Environ. Sci. Technol. 1992, 26, 935–943

66/79351

Results of the National Alachlor Well Water Survey

Larry R. Holden* and Jeffrey A. Graham

Monsanto Company, 700 Chesterfield Parkway North, St. Louis, Missouri 63198

Roy W. Whitmore, W. Joseph Alexander, Richard W. Pratt, Susan K. Liddle, and Lanny L. Piper

Research Triangle Institute, P.O. Box 12194, Research Triangle Park, North Carolina 27709

■ The frequency of occurrence of alachlor and several other agrichemicals in water from private, rural domestic wells was determined for all counties in the United States where alachlor is sold. The three-stage, stratified, unequal probability selection procedure yielded water samples from 1430 wells in 89 counties. Of the estimated 6 million existing private domestic wells in the target area, less than 1% have detectable levels of alachlor. Similar occurrence frequencies were found for metolachlor and simazine. Atrazine was the most commonly detected pesticide in the alachlor use area with an occurrence frequency near 12%. Concentrations of all detected pesticides in rural well water are very low and are rarely expected to exceed any health-based standard. The occurrence of nitrate/nitrite, however, is more common. Over 50% of the wells in the alachlor use area have detectable levels of nitrate/nitrite. Nearly 5% exceed the 10 mg/L maximum contaminant level for nitrate/nitrite (expressed as total nitrogen). The occurrence of all chemicals is correlated with various measures of chemical use near the well and with measures of groundwater vulnerability. The likelihood of finding other agrichemicals in a well is significantly increased when nitrate and atrazine are also present.

Introduction

Alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide] is an active ingredient in Lasso, Lariat, Bronco, and a variety of other herbicides that are primarily applied for the control of annual grasses and certain broadleaf weeds in corn, soybeans, and peanuts. The major modes of alachlor dissipation in field soils include microbial degradation and volatilization. Among most soil-applied herbicides, alachlor is moderately mobile ($K_{oc} \approx 170$) but relatively nonpersistent with a soil half-life averaging approximately 2 weeks (*1*).

Extensive studies performed by Monsanto have shown that alachlor can cause tumors in some laboratory animals subjected to lifetime exposures at high doses [e.g., 126 mg of alachlor (kg of body weight)$^{-1}$ day^{-1} in rats] (*2*). The Environmental Protection Agency (EPA) has established a maximum contaminant level (MCL) for the average annual concentration of alachlor in drinking water at 2 μg/L. According to the EPA, "Drinking water that meets this standard is associated with little to no [health effect] risk and is considered safe with respect to alachlor" (*3*).

Since 1985, Monsanto has conducted several large-scale surface water and groundwater studies designed to assess the potential exposure of the U.S. population to alachlor via drinking water. Surveys of over 50 community water systems that rely on surface water in regions of alachlor use were conducted in 1985 and 1986. Few of the systems sampled in these surveys had annualized mean alachlor concentrations exceeding 1 μg/L. When alachlor was detected in a water system, it was present only during the first few months after application (*4*, *5*).

In 1985, Monsanto also conducted a well water survey designed primarily to assess the occurrence of alachlor in rural wells in counties with the greatest alachlor sales (*6*). In this survey, alachlor was detected in 4% of 242 private rural wells sampled from 15 counties. This study found no significant association between alachlor occurrence and soil vulnerability as estimated from organic matter content and permeability.

One of the most extensive drinking water studies ever considered for alachlor, the National Alachlor Well Water Survey (or NAWWS), began actual survey activities in mid-1987 and is the subject of this paper. The NAWWS, designed with the active participation of the Environmental Protection Agency, is a statistically-based sampling survey of alachlor occurrence targeted to private, rural domestic wells in counties where alachlor is used. The primary goal of the NAWWS was to estimate, with specified precision, the proportion of wells with detectable concentrations of alachlor. This proportion was to be determined for wells in counties where alachlor is sold and other subpopulations of special interest. The most stringent precision requirements were established for subpopulations corresponding to wells in areas of (a priori) higher groundwater vulnerability and higher alachlor sales (*7*). To obtain the most useful information, statistically-based survey methods similar to those proposed for the EPA's National Pesticide Survey (*8*, *9*) were employed.

In addition to alachlor, the occurrence of four other herbicides (metolachlor, atrazine, cyanazine, and simazine) and nitrate were studied in the NAWWS. These chemicals are widely used in the same areas as alachlor, and all have been reported to have been found in well water to some extent. All herbicides but simazine have primary uses in corn. Alachlor and metolachlor are used in soybean fields as well.

Survey activities of the NAWWS continued from mid-1987 through the end of 1989. The results of the alachlor survey were presented to the Environmental Protection Agency in February of 1990. This paper summarizes these earlier results and the results of further analyses on the extensive NAWWS data base.

Survey Methodology

Survey Design. The target population for any survey consists of those units from which a sample was selected with known, positive probabilities for observation and measurement. In the NAWWS these units are defined both spatially and temporally. Spatially, the population consists of all private, rural domestic wells located in counties where alachlor was sold in 1986. This area, shown in Figure 1, and referred to subsequently as the alachlor use area coincides, for the most part, with major regions of the United States where corn, soybean, or peanuts are grown. Domestic wells are those that supply water for drinking, cooking, or bathing. Irrigation and stock wells would be excluded from the NAWWS target population unless they also supplied water for domestic use.

Temporally, the target population consists of the 12 months during which water samples could have been collected (June 1988 through May 1989). Therefore each population unit can be visualized as a well-month and the

0013-936X/92/0926-0935$03.00/0

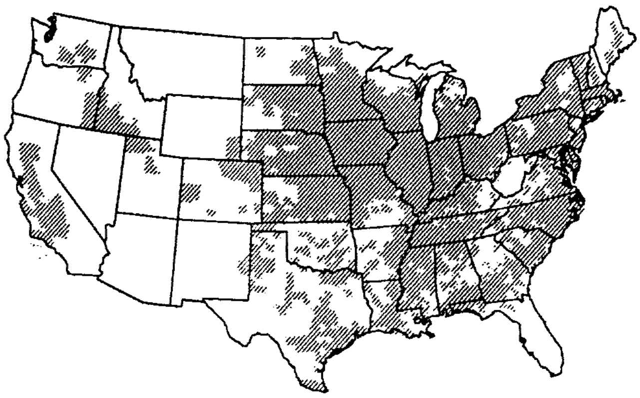

Figure 1. Alachlor use area. Shaded regions indicate all counties having alachlor sales in 1986.

proportion of well-months for which a detectable level of alachlor can be found is an important population characteristic to be estimated from the data. Temporal sampling methods used in the NAWWS are discussed in more detail in Liddle et al. (*10*).

