Michigan Department of Agriculture
Groundwater Monitoring Program
Domestic Supply Well
Baseline Study Report

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EXECUTIVE SUMMARY

The mission of the Michigan Department of Agriculture (MDA) Groundwater Monitoring Program is to determine the nature and extent of pesticide and nitrogen fertilizer contamination in Michigan's groundwater, to reduce the potential for negative health impacts associated with the use of low-quality groundwater, and to use the information gathered to improve communication about the risks to groundwater resources associated with different land-use activities. Over 2.5 million residents, 27.3 percent of Michigan's population, rely on domestic wells for their water supply (1990 U.S. Census).

The MDA groundwater monitoring program conducted a study of domestic well water quality between 1997 and 2000. It provides statistically meaningful estimates of domestic well water quality in rural areas of the state. The estimates apply to wells serving 83.5% of Michigan residents using domestic wells. Estimates for domestic supply wells in urban/suburban areas, serving the remaining 16.5% of Michigan residents using domestic wells, could not be made due to the nature of the study.

Samples from 391 wells selected at random were tested at the Michigan Department of Environmental Quality Drinking Water Laboratory for 75 pesticides, 66 volatile organic compounds, nitrite, and nitrate. The results have been weighted to correct for differences between the number of wells in the sample from each sub-population, and the number of wells in the state used by each sub-population. Detection frequencies are a function of detection limits, analytical methods, and the products detectable by the analyses used, other factors being equal. The results are summarized in the table below.

Parameter	Concentration	Estimated Frequency and 95% Confidence Interval		
		Rural Non-Farm	Farm	All Rural
Nitrate-N	> MCL	< 1.7%	3.9%; 2.0%-7.7%	< 1.9%
	> 20% MCL	9.2% ± 4.3%	12.7% ± 4.6%	9.3% ± 4.3%
	No impact observed	90.8% ± 4.3%	83.3% ± 5.1%	90.5% ± 4.3%
Pesticides (Listed in report Appendix A)	> MCL	< 1.7%	< 1.5%	< 1.7%
	> 20% MCL	< 1.7%	< 1.5%	< 1.7%
	Detected	< 1.7%	0.5%; 0.1%-2.7%	< 1.75%
	Not detected	> 98.3%	> 97.6%	> 98.25%
Volatile Organics (Listed in report Appendix A)	> MCL	< 1.8%	< 1.5%	< 1.8%
	> 20% MCL	< 1.8%	1.5%; 0.5%-4.5%	< 1.9%
	Detected	7.2% ± 3.9%	5.5% ± 3.2%	7.1% ± 3.9%
	Not detected	92.8% ± 3.9%	93.0% ± 3.5%	92.8% ± 3.9%

MCL Maximum Contaminant Level. Public water supplies must keep contaminant levels below the MCL. Domestic supply wells are *not* public water supplies.

Based on the results, it's estimated that *less than* 1.9 percent of all rural domestic wells in the state have nitrate-N levels above the public water supply Maximum Contaminant Level (MCL) of 10 ppm. Rural domestic wells include both farm and rural non-farm wells. The lack of detections of wells above 10 ppm nitrate-N in the rural non-farm group prevents a closer estimate. It's estimated that 3.9 percent of domestic wells on Michigan farms have nitrate-N levels of 10 ppm or higher, with a 95% confidence interval from 2.0% - 7.7%. No estimates of the frequency of wells with nitrate-N above 10 ppm were possible for urban/suburban wells, due to the lack of detections and the low number of wells sampled.

Approximately 9.3 percent of Michigan rural domestic wells, ± 4.3 percent, have been impacted by human-related nitrate sources, shown by nitrate-N levels between 2 and 9.9 ppm. Farm wells are somewhat more likely to have nitrate-N levels above 5 ppm than are rural non-farm wells ($p=0.078$). The study indicates that 90.5 percent of the state's rural domestic wells, ± 4.3 percent, have nitrate-N levels lower than 2 ppm, the threshold for nitrate-N levels associated with human-related impacts.

One known pesticide, atrazine, was detected in one well, at a level of 0.2 parts-per-billion (ppb), 6.7 percent of the public water supply MCL. This represents 0.5 percent of the farm domestic wells sampled, with a 95 percent confidence interval of 0.1 - 2.7 percent. The percentage of all rural domestic wells with a detectable level of one or more of the pesticides covered in this study is estimated to be *less than* 1.75 percent. Because only 12 urban/suburban wells were sampled, no meaningful estimate of the pesticide contamination frequency for this subgroup is possible.

Volatile organic compounds (VOCs) are estimated to occur in 7.1 percent, ± 3.9%, of rural domestic wells in Michigan based on this study. Fifteen different VOCs were detected, including products associated with well construction, maintenance, and disinfection; solvents associated with dry cleaning and/or metal degreasing; fuel components; and miscellaneous VOCs. One VOC, 1,2-dichloroethane, detected in one well, has been used both as a solvent and in soil fumigants. There was insufficient information to determine the source of this product. Tetrachloroethylene, also known as perchloroethylene or "perc", was detected in one well at a level of 2.7 ppb, equivalent to 54 percent of its MCL. Other than some nitrate detections, this was the highest concentration relative to the MCL found in this study. Other VOCs detected included carbon disulfide, carbon tetrachloride, chlorodifluoromethane, and chlorobenzene.

Methyl-*tert*-butyl ether (MTBE), a gasoline additive, was detected in one well at a level of 10 ppb. This falls in the range of 25 to 50 percent of the MCL, depending on where the U.S. EPA establishes the final MCL for MTBE.

It appears that contamination of rural domestic wells by VOCs is more common than pesticide contamination. The most likely VOC contaminants are those associated with well construction, maintenance, and disinfection (trihalomethanes and tetrahydrofuran); and with metal degreasing and dry-cleaning (chlorinated ethanes and ethylenes).

Of the compounds covered by this study, nitrate is the one most likely to be detected at a level above the public water supply MCL. Infants under the age of six months are most at risk from high nitrate levels, which can lead to a condition called *methemoglobinemia*. This condition reduces the capacity of infants' red blood cells to carry oxygen, and acute cases can be fatal.

Recommendations from the study are to continue monitoring domestic wells. Researchers and agencies must be aware of emerging monitoring issues, such as the presence of pesticide metabolites and degradates, contamination from pharmaceutical and veterinary products, and new toxicological, epidemiological, and fate and transport data showing changes in groundwater contamination risks.

The benefit/cost ratio of groundwater monitoring may be optimized by combining focused and statistical groundwater monitoring in the context of information needs. It's important to evaluate the water quality of urban/suburban domestic wells, given that over 400,000 Michigan residents rely on them. The MDA Groundwater Monitoring Program will be sampling urban/suburban domestic wells in FY 2001 and beyond to accomplish this goal.

There are many opportunities for cooperation in groundwater monitoring between federal, state, local, business, and non-profit organizations. Overcoming institutional inertia is the key to increasing cooperation in this discipline and reaping its rewards.

INTRODUCTION TO THE MICHIGAN DEPARTMENT OF AGRICULTURE GROUNDWATER MONITORING PROGRAM

The mission of the Michigan Department of Agriculture (MDA) Groundwater Monitoring Program is to determine the nature and extent of pesticide and nitrogen fertilizer contamination in Michigan's groundwater, to reduce the potential for negative health impacts associated with the use of low-quality groundwater, and to use the information gathered to improve the way we communicate the risks to groundwater resources associated with different land-uses.

Program Objectives

The groundwater monitoring program monitors private wells across the state to meet the objectives listed below. Sampling conducted under the program is focused based on information needs.

Baseline. The purpose of the baseline portion of the groundwater monitoring program is to provide data on groundwater quality throughout the state, so that decisions can be based on accurate and timely information. The program samples wells across Michigan for analysis using laboratory methods such as gas chromotography and mass spectroscopy (GC / MS), and screening methods such as enzyme-linked immunosorbent assay (ELISA, also known as immunoassay) to evaluate private well water quality in the state. The program also samples wells to develop a statistically valid analysis of pesticide and fertilizer problems in private water supplies.

Pesticide State Management Plans. The objective in this area is to meet the monitoring requirements of EPA Pesticide Management Plans (PMP) and to retain pesticide product registrations where those products can be used without negative impacts on groundwater quality. Wells in areas of high PMP chemical use are sampled to determine their impact on Michigan's groundwater.

Aquifer Vulnerability. The groundwater monitoring program has focused on a number of different site-types for the aquifer sensitivity part of the program, including bulk storage facilities, atrazine use, high-density animal, aerial applicators, and dairy. The program looks for pesticide uses that increase the risks of groundwater contamination, and then evaluates the frequency and severity of contamination for that site-type.

Confirmation and Envelope monitoring. The purpose of this portion of the groundwater monitoring program is to carry out the groundwater sampling and envelope monitoring necessary to complete site investigations and groundwater activity plans. Envelope monitoring refers to the sampling of wells around a known contamination in order to determine the extent of the contamination.

Program Staff

Groundwater monitoring program coordinator. The groundwater monitoring program coordinator manages the program. This individual designs individual monitoring programs, represents the department in groundwater monitoring matters with other agencies and institutions, writes project and program reports, and presents program and project information to other groups. This individual coordinates sampling between field and laboratory staff, supervises data entry, creates and maintains groundwater monitoring database forms, reports, and queries; communicates data and findings to well owners and agency staff, and participates in investigations of contaminated wells.

Regional groundwater specialists. These individuals carry out a variety of duties for the MDA Environmental Stewardship Division (ESD). With regard to the groundwater monitoring program they sample wells, particularly as part of contamination confirmation and envelope monitoring, and they participate in groundwater contamination investigations. There are 6 regional groundwater specialists.

Student assistants. The ESD hires student assistants to conduct routine well sampling and to carry out tasks such as data entry and basic data analysis.

Program Sampling and Analysis

The groundwater monitoring program conducts both random and focused monitoring to estimate drinking water well contamination frequencies and the relative risk of contamination caused by different land uses, different pesticides, and different locations. Samples are analyzed at the Michigan Department of Environmental Quality Drinking Water Laboratory (MDEQ-DWL) or at the MDA Pesticide and Environment (P & E) Laboratory.

The MDEQ-DWL typically analyzes MDA groundwater monitoring program samples for 75 pesticides, 66 volatile organic compounds (VOCs), and 8 water chemistry parameters (Appendix A). Some of the VOCs have been or still are used in pesticide formulations. The MDA P & E Lab analyzes samples for acetochlor, alachlor, atrazine, cyanazine, metolachlor, and simazine.

The program also screens drinking water well samples around the state using ELISA methods. Samples are screened for triazines using ELISA methods, and for nitrate and nitrite-nitrogen using a simple colorimetric strip test.

Virtually all wells sampled by the MDA groundwater monitoring program are existing domestic drinking water wells. Participation by well owners is voluntary, and monitoring results are confidential.

The program has carried out several projects in the past few years to meet the program objectives described above. In addition to this baseline study, the program has sampled wells of producers using PMP products, has conducted well screenings using the ELISA portable lab, and has carried out confirmation and envelope monitoring as necessary. The program also took part in a cooperative study with the United States Geological Survey (USGS) examining the impacts of recent urbanization on shallow and drinking water aquifers in southeast Michigan. The program has also been sampling drinking water wells serving migrant labor housing for the past three years. Reports and papers describing some of these projects are being prepared by groundwater monitoring program staff. Contact the MDA Groundwater Monitoring Program for more information.

BASELINE STUDY DESIGN

The target population of the baseline study was all Michigan households using a domestic water well (Figure 1). The groundwater monitoring program has carried out a two-phase study of this population, as described below. Approximately 1,121,000 of Michigan's 3,848,000 housing units, or 29.2 percent, of Michigan's housing units, rely on

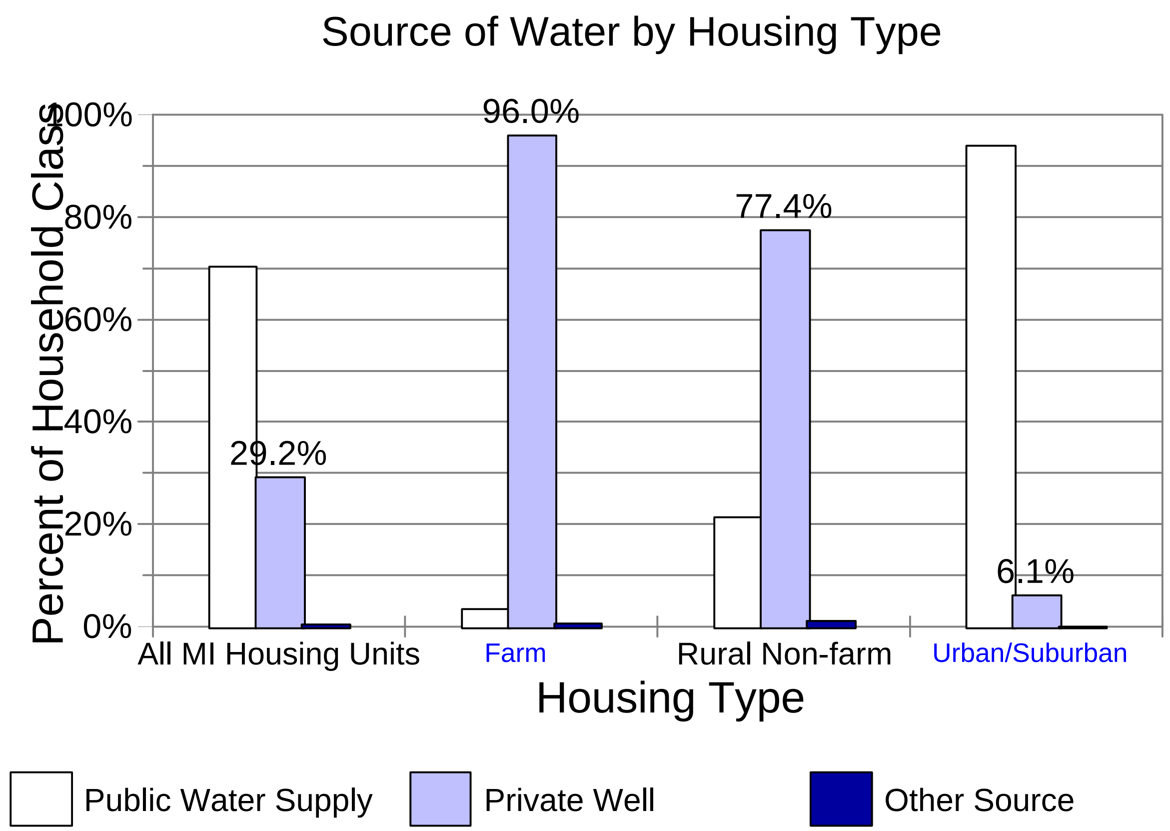


Figure 1. Source of water for different Michigan housing types, with percentage of housing units using domestic wells (U.S. Census 1990 PUMS)

domestic water supply wells as the source of their water (STF3A, U.S. Census, 1990). These figures include vacation and other seasonal homes, as well as vacant housing units.

The 1990 population estimates for Michigan, for groups used to stratify the population for this study, and for infants 6 months and younger are shown in Table 1. The population estimates for the infants were calculated as one-half of the population of Michigan residents under 1 year of age, and are included because infants younger than 6 months are most at risk of health problems when consuming water high in nitrate.

Table 1. Estimates of Population Using Domestic Supply Wells in Michigan. 1990 Census and 1990 Census Michigan 5% PUMS.

