U.S. Department of the Interior
U.S. Geological Survey

In cooperation with the
Idaho State Department of Agriculture

Probability of Detecting Atrazine/Desethyl-Atrazine and Elevated Concentrations of Nitrate ($NO_2 + NO_3 - N$) in Ground Water in the Idaho Part of the Upper Snake River Basin

Water-Resources Investigations Report 98–4203

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By Michael G. Rupert

Water-Resources Investigations Report 98–4203

In cooperation with the
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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
acre	4,047	square meter
acre-foot (acre-ft)	1,233	cubic meter
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
foot (ft)	0.3048	meter
foot per mile (ft/mi)	0.1894	meter per kilometer
[1] foot squared per day (ft^2/d)	0.0929	meter squared per day
inch (in.)	25.4	millimeter
gallon per minute (gal/min)	0.06309	liter per second
mile (mi)	1.609	kilometer
square mile (mi^2)	2.590	square kilometer

[1] The standard unit for transmissivity is cubic foot per day per square foot times foot of aquifer thickness [$(ft^3/d)/ft^2$]ft. In this report, the mathematically reduced form, foot squared per day (ft^2/d), is used for convenience.

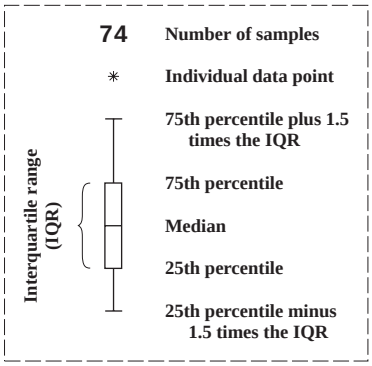
Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Abbreviated water-quality units:

µg/L micrograms per liter
mg/L milligrams per liter

EXPLANATION FOR BOXPLOTS

(Figures 5, 10, 12)



Probability of Detecting Atrazine/Desethyl-Atrazine and Elevated Concentrations of Nitrate ($NO_2 + NO_3 - N$) in Ground Water in the Idaho Part of the Upper Snake River Basin

By Michael G. Rupert

ABSTRACT

Draft Federal regulations may require that each State develop a State Pesticide Management Plan for the herbicides atrazine, alachlor, cyanazine, metolachlor, and simazine. This study developed maps that the Idaho State Department of Agriculture might use to predict the probability of detecting atrazine and desethyl-atrazine (a breakdown product of atrazine) in ground water in the Idaho part of the upper Snake River Basin. These maps can be incorporated in the State Pesticide Management Plan and help provide a sound hydrogeologic basis for atrazine management in the study area.

Maps showing the probability of detecting atrazine/desethyl-atrazine in ground water were developed as follows: (1) Ground-water monitoring data were overlaid with hydrogeologic and anthropogenic data using a geographic information system to produce a data set in which each well had corresponding data on atrazine use, depth to ground water, geology, land use, precipitation, soils, and well depth. These data then were downloaded to a statistical software package for analysis by logistic regression. (2) Individual (univariate) relations between atrazine/desethyl-atrazine in ground water and atrazine use, depth to ground water, geology, land use, precipitation, soils, and well depth data were evaluated to identify those independent variables significantly related to atrazine/desethyl-atrazine detections. (3) Several preliminary multivariate models with various combinations of independent variables were constructed. (4) The multivariate models which best predicted the presence of atrazine/desethyl-atrazine in ground water were selected. (5) The multivariate models were entered into the geographic information system and the probability maps were constructed.

Two models which best predicted the presence of atrazine/desethyl-atrazine in ground water were selected; one with and one without atrazine use. Correlations of the predicted probabilities of atrazine/desethyl-atrazine in ground water with the percent of actual detections were good; r-squared values were 0.91 and 0.96, respectively. Models were verified using a second set of ground-water quality data. Verification showed that wells with water containing atrazine/desethyl-atrazine had significantly higher probability ratings than wells with water containing no atrazine/desethyl-atrazine ($p < 0.002$).

Logistic regression also was used to develop a preliminary model to predict the probability of nitrite plus nitrate as nitrogen concentrations greater than background levels of 2 milligrams per liter. A direct comparison between the atrazine/desethyl-atrazine and nitrite plus nitrate as nitrogen probability maps was possible because the same ground-water monitoring, hydrogeologic,

and anthropogenic data were used to develop both maps. Land use, precipitation, soil hydrologic group, and well depth were significantly related with atrazine/desethyl-atrazine detections. Depth to water, land use, and soil drainage were significantly related with elevated nitrite plus nitrate as nitrogen concentrations. The differences between atrazine/desethyl-atrazine and nitrite plus nitrate as nitrogen relations were attributed to differences in chemical behavior of these compounds in the environment and possibly to differences in the extent of use and rates of their application.

INTRODUCTION

Ground-water quality is a water resource management concern in Idaho where ground water supplied more than 85 percent of public water supplies in 1990 (Solley and others, 1993). Pesticides (a generic term for herbicides, insecticides, nematocides, and rodenticides) have been detected in ground water in several areas (Crockett, 1995; Rupert, 1994; Rupert and others, 1996). In the Burley area, water from more than 80 percent of the 60 wells sampled by the U.S. Geological Survey (USGS) contained at least one detectable pesticide (Rupert and others, 1996). Atrazine was the most commonly detected pesticide in ground water sampled statewide (Crockett, 1995).

Draft Federal regulations may require that each State develop a State Pesticide Management Plan (SMP) for the herbicides atrazine, alachlor, cyanazine, metolachlor, and simazine. The Idaho State Department of Agriculture (ISDA) is in the process of developing an SMP and would benefit from a map that might be used to predict the probability of atrazine in ground water. These maps could be incorporated into the SMP and help provide a sound hydrogeologic basis for pesticide management in Idaho. Other organizations and programs that might benefit from such a map include the agri-chemical industry; agricultural producers; the Shoshone-Bannock Tribes; county and city governments; planning and zoning commissions; education programs for applicators; and State programs related to Wellhead Protection, Drinking Water, Home-A-Syst, and Best Management Plans (BMPs).

Ground-water probability maps are designed to predict the predisposition of areas to ground-water contamination based on natural and anthropogenic (related to human activities) factors. Ground-water probability maps are similar to ground-water vulnerability maps developed using the DRASTIC mapping technique (Aller and others, 1985) but are based upon statistical correlations with actual ground-water monitoring data. Ground-water probability maps are superior predictive tools over vulnerability maps developed with the DRASTIC mapping technique because they are statistically based on actual contaminant concentrations and can quantify the actual probability of the detection of a particular contaminant.

Background

Probably the most widely known ground-water vulnerability mapping procedure is the DRASTIC model (Aller and others, 1985). It was designed to evaluate the potential for ground-water contamination in a given area on the basis of hydrogeologic factors. The DRASTIC acronym refers to the seven factors considered in the model: **d**epth to water, net **r**echarge, **a**quifer media, **s**oil media, **t**opography, **i**mpact of vadose zone media, and hydraulic **c**onductivity of the aquifer (Aller and others, 1985, p. iv). The DRASTIC model has been used to develop ground-water vulnerability maps in many parts of the Nation; the effectiveness of the model has met with mixed success (Koterba and others, 1993, p. 513; Barbash and Resek, 1996; Rupert, 1997). DRASTIC maps usually are not calibrated to actual contaminant concentrations.

The first published map of ground-water vulnerability in Idaho was developed by Rupert and others (1991), who used a modified form of the DRASTIC model. Three of the seven DRASTIC factors—depth to water, net recharge (land use), and soil media were used because they were believed to be the most important factors with respect to ground-water vulnerability, and because they were the most readily accessible data. Land use was used as a surrogate for net recharge because irrigated agricultural areas provide the largest amount of recharge in southern Idaho. The resultant map was named “relative ground-water vulnerability” because the vulnerability ratings (low, medium, high, and very high) were determined relative to each other and were not based on actual ground-water quality data. Rupert and others (1991, p. 23) stated that the point rating schemes used to develop the map may need to be adjusted to conform with ground-water monitoring data.

Chang and others (1994) correlated nitrate concentrations in ground water with the relative ground-water vulnerability map developed by Rupert and others (1991). Chang and others (1994, p. 10) determined that there was a "statistically significant, but weak, relationship between the rating system and nitrate observations."

Rupert (1997) significantly improved the effectiveness and accuracy of the earlier vulnerability map by Rupert and others (1991) by calibrating (adjusting) the vulnerability point ratings to measured nitrite plus nitrate as nitrogen (NO_2+NO_3–N) concentrations in ground water using nonparametric statistical tests. The maps were termed probability maps instead of vulnerability maps because (1) the probability categories were based on the results of statistical comparisons, and (2) the term probability more clearly states what the maps portrayed; whether an area has a high or low probability for NO_2+NO_3–N contamination of ground water. Calibration of the probability maps with measured water-quality data made them a superior predictive tool over the relative ground-water vulnerability map produced using the modified DRASTIC method.

Improvements have been made in the effectiveness of ground-water vulnerability/probability maps by using logistic regression to relate water-quality data to hydrogeologic and anthropogenic factors (Koterba and others, 1993; Druliner and others, 1996; Nolan and Ruddy, 1996; Nolan and Clark, 1997; Tesoriero and Voss, 1997). Logistic regression is an improvement over the nonparametric statistical methods used in previous probability mapping in Idaho (Rupert, 1997) because the actual probabilities of a detection are quantified.

Purpose and Scope

The main purpose of this report is to present maps that might be used to predict the probability of atrazine/desethyl-atrazine (atrazine/DEA) and elevated NO_2+NO_3–N in ground water in the Idaho part of the upper Snake River Basin. Relations between atrazine/DEA and NO_2+NO_3–N in ground water and hydrogeologic and anthropogenic factors were examined using a geographic information system (GIS). Statistical models that predict the probability of detecting atrazine/DEA and NO_2+NO_3–N in ground water were developed using logistic regression statistical methods. Atrazine/DEA is the only pesticide for which a probability map was developed because it is the only pesticide compound with a sufficient number of detections for statistical analysis. A model predicting the probability of elevated NO_2+NO_3–N concentrations also was developed to compare differences in models for atrazine/DEA and NO_2+NO_3–N. Comparisons were performed to determine whether NO_2+NO_3–N might be used as a surrogate for predicting contamination by other compounds.