Selection of Wells. The NAWWS sample of well-months was obtained in three stages. At the first stage, county-months (i.e., a county and the month of water collection) were randomly selected. During the second stage of the sampling process, a set of household clusters was selected within each sample county-month. After all eligible wells in each household cluster were identified, via on-site interviews, a third-stage sample of wells (representing well-months) was selected from each cluster. This multistage design was necessary both for its efficiency and because no national list of wells exists from which to draw a single-stage sample.

Stratified sampling was employed at both the first and second stages of the selection process. First-stage strata were based upon measures of groundwater vulnerability to pesticide contamination, alachlor sales, and peanut cropping. County-level DRASTIC scores, developed for the EPA's National Pesticide Survey (NPS), were used as a measure of relative groundwater vulnerability. DRASTIC is an acronym for a numerical classification system designed to evaluate an aquifer's vulnerability to chemical contamination. The pesticide DRASTIC system was designed by the National Water Well Association (now the National Ground Water Association), under contract with the U.S. EPA, to provide a systematic numerical approach to evaluating the potential for groundwater pollution (*11*). The complete DRASTIC score is a weighted sum of seven DRASTIC component scores. Each component score is an index describing the influence, in the area under consideration, of a hydrogeologic factor considered relevant to groundwater contamination. The seven factors used in the DRASTIC system are depth to saturated zone, net recharge, type of aquifer media, type of soil media, slope of land surface, impact of vadose zone, and hydraulic conductivity of the aquifer. The larger values of each component score, and hence of the total DRASTIC score, predict a greater potential for groundwater contamination.

Second-stage strata were based upon estimates of alachlor use and vulnerability within each sample county. County-specific hydrogeologic information was compiled and used by study hydrogeologists to develop DRASTIC scores for each hydrogeologic setting in each sample county. These scores, along with other information obtained from county agent interviews, were used for stratifying household clusters prior to selecting the second-stage sample. In addition, the 12 months of potential water collection for each county were temporally stratified by low, moderate, and high historic groundwater recharge levels.

The requisite number of sample units selected from each stratum at each of the three stages of sampling resulted from the application of the design optimization procedure of Chromy (*12*) to the set of precision requirements jointly established by Monsanto and the EPA (*7*). The most stringent precision requirements were established for domains associated with higher groundwater vulnerability and higher alachlor sales. As a result of these requirements, wells in strata corresponding to higher alachlor use and vulnerability had higher probabilities of selection. The three-stage, stratified, unequal probability selection procedure resulted in a final sample of 1604 wells in 89 sample counties. Because some counties were selected for more than one temporal stratum, the total number of county-months selected was 97. Water samples were collected from 1430 of these wells. Additional details concerning the design of the NAWWS, including a list of the counties selected in each of the spatial and temporal strata, can be found in refs 7 and 10.

Well water sample collection began in June 1988 and continued through May 1989. Well water sampling kits were prepared and shipped to sampling personnel in the field on a continuing basis. Well water samples were collected using a strict sampling protocol. Each member of the sampling staff was trained in the field and was provided a comprehensive water-sampling and data-collection manual. The sampling equipment included labeled sample bottles, disposable beakers, a flowthrough cell, a digital thermometer, and insulated containers. Water samples were carefully taken from regular water taps using a flowthrough cell and a digital thermometer to establish a stabilized water temperature. The stabilized water temperature insured that the sample was "fresh" from either a large storage tank or the aquifer. After water collection, the labeled sample bottles were carefully packed in a chilled insulated container and shipped overnight to the laboratory for chemical analyses. In addition to collecting well water, sampling staff were responsible for administering participant questionnaires and completing a brief assessment of each well site.

NAWWS Questionnaires. County agricultural agents were interviewed to obtain data on cropping practices and alachlor use, both of which were necessary for stratifying the household clusters at the second stage of sampling. These data were collected for all U.S. Census enumeration districts and block groups in the rural portion of each sampled county.

A mail questionnaire was used to collect expert opinions concerning agricultural activities and herbicide use within a half-mile radius of each sample well. Questions were also asked regarding the likelihood of other sources of nitrate (e.g., feed lot, barnyard) and the existence of agrichemical dealers in the half-mile area. The questionnaire, along with a map showing the location of each sample well, was sent to local agricultural experts (primarily USDA Extension Service agents) in each of the 89 sample counties. Extensive follow-up procedures achieved a 100% response rate.

At each well water collection site, a household questionnaire was administered to an adult resident of the household. Its purpose was to collect information about household characteristics, well construction characteristics, and the area around the well. Whenever the respondent to the household questionnaire reported that the well was located on farm property, a farm questionnaire was also administered to the person who farmed the property. Its purpose was to obtain information about farming practices near the well, including crops grown and fertilizer stored, as well as storage, use, disposal, and spills of alachlor products near the well.

After the water samples were collected, the field samplers also completed an Observational Data Collection Form for each well. The purpose of this instrument was to provide information about the water sample collection, the visible construction characteristics of the well, the immediate environment of the well site, and other factors in the near vicinity of the well that could influence the quality of the water and the potential for direct, down-hole contamination.

Chemical Analysis of Water Samples. Chemical analysis results were obtained for all 1430 well water samples collected. Concentrations of the five herbicides were determined by capillary gas chromatography–mass spectrometry (GC–MS) in the selected-ion monitoring mode. Quantitation was based upon stable isotope-labeled internal standards of each of the five herbicide analytes as reported previously (*13*). Detection decisions for these herbicides were based upon multiple criteria applied to each well water sample and not just on the typically-used global concentration thresholds. The smallest actual concentration of the analyte that could be in the water samples and still yield consistent detection using these criteria was approximately 0.03 μg/L (or parts per billion) for all herbicides but cyanazine. For cyanazine, this minimum detectable amount was approximately 0.1 μg/L. Nitrate/nitrite (expressed as total nitrogen) in the well water samples was determined colorimetrically using a procedure based on the ASTM Standard Test Method (*14*). For observed nitrate measurements, a simple global threshold of 0.1 mg/L (or parts per million) was used to classify samples as detections.

Upon completion of chemical analyses of well water samples, a report of the findings for each well was mailed to each survey participant and well owner (if not the same person) within 2 months. When target analytes were detected, participants were also provided with the names and numbers of local officials who agreed to provide information on possible health effects of the products and information on proper well construction. In the event that product levels exceeded any health-based standards, participants were notified as soon as possible (usually within 48 h) and provided with the name of a local health department official who could provide advice.

Well-Level Hydrogeological Assessments. Three well-specific hydrogeologic measures were constructed by study hydrogeologists for each sample well in the survey for use in the statistical analysis of chemical occurrence. One measure, the well-specific vulnerability, classifies the aquifer the well most likely taps as surficial (most vulnerable), confined (least vulnerable), and intermediate (moderately vulnerable). Using these broad categories rather than more complex functions reduces the potential for bias resulting from the sizable portion of missing or unreliable participant data on well depth.