	Estimated Population	Estimated no. of infants 6 months or younger	Estimated population using domestic well	Estimated no. of infants 6 months or younger in households using domestic wells
Farm	121,647	642	116,781	610
Rural Non-farm	2,568,363	16,622	1,996,089	13,047
Urban/Suburban	6,586,971	46,417	418,974	2,350
Total	**9,276,981**	**63,687**	**2,531,844**	**16,013**

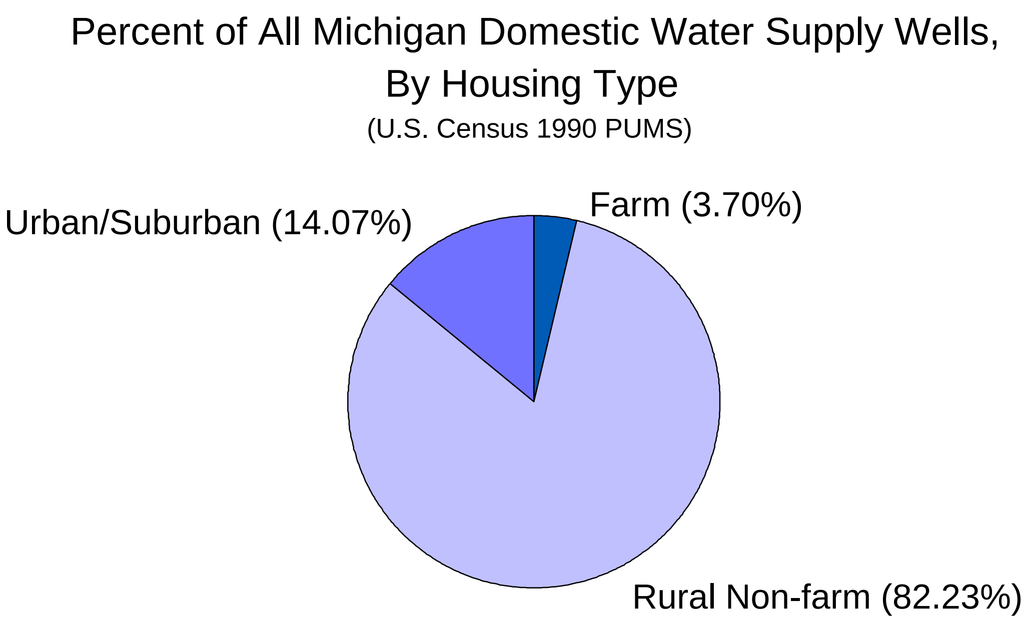


Figure 2. All Michigan domestic water supply wells, proportional by housing type.

The proportion of all domestic water supply wells in Michigan, categorized by housing type, is shown in Figure 2. Note that over 80 percent of all domestic supply wells in the state are used by rural non-farm housing units.

A stratified random sample of 200 urban / suburban households, and 800 rural households was drawn from a commercial database of all households with listed telephone numbers in the state (Survey Sampling Inc., 1996). This means that households with unlisted telephone numbers were not included in the sample. It also means that vacation and other seasonal homes with a phone number were included in the sample. A random sample of 400 farms households was drawn by the Michigan Agricultural Statistics Service (MASS), and this sample was included in the study. The primary purpose of this study was to obtain information using a mail survey instrument about participants' knowledge of basic groundwater concepts and of the Michigan Groundwater Stewardship Program.

Distinctions between urban/suburban and rural non-farm household types were based on Zipcodes. All non-urban Zipcodes were considered to be rural. The MASS followed the U.S. Census definition of a farm as any household living on 1 or more acres of land with $1,000 or more in sales of agricultural products in 1989.

When producing the mailing lists no effort was made to distinguish between households using domestic wells or public water supplies. Farm households were sampled for the mail survey at a higher relative frequency than other groups because of the pivotal nature they play in the implementation of the Michigan Groundwater Stewardship Program, and because of the comparatively high per capita impact (both positive and negative) the groundwater stewardship program has had on farmers, as compared to other nitrogen fertilizer and pesticide users.

Those selected were mailed a survey instrument to determine their knowledge, attitudes, and practices regarding groundwater stewardship. Respondents with private domestic wells were offered the opportunity to receive free water analyses. A questionnaire, cover letter, free water analysis request card, and a gift for filling out the questionnaire (rubber jar opener) were mailed to the sample population on March 18, 1996. A follow up postcard was mailed on March 28, 1996. A second questionnaire, cover letter, and free water analysis request card were mailed to non-respondents on April 11, 1996. A third and final questionnaire, cover letter, and free water analysis request card were mailed to non-respondents on May 10, 1996.

Of the 1,400 surveys mailed, 150 (10.7 percent) were undeliverable. Usable surveys from 663 households were submitted, for a response rate of 53 percent (663/1250) of the delivered surveys. Among respondents, 418 (63 percent) indicated that their water came from a private well. The remaining 245 respondents (37 percent) said that they received their water from public water supplies.

Of the 418 respondents that use a private well, 280 requested a free water analysis. The distribution of the requests for water analysis by housing type is shown in Table 2.

Table 2. Phase 1 requests for free water analysis, by household type. Percent of household types using domestic wells from the 1990 U.S. Census Michigan 5 percent extract PUMS.

Housing Type	Initial Mail Sample	Est. No. of Analysis Offers Delivered*	Percent Housing Type Using Well	Est. No. of Analysis Offers Delivered to Well Users	Number of Analysis Requests	Analysis Requests as Percent of Est. No. of Analysis Offers Delivered to Well Users
Farm	400	357	96.0%	343	155	45.2%
Rural Non-farm	800	714	77.4%	553	109	19.7%
Urban/Suburban	200	179	6.1%	11	16	146.9%
Total	1400	1250	72.5%	907	280	30.9%

* Assumes 10.7 percent undeliverable for all household types.

The estimated response rate for the free water analysis request as shown in Table 2 is about 31 percent. This raises the question of whether or not the monitoring sample was representative of those receiving the mail survey, and the population represented by the mail survey. There is, however, reason to believe that rural non-farm residents may not have received the same proportion of free analysis offers. Data from the 1990 U.S. Census 5 % Public Use Microdata Series for Michigan show that 25% of rural Michigan housing units were vacant. The majority, 19.7%, were classified as seasonal, recreational, or other occasional use. The remaining rural housing units were vacant because they were for sale or rent, because they were not yet occupied, or for other reasons. All rural non-farm housing units with a telephone were included in the population to be sampled. Given that matching rural addresses is more difficult than matching urban addresses, and given the high vacancy rate, it’s quite feasible that surveys and offers were not delivered proportionally to rural non-farm housing units (that is, they were a higher relative proportion of the undeliverable surveys, *and* that surveys were delivered to vacant vacation units, and possible participants did not receive them until either their mail was forwarded or they visited their cabin.

If the proportion of households with domestic water supply wells was the same for both the respondents to the initial baseline mail survey and the non-respondents, then approximately 788 households with a domestic water supply received an offer for a free water analysis (63% of 1250), and 35 percent (280 respondents) accepted the free water analysis offer.

There is evidence that not as many rural non-farm housing units received surveys and free analysis offers as expected. The baseline survey study indicated that responses were distributed as follows: 32.1 percent from city or town areas; 33.6 percent from outside a city or town but not on a farm, and 31.8 percent from farms or ranches. This means 213 responses came from households inside a city or town, while only 200 surveys were mailed to urban/suburban households (Krueger and Suvedi, 1996). One possible explanation is that some of the respondents in the rural non-farm subsample were from small towns, and indicated that they lived in a town or city area.

The relatively high proportion of respondents requesting a free water analysis from the urban/suburban subsample is another indication that the rural non-farm and urban/suburban subsamples may have overlapped, given that the response rate from this group was 3 to 4 times higher than was expected.

Phase I Sampling Methods

Initially, it was decided to have well owners collect their own samples and mail them back to the MDA groundwater monitoring program. Sampling kits were shipped to respondents, beginning in October 1996 (FY 1997). This method proved to be impracticable for this project for several reasons. Despite writing instructions in the simplest language consistent with sampling requirements, and pretesting the instructions, we received a number of complaints or comments that the instructions or the sampling were too complicated (One suggestion received after this phase was to include a video of the sampling procedures as well). Although all respondents had requested the well water analysis, the return rate for the kits, using prepaid shipping, was less than 75%. Of the kits returned, 12.8% had volatile organic compound (VOC) samples that were not usable, due to the presence of large air bubbles. This method also required a great deal of handling and preparation time. The last set of kits mailed to respondents was shipped in April 1997.

It was decided in May 1997 to have regional groundwater specialists collect the remaining baseline samples, using standard MDA groundwater monitoring procedures. A total of 116 baseline wells were sampled using both methods in FY 1997. MDA staff completed Phase I baseline monitoring in FY 1998, sampling 96 baseline wells.

Due to the two year lag between the initial survey and the baseline sampling in FY 1998, MDA staff were unable to contact a number of well owners. The remaining well owners were no longer willing to participate in the study, with most citing the extensive delays in the project and the program's failure to meet projected schedules. In all, 68 well owners could no longer be contacted or withdrew from the study. The distribution of household types was quite similar between the initial sample, based on free analysis requests, and the final distribution based on those actually sampled. There was a slight decrease in the percentage of urban/suburban wells sampled, and a corresponding increase in the percentage of farm wells sampled. The comparison is shown below, in Table 3.

Table 3. Comparison of requests for water analysis and wells sampled for Phase I, by household type.

Household Type	Number of analysis requests	Requests as Percent of Analysis Requests	Number of Wells Sampled	Wells Sampled as Percent of Phase I
Farm	155	55.4%	125	59.0%
Rural non-farm	109	38.9%	79	37.3%
Urban/Suburban	16	5.7%	8	3.8%
Total	280	100.0%	212	100.0%

Phase I Analytical Methods

Samples collected during FY 1997 of the Phase I baseline study were analyzed at the Michigan Department of Environmental Quality Drinking Water Lab for the following analytes. A complete list of analytes by sampling year, with methods, is presented in Appendix A. A brief description is presented below.

The automated partial chemistry battery is a test for water quality parameters such as hardness, iron, fluoride, sodium, nitrate, and nitrite. The pesticide screening by Nitrogen-Phosphorous Detector (NPD) examines samples for triazines such as atrazine and simazine, acetanilides such as alachlor and metolachlor, and other herbicides. The chlorinated acid herbicide scan covers 2,4-D; bentazon, other herbicides, and the wood treatment product pentachlorophenol. The carbamates by High-Performance Liquid Chromatography / Photo-Conductivity Detector (HPLC / PCD) scan is a test for insecticides such as aldicarb, methiocarb, carbaryl, and carbofuran. The UV active pesticide by HPLC / Ultra-Violet (HPLC / UV) is a test for chemically related herbicides linuron, diuron, fluometuron, and others. The test for organic solvents by Ion-Trap Detector (ITD) is a test for trihalomethanes such as chloroform, for former fumigants such as 1,2-dichloropropane and ethylene dibromide, solvents such as trichloroethylene, toluene, and benzene; and a host of other organic solvents.

Due to reductions in MDEQ lab support for the MDA groundwater monitoring program, samples collected in FY 1998 were analyzed for the analytes shown in Table 5.

The CXLU scan was dropped from the study, and the CXPT scan was substituted for the CXNP scan. The net effect was to reduce analysis costs while adding analytes of

Table 4. Analyses performed on MDA baseline samples collected in FY 1997

TEST DESCRIPTION	SCAN CODE	TEST METHOD	NUMBER OF ANALYTES	RANGE OF DETECTION LIMITS
Automated Partial Chemistry Battery	CRA	MDEQ	8	0.05 - 10 mg/L
Pesticides Screening by NPD	CXNP	EPA 525.1	20	0.0001 - 0.005 mg/L
Chlorinated Acid Herbicides	CXHB	EPA 515.2	9	0.00006 - 0.004 mg/L
Carbamates by HPLC/PCD	CXLP	EPA 531.1	10	0.0002 - 0.002 mg/L
UV Active Pesticides by HPLC/UV	CXLU	MDEQ	7	0.001 - 0.005 mg/L
Organic Solvents by ITD	CXVO	EPA 524.2	66	0.0002 - 0.05 mg/L

interest, and dropping analytes that had never been detected in groundwater in MDA samples. The pesticide screening by Electron Capture Detector (ECD) and NPD is a test for triazines, acetanilides, other herbicides, and in addition tests for organochlorines such as DDT, chlordane, heptachlor, and PCBs.

Phase II Sampling Methods

The decision was made to replicate the sample selection method of Phase I in order to be able to combine the results and increase the accuracy and precision of the study, if warranted by the data. Wells were selected for Phase II of the baseline study in the following manner. A stratified random sample of 150 urban and suburban households and 650 rural households was drawn from telephone directories using 1990 U.S. Census definitions of rural and urban places. A random sample of 325 farm households was drawn by the Michigan Agricultural Statistics Service. Letters to the sample population were mailed, offering a free set of water analyses to the first 200 respondents with a private drinking water well. All letters were mailed May 28, 1999. Because this was simply an offer for a free water analysis, no follow-up mailings were made. Requests for participation were screened to be sure no Phase 1 participants were included in Phase II. None of the Phase II respondents had taken part in Phase I.

Table 5. Analyses performed on MDA baseline samples collected from FY 1998 through FY 2000

TEST DESCRIPTION	SCAN CODE	TEST METHOD	NUMBER OF ANALYTES	RANGE OF DETECTION LIMITS
Automated Partial Chemistry Battery	CRA	MDEQ	8	0.05 - 10 mg/L
Pesticides Screening by ECD & NPD	CXPT	EPA 525.1	56	0.00002 - 0.005 mg/L
Chlorinated Acid Herbicides	CXHB	EPA 515.2	9	0.00006 - 0.004 mg/L
Carbamates by HPLC/PCD	CXLP	EPA 531.1	10	0.0002 - 0.002 mg/L
Organic Solvents by ITD	CXVO	EPA 524.2	66	0.0002 - 0.05 mg/L

Of the 1,125 free water analysis offers mailed, 64 (5.7 percent) were undeliverable. This

rate is substantially lower than the 10.7 percent undeliverable rate for the Phase I mailing. Eligible requests for water analyses from 193 households were returned.

The Phase II respondents requesting free water analyses are shown by category in Table 6. The poor response from farm households, relative to Phase I, is most likely due to the fact that the free analysis offers were mailed at a very busy time of the year for farmers, and they did not want to take the time to deal with the request and the sampling. Response from the rural non-farm households was quite similar to Phase I. Response from the urban/suburban households was much lower proportionally, but in absolute terms was only 12 wells less than Phase I. A follow-up mailing would undoubtedly have improved the response rate for all groups.

Table 6. Phase II requests for free water analysis, by household type. Percent of household types using domestic wells from the 1990 U.S. Census Michigan 5 percent extract PUMS.

Housing Type	Initial Mail Sample	Est. No. of Analysis Offers Delivered*	Percent Housing Type Using Well	Est. No. of Analysis Offers Delivered to Well Users	Number of Analysis Requests	Analysis Requests as Percent of Est. No. of Analysis Offers Delivered to Well Users
Farm	325	306	96.0%	294	88	29.9%
Rural Non-farm	650	613	77.4%	474	101	21.3%
Urban/Suburban	150	141	6.1%	9	4	46.4%
Total	1125	1061	73.2%	777	193	24.9%

* Assumes 5.7 percent undeliverable for all household types.

