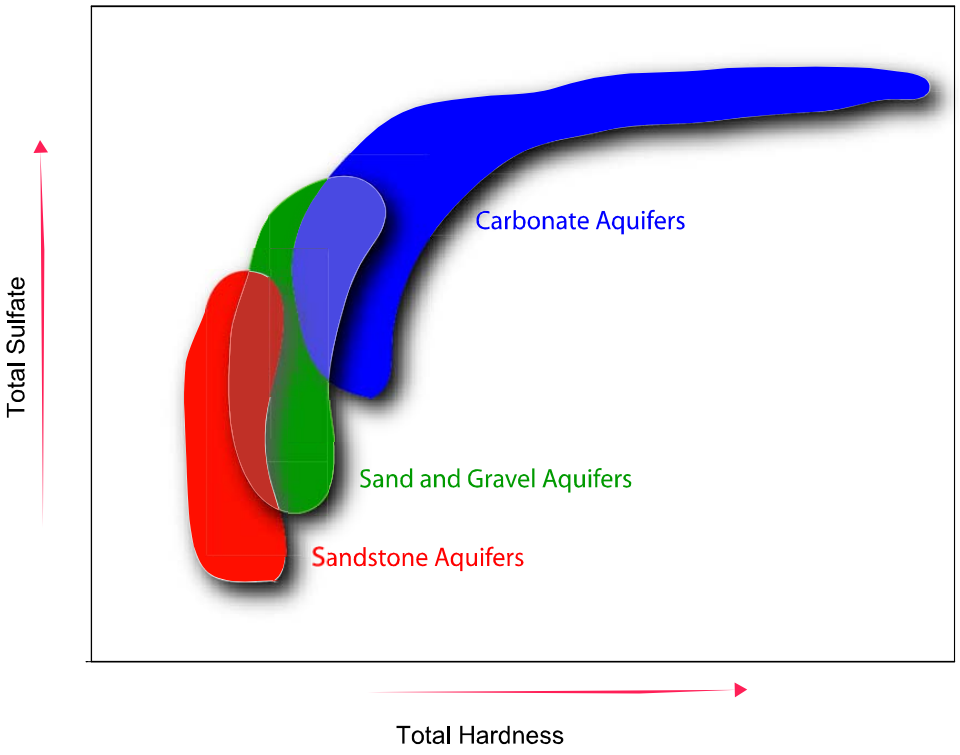
State of Ohio
Environmental Protection Agency

Division of Drinking and Ground Waters

2002 305(b) Report Ohio's Ground Water Quality



May 2003

Bob Taft, Governor
Chris Jones, Director

2002 305(b) Report

Ohio's Ground Water Quality

Prepared by Ohio Environmental Protection Agency
Division of Drinking and Ground Waters

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May 30, 2003

ACKNOWLEDGMENTS

Ohio EPA, Division of Drinking and Ground Waters (DDAGW) wishes to recognize the contribution of groups and individuals who provided guidance and support in the compilation of this document. Water sample and data collection efforts by numerous Ohio EPA district DDAGW personnel are gratefully acknowledged. Special thanks go to our data base management team of Andrew Hoyte and Jackson Chiang for their excellent guidance, and to Richard McClish and Dave White for providing Geographic Information Systems support. Ohio EPA Department of Environmental Services provided laboratory data analyses for all of the Ambient Monitoring Network water samples. The writers include Christopher Kenah, Michael Slattery, and Linda Slattery; questions should be directed to them. Substantial review and comment by Michael Eggert (DDAGW) and other DDAGW staff, and the Ohio EPA's Public Interest Center are appreciated and have improved the document. Section 106 grant funds of the 1996 Clean Water Act support the Ambient Ground Water Monitoring Network and the compilation of the biennial 305(b) report.

Cover Illustration: Plot of Total Sulfate vs. Total Hardness illustrates the intermediate relationship of the water chemistry in the sand and gravel aquifers between the sandstone aquifers and the carbonate aquifers. This relationship results from the erosion of sandstone and carbonate bedrock to produce the bulk of the material for the sand and gravel aquifers. See section on Ground Water Quality by Aquifer Type and Figure 10 for additional explanation.

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EXECUTIVE SUMMARY

2002 305(b) Report -- Ohio's Ground Water Quality

Ground water quality monitoring programs and ground water quality data analyses for the state of Ohio are summarized in the 2002 305(b) report as required in section 106(e) of the Clean Water Act. Programs to monitor, evaluate, and protect ground water resources in Ohio are carried out by various state, federal and local agencies. Ohio Environmental Protection Agency (Ohio EPA) is the designated agency for monitoring and evaluating ground water quality conditions and assessing ground water contamination problems for the state of Ohio. Within Ohio EPA, the Division of Drinking and Ground Waters (DDAGW) carries out these functions, and coordinates various ground water monitoring efforts with other state programs through the Ohio Water Resources Council and the State Coordinating Committee on Ground Water. The 2002 305(b) Ground Water Report provides DDAGW the opportunity to enhance our characterization of state-wide ground water quality through improved data analysis and presentation, as well as meeting the 305(b) reporting requirements.

Two main sources of information are used to characterize Ohio's ground water quality in the 2002 305(b) Report. The Ambient Ground Water Monitoring Program (AGWMP) is the DDAGW program created to monitor "raw" (untreated) ground water. This program's goal is the collection, maintenance, and analysis of ground water quality data to measure changes in the water quality of the State's major aquifer systems. The second source of information is the public water system (PWS) compliance data, which is compiled from information on treated (processed) ground water. These two data sources compliment one another and provide water quality data from most of the state.

The geologic settings and distribution of Ohio's three major aquifer types, sand and gravel, sandstone, and carbonate, are described. The sand and gravel aquifer system, which is superimposed on the bedrock of the eastern, central, and southwestern portions of the state, comprise Ohio's most productive and sensitive aquifers. These buried valley aquifers are composed of bands of permeable unconsolidated sand and gravel (20 to 200 + feet thick) filling old river valleys which were cut by glacial meltwater and preglaical streams. The sandstone aquifer system, is found throughout the eastern portion of Ohio. These aquifers are characterized by gently dipping strata of sandstone, shales, and other units which yield moderate to high volumes of water, although in the southeast the yields may drop to low production levels due to the presence of interbedded shales, coals, and clays. The carbonate bedrock aquifer is found in the western half of the state. These carbonates can be thick (up to 600 feet), and may yield over 500 gallons of water per minute in fractured zones with solution channels.

Water quality data for the three main aquifer types are presented in this report. Ground water quality across the state is generally of high quality as documented by AGWMP data. Table 3 of this report presents summary statistics for the inorganic parameters grouped by major aquifer types. This table establishes typical chemical concentrations based on 30 years of sampling and illustrates major element variation as a function of aquifer type. This information is useful for evaluating ground water quality impacts. Figure 1 represents the variation of total dissolved solids (TDS) between the three major aquifer types and illustrates the intermediate concentrations of TDS in the sand and gravel aquifer compared to the carbonate and sandstone aquifers. The high TDS concentrations in the carbonate system are clearly

represented in this figure. The association of higher TDS with the sand and gravel aquifer compared to the sandstone aquifer is attributed to the rock composition of the aquifers. The sand and gravel aquifers are dominated by carbonate rock debris deposited by glacial processes, and consequently, the water quality is similar to the carbonate aquifer water quality. The lower TDS of the sandstone aquifers is attributed to the higher silica sand and lower carbonate rock content of the sandstone aquifers. Similar plots are provided for all the inorganic parameters in Appendix I.

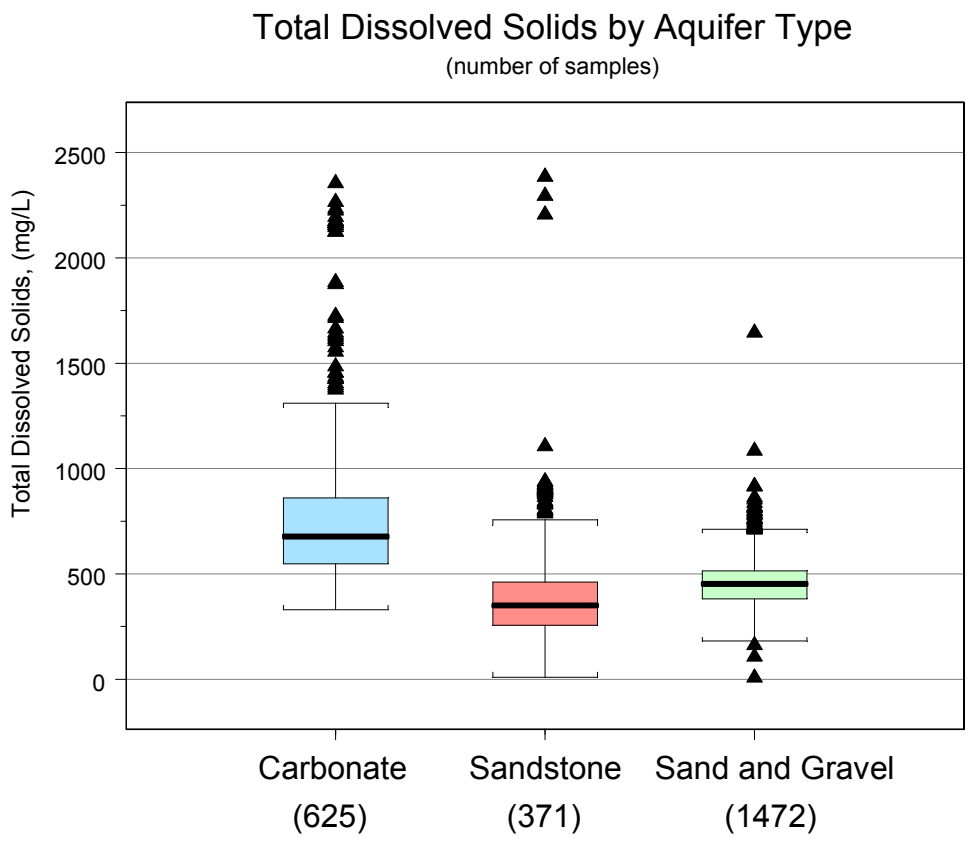

Figure 1. Total dissolved solids by aquifer type.

Over the past year, much of our ground water quality analysis focused on using nitrate concentrations to identify sensitive aquifers in Ohio. This approach revealed two main geologic settings in which ground water is most vulnerable to immediate and direct recharge of surface water and its potential contaminant load: 1) buried valley and outwash (sand and gravel) aquifers; and 2) bedrock aquifers underlying thin till and lacustrine deposits. Figure 2 illustrates the association of these sensitive aquifer settings with public water systems having elevated nitrate concentrations. Statistical analysis of nitrate data from 4,136 public water systems confirms that the buried valley aquifers and the bedrock aquifers below thin glacial material are the most vulnerable aquifers in Ohio.

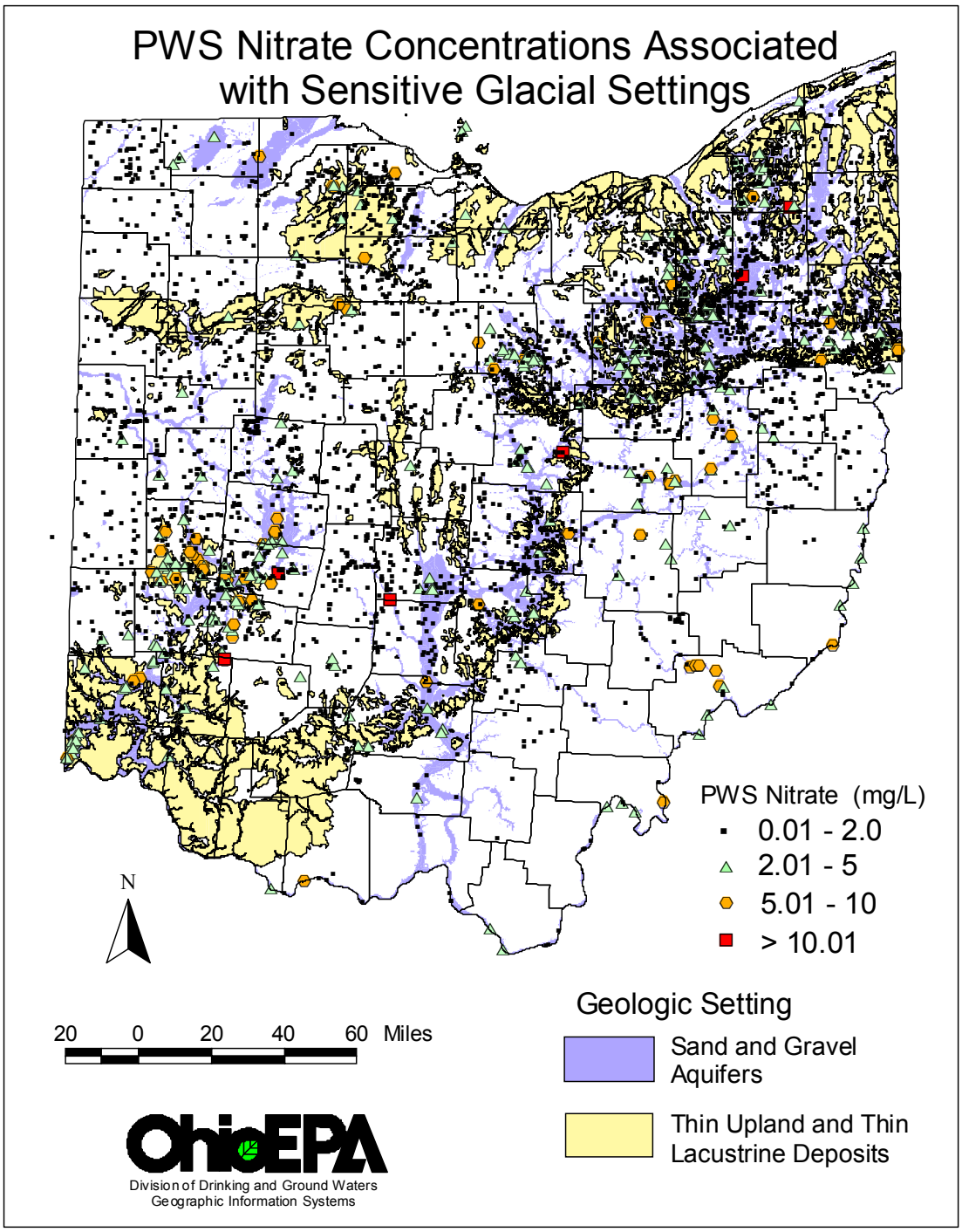

Figure2. Public water systems in Ohio with elevated nitrate concentrations.

To build on the statewide identification of sensitive aquifers, we examined the nitrate time-series of 203 individual water systems using AGWMP data. These time-series reveal a surprisingly consistent division of three behavior modes: 1. *Nitrate Unstable* – no detections of nitrate; 2. *Transient* – irregular, isolated detections of nitrate; and 3. *Nitrate Stable* – detections of nitrate are common. The nitrate concentration and its variation at any site is the result of the interaction of nitrate source availability, source timing, volume of recharge, transport pathways, rate of recharge movement, rate of microbial activity, and dominant oxidation-reduction conditions. These modes of behavior illustrate the transition from the relatively open and oxidized nature of shallow aquifers in sensitive hydrogeologic settings to deeper, less sensitive and more reduced aquifer settings. Tritium and water temperature data from these same sites support the interpretations of recharge and pathway length control and provide further evidence for the physical basis which underlies the empirical nitrate behavior modes.

The strong association between land use and nitrate concentration was also analyzed with preliminary land use/land cover data. More detailed analysis awaits improved land use data. As expected, the preliminary analysis shows correlations of elevated nitrate with agriculture land, but elevated nitrate is also associated with high percentages of urban recreational grasses. In both cases the nitrate concentrations are well below the maximum contaminant level (MCL), but the analysis points to the importance of managing all land uses in drinking water protection areas.

