing monitoring data, and 4) recommend methods that show promise as ground water quality management tools.

Results from the study indicate that kriging is a very useful method for documenting statistically significant trends, and was most successful with the nitrate data. The results from Welhan (2004) are summarized in Table 4, and an example is shown in Figure 14.

**Table 4.** Kriging conclusions from Welhan (2004)

Analysis	Conclusion
Spatial Outlier	Omit outliers that are not representative of the area.
Temporal Change	Effective for nitrate Statewide and arsenic in select areas.
Probability Mapping	Useful for showing areas where a constituent most likely exceeds a regulatory standard, and for making chronic exceedence maps.
Cokriging	Not found to be effective.
Spatial-temporal.	The most significant result of this study – strong temporal autocorrelation of nitrate levels among wells across time.

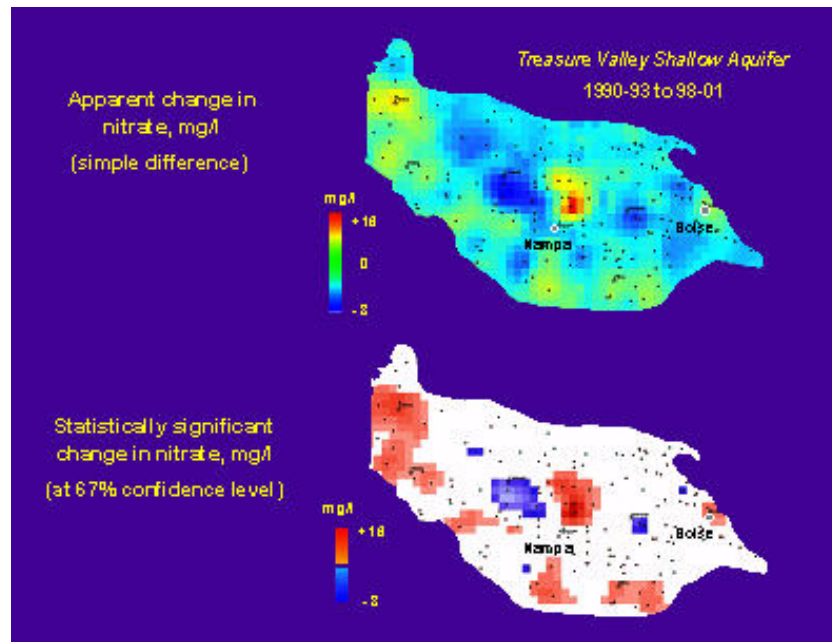


Figure 14. An example from Welhan (2004) which shows the utility of using Kriging map techniques to analyze nitrate concentrations from Statewide Program sites.

## Conclusions

Nitrate data collected through the Idaho Statewide Program have been valuable for determining where some ground water quality problems exist. Nitrate impacts to ground water occurred in southwestern, south central, and eastern Idaho. Five percent of the monitoring sites had nitrate over the MCL of 10 mg/L. Another 11 percent had elevated nitrate concentrations that ranged from greater than 5 mg/L to 10 mg/L.

**Table 5.** Summary of nitrate trends for Hydrogeologic Subareas, Nitrate Priority Areas, and Annual Sites using Statewide Program data.

Area	Trend <sup>1</sup>	FR-SR	SR-TR	FR-TR
Subareas N = 20	Inc. Trend	10	1	6
	No Trend	10	18	14
	Dec. Trend	0	1	0
Priority Areas N = 13	Inc. Trend	5	1	3
	No Trend	8	10	10
	Dec. Trend	0	2	0
Annual Sites N = 99	<b>From Initial Sample to Sample in 2004</b>			
	Inc. Trend	18		
	No Trend	65		
	Dec. Trend	16		

<sup>1</sup> A trend is increasing (Inc.) or decreasing (Dec.) if analytical tests indicate significance at the 95% CL.

Trend analyses indicate that increases in nitrate in Idaho ground water have been more common than decreases for the time period from 1991 through 2003. Analyses for Hydrogeologic Subareas, Nitrate Priority Areas, and Annual Sites all confirm the overall increasing trend (Table 5). Increases were greater between the 1<sup>st</sup> and 2<sup>nd</sup> Rounds than between the 2<sup>nd</sup> and 3<sup>rd</sup> Rounds. Further study is needed to determine how factors such as land use, soil type, irrigation practices, and nitrogen loading impact nitrate levels.

## Preventing Nitrate Impacts to Ground Water

Since nitrate can persist in ground water for a long time, prevention is the best course of action. Some methods that can help keep nitrate from entering the ground water are:

1. Good Well Construction. Seal wells properly, and use casing designs that will prevent cross-contamination.
2. Best Management Practices. Reduce nitrate input, reduce leaching with efficient irrigation, and use nitrogen-fixing crops in rotation.
3. Waste Management. Carefully supervise the disposal of human and animal wastes, and design wastewater applications to prevent excessive nitrate loading.

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