Acknowledgments

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STUDY AREA DESCRIPTION AND HYDROGEOLOGY

The 35,800-mi^2 upper Snake River Basin (USNK) extends from Yellowstone National Park in Wyoming to King Hill in south-central Idaho (fig. 1). The 10,800-mi^2 eastern Snake River Plain is about 60 mi wide and 200 mi long. About 50 percent of the entire USNK is rangeland, about 21 percent is agricultural land, and about 23 percent is forest land (Maupin, 1995, p. 22). Most of the 4.7 million acres of agricultural land are near the Snake River and near the mouths of tributary basins (fig. 2). Most of the cities and industrial centers

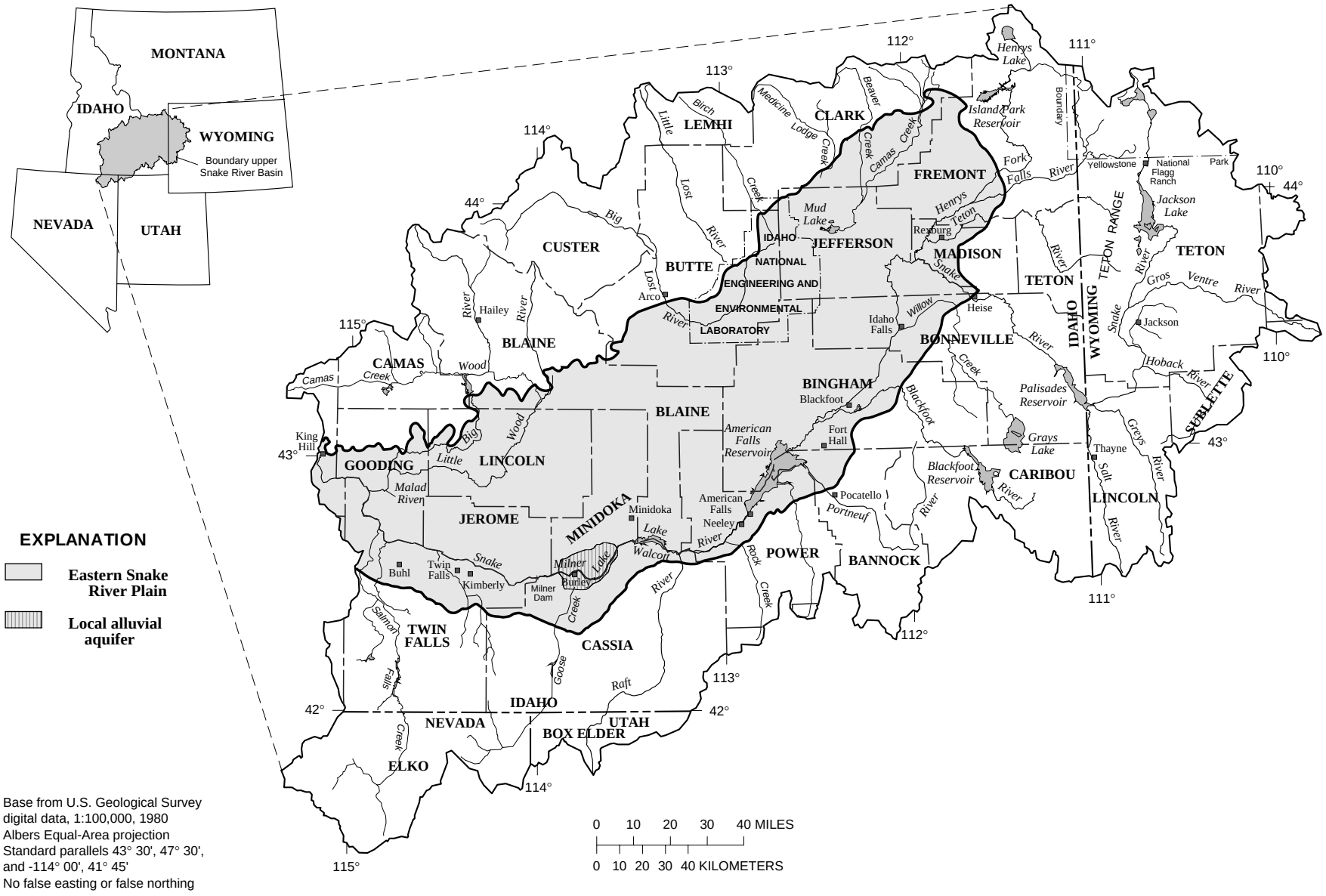

Figure 1. Location of the upper Snake River Basin and eastern Snake River Plain.

Figure 2. Major land-use classifications in the Idaho part of the upper Snake River Basin.
(60 k)

Can be accessed from the home page for this report.

Figure 3. Mean annual precipitation in the Idaho part of the Upper snake River Basin, 1961–90.
(60 k)

Can be accessed from the home page for this report.

are near the Snake River. Predominant native vegetation includes fir and pine forests in the mountains, and sagebrush and bunchgrass in valleys and on the plain. Large parts of the plain are sparsely vegetated outcrops of basalt of Quaternary age.

The climate of most of the basin is semiarid (fig. 3). Mean annual precipitation ranges from less than 10 in. on much of the plain to as much as 50 in. in Blaine County. The basin is characterized by moderately to severely cold winters and hot, dry summers. The average length of the growing season is about 120 to 160 days.

Land-surface altitude of the entire USNK ranges from about 2,500 ft above sea level at the western edge of the basin to 13,770 ft in the Teton Range in western Wyoming. The northern and northwestern parts of the basin are characterized by deep intermontane valleys and mountains that, in places, exceed 12,000 ft in altitude. The relatively flat eastern Snake River Plain is 2,500 to 6,000 ft above sea level.

Idaho ranks third in the Nation behind California and Texas in total water use (Rupert, 1994, p. 5). In 1990, 2.5 million acres on the eastern Snake River Plain were irrigated with 6.6 million acre-ft of ground water and 7.6 million acre-ft of surface water (Maupin, 1995, p. 33). Seventy-one percent of all irrigated acreage in Idaho in 1990 was in the Idaho part of the USNK; potatoes, wheat, sugar beets, hay, and barley were the predominant crops.

Three major types of aquifers are present in the entire USNK: a regional basalt aquifer, local alluvial aquifers, and tributary valley aquifers. The regional aquifer underlying the eastern Snake River Plain is composed primarily of fractured basalt, although in some areas, particularly along the margins of the plain, alluvial deposits and silicic volcanic rocks constitute the aquifer. Locally overlying the eastern Snake River Plain aquifer are alluvial aquifers, some of which are perched. Seepage from streams that flow onto the plain and underflow (subsurface ground-water flow) from tributary valley aquifers are major sources of recharge to the eastern Snake River Plain aquifer. Tributary valley aquifers are composed primarily of alluvium. Greater emphasis is placed on the eastern Snake River Plain aquifer throughout this report because most water-quality data are for the plain and most water use is on the plain.

Snake River Plain Aquifer

The eastern Snake River Plain is underlain predominantly by a series of vesicular and broken olivine basalt flows (Quaternary age) of the Snake River Group. Individual flows average 20 to 25 ft in thickness; geophysical data and drillers' logs indicate that total thickness of the basalt is as much as 5,000 ft (Whitehead, 1992, p. B1). Basalt is generally less than 10 ft below land surface in the central part of the plain and is generally less than 100 ft below land surface elsewhere.

Layered basalt flows underlying the eastern Snake River Plain contain and yield exceptionally large volumes of water to wells and springs. Wells open to less than 100 ft of the aquifer yield as much as 7,000 gal/min; yields of 2,000 to 3,000 gal/min with only a few feet of drawdown are common (Whitehead, 1992, p. 22–25; Lindholm, 1996, p. 18–22). Individual well yields from the Snake River Plain aquifer are some of the largest in the Nation. Transmissivity of the predominantly basalt aquifer commonly exceeds 100,000 ft^2/d and locally is as much as 1,000,000 ft^2/d (Whitehead, 1992, p. 22).

Regionally, water in the Snake River Plain aquifer moves from northeast to southwest (Rupert, 1997, p. 6). The potentiometric surface descends 2,000 ft along a 200-mi-long flowpath at an average gradient of 10 ft/mi (Lindholm and others, 1988). Flow velocities average about 10 ft/d (Robertson and others, 1974, p. 13). Ground-water traveltimes from the far upgradient side to the far downgradient side are as much as 350 years (Ackerman, 1995, p. 1). Depth to first-encountered water ranges from less than 3 ft in alluvium along the Snake River (Maupin, 1992) to about 1,000 ft in the north-central part of the eastern plain.

Ground water is discharged from the Snake River Plain aquifer mainly as spring flow and as seepage to the Snake River between Milner Dam and King Hill (fig. 1). Northside discharge to this reach was about 6,000 ft^3/s in 1980 (Kjelstrom, 1992, fig. 2). Ground-water discharge increased considerably from about 1910 through the early 1950's (Kjelstrom, 1992, fig. 2). The increase is attributed to recharge from surface-water irrigation north and east of the springs. Since the early 1950's, ground-water discharge has decreased as a result of (1) increased ground-water withdrawals for irrigation (Moreland, 1976, p. 9), (2) the introduction of more efficient irrigation practices such as conversion from gravity-fed to sprinkler irrigation, and (3) local

droughts (Kjelstrom, 1992, p. 2). Changes in ground-water levels reflect the same long-term downward trend as does spring discharge (Kjelstrom, 1992; Rupert, 1997, p. 8).

Local Alluvial Aquifers

Local alluvial aquifers that overlie the Snake River Plain aquifer in some areas (Young, 1984; Lindholm and others, 1988) typically are composed of alluvium deposited by tributary streams and the Snake River.

In the Burley area, an alluvial aquifer is perched above a blue-clay layer about 60 to 120 ft below land surface (Rupert, 1997, p. 8). The top of the clay layer was mapped by Ken Skinner (U.S. Geological Survey, written commun., 1996), who reviewed several hundred well-driller records. The water table in the local alluvial aquifer is relatively flat over much of its extent, compared with that of the regional aquifer (Rupert, 1997, p. 7). Ground-water flow in the local alluvial aquifer is generally northward near the southern boundary and westward near the western boundary. Water levels are about 100 ft higher in the perched aquifer than in the regional aquifer. Recharge to the local alluvial aquifer is predominantly infiltration of irrigation water. According to local accounts, the alluvial aquifer in the Burley area was dry prior to 1907 when a canal network was constructed to transport irrigation water from Lake Walcott. Reportedly, several wells completed in the local alluvial aquifer go dry seasonally, after irrigation ceases; these wells become operational again less than 2 weeks after the start of the next irrigation season.

Tributary Valley Aquifers

Seepage from streams that flow onto the eastern Snake River Plain and underflow from tributary valleys on the north, east, and south sides of the plain recharge the regional aquifer. Aquifers in tributary valleys are predominantly alluvial deposits. Near the mouths of several valleys, basaltic lava flows of the Snake River Group interfinger with and overlie the alluvium. Prominent northwest-trending mountain ranges north and south of the plain separate the tributary valleys. A more complete description of these tributary valleys is provided by Mundorff and others (1964).

MODEL DEVELOPMENT APPROACH

Maps showing the probability of atrazine/DEA detections in ground water of the Idaho part of the USNK were developed in several steps. The first was to compile all ground-water monitoring data on atrazine/DEA in ground water of the study area. Once compiled, relations between the atrazine/DEA data and hydrogeologic and anthropogenic data were evaluated using a GIS and logistic regression statistical methods. Univariate relations were evaluated between atrazine/DEA detections in ground water and atrazine use, depth to ground water, geology, land use, precipitation, soils, and well depth to identify and eliminate those independent variables not significantly related to the presence of atrazine/DEA. Multivariate models with various combinations of independent variables were developed using logistic regression. The two most effective multivariate statistical models that predicted the presence of atrazine/DEA in ground water were selected—one with and one without atrazine use. The models then were entered into a GIS, and the maps were produced.

GROUND-WATER QUALITY DATA

Ground-water quality data evaluated in this report (fig. 4) were collected as part of the Idaho Statewide Ground-Water Monitoring Program (ISGWMP) and the USGS National Water-Quality Assessment (NAWQA) Program. All data were collected during the same time period and analyzed by the same laboratory using the same laboratory methods.

Two laboratory analytical methods were used to determine pesticide concentrations in ground water; gas chromatography/mass spectrometry analysis (GC/MS) and enzyme-linked immunosorbent assay (ELISA). The GC/MS data were used to calibrate the models; ELISA data were used to verify them.