Analysis of the distribution of total arsenic concentrations across Ohio has continued to help evaluate the impact of the arsenic MCL reduction from 50 ug/L to 10 ug/L by U.S. EPA. Elevated total arsenic concentrations in Ohio are often associated with wells developed in the sand and gravel units; this correlation holds for both Ambient and PWS data. Study of the spatial distribution of arsenic values suggests that arsenic is released through dissolution of aquifer materials under slightly reducing to reducing conditions rather than through point source contamination of an aquifer. General geochemical guidelines for the presence of arsenic are discussed, but the random and widespread nature of arsenic in geologic materials requires a site specific evaluation for its presence.

Future water quality efforts will focus on integrating water quality information with other Ohio EPA and U.S. EPA ground water programs. We will continue to work to increase the quality of the AGWMP data, to incorporate improvements in data management tools, and to improve our data analysis capabilities. These efforts will allow ground water quality data to be used to help target priority areas for ground water protection activities in support of DDAGW programs. Activities will include:

- listing and cataloging ground water resources impacted from land use activities;
- transferring the AGWMP data into STORET;
- increasing our understanding of the ground water resources of Ohio;
- continuing to identify sensitive aquifers;
- supporting effective implementation of new SDWA rules; and
- incorporating SWAP sensitivity analyses into our water quality analysis.

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INTRODUCTION

Ground water is a vital resource in Ohio. Approximately 1,050 of Ohio's 1,350 community water systems utilize ground water, including three of Ohio's largest cities (Dayton, Canton and Springfield). The cities of Columbus and Cincinnati use ground water to meet part of their daily water needs. About 99 percent of the 4,300 non-community public water systems, (schools, small industries or businesses, service stations, golf courses, etc.) use ground water. In addition, approximately one million rural homes use ground water. Four-and-a-half million Ohio residents, approximately 40 percent of the state's population, depend upon wells for water. Ground water is critical in meeting the demands of industry, agriculture, commercial establishments, and households. Total ground water pumped in Ohio for all uses is estimated at one billion gallons per day.

The Ohio Environmental Protection Agency (Ohio EPA) is the designated state ground water quality management agency for preventing and addressing ground water quality problems. To meet this responsibility, Ohio EPA characterizes ambient ground water quality conditions; identifies ground water contamination; determines cause and effect relationships; and recommends strategies for preventing contamination. The Division of Drinking and Ground Waters (DDAGW) has the lead role for these activities within Ohio EPA. In addition, DDAGW coordinates ground water monitoring efforts with other state programs.

The 2002 305(b) Report summarizes DDAGW's efforts to characterize the quality of Ohio's ground water since the 2000 305(b) report was completed. These efforts have focused on maintaining the data collection programs, continuing to improve our capabilities for manipulating the available data, and incorporating Geographical Information Systems (GIS) and other graphic tools to improve the analysis of data and the presentation of the analytical results. The primary focus of these activities is to define background water quality for Ohio aquifers, to identify natural geochemical variation within the state aquifers, and to help define sensitive aquifers in the state. The goal is to utilize these water quality data to help identify areas where ground water quality has been affected by human activities in order to help prioritize ground water protection efforts.

This 305(b) Report allows Ohio EPA to document the progress we have made in evaluating water quality in the state aquifers. The report is organized to provide a summary of state ground water programs followed by a general description of the DDAGW's programs. Then, a description of the major aquifer types in Ohio is provided. Analytical efforts of the Ground Water Quality Characterization Program to characterize the water quality of Ohio's three major aquifer types is consistent with U.S. EPA's request to assess the water quality for selected aquifers or hydrogeologic settings.

In the past year significant effort was focused on evaluating nitrate data to identify sensitive aquifers. Analysis of nitrate time series identified three classes of nitrate behavior related to the sensitivity of the aquifer. These relationships are summarized in the Sensitive Aquifer section. The identification of sensitive aquifers and evaluation of the associated ground water quality data emphasize the importance

of land use data for understanding land use impacts in sensitive aquifers. Consequently, land use analysis around Ambient Ground Water Monitoring Program wells was initiated and is summarized after the sensitive aquifer discussion. Finally, a summary of the effort to describe the distribution of arsenic in Ohio public water systems that use ground water is included.

OHIO GROUND WATER PROGRAMS

On July 1, 2001, Governor Bob Taft established a permanent Ohio Water Resources Council (OWRC) with the mission: To guide the development and implementation of a dynamic process to advance the management of Ohio's water resources. The State Agency Coordination Group, with representatives from the state agencies dealing with water issues, was also established to serve as a technical resource for the OWRC. In March 2002, the Ohio Water Resources Council Four-Year Strategic Plan was published. The heart of the strategic plan is a list of seven goals and 29 objectives and action items to help meet the goals. The goals and objectives are listed on the OWRC web site: www.dnr.state.oh.us/owrc/goals.htm . Many of these goals relate to assessing and protecting Ohio's ground water resources..

The State Coordinating Committee Ground Water (SCCGW) was created in 1992 by the directors of the state agencies with ground water responsibilities. The purpose of the SCCGW is to promote and guide the implementation of a coordinated, comprehensive, and effective ground water protection and management program for Ohio. Overlapping membership of the SCCGW and the OWRC's State Agency Coordination Group helps to coordinate water management issues, and the SCCGW is directing its efforts to achieve the OWRC goals and objectives.

Programs to monitor, evaluate, and protect ground water resources in Ohio are carried out by various federal, state and local agencies. Ground water related activities at the state level are conducted by Ohio EPA, the Public Utilities Commission, and the Ohio Departments of Agriculture, Commerce (Division of State Fire Marshal), Health, Natural Resources, and Transportation. The United States Geological Survey (USGS), Water Resources Division, contributes to these efforts with water resource research. Figure 1 illustrates the ground water monitoring programs in Ohio. Short descriptions of these ground water monitoring programs are provided in the following paragraphs. Additional information is available from the agencies in charge of specific monitoring programs.

Ohio EPA's ground water related activities include ground water quality monitoring and assessment, as well as evaluation, prevention, and remediation of ground water pollution from existing and proposed treatment, storage and disposal sites. Ohio EPA's Division of Drinking and Ground Waters (DDAGW), functions as a technical support unit for other Ohio EPA programs by providing technical expertise on local hydrogeology and ground water quality. Specific activities of the ground water staff include: waste disposal treatment and storage site investigations; ground water complaint response; review of plans and site feasibility reports to ensure adequate ground water protection; and surveillance at land disposal sites. The division also maintains a statewide ground water quality monitoring program; oversees activities associated with underground injection wells (Class I, IV, and V); carries out the state public water system supervision program; and is responsible for implementing Ohio's Source Water Protection Program (SWAP). Legal authority to support Ohio EPA ground water functions is included in Sections 6109, 6111, 3734, and 3745, Ohio Revised Code (ORC). Other divisions and units within Ohio EPA also have major ground water responsibilities, including the Divisions of Solid and Infectious Waste Management,

Hazardous Waste Management, Emergency and Remedial Response, Surface Water and Ohio EPA's Office of Federal Facilities Oversight.

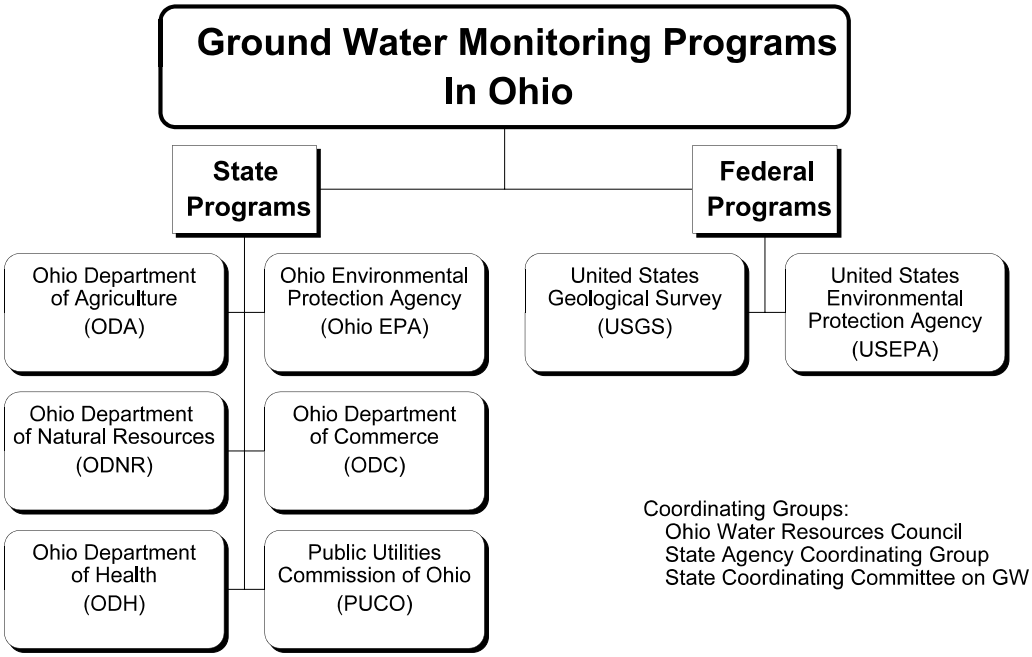


Figure 1. Ground water monitoring programs in Ohio.

The **Ohio Department of Natural Resources** (ODNR), **Division of Water** is responsible for the quantitative evaluation of ground water resources. Specific functions include: ground water mapping, administering Ohio's well log and drilling report laws, special hydrogeologic investigations, water quantity assessment, and technical assistance to municipalities, industries, and the general public regarding local geology, well drilling, and water development. Statutory authority for these activities is contained in Sections 1521 and 1523 of the ORC. The Division of Water is also compiling existing hydrogeologic data from their files to generate potentiometric maps to help complete SWAP assessments and continues to produce Ground Water Pollution Potential Maps (DRASTIC criterion) for Ohio counties. The Division of Water has completed computerization of the well log system and is distributing the recently completed State Aquifer Maps, both of which contribute to data available for evaluating ground water. The State Aquifer Maps are GIS coverages that include a Glacial Aquifer Map with five attributes describing the aquifer (thickness, aquifer setting, yield, lithology, and local name) and multiple bedrock coverages with three attributes describing the aquifer (yield, thickness, and name). The Aquifer Maps are valuable tools for analysis of ground water resources when combined with other GIS based information, such as well location or water quality data.

The **ODNR Division of Mineral Resources Management**, acting under authority of Sections 1509, 1513, and 1514, of the ORC, administers rules and regulations to manage oil and gas reserves and to control pollution from activities associated with petroleum production. Major functions that directly relate to ground water protection include regulating well drilling, well casing and well abandonment techniques, and regulating storage and disposal practices for associated waste fluids. The division administers the state's underground injection control programs for mineral extraction wells, enhanced oil recovery operations, and brine disposal (Class II and III injection wells). Additionally, the division oversees mining activities in the state and may require ground water monitoring and follow-up corrective actions around newly permitted coal strip mining areas.

Other divisions within ODNR also have ground water related responsibilities. The **Division of Soil and Water Conservation** (Section 1511, ORC) is responsible for developing programs which abate water pollution associated with soil erosion and animal waste handling activities. The **Division of Geological Survey** collects, interprets, and disseminates information on Ohio's bedrock and glacial geology. Ongoing programs for geologic mapping, geophysical testing, and test drilling provide a better understanding of the geologic framework of Ohio aquifers. The Division of Geological Survey is working with the Central Great Lakes Mapping Coalition to develop 3-D maps of selected topographic quadrangles in Ohio.

The **Ohio Department of Health** (ODH) is responsible for programs to regulate the siting, design, operation, and maintenance of private, residential water supply systems and sewage disposal systems which may have direct impacts upon local ground water quality and drinking water safety. ODH has adopted rules governing specific well construction practices and a well permit system, effective January 1, 2000 (Chapter 3701-28, OAC). These rules are administered in cooperation with local health departments. Local health departments and ODH investigate complaints of private wells that are suspected of being contaminated. ODH programs are mandated by Section 3701of the ORC, and include a registration program for private water system contractors.

ODH continues to investigate the distribution of arsenic in private wells in various counties. Increased awareness of arsenic in ground water has raised concerns about private wells in areas where compliance sampling for public water systems has identified high arsenic values. Samples collected were analyzed for arsenic, total iron, phosphorous, nitrate, and total coliform. The studies found that most of the wells with arsenic detections were completed in buried valley aquifers or in the sandstone formation immediately underlying the buried valley deposits. These studies have also confirmed that the presence of arsenic can be a very localized phenomenon.

In the **Ohio Department of Commerce**, Division of State Fire Marshal, the Bureau of Underground Storage Tank Regulations (BUSTR) is responsible for the registration of underground storage tanks (UST) for petroleum products and the implementation of rules for underground tank installation, testing, and abandonment. BUSTR staff investigate and direct UST removal and associated ground water cleanup activities in conjunction with local fire departments.

The **Ohio Department of Agriculture** (ODA), through the Pesticide Regulation Section, administers programs regulating the use of agricultural pesticides and oversees pesticide applicator training programs. ODA was the lead agency for developing the state's Pesticide Management Plan (PMP) to protect Ohio's ground waters from pesticide contamination. After receiving verbal concurrence for Ohio's PMP in

1999, written approval was received in August 2000 after the directors of ODH, ODNR, and Ohio EPA signed a cooperative commitment to implement the Pesticide Management Plan for the State of Ohio. As outlined in Ohio's PMP, ODA's Pesticide Regulation Section is currently sampling production wells at agricultural sites throughout the state. Ohio's PMP ranked areas of the state for vulnerability to ground water contamination based on soil type, geology, and land use. The PMP sampling program targets high vulnerability areas for initial sampling in which one hundred wells are sampled each year. Previous years of limited well sampling at bulk pesticide storage and handling sites identified contaminated wells at some sites. ODA continues to work with the identified facilities to implement best management practices to prevent further contamination.

In addition to the pesticide programs, various ODA divisions sample ground water for pathogens in wells that produce water used in food processing. In July 2002, primary regulatory authority for approval of confined animal feeding operations (CAFOs) moved from the Ohio EPA Division of Surface Water to the ODA Livestock Environmental Permitting Program. The Ohio EPA Division of Surface Water retains responsibility for issuing discharge permits for these facilities.

The **USGS Water Resources Division** focuses efforts on collecting and interpreting ground water data to examine the sustainability of ground water resources. Relevant research includes description and evaluation of water resources, mapping of water levels, ground water discharge of regional aquifers, local and regional modeling of ground water flow, local studies using federal and state cooperative funds, and the National Water Quality Assessment Program (NWQAP), as well as summary reports on national trends of water quality.

U.S. EPA collects ground water monitoring data at hazardous waste sites for which they oversee cleanup or which are permitted by U.S. EPA. Federal legislation overseen by U.S. EPA certainly drives much of the ground water monitoring and analysis completed in the state, such as the requirement for the 305(b) Report. Ohio EPA's Office of Federal Facilities Oversight (OFFO) collects ground water data from federal facilities in their oversight capacity.

OHIO EPA GROUND WATER CHARACTERIZATION PROGRAM

DDAGW is responsible for characterizing Ohio's ground water quality. Ground water quality monitoring information is collected through the new well approval process for public water supply wells, compliance sampling for public drinking water systems, sampling of the Ambient Ground Water Network wells, and various special studies. The division also receives or has access to water quality data collected from permitted solid waste sites, RCRA-regulated hazardous waste sites, and Ohio EPA Division of Emergency and Remedial Response (DERR) sites. Progress continues to be made to utilize these data to characterize Ohio's water quality. The goal is to employ water quality data to identify baseline water quality information for the main aquifer types, and to characterize the natural geochemical variation within the aquifer types on a regional and temporal basis. These data can then be used to identify areas of contaminated ground water within Ohio. Once identified, areas of ground water impact can be investigated and analyzed to identify likely causes. This process will improve our understanding and delineation of sensitive aquifers which will in turn allow Ohio EPA to focus protection strategies in priority areas. Figure 2 illustrates the hierarchy of DDAGW water quality monitoring data.