For Phase II, 179 wells were sampled. The remaining well owners declined to participate when they were contacted to arrange a sampling appointment, or could not be reached by phone and did not respond to attempts to schedule sampling by mail.

Phase II water samples were analyzed at the MDEQ Drinking Water Laboratory for the same set of parameters as the samples collected in FY 1998. See Table 5 for details. The individual compounds covered by the scans are shown in Appendix A.

All samples were collected by MDA regional groundwater specialists and by MDA student assistants, using standard MDA groundwater monitoring procedures.

Aggregation of Results

A fundamental question that must be addressed at this time is whether or not the monitoring results from the two phases of this study can be aggregated meaningfully. Phase II sampling was designed specifically to allow the results to be combined with the Phase I results. The null hypothesis, or basic assumption, is that the two phases come from the same population, and that the data may be aggregated. The analysis of the null hypothesis is presented below.

Results from the automated partial chemistry tests for the two phases were compared. This was done for a number of reasons. The analytes compared—chloride, fluoride, hardness, iron, sodium, and sulfate—are conservative; that is, they do not react or change concentration rapidly in groundwater environments. The second reason is that most of these analytes are present to some extent in most samples, which allows a solid basis of comparison between the two phases. *The inherent assumption is that if the partial chemistry data for the two phases indicates no reason to reject the null hypothesis that the two* *phases come from the same population, then the pesticide and volatile organic compound results can safely be aggregated as well.*

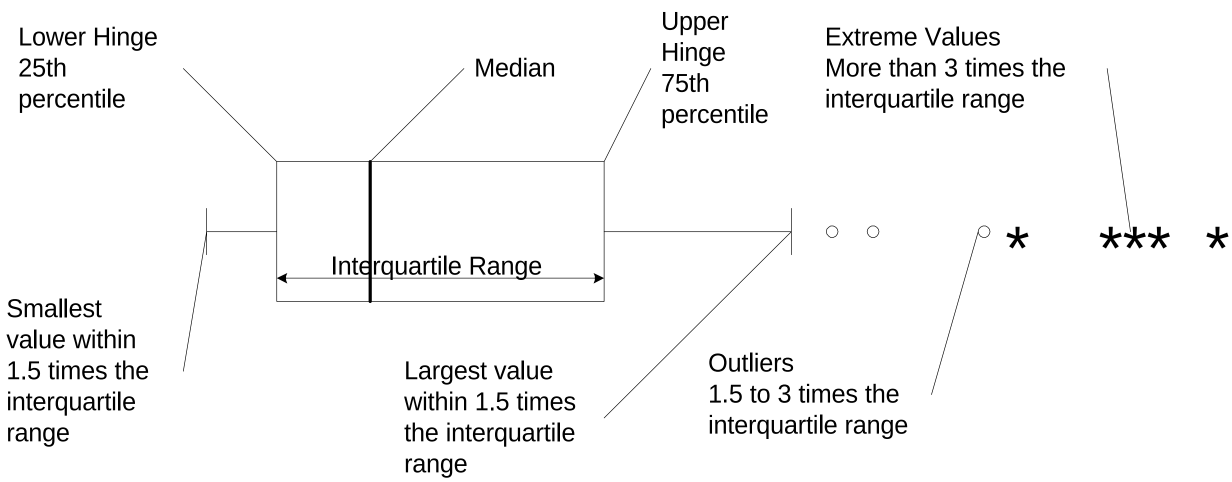


Figure 3. Diagram of boxplot (or box and whisker plot). Helsel and Hirsch, 1993, pp 24-26, 451-453; Norušis, 1998, pp 100-101.

First, data from the two phases were compared by the use of boxplots. Boxplots are summary plots based on the median, quartiles, and extreme values of the data. Descriptions of the different elements of a boxplot are shown in Figure 3. The box represents the interquartile range (from the 25th percentile to the 75th percentile), containing 50% of the values. A line across the box indicates the median. Strictly speaking, the upper and lower ends of the box, as used in this paper, are Tukey hinges, the median of all values greater than (or less than) the sample median. For samples larger than about 30 values, the hinges are essentially equivalent to the 25th and 75th percentiles. The whiskers are lines that extend from the box to the highest and lowest values within 1.5 box lengths (1.5 times the interquartile range). Outliers in the plots presented are values from 1.5 to 3 times the interquartile range, and are indicated by circles. Extreme values are values more than 3 times the interquartile range, and are represented by asterisks (Norušis, 1998). The presence of outliers and extreme values in a standard boxplot is a strong indication that the data are not from a normal distribution. In the boxplots presented, detection limits are indicated and no data below the detection limits are shown. For some variables not all outliers and extreme values were plotted, in order to show the boxes and whiskers more clearly.

As can be seen by examining the boxplots in Appendix B, in which data from the two phases are plotted side by side, there is a great deal of similarity in the distributions and medians of the data. With the possible exception of the dissolved iron and nitrate data, the boxplots for each of the water chemistry parameters appear quite similar. The presence of numerous outliers and extreme values indicates that the data are not from a normal distribution (Helsel and Hirsch, 1993, p. 25-26).

What boxplots do not tell us is whether or not the differences that can be seen are statistically significant. There are a number of statistical tests to determine if two independent samples, such as the Phase I and Phase II baseline sample sets, have the same central tendencies and distribution: that is, to determine whether or not they appear to be from the same population. In general, the methods can be distinguished as either parametric or nonparametric. Parametric methods require that data (or a transformation of the data) have a normal distribution. The normal distribution refers to a Gaussian probability distribution that is commonly described as bell shaped. Any non-trivial violation of this assumption results in a significant loss of power for the parametric methods, meaning that the tests will be unable to distinguish significant differences between samples that are actually present. "When parametric tests are applied to non-normal data, their power to detect differences which are truly present is much lower than that for the equivalent nonparametric test." (Helsel and Hirsch, 1993, p. 127)

Helsel and Hirsch (1993, pp. 2-3) describe characteristics of water resources data that certainly apply to the data from this study.

- No negative values for the phenomena being studied (flow, concentrations, etc.) are possible.
- Outliers, and/or extreme values, are regularly present. Outliers are more common on the high end of the distribution.
- The distribution of data is positively skewed, which is expected when outlying values occur almost entirely on the high end of the distribution. This is evident in the boxplots of the baseline results.
- Basic water resources data are typically non-normal in distribution, due to the first three factors.
- Another common characteristic, and one that is significant for the baseline study, is that some data are reported only as below a particular level (i.e., not detected, at a level varying for each analyte). These results are called censored data. The presence of censored data also limits or prohibits the use of certain statistics.

As a result of these characteristics, the use of nonparametric statistical methods is indicated.

The rank-sum test, also known as the Wilcoxon rank-sum test or the Wilcoxon-Mann-Whitney rank-sum test is typically used to determine whether two independent samples come from the same population (same median and other percentiles), or if they differ only in location (central value or median). No assumptions are required about how the data are distributed; only that the distribution of the two samples be equal. The test can handle two different sample sizes. Because it is meant to be used with continuous variables, the number of tied ranks relative to the number of observations should be low, and should definitely be less than 50%. The only data set from the partial chemistry analysis that meets these criteria is the water hardness data.

Upon running the rank-sum test, the test statistic Z was calculated as -0.459. Z is used as the test statistic in the rank-sum test for large samples such as the two baseline phases. The two-tailed significance level is 0.646. In other words, for samples of this size, there is almost a 65% chance of observing differences in the rank of hardness concentrations equal to those found in this analysis when two independent samples are drawn from the same population. This means that there is no reason to believe the two samples came from different populations with regard to water hardness (SPSS for Windows, Release 10.0.0, 1999).

Water hardness is only one parameter. If the two phases were from the same population we would expect that the other partial chemistry parameters would show similar results. Because of the large number of non-detects and tied values, however, the rank-sum test is not appropriate for these data. Instead, a categorical analysis was used. In the particular analysis used, the Kruskal -Wallis test for ordered categorical responses, the results were categorized by phase and by response category. For example, nitrate results were separated by sampling phase, and then the number of observations falling into the following categories were counted:

- not detected
- detected, at possible background levels
- detected above background levels but below the Maximum Contaminant Level (MCL) of 10 ppm nitrate-N
- at or above the MCL.

This results in a 2 x 4 table. Average row and column ranks are calculated, and the Kruskal-Wallis test statistic is calculated. To evaluate its significance, the test statistic is compared to the chi-square distribution with the appropriate degrees of freedom. The results of this analysis are shown in Table 7.

As can be seen, in each case the Kruskal-Wallis test statistic was smaller than the corresponding chi-square value, meaning there was no significant difference in the results of the two phases at a 0.05 level of significance. In fact, there was no significant difference between results even at the relaxed significance level of 0.10. This means there is no reason to reject the hypothesis that the two phases come from the same population, based on the comparison of partial chemistry results. The results of the baseline study will be presented with the two phases combined.

Table 7. Kruskal -Wallis test for ordered categorical responses, from *Statistical Methods in Water Resources, pp. 382-385.*

Analytes	K, Kruskal-Wallis test statistic	Chi-Square Statistic (.95, deg. of freedom)	Chi-square cumulative distribution
Iron, dissolved	3.39	5.99, 2 deg. of freedom	0.183
Fluoride	0.335	5.99, 2 deg. of freedom	0.846
Chloride	0.831	5.99, 2 deg. of freedom	0.660
Sodium	0.069	5.99, 2 deg. of freedom	0.966
Nitrate	3.16	7.81, 3 deg. of freedom	0.367
Sulfate	0.677	5.99, 2 deg. of freedom	0.713

BASELINE STUDY RESULTS

The results of the groundwater monitoring baseline study are presented below. The discussion of results will focus on analytes of interest such as nitrate, nitrite, pesticides, and volatile organic compounds. However, before beginning this discussion a word of caution is necessary. The detection of analytes, including contaminants, is a function of a variety of factors, including :

- What is looked for. If an analyte is not included in the lab methods, it will not be found.
- Where we look. Analytes are associated with geologic conditions, land uses, population density, precipitation, and other factors.
- How we look. The selection of sampling and analysis methods clearly affects the detection of analytes. Certain methods are more likely to detect certain analytes.
- Detection limits. Even when the same method is used, detection limits can vary, and will directly affect the number of detections found. For example, the U.S. Geological Survey typically uses method detection limits that are one to two orders of magnitude lower than many of the MDEQ DWL detection limits. Obviously, they will find more detections.

Project design must take into account data needs, and manipulate the factors above to meet those needs within program constraints. It is up to scientists, project managers, and decision makers to evaluate results in the context of public and environmental health, and to take appropriate actions.

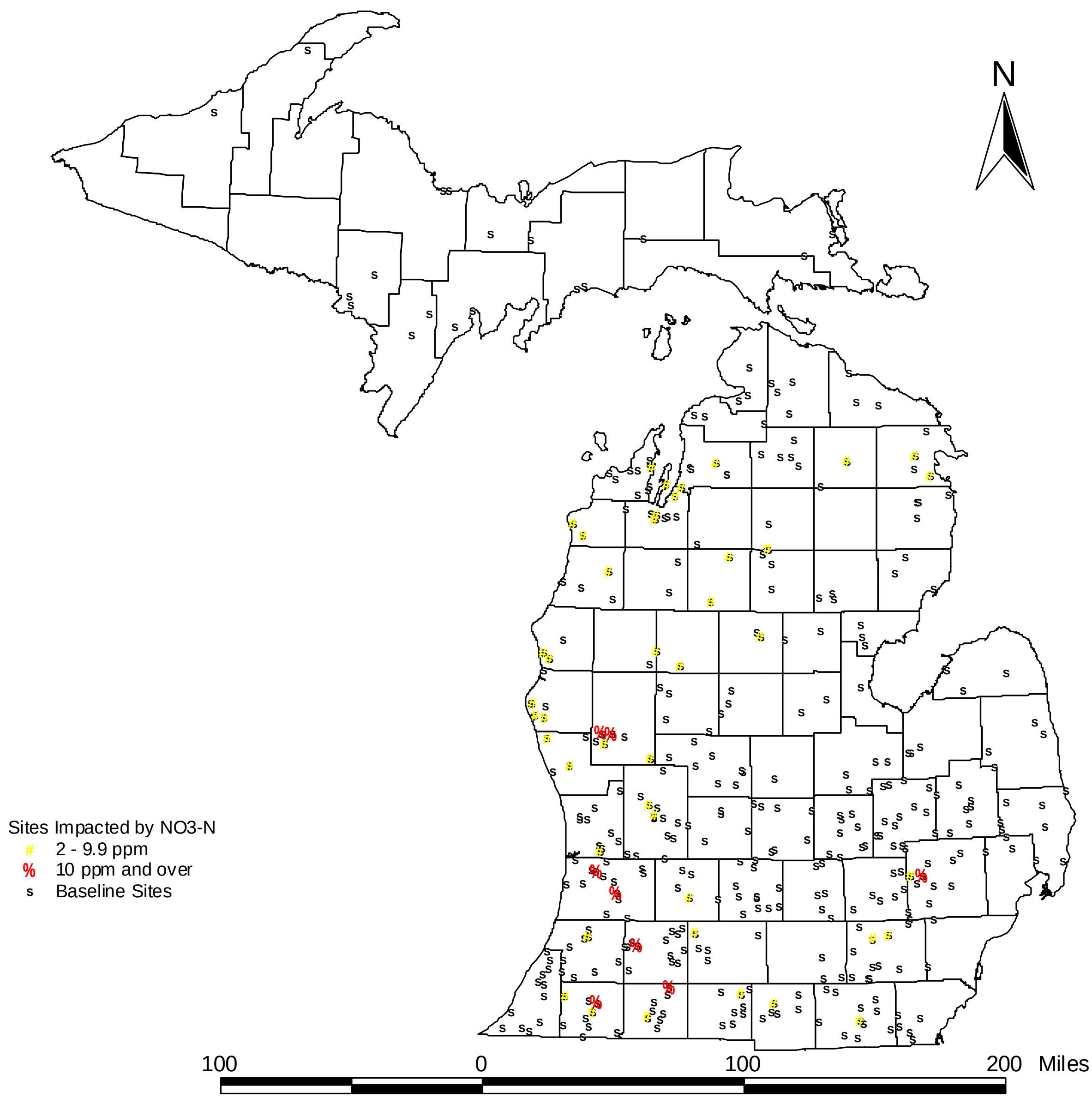
The results will be presented by weighting them to represent the proportion of wells in the respective subsamples. A map of wells sampled for nitrate and nitrite is shown in Figure 4. A map of wells sampled for pesticides and VOCs is shown in Figure 5.

Nitrate-N Results

Samples from 390 wells were analyzed for nitrate-as-nitrogen (NO3-N or nitrate-N). One sample was lost or destroyed in a lab accident. Results are shown in Figure 6 and Table 8.