Idaho Statewide Ground-Water Monitoring Program

The ISGWMP is a cooperative program between the USGS and the IDWR. Primary objectives of the program are to (1) characterize the quality of water in Idaho's aquifers, (2) identify temporal trends in water quality in individual aquifers, and (3) identify aquifers

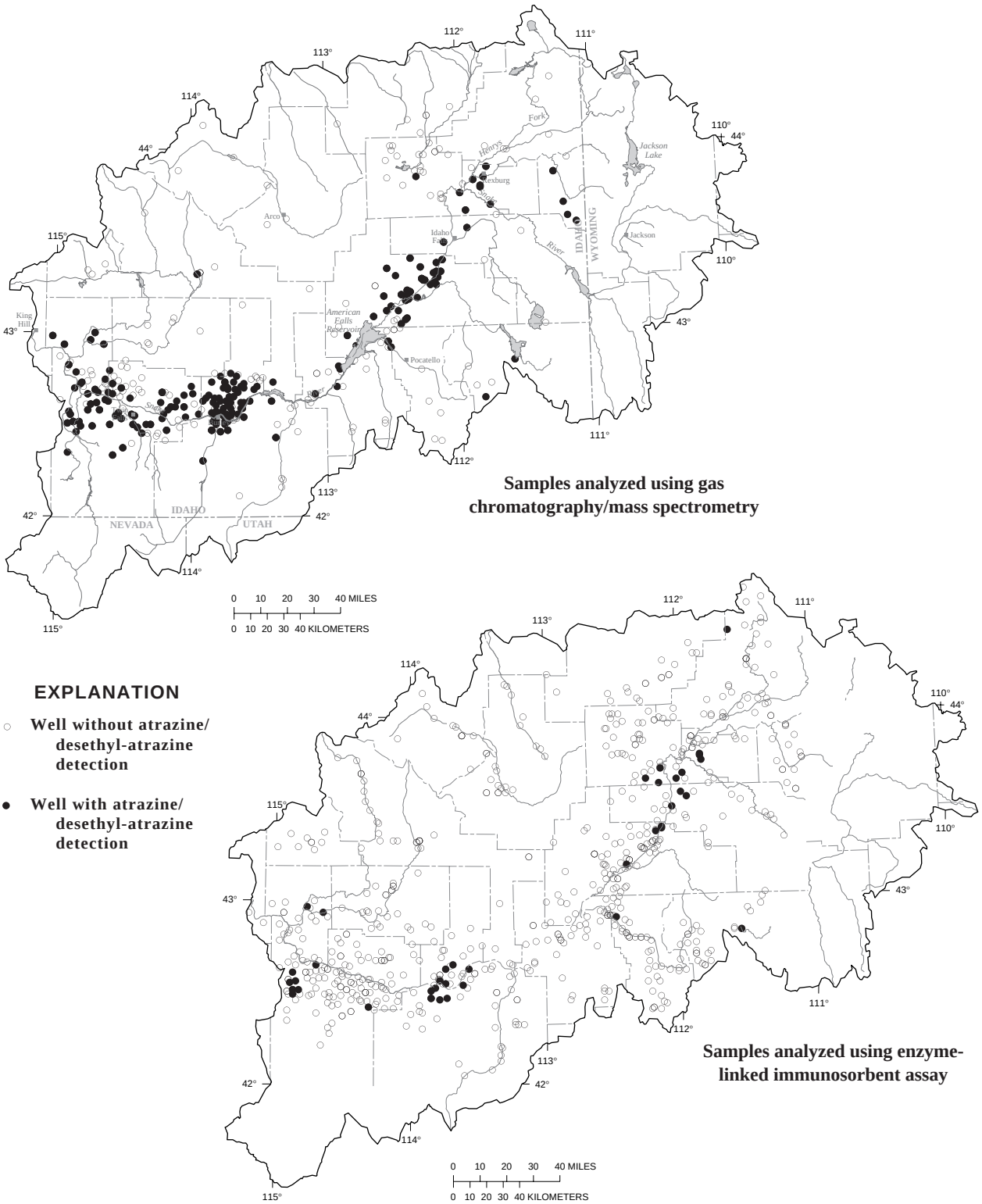

Figure 4. Ground-water samples with and without atrazine/desethyl-atrazine detections in the Idaho part of the upper Snake River Basin. (Samples analyzed using gas chromatography/mass spectrometry were collected for the Idaho Statewide Ground-Water Monitoring Program and the U.S. Geological Survey National Water-Quality Assessment Program, 1993–96. Samples analyzed using enzyme-linked immunosorbent assay method were collected for the Idaho Statewide Ground-Water Monitoring Program, 1993–96)

or geographic areas where water-quality problems may exist or be emerging (Idaho Department of Water Resources, 1991; Neely and Crockett, 1992; Neely, 1994; Crockett, 1995). Water-quality data generated by the program are stored in the USGS National Water Information System data base and the IDWR Environmental Data Management System data base. The first samples were collected from 97 wells statewide in the summer of 1990. During 1991–94, approximately 400 additional wells were sampled each year, forming a network of approximately 1,600 wells total. Beginning in 1995, the wells sampled in 1991 were resampled as part of the trend-monitoring phase of the project. During this phase, most of the 1,600 wells will be sampled once every 4 years, and a subset will be sampled annually. Data collected in 1993–96 (fig. 4) were evaluated for this study to cover a 4-year sampling cycle of the ISGWMP.

Wells were selected for the ISGWMP using a statistically based stratified-random approach. The State was subdivided into 22 hydrogeologic subareas on the basis of aquifer type, water chemistry, and ground-water flow characteristics (Neely and Crockett, 1992). Ten of these subareas are in the Idaho part of the USNK.

The number of wells in each hydrogeologic subarea was determined using the Neyman Optimal Allocation method (Snedecor and Cochran, 1967). This method takes into account the human population within each subarea, the size of the subarea, and the variability of water quality based on specific conductance. Subareas with the most wells sampled were those with the largest human population, largest area, and most variation in water quality.

Sections of the township-range-section coordinate system within each subarea were selected randomly. Only wells that met the following criteria were selected for sampling: (1) known well depth, (2) existence of driller's record, (3) operational pump, and (4) completed in only one aquifer. Water from wells selected is used for a wide variety of purposes, including irrigation, domestic, commercial, stock, or public supply (fig. 5).

Samples for the ISGWMP were collected by USGS personnel, and most samples were analyzed at the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo. Wells were purged prior to sampling until field parameters of specific conductance, pH, and temperature stabilized (at least 15 minutes).

U.S. Geological Survey National Water-Quality Assessment Program

Water samples from 104 wells in Cassia, Jerome, Gooding, Lincoln, and Minidoka Counties were collected as part of the USGS NAWQA Program, 1993–95 (Rupert, 1997). A systematic method was used to select wells sampled; sections of the township-range-section coordinate system were selected randomly using a computer program developed by Scott (1990). All wells in each selected section were evaluated for their suitability for sampling. Well selection criteria included (1) existence of a driller's record, (2) a good surface seal, (3) a short plumbing line, (4) a sampling port upflow from any pressure tank or treatment equipment, (5) permission to sample from the well owner, and (6) access for water-level measurement.

Samples were collected using vehicles and equipment dedicated for water-quality sampling. In addition to the well plumbing system, samples contacted only teflon hoses and stainless-steel connectors. Enclosed sampling and preservation chambers were used to isolate samples from potential atmospheric contamination. Wells were purged for at least 25 minutes prior to sampling. Field measurements of dissolved oxygen, pH, specific conductance, temperature, and turbidity were observed during purging; samples were collected after three consecutive measurements, 5 minutes apart, showed no change. All samples were analyzed by the USGS NWQL in Arvada, Colo.

Pesticide Analytical Methods

GC/MS and ELISA analytical methods were used to determine pesticide concentrations in ground water for this study (table 1). The GC/MS method started with solid-phase extraction of analytes followed by GC/MS analysis at the NWQL (Zaugg and others, 1995). Samples were filtered through a 0.45-µm baked glass fiber filter and concentrated on a solid-phase extraction cartridge. The analytes then were eluted from the cartridge using hexane-isopropanol and analyzed by capillary-column GC/MS. The reporting limit for atrazine using the GC/MS method is 0.001 µg/L. All samples collected as part of the NAWQA Program were analyzed with this method, whereas only a subset of samples collected as part of the ISGWMP were similarly analyzed. This subset of ISGWMP wells was selected ran-

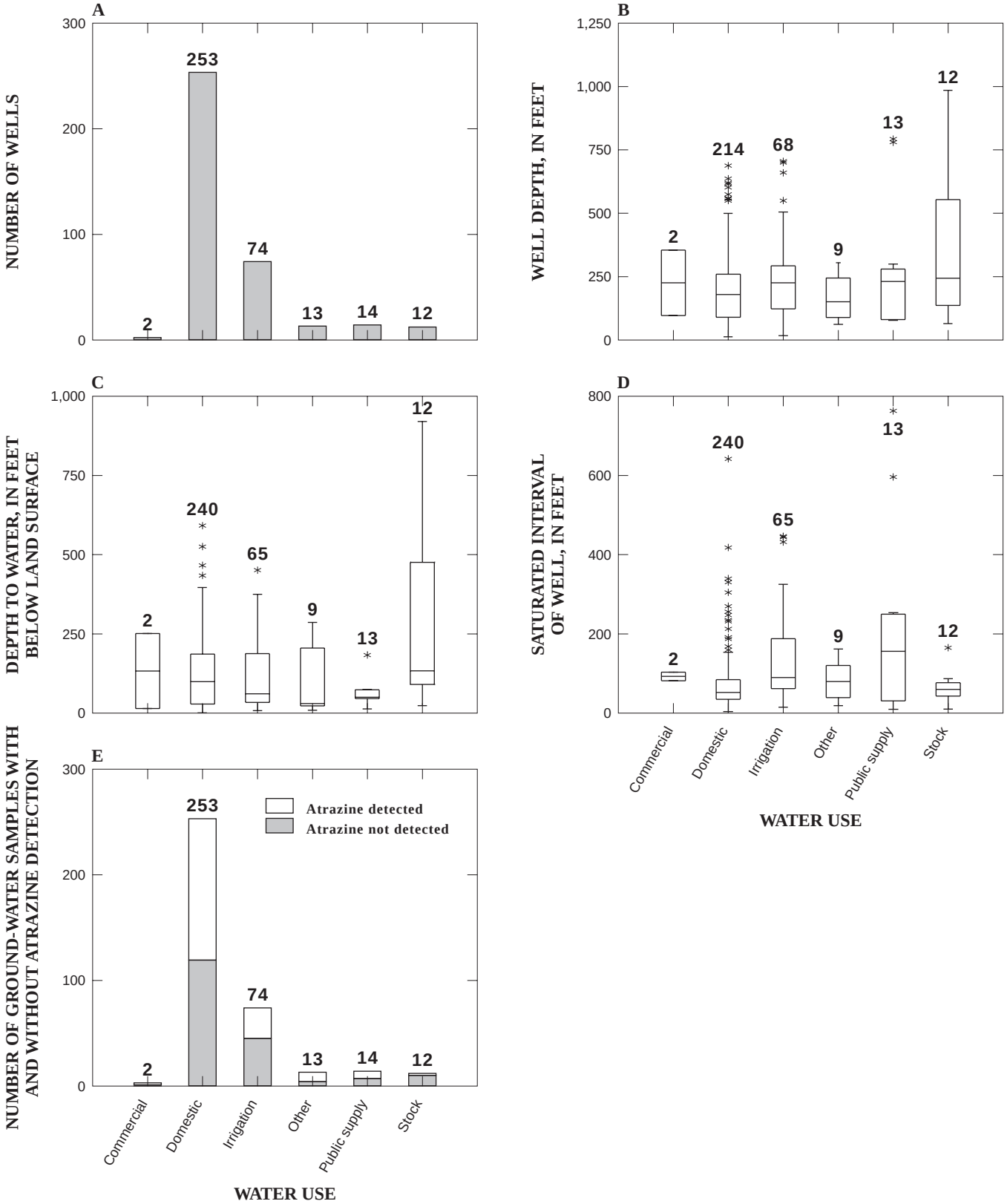

Figure 5. Relations between water use and well depth, depth to water, saturated interval of well, and number of ground-water samples with and without atrazine detections in the Idaho part of the upper Snake River Basin, 1993–96.