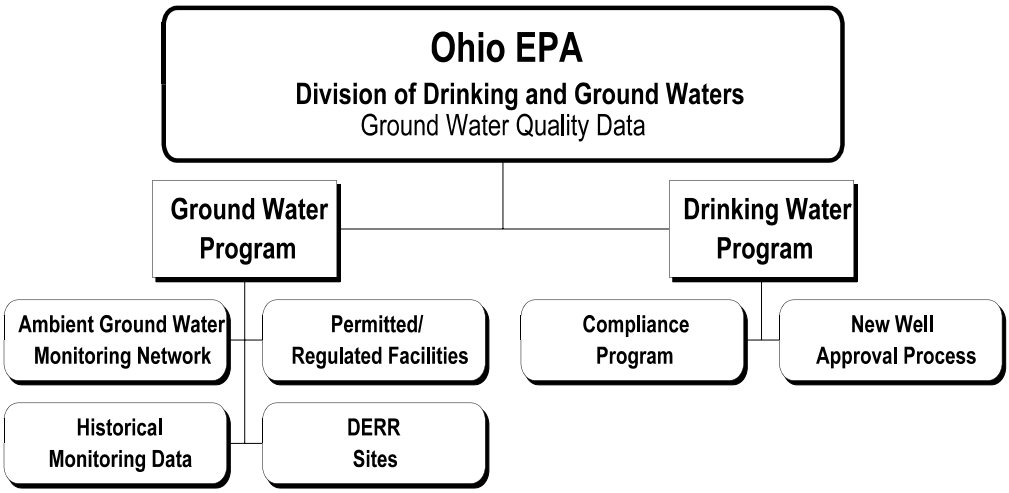


Figure 2. DDAGW ground water quality data sources.

The water quality analysis presented in this report utilizes Ambient Ground Water Monitoring Program (AGWMP) data and, to a lesser extent, public water system (PWS) compliance data. AGWMP utilizes raw (untreated) water quality data. In contrast, PWS compliance data is generally treated or distribution water quality data. The AGWMP was specifically designed for broad-based water quality analyses of Ohio's major aquifers. The PWS compliance data is collected to ensure that PWSs are meeting water quality standards, and consequently is more restrictive in parameter selection. Nevertheless, the wide geographic distribution of PWSs makes these data useful for statewide studies. Because of the importance of the AGWMP and PWS compliance data to the water quality analysis presented in this report, these data are described in separate sections below.

Another DDAGW ground water monitoring program identified in Figure 2 is the Historical Monitoring Data, which will eventually contribute to the water quality characterization effort. DDAGW staff have evaluated and organized paper files containing older ground water sample data, collected primarily between 1973 and 1985. These files include data collected during complaint investigations, litigation sampling, and pollution source investigation sampling. Data with accurate location and basic geologic information are being selected for transcription into an electronic format. AGWMP staff are just beginning to incorporate these historic data into our water quality analysis.

The monitoring data received from permitted/regulated facilities and DERR sites are another source of ground water quality information. Most of these data are submitted in formats dictated by the regulatory program, but the effort to organize this information into a water quality database for statewide analysis has not been initiated. The division completes special studies that focus on nonpoint sources such as arsenic, radon, pesticides or nitrates, which provide additional sources of data for water quality characterization. Finally, the required analysis of a raw water sample for a new PWS well includes an extensive suite of parameters, and provides a PWS raw water sample that can be used to help characterize

Ohio's water quality. In the case of transient public water systems, this new well sample is the only required monitoring for a broad spectrum of geochemical parameters.

Other Ohio EPA divisions have data relevant to ground water quality. The Division of Surface Water has extensive surface water sampling data that will be important for evaluating ground water and surface water interactions. In addition, their nonpoint source programs collect data that are relevant to potential ground water impacts. The Division of Emergency and Remedial Response collects ground water data for complaint and enforcement site investigations and they receive some ground water monitoring data from Voluntary Action Program sites that could be incorporated with ground water monitoring data from regulated sites. As DDAGW's Ground Water Quality Characterization Program matures, we will incorporate these data into our water quality analysis.

Ambient Water Quality Data

As part of the effort to characterize general water quality conditions in Ohio, DDAGW maintains the Ambient Ground Water Monitoring Program (AGWMP). Data collection activities occur at the district offices, and compilation, database design, and data analysis are completed mainly in the Central Office. This program to sample raw water was originally established in 1973 to measure seasonal and annual changes in water quality in the state's major aquifers. The network consisted of approximately 45 wells in 1973. The program expanded to 60 wells in the mid 1970s, but sampling of these wells decreased steadily to the mid 1980s. In 1986, the AGWMP was re-energized with 150 samples collected from about 100 active wells. To provide better representation of the primary aquifers in Ohio, a large number of bedrock wells were added to the network in the mid 1990s.

The program currently includes approximately 203 wells at approximately 198 sites. The distribution of AGWMP wells is illustrated in Figure 3. Of the total sites, roughly 92 percent are public water systems, and the rest (8 percent) are industrial, commercial enterprises or private residences. Raw water samples are analyzed for inorganics every 6 or 18 months depending on the total number of samples that have been collected and the stability of the geochemistry of major elements at the site. Table 1 lists the inorganic parameters for which AGWMP samples are analyzed. Samples are analyzed for volatile organic compounds once every 18 months. Starting in the mid 1990s, pesticides and semi-volatile organic compounds (SVOC) samples were collected every 18 months. These analyses were discontinued in 1999 because few compounds were detected for the significant added expense.

The primary objective of the AGWMP is to collect raw water quality data to characterize the general ground water quality across the state, the source water for ground water based PWSs in Ohio. To accomplish this goal, wells included in the AGWMP should not be significantly impacted by local spills or other local waste concerns. To evaluate the effect of volatile organic compounds (VOCs) on the AGWMP wells, all VOC detections from AGWMP samples were reviewed. Criteria were developed to identify AGWMP wells with "significant" VOC detections, including:

- A VOC hit requires VOC detections from more than one sampling event at a given well;
- Disinfection byproducts and common lab contaminants were excluded from consideration; and
- Tentatively Identified Compounds (TICs) were use in this analysis only if they were reported at concentrations above 5.0 ug/L (R. Khidekel, pers. comm., 2002).

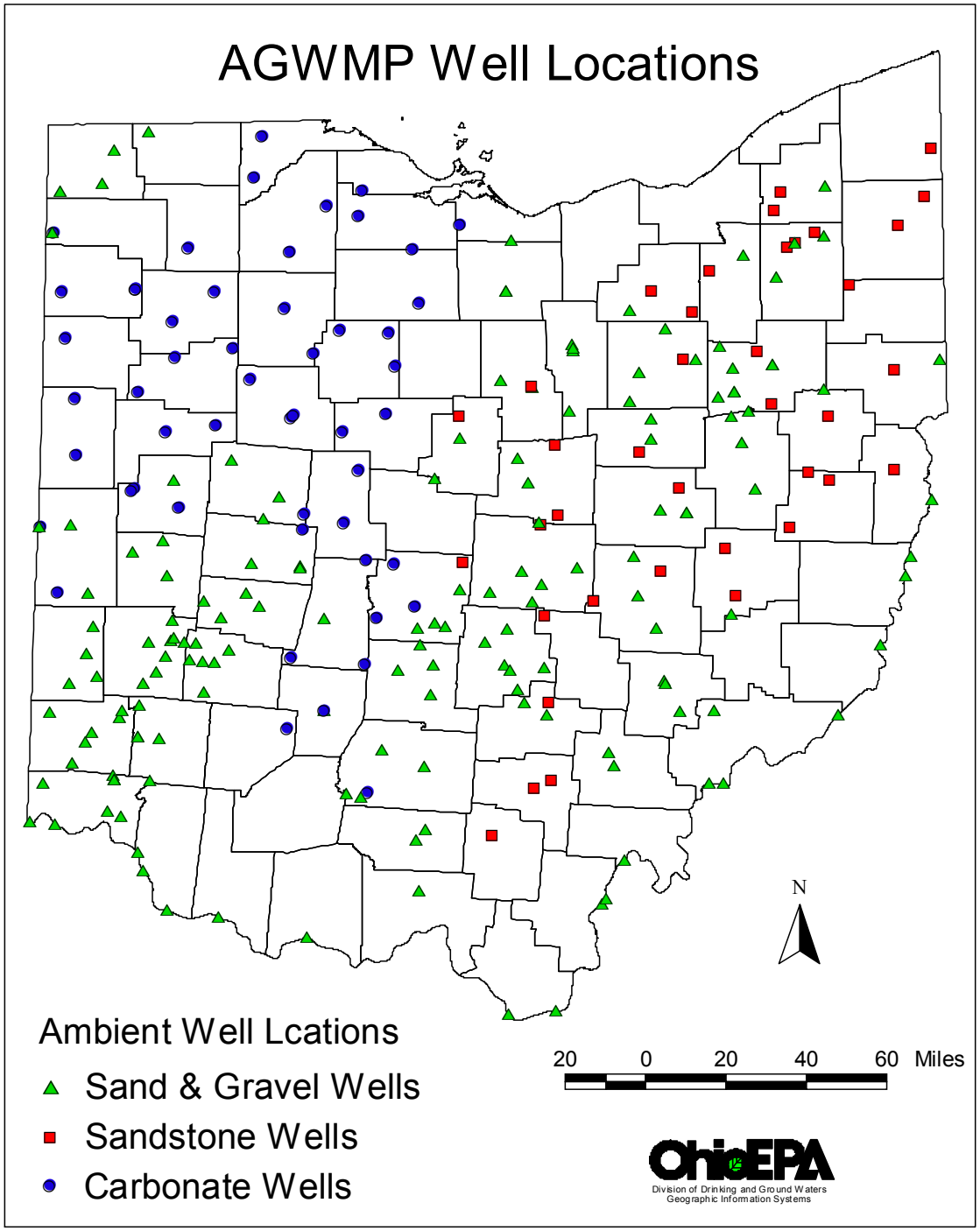


Figure 3. AGWMP well locations and aquifer type.

Using these conservative criteria, 19 of the active AGWMP wells exhibit low-level VOC impacts. All of the VOC detections are well below the Maximum Contaminant Level (MCL), but these wells may be used to help identify sensitive aquifers. With the identification of this subset of AGWMP wells, the ground water staff is considering how to include these wells in general geochemical summaries.

Locational and lithologic information have been updated for all of the 203 active ambient wells in the AGWMP database for effective geochemical and GIS analysis. Of the active wells, 61 percent produce from unconsolidated sand and gravel aquifers, 23 percent from carbonate bedrock aquifers, and 16 percent from sandstone bedrock aquifers. The unconsolidated wells are predominantly sand and gravel wells, but four of the well logs identify the screened zone as gravel and two well logs identify the screened zone as sand. In general terms, we refer to all the unconsolidated wells as sand and gravel aquifers. The sandstone wells produce from Pennsylvanian and Mississippian sandstones. Of the sandstone wells, eight are identified as sandstone/shale wells and two wells are identified as shale. This distinction is based on the well logs, but bedrock wells are generally open bore holes below the casing, so some water contribution from the stratigraphic section below the casing might be expected. From this perspective, all the sandstone wells could be called sandstone/shale wells. Most of the carbonate wells are producing from Silurian dolomites, but wells in the Devonian limestones account for six of the carbonate wells. These aquifers are discussed in the following "Major Aquifer Types" section.

There are limitations to using AGWMP data to characterize statewide ground water quality. The most significant limitation is the range of well types (high-production public versus low-production public versus domestic). The bulk of the AGWMP wells are of the high-yield public water supply type. The high production wells in the unconsolidated units are generally deeper and have long well screens. Bedrock wells are typically cased to the bedrock with open boreholes in the bedrock. These types of wells may allow a certain amount of natural mixing of waters between stratigraphic or hydro-stratigraphic units. Other possible sources of bias include the number and variety of sampling personnel and the somewhat irregular sampling frequencies. On the other hand, a single laboratory is used for all Ambient Program chemical measurements statewide, providing strong analytical consistency. Despite these potential error sources, the data set quality is quite high; the geochemical variability between the aquifer types is easily discerned, as illustrated in the Ohio Water Quality Characterization Section of this report.

Since the completion of the 2000 305(b) Report, the AGWMP staff have continued to work to increase the quality of the AGWMP water quality database, to implement the standard procedures for data management developed in 1999, and to research and update the hydrologic data associated with the AGWMP wells. These efforts maintain our high confidence in the AGWMP data. The following AGWMP data management and QA/QC procedures have been completed:

- All old organic AGWMP data were entered and QA/QC procedures completed;
- The End-of-Round report format was developed and this report is now generated at the end of each sampling round in order to assure QA/QC procedures are completed for new data;
- Refined the sampling period for the spring and fall sampling rounds to provide a firm sampling completion date to allow End-of-Round Report completion;
- The Operating Procedures Document (OPD), the quality assurance and procedure document for the AGWMP, was expanded, reorganized, and rewritten;

Table 1

AGWMP Inorganic Chemical Parameters

PARAMETERS	CURRENT REPORTING LIMITS
Major Constituents	**mg/L**
Alkalinity, Total as $CaCO_3$	5
Calcium (Ca)	2
Chloride (Cl)	5
Hardness as $CaCO_3$	10
Magnesium (Mg)	1
Potassium (K)	2
Sodium (Na)	5
Sulfate (SO_4)	5
Total Dissolved Solids (TDS)	10
Trace Constituents	**µg/L**
Aluminum (Al)	200
Arsenic (As)	2
Barium (Ba)	15
Cadmium (Cd)	0.2
Chromium (Cr)	30
Copper (Cu)	10
Fluoride (F)	0.10 mg/L
Iron (Fe)	50
Lead (Pb)	2
Manganese (Mn)	10
Nickel (Ni)	40
Selenium (Se)	2
Strontium (Sr)	30
Tritium (^3H)	0.8 T.U.
Zinc (Zn)	10
Nutrients	**mg/L**
Ammonia (NH_3)	0.05
Chemical Oxygen Demand (COD)	10
Nitrate/Nitrite (as N)	0.10
Phosphorus (P)	0.05
Total Kjeldahl Nitrogen (as N)	0.2
Total Organic Carbon (TOC)	2
Field Analysis	**Relative Accuracy**
pH	± 0.02 S.U.
Specific Conductance (µmhos/cm)	± 0.5 %
Temperature	± 0.1 °C

- Completed a review of the all of the AGWMP files to correct and update the hydrologic data, including a review of geologic (using ODNR Aquifer Maps) and well construction data;
- Developed criteria for resampling AGWMP wells;
- Decided to transfer AGWMP data to STORET rather than rewrite the data management program and initiated STORET training and data mapping;
- Drafted a sampling proposal for more frequent sampling at sensitive AGWMP wells to study seasonal variation, GW-SW interaction, and contaminant transport in sensitive aquifers; and
- Site Information Forms were developed for each active AGWMP well to ensure the correct well is sampled and the sampler is aware of special circumstances at sites.

With these efforts, the AGWMP water quality data continues to be the best raw water-quality data that DDAGW has to characterize statewide ground waters. Consequently, we have utilized these data extensively in this report to characterize the water quality of the three major aquifer types in Ohio. The expertise of the GIS staff and the continued development of expertise with data analysis programs are critical parts of the efforts to examine these data and present them in effective ways.

Public Water System Data

ODH began water quality sampling and analysis of public water supplies in the early 1940s. With the formation of Ohio EPA in 1972, these duties were transferred to Ohio EPA. Samples of both raw and finished water from community water suppliers were collected and analyzed through the mid-1970s. The analyses provided a continuing record of public water supply quality to ensure that violations of recommended health (primary) or aesthetic (secondary) standards in drinking water were identified and corrected. Between 1950 and 1977, over 15,000 raw water chemical analyses of the state's public ground water supplies were obtained. Since around 1977, only finished (treated) water has been tested on a regular basis, and analyses are limited to primary (health related) drinking water parameters. In proposed new wells, however, raw water is required to be tested for all primary and secondary parameters.