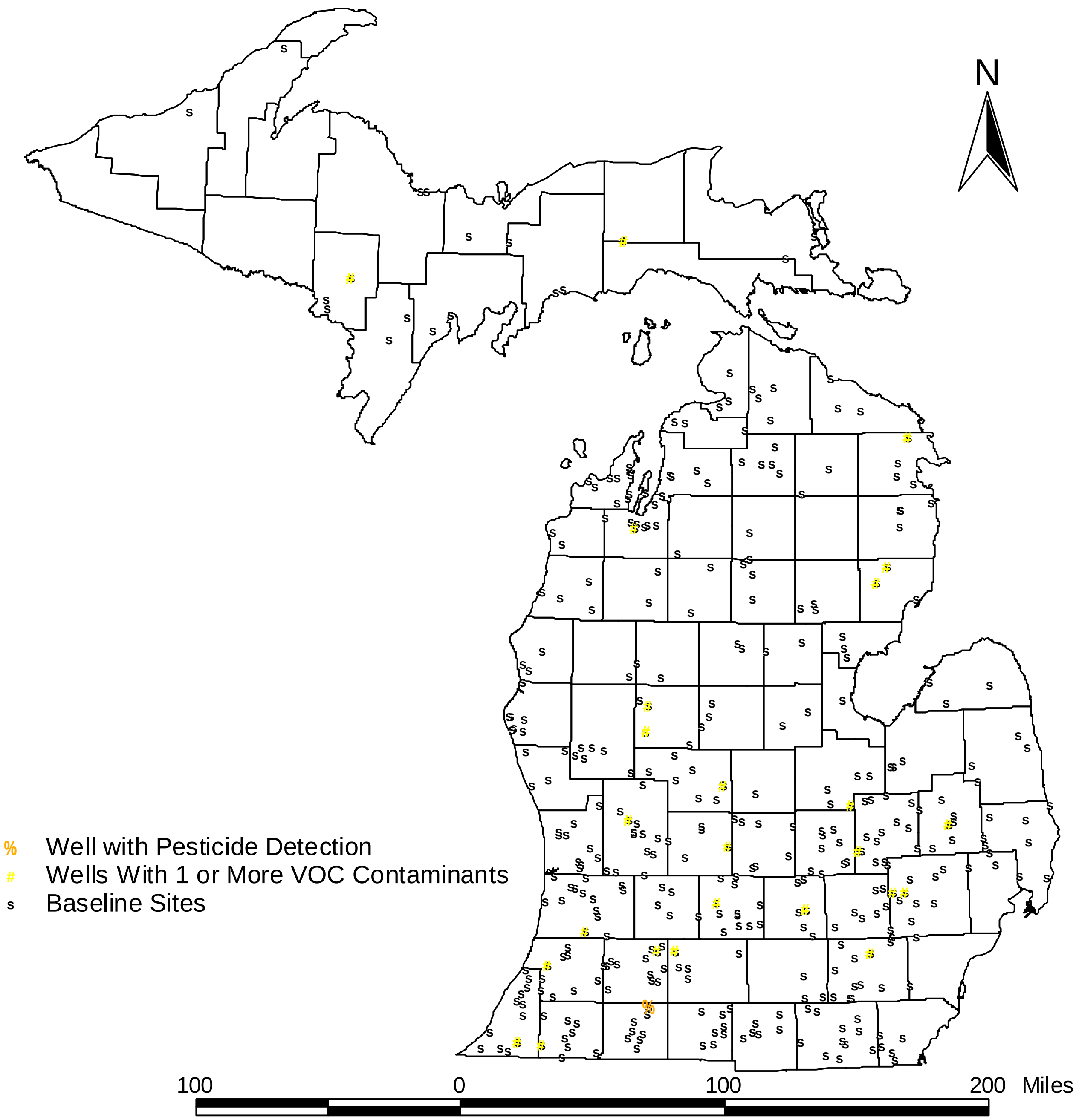
Nitrate results are shown broken down by categories related to human use or impact on groundwater in Table 8. The Maximum Contaminant Level (MCL) for nitrate-N is 10 mg/L. The category of results from 2 to 9.9 mg/L reflects the percent of wells that appear to have been impacted by human-related sources of nitrates. The range of results from “Not Detected” to 1.9 mg/L represents wells that do not yet show signs of human-related nitrate sources (Mueller and Helsel, 1996).

MDA Baseline Sites
Sampled for Nitrate



Lambert Conformal Conic Projection
Michigan State Plane Central Zone
North American Datum 1983

MDA Baseline Sites
Sampled for Pesticides and VOCs



Lambert Conformal Conic Projection
Michigan State Plane Central Zone
North American Datum 1983

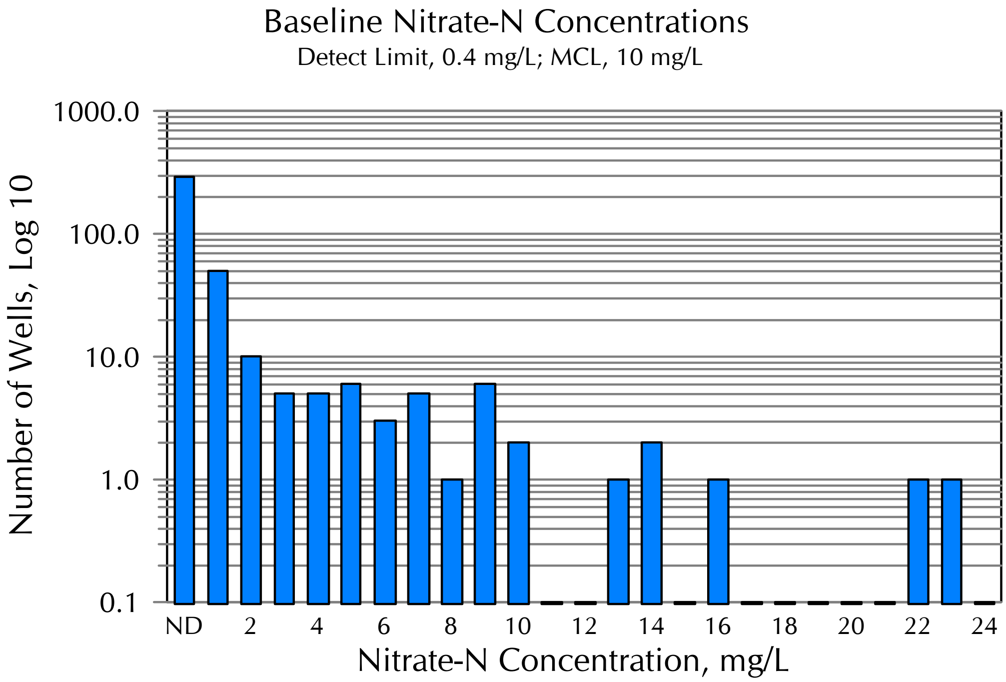


Figure 6. Distribution of nitrate detections for MDA baseline study

The number of wells at each nitrate-N detection level is shown in Figure 6. All nitrate detections are shown. The log-base 10 scale is used due to the wide spread on the scale.

Regarding confidence intervals, we can say that over time, if many samples were collected from the same population sampled for this study, approximately 95% (or whatever the confidence interval is) of the intervals will correctly cover the true population proportions.

Table 8. Distribution of nitrate-N results by subpopulation.

Detection Range	**Number of Wells**			
	Farm	Rural	Urban-Suburban	Total
10 mg/L or higher	8	0	0	8
2 - 9.9 mg/L	26	16	1	43
Not Detected - 1.9 mg/L	170	158	11	339

The percentage of rural domestic wells with detections at or above 10 mg/L NO3-N is much lower than the corresponding percentage of farm wells, because farm wells make up only 4.3 percent of all rural domestic wells, and no NO3-N detections at or above 10 mg/L were found in rural non-farm wells.

Table 9. Proportion of rural Michigan domestic supply wells, by nitrate-N levels, weighted by sampling proportion.

Detection Range	Rural Non-Farm	Farm	All Rural	Significance Level of C. I.
10 mg/L or higher	< 1.7%	3.9%; 2.0%-7.7%	< 1.9%	95.0%[a]
2 - 9.9 mg/L	9.2% ± 4.3%	12.7% ± 4.6%	9.3% ± 4.3%	95.0%[b]
Not detected - 1.9 mg/L	90.8% ± 4.3%	83.3% ± 5.1%	90.5% ± 4.3%	95.0%[b]

[a] Confidence Interval calculated from Poisson cumulative distribution
[b] Confidence Interval calculated from large sample normal approximation to the binomial distribution.

Nitrite-N Results

Samples from 390 wells were sampled for nitrite-as nitrogen, or nitrite-N. One sample was lost or destroyed in a lab accident. The results are shown in Table 10 and in Figure 7 below.

Table 10. Groundwater monitoring baseline study nitrite-N results, with confidence intervals. Detection limit is 0.05 mg/L, the MCL is 1.0 mg/L.

Detection Range	Rural Non-Farm	Farm	All Rural Wells	Significance Level of C. I.
1 mg/L or higher	0.00%	0.00%	< 1.7%	95.0%[a]
0.21 – 0.99 mg/L	0.6%	0.0%	0.6%; 0.1% – 2.8%	95.0%[a]
0.05 – 0.2 mg/L	2.3%	2.9%	2.3%; 1.0% – 5.9%	95.0%[a]
Not Detected	97.1%	97.1%	97.1%; ± 2.4%	95.0%[b]

[a] Confidence Interval calculated from Poisson cumulative distribution
[b] Confidence Interval calculated from exact binomial distribution.

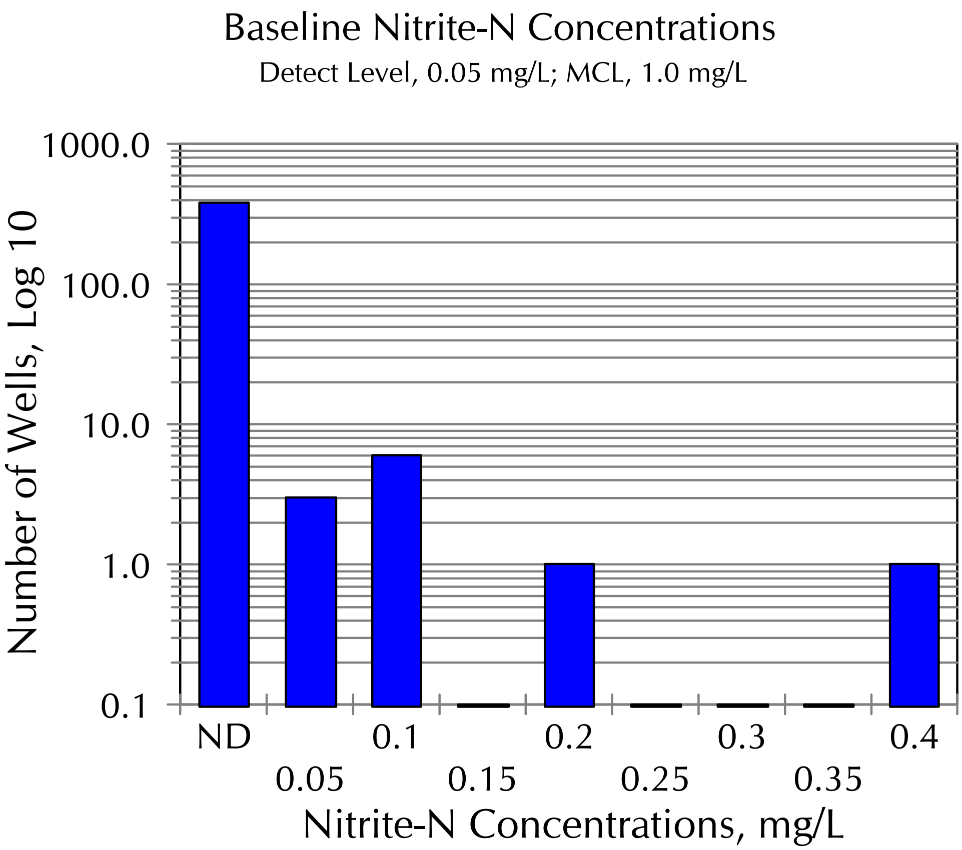


Figure 7. Distribution of nitrite detections for MDA baseline study

Of the wells sampled, 379 had no nitrites detected, at a detection limit of 0.05 mg/L. Only 1 well had a nitrite-N detection in a range indicating human impact (0.36 mg/L). No wells exceeded the nitrite-N MCL of 1.0 mg/L. The remaining 10 wells were in a range which could be considered background level, from 0.05 - 0.2 mg/L nitrite-N.

Pesticide Detections

Only 1 well out of 391 sampled for pesticides tested positive for a product known to be a pesticide. The volatile organic compounds (VOC) detections included several products, used currently or historically, both for agricultural and commercial use. VOC detections will be discussed in the VOC section.

Atrazine was detected in a farm well at a level of 0.2 µg/L (micrograms/liter), a level right at the MDEQ DWL detection limit. No other pesticides were detected in any wells sampled for this study. This represents a proportion of 0.5% of the farm wells sampled.

Table 11. Distribution of pesticide detections by subpopulation. See Appendix A for list of analytes, detection limits, and MCLs.

Detection Range	**Number of Wells**			
	Farm	Rural	Urban-Suburban	Total
> MCL	0	0	0	0
> 20% MCL	0	0	0	0
Detected	1	0	0	1
Not detected	204	174	12	390

Atrazine is the most widely used restricted use pesticide in Michigan, based on pounds of active ingredient sold. It is a triazine herbicide used on corn. Assuming the sample represented the likelihood of detecting the analytes covered by the lab analyses, the confidence interval for the proportion of wells with a detectable level of pesticide is *less than* 1.75%. The significance level of the confidence interval is 95.0%. This was calculated from the Poisson cumulative distribution which left an upper rejection region of no more than 5.0%. In other words, using similar methods we would expect to see pesticide detection frequencies in rural domestic wells greater than 1.75% less than 5% of the time. The significance of these results will be discussed in the Conclusions.

Table 12. Groundwater monitoring baseline study pesticide results, with confidence intervals. See Appendix A for list of analytes, detection limits, and MCLs.

Detection Range	Rural Non-Farm	Farm	All Rural Wells	Significance Level of C. I.
> MCL	< 1.7%	<1.5%	< 1.7%	95.0%[a]
> 20% MCL	< 1.7%	< 1.5%	< 1.7%	95.0%[a]
Detected	< 1.7%	0.5%; 0.1%–2.7%	< 1.75%	95.0%[a]
Not detected	> 98.3%	> 97.6%	> 98.25%	95.0%[a]

[a] Confidence Interval calculated from Poisson cumulative distribution

Volatile Organic Compound Detections

One or more VOCs were detected in 26 of the 379 wells sampled for VOCs in the study. This represents 6.9% of the wells sampled for VOCs in the study. The products detected are or have been used for a variety of purposes. Twelve samples collected by well owners in the initial stage of Phase I were received with large air bubbles. These samples were not submitted for analysis, as the air bubbles precluded an accurate VOC analysis.

The distribution of VOC contamination by sub-population is shown in Table 13. The weighted proportion of VOC contaminated wells is shown in Table 14.

The two project phases were compared using the number of wells with VOCs detected in a contingency table. The Chi-squared distribution of 0.602, from the contingency table test statistic of 0.271 with 1 degree of freedom, indicates that 60.2% of the time, one would expect to see differences caused by chance at least as great as those observed between the two project phases in the rate of VOC contamination. In other words, the two phases showed results that would be expected if VOC detections were randomly distributed between the two phases.

Table 13. Distribution of VOC by subpopulation.