Table 1. Nitrite plus nitrate as nitrogen and selected pesticides in ground water in the Idaho part of the upper Snake River Basin, 1993–96

[Data were collected as part of the Idaho Statewide Ground-Water Quality Monitoring Program (ISGWMP), and the USGS National Water-Quality Assessment Program, 1993–96; concentrations of nitrite plus nitrate as nitrogen (NO_2+NO_3–N) are in milligrams per liter; concentrations of alachlor, atrazine, desethyl-atrazine, cyanazine, metolachlor, and simazine are in micrograms per liter; GC/MS, analyzed using gas chromatography/mass spectrometry by the U.S. Geological Survey National Water Quality Laboratory; ELISA, analyzed using enzyme-linked immunosorbent assay (immunoassay) by the ISGWMP; No., number; NA, not applicable; <, less than; e, laboratory estimate; MCL, maximum contaminant level; HA, health advisory level; RSD, risk-specific dose; —, no standard available]

Constituent	Method of analysis		No. of wells sampled	No. of samples with detections	Minimum reporting level	Minimum concentration measured	Percentile					Maximum concentration measured	MCL, HA, or RSD
	GC/MS	ELISA					10	25	50	75	90		
Nitrite plus nitrate, dissolved, as nitrogen (NO_2+NO_3–N)	NA	NA	808	766	0.05	<0.05	0.23	0.68	1.5	3.4	6.0	78	10
Alachlor	X		369	3	.002	<.002	<.002	<.002	<.002	<.002	<.002	.055	2
Alachlor		X	695	4	.05	<.05	<.05	<.05	<.05	<.05	<.05	.45	2
Atrazine	X		369	184	.001	<.001	<.001	<.001	.001	.008	.033	1.27	3
Atrazine, desethyl	X		369	173	e.002	<.002	<.002	<.002	<.002	e.005	e.017	e.287	—
Atrazine		X	695	41	.046	<.046	<.046	<.046	<.046	<.046	<.046	1.71	3
Cyanazine	X		369	0	.004	<.004	<.004	<.004	<.004	<.004	<.004	.013	1
Cyanazine		X	552	5	.035	<.035	<.035	<.035	<.035	<.035	<.035	.15	1
Metolachlor	X		369	14	.002	<.002	<.002	<.002	<.002	<.002	<.002	.16	100
Metolachlor		X	695	2	.05	<.05	<.05	<.05	<.05	<.05	<.05	.2	100
Simazine	X		369	72	.005	<.005	<.005	<.005	<.005	<.005	.007	.39	4
Simazine		X	191	7	.03	<.03	<.03	<.03	<.03	<.03	<.03	1.18	4

domly from the total population of ISGWMP wells in the study area.

The ELISA method is an enzyme-linked immunosorbent assay (ELISA) (Vanderlaan and others, 1990) and was performed on unfiltered samples using a spectrophotometer at a bench laboratory at the IDWR. The ELISA method is designed to measure atrazine concentrations but also has cross reactivity to many different triazine compounds, including desethyl-atrazine, ametryn, cyanazine, propazine, prometon, simazine, terbutryn, and terbutylazine. If more than one of these compounds are present in a sample, the ELISA method will measure the additive concentrations of all the compounds. A disadvantage of the ELISA method is that the reporting limit for atrazine (0.046 µg/L) is much higher than the GC/MS method reporting limit (0.001 µg/L) (table 1). Almost every sample collected for the ISGWMP was analyzed with the ELISA method; none of the wells sampled for the NAWQA Program were analyzed with this method.

Quality Assurance

Quality-assurance and quality-control (QA/QC) practices for samples analyzed using the GC/MS method included equipment blank, spike, and spike replicate samples. Equipment blanks help evaluate whether samples are contaminated by sampling equipment. Spike and spike replicate samples help define the accuracy (bias) and precision (variation) of the sampling methods and laboratory analyses. None of the equipment blanks contained detectable concentrations of pesticides (Ott, 1998, table 2). Spike and spike replicate atrazine samples had 97 percent mean recoveries with 14 percent standard deviation (Ott, 1998, table 8). These QA/QC data suggest that all sampling and analytical methods were acceptable.

The NWQL maintains its own internal program of blank, replicate, and spike samples for USGS Laboratory Schedule 2001 to assure accurate analysis of water-quality samples (Pritt and Raese, 1995). The Quality Assurance Unit of the NWQL routinely submits blind reference and blank samples to the NWQL. The USGS Branch of Technical Development and Quality Systems, which is independent of the NWQL, also submits blind samples to the NWQL. These data were all within acceptable limits (within two standard deviations of the expected mean).

The field QA/QC practices for the ELISA samples included replicate samples at approximately 5 percent of the sites. Laboratory QA/QC practices included 10 percent laboratory replicate samples and two spikes

for every "batch" of 10 to 60 samples. Water samples with a positive detection were reanalyzed for confirmation. These data suggest they are within acceptable limits (Janet Crockett, Idaho Department of Water Resources, oral commun., 1998).

Pesticide Detections in Ground Water

Ground-water quality data used in this study (Harenberg and others, 1993, 1994; Brennan and others, 1995, 1996; Ott, 1997) provided a good characterization of the spatial distribution and concentrations of NO_2+NO_3–N and pesticides in the basin (fig. 4, table 1). The random well selection process used for the ISGWMP and NAWQA Program provided a wide distribution of wells throughout the basin and produced data suitable for statistical analysis. Of the wells sampled for atrazine analysis using the GC/MS method, 69 percent were for domestic use, 20 percent for irrigation, 3 percent for stock, 4 percent for public supply, 1 percent for commercial, and 3 percent for other uses (fig. 5A). Wells were 14 to 985 ft deep; median well depth was 185 ft (fig. 5B). Depth to water was 0 to 920 ft; median depth was 87 ft (fig. 5C). Saturated interval in wells, or interval between the water table and the bottom of the well, was 4 to 763 ft; median saturated interval was 61 ft (fig. 5D).

Atrazine and desethyl-atrazine were the most commonly detected pesticide compounds, followed by simazine, metolachlor, and alachlor (table 1). No pesticide detections exceeded maximum contaminant levels or health advisories. Atrazine was detected most frequently in water from domestic wells (fig. 5E). Most atrazine detections were in the central part of the USNK near the Snake River (fig. 4). Samples analyzed using the GC/MS method had a greater frequency of atrazine detections than those analyzed using the ELISA method, which has lower reporting levels. All samples with metolachlor or simazine detections also had atrazine or desethyl-atrazine detections.

RELATIONS OF ATRAZINE CONCENTRATIONS DETERMINED USING THE GAS CHROMATOGRAPHY/MASS SPECTROMETRY METHOD WITH CONCENTRATIONS DETERMINED USING THE ENZYME-LINKED IMMUNOSORBENT ASSAY METHOD

To examine the relation between GC/MS- and ELISA-determined atrazine concentrations, samples analyzed by both methods were tested using the Spearman rank-order test (Ott, 1993, p. 465). Spearman rank-order test measures whether y increases (or decreases) with x, even when the relation between y and x is not necessarily linear. For instance, Spearman rank-order test can determine whether atrazine concentrations determined using the GC/MS method are significantly correlated with atrazine concentrations determined using the ELISA method. Spearman rank-order test calculates two parameters—a p-value and a Spearman correlation. The relation is significant if the p-value is less than 0.05 and Spearman correlation is near 1; the relation is not significant if the p-value is greater than 0.05 and the Spearman correlation is near 0. A Spearman correlation matrix (matrix showing relations of all variables) can be calculated if there are more than two variables.

For every sample in which atrazine was detected using the GC/MS method, there was a corresponding detection using the ELISA method. A regression of atrazine concentrations using the GC/MS and ELISA methods (fig. 6) resulted in an r-squared (linear correlation coefficient) value of 0.955, suggesting consistent performance by both methods at the concentrations measured. The slope of this regression was 0.797, suggesting the ELISA method produced higher values (high bias). A potential explanation for this high bias may be the cross reactivity of the ELISA method to other pesticide compounds. The ELISA method also showed a positive detection to desethyl-atrazine and simazine, both of which were detected in most of the corresponding GC/MS analyses. Concentrations of atrazine, desethyl-atrazine, and simazine analyzed by the GC/MS method were added together and compared with the concentrations analyzed by the ELISA method. A slightly better correlation was obtained (slope = 0.857), but the ELISA data still showed a high bias when compared with the GC/MS data. The GC/MS and ELISA data also were positively correlated by using Spearman rank-order test; the p-value was less than 0.001 and the Spearman value was 0.906. In summary, there is a linear relation between detections produced using both the GC/MS and ELISA methods, but the ELISA method produced higher values (had a high bias).

Goolsby and others (1991) also compared GC/MS-determined atrazine data with ELISA-determined atrazine data. Their results suggested a good correlation for concentrations below 0.2 µg/L, but relations became nonlinear when concentrations exceeded

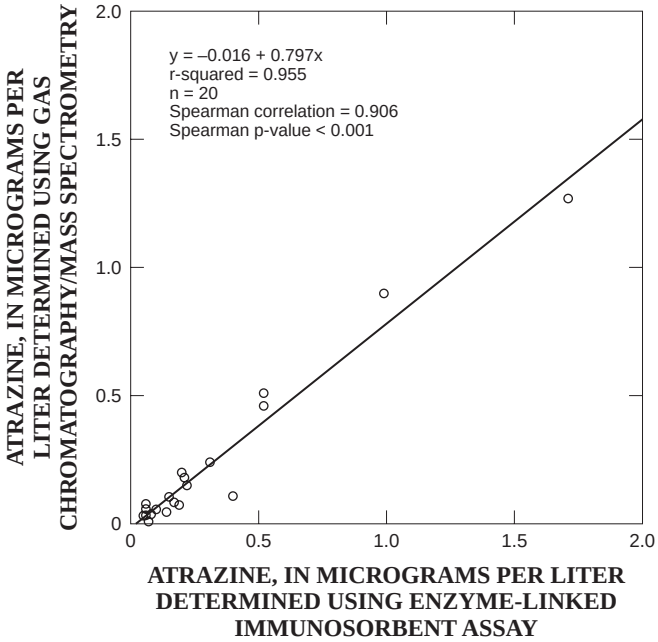

Figure 6. Relation of atrazine concentrations determined using gas chromatography/mass spectrometry with concentrations determined using enzyme-linked immunosorbent assay.

0.2 µg/L. Only 10 out of 184 GC/MS-determined atrazine detections in this study exceeded 0.2 µg/L. Hottenstein and others (1996) observed a good correlation of results between GC/MS and ELISA methods; sample recoveries averaged 100 percent ±8 percent and the correlation coefficient (r) was 0.993. They observed that the ELISA method produced higher values than did the GC/MS method and attributed the difference to loss during sample extraction and concentration steps of the GC/MS method, or the presence of cross-reacting compounds in the samples. Thurman and others (1990) also noted a correlation between GC/MS and ELISA methods, with a correlation coefficient (r) of 0.99.

The GC/MS method also detects desethyl-atrazine, a breakdown product of atrazine. Desethyl-atrazine has a low laboratory recovery because of its poor absorbency on the solid-phase extraction cartridge (Zaugg and others, 1995, p. 35). Desethyl-atrazine also is detected using the ELISA method because of its cross reactivity. Desethyl-atrazine was detected using both the GC/MS and ELISA methods whenever its concentration exceeded the ELISA reporting limit; however, there was a large variation in concentrations. Regression analysis produced an r-squared value of 0.468, and Spearman's rank-order test produced a correlation value of 0.476. This large variation in concentrations presumably is due to the poor laboratory recovery by the GC/MS method.

Concentrations of alachlor, metolachlor, and simazine determined using GC/MS and ELISA methods were compared (table 1). Alachlor was detected in only one sample using both GC/MS (0.055 µg/L) and ELISA (0.16 µg/L) methods. The same was true for metolachlor, which had a GC/MS-determined concentration of 0.16 µg/L and an ELISA-determined concentration of 0.18 µg/L. Simazine was detected by both methods in five samples; ELISA-determined concentrations were higher than corresponding GC/MS-determined concentrations.