A second hydrogeological measure developed for the NAWWS was the estimated water level (expressed as low, moderate, or high level) at the time of water collection relative to the previous 5 years. Relative well water levels were estimated using hydrographs from nearby observation wells for the specific aquifers likely to be tapped by each sample well. Rainfall data were used as a surrogate in the few cases for which hydrographs were unavailable.

Lastly, DRASTIC scores were developed for each of the aquifers tapped by the 1430 sample wells. The seven DRASTIC components were estimated for each hydrogeological setting in each county potentially containing a sample well. The well-level DRASTIC score used was the weighted sum of the seven DRASTIC components estimated for the aquifer most likely containing the sample well. Average scores were used in cases where distinct aquifers could not be identified for a sample well.

Table I. Selected Descriptive Characteristics of Wells in the Target Population[a]

characteristic	estimate	std error
no. of wells	6 040 000	280 000
households served by wells	6 460 000	260 000
persons served by wells	19 700 000	940 000
wells used for drinking water, %	97.9	1.3
wells on farms, %	25.7	2.9

[a] Based on information from household questionnaires.

Statistical Analysis of Results. A stratified, multistage process with unequal sampling probabilities was used to select wells for the NAWWS. Consequently, procedures that account for this complex sampling design were used to properly analyze the survey data. Analysis weights, needed to compute proper estimates of population parameters from the data, were obtained for each sample well as the inverse of the probability of selection (*15*). In addition, weight adjustments to compensate for both unit nonresponse (all data missing) and item nonresponse (partial data available from a sample unit) were used. These adjustments reduced the potential for nonresponse bias (*16*).

The numbers of well-months in the target population and subpopulations were estimated as the sum of the analysis weights of the sample wells in the subpopulation. Dividing this number by 12 results in an estimate of the annual average number of wells in a subpopulation. For simplicity, each annual average is referred to simply as the "number of wells" in this paper. Of primary interest are the proportions of wells possessing specific characteristics (e.g., alachlor detections). These proportions can be expressed as the ratio of two (annual average) population totals. (For example, the proportion of wells with alachlor detections is the number of wells with alachlor detections divided by the total number of wells in the target population.) The standard errors of all these ratio estimates were computed using the Taylor series linearization method as described in Wolter (*17*) and Rao (*18*) and the assumed replacement estimator described in Chromy (*19*).

Tests for the differences in two proportions were performed by comparing the difference, divided by the Taylor series linearization estimate of its standard error, to the standard normal reference distribution. Weighted logistic regression was used to estimate trends in proportions—the weights being the analysis weights described above. The standard errors of these regression coefficients were again computed using Taylor series linearization methods. One- or two-tailed versions of all significance tests were applied as appropriate. In all cases, the threshold for statistical significance was considered to be at the 5% level ($p < 0.05$).

Results

Target Population Description. Tables I–III summarize important descriptive characteristics of wells in the alachlor use area. These estimates are based on information about each sample well obtained from household residents, county experts, and field samplers. As indicated in Table I, there were an estimated 6 million private, rural, domestic wells in the alachlor use area, on the average, from June 1988 through May 1989. These wells served an

Table II. Estimated Frequency of Selected Chemical Usage Characteristics of Wells in the Target Population

characteristic	estimate[a]	std error[a]
well within 300 feet of[b]		
cropped area, field, or pasture	64.3	3.4
corn, soybeans, or peanut crops	39.6	2.8
feedlot or barnyard	29.5	3.5
well within 1/2 mile of[c]		
any agriculture activity[d]	94.2	2.4
intense agricultural activity[d,e]	42.9	6.2
any row cropping[d]	85.3	3.2
intense row cropping[d,e]	18.4	2.1
any nitrogen fertilizer used[d]	93.4	2.4
intense nitrogen fertilizer use[d,e]	22.4	3.5
probable alachlor use[f]	58.8	5.3
probable metolachlor use[f]	47.3	4.3
probable atrazine use[f]	55.1	4.7
probable cyanazine use[f]	39.6	5.0
probable simazine use[f]	29.9	4.1

[a] Values are in percent of wells. [b] Evidence determined by observation at the time of water collection; these are most likely underestimates. [c] Opinions reported by county experts. [d] Within the previous year. [e] Intense denotes more than 50% of the land area devoted to the activity. [f] Within the previous 5 years.

Table III. Estimated Frequency of Selected Vulnerability Characteristics of Wells in the Target Population

characteristic	estimate[a]	std error[a]
deep and confined aquifer tapped[b]	19.4	5.4
shallow and unconfined aquifer tapped[b]	32.4	4.0
less than 50 feet deep[c]	12.1	2.1
unknown depth[c]	23.6	3.3
over 20 years old[c]	30.4	1.8
unknown age[c]	19.1	3.2
within 100 feet of nonoperating well[d]	17.4	2.1
with absent or cracked pad[d]	56.5	4.5
pad unobserved[d]	29.8	4.5
wellhead below ground surface[d]	22.0	2.9

[a] Values are in percent of wells with characteristic. [b] The most likely aquifer tapped as determined by the best available evidence. [c] Based on information supplied by household respondents. [d] Based on observations made at time of water collection.

Table IV. Estimated Percent Occurrence of Nitrate in the Alachlor Use Area

nitrate[a] levels, mg/L	% of wells	std error
<0.1[b]	47.7	4.5
0.1–3[c]	28.7	3.7
3–10	18.7	1.9
>10[d]	4.9	1.1

[a] Nitrate/nitrite reported as total nitrogen. [b] Not detected. [c] Detections in this range could be due to natural background levels in the well water. [d] 10 mg/L is the maximum contaminant level (MCL) for nitrate/nitrite.

estimated 6.5 million households containing 20 million people. Almost all of the domestic wells in the target population are used for drinking water.

Table II summarizes the nature of agricultural activities in the vicinity of target population wells. While only 26% of the wells in the target population are located on farm property, a majority are within 300 ft of a cropped area, field, or pasture. On the basis of field observations, we estimate that at least one of the major alachlor target crops (corn, soybeans, or peanuts) is grown within 300 ft of 40% of the wells. County expert responses indicate that most of the wells have some agricultural production within a half mile and an estimated 85% have row crops (e.g., corn, soybeans) grown within a half mile. Nearly 20% of the wells are located in intense row cropping areas (i.e., where the activity comprises at least 50% of the land area).

The survey estimates in Table II also indicate widespread use of the target herbicides in the alachlor use area. Alachlor and atrazine are the most commonly used, whereas the proportion of target population wells near metolachlor, cyanazine, and simazine use is smaller. Nearly all of the wells in the alachlor use area have nitrogen fertilizer applied within a half mile. Twenty-two percent of these wells are located in what was categorized as intense fertilizer application areas.

The results given in Table III suggest that a sizable portion of rural wells in the target population is potentially vulnerable to the introduction of trace levels of agricultural chemicals from point as well as nonpoint sources. On the basis of hydrogeological assessments, nearly one-third of the 6 million wells in the target population are tapping vulnerable surficial aquifers. An estimated 19% of wells are tapping low vulnerability confined aquifers, and the remainder are tapping aquifers of intermediate vulnerability. Abandoned or nonoperating wells are within 100 ft of 17% of the wells.