Detection Range	Number of Wells			
	Farm	Rural	Urban-Suburban	Total
> MCL	0	0	0	0
> 20% MCL	3	0	0	3
Detected	11	12	0	23
Not detected	187	155	11	353

Table 14. Estimated proportion of farm and rural non-farm wells with 1 or more VOC contaminants, weighted proportionally by baseline subgroups. See Appendix A for list of analytes, detection limits, and MCLs

Concentration	Rural Non-Farm	Farm	All Rural	Significance Level of C. I.
> MCL	< 1.8%	< %1.5	< 1.8%[a]	95.0%[a]
> 20% MCL	< 1.8%	1.5%; 0.5%-4.5%	< 1.9%[a]	95.0%[a]
Detected	7.2% ± 3.9%	5.5% ± 3.20%	7.1% ± 3.9%[b]	95.0%[b]
Not detected	92.8% ± 3.9%	93.0% ± 3.5%	92.8% ± 3.9%[b]	95.0%[b]

[a] Confidence Interval calculated from Poisson cumulative distribution.
[b] Confidence Interval calculated from exact binomial distribution.

A contingency table comparison of **farm** and **rural non-farm** wells showed no significant differences between the number of farm and rural non-farm wells with one or more VOC detections. The Chi-squared distribution of 0.935, from the contingency table test statistic of .0068 with 1 degree of freedom, indicates that 93.5% of the time, one would expect to see differences caused by chance at least as great as those observed between the two groups of wells in the rate of VOC contamination. Due to an insufficient number of observations, results from the urban-suburban subsample were not included in the contingency table.

Table 15. MDA baseline study VOC detections, and typical product uses (Merck Index, National Pesticide Information Retrieval System Product Ingredient List).

VOC	Use
1,1,1-trichloroethane	degreasing metal, (septic tank degreaser?)
1,1-dichloroethane	breakdown product of trichloroethane
1,1-dichloroethylene	intermediate in manufacture of plastic wrap, breakdown product of trichloroethane
1,2-dichloroethane	solvent, fumigant ingredient
Benzene	gasoline component, solvent
Carbon disulfide	solvent, chemical feedstock, in soil fumigants
Carbon tetrachloride	solvent, chemical feedstock, grain fumigant, formerly in fire extinguishers
Chlorobenzene	paint solvent, feedstock for chemical manufacturing
Chlorodifluoromethane	refrigerant (chlorofluorocarbon)
Methyl Tert-Butyl Ether	gasoline oxygenate
Multi-C Hydrocarbon	fuel oil (based on detection note)
Tetrachloroethylene	dry cleaning, degreasing metals, solvent
Tetrahydrofuran	solvent for PVC (incl. plumbing)
Toluene	solvent, gasoline component

Table 15 lists the VOCs detected and typical uses for the products. Note that 1,2-dichloroethane has been used extensively as an ingredient in a number of fumigant products.

The number of detects for each VOC analyte is shown in Figure 8.

For those volatile organic chemicals with an established MCL or Lifetime Health Advisory Level (HAL), all baseline study VOC detections are shown as a percentage of the respective MCL / HAL in Figure 9.

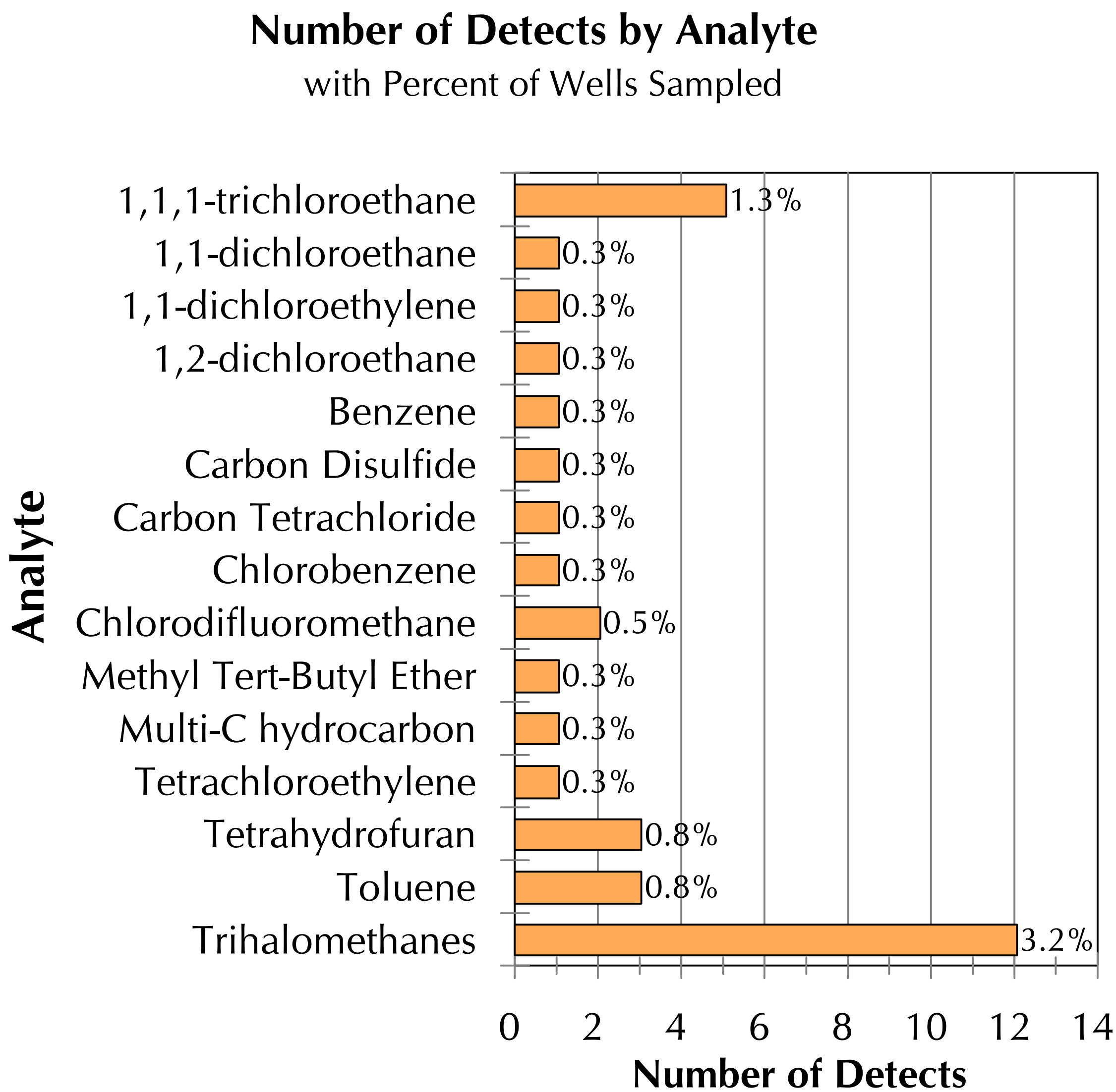


Figure 8. Number of VOC detections by analyte, and as a percentage of wells sampled.

VOC Detections as a Percent of MCL

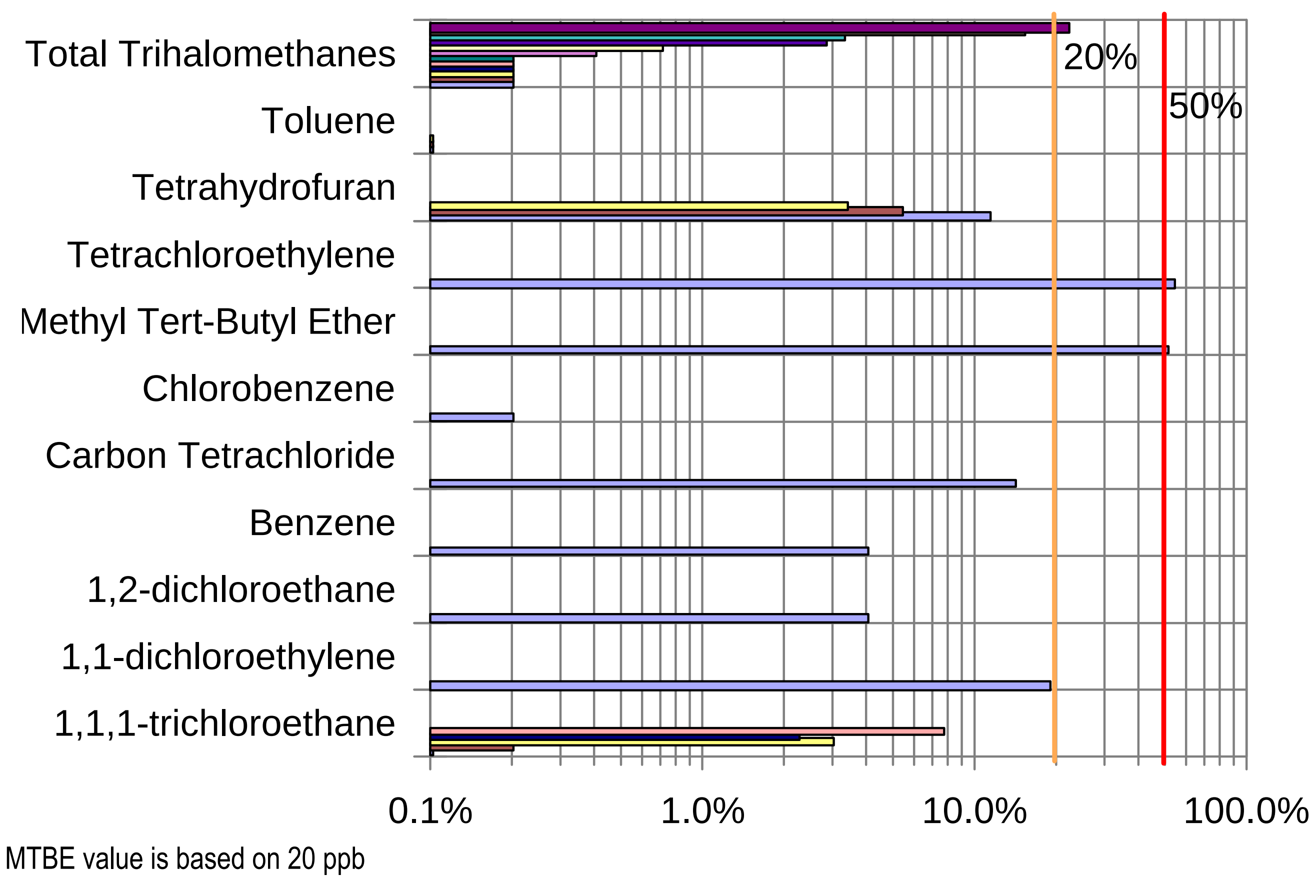


Figure 9. VOCs detected as a percentage of their MCLs.

DISCUSSION & CONCLUSIONS

The results of this study indicate that pesticide contamination of domestic supply wells in Michigan is a limited problem at this time, at least at the levels of detection used in this study, from micrograms / liter to tenths of a microgram / liter. One pesticide, atrazine, was detected in one well, at a concentration of 0.2 µg / L. This is equal to 6.7 percent of the atrazine MCL. Assuming that the probability a well chosen at random contains one or more pesticides can be modeled by the Poisson distribution, it's estimated that *less than* 2.4 percent of farm domestic wells contain one or more pesticides. Similarly, it's estimated that *less than* 1.7 percent of rural non-farm wells contain one or more pesticides. Because only 12 urban / suburban wells were sampled, and no pesticides were detected, no meaningful estimate of the maximum likely pesticide contamination frequency for this subgroup is possible.

It is important to remember that groundwater quality in general, and domestic well water quality in particular, are lagging indicators. Infiltration and percolation of water from the surface to domestic well screens can take generations in some cases. The impacts of land use may not be reflected in domestic well water quality for several decades or longer. For example, research carried out the USGS in southeast Michigan indicated that 10 of 28 domestic supply wells (36%), which had been selected essentially at random, supplied water older than 47 years, based on tritium dating (Thomas, 2000). This is evidence, albeit limited, that the water quality of a significant fraction of domestic supply wells in Michigan has not yet been impacted by post-Second World War and Green Revolution land use practices.

A number of the products which were searched for in this study are both relatively mobile and resistant to degradation, once they have migrated below biologically active zones. Under many situations, these products will eventually appear in groundwater supplies, though the amount which reaches domestic water supplies may be detectable only by trace chemistry, using detection limits on the order of nanograms / liter (parts-per-trillion) or lower. As water impacted by pesticides reaches domestic supply wells, we may see pesticide detection frequencies increase relative to present figures.

Other projects carried out by the MDA indicate that, in at least some areas, the number of domestic wells with pesticide contaminants may be an order of magnitude higher than the level estimated in this study. The MDA has confirmed one or more pesticides in 2.4% of the wells sampled through the groundwater monitoring program. Most of the sampling is directed towards areas where pesticides are used, to determine the impact to groundwater resources.

Enzyme-linked immunosorbent assay, or immunoassay, methods have been used by the MDA to screen domestic well samples at events around Michigan. Approximately 2% of the samples test positive for a triazine compound, at a level of 0.1 ppb or higher. A voluntary well screening program run by the Water Quality Laboratory of Heidelberg College in Ohio had a detection frequency of 9.8% using an immunoassay method similar to that used by the MDA, though at a detection level of 0.05 ppb. Most of the samples from that project were from Kentucky, Ohio, and Indiana (Baker et. al, 1994).

Triazines are a family of herbicides that include atrazine, simazine, and cyanazine. The immunoassay test reacts with a number of triazine herbicide degradates or metabolites as well, which can make it difficult to confirm detections, particularly low-level detections, when using standard lab methods based on the parent products. This was a self-selecting sample, in that the water screenings are open to all domestic well users, and those who submit a sample may be those with concerns about their water quality. Still, immunoassay methods are a useful means of assessing a great many samples quickly.

No detections of *nitrite* were found at or above the MCL of 1 ppm nitrite-N. The study showed only one well that appeared to have *nitrite* levels in a range associated with human activities. This is good news for domestic well users in the state, and is consistent with data gathered from other MDA studies. High levels of nitrite-N in well water (above 1 part per million) can be a sign of microbiological contamination from animal or human waste (such as manure or septic system waste) .

The results of the nitrate testing, when weighted proportionally according to the sub-populations sampled, indicated that *less than* 1.9 percent of all rural domestic wells in Michigan have nitrate-N levels of 10 mg/l (equivalent to parts-per-million) or higher. This is in sharp contrast to directed monitoring by the department, which has found nitrate levels of 10 ppm or higher in 9.3% of the wells sampled. In the directed monitoring carried out the MDA, however, clustering is known to occur, and high nitrate levels in groundwater are a direct result of high input rates in combination with vulnerable soil conditions.

Data from the study indicate that farm wells are more likely to have nitrate-N levels above 5 mg/L than are rural non-farm wells. The likelihood of this difference being due to chance was 7.7%. To put it a different way, if this same study were to be carried out 1,000 times, and nitrate levels in the state did not change during that time, we would expect to see differences as great or greater, with farm wells having higher nitrate-N levels, approximately 923 times. These results are not significant at the 0.05 significance level, but are at a significance level of 0.10.

Focused monitoring by the MDA has found nitrate-N at or above 10 mg/L in 9.3 percent of the wells sampled by the program. *Focused monitoring* is non-random monitoring the MDA has done is areas with a higher likelihood of groundwater quality problems. The USGS found that, nationwide, 12 percent of domestic supply wells in agricultural areas exceeded the MCL of 10 mg/L nitrate-N. This was based on approximately 3,200 samples from wells in National Water-Quality Assessment (NAWQA) study areas and additional USGS study areas (Mueller and Helsel, 1996). Elevated nitrate levels in domestic supply wells in agricultural areas are likely to be caused by a combination of nitrate from livestock feeding areas, fertilized cropland, and/or septic systems (Mueller and Helsel, 1996; Koelliker et. al, 1992).