RELATIONS OF ATRAZINE CONCENTRATIONS WITH NITRITE PLUS NITRATE AS NITROGEN

Relations between GC/MS-determined atrazine concentrations and NO_2+NO_3–N concentrations were examined to determine whether NO_2+NO_3–N data may be used as a surrogate for atrazine data in subsequent correlations with hydrogeologic and anthropogenic factors. Atrazine concentrations determined using the ELISA method and desethyl-atrazine concentrations determined using the GC/MS method were not evaluated because of their respective high bias and high variability. A regression of atrazine and NO_2+NO_3–N concentrations produced an r-squared value less than 0.001, and a Spearman rank-order test produced a Spearman correlation of 0.352 and a p-value less than 0.001 (fig. 7). This suggests a poor correlation of atrazine concentrations to NO_2+NO_3–N concentrations. These results are consistent with those of Barbash and Resek (1996), who determined that NO_2+NO_3–N is generally a poor predictor of pesticide occurrence. Therefore, for this study, NO_2+NO_3–N was not used as a substitute for atrazine in correlations with hydrogeologic and anthropogenic factors.

HYDROGEOLOGIC AND ANTHROPOGENIC DATA

Hydrogeologic and anthropogenic data used in this study included atrazine use, depth to ground water, geology, land use, precipitation, soils, and well depth. These data were available in GIS format from a variety of sources.

Gianessi and Anderson (1995) estimated atrazine use on the basis of suggested application rates and the acres of corn grown in each of the 22 counties in the Idaho part of the USNK. These data were used in this study because data were not available on sales or use of atrazine in the study area. A major disadvantage of Gianessi and Anderson's approach is that data were available only at a county level. Conversations with local Cooperative Extension System personnel indicated that substantial amounts of atrazine also may be used for noncrop purposes such as roadside weed control. Several formulations that contain atrazine as an active ingredient are available for noncrop weed control. However, conversations with the Idaho Department of Transportation and county weed control officers have indicated that they have not used atrazine for roadside weed control since the mid-1970's because kochia (*Kochia scoparia*), a major problem weed in Idaho, became resistant to atrazine. Instead, diuron, bromacil, 2-4-D, and (or) dicamba are used for this purpose. Although reported use of atrazine by governmental agencies for noncrop purposes is minor, atrazine detections where little or no corn is grown suggests some use of atrazine by nongovernmental entities.

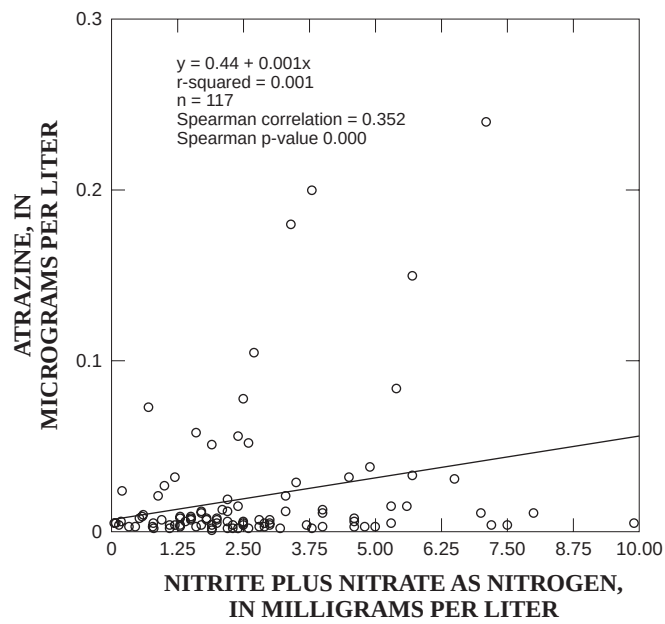

Figure 7. Relation of atrazine concentrations determined using gas chromatography/mass spectrometry with nitrite plus nitrate as nitrogen concentrations in ground water in the Idaho part of the upper Snake River Basin.

Depth to first-encountered ground water in the eastern Snake River Plain was mapped by Maupin (1992), who divided depth to water into five categories; 0 to 100, 101 to 300, 301 to 600, 601 to 900, and greater than 900 ft. Depth to first-encountered ground water in the upper Big Wood, Big Lost, Little Lost, and Birch Creek valleys (fig. 1) was mapped by Berenbrock and others (1994), who divided depth to water into four categories; 0 to 50, 51 to 100, 101 to 150, and greater than 150 ft. Data from both studies were combined into one GIS coverage. Data from the study by Berenbrock and others (1994) took precedence in areas common to both because Berenbrock's data are more recent and were mapped at a larger scale (greater detail).

Land-use data from the IDWR and the Bureau of Reclamation (BOR) were evaluated for this study. IDWR combined data from (1) a map denoting vegetation types, (2) a map differentiating between sprinkler- and gravity-fed irrigation, and (3) a map differentiating dryland agriculture from irrigated agriculture (Rupert and others, 1991, p. 12). Dewayne McAndrews (Bureau of Reclamation, unpublished data, 1987, 1992) mapped land cover using 1:40,000-scale, high-altitude aerial photographs taken in 1987 and field checked in 1992. Each land-use data set had its own unique advantages. The IDWR data were mapped at a small scale (1:100,000) and included classifications for lava flows, dryland agriculture, rangeland, and forest land. The BOR data were mapped at a larger scale (1:40,000) but combined forest, lava flows, and rangeland into one classification, native lands. The BOR data have the advantage of being field checked and differentiating as to sprinkler or gravity irrigation. Both sets of land-use data were evaluated to determine which produced the best correlation with atrazine/DEA detections in ground water.

Precipitation data for 1961 through 1990 (fig. 3) were obtained from an isohyetal map (Molnau, 1995). Surficial geology was mapped by Whitehead (1986) and later digitized into GIS format.

Soils data (fig. 8) were obtained from the State Soil Geographic Data Base (STATSGO) and developed by the U.S. Natural Resources Conservation Service (U.S. Department of Agriculture, 1991). STATSGO soils data were aggregated from many large-scale soil surveys (1:12,000 to 1:62,500) into one large data base at an approximate scale of 1:250,000 (U.S. Department of Agriculture, 1991, p. 1, 2). Soil criteria evaluated during this study were clay content, drainage, hardpan occurrence, hydrologic group, percentage of organic matter, and permeability.

Figure 8 Hydrologic group soil classifications for the Idaho part of the upper Snake River Basin.
(60 k)

Can be accessed from the home page for this report.

Well depth was retrieved from the USGS data base. These data then were merged with the GIS coverages containing ground-water quality information.

ESTIMATING THE PROBABILITY OF DETECTING ATRAZINE/DESETHYL-ATRAZINE IN GROUND WATER

Maps showing the probability of detecting atrazine/DEA in ground water were constructed using a GIS and logistic regression statistical methods. Hosmer and Lemeshow (1989, p. 82–91) provided an overview of how to develop a predictive model using logistic regression.

The probability maps were produced as follows: (1) Ground-water monitoring data were overlaid with hydrogeologic and anthropogenic data using a GIS to produce a data set in which each well had corresponding data on atrazine use, depth to ground water, geology, land use, precipitation, soils, and well depth. These data then were downloaded to a statistical software package for analysis by logistic regression. (2) Individual (univariate) relations between atrazine/DEA in ground water and atrazine use, depth to ground water, geology, land use, precipitation, soils, and well depth data were evaluated to identify those independent variables significantly related to atrazine/DEA detections. (3) Several preliminary multivariate models with various combinations of independent variables were constructed. (4) The multivariate models which best predicted the presence of atrazine/DEA in ground water were selected. (5) The multivariate models were entered into the GIS and the probability maps were constructed.

Data collected as part of the ISGWMP and NAWQA Program, and analyzed using GC/MS analytical methods, were used to calibrate the logistic regression models. Data collected for the ISGWMP and analyzed using the ELISA method were used to verify the performance of the models. All data on atrazine/DEA concentrations in ground water were converted to detection/nondetection status to satisfy the input data requirements of logistic regression. To produce the largest possible sample set, atrazine/DEA data analyzed using the GC/MS method were combined into one dependent variable for model calibration.

Atrazine use, depth to ground water, precipitation, soil clay content, percent of soil organic matter, and soil permeability were modeled as continuous variables. Depth to water and precipitation values were determined from contour maps; values were set at half of the contour interval. For instance, wells lying between precipitation contour intervals of 10 and 20 in. were assigned precipitation values of 15 in. Because of their categorical nature, geology, land use, soil drainage, and soil hydrologic group were modeled as discrete (design) variables; the reference group was assigned to a category that had no atrazine/DEA detections. For example, no atrazine/DEA was detected in water from wells completed in sedimentary and metamorphic rocks of pre-Cretaceous age, so that unit was used as the reference group.

Previous authors converted land-use data to percent of a particular land use within a certain distance from a well (Eckhardt and Stackelberg, 1995; Tesoriero and Voss, 1997) to address the patchwork nature of land use in highly developed and highly diverse locations. These conversions were not needed for this study because of the homogeneous nature of land use in the USNK.

Statistical Methods and Regression Models

Logistic regression (Hosmer and Lemeshow, 1989) was used to develop algorithms that predict the probability of detecting atrazine/DEA in ground water by quantifying relations between ground-water quality and hydrogeologic and anthropogenic data. Logistic regression is conceptually similar to multiple regression, because relations between one dependent variable and several independent variables are evaluated. In logistic regression, the dependent variable (for this study, atrazine/DEA detection) is transformed to a binary variable (detection or nondetection). A major advantage of logistic regression over multiple regression is that it does not require normally distributed data; data transformations to approximate normality are not required.

Logistic regression calculates several statistical parameters that determine the predictive success of the model. The log-likelihood ratio measures the success of the model as a whole by comparing observed with predicted values (Hosmer and Lemeshow, 1989, p. 13); specifically, it tests whether model coefficients are significantly different from 0. The most effective model is the one with the highest log-likelihood ratio, taking into account the number of independent variables

(degrees of freedom) used in the model. The log-likelihood ratio follows a chi-squared distribution, and the computed p-value indicates whether model coefficients are significantly different from zero. In other words, the computed p-value is the significance level attained by the data; the smallest p-value suggests the best model. A p-value of 0.05 suggests a significance level of 95 percent; a p-value of 0.01 suggests a significance level of 99 percent. McFadden's rho-squared (SPSS Inc., 1997, p. 86) is a transformation of the log-likelihood statistic and is intended to mimic the r-squared of linear regression. Rho-squared is always between 0 and 1; a rho-squared approaching 1 corresponds to more significant results. Rho-squared tends to be smaller than r-squared, so a small number does not necessarily imply a poor fit. Values between 0.20 and 0.40 suggest good results (SPSS Inc., 1997, p. 86). The percent of correct predictions is a measure of how many actual atrazine/DEA detections and nondetections are present, compared with what was predicted by the model; the largest number denotes the best model. The percent correct responses is calculated as the number of observed detections predicted by the model as detections, plus the number of observed nondetections predicted as nondetections, divided by the combined number of observed detections and nondetections (Nolan and Clark, 1997, p. 855). The odds ratio is a measure of the relative influence of an independent variable on the model; higher odds ratios suggest a greater effect of that particular independent variable on the model. The partial-likelihood ratio was used to compare nested models to determine the significance of adding one or more new variables (Helsel and Hirsch, 1992; Nolan and Clark, 1997). A nested model contains all of the independent variables in the original model, plus one or more additional independent variables. To determine whether the model is improved by adding the independent variable, the logistic regression model is calculated without that new variable. Logistic regression calculates a partial-likelihood ratio. The logistic regression model then is rerun, this time with the additional new independent variable; the second model also calculates a partial-likelihood ratio. The difference in partial-likelihood ratios between the two models is calculated and a chi-squared approximation is calculated with degrees of freedom equal to the number of additional variables in the new model. If the p-value from the chi-squared distribution is less than 0.05, the model has been significantly improved at the 95-percent significance level.

Using logistic regression, a model is generated that predicts the probability (P) of detecting atrazine/DEA in ground water as follows:

$$Prob = \frac{e^{(a + b_1(AU) + b_2(LU) + b_3(P) + b_4(S) + b_5(W))}}{1 + e^{(a + b_1(AU) + b_2(LU) + b_3(P) + b_4(S) + b_5(W))}} \quad (1)$$

where

$Prob$ = the probability of detecting atrazine/DEA in ground water;
a = intercept;
b_1 = slope coefficient for atrazine use;
AU = atrazine use, in pounds of active ingredient applied per county;
b_2 = slope coefficient for land use;
LU = land use;
b_3 = slope coefficient for precipitation;
P = precipitation, in inches per year;
b_4 = slope coefficient for soils;
S = soils;
b_5 = slope coefficient for well depth; and
W = well depth.