Some common well construction features also increase the chance of chemical contamination. For example, in this study we find that the wellhead is below the surface of the ground for many of the wells and less than half have a concrete pad. As a class, older wells are more likely to be in poor condition and thus vulnerable to chemical contamination. As seen in Table III, approximately one-third of the 6 million wells in the alachlor use area are predicted to be over 20 years old. For an additional 20% of the wells, the ages could not be determined.

Nitrate and Herbicide Occurrence. This survey finds that nitrate occurrence in rural well water is common. As seen in Table IV, over half of the 6 million wells in the alachlor use area are estimated to have detectable nitrate/nitrite levels. Only one-fourth of the wells, however, have levels exceeding 3 mg/L, sometimes regarded as the threshold concentration indicative of human sources (*20*). About 5% (or 300 000) of the rural wells in alachlor use counties are expected to deliver water that contains levels in excess of 10 mg/L, the nitrate/nitrite maximum contaminant level.

The predicted frequencies of occurrence of the five herbicides studied are given in Table V. Atrazine is the

Table V. Estimated Percent Occurrence of the Five Herbicides in the Alachlor Use Area

chemical	estimated % of wells at or above[a]				
	detection	0.1 μg/L	0.2 μg/L	0.5 μg/L	1 μg/L
alachlor	0.78 (0.29)	0.36 (0.22)	0.32 (0.20)	0.06 (0.03)	0.03 (0.02)
atrazine	11.68 (5.13)	2.32 (0.75)	1.11 (0.40)	0.23 (0.11)	0.16 (0.11)
cyanazine	0.28 (0.20)	0.08 (0.06)	*b*	*b*	*b*
metolachlor	1.02 (0.38)	0.40 (0.21)	0.40 (0.22)	0.29 (0.20)	0.22 (0.20)
simazine	1.60 (0.87)	0.10 (0.08)	0.01 (0.01)	0.01 (0.01)	<0.01 (<0.01)

[a] Standard errors are given in parentheses. [b] No occurrences of cyanazine at or above this level were found in the sample.

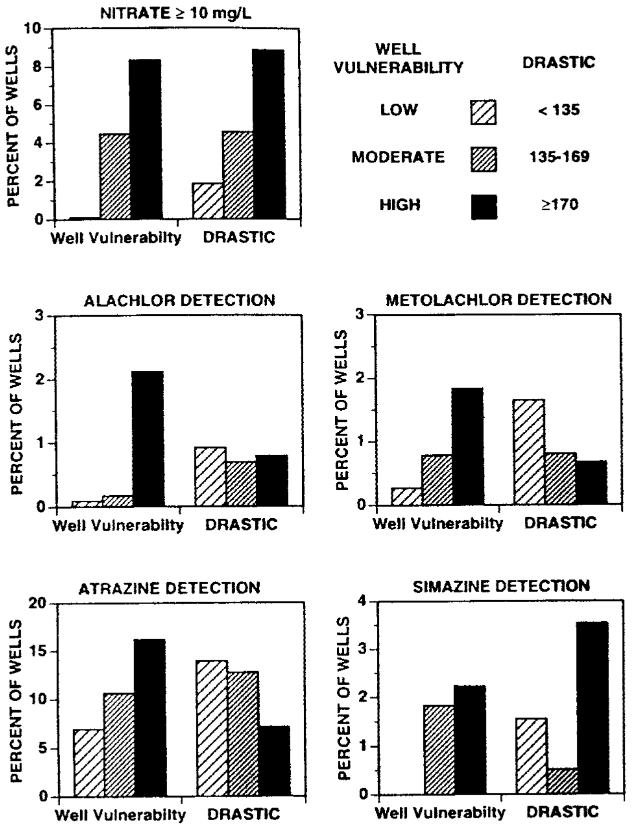

Figure 2. Association of chemical occurrences with the NAWWS well vulnerability index and well-specific DRASTIC scores. The vertical axes represent frequency of occurrence.

most commonly detected herbicide in the alachlor use area. Simazine, metolachlor, and alachlor all have detection frequencies near 1% and do not differ statistically. An estimated 0.3% of the wells in the target population are expected to have cyanazine at levels detectable by our methods. Since both atrazine and alachlor have similar likelihoods of use within a half mile of rural wells, the disparity in occurrence between them is likely related to the longer soil half-life of atrazine (60 days) compared with alachlor (15 days) (*1*).

Table V also predicts that most of the detections of herbicides, especially atrazine, in the target population will occur at low levels (e.g., <0.5 μg/L). Less than half of alachlor and metolachlor detections, one-tenth of the atrazine detections, and practically none of the simazine detections are at levels exceeding 0.2 μg/L. Alachlor is expected to occur at levels exceeding its 2 μg/L MCL in 0.02% (or about 1200) of the 6 million rural wells. The projected percentage of atrazine occurrences exceeding the 3 μg/L MCL is 0.1%, corresponding to about 5700 wells.

Vulnerability and Chemical Occurrence. Figure 2 shows the estimated frequency of chemical occurrence within each of the three categories of well-specific groundwater vulnerability (based on the most likely aquifer type tapped). For all herbicide detections and for nitrate levels exceeding 10 mg/L, the estimated frequency increases as the vulnerability goes from low (deeper and confined aquifers) to high (shallow and unconfined aquifers). The differences between frequencies of high- and low-vulnerability wells were statistically significant for nitrate/nitrite, alachlor, metolachlor, and simazine and nearly significant for atrazine. The relationship of the well-specific DRASTIC score to chemical occurrence, however, is less clear. Significant positive trends with three DRASTIC classes (lower, moderate, and higher vulnerability) were found only for simazine detection and nitrate/nitrite levels over 10 mg/L. The occurrence of other herbicides showed no significant correlation with the well-level DRASTIC index. In fact, a near-significant negative trend with this index was seen for atrazine detections.

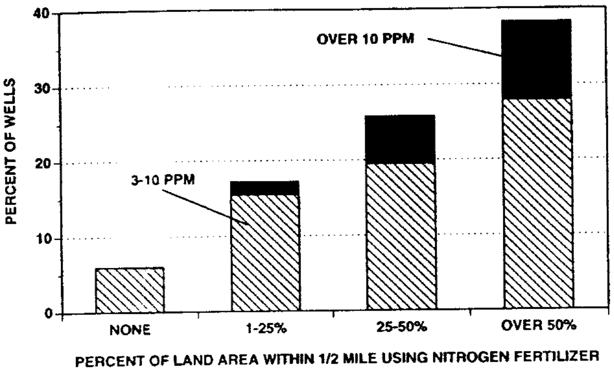

Figure 3. Occurrence of nitrate/nitrite levels exceeding 3 μg/L in the alachlor use area.