Based on random sampling, it's estimated that 9.3 percent of Michigan domestic wells, ± 4.3 percent, have been *impacted* by human-related nitrate sources. Human impact is deduced from nitrate-N levels between 2 and 9.9 ppm, that is, nitrate levels below the MCL of 10 ppm NO3-N, but above background levels. More extensive sampling of the rural non-farm and urban-suburban sub-populations would allow us to further refine this estimate, but it is unlikely to vary outside of the confidence interval presented, that is, between 5.0 and 13.6 percent of the domestic wells in Michigan.

The good news is that the study indicates that 90.5 percent of the state's domestic wells, ± 4.3 percent, have nitrate-N levels lower than 2 ppm. These are the wells that do not (yet) show evidence of impact by human activities, based on their nitrate levels. Additional sampling of the rural non-farm and urban-suburban sub-populations would allow us to further refine this estimate as well. One of the goals of the groundwater monitoring program in the next few years will be to improve the accuracy of the estimates of nitrate-N contamination in domestic wells.

It is estimated that using methods similar to those in this study, one or more volatile organic compounds could be detected in 7.1 percent of Michigan rural domestic supply wells. If the study were repeated a number of times using methods similar to this study, 95 percent of the time the estimated proportion would fall between 4.4 and 9.9 percent. Trihalomethanes, formed by the action of free chlorine on organic matter, were the most frequently detected, found in 12 of the 26 wells with a VOC detection. They are associated with well disinfection using chlorine-based products, which accounts for their relatively high frequency. The highest concentration of trihalomethanes detected was 21.7 µg/L (micrograms/liter), which is equivalent to 21.7 percent of the MCL for total trihalomethanes of 100 µg/L.

VOCs *not* associated with well construction, disinfection, and/or plumbing, were detected in 12 of 379 wells, or 3.2 percent. Chlorinated ethanes and/or ethylenes were detected in five wells. These products are typically used as solvents, particularly for degreasing metal, such as cleaning auto and machinery parts, and in dry cleaning. It's possible that the detection of 1,2-dichloroethane was due to its use in soil fumigants, but there was insufficient information to determine the source of this product. Tetrachloroethylene was detected at a concentration of 2.7 µg/L, equal to 54 percent of the MCL. This was the highest concentration relative to the MCL of any of the volatile organic compounds detected. Other VOCs detected included a refrigerant (chlorodifluoromethane, one of the Freons), a paint solvent and ingredient (chlorobenzene), and other solvents.

Methyl tert-butyl ether (MTBE) was detected in one well at a concentration of 10 µg/L. MTBE is used to increase the oxygen content of gasoline, to reduce auto emissions, and as an octane booster. The U.S. EPA is presently reviewing the MCL for MTBE, and is likely to set it in the range of 20 to 40 µg/L. Many people can taste MTBE at concentrations near 40 µg/L, and due to its extremely unpleasant taste will not consume water contaminated at or above the taste threshold.

Some of the means by which these VOCs reach groundwater are: leaking gasoline storage tank or spilled gasoline (for MTBE), migration of septic-system effluent containing household chemicals, spills or improper disposal of chemicals used for home or machinery maintenance, or migration from neighboring or previous land use (Thomas, 2000).

In conclusion, it appears that contamination of Michigan domestic wells by VOCs and nitrate is more widespread than pesticide contamination. The study showed some evidence that farm domestic wells are more likely to have nitrate-N levels above 5 mg/L than are rural non-farm wells ($p=0.078$). The final section of this report will present recommendations based on the results and conclusions.

RECOMMENDATIONS

The recommendations below refer to groundwater and domestic well monitoring in Michigan, but should not be interpreted as stating that the MDA should carry out all or part of any particular recommendation.

Continue on-going monitoring of Michigan domestic wells

Evidence of impact to state groundwater resources used for domestic wells by nitrate, VOCs, and in some locations, pesticides, demonstrates a need to continue to monitor domestic wells. As it is possible that a significant fraction of the state's domestic wells are supplying water that pre-dates more widespread use of fertilizers, pesticides, and VOCs, it would be very useful to include additional studies of groundwater age.

Researchers and agencies must also modify monitoring programs as necessary to address emerging contamination issues, such as contamination from pharmaceutical compounds (including those used on animals), from other compounds not presently covered in monitoring studies, including pesticide degradates and metabolites; and new toxicological or epidemiological data indicating increased (or decreased) risks from contaminants.

Additional monitoring research, particularly for urban and suburban domestic wells, and focused monitoring in higher-risk areas

Data from this study are not sufficient to determine probable contamination frequencies in urban-suburban areas, due to the study's focus on agricultural and rural areas. Given that over 400,000 Michigan urban-suburban residents use domestic wells, it's important to evaluate the water quality being supplied by these wells.

The study indicated that pesticide contamination does not appear to be a widespread problem at this time, and provided evidence that agricultural wells are more likely to have higher levels of nitrate. There is an opportunity to focus research and resources on high-risk areas, maximizing many of the benefits of monitoring while keeping costs contained.

Address the problems and issues raised by monitoring studies

There's little point to searching for contaminated groundwater if nothing will be done once it is found. The Michigan Groundwater Stewardship Program has provided state-wide leadership in tackling many of the problems that can lead to groundwater contamination. The MDA and other organizations need to continue to work to prevent groundwater contamination and to mitigate groundwater contamination when it is found. This leads to the final recommendation.

Cooperation between agencies, non-profits, and private institutions

There are many opportunities for cooperation in groundwater monitoring and groundwater protection between federal, state, local, business, and non-profit organizations. The MDA has worked with the USGS, the U.S. EPA, the MDEQ, MSU Extension, Conservation Districts, district health departments, universities, pesticide manufacturers and registrants, and other groups on groundwater monitoring and protection projects.

The advantages of cooperation include economies of scale, research which addresses more needs, a wider audience for the research, access to more expertise, and coordinated responses to issues and problems. Disadvantages of cooperation can include loss of control of the issue and higher transaction costs, such as needs for more review and the concomitant delays. Overcoming institutional inertia is one of the keys to increasing cooperation and reaping its rewards.

Improvements in land use and resource management practices may not affect domestic well water quality for years to come, for reasons discussed in this report. This is no excuse not to manage our natural resources to the best of our ability. It reminds us to use a variety of methods and measures when evaluating the impacts, both negative and positive, of our activities.

APPENDIX A: ANALYTES INCLUDED IN MDA BASELINE STUDY LABORATORY ANALYSES

WATER TESTING ANALYTES AND DETECTION LIMITS: 1997 SEASON

Tables 1-3 list the general chemistry, pesticide, and volatile organic compound (VOC) chemicals that are included in the Michigan Department of Public Health (MDPH) analyses of MDA water supply samples. Analyte detection limits are included.

Table 1. General Chemistry Analyte Detection Limits and Levels of Concern, from MDPH Lab "Interpretation of Common Tests."

Analyte	Detection Limit (ppm)	Excellent (ppm)	Satisfactory (ppm)	Objectionable (ppm)	Related Problems
Chloride	2	nd[1]-20	20-250	> 250	Taste and Corrosion
Fluoride	0.1	0.3.-1.7	1.7-4.0	> 4.0	Lower levels beneficial in reducing tooth decay. Mottling of teeth at high levels.
Hardness as $CaCO_3$	10	25-100	100-250	> 250 or < 25	Scaling of water fixtures, laundry problems, water spotting, discoloration at high levels. Corrosion at low levels.
Iron	0.1	nd-0.20	0.2-0.5	> 0.5	Staining, turbidity, taste, color, and odor.
Nitrate as Nitrogen	0.2	nd	nd-5.0	> 10	Levels greater than 10 ppm are a health hazard for infants less than one year of age. Levels greater than 5 ppm generally indicate some wellhead vulnerability.
Nitrite as Nitrogen	0.02	nd-0.2	0.2-1.0	> 1.0	Levels greater than 1.0 ppm are an established health hazard. Levels greater than 0.2 generally indicate some well vulnerability.
Sodium	2	nd-20	20-250	> 250	Values related to taste and corrosion. Persons on restricted salt diets should notify their physician of their water supply sodium content.
Sulfate	2	nd-20	20-400	> 400	Odor problems. Higher levels may have laxative effect.

[1] non-detect, compound not in water supply or present at a concentration lower than the detection limit.

">" = "greater than"; "<" = "less than."

Table 2. Pesticide Analytes and detection limits[1]

Analyte	Detection Limit (ppb)[3]	Analyte	Detection Limit (ppb)[3]
Acifluorfen	2	Eptam	1
Alachlor	0.2	Fluometuron	1
Aldicarb	0.5	3-Hydroxycarbofuran	0.2
Aldicarb Sulfone	0.5	Hexazinone	3
Aldicarb Sulfoxide	0.5	Linuron	1
Ametryn	1	Methiocarb	0.2
Atrazine	0.1	Methomyl	0.2
Barban	5	Metolachlor	1
Baygon (Propoxur)	0.2	Metribuzin	1
Bentazon	2	Neburon	1
Butachlor	2	Oxamyl	2
Butylate	2	Pentachlorophenol	0.06
Carbaryl	0.2	Picloram	2
Carbofuran	0.5	Prometon	1
Carboxin	2	Pronamide	1
Cyanazine	1	Propachlor	3
Cycloate	2	Propanil	2
Cyprazine	1	Propazine	1
2,4-D	2	Propham	5
Dalapon	20	Simazine	0.1
Dicamba	2	2,4,5-T	1
Dinoseb	0.3	2,4,5-TP (Silvex)	0.3
Diphenamid	1	Tebuthiuron	5
Diuron	1	Trifluralin	1

[1] Detection Limit: The lowest concentration detectable by the lab.

[2] (ppm): Parts-per-million, equivalent to milligrams-per-liter (mg/l)

[3] (ppb): Parts-per-billion, equivalent to micrograms-per-liter (µg/l)

Table 3. Volatile Organic Compound Analytes and Detection Limits [1]

Analyte	Detection Limit (ppb)[3]	Analyte	Detection Limit (ppb)[3]
Benzene	0.2	Dichloropropene (1,3-trans)	0.5
Bromobenzene	0.5	Ethylbenzene	0.2
Bromochloromethane	0.5	Dibromomethane (1,2) (EDB)	0.5
Bromoform (THM)	0.2	Fluorotrichloromethane	1
Bromomethane	20	Hexachlorobutadiene	0.5
Butylbenzene-Norm	0.5	Hexachloroethane	0.5
Butylbenzene-Sec	0.5	Isopropylbenzene	0.5
Butylbenzene-Tert	0.5	Isopropyltoluene-p	0.5
Carbon Tetrachloride	0.2	Methyl Ethyl Ketone	20
Chlorobenzene	0.2	Methyl Isobutyl Ketone	20
Chlorodibromomethane (THM)	0.2	Methyl Tert-Butyl Ether (MTBE)	1
Chloroethane	20	Methylene Chloride	0.3
Chloroform (THM)	0.2	Naphthalene	1
Chloromethane	50	Propylbenzene-Norm	0.5
Chlorotoluene (Combined)	0.5	Styrene	0.5
Dibromo-3-chloropropane (1,2)	2.5	Tetrachloroethane (1,1,1,2)	0.5
Dibromomethane	0.5	Tetrachloroethane (1,1,2,2)	0.5
Dichlorobenzene-m	0.2	Tetrachloroethylene	0.2
Dichlorobenzene-o	0.5	Tetrahydrofuran	5
Dichlorobenzene-p	0.2	Toluene	0.2
Dichlorobromomethane	0.2	Total Trihalomethanes	0.2
Dichlorobutane (1,4)	0.5	Trichlorobenzene (1,2,3)	0.5
Dichlorodifluoromethane	1	Trichlorobenzene (1,2,4)	0.2
Dichloroethane (1,1)	0.5	Trichloroethane (1,1,1)	0.2
Dichloroethane (1,2)	0.2	Trichloroethane (1,1,2)	0.4
Dichloroethylene (1,1)	0.2	Trichloroethylene	0.2
Dichloroethylene (1,2-cis)	0.2	Trichloropropane (1,2,3)	0.5
Dichloroethylene (1,2-trans)	0.2	Trimethylbenzene (1,2,4)	0.5
Dichloropropane (1,2) [4]	0.2	Trimethylbenzene (1,3,5)	0.5
Dichloropropane (1,3)	1	Vinyl Chloride	0.3
Dichloropropane (2,2)	1	Xylene- m & p	0.5
Dichloropropene (1,1)	0.5	Xylene- o	0.5
Dichloropropene (1,3-cis)	0.5	Xylene (Total)	0.5

[1] Detection Limit: The lowest concentration detectable by the lab.

[2] (ppm): Parts-per-million, equivalent to milligrams-per-liter (mg/l) .

[3] (ppb): Parts-per-billion, equivalent to micrograms-per-liter (µg/l).

[4] 1,2-dichloropropane has been used as a pesticide.

All water analyses performed by the Michigan Department of Environmental Quality Drinking Water Laboratory (formerly the Michigan Department of Public Health Drinking Water Laboratory), Lansing, Michigan.

Pesticide Analytes, Scans, and Detection Limits for MDA Samples, 1998 - 2000 Season

Analyte	Scan	* Detection Limit (ppb)
2,4-D	XHB	2
2,4,5-T	XHB	1
2,4,5-TP (Silvex)	XHB	0.3
Acifluorfen	XHB	4
Bentazon	XHB	2
Dicamba	XHB	2
Dinoseb	XHB	0.3
Pentachlorophenol	XHB	0.08
Picloram	XHB	2
3-hydroxycarbofuran	XLP	0.2
Aldicarb	XLP	1
Aldicarb Sulfone	XLP	1
Aldicarb Sulfoxide	XLP	1
Baygon (Propoxur)	XLP	0.2
Carbaryl	XLP	0.2
Carbofuran	XLP	1
Methiocarb	XLP	0.2
Methomyl	XLP	0.2
Oxamyl	XLP	2
Alachlor	XPT	0.2
Ametryn	XPT	1
Atrazine	XPT	0.2
Butachlor	XPT	2
Butylate	XPT	2
Carboxin	XPT	2
Cyanazine	XPT	1
Cycloate	XPT	2
Cyprazine	XPT	1
Diphenamid	XPT	1
Eptam	XPT	1
Hexazinone	XPT	3
Metolachlor	XPT	1
Metribuzin	XPT	1
Prometon	XPT	1
Pronamide	XPT	1
Propachlor	XPT	3
Propazine	XPT	1
Simazine	XPT	0.2
Tebuthiuron	XPT	5
Trifluralin	XPT	1
Endrin	XPT	0.05
Lindane (gamma-BHC)	XPT	0.04
Methoxychlor	XPT	0.2
Aldrin	XPT	1
Hexachlorocyclohexane (α-BHC)	XPT	1

Pesticide Analytes, Scans, and Detection Limits for MDA Samples, 1998 - 2000 Season