Kruskal-Wallis and Wilcoxon rank-sum nonparametric statistical tests (Ott, 1993, p. 279, 793) were used to determine whether there were statistically significant differences in concentrations among the various data groups; for example, whether probability ratings were significantly higher for water from wells with atrazine/DEA detections than for water from wells without atrazine/DEA detections. Both tests calculate a p-value; if the resulting p-value is less than 0.05, the data sets are significantly different at the 95-percent significance level. If the p-value is less than 0.01, the data sets are significantly different at the 99-percent significance level. In this study, the 95-percent significance level was the cutoff value for determining whether the data sets were significantly different.

Univariate Analysis of Each Variable

Individual (univariate) relations between atrazine/DEA detections and atrazine use, depth to water, geology, land use, precipitation, soils, and well depth were evaluated to make an initial determination of which variables were significantly related. Logistic regression, Spearman rank-order test, and Wilcoxon statistical tests were performed on all data. The log-likelihood and Wilcoxon rank-sum test p-values for all independent variables except hardpan occurrence and permeability were less than 0.05, suggesting that these variables are significantly related to atrazine/DEA detec-

tions (table 2). Hardpan occurrence and soil permeability also had the smallest Spearman correlations. Hardpan occurrence and soil permeability were omitted from further analysis and all other independent variables were evaluated further in the multivariate analysis.

Multivariate Analysis

Multivariate analysis incorporates several independent variables into the logistic regression model. All possible combinations of independent variables were evaluated to develop the most effective models. The models were built by including each individual variable in the model and evaluating the resulting test statistics. All models were built by first including land use in the model, and then individually adding the other independent variables to test their significance. Land use was the first variable included because it had the most significant correlation with atrazine/DEA detections in the univariate analysis (table 2). One of the most useful methods to determine whether addition of a particular independent variable made a significant improvement to the model was to compare the partial-likelihood ratios calculated before and after addition of that variable to the model. As described in the statistical methods section, the independent variable was determined to significantly improve the model if the chi-squared p-value calculated from the difference of the partial-likelihood ratios was less than 0.05.

Comparisons Among the Preliminary Logistic Regression Models

Four preliminary multivariate models were developed. Models 1 and 2 included land-use data developed by the BOR; models 3 and 4 included land-use data developed by the IDWR (table 3). Models 1 and 3 did not include atrazine-use data, whereas models 2 and 4 did.

Land use, precipitation, soil hydrologic group, and well depth significantly improved the ability of all the models to predict the probability of atrazine/DEA in ground water (table 3). Depth to ground water, geology, soil clay content, soil drainage, and soil organic matter did not significantly improve the effectiveness of any of the multivariate models. All independent variables significantly related using the BOR land-use data also were significantly related using the IDWR land-use data. No significant interactions were observed between any of the independent variables in any of the models.

All models had low log-likelihood ratio p-values ($p < 0.001$), suggesting significance levels greater than 99 percent (table 4). Of the models that included atrazine use, model 2 had the largest log-likelihood ratio

Table 2. Statistical results from univariate correlations of atrazine/desethyl-atrazine detections in ground water with several independent variables in the Idaho part of the upper Snake River Basin

[BOR, land-use data developed by the Bureau of Reclamation; IDWR, land-use data developed by the Idaho Department of Water Resources; LLR, log-likelihood ratio of logistic regression model; DF, degrees of freedom of log-likelihood ratio; LLR-P, chi-squared p-value calculated from log-likelihood ratio; McF, McFadden's rho-squared calculated with logistic regression; Spear, Spearman correlation; Wil, p-value calculated with Wilcoxon rank-sum test; <, less than]

Independent variable	LLR	DF	LLR-P	McF	Spear	Wil
Atrazine use	8.869	1	0.003	0.017	0.188	< 0.001
Geology	17.467	5	.004	.034	.152	.003
Land use, BOR	50.024	4	< .001	.099	.317	< .001
Land use, IDWR	36.319	5	< .001	.072	.292	< .001
Precipitation	7.857	1	.005	.015	- .103	.039
Soil clay content	7.741	1	.005	.015	- .109	.011
Soil drainage	17.420	4	.002	.034	.154	.001
Soil hardpan	.877	1	.349	.001	.088	.313
Soil hydrologic group	12.238	3	.007	.024	.186	.001
Soil permeability	.562	1	.453	.001	.033	.405
Well depth	21.251	1	< .001	.044	- .237	< .001

Table 3. Summary of independent variables significantly related in multivariate relations with the detection of atrazine/desethyl-atrazine and elevated nitrite plus nitrate as nitrogen concentrations in ground water in the Idaho part of the upper Snake River Basin

[IDWR, land-use data developed by the Idaho Department of Water Resources; BOR, land-use data developed by the Bureau of Reclamation; X, significant relation with atrazine detections in ground water; —, no relation observed; NO_2+NO_3–N, nitrite plus nitrate as nitrogen]

Independent variable	Model 1	Model 2	Model 3	Model 4	NO_2+ NO_3–N
Atrazine use		X		X	
Depth to ground water					X
Geology	—	—	—	—	—
Land use, IDWR			X	X	X
Land use, BOR	X	X			
Precipitation	X	X	X	X	
Soil clay content	—	—	—	—	—
Soil drainage					X
Soil hydrologic group	X	X	X	X	
Soil organic matter content	—	—	—	—	—
Well depth	X	X	X	X	

and the largest McFadden's rho-squared. Taking all these factors into account, model 2 was the most effective in defining the probability of atrazine/DEA detections in ground water. Of the models that did not include atrazine use, model 1 was the most effective because it had the largest log-likelihood ratio and the largest McFadden's rho-squared.

Regressions were made between the percentage of actual atrazine/DEA detections and the predicted probability of atrazine/DEA detections (fig. 9). The percentage of actual atrazine/DEA detections was determined by dividing the probability ratings for the entire study area into groupings of 10 percent (0–10, 10–20, 20–30, and so on). The percentage of atrazine detections within each group then was calculated and included in the regressions shown in figure 9. Of the two models that included atrazine use, model 2 yielded the best results; r-squared was the largest, and slope of the regression line was closer to 1. Of the two models that did not include atrazine use, model 1 yielded the best results; r-squared was the largest and slope of the regression line was closest to 1. Of all four models, model 1 yielded the best results when compared with ground-water quality data.

A Spearman correlation matrix was developed to compare the percentage of actual atrazine/DEA detections with the predicted probability of atrazine/DEA detections (table 4). Of the two models that included atrazine use, model 2 had the largest Spearman correlation; of the two models that did not include atrazine use, model 1 had the largest Spearman correlation.

The Wilcoxon test was used to quantify the differences in probability ratings between water from wells with and without atrazine/DEA detections (table 4, fig. 10). All tests had a p-value less than 0.001, suggesting water from wells with atrazine/DEA detections had higher probability ratings at greater than the 99.9 percent significance level.

As suggested in the preceding discussion, model 1 was the most effective of the models that did not include atrazine-use data in predicting the probability of atrazine/DEA detections in ground water; model 2 was the most effective of the models that included atrazine use. Comparison between models 1 and 2 results demonstrates the effectiveness of adding atrazine use to the model.

Construction of Probability Maps

Maps showing the probability of detecting atrazine/DEA in ground water in the Idaho part of the USNK were constructed by combining the atrazine

Table 4. Statistical results from four preliminary models used to predict atrazine/desethyl-atrazine in ground water in the Idaho part of the upper Snake River Basin

[LLR, log-likelihood ratio of logistic regression model; DF, degrees of freedom of log-likelihood ratio; LLR-P, chi-squared p-value calculated from log-likelihood ratio; McF, McFadden's rho-squared calculated with logistic regression; Spear, Spearman correlation; Spear-P, p-value calculated with Spearman correlation; Wil, p-value calculated with Wilcoxon rank-sum test; BOR, land-use data developed by the Bureau of Reclamation; AU, atrazine use included in the model; IDWR, land-use data developed by the Idaho Department of Water Resources; <, less than]

Model	LLR	DF	LLR-P	McF	Spear	Spear-P	Wil	Comments
1	79	9	< 0.001	0.163	0.404	< 0.001	< 0.001	BOR
2	96	10	<.001	.20	.408	<.001	<.001	BOR, AU
3	69	10	<.001	.142	.348	<.001	<.001	IDWR
4	87	11	<.001	.178	.384	<.001	<.001	IDWR, AU

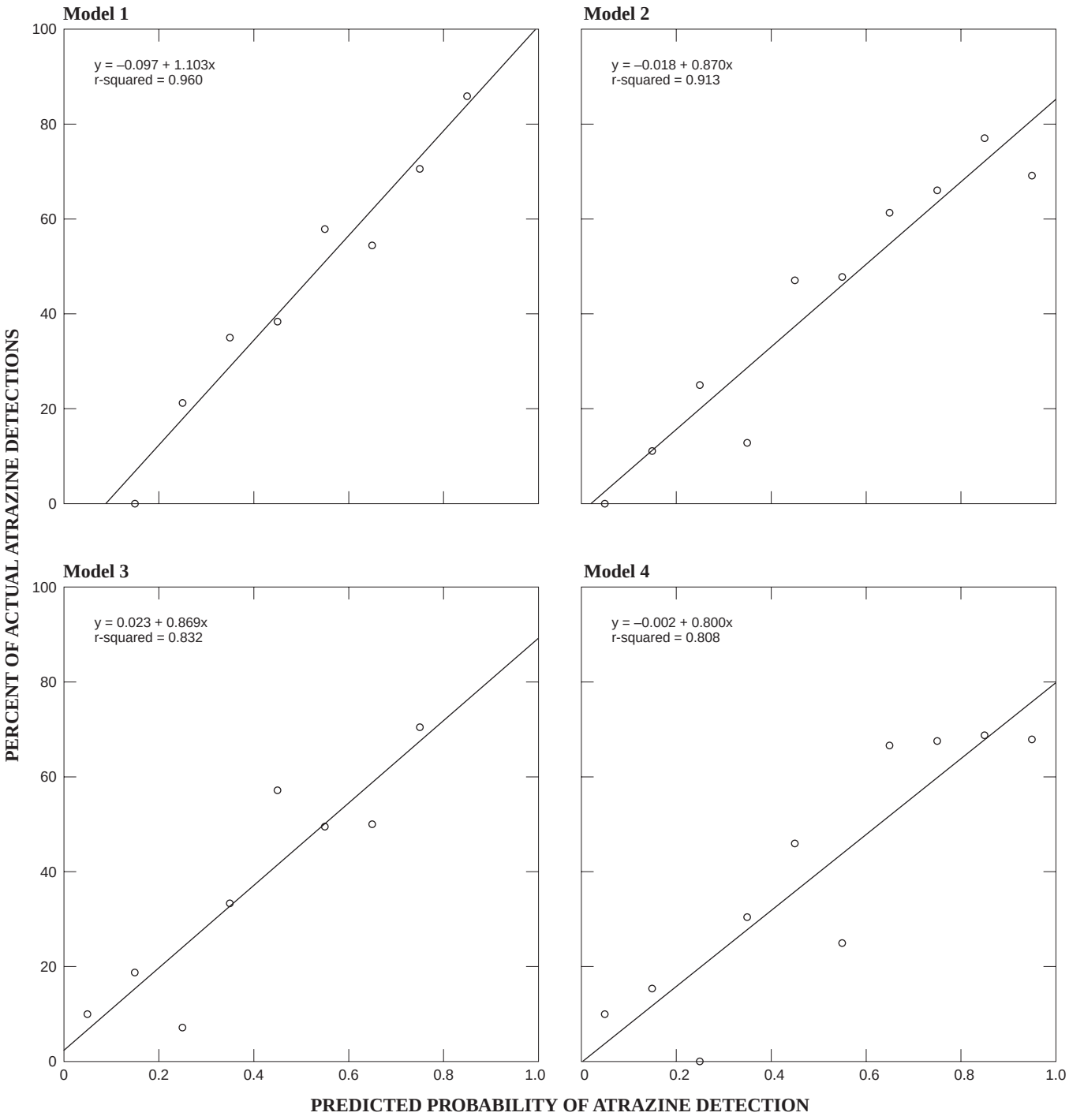

Figure 9. Relations of percent of actual atrazine/desethyl-atrazine detections in ground water with predicted probabilities of detections in the Idaho part of the upper Snake River Basin.