Except for nitrate/nitrite, no detectable correlation was found between chemical occurrence and participant-reported well depth. The percentage of wells with nitrate/nitrite exceeding 10 mg/L was significantly greater for wells reported to be less than 50 ft deep (9%) than for wells greater than 200 ft deep (2%). No consistent associations were found between chemical occurrence in the well and various well construction characteristics. Any such influences that may exist in the population are below the level of statistical resolution in this survey.

No statistically significant differences in herbicide and nitrate/nitrite occurrence were found among classes based on actual water level relative to the past 5 years. The same comparisons restricted just to wells tapping surficial and unconfined aquifers also failed to show any significant effect of water level. The magnitude of any association of water level (either negative or positive) with chemical occurrence that may exist is too small or too variable to be detected in this survey.

Chemical Use and Occurrence. As the likelihood and extent of chemical use increase in the vicinity of a well, the chance that it will be found in the well water should also increase. Here, as with most monitoring studies, the degree of chemical use in each well vicinity is not known precisely. (In fact, the complexity of chemical transport mechanisms in the soil makes it difficult to establish a meaningful definition of well vicinity.) In the NAWWS, however, we did have available several surrogate measures (e.g., those listed in Table II) for actual chemical use. In the case of nitrate/nitrite, for example, Figure 3 shows that the frequency of occurrence is strongly (and significantly) correlated with the land area devoted to nitrogen fertilizer application (in the opinion of county experts). A significant difference in the occurrence of nitrate/nitrite levels exceeding the 10 mg/L MCL is also found between wells located on farms (10%) and those not on farm property (3%). If the farm well is also within an area of intense fertilizer application, the likelihood of exceeding the 10 mg/L MCL increases to 14%.

Table VI compares the estimates of herbicide detections for wells within a half mile of herbicide use (in the opinion of county experts) with those for more distant wells. As expected, the estimated frequency of detection is greater for wells most likely to be near herbicide use. Logistic regressions of chemical detection on the likelihood of use (0, definitely not used; 1, probably not used; 2, probably used; and 3, definitely used) yield statistically significant positive trends for all herbicides.

Table VI. Estimated Percent of Wells with Detections Classified by Probable Use of Herbicides within 1/2 Mile[a]

herbicide	probably used[b]	probably not used[b]
alachlor	1.32 (0.50)	0.02 (0.02)
metolachlor	1.55 (0.58)	0.54 (0.50)
atrazine	16.36 (3.17)	5.94 (2.23)
cyanazine	0.70 (0.51)	*c*
simazine	3.71 (2.63)	0.70 (0.38)

[a] Values are percent of wells with detections of the indicated herbicide; standard errors are in parentheses. [b] Based on opinions reported by county experts. [c] No occurrences in the sample.

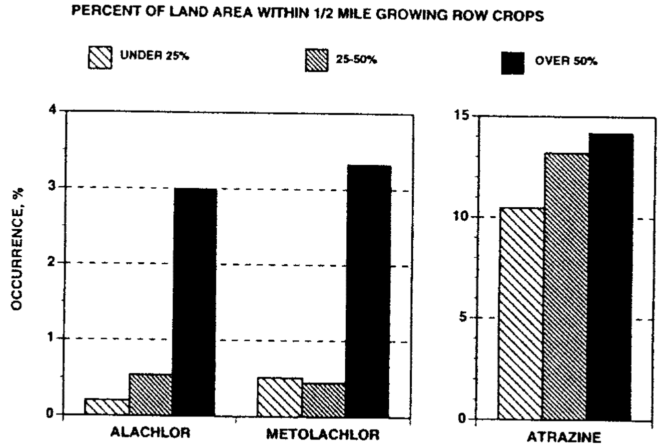

Figure 4. Association of alachlor, metolachlor, and atrazine with intensity of row cropping near the well.

Subpopulations defined by other surrogate use measures also show increased herbicide occurrence. An estimated 1.3% of rural wells within 300 feet of visible corn, soybeans, or peanut fields (primary alachlor crops) have detectable alachlor levels compared to only 0.4% for wells not in this class. The significant increase in alachlor, metolachlor, and atrazine detections with the estimated percent of surrounding land in row crops is illustrated in Figure 4. In fact, the subpopulation of wells near intense row cropping (i.e., over 50% of land area within a half mile in row crops) shows the highest estimated frequency of alachlor and metolachlor detections (3% and 3.3%, respectively) of any use surrogate category. As indicated in Table II, these wells make up almost 20% of the 6 million rural domestic well population in the alachlor use area. Unlike the case for nitrate/nitrite occurrence, however, no significant differences in any herbicide occurrence were found between wells on farm and those on nonfarm properties.

The NAWWS found large detection frequencies of herbicides for the very small percentage of wells (≈2%) located within a half mile of pesticide dealers, formulators, or applicators (12%, 19%, 11%, and 11% for alachlor, atrazine, metolachlor, and simazine detections, respectively). The standard errors for these estimates are quite large, however, due to the small number of wells sampled in this class. These results, however, coupled with those from other studies (*21*, *22*), do suggest that wells near agrichemical dealers may, as a class, be at increased risk of contamination. Pesticide surveys focusing on this population of wells are needed.

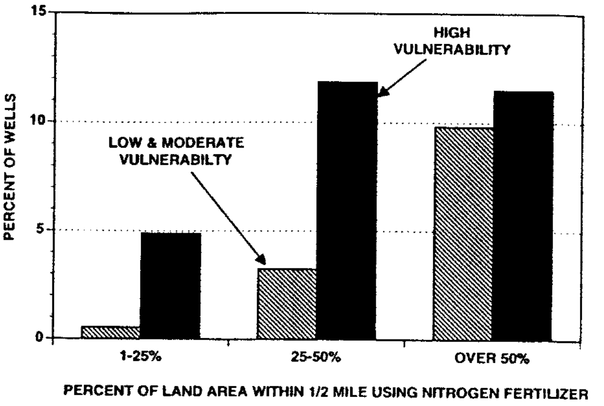

Figure 5. Association of nitrate/nitrite levels exceeding the 10 mg/L MCL with use and vulnerability.

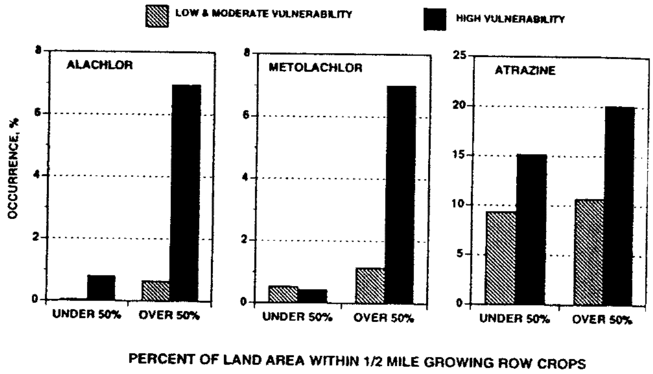

Figure 6. Association of chemical occurrence with use and vulnerability.