Even though public drinking water compliance sampling targets only treated water, the wide distribution and large number of public water systems make these data useful in characterizing Ohio's ground water. The data from treated water (compliance sampling), as well data from the untreated (raw) water from public water supplies, are hereafter collectively referred to as public water system (PWS) data. In the case of nitrate, we make the assumption that most PWSs do not have treatment processes that significantly reduce nitrate concentration in the sampled water. Other parameters, however, may be reduced in the treatment process. For example, if a PWS is removing iron, and arsenic is also present, the arsenic concentration will be reduced with iron removal.

Treated water from Ohio's public water systems is currently being monitored for compliance purposes on a continuing basis in accordance with the Federal Safe Drinking Water Laws and Chapter 6109 of the Ohio Revised Code. Sampling is based on three-year cycles, but sampling schedules for each contaminant group are different. Individual sampling schedules are produced for each public water supplier by DDAGW based on past sampling results and various waiver programs. Guidelines for public drinking water monitoring for ground water based systems are provided in Table 2.

Table 2

Drinking Water Monitoring Requirements for Public Water Supply Wells.			
Contaminant Group	**Community PWS**	**Non-Transient, Non-Community PWS**	**Transient Non-Community PWS**
Radiological [a]	✘		
Trihalomethanes	✘		
Asbestos [b]	✘	✘	
Inorganic Constituents [c]	✘	✘	
Synthetic Organic Compounds (SOCs) [d]	✘	✘	
Volatile Organic Compounds (VOCs) [e]	✘	✘	
Lead and Copper [f]	✘	✘	
Microbiological [g]	✘	✘	✘
Nitrate and Nitrite [h]	✘	✘	✘

[a] Must monitor for gross alpha radioactivity once every three years. New community systems must complete four consecutive quarterly samples the first year of operation.
[b] Asbestos concentration must be analyzed once every nine years.
[c] Required to sample for 12 inorganic constituents once every 3 years.
[d] All ground water systems are required to sample for alachlor, atrazine, and simazine once every 3 years. Systems with detections are required to monitor these compounds on a quarterly schedule until they are reliably and consistently below the maximum contaminant level (MCL). Systems that had one or more nitrate detections above 2.0 mg/L are required to monitor the other 15 SOCs once every 3 years.
[e] Required to sample for 21 compounds. Initially, samples are required on a quarterly basis for one year, then a public water system can reduce sampling frequency to once a year. After three years of annual samples without VOC detections, sampling frequency can be reduced to once every three years.
[f] Action levels, not MCLs
[g] All ground water-based public water systems are required to monitor for total coliform at least once every quarter. A community system must sample for total coliform at least once per month. If any sample is positive for total coliform then the sample must be analyzed for fecal coliform or E.coli.
[h] All ground water-based public water systems are required to monitor for nitrate at least once per year. Nitrite is required once every 9 years. If the nitrate exceeds 50 percent of the MCL (i.e., 5 mg/L), or if nitrite exceeds 50 percent of the MCL (i.e., 0.5 mg/L), quarterly samples are required until the system is reliably and consistently below the MCL. Ground water systems designated as under the direct influence of surface water are required to sample for nitrate monthly.

MAJOR AQUIFER TYPES

Ohio has abundant surface and ground water resources. Average rainfall ranges between 30 to 44 inches a year (increasing from northwest to southeast), which drives healthy stream flows, except in prolonged periods of drought. Infiltration of a small portion of this rainfall recharges the states aquifers and keeps the streams flowing between rains. Ohio's aquifers can be divided into three major types of productive aquifers which are present throughout most of the state. Nevertheless, there are significant areas of the state where local aquifers exhibit limited water production potential. The three major, productive aquifers are illustrated in Figure 4 along with a low yielding aquifer in Southwest Ohio. Where present, the major aquifers provide abundant ground water to Ohio citizens.

The most productive aquifers are the sand and gravel units that occur in old stream valleys across the state. The sandstone bedrock aquifer setting provides water to the eastern portions of the state that do not use the sand and gravel units. The sandstone bedrock production is limited along the southeast border of the state. The carbonate bedrock setting provides water to the western part of the state. The interbedded shale and carbonate aquifer in the southwestern portion of Ohio is generally a very low-yielding aquifer, and its use is limited. The quantity of water obtained from wells is highly variable across the state and is dependent upon the local geology in the aquifer setting, and the user's needs. Each of these aquifer settings is described in the following sections.

Sand and Gravel Aquifers

Ohio's most productive water bearing formations or aquifers are valley outwash deposits of sand and gravel that were deposited by glacial meltwater. They are found beneath and adjacent to the Ohio River, its major tributaries, and other pre-glacial stream channels. The distribution of these Quaternary sand and gravel units is presented in a generalized manner as thin bands of green in Figure 4, which is simplified from the ODNR Glacial Aquifer Maps (ODNR, 2000). The Glacial Aquifer Map provides detail on the distribution of sand and gravel deposited by glacial and alluvial processes. Figure 4 illustrates the general distribution of the old river valleys cut by glacial meltwater which were subsequently filled in by glacial deposits as the glaciers receded. Based on their depositional environment, the sand and gravel units are frequently referred to as buried valley aquifers, although this is not an accurate description of all the sand and gravel deposits that provide water to Ohio wells. For instance, in the northwest corner of the state, the wide area of sand and gravel units include sheets of outwash or gravel deposits that occur between sheets of glacial till. Present day stream processes deposit alluvial sand and gravel deposits that can also be used as aquifers. Other hydrogeologic settings included in the sand and gravel aquifers are the outwash/kame and beach ridge deposits (including the Oak Opening Sands). Although all of these units are not included in Figure 4, they are identified in the ODNR Aquifer Maps.

Water production from the coarser grained and thicker sand and gravel deposits ranges from 500 to 1,000 gallons per minute. Lower yields from sand and gravel aquifers are more common. The production rate depends on the type, distribution, extent, and thickness of permeable glacial/alluvial deposits as well as on well construction parameters, such as well diameter and length of well screen.

Sandstone Aquifers

In the eastern portions of Ohio where buried valley aquifers are not present, the common aquifer is sandstone (Figure 4). Upper Paleozoic siltstone, sandstone, and conglomerate formations (Permian to Mississippian age) in eastern Ohio occur as numerous layers of variable thickness and areal

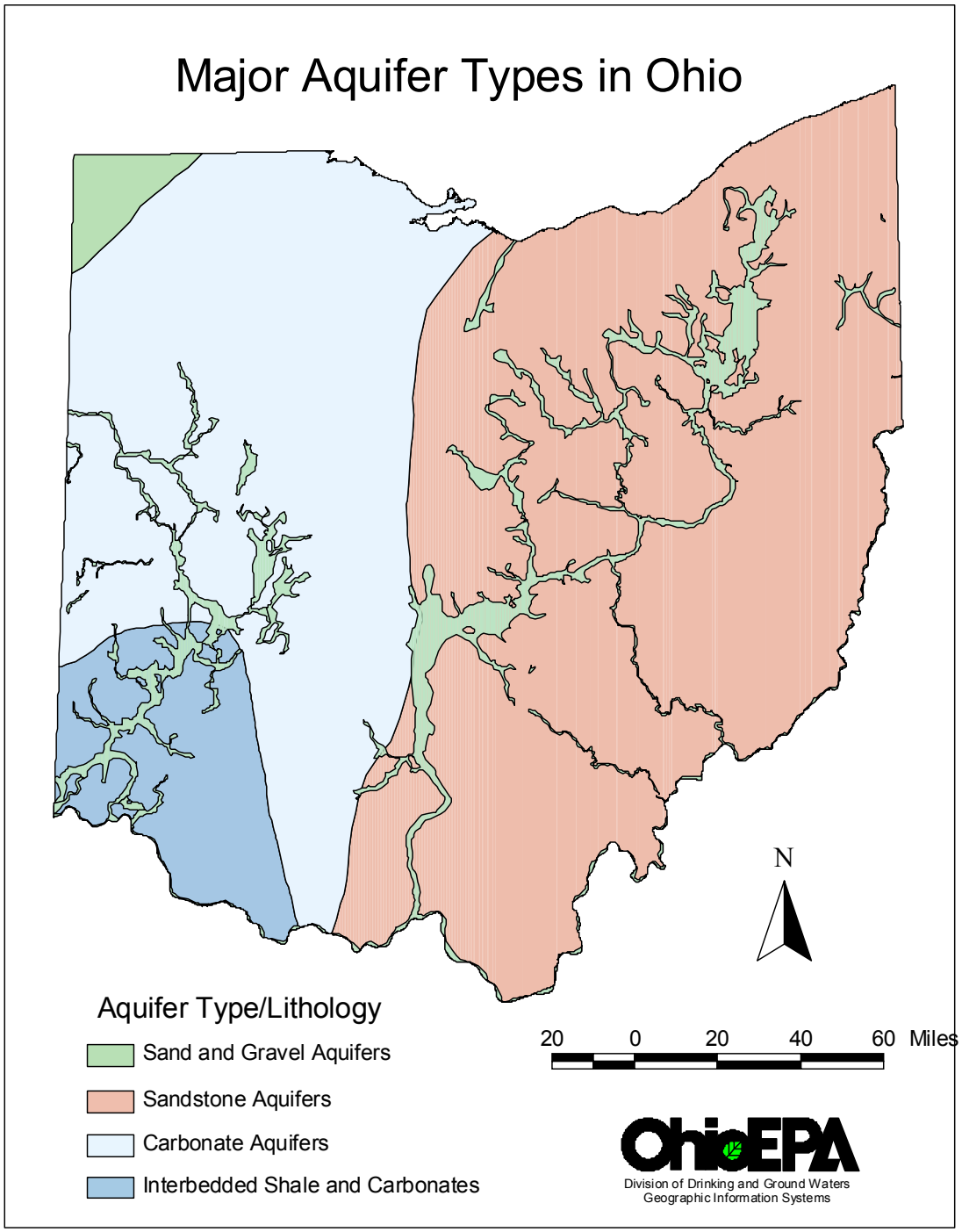


Figure 4. Aquifer types in Ohio modified from ODNR Aquifer Map (ODNR, 2000)

extent separated by layers of shale and minor amounts of limestone, clay and coal. The sandstone units generally dip a few degrees to the southeast. Some of the thicker sandstones and conglomerates are capable of yielding 50 to 100 gallons per minute to individual wells, but 25 gallons a minute is generally a good yield for the sandstone aquifers. The more productive stratigraphic units include Mississippian Berea Sandstone, Cuyahoga Group, Logan and Blackhand Formations, Pennsylvanian Massillon through Sharon Formations, and the Homewood Sandstone within the undivided Allegheny and Upper Pottsville Groups, in stratigraphic order of deposition.

In southeastern Ohio, the Permian and Upper Pennsylvanian stratigraphic section includes low yielding aquifers. The bedrock consists of massive shales or varied sequences of thin bedded shales, limestones, sandstones, clays, and coals, which do not yield much water to wells. A yield of 0-5 gallons per minute is not uncommon in these areas. These low yielding units include the Pennsylvania Undivided and the Permian Dunkard Group in stratigraphic order (bottom to top), as defined in the ODNR Aquifer Maps.

Carbonate Aquifers

Ohio's third major aquifer type is the carbonate bedrock, the dominant aquifer in the western part of the state (Figure 4). Lower Devonian and Silurian limestones and dolomites reach a total thickness of 300 to 600 feet, and are capable of yielding from 100 to over 500 gallons of water per minute. Higher production units are associated with fractures and dissolution features that increase the permeability of the carbonate bedrock. The high production aquifers are the Silurian Lockport/sub-Lockport Dolomite, the Salina Group, consisting of the Tymochtee and Greenfield Dolomites, and the Undifferentiated Salina Dolomite. The Devonian Delaware and Columbus Limestone, exposed on the eastern edge of the Silurian Dolomites, and equivalent Devonian units in the northwest corner of Ohio (Traverse Group, Dundee Limestone, and Detroit River Group) are also included with the carbonate aquifers.

Interbedded Shale and Carbonate Aquifers

In the southwestern portion of the state, the interbedded shale and carbonate aquifer (undivided Ordovician) is dominated by shale (Figure 4). These rocks have a relatively low potential for yielding ground water due to the predominance of shales and other impervious rocks. Well yields are generally less than 10 gallons per minute, and in many areas are less than one gallon per minute. In southwest Ohio, public water systems depend on the buried valley aquifers as the main ground water source. The interbedded shale and carbonate aquifer with low yields are only practical for low volume water users, and consequently, this aquifer is not discussed further in this report.

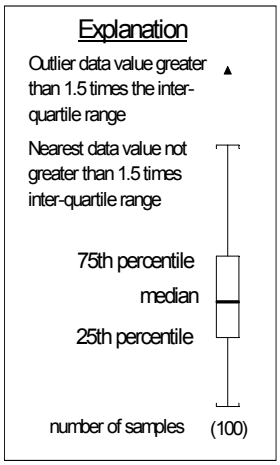
GROUND WATER QUALITY BY AQUIFER TYPE

Introduction

The overall ground water quality within the State of Ohio is described here using the Ambient Ground Water Monitoring Program database, consisting of over 3,250 water quality samples distributed across 203 sites (Figure 3). The major aquifer types are used to delineate ground water quality differences between the unconsolidated sand and gravel units, sandstone bedrock, and carbonate bedrock (Figure 4). The majority of the wells used in this evaluation are production wells associated with public water supplies, usually developed within higher yielding zones of generally good water quality. This is consistent with the goals of the AGWMP, to collect, analyze, and describe the background (ambient) ground water quality used by public water systems across the state.

Of the factors that contribute to the chemical makeup of ground water, the most significant are the composition of the recharge (percolation) water, the soil and vadose zone composition, the composition and porosity of the aquifer solids, and the residence time of the ground water. These factors vary widely across the three main aquifers in Ohio, but some general observations on their effect on water quality are indicated based on aquifer types. In general, the initial composition of percolation water across the state is similar. Long-term average precipitation for Ohio is 38 inches per year while ground water recharge rate estimates range from 3 inches to 16 inches per year, with a median of 6 inches per year (Dumochelle and Schiefer, 2002). Composition and solubility of soil and vadose materials, however, is highly variable across the state, leading to recharge waters with dissimilar initial compositions. Thus, the thick glacial tills (clayey soils) found across much of north, central, and west Ohio affect the initial percolation water quality much differently than the thin loess soils of southeast Ohio. The permeability of these thick soils tends to increase the residency time, however, agriculture tile drains in these thick soils short circuit flow paths to surface water and influences the volume of recharge reaching the aquifer.

Increased residence time in an aquifer will typically lead to higher salinity and greater mineralization of the water, depending on the solubility of the aquifer minerals present. The sand and gravel units, for example, have typically short residence times, leading to lower salinities in these waters. These younger waters are generally more shallow, and, if affected by surface contamination, are more likely to reflect this impact. Older, deeper waters, such as in the carbonate aquifers of northwestern Ohio, may follow much longer flow paths, allowing the water ample time to establish a geochemical equilibrium with the rock system. Figure 5 is a box plot indicating the distribution of well depths by aquifer type for the AGWMP wells. The median depth of the carbonate aquifers (about 220 feet) is greater than the median depth of the sandstone aquifers (about 175 feet). The median depth for the sand and gravel aquifers is significantly shallower, just under 100 feet. The range of the carbonate and sandstone well depths is roughly twice the range of the sand and gravel wells.



Box and Whisker Plots

Box and Whisker Plots are an efficient method to visualize how individual points are distributed in data sets. The "box" itself outlines the range of half the data (25th to 75th percentiles). The median, or 50th percentile, is shown by the bar inside the box. Two whiskers (vertical lines extending from the box) indicate the distance to the highest and lowest data points which are not outliers. Outliers are indicated by points above or below the whiskers. If the median is located midway between top and bottom of the box, the data are normally distributed.