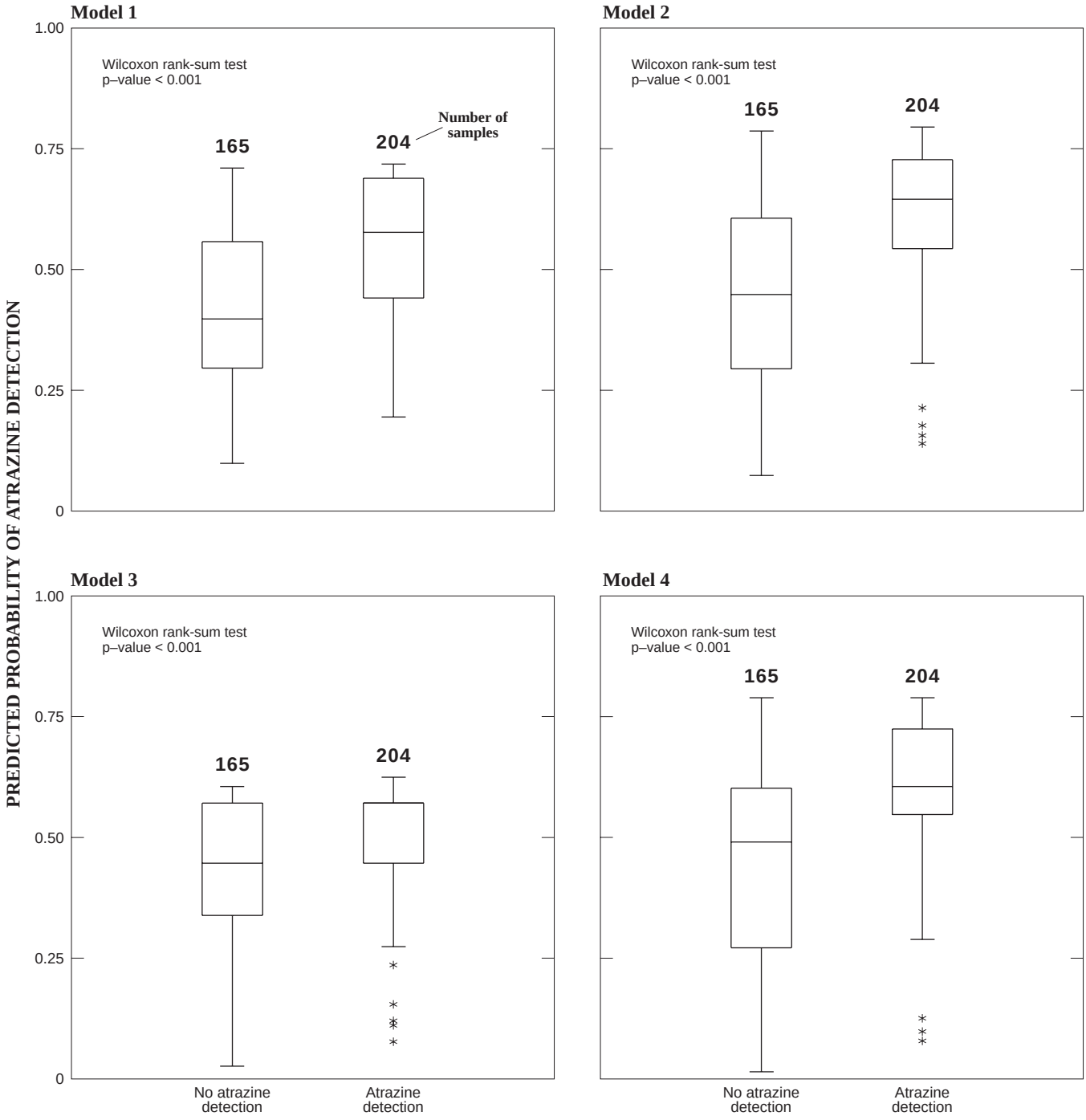

Figure 10. Correlations of predicted probability of detecting atrazine/desethyl-atrazine, determined using gas chromatography/mass spectrometry, with actual detections or nondetections in ground water in the Idaho part of the upper Snake River Basin.

use, land use, precipitation, soils, and well depth data into one master coverage using a GIS. Using equation (1), a probability rating then was calculated for each of the 56,000 resulting polygons to define the maps (pl. 1, fig. 11).

Well depth was set at 150 ft, which is slightly less than the median well depth of 165 ft that was measured in domestic wells evaluated for this study. The same approach was used by Tesoriero and Voss (1997) for NO_2+NO_3–N.

DISCUSSION OF PROBABILITY MAPS

The ideal approach to demonstrate model effectiveness is to compare model results with a second independent set of ground-water monitoring data, similar to what Tesoriero and Voss (1997) demonstrated for NO_2+NO_3–N. Water samples from wells with atrazine detections and analyzed using the ELISA method had significantly higher probability ratings ($p = 0.002$) than samples with no detections (fig. 12). All ELISA data for samples from the same wells used in model calibration were excluded from this comparison to help ensure that the ELISA data represented an independent data set. There were a small number of atrazine/DEA detections in the data analyzed using the ELISA method be-cause of the high reporting limits; this small number of detections precluded more complex correlations be-tween the ELISA data and the probability maps. An alternate approach was attempted to validate the models—the GC/MS data were halved; one-half were used to construct the models, the other half to validate the models. Unfortunately, data were insufficient to complete this approach successfully.

The effectiveness of the probability maps likely would be improved if data on noncrop use of atrazine were available. Correlation of percent atrazine/DEA detections with the 1995 estimates of Gianessi and Anderson showed a good relation at moderate to high use (fig. 13); however, several counties had a high percentage of atrazine/DEA detections, although little or no atrazine/DEA was used for the production of corn. These detections may be due to noncrop use of atrazine in the USNK, as discussed previously.

The BOR land-use data consistently produced more significant relations than the IDWR land-use data produced (table 4). This may be because the BOR data are more accurate in agricultural areas, where most atrazine/DEA detections were located.

The probability maps for model 1 (pl. 1) and model 2 (fig. 11) were developed for well depths of 150 ft; probability ratings decreased by approximately 5 percent in both models 1 and 2 when well depths were increased to 200 ft.

Atrazine/DEA detections were inversely related with precipitation, possibly because corn is grown in lower altitudes where climate is warmer and drier. Rupert (1997) observed no significant relation between precipitation and NO_2+NO_3–N.

Accuracy of the probability maps likely would be improved if (1) larger scale soils data were available in digital form; and (2) additional hydrogeologic data, such as vadose zone characteristics, were included. Some site-specific variables, such as poor well construction and localized spills, were not accounted for in the models.

Previous authors (U.S. Environmental Protection Agency, 1993; Erwin and Tesoriero, 1997; Tesoriero and Voss, 1997) have used the term aquifer sensitivity, or hydrologic susceptibility, to name maps that show the predisposition of areas for ground-water contamination based upon hydrogeologic characteristics such as soil and geology. Taking this definition into account, model 1 (pl. 1) can be considered a sensitivity/susceptibility map. Those same authors defined vulnerability as the combination of sensitivity/susceptibility with additional data on source and amounts of contaminants; therefore, figure 11 can be considered a vulnerability map. The maps produced during this study are termed probability maps because they are based on correlations with actual ground-water quality data, which distinguishes them from vulnerability maps developed using the DRASTIC technique.

It is possible that model 1 (pl. 1) can be used to predict the probability of detecting pesticide compounds other than atrazine/DEA. Table 5 summarizes the pesticide compounds detected in the Idaho part of the USNK in samples collected for the ISGWMP and the NAWQA Program and analyzed using the GC/MS method. Atrazine/DEA was detected in almost 50 percent of the samples. Many samples in which atrazine/DEA was detected also had corresponding detections of other compounds, suggesting that these compounds may behave similarly in the environment. This is particularly true for metolachlor and simazine, which had a high frequency of detection and were always associated with atrazine/DEA. There was partial correlation of atrazine/DEA detections and p,p'DDE, EPTC (Eptam), and metribuzin detections, suggesting that

Figure 11. Probability of detecting atrazine/desethyl-atrazine concentrations greater than 0.001 micrograms per liter in water from wells 150 feet deep using model 2, atrazine use included, in the Idaho part of the upper Snake River Basin. *(60 k)*

Can be accessed from the home page for this report.

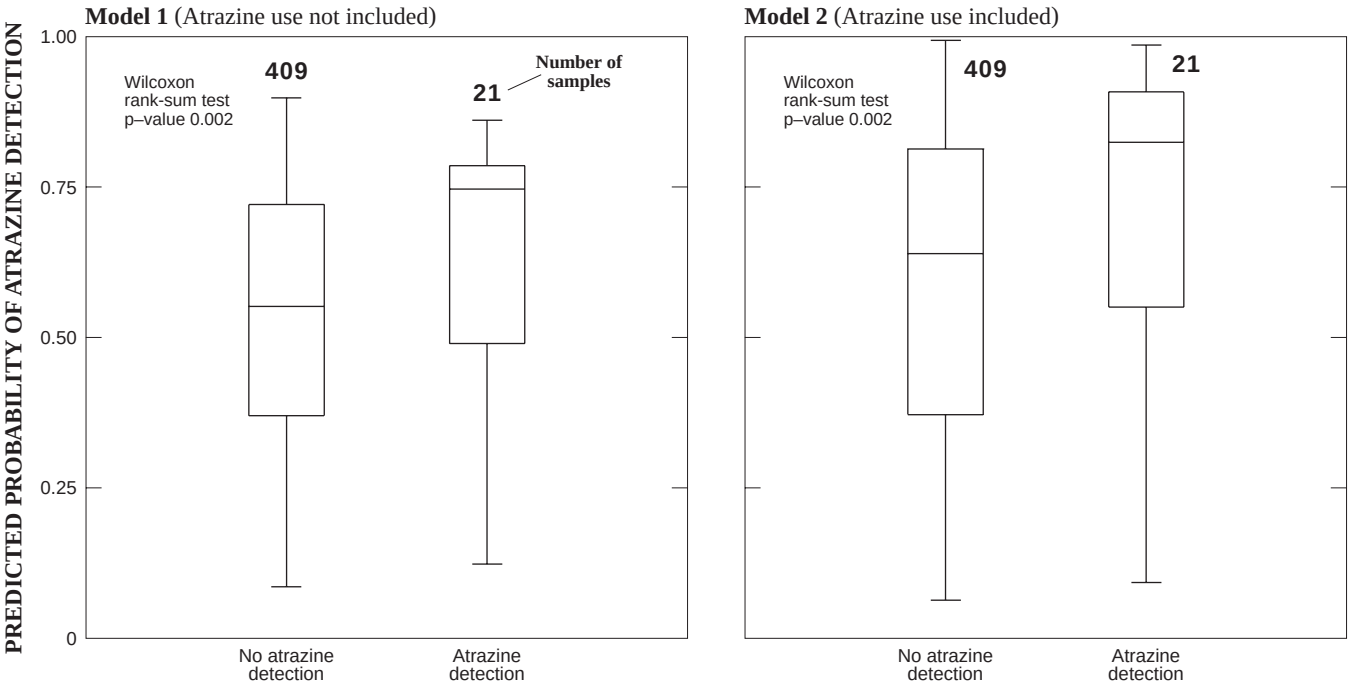

Figure 12. Correlations of predicted probability of detecting atrazine/desethyl-atrazine, determined using enzyme-linked immunosorbent assay, with actual detections or nondetections in ground water in the Idaho part of the upper Snake River Basin.

model 1 is probably a poor predictor of detections of these compounds. The low total number of detections of other compounds made it impossible to determine whether they were associated with atrazine/DEA. Additional comparisons between the occurrence of atrazine/DEA and other pesticide compounds should be made before using model 1 to predict the presence of those compounds. Chemical characteristics of the compounds, such as solubility and sorption coefficient (Kd) also should be taken into account.