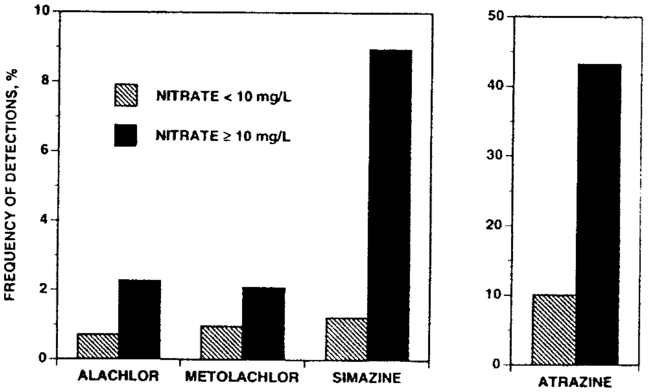

Figure 7. Association of herbicide detection with nitrate/nitrite levels exceeding the 10 mg/L MCL.

Joint Effect of Use and Vulnerability. Since chemical occurrence in rural wells in the alachlor use area is positively correlated with measures of use and vulnerability, it is reasonable to expect more detections in wells that are classified as vulnerable and are also located near intensive use of the chemical. Figure 5 illustrates the interaction between nitrogen fertilizer use and well vulnerability on the occurrence of nitrate levels exceeding the MCL. It is clear that higher vulnerability wells are more susceptible to nitrate contamination, especially at intermediate levels of fertilizer use. Figure 6 shows the frequency of occurrence of alachlor, atrazine, and metolachlor for four partitions of the alachlor use area defined by percent of land in row crops and aquifer vulnerability. It is obvious that detection frequency is greatest for those vulnerable wells most likely to be in areas of intense row crop activity. Both alachlor and metolachlor are expected to occur in an estimated 7% of the approximately 400 000 vulnerable wells in areas of intense row cropping. Detectable levels of atrazine are expected to occur in 20% of these wells. Although not shown in Figure 6, an estimated 11% of wells have nitrate/nitrite levels exceeding 10 mg/L in this group. Frequencies of occurrence of chemicals outside this highly vulnerable supbpulation are much lower, especially for alachlor and metolachlor.

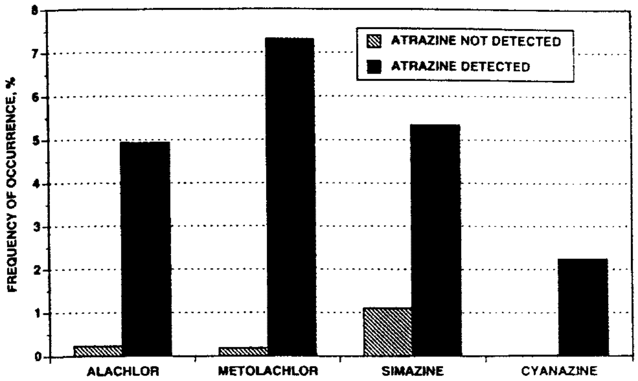

Figure 8. Association of herbicide detection with atrazine detection.

Joint Occurrences of Chemicals. The association between herbicide detections and nitrate/nitrite levels of 10 mg/L or greater was found to be significant for alachlor, atrazine, and simazine. This association between nitrate/nitrite and detectable levels of herbicides in well water is clearly evident in Figure 7. Nearly one-half (43%) of the approximately 300000 wells in the target population with nitrate/nitrite levels predicted to exceed the 10 mg/L MCL are estimated to have detectable levels of atrazine. Metolachlor, although not yielding a statistically significant association with the occurrence of high nitrate, does show the same pattern consistent with the other herbicides. Approximately half of the wells containing nitrate at levels exceeding the 10 mg/L MCL are also expected to contain at least one of the five herbicides studied here.

There is an even more striking association between the occurrence of atrazine and that of the other herbicides. As is clearly shown in Figure 8, there are highly significant associations between observing detectable levels of atrazine and observing detectable levels of alachlor, metolachlor, simazine, and cyanazine.

Discussion

The National Alachlor Well Water Survey differs from most other monitoring studies for alachlor in that it has a well-defined target population: all private, rural, domestic wells in counties where alachlor was sold in 1986. This region of the United States where alachlor is used coincides primarily with areas of corn and soybean production and contains an estimated 6 million private, rural domestic wells, serving 20 million people. An equally important advantage of the NAWWS is the use of probability sampling methods for well selection. This is the only defensible means for obtaining unbiased estimates of the occurrence of low levels of alachlor and the other chemicals. Many studies purporting to be surveys are nonstatistical efforts in which monitoring sites are subjectively selected in the hope of representing some vague "worst-case" population. Such studies may, in some cases, be cost effective for determining if contamination exists but can never provide valid descriptions of the frequency and magnitude of chemical occurrence.

The NAWWS finds that nitrate is the most common contaminant of rural wells with an estimated 300000 wells exceeding the health-based standard. There is a strong correlation of high nitrate occurrence with degree of nitrogen fertilizer application near the wells. The highly significant difference found in nitrate occurrence between farm and nonfarm wells is also particularly interesting since no such effect was seen for any of the herbicides.

The five herbicides studied here occur less frequently in rural wells than does nitrate. Alachlor, metolachlor, and simazine detection frequencies are all near 1% in the alachlor use area and are rarely expected to exceed any health-based standard. Even atrazine, which has the largest detection frequency (12%), is expected to exceed its 3 μg/L MCL in only 0.1% of the wells.

In general, the overall frequencies of occurrence of the five herbicides seem consistent with their persistence in the soil and their likelihood of use throughout the target population. Both alachlor and cyanazine have soil half-lives of approximately 2 weeks whereas those of atrazine, metolachlor, and simazine are 2–3 months (*1*). Since atrazine is both persistent and widely used in the target population (Table II), it is not surprising that it is the most frequently detected well water contaminant. Alachlor is less persistent in the soil than metolachlor but has greater use throughout the target population. Consequently both chemicals have similar detection frequencies in well water.

As might be expected, detections are more frequent near the more intensive use of the chemical. Most factors that are correlated with likelihood and intensity of chemical use, such as percent of land used for row cropping, show the same positive relationship with chemical occurrence. Wells which tap shallow and unconfined aquifers also have a higher likelihood of chemical contamination than do wells in deeper and more confined aquifers. The fraction of wells with detectable herbicide levels is greater for vulnerable wells that are also located in intense row cropping areas. Most of these detections, however, still occur at low levels.