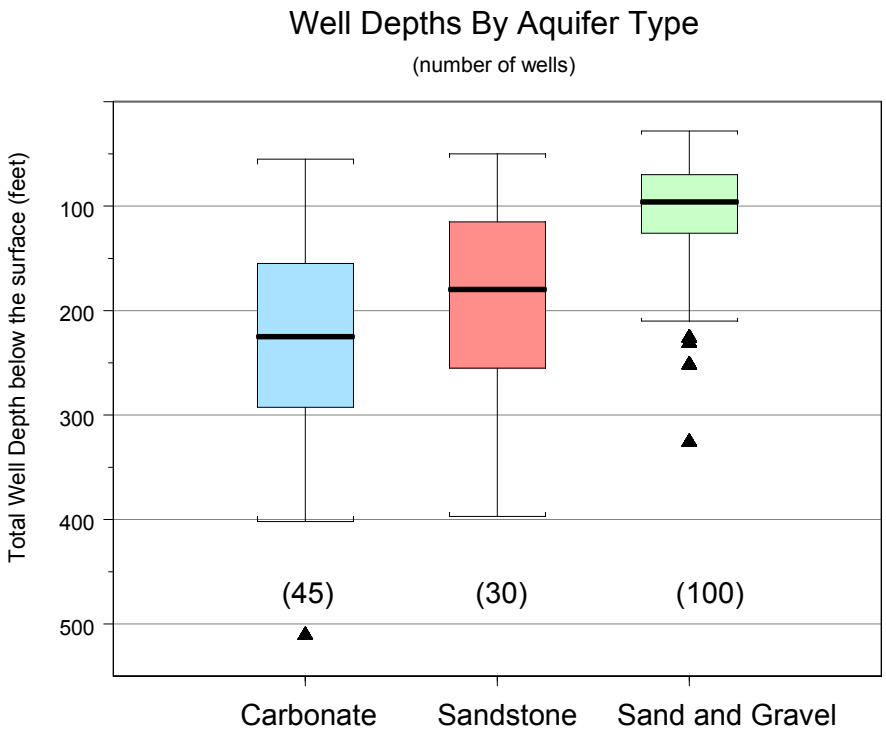


Figure 5. Box plot of AGWMP well depths by aquifer type.

Parameter Means

Ground water across the state is generally of very high quality, as indicated by the mean aquifer geochemistry summarized in Table 3. This table provides the arithmetic mean, median, minimum value, maximum value, total number of samples, number of samples below the reporting limit, and the percent censored for each parameter in each aquifer type as of July, 2002. The "percent censored" column records the percent of analyses measured below the current reporting limit (rounded to the nearest percent). The presence of a less than sign (<) in the minimum value field (column 5) indicates the minimum value is the reporting limit. The minimum value (column 5) in Table 3 may not always coincide with the modern reporting limit (Table 2) due to changes over time in analytical methods or errors in data transcription. Estimates of the number and percentages of censored data (columns 8 and 9, Table 3) may be similarly affected.

Table 3 represents the accumulation of over 80,000 raw, inorganic ground-water data points gathered at more than 200 sites across Ohio from over 30 years of ground water sampling. Thus, Table 3 records one of the most significant summaries of ambient ground water chemistry available for the State of Ohio and separates these data into the major aquifer types. Consistency in sampling protocol, analytical procedures and stability of site histories over time combine to lend a unique significance to the ground water data base developed through Ohio EPA's Ambient Ground Water Monitoring Program. A significant

consequence of the long history of the AGWMP is the ability to track ground water quality at individual wells over long periods of time. The topic of nitrate time series is examined in the Sensitive Aquifer section of this report and this analysis illustrates the value of AGWMP data collected at a well over a significant time period.

The ground water parameter data in Table 3 are grouped into four categories, identified in the first column:

- **Field Parameters** – measured in field (pH, water temperature, and specific conductance);
- **Major Constituents** – such as calcium or sulphate, concentrations in the range of mg/L (ppm);
- **Trace Constituents** – such as arsenic or cadmium, concentrations in range of ug/L (ppb); and
- **Nutrients** – components required by some organic systems for nutrient balance, concentrations in mg/L (ppm).

To illustrate the utility of Table 3, a simple example is provided. To find which major aquifer has the most manganese, find the Manganese row in Column 1 (under Trace Constituents), and read off the mean values for each aquifer type from column three. In this case, we see that the sandstone bedrock system has the greatest overall mean manganese concentration (232.8 ug/L), while the carbonate system has the lowest, at 29.3 ug/L. Suppose now you were interested in looking up the probabilities of encountering a manganese detection in each of the three aquifer types. To do this, follow the manganese row across to column 9 (Percent Censored). Here we find that within the sand and gravel units, only seven out of every 100 water samples is recorded below the reporting limit, so we would expect to find a manganese detection with greater than a 90 percent probability. In the case of the carbonate bedrock system in Ohio however, we find the percent censored for manganese is 73, indicating that only a 27 percent chance exists that a water sample from this aquifer type will yield a detection for manganese. It should be noted that these censored values are not probabilities in the stricter sense of a probability distribution, but rather observed percentages. Thus they are useful values for estimating expected levels of non-detects, based on the long-term sampling history of AGWMP wells.

Use of Primary and Secondary MCLs

The following analysis of AGWMP ground water quality data utilizes Maximum Contaminant Level (MCL) and Secondary Maximum Contaminant Level (SMCL) as convenient benchmarks for discussion. However, MCLs (regulated as the maximum permissible level in delivered water) and SMCLs (advisory limit only) are applied strictly to treated water at public water systems for regulatory purposes. Since AGWMP data are obtained entirely from raw (untreated) ground water, any exceedence of an MCL or SMCL by an AGWMP data point has no legal or regulatory consequence. The usefulness of the comparison is only that MCLs and SMCLs are widely known and understood, and thus represent a practical benchmark for discussion.

Seven of the enforceable primary drinking water standards with defined MCLs applicable to finished drinking water are monitored through the AGWMP. The MCLs are: arsenic (50 ug/L, lowered to 10ug/L effective January 2006), barium (2 mg/L), cadmium (5 ug/L), chromium (100 ug/L), fluoride (4 mg/L), nitrate-nitrite as N (10 mg/), and selenium (50 ug/L). Additionally, both lead (0.015 mg/L) and copper (1.3 mg/L) are covered by action levels (not MCLs) for drinking water and are monitored by the drinking water program.

As indicated by Table 3, no chemical parameters exceed their MCL based on averages by aquifer type. Mean arsenic concentrations for all three aquifer systems were well below the MCL of 50ug/L and the new MCL of 10 ug/L (sand and gravel =7.0 ug/L, sandstone = 2.99 ug/L, carbonate = 3.89 ug/L). Only a single (sand and gravel) well recorded a mean arsenic (As) concentration above the current MCL. The new arsenic MCL raises concerns for those systems close to and above the new standard. A summary of the arsenic geochemistry and distribution in Ohio is provided later in this report. Mean concentrations for barium, cadmium, chromium, fluoride, nitrate-nitrite, and selenium were also below the associated MCLs for these parameters within all three aquifer systems. Individual station means indicate no primary MCL exceedences for barium, cadmium, chromium, fluoride, and selenium.

In addition to the seven primary drinking water standards, eight parameters with established SMCLs are monitored by the AGWMP. Elevated levels of these parameters are associated with aesthetic degradation of water quality. The SMCLs covered by this program are: aluminum (0.05 - 0.2 mg/L), chloride (250 mg/L), iron (0.3 mg/L), manganese (0.05 mg/L), pH (7-10.5 SU), sulfate (250 mg/L), total dissolved solids (TDS, 500 mg/L), and zinc (5 mg/L). Since these parameters are more closely related to general ground water quality, they will be discussed in the aquifer type sections below.

Influence of Nitrate

One of the accomplishments of the past years activities has been the identification of AGWMP wells with elevated nitrate derived from surface and near surface sources. Wells were included in this category if they exhibited levels of nitrate greater than 2.0 mg/L. This criterion is similar to the one used in the Source Water Assessment and Protection Program (SWAP) Susceptibility Analysis, and is also based on USGS reports citing nitrate background levels as being less than 2.0 mg/L. This effort has allowed the wells influenced by surface and near surface sources of nitrate to be excluded from Table 3. Thus, Table 3 is the best summary available for the general water quality of Ohio's major aquifers, the source water for Ohio's public drinking water systems using ground water. This is not to say that there is no anthropogenic impact in the data presented in Table 3, but that the impact from surface and near surface derived nitrate and its consequences have been, according to our stated tolerance, expressly removed. The incentive for the removal of those wells affected by elevated nitrate concentrations from Table 3 is to provide the most representative "background" characterization of ground water possible.

With the removal of the nitrate-influenced wells, as expected, the nitrate means and maximums in Table 3 are significantly reduced from the values reported in the 2000 305(b) Table 3. The sand and gravel maximum of 4.92 mg/L is a single value at a well in which all the other nitrate results are non detect. No well was identified as influenced on the basis of a single sample, so this elevated result is correctly reported in Table 3. Other differences in Table 3, resulting from the removal of nitrate influenced wells, appear to reflect oxidation and reduction controls. Thus, the parameters that are more soluble in reduced conditions exhibit increased means as a result of removing the nitrate-influence (oxygenated) water data. These increases are generally small for Ba, Mn, and As. A more significant increase is seen in iron concentrations, with an increase from 1,170 to 1,598 ug/L in the sand and gravel aquifers and from 1,382 to 1,784 ug/L in the sandstone aquifers. For the major elements, the difference between the 2000 and 2002 means reported in Table 3 are not significantly different. For example, the hardness and total dissolved solids are little changed. Because nitrate-nitrite concentrations are useful indicators of human activity, nitrate will be discussed in more detail in the Sensitive Aquifer section of this report.

Table 3. Ambient Network Data Summary by Major Aquifer as of July 2002.

Parameter and Units	Major Aquifer	Mean Value	Median Value	Min. Value	Max. Value	Number of Samples	Number Below Rep. Limit	Percent Censored
FIELD PARAMETERS				‡			§	§
pH, Field S.U.	Sand and Gravel	7.32	7.3	5.8	8.9	1135	na	na
	Sandstone	7.27	7.3	5.9	8.7	257	na	na
	Carbonate	7.25	7.2	5.6	8.7	578	na	na
Specific Conductivity umhos/cm	Sand and Gravel	598	590	1	1503	1207	na	na
	Sandstone	571	480	20	3700	269	na	na
	Carbonate	850	760	275	2790	600	na	na
Water Temperature Degrees C	Sand and Gravel	13.4	13.1	5.8	25.0	1220	na	na
	Sandstone	12.8	12.5	7.0	28.7	268	na	na
	Carbonate	13.4	13.1	8.0	25.0	603	na	na
MAJOR CONSTITUENTS								
Alkalinity, Total as $CaCO_3$ mg/L	Sand and Gravel	265	274	< 5.0	1500	1509	0	0
	Sandstone	215	196	< 5.0	1500	369	0	0
	Carbonate	292	301	102	648	645	0	0
Calcium, Total mg/L	Sand and Gravel	93.3	93	< 2	300	1566	2	0
	Sandstone	57.3	50	< 2	74	384	1	0
	Carbonate	136.4	116	60	613	666	1	0
Chloride mg/L	Sand and Gravel	34.5	28.0	< 2.0	247	1548	51	3
	Sandstone	40.5	21.0	< 2.0	286	377	47	12
	Carbonate	27.9	14.0	< 2.0	420	636	66	10
Hardness, Total as $CaCO_3$ mg/L	Sand and Gravel	358	362	< 10	953	1168	2	0
	Sandstone	227	201	< 10	630	282	1	1
	Carbonate	554	471	209	2010	489	0	0
Magnesium, Total mg/L	Sand and Gravel	29.8	30	< 1	74	1569	3	0
	Sandstone	18.0	16	< 1	66	384	1	0
	Carbonate	50.6	44	26	134	668	1	0
Potassium, Total mg/L	Sand and Gravel	2.3	2.0	< 1	56.0	1496	221	15
	Sandstone	2.6	2.0	< 0.5	8.0	373	69	18
	Carbonate	3.0	3.0	1.3	8.4	615	3	0
Sodium, Total mg/L	Sand and Gravel	25.5	21	< 4	427	1569	36	2
	Sandstone	63.1	28	< 5	774	384	18	5
	Carbonate	35.3	27	< 5	202	667	7	1
Sulfate mg/L	Sand and Gravel	81.5	70.0	< 5	640	1548	6	1
	Sandstone	77.1	43.5	< 5	1320	382	37	10
	Carbonate	280.7	201.0	< 5	1410	662	1	1
Total Dissolved Solids mg/L	Sand and Gravel	461	452	12	1650	1472	0	0
	Sandstone	415	350	< 10	2390	371	1	0
	Carbonate	769	670	330	2360	625	0	0
TRACE CONSTITUENTS								
Aluminum ug/L	Sand and Gravel	200.6	200.0	84.0	1510	1093	1090	100
	Sandstone	200.2	200.0	< 200.0	234	315	313	99
	Carbonate	207.9	200.0	< 200.0	1810	424	417	98
Arsenic, Total ug/L	Sand and Gravel	7.00	4.0	< 2.0	95	1472	535	36
	Sandstone	2.99	2.0	< 2.0	30	363	274	75
	Carbonate	3.89	2.0	< 2.0	21	630	367	58
Barium ug/L	Sand and Gravel	192.0	139.0	15.0	2160	1444	19	1
	Sandstone	173.3	69.0	15.0	2080	353	6	2
	Carbonate	65.8	40.0	7.0	301	629	68	11
Cadmium, Total ug/L	Sand and Gravel	0.22	0.2	< 0.2	5.0	1313	1297	99
	Sandstone	0.22	0.2	< 0.2	6.0	364	356	98
	Carbonate	0.25	0.2	< 0.2	10.2	609	599	98

Parameter and Units	Major Aquifer	Mean Value	Median Value	Min. Value ‡	Max. Value	Number of Samples	Number below Rep. Limit	Percent Censored
Chromium, Total ug/L	Sand and Gravel	27.0	30.0	< 0.2	50	1338	1325	99
	Sandstone	27.4	30.0	< 10.0	30	370	367	99
	Carbonate	28.2	30.0	< 0.2	50	619	607	98
Copper, Total ug/L	Sand and Gravel	10.80	10.0	< 2.0	233	1188	1035	87
	Sandstone	10.65	10.0	< 2.0	93	349	274	79
	Carbonate	13.58	10.0	< 2.0	367	489	344	70
Fluoride mg/L	Sand and Gravel	0.49	0.3	< 0.1	2.3	958	111	9
	Sandstone	0.36	0.3	< 0.1	2.1	287	39	10
	Carbonate	1.40	1.4	< 0.1	3.2	423	5	1
Iron, Total ug/L	Sand and Gravel	1598.0	1400.0	21.0	14000	1571	104	7
	Sandstone	1784.3	516.0	< 50.0	21500	382	53	14
	Carbonate	1004.1	690.0	< 50.0	10200	669	68	10
Lead, Total ug/L	Sand and Gravel	2.52	2.0	1.0	101	1462	1343	92
	Sandstone	2.52	2.0	< 2.0	40	369	335	91
	Carbonate	3.14	2.0	< 2.0	167	583	493	85
Manganese, Total ug/L	Sand and Gravel	197.1	125.0	5.3	5130	1533	108	7
	Sandstone	232.8	94.5	9.0	1810	377	42	11
	Carbonate	29.3	17.0	10.0	300	620	454	73
Nickel, Total ug/L	Sand and Gravel	36.5	40.0	1.0	74	1147	1139	99
	Sandstone	38.3	40.0	< 20.0	144	332	320	96
	Carbonate	38.1	40.0	< 20.0	100	457	454	99
Selenium, Total ug/L	Sand and Gravel	2.07	2.0	< 2.0	10	1211	1167	96
	Sandstone	2.05	2.0	< 2.0	10	355	293	85
	Carbonate	2.15	2.0	< 2.0	10	454	428	94
Strontium, Total ug/L	Sand and Gravel	2248.0	537.5	< 30.0	30800	1138	2	0
	Sandstone	489.8	375.0	10.0	4800	324	2	1
	Carbonate	18404.0	16200.0	< 30.0	66200	462	3	1
Tritium T.U.	Sand and Gravel	9.0	10.0	< 0.8	23	108	7	6
	Sandstone	8.3	9.1	< 0.8	19	26	5	19
	Carbonate	4.3	1.8	< 0.8	13	44	14	32
Zinc, Total ug/L	Sand and Gravel	23.6	10.0	< 10.0	3620	1198	814	68
	Sandstone	32.6	14.0	< 10.0	426	348	134	39
	Carbonate	58.9	12.0	< 10.0	1210	459	202	44
NUTRIENTS								
Ammonia-N mg/L	Sand and Gravel	0.27	0.14	0.01	3.4	1525	391	26
	Sandstone	0.38	0.22	< 0.05	2.2	375	78	21
	Carbonate	0.39	0.32	< 0.05	5.1	651	57	9
Chemical Oxygen Demand mg/L	Sand and Gravel	11.4	10.0	< 10.0	200	1110	1025	92
	Sandstone	10.6	10.0	< 10.0	55	314	293	93
	Carbonate	12.5	10.0	< 10.0	371	481	397	83
NO2+NO3 as N mg/L	Sand and Gravel	0.22	0.10	< 0.01	4.9	1465	1125	77
	Sandstone	0.12	0.10	0.10	1.9	366	316	86
	Carbonate	0.12	0.10	< 0.05	1..5	618	571	92
Phosphorus, Total mg/L	Sand and Gravel	0.10	0.05	0.02	10.5	1297	990	76
	Sandstone	0.12	0.05	< 0.05	4.4	318	195	61
	Carbonate	0.07	0.05	< 0.05	1.4	531	411	77
Total Kjeldahl N mg/L	Sand and Gravel	0.42	0.3	< 0.2	3.3	514	181	35
	Sandstone	0.59	0.4	< 0.2	2.8	170	47	28
	Carbonate	0.57	0.5	0.1	5.3	238	36	15
Total Organic Carbon mg/L	Sand and Gravel	3.2	2.0	< 1.0	75	1172	1085	93
	Sandstone	2.7	2.0	< 1.0	16	321	299	93
	Carbonate	3.1	2.0	< 1.0	73	481	403	84