Areas near Burley, Jerome County, Minidoka, Mud Lake, Rexburg, and Twin Falls County had high probability ratings (fig. 11, pl. 1), due primarily to a combination of irrigated agricultural land use, small amounts of precipitation, and soils with high infiltration rates. Several of the areas also have a history of high NO_2+NO_3–N concentrations in ground water (Parliman and Young, 1987, 1988, 1989; Young, Parliman, and Jones, 1987; Young, Parliman, and O'Dell, 1987; Rupert, 1994, 1996, 1997).

Model 2 (atrazine use included, fig. 11) results indicated high probability ratings in Jerome, Gooding, and Twin Falls Counties where most corn in the basin is grown. Probability ratings sometimes changed abruptly across county lines because atrazine-use data are available only at a county level. More detailed atrazine-use data would help reduce these abrupt changes.

COMPARISON OF THE PROBABILITY OF DETECTING ATRAZINE/DESETHYL-ATRAZINE WITH THE PROBABILITY OF DETECTING ELEVATED NITRITE PLUS NITRATE AS NITROGEN IN GROUND WATER

Logistic regression also was used to develop a preliminary model which predicts the probability of NO_2+NO_3–N concentrations greater than 2 mg/L in ground water of the Idaho part of the eastern Snake River Plain (fig. 14). Background concentrations of NO_2+NO_3–N in ground water are typically less than 2 mg/L (Rupert, 1996). The ground-water monitoring, hydrogeologic, and anthropogenic data used to create the NO_2+NO_3–N probability map were the same as those used to create the atrazine/DEA map, thus allowing a direct comparison between atrazine/DEA and

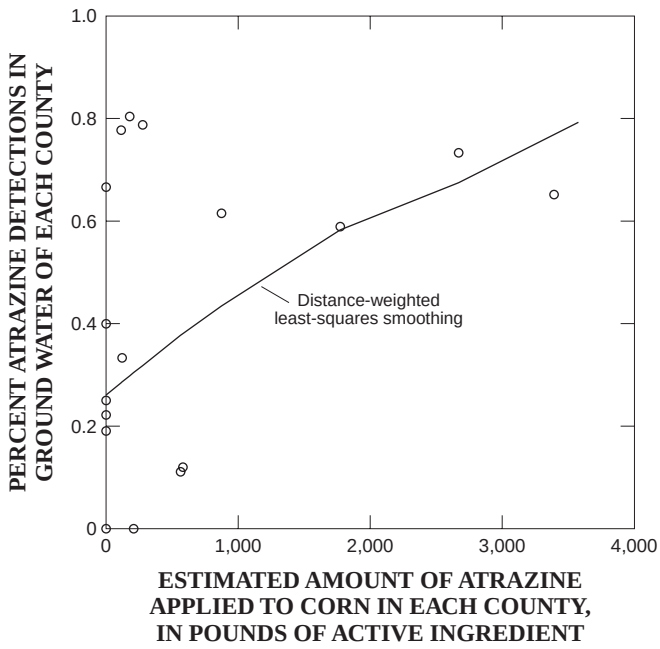

Figure 13. Percent atrazine/desethyl-atrazine detections in ground water in relation to the amount of atrazine applied to corn in each county. (Atrazine application estimates are from Gianessi and Anderson, 1995)

NO_2+NO_3–N detections. The NO_2+NO_3–N probability map is restricted to that part of the eastern Snake River Plain and tributary valleys where depth to ground water has been mapped (Maupin, 1992; Berenbrock and others, 1994). The straight line along the southern edge of the map marks the extent of Maupin's depth-to-water map.

The atrazine/DEA and NO_2+NO_3–N models produced different results (table 3). For example, precipitation, soil hydrologic group, and well depth had statistically significant relations with atrazine/DEA detections but not with elevated NO_2+NO_3–N concentrations. Depth to water and soil drainage had statistically significant relations with elevated NO_2+NO_3–N concentrations but not with atrazine/DEA detections. The differences between atrazine/DEA and NO_2+NO_3–N relations were attributed to differences in chemical behavior of these compounds in the environment and possibly to differences in the extent and rates of their application.

Model results indicate that atrazine/DEA is related with soil hydrologic group and NO_2+NO_3–N is

Table 5. Summary of pesticide detections and the co-occurrence of atrazine/desethyl-atrazine with other pesticide compounds in ground water in the Idaho part of the upper Snake River Basin, based on results of the U.S. Geological Survey National Water-Quality Assessment Program and the Idaho Statewide Ground-Water Monitoring Program, 1993–96

[No., number; <, less than; NA, not applicable]

Pesticide name	Total No. of analyses	Total No. of detections	Percent detections	No. of wells with co-occurrence of atrazine and other compounds	No. of wells with no co-occurrence of atrazine and other compounds
Alachlor	369	3	<1	3	0
Atrazine	369	184	50	NA	NA
Atrazine, desethyl	369	173	47	NA	NA
Carbaryl	369	3	<1	3	0
Carbofuran	369	1	<1	0	1
DDE, p,p'	369	18	5	10	8
Diazinon	369	2	<1	2	0
Dieldrin	369	1	<1	0	1
EPTC (Eptam)	369	17	5	10	7
HCH, Alpha	369	1	<1	0	1
Metolachlor	369	14	4	14	0
Metribuzin	369	38	10	26	12
Permethrin, cis	369	1	<1	1	0
Prometon	369	28	8	26	2
Propachlor	369	2	<1	1	1
Propanil	369	5	1	4	1
Simazine	369	72	19	72	0
Tebuthiuron	369	3	<1	3	0
Triallate	369	1	<1	1	0
Terbacil	369	3	<1	3	0
Trifluralin	369	1	<1	1	0

Figure 14 Probability of detecting nitrate plus nitrate as nitrogen concentrations greater than background levels (2 milligrams pr iter), in ground water in the Idaho part of the upper Snake River Basin. *(60 k)*

Can be accessed from the home page for this report.

related with soil drainage. Soil drainage denotes the frequency and duration of wet periods of the soil (U.S. Department of Agriculture, 1993, p. 98). Soils with poor drainage are typically saturated with water and can have reducing (anaerobic) conditions. Reducing conditions can lead to denitrification that can in turn minimize NO_2+NO_3–N concentrations. Correlations with soil drainage categories probably reflect these processes. Hydrologic group is related with infiltration rate of the soil and with atrazine/DEA detections because soils with high infiltration rates allow atrazine/DEA to migrate to the water table.

Model results obtained for NO_2+NO_3–N were more significant using the IDWR land-use data than those obtained using the BOR land-use data, probably because the IDWR data differentiate unimproved land into classifications of lava flows, dryland agriculture, rangeland, and forest land.

SUMMARY AND CONCLUSIONS

Ground-water probability maps are designed to predict the predisposition of land areas as to their potential for ground-water contamination based on hydrogeologic and anthropogenic factors. Ground-water probability maps are similar to ground-water vulnerability maps developed using the DRASTIC mapping technique, except that probability categories are based on statistical correlations with actual ground-water monitoring data. Ground-water probability maps are superior predictive tools over vulnerability maps developed with the DRASTIC mapping technique because they are statistically based and show a quantified expression of the probability of detecting a particular contaminant.

Ground-water probability maps can be used by resource protection agencies to focus pollution prevention programs in areas of greatest concern and to focus ground-water sampling programs in areas of greatest potential for contamination. Draft Federal regulations may require that each State develop a State Pesticide Management Plan (SMP) for the herbicides atrazine, alachlor, cyanazine, metolachlor, and simazine. This study was designed to assist the Idaho State Department of Agriculture by developing maps that might be used to predict the probability of detecting atrazine and desethyl-atrazine (DEA, a breakdown product of atrazine) in ground water. The maps can be included in the SMP and help provide a sound hydrogeologic basis for atrazine management in the Idaho part of the upper Snake River Basin.

Atrazine/DEA ground-water monitoring data used in this study were collected as part of the Idaho Statewide Ground-Water Monitoring Program (ISGWMP) and the USGS National Water-Quality Assessment (NAWQA) Program. Data collected during 1993–96 from about 800 wells were evaluated for this study. The ISGWMP used two analytical methods to determine atrazine/DEA concentrations in ground water; the gas chromatography/mass spectrometry (GC/MS) method, and the enzyme-linked immunosorbent assay (ELISA) method. Because of low cost, most samples collected for the ISGWMP were tested using the ELISA method; only a subset of the samples also were tested using the more costly GC/MS method. All samples collected as part of the NAWQA Program were analyzed using the GC/MS method. All GC/MS data were used to calibrate the models; ELISA data were used to verify the models.

Hydrogeologic and anthropogenic (related to human activities) data used in this study included atrazine use, depth to ground water, geology, land use, precipitation, soils, and well depth. These data were available in geographic information system (GIS) format from a variety of sources.

Two maps, one with and one without atrazine use, showing the probability of detecting atrazine/DEA in ground water were constructed using a GIS and logistic regression statistical methods. The probability maps were produced as follows: (1) Ground-water monitoring data were overlaid with hydrogeologic and anthropogenic data using a GIS to produce a data set in which each well had corresponding data on atrazine use, depth to ground water, geology, land use, precipitation, soils, and well depth. These data then were downloaded to a statistical software package for analysis by logistic regression. (2) Individual (univariate) relations between atrazine/DEA in ground water and atrazine use, depth to ground water, geology, land use, precipitation, soils, and well depth data were evaluated to identify those independent variables significantly related to atrazine/DEA detections. (3) Several preliminary multivariate models with various combinations of independent variables were constructed. (4) The multivariate models which best predicted the presence of atrazine/DEA in ground water were selected. (5) The multivariate models were entered into the GIS and the probability maps were constructed.

Two models that best predicted the presence of atrazine/DEA in ground water were selected, one with and one without atrazine use. Correlations of the predicted probabilities of detecting atrazine/DEA in ground water with the percent of actual detections were good; r-squared values were 0.91 and 0.96, respectively. Models were verified using a second set of ground-water quality data. Verification showed that probability ratings were significantly higher ($p < 0.002$) for wells in which atrazine/DEA was detected than for wells in which atrazine/DEA was not detected.

Model effectiveness might be improved if data on noncrop use of atrazine, vadose zone characteristics, and larger scale soils data were included. The models also might be improved if additional GC/MS ground-water monitoring data with low reporting limits were available. The model without atrazine use may be applicable for compounds other than atrazine. Metolachlor and simazine had a high frequency of detection in ground water and always were associated with atrazine/DEA, suggesting that these compounds might behave similarly in the environment.

Logistic regression also was used to develop a preliminary model to predict the probability of detecting nitrite plus nitrate as nitrogen (NO_2+NO_3–N) concentrations greater than background levels (2 milligrams per liter). A direct comparison between the atrazine/DEA and NO_2+NO_3–N probability maps was possible because the same ground-water monitoring, hydrogeologic, and anthropogenic data were used to develop both maps. Land use, precipitation, soil hydrologic group, and well depth had statistically significant relations with atrazine/DEA detections. Depth to water, land use, and soil drainage had statistically significant relations with elevated NO_2+NO_3–N concentrations. The differences between atrazine/DEA and NO_2+NO_3–N relations were attributed to differences in chemical behavior of these compounds in the environment and possibly to differences in the extent of use and rates of their application.

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