The well vulnerability classification system, based on expert opinions of study hydrogeologists concerning well depth and the presence/absence of confining layers, showed very good correlation with chemical occurrence. This or similar simple classification systems show promise as a general way to delineate potential contamination sites. The usefulness of the DRASTIC index, on the other hand, is less clear. The NAWWS found little, if any, association between DRASTIC scores and herbicide occurrence. It may be that the complex weighting and coding procedures used in DRASTIC scoring are self-defeating. Simpler classification systems, focusing on only a few major vulnerability factors, look to be more useful than DRASTIC in the short term.

No discernible association was found in this study between yearly water levels (relative to the 5-year norm) and chemical occurrence in rural wells. Any effect of water level that might exist must be too small and/or complex to be seen in a national sample. Existence of local differences in chemical occurrence due to changes in recharge and water level, however, cannot be ruled out.

Results of this survey are consistent with other groundwater studies that report an association between the occurrence of herbicides and high nitrate levels (*23*–*26*). Nitrate occurrence in a well, especially at levels near the 10 mg/L MCL, is most likely a surrogate for higher well vulnerability to both point and nonpoint source contamination. Although the association is not perfect, the presence of higher nitrate levels is still valuable as an indicator for the occurrence of other chemicals. Similarly, wells in which any herbicide, especially atrazine, is detected are also more likely to contain other chemicals.

Many of the NAWWS rural wells are, in fact, vulnerable to contamination from point as well as nonpoint sources. In addition to tapping vulnerable aquifers, many are also located near potential conduits for aquifer contamination. The alachlor use area has many older wells, and many may be improperly constructed. Although no significant correlation was seen here between such well construction characteristics and chemical occurrence in the entire target population, many other studies have documented such effects on a smaller scale (e.g., ref 27). Thus the possibility that the agrichemicals found in any NAWWS sample well were due to contamination from point sources (e.g., pesticide dealers, mixing and loading operations, spills) or as a consequence of improper construction cannot be ruled out. Estimates based upon this and similar surveys, therefore, can be viewed only as "upper bound" frequencies of chemical occurrence resulting from nonpoint sources.

Of course, alachlor or any other herbicide may occur in wells in specific local areas at frequencies and at levels greater than those estimated by the NAWWS. The NAWWS was designed to estimate the occurrence of alachlor in the alachlor use area and large subpopulations thereof. It was not designated to predict herbicide occurrences in local areas such as counties or even states. Surely such "hot spot" areas do exist. The nature of probability sampling, however, ensures that these areas still correctly enter into the overall estimates of contamination frequency.

To our knowledge only three states have conducted surveys for alachlor occurrence that can validly draw inferences beyond the wells actually sampled to a well-defined population: the Wisconsin Dairy Farm Well Survey (*23*), the Iowa State Wide Rural Well Survey (*28–32*), and a series of surveys conducted from 1985 to 1987 in Nebraska (*24*, *33–35*). Although detection limits vary, making comparisons of chemical occurrence difficult, the frequency of occurrence of alachlor in well water ranges from 0% to 1.2% in these surveys. While the alachlor occurrence in a specific state need not reflect that of the entire alachlor use area, the NAWWS estimate of 0.78% is consistent with these results.

As is the case with NAWWS, these state surveys find atrazine to be the most commonly occurring pesticide with frequencies ranging from 3.8% to 12%. Similarly, nitrate is the most commonly found well contaminant in these studies. In the state surveys the frequency of nitrate/nitrite levels exceeding the MCL ranges from 8.4% to 29.1%. These are higher than the NAWWS estimate for the entire alachlor use area (4.9%) but are consistent with NAWWS estimates of 10–14% for wells near greatest nitrogen fertilizer application.

The Environmental Protection Agency has recently announced Phase I results from the National Pesticide Survey (NPS), a survey of pesticides in all U.S. drinking water wells (*36*). The NPS comprises two separate surveys: one of community well water systems and another of private, rural, domestic wells. The NPS domestic well component used sampling procedures similar to those of the NAWWS. The NPS domestic well target population is the 10.5 million private, domestic, rural wells in the entire nation, including the 6 million wells in the alachlor use area. The NPS sampled water from 752 rural wells in 90 U.S. counties, whereas the NAWWS sampled 1430 wells in 89 alachlor sales counties. Both surveys used complex multistage stratified sampling methods. The NPS tested for 127 different analytes in each sample well, including all six of those studied by the NAWWS. With the exception of nitrate/nitrite, however, the detection limits of the NAWWS analytes were at least 1 order of magnitude lower than those of the NPS.

While the two target populations are somewhat different, results of both the NPS and the NAWWS are consistent. For example, the percent of wells having concentrations of nitrate/nitrite (expressed as nitrogen) over 0.15 mg/L is 57% and 51% for the NPS and NAWWS, respectively. The percent of wells with nitrate/nitrite exceeding the MCL is 2.4% for the entire nation (NPS) compared with 4.9% for the more agricultural alachlor use area (NAWWS). The NPS estimates a national frequency of detection in private rural wells less than 0.1% for alachlor and 0.7% for atrazine. The detection limits for these two compounds, however, were 0.5 and 0.12 μg/L, respectively. The frequency of alachlor and atrazine occurrences exceeding these levels derived from the NAWWS are 0.06% and 2.2%, respectively. The NPS domestic well survey also found similar correlations between nitrate occurrence and measures of use and vulnerability.

The NAWWS and the NPS together provide a consistent nationwide picture of alachlor occurrence in drinking water wells. The NPS provides a broad picture of chemical occurrence in domestic and in community water system wells. With its lower detections limits, however, the NAWWS gives a much greater resolution picture for alachlor and for some important agrichemicals in counties where alachlor is sold. The agreement between these large-scale surveys is due, in large part, to careful probability sampling from a well-defined target population.

Acknowledgments

We thank Dr. Ronald G. Smith, Dr. Sheila A. Schuette, and Ms. Marlene L. Schott for their outstanding efforts in the chemical analysis of well water samples. We also acknowledge the efforts of Dr. David I. Gustafson who designed and conducted the county expert mail survey and provided invaluable advice during the entire study. Finally, we thank the many interviewers and samplers at RTI who traveled thousands of miles in search of wells.

Registry No. Alachlor, 15972-60-8; metolachlor, 51218-45-2; atrazine, 1912-24-9; simazine, 122-34-9.

Literature Cited

(1) Wauchope, R. D.; Buttler, T. M.; Hornsby, A. G.; Augustijn-Beckers, T. W. M.; Burt, J. P. In *Reviews of Environmental Contamination and Toxicology*; Ware, G. W., Ed.; Springer-Verlag: New York, 1991; Vol. 123.

(2) *Fed. Regist.* **1987**, *52*, 49480–49503.

(3) *Fed. Regist.* **1991**, *56*, 3588.

(4) Gustafson, D. I. *J. Environ. Sci. Health, Part B* **1990**, *B25*, 665–687.

(5) Klein, A. J.; Basziz, S. R.; Horner, L. H.; Lauer, R.; Rupel, F.; Smith, R. G.; Triebe, F. M. Presented at the 193rd National Meeting of the American Chemical Society, Denver, CO, Mar 1987.