‡ records with '<' represent reporting limit

§ na denotes not applicable

General Water Types

Based on major ion composition, the three general water types encountered in Ohio's major aquifers are a calcium-bicarbonate type in the sand and gravel aquifers, a calcium-sodium-bicarbonate type in the sandstone aquifers, and a calcium-bicarbonate-sulfate type in the carbonate aquifers. This information is displayed graphically in Figure 6,which compares the mean major ion composition of the three aquifer systems. While all three water types are based on the calcium-bicarbonate model, the sandstone aquifer waters are highest in sodium and chloride. The carbonate ground waters have the highest bicarbonate, calcium, magnesium, and sulfate ion concentrations. Also notable is the fact that the carbonate waters have the highest mean ionic strength of the three aquifer types; this correlates well with the longer residence time within the carbonate system. The lower total dissolved solids (TDS) of the sandstone aquifers is attributed to the higher silica sand and lower carbonate rock content in the sandstones. These same data are presented on a Piper diagram in Figure 7. The Piper diagram provides a summary of cation data (left triangle), anion data (right triangle) and composite data (center diamond) to visually distinguish waters of different chemistries and origin.

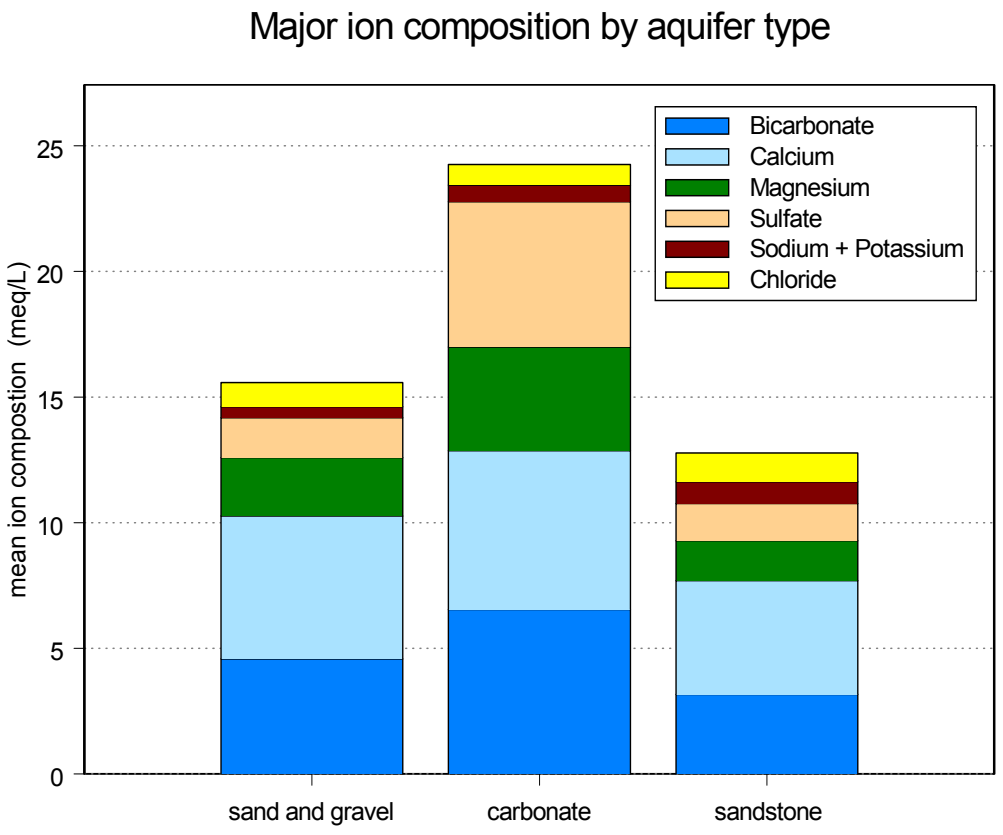


Figure 6. Mean major ion composition of the three aquifer systems.

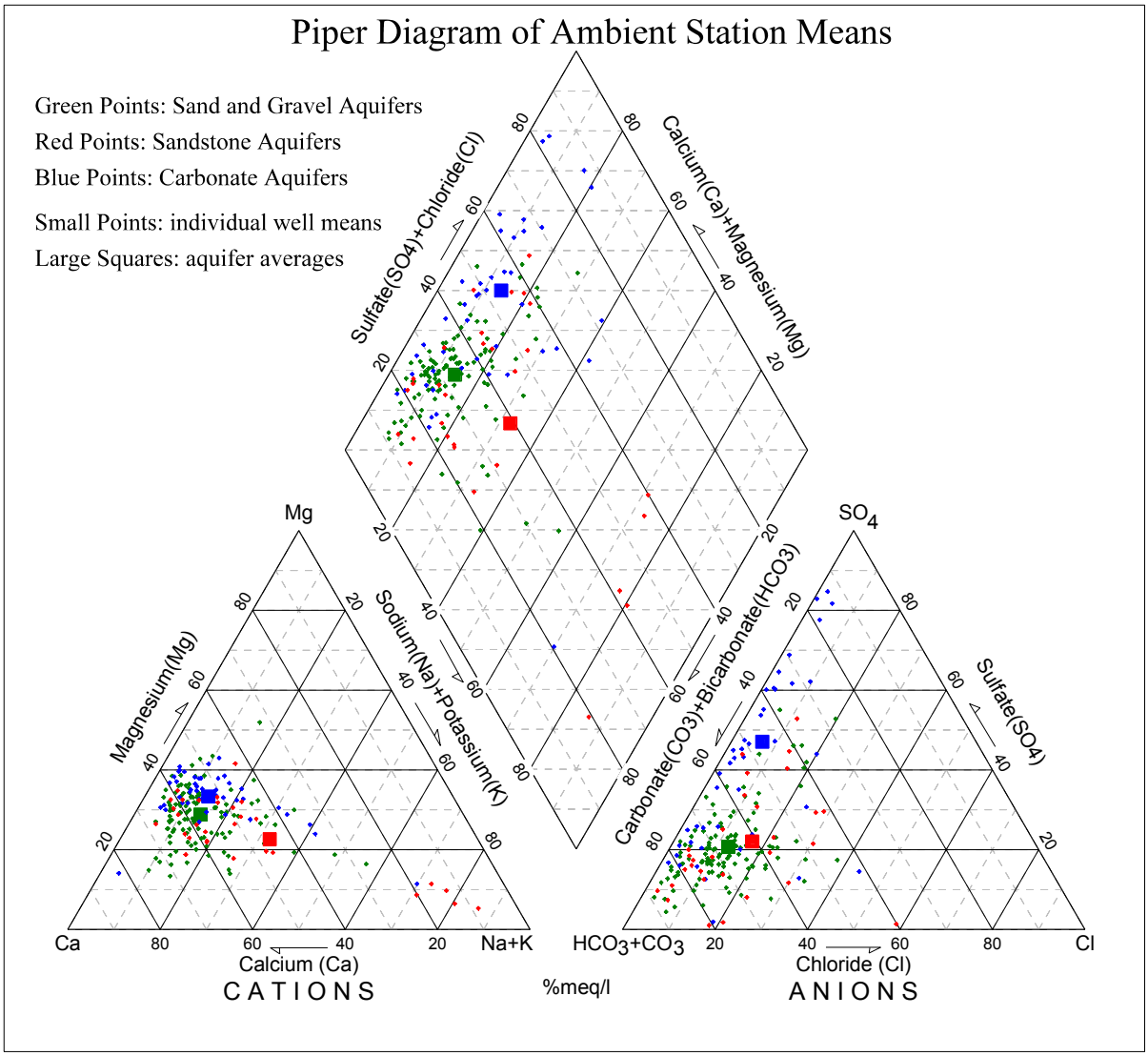


Figure 7. Piper diagram of individual data points and aquifer means for AGWMP wells.

The carbonate ground waters in Figure 7 (blue plotting points) trend toward a more sulfate-rich composition, reflecting the dissolution of strontium, calcium, and sulfate-bearing minerals. These waters display a wide range of alkalinity concentrations. The overlap between the carbonate and sand and gravel aquifer water chemistries (green plotting points) is due to the fact that much of the aquifer material in the unconsolidated (sand and gravel) units is actually eroded from carbonate rocks. The sandstone water chemistry (red plotting points) reveals a higher mean sodium, potassium, and chloride content than the other two systems, indicating a probable natural source for these ions, apparently from dissolution of simple salts or matrix cements.

The following sections discuss the water quality exhibited by each of the major aquifer types and the relationships between the major aquifer types utilizing the data summarized in Table 3. Several of the relationships presented here are repeated from the 2000 305(b) report because they clearly present differences between the aquifers. Other illustrations are new for this report. The reader is referred to the previous report for additional graphic representations of aquifer water quality differences.

Sand and Gravel Unit Ground Water Quality

The unconsolidated sand and gravel units, typically associated with the buried valley aquifer system, are the highest water-yielding units across the state. These systems are cut into the bedrock, and occur throughout much of the state (Figure 4). The ambient database for this system consists of about 2,100 samples from 123 sites, and their mean water chemistry is summarized in Table 3 (excluding the nitrate "impacted" wells, see page 19). The ground water from this group of aquifers is characterized by relatively low TDS, zinc, fluoride, and sulfate. The sand and gravel aquifers are geochemically related to the carbonate bedrock aquifers since the clastic material making up the buried valleys may be dominated by carbonate rock debris. This similarity is displayed in their ground water chemistries, for example, the sand and gravel aquifer waters plot closely to the carbonate waters on the cation triangle of Figure 7. In the anion triangle of Figure 7 however, the carbonates are heavily influenced by the high sulfate concentrations. In Figure 8 the distribution of the total dissolved solids data (all data points, not just the means) is illustrated in a box plot for each of the aquifer types. The TDS concentrations of the sand and gravel aquifers are intermediate between the carbonate and sandstone aquifers. This relationship is illustrated in the median values and the range of the outliers in Figure 8 as well as the mean values for TDS in Table 3.

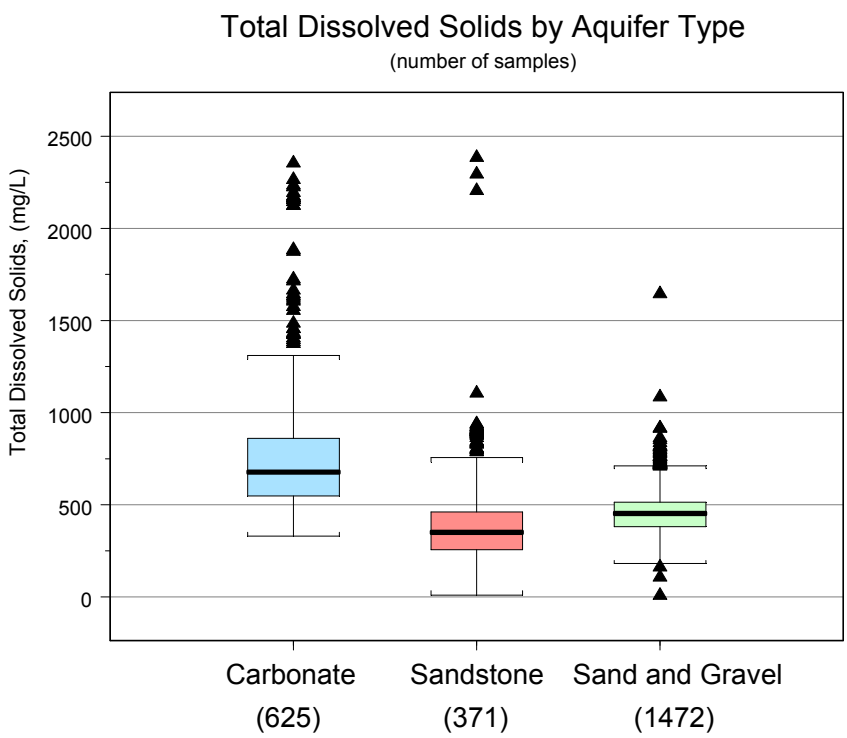


Figure 8. Box plot of total dissolved solids for AGWMP data.

Other parameters for which the sand and gravel and gravel water samples appear geochemically associated to the carbonate aquifer waters due to clastic debris are alkalinity, calcium, magnesium, hardness, fluoride, and strontium. The mean total iron and manganese concentrations for the sand and gravel aquifers are 1,598 ug/L, and 197 ug/L respectively. These values both significantly exceed the associated SMCL (300 ug/L and 50ug/L, respectively). Consequently, it is not uncommon for iron removal to be included as a treatment component at a PWS using a deep sand and gravel aquifer.

Sandstone Bedrock Aquifer Ground Water Quality

The Mississippian/Pennsylvanian sandstone bedrock systems contain most of the major bedrock ground water wells in the eastern half of the state (Figure 4). The Ambient database for this system consists of about 375 samples from 29 sites whose mean water chemistries are provided in Table 3. These waters are characterized by low (bicarbonate) alkalinity. A significant trend for some sandstone waters is toward increasing chloride and sodium composition shown in Figure 7. This suggests that these waters may have long residence times, and/or may represent mixing with saline sodium-chloride type water expressed from bedrock shales or with deeper formation waters. The distribution of sodium data is illustrated in box plots for each of the aquifer types in Figure 9 (log scale for vertical axis). The elevated sodium in the sandstone aquifers is clearly illustrated. Although the median sodium value for the sandstone and carbonate aquifers are similar (27-28 mg/L), the mean value for the sandstones is 63.1 mg/L versus 35.3 mg/L for the carbonates. This higher sandstone mean is explained by numerous elevated values in the strongly asymmetric sodium distribution for the sandstone aquifers. In addition, most of the higher sodium concentrations occur at depth, supporting the suggested control by deeper formation waters or residence time.