Analyte	Scan	* Detection Limit (ppb)
Hexachlorocyclohexane (β-BHC)	XPT	1
Hexachlorocyclohexane (Δ-BHC)	XPT	1
Chlordane, alpha	XPT	0.2
Chlordane, gamma	XPT	0.2
DDD,4,4'-	XPT	1
DDE,4,4'-	XPT	1
DDT,4,4'-	XPT	1
Endosulfan, alpha	XPT	1
Endosulfan,beta	XPT	1
Endrin aldehyde	XPT	1
Heptachlor	XPT	0.08
Heptachlor epoxide	XPT	0.04
Hexachlorobenzene	XPT	0.1
Hexachlorocyclopentadiene	XPT	0.2
Octachlorocyclopentadiene	XPT	1
Polybrominated biphenyls	XPT	1
PCB (Aroclor 1016)	XPT	0.2
PCB (Aroclor 1221)	XPT	0.2
PCB (Aroclor 1232)	XPT	0.2
PCB (Aroclor 1242)	XPT	0.2
PCB (Aroclor 1248)	XPT	0.2
PCB (Aroclor 1254)	XPT	0.2
PCB (Aroclor 1260)	XPT	0.2
Dieldrin	XPT	1
Toxaphene	XPT	2
Bromacil	XPT	2
Chlorothalonil	XPT	1
Dacthal	XPT	1
Terbacil	XPT	2
Benzene	XVO	0.2
Bromobenzene	XVO	0.5
Bromochloromethane	XVO	0.5
Bromoform (THM)	XVO	0.4
Bromomethane	XVO	20
Butylbenzene-Norm	XVO	0.5
Butylbenzene-Sec	XVO	0.5
Butylbenzene-Tert	XVO	0.5
Carbon Tetrachloride	XVO	0.4
Chlorobenzene	XVO	0.5
Chlorodibromomethane (THM)	XVO	0.4
Chloroethane	XVO	20
Chloroform (THM)	XVO	0.4
Chloromethane	XVO	50
Chlorotoluene (Combined)	XVO	0.5
Dibromo-3-chloropropane (1,2)	XVO	2.5
Dibromomethane	XVO	0.5

* Detection limit is Practical Quantitation Limit. "Not Detected" assures levels below this value. If testing response indicates the confirmed presence of a compound below this value, the lab may report by comment (e.g., "Trace").

ppb: Parts-per-billion, equivalent to micrograms-per-liter (μg/l)

ppm: Parts-per-million, equivalent to milligrams-per-liter (mg/l)

Pesticide Analytes, Scans, and Detection Limits for MDA Samples, 1998 - 2000 Season		
Analyte	**Scan**	*** Detection Limit (ppb)**
Dibromoethane (1,2) (EDB)	XVO	0.5
Dichlorobenzene-m (1,3)	XVO	0.4
Dichlorobenzene-o (1,2)	XVO	0.5
Dichlorobenzene-p (1,4)	XVO	0.4
Dichlorobromomethane (THM)	XVO	0.4
Dichlorobutane (1,4)	XVO	0.5
Dichlorodifluoromethane	XVO	1
Dichloroethane (1,1)	XVO	0.5
Dichloroethane (1,2)	XVO	0.5
Dichloroethylene (1,1)	XVO	0.5
Dichloroethylene (1,2-cis)	XVO	0.4
Dichloroethylene (1,2-trans)	XVO	0.4
Dichloropropane (1,2)	XVO	0.4
Dichloropropane (1,3)	XVO	1
Dichloropropane (2,2)	XVO	1
Dichloropropene (1,1)	XVO	0.5
Dichloropropene (1,3-cis)	XVO	0.5
Dichloropropene (1,3-trans)	XVO	0.5
Ethylbenzene	XVO	0.5
Fluorotrichloromethane	XVO	1
Hexachlorobutadiene	XVO	0.5
Hexachloroethane	XVO	0.5
Isopropylbenzene	XVO	0.5
Isopropyltoluene-p	XVO	0.5
Methyl Ethyl Ketone	XVO	20

Analyte	Scan	* Detection Limit (ppm)
Chloride	R	4
Fluoride	R	0.1
Hardness as CaCO3	R	10
Iron	R	0.1
Nitrate as Nitrogen	R	0.4
Nitrite as Nitrogen	R	0.05
Sodium	R	5
Sulfate	R	5

Pesticide Analytes, Scans, and Detection Limits for MDA Samples, 1998 - 2000 Season		
Analyte	**Scan**	*** Detection Limit (ppb)**
Methyl Isobutyl Ketone	XVO	20
Methyl Tert-Butyl Ether (MTBE)	XVO	1
Methylene Chloride	XVO	0.6
Naphthalene	XVO	1
Propylbenzene-Norm	XVO	0.5
Styrene	XVO	0.5
Tetrachloroethane (1,1,1,2)	XVO	0.5
Tetrachloroethane (1,1,2,2)	XVO	0.5
Tetrachloroethylene	XVO	0.4
Tetrahydrofuran	XVO	5
Toluene	XVO	0.5
Total Trihalomethanes	XVO	0.4
Trichlorobenzene (1,2,3)	XVO	0.5
Trichlorobenzene (1,2,4)	XVO	0.5
Trichloroethane (1,1,1)	XVO	0.4
Trichloroethane (1,1,2)	XVO	0.5
Trichloroethylene	XVO	0.4
Trichloropropane (1,2,3)	XVO	0.5
Trimethylbenzene (1,2,4)	XVO	0.5
Trimethylbenzene (1,3,5)	XVO	0.5
Vinyl Chloride	XVO	0.5
Xylene- m & p	XVO	0.5
Xylene- o	XVO	0.5
Xylene (Total)	XVO	0.5

Detection limit is Practical Quantitation Limit. "Not Detected" assures levels below this value. If testing response indicates the confirmed presence of a compound below this value, the lab may report by comment (e.g., "Trace").

ppb: Parts-per-billion, equivalent to micrograms-per-liter (μg/l)

ppm: Parts-per-million, equivalent to milligrams-per-liter (mg/l)