(6) Graham, J. A.; Holden, L. R. Presented at the National Water Well Association Agricultural Impacts on Ground Water Conference, Des Moines, IA, March 21–23, 1988.

(7) Holden, L. R.; Whitmore, R. W.; Graham, J. A. In *Proceedings of the Agricultural Impacts on Ground Water—A Conference*; National Water Well Association: Dublin, OH, 1988; pp 237–254.

(8) *National Pesticide Survey. Pilot Evaluation Summary Report*; Office of Drinking Water, Office of Pesticide Programs, U.S. Environmental Protection Agency: Washington, DC, 1987.

(9) Mason, R. E.; Piper, L. L.; Alexander, W. J.; Pratt, R. W.; Liddle, S. K.; Lessler, J. T.; Ganley, M. C. National Pesticide Survey Pilot Evaluation Technical Report. RTI/7801/06-02F; Research Triangle Institute: Research Triangle Park, NC, 1987.

(10) Liddle, S. K.; Whitmore, R. W.; Mason, R. E.; Alexander, W. J.; Holden, L. R. *Ground Water Monit. Rev.* **1990**, *10*, 142–146.

(11) Aller, L.; Bennett, T.; Lehr, J. H.; Petty, R. J.; Hackett, G. *DRASTIC: A standardized system for evaluating ground water pollution potential using hydrogeologic settings*; EPA 600/2-87-035; U.S. Environmental Protection Agency: Washington, DC, 1987.

(12) Chromy, J. R. In *1987 Proceedings of the Section on Survey Research Methods*; American Statistical Association:

Washington, DC, 1988; pp 194–199.

(13) Schuette, S. A.; Smith, R. G.; Holden, L. R.; Graham, J. A. *Anal. Chim. Acta* **1990**, *236*, 141–144.

(14) Standard Test Methods for Nitrite–Nitrate in Water. Section 11 on Water and Environmental Technology, Volume 11.01, Method D 3867-85. In *Annual Book of ASTM Standards*; American Society for Testing and Materials: Philadelphia, PA, 1986; pp 598–610.

(15) Kendall, M.; Stuart, A.; Ord, J. K. *The Advanced Theory of Statistics, Vol. 3: Design and Analysis, and Time-Series*, 4th ed.; MacMillan: New York, 1983; pp 184–233.

(16) Oh, H. L.; Scheuren, F. J. In *Incomplete Data in Sample Surveys, Volume 2: Theory and Bibliographies*; Madow, W. G., Olkin, I., Rubin, D. B., Eds.; Academic Press: New York, 1983; pp 143–184.

(17) Wolter, K. M. *Introduction to Variance Estimation*; Springer-Verlag: New York, 1985; pp 221–247.

(18) Rao, J. N. K. In *Sampling*; Krishnaiah, P. R., Rao, C. R., Eds.; Handbook of Statistics; North-Holland: New York, 1988; Vol. 6, Chapter 17.

(19) Chromy, J. R. In *Current Topics in Survey Sampling*; Krewski, D., Platek, R., Rao, J. N. K., Eds.; Academic: New York, 1981; pp 329–347.

(20) Madison, R. J.; Burnett, J. O. In *National Water Summary 1984—Water-Quality Issues*; U.S. Geological Survey: Denver, CO, 1984; pp 93–105.

(21) Long, T. *Ground water contamination in the vicinity of agrichemical mixing and loading facilities*; Illinois Department of Energy and Natural Resources: Chicago, 1988.

(22) *ODA Pesticides in Ground Water Survey*; Ohio Department of Agriculture: Columbus, 1989.

(23) LeMasters, G.; Doyle, D. J. *Grade A Dairy Farm Well Water Quality Survey*; Wisconsin Department of Agriculture, Trade, and Consumer Protection and Wisconsin Agriculture Statistics Service: Madison, 1989.

(24) Spaulding, R. F.; Burbach, M. E.; Exner, M. E. *Ground Water Monit. Rev.* **1989**, *9*, 126–133.

(25) Baker, D. B.; Wallrabenstein, L. K.; Richards, R. P.; Creamer, N. L. *Nitrates and pesticides in private wells of Ohio: A state atlas*; The Water Quality Laboratory, Heidelberg College: Tiffin, OH, 1989.

(26) Klaseus, T. G.; Buzicky, T. G.; Schneider, E. C. *Pesticides and Groundwater: Surveys of selected Minnesota wells*; Minnesota Departments of Health and Agriculture: St. Paul, MN, 1988.

(27) Exner, M. E.; Spalding, R. F. *Ground Water* **1985**, *23*, 26–34.

(28) Hallberg: G. R.; Dross, B. C.; Libra, R. D.; Burmeister, L. F.; Weih, L. M. B.; Lynch, C. F.; Bruner, D. R.; Lewis, M. Q.; Cherryholmes, K. L.; Johnson, J. K.; Culp, M. A. *The Iowa State-Wide Rural Well-Water Survey Design Report: A systematic Sample of Domestic Drinking Water Quality*; Technical Information Series 17; Iowa Department of Natural Resources: Iowa City, 1991.

(29) Iowa State-Wide Rural Well-Water Survey, Summary of State-Wide Results and Study Design. Report SWRL H-1; Iowa Department of Natural Resources and The University of Iowa: Iowa City, 1990.

(30) Iowa State-Wide Rural Well-Water Survey, Summary of Results: Pesticide Detections. Report SWRL H-2; Iowa Department of Natural Resources and The University of Iowa: Iowa City, 1990.

(31) Iowa State-Wide Rural Well-Water Survey, Summary of Results: Nitrate and Bacteria. Report SWRL H-3; Iowa Department of Natural Resources and The University of Iowa: Iowa City, 1990.

(32) Iowa State-Wide Rural Well-Water Survey, Summary of Results: Atrazine Detections. Report SWRL H-4; Iowa Department of Natural Resources and The University of Iowa: Iowa City, 1990.

(33) Jacobs, C. A. *Domestic Well Water Sampling in Nebraska, 1985 Laboratory Findings and Their Implications*; Nebraska Department of Health: Lincoln, 1985.

(34) Jacobs, C. A. *Domestic Well Water Sampling in Nebraska, 1986 Laboratory Findings and Their Implications*; Nebraska Department of Health: Lincoln, 1986.

(35) Jacobs, C. A. *Domestic Well Water Sampling in Nebraska, 1987 Laboratory Findings and Their Implications*; Nebraska Department of Health: Lincoln, 1987.

(36) *National Survey of Pesticides in Drinking Water Wells, Phase I Report*; EPA-570/9-90-015; U.S. Environmental Protection Agency, Office of Water, Office of Pesticides and Toxic Substances, U.S. Government Printing Office: Washington, DC, 1990.

Received for review September 6, 1991. Revised manuscript received January 15, 1992. Accepted January 21, 1992.