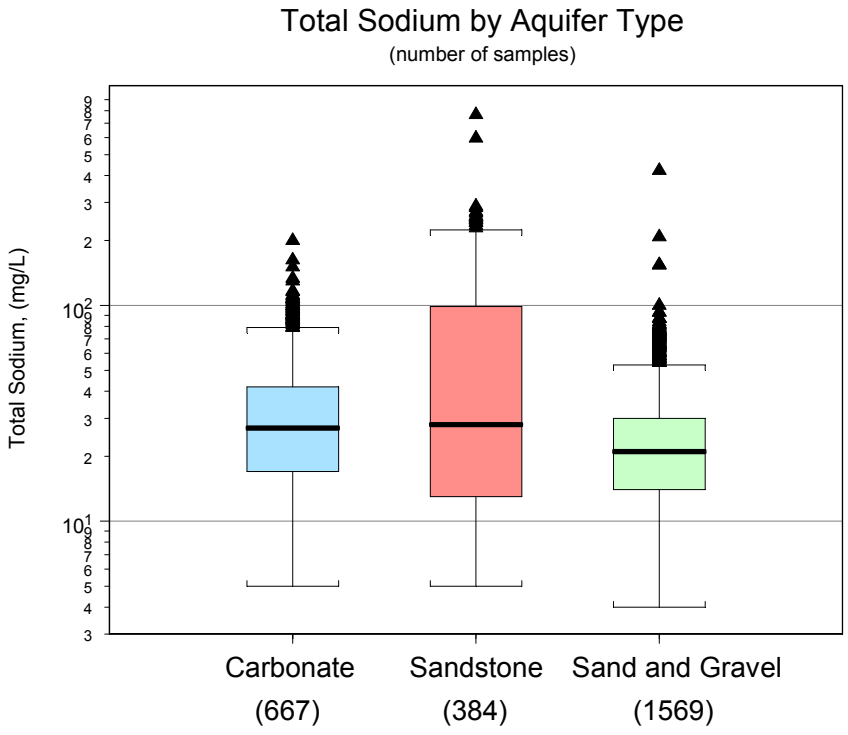


Figure 9. Box plot of sodium for AGWMP data.

Carbonate Bedrock Aquifer Ground Water Quality
The bedrock of the Silurian/Devonian carbonate systems hosts the major aquifers in the western half of the state (Figure 4). The Ambient database for this system consists of about 675 samples from 44 sites. Most ground water in the carbonate bedrock is of the calcium-bicarbonate-sulfate type, as depicted in the Piper diagram (Figure 7), and is slightly alkaline in pH.

This aquifer type exhibits the greatest mean concentrations for calcium, magnesium, sulfate, TDS, alkalinity, strontium, hardness, and conductivity of the three aquifer types. Mean hardness (554 mg/L) is at levels which typically require treatment to remove calcium and magnesium in the finished water. The mean concentrations of TDS (769 mg/L), iron (1004 ug/L), and sulphate (280 mg/L) are all above their respective SMCLs (500 mg/L, 0.3mg/L, and 250 mg/L). About 40 percent of the individual samples from carbonate aquifers exceed the SMCL for sulfate (250 mg/L). Mean fluoride is highest in the carbonate system (1.4 mg/L) and is probably controlled by the dissolution of fluorine bearing minerals such as apatite and fluorite. Thus, the carbonate bedrock routinely displays ground water chemistry averages above secondary drinking water standards.

These elevated concentrations in the carbonate system relative to the other aquifer settings may be related to longer residence times within the system, as well as the relatively high solubilities of minerals in the host bedrock. Figure 10 illustrates the relationship between sulfate and hardness (hardness is a

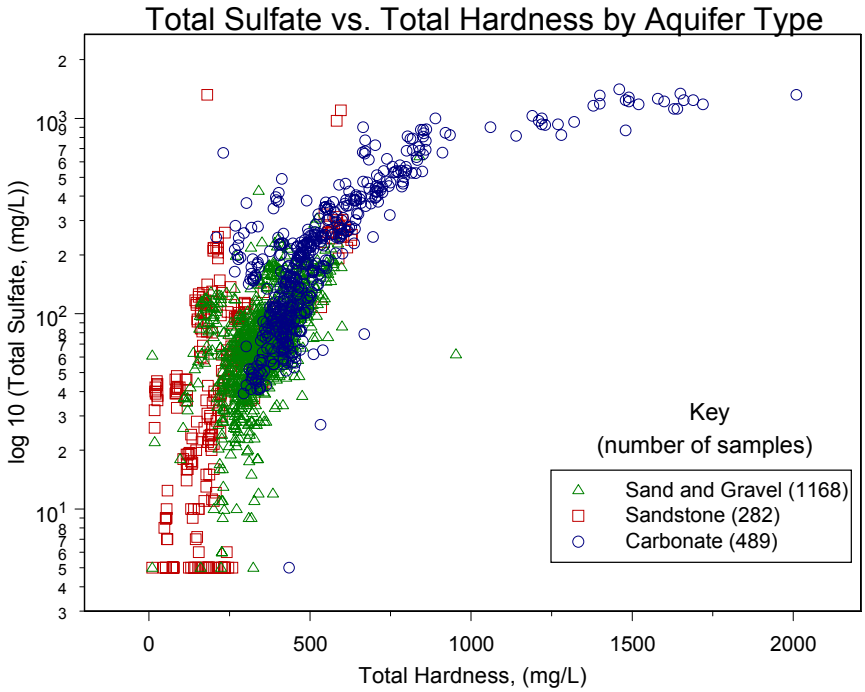


Figure 10. Hardness vs. Sulfate for AGWMP data.

sum of the ions Ca and Mg) by aquifer type for about 2,600 samples. The higher concentrations of hardness and sulfate in the carbonate aquifers are clearly illustrated in Figure 10. The intermediate nature of the sand and gravel aquifer water quality occurring between the sandstone and carbonate aquifer values is also exhibited. The fact that the carbonate aquifers have the higher mean values for most parameters is consistent with the high mean TDS value for the carbonate aquifers illustrated in Table 3, Figure 6, and Figure 8. The three elevated sulfate values for the sandstone aquifer (1,000 mg/L) are from a new well completed in an area of reclaimed land and are clearly anomalous for the sandstone aquifers.

The geographic distribution of mean TDS for AGWMP wells is presented in Figure 11 with the major aquifers as the base map. This illustrates the elevated TDS associated with the carbonate aquifers as compared to the sandstone and sand and gravel aquifers.

The TDS relationships to well depth and aquifer type are illustrated in Figure 12. All of the AGWMP TDS data are plotted and clusters of data (most obvious in areas of low data density) represent the range of TDS concentrations at individual wells. Figure 12 demonstrates the generally high TDS concentrations for the carbonate aquifers and the increasing TDS concentration and variability with well depth for the carbonate aquifers. In contrast, the sand and gravel aquifers exhibit significantly less variability than the carbonate aquifers. They also are characterized by lower TDS values. The sandstone aquifers include several AGWMP wells with elevated TDS (the highest data points are from a well located in a reclaimed surface coal mine area), but generally, TDS in the sandstone aquifers is low.

These relationships are consistent with residence time in the aquifer and the geology of these aquifers. It is common for longer flow paths to correlate with a chemical evolution toward higher mineralization, and the greater depth of the carbonate wells correlates well with the longer flow paths/residence time. In addition, silica sand present in the sandstones is significantly less soluble than the calcite and dolomite in the carbonate aquifers, so calcium and magnesium concentrations would be expected to be relatively high in a carbonate setting. The presence of soluble evaporates (mostly gypsum) in the Salina Dolomite can also contribute to the calcium and sulfate concentrations. The sand and gravel aquifers are composed largely of debris from eroded carbonate rocks with dilution from Canadian shield material and local bedrock. Consequently, the geochemistry of water from the sand and gravel aquifers is similar to the water from the carbonate aquifers but the concentrations of most components are reduced relative to the carbonate aquifers.

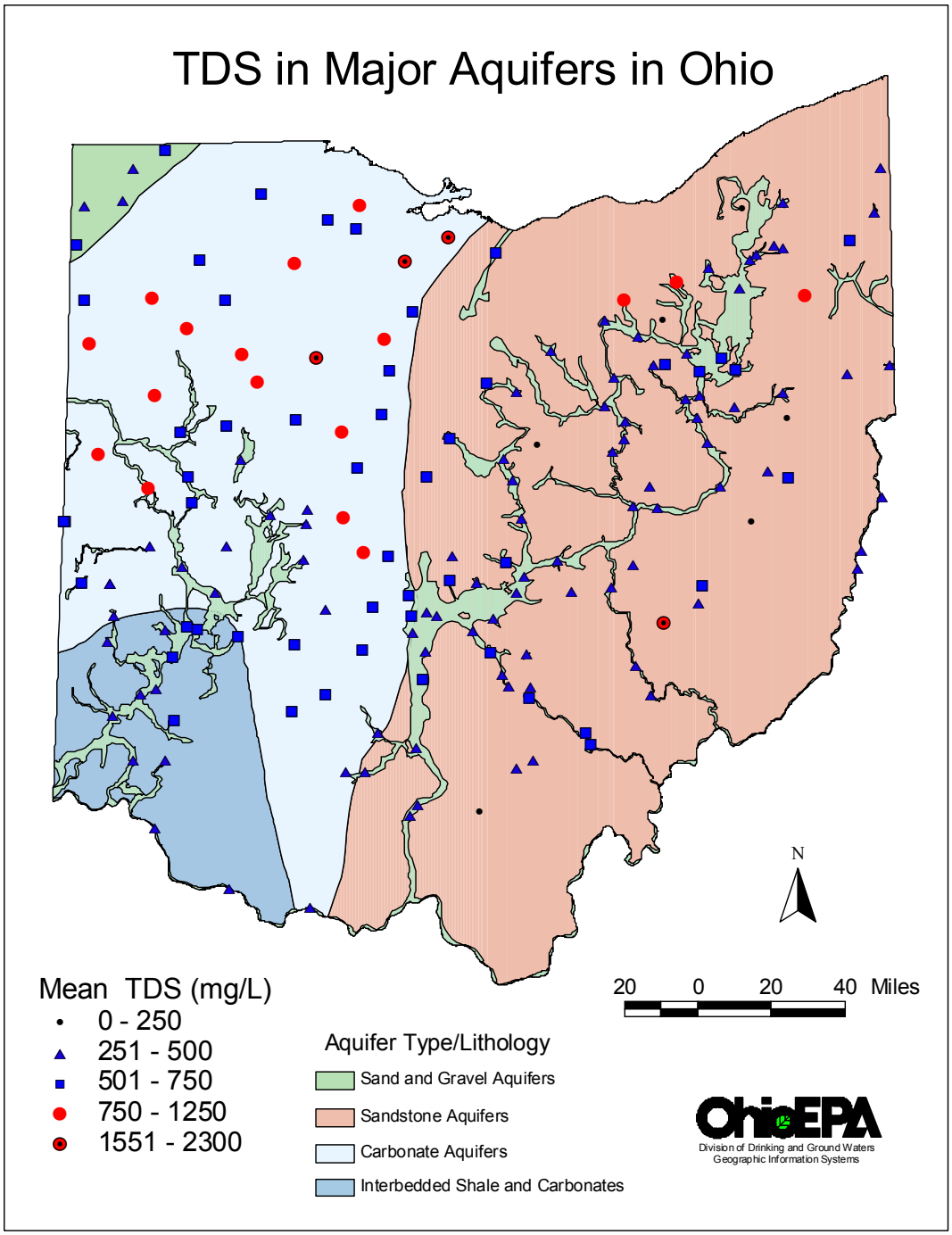


Figure 11. Geographic distribution of the mean TDS values for AGWMP wells.

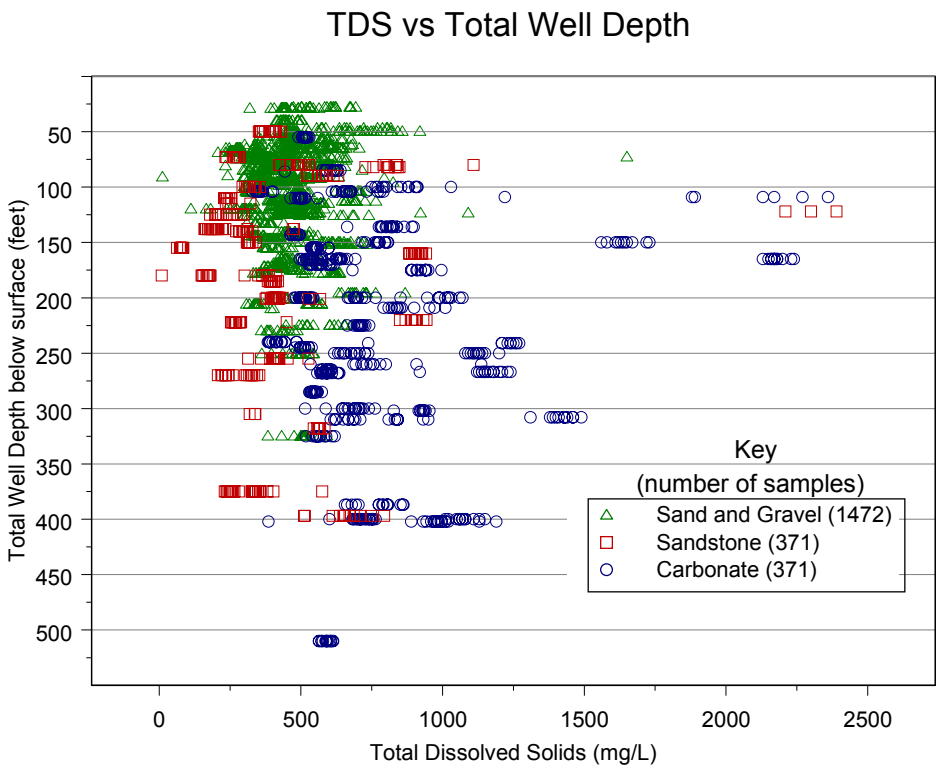


Figure 12. AGWMP TDS data relative to well depth and aquifer type.

GROUND WATER TEMPERATURES

AGWMP ground water temperatures reflect influences of both the atmosphere and the subsurface. Changes in ground water temperatures are induced by changes in seasonal air and recharge temperatures, but are quickly moderated by the soil column, the mass of the host rock material, and existing ground water. The temperature of a ground water sample, taken at the surface, is a composite of these factors, as well as others such as changes in sample temperature due to bringing the sample to the surface, the speed of sampling, etc.

The relationship between air- and ground water-temperature is illustrated in Figure 13, in which all archived AGWMP ground water sample temperatures (open black circles) are plotted against the sample month. The monthly means of this ground water data set (orange squares and line) indicate that monthly and seasonal changes in ground water temperatures are small but predictable, even against a background of high variability in individual measurement. The means show a relatively smooth increase to a July maximum of 15° C (59° F), decreasing to a December minimum of 12° C (53.6° F), with a range of 3° C (5.4° F) . Note that the semi-annual AGWMP sampling cycle is revealed in the data distribution in Figure 13, with data concentrated in the spring and fall months.

Mean daily air temperatures taken at Delaware, OH, for the period 1961-1990, aggregated by month, are also shown on Figure 13 as solid blue triangles and a blue line (Easterling, et al.,1996). The highest mean monthly air temperature (22.4° C = 72.3 ° F) occurs in July, and corresponds with the ground water temperature maximum in July. The minimum air temperature of - 4.3° C (24.3 ° F) occurs in January, and lags the ground water minimum temperature by one about month.