APPENDIX B: BOXPLOTS OF MDA BASELINE STUDY WATER CHEMISTRY PARAMETERS

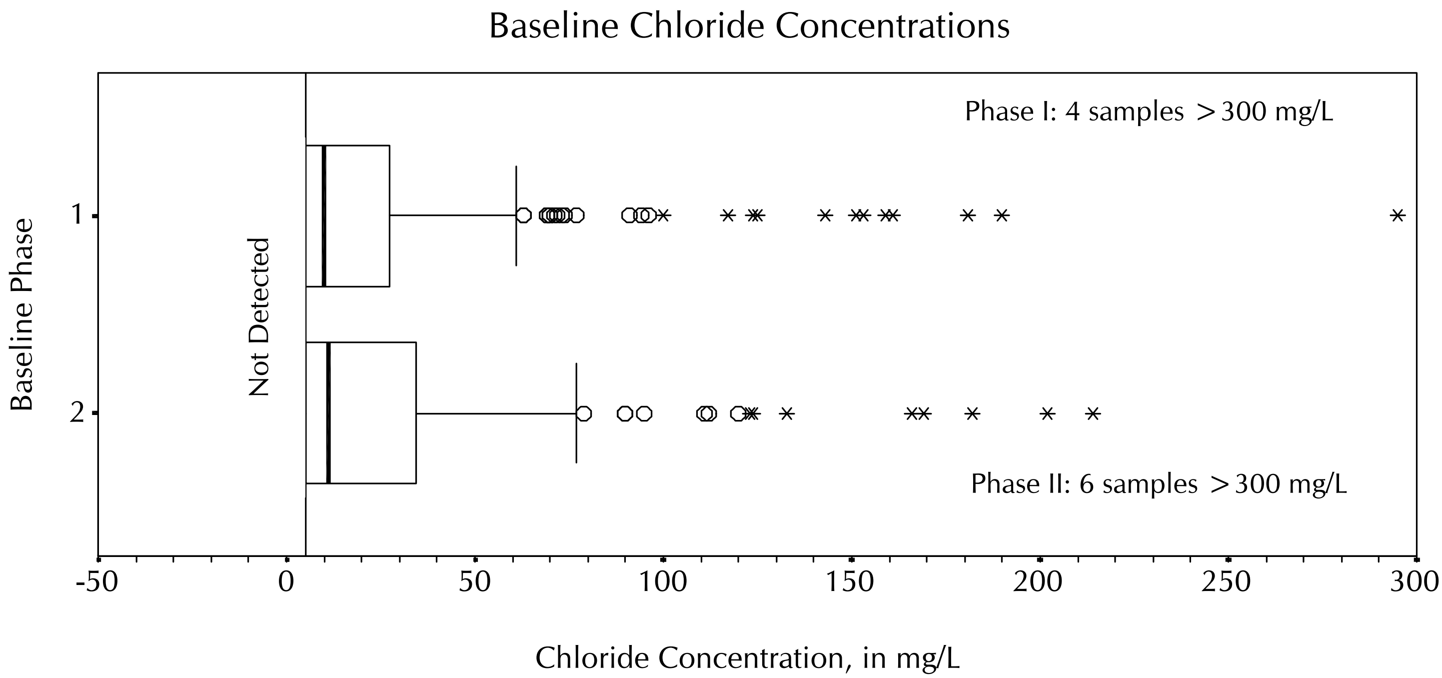


Figure 10. Boxplot of chloride concentrations by sampling phase

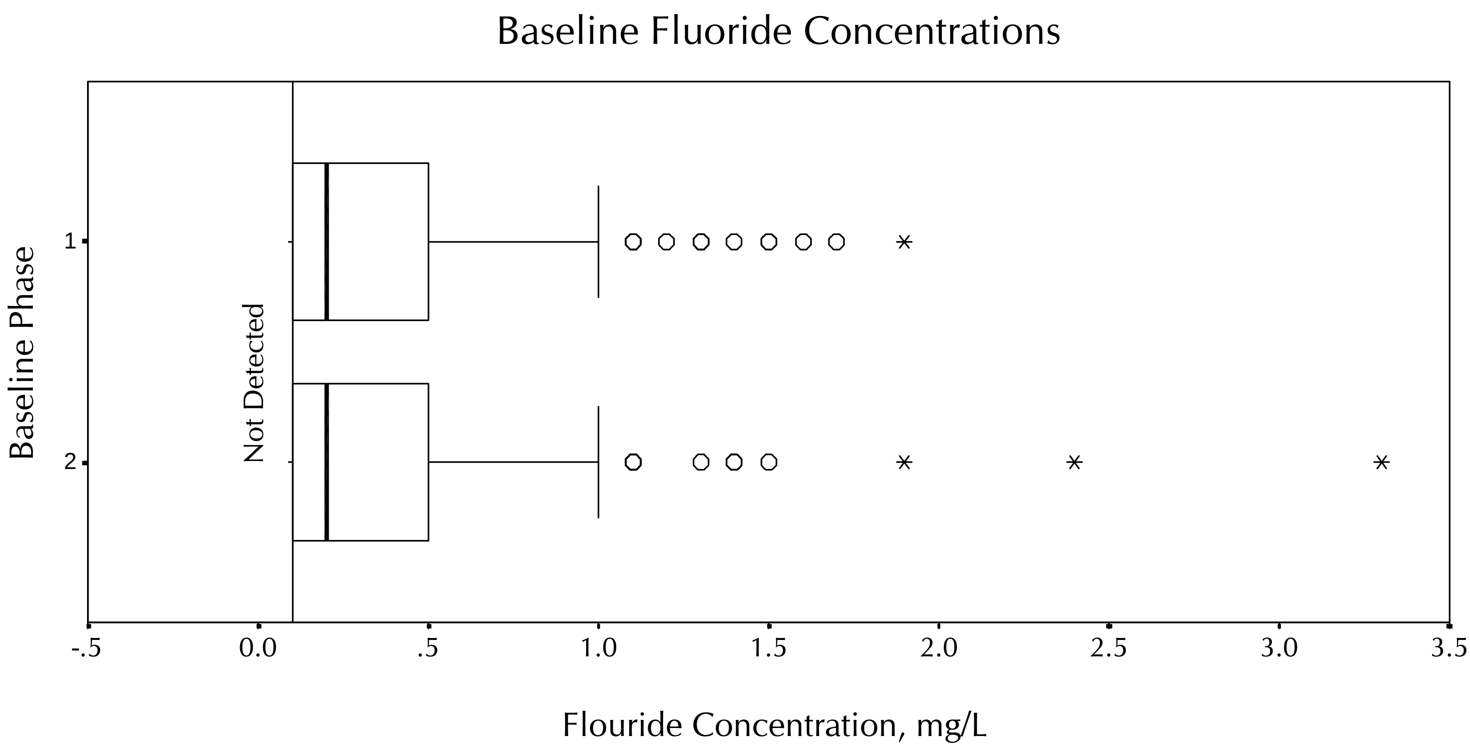


Figure 11. Boxplot of fluoride concentrations by sampling phase

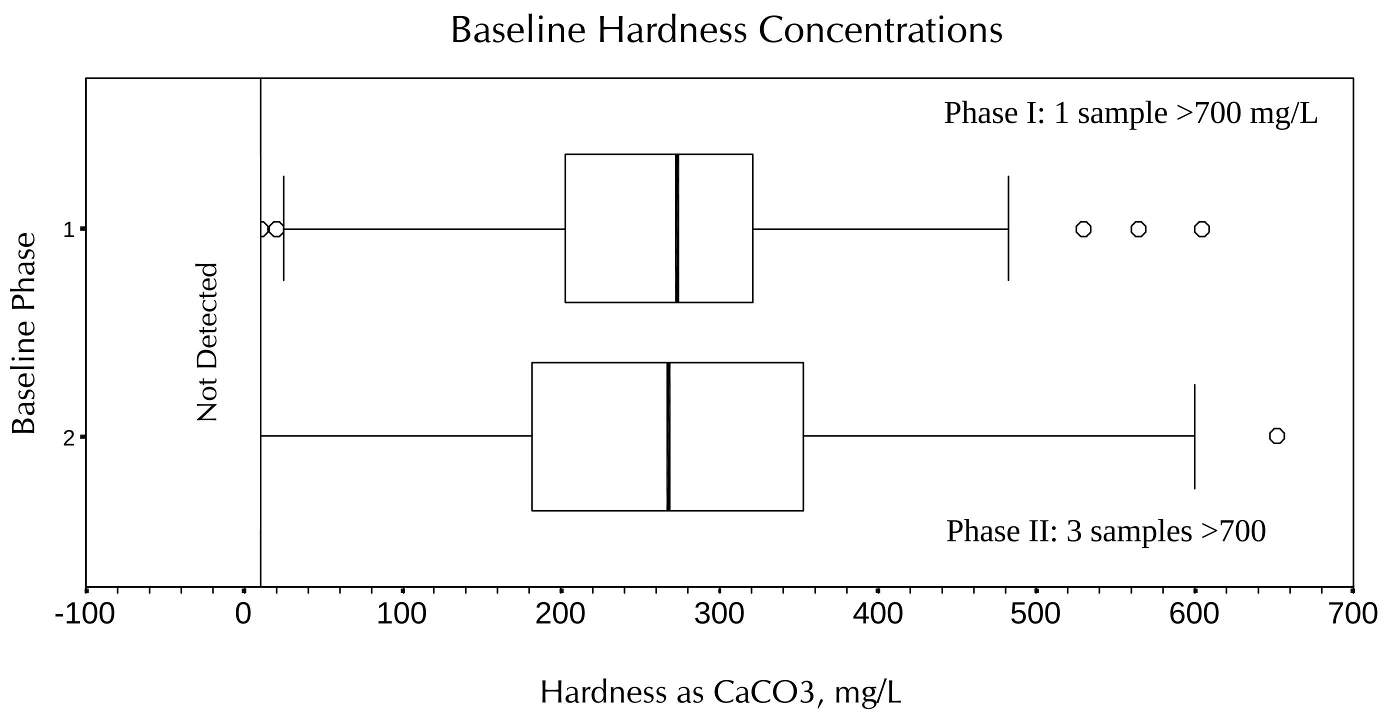


Figure 12. Boxplot of hardness as CaCO3 by sampling phase

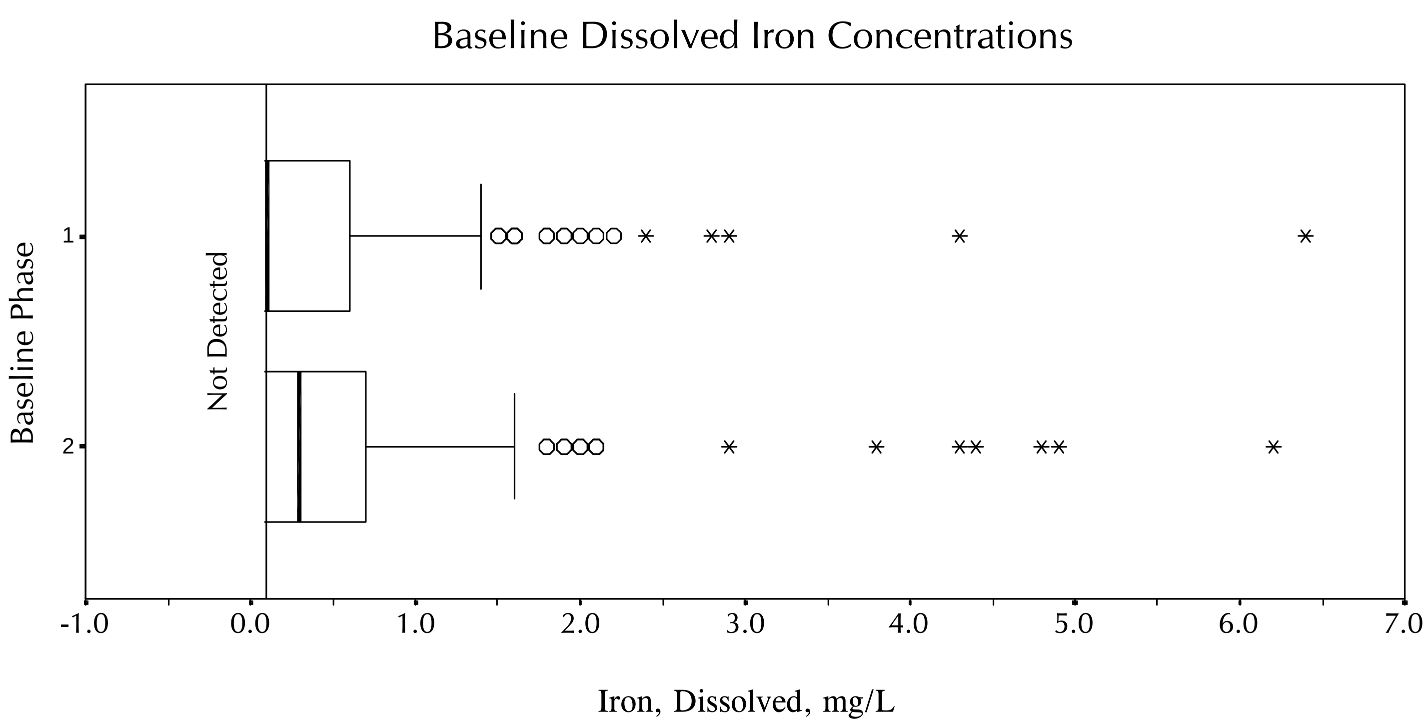


Figure 13. Boxplot of dissolved iron concentrations by sampling phase

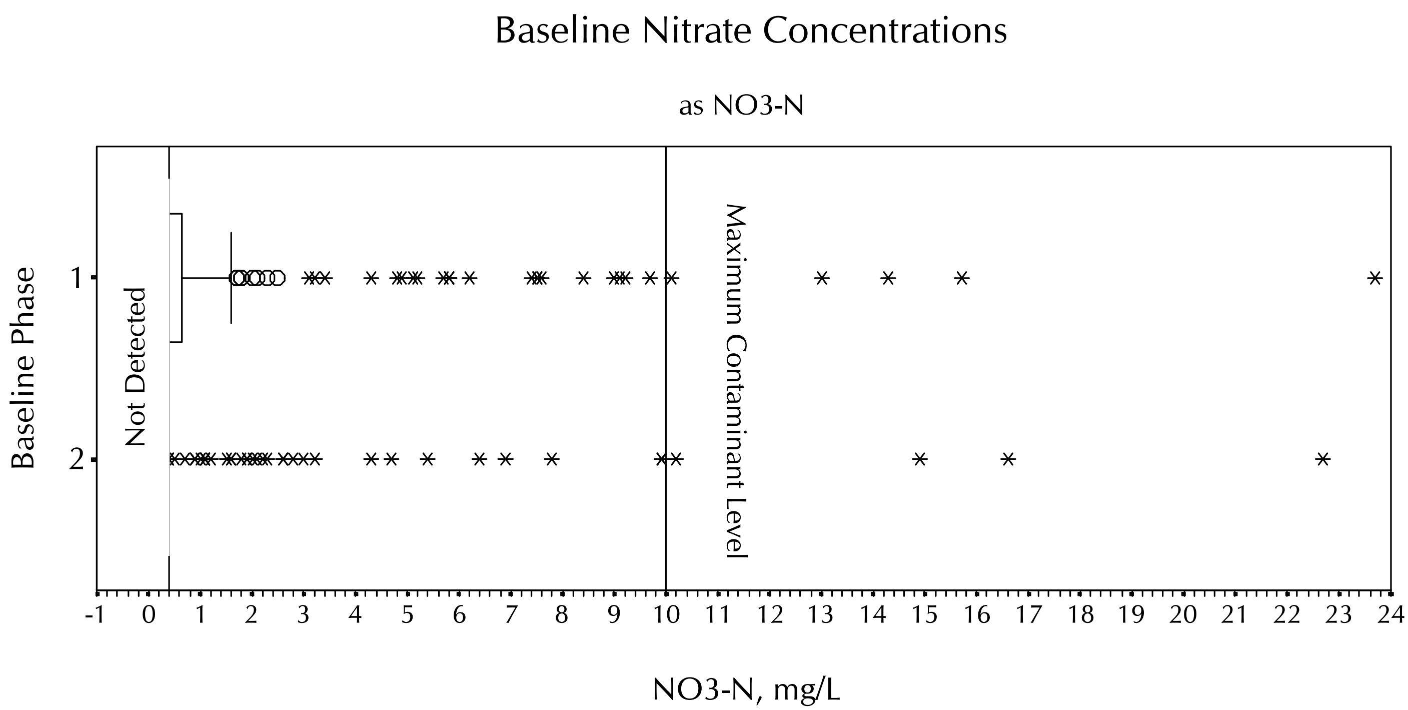


Figure 14. Boxplot of nitrate-N concentrations by sampling phase

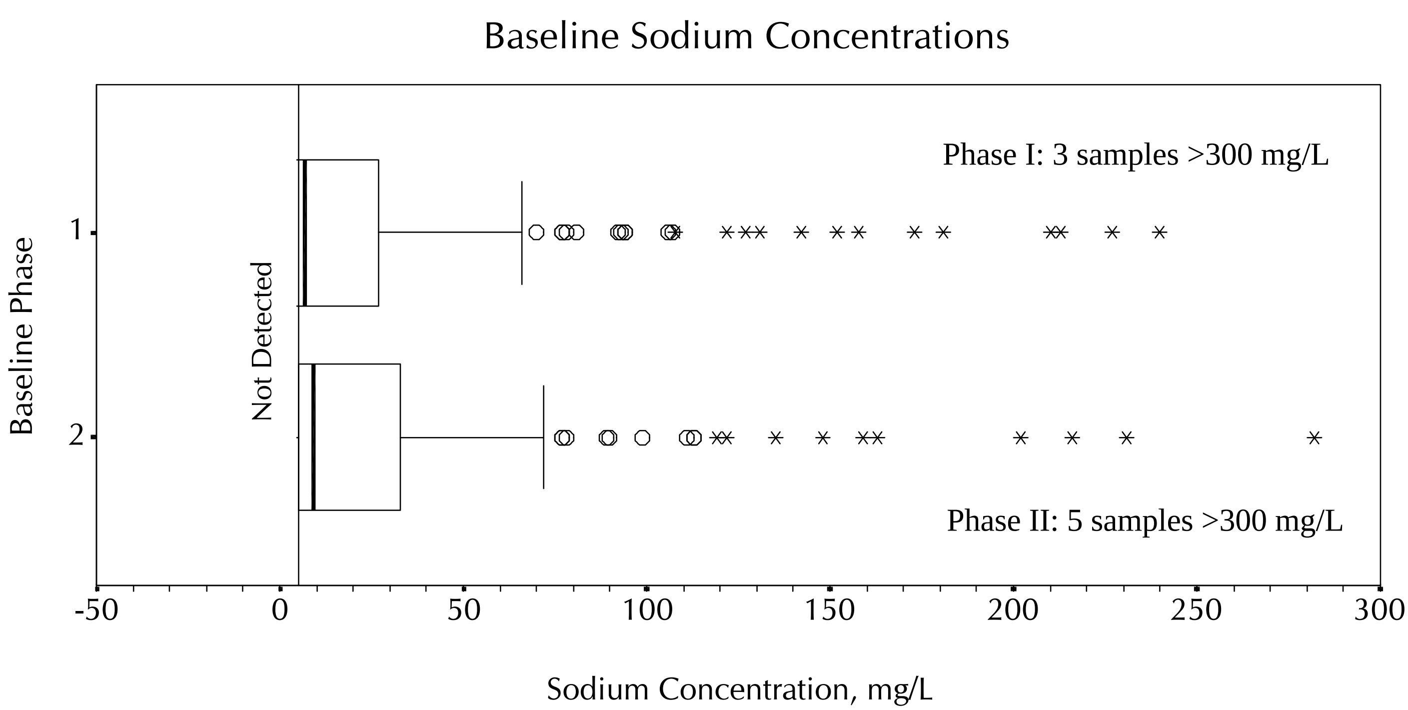


Figure 15. Boxplot of sodium concentrations by sampling phase

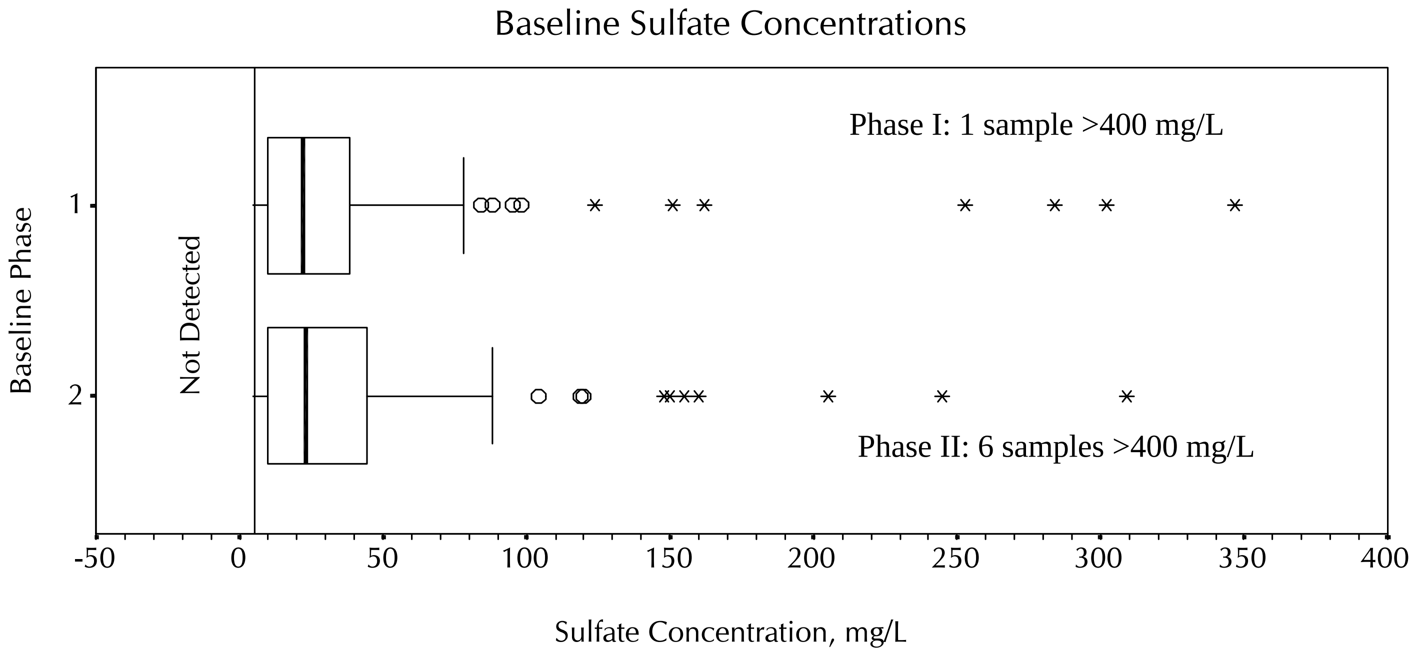


Figure 16. Boxplot of sulfate concentrations by sampling phase

APPENDIX C: COVER LETTERS AND WATER ANALYSIS OFFERS MAILED TO SAMPLE POPULATION

Phase I Request for Free Water Analysis, Included With Initial Baseline Survey

Text of response card is shown below. Actual response card was a 3" by 5" card, with landscape printing.

Private Drinking Water Well Baseline Survey
MI Dept. of Agriculture Groundwater Program

I have completed and returned the written baseline survey. My household gets its drinking water from a private well, and I would like to have this same well tested for a variety of man-made chemicals. I understand that I will not be charged for this test. I also understand that the results from my test will be confidential.

Please fill in the information below, and mail the card. An MDA representative will contact you.

Name ____

Address ____

City, State, Zip ____

Phone Number ____

The best time to reach me is ______ am pm (please circle one) on ____ (please list days of the week).

Phase II Cover Letter

May 27, 1999

Dear Sir or Madam:

The Michigan Department of Agriculture (MDA) will be conducting FREE tests of drinking water well quality throughout Michigan, to the first 200 people who respond to this letter. These tests normally cost home owners $353. Your name was chosen at random, and if you use your own well for drinking water, we would like you to participate in the MDA study. Wells will be sampled between May and September and we will mail you a copy of the results. Your water test results will be completely confidential.

The MDA is conducting this study to gather enough information to know the present state of private drinking well water quality in Michigan, since very little is known about this subject. Samples will be analyzed for nitrates, many pesticides, and a wide variety of compounds used in fuels, solvents, and industrial chemicals.

A question some well owners ask is "What will happen if you find something in my water?" Past MDA studies have shown that fewer than 1 well out of 100 are contaminated at a level above public drinking water standards. If a problem *is* found, the first step we take is to inform the well owner of the possible contamination. The well is then retested to determine if there really is a problem. If the contamination is confirmed, the MDA conducts additional monitoring in the area and works with local well owners and land owners to solve the problem. All problems to date have been solved through voluntary efforts.

If you would like to participate, please complete the attached form, place it in the return envelope, and mail it as soon as possible, since participation is limited. If you are one of the first 200 people to respond, an MDA groundwater program staff member will call to arrange a time to collect a water sample from your well during the next few months. Sampling will begin in June and is scheduled to be completed in September.

If you have any questions, please call Robert Pigg at 517-373-6893.

Sincerely,

Robert W. Pigg
MDA Groundwater Monitoring Program Coordinator

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