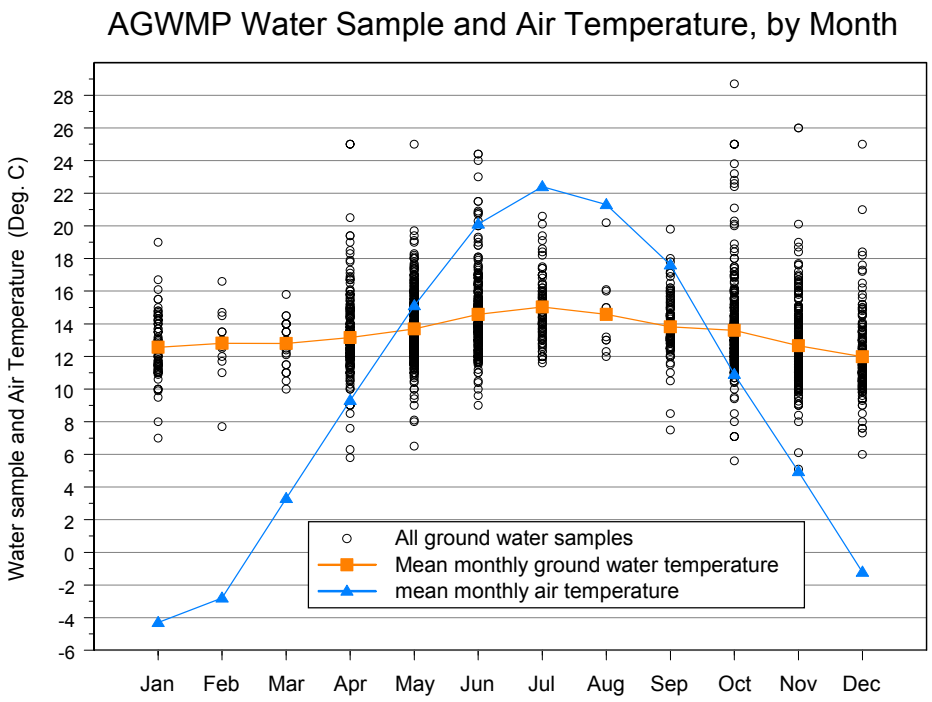


Figure 13. AGWMP water temperature by month.

Overall, there is good correspondence between the two data sets. The temperature of the ground water system is essentially a damped version of the air temperatures. Ground water and air temperatures are the same twice a year, once about mid-April, and again in mid-September. These points reflect the transition to and from the summer months, where the maximum difference between ground and air temperature is about 7° C (12.6 ° F). Much like a root cellar in summer, an aquifer system (host rock and subsurface water) will moderate the rise in summer temperature due to its large thermal mass. We surmise that this moderation is more pronounced for deeper systems, which are more isolated from atmospheric changes. In the winter months, the difference between near-surface air temperatures and mean ground water temperatures is greater than during the summer months. Again, this is due to the moderating influence of the large mass of the earth material, but also because the subsurface may be isolated from the open air by frozen ground.

SENSITIVE AQUIFERS

Overview

Recent data analysis efforts have been directed toward identifying sensitive aquifers (aquifers mostly likely to be affected by land use activities). The surface areas above sensitive aquifers exhibit high recharge rates, resulting in rapid transport of surface water to the ground water resource. This recharge can transport surface contaminants along with oxygenated surface water to the subsurface and significantly affect ground water chemistry. The active recharge processes create a dynamic system where pulses of recharge disrupt or dominate the stable ground water environment. Generally, sand and gravel aquifers and bedrock aquifers overlain by thin till are considered to be the most sensitive aquifers in Ohio.

Water quality parameters were used to identify Ambient Ground Water Monitoring Program (AGWMP) sites and public water systems (PWSs) that exhibit ground water quality changes associated with land use activities. Geologically sensitive aquifers were identified by analyzing water quality data from AGWMP wells and PWS compliance data using elevated nitrate concentrations as the criterion (> 2.0 mg/L). Analysis of nitrate time series of the active AGWMP wells revealed interesting relationships to surface water recharge. These efforts are describe in the following sections.

AGWMP Data - Geographic Analysis

We know that the AGWMP includes wells in which the water quality is "impacted" by land use activity. The approach used for identifying the wells that exhibit nitrate and organic impacts parallels the SWAP Ground Water Susceptibility Analysis (2002) water quality criteria. For nitrate, if the water quality data includes more than one result greater than 2 mg/L it is considered "impacted." If there is only one result greater than 2.0 mg/L, but there are additional results close to 2 mg/L (which tend to support the existence of nitrate in the well), the well is also considered "impacted." No well is considered "impacted" on the basis of one sample result alone.

There is no simple or general approach for combining the multiple parameters analyzed in the organic scans. Our analysis of VOC impacts combined detections of organic parameters at wells. A well was identified as "impacted" if organics were detected at a well in more than one sample. Trihalomethanes (THMs), common lab contaminants, and detections of elemental organic sulfur were excluded as valid detections. The current analysis includes tentatively identified compounds (TICs) that are reported at concentration greater than 5.0 ug/L. The reasoning for including the TICs is that they are real results, but they are not quantified accurately since they are not compared to a target standard. Consequently, the result ranges from 10 times less to 2 times higher than the reported concentration. To be conservative, we selected 10 times the detection limit as the minimum TIC concentration as a threshold for valid detection.

These criteria were applied to the AGWMP well water quality results, and revised status codes were used to identify the "impacted" well. This analysis was applied to active and inactive AGWMP wells and identified 30 wells with nitrate impacts, 12 wells with VOC impacts, and 10 wells with nitrate and VOC impacts. Of these wells, 12 were inactive sites, and several of the active wells are in the network to monitor the VOC impacts. These wells are plotted in Figure 14. It is important to note that the concentrations in these 'impacted' wells are far below the MCL standards for nitrate and VOCs.

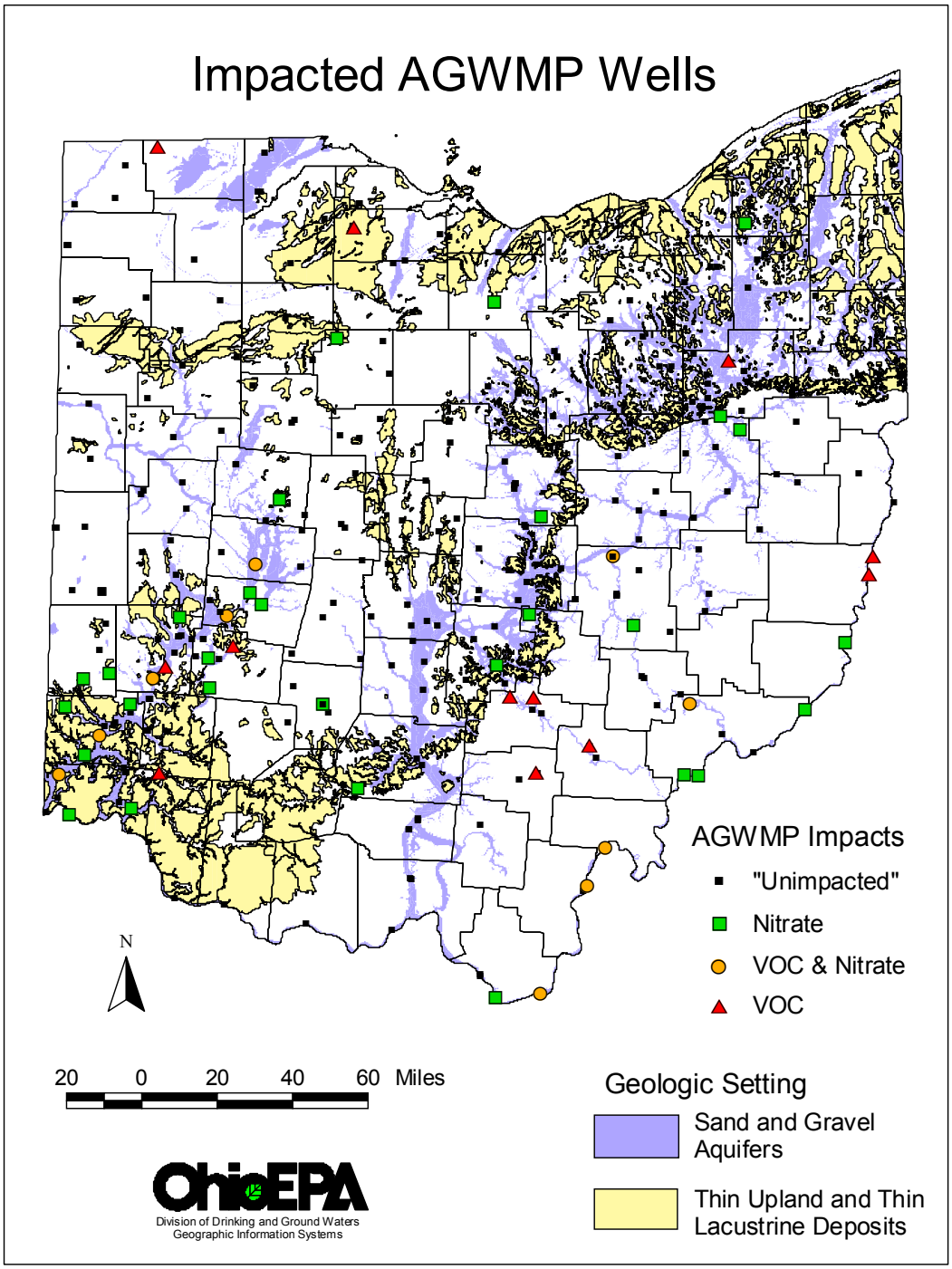


Figure 14. Impacted AGWMP wells.

The base map of Figure 14 is sand and gravel aquifers and thin till over bedrock aquifers (based on the ODNR Aquifer Maps) since these aquifers are considered to be most sensitive. Figure 14 illustrates a good association between "impacted" sites and buried valley aquifers or areas of thin till overlying bedrock aquifers. Several of the VOC impacted wells are not within one of these hydrologic settings. This is believed to be related to the strong point source control for VOC impact. VOC sources are more typical of point sources with concentration of sources in developed areas, whereas, nitrate sources are widespread, diffuse nonpoint sources. A concentrated source in a less sensitive aquifer may result in ground water impact. Although Figure 14 exhibits a strong association between impacts and sensitive aquifers, this small subset of wells does not provide statistically convincing support for identifying sensitive aquifers. Due to the additional uncertainly of the VOC analysis resulting from the method of combining multiple parameters and the site specific nature of point sources, the VOC criteria for identifying "impacted" wells, will be re-evaluated for the next 305(b) report.

Public Water System Compliance Data - Geographic Analysis

The PWS compliance data from 1991 to present were analyzed to identify system means and maximums for nitrate concentrations in treated water for each PWS. In most cases the treatment for ground water is minimal, and systems with more extensive treatment for ground water in Ohio are not designed to reduce nitrate concentrations significantly. Consequently, the drinking water compliance data is a useful measure of local nitrate concentration. The PWS water quality data was attached to a single well in order to associate the wellfield to a glacial aquifer setting using the ODNR Aquifer Maps. This analysis includes 4,136 PWSs which have recently updated GPS locations for their wells.

This data manipulation allowed us to associate the ODNR Glacial Aquifer Map attributes with water quality data from individual PWSs. Thus the PWSs with elevated nitrate concentrations can be displayed with their glacial aquifer setting or the aquifer lithology at selected map scales. It is important to note that many of the public water systems are drilling and casing wells through the glacial aquifers and producing water from underlying bedrock aquifers. This is generally the case in areas where the glacial units are thin or exhibit low permeability. On the other hand, in many areas the glacial aquifers are the production aquifers. If the glacial aquifer setting is not the production aquifer, the glacial aquifer is part of the overlying material through which vertical recharge must travel. In both situations, the glacial aquifer materials directly influence the subsequent water quality.

Nitrate greater than 2.0 mg/L was the criterion used to identify wells with significant land use effects. This threshold nitrate value is consistent with nitrate water quality evaluation used in Ohio's Source Water Protection Program Susceptibility Analysis, as discussed in the previous section. Significantly, this selection does not indicate a well is unsafe for use by a PWS, since this concentration is well below the Maximum Contaminant Level (MCL) of 10 mg/L for nitrate. The impact indicates that a pathway from the ground surface to the aquifer is present and utilized for nitrate migration.

Figure 15 illustrates the distribution of public water systems in Ohio with elevated nitrate concentrations in association with spatially correlated hydrogeologic settings of the ODNR Glacial Aquifer Map. Visually there is a strong association between the sand and gravel aquifers represented by the blue shading and the public water systems with nitrate means greater than 2.0 mg/L as indicated by the colored shapes (green, orange, and red). The buried valley, valley fill (Ohio River), outwash/kame,

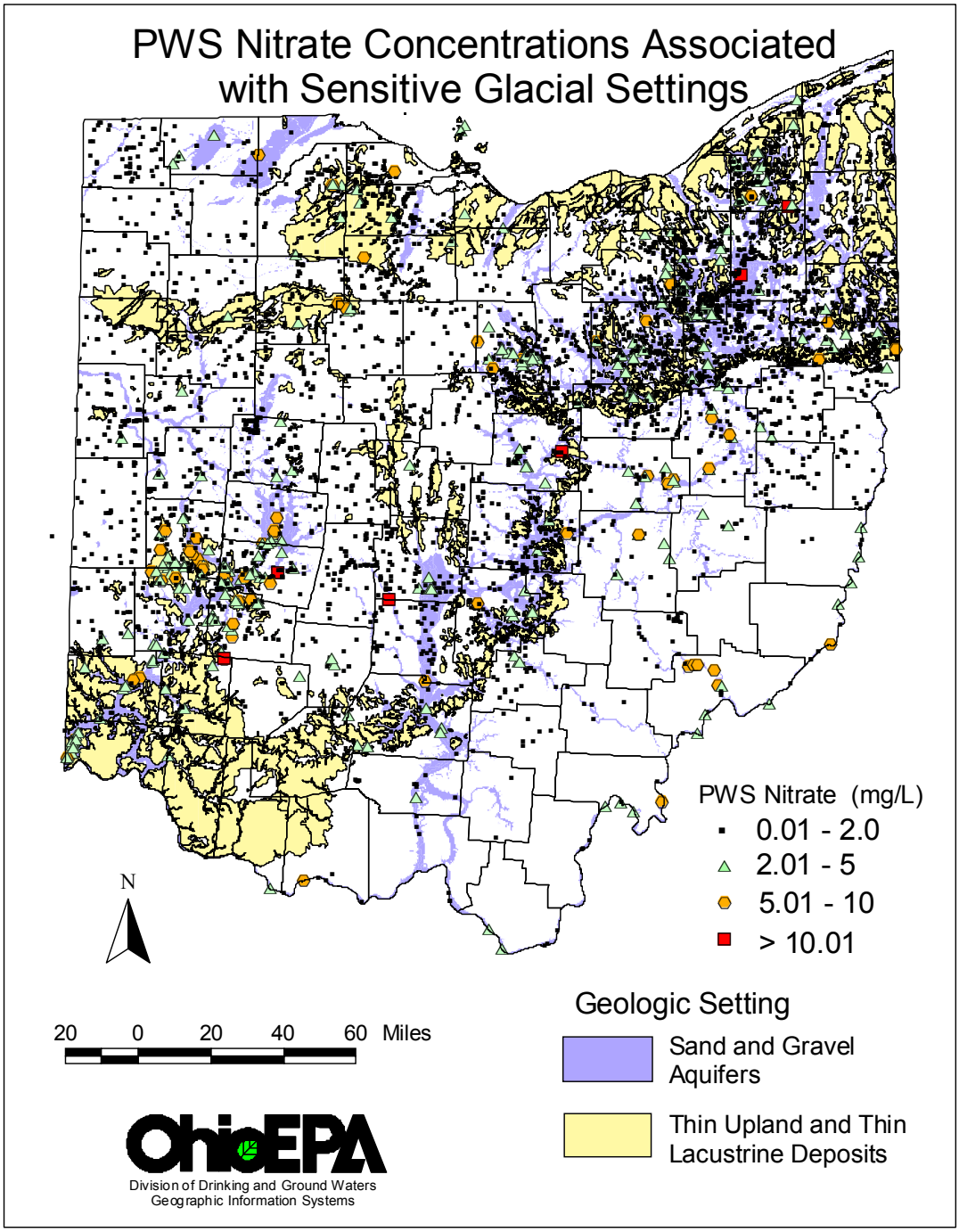


Figure 15. PWSs in Ohio with elevated nitrate concentrations.

and beach ridge aquifer settings from ODNR's Glacial Aquifer Map were combined in the blue color to simplify the presentation in Figure 15. The association of sensitive aquifers with sand and gravel glacial deposits is generally accepted for dissolved components, and this analysis provides additional confirmation of this relationship. It is important to note that the sensitivity of these aquifers does not necessarily apply to pathogens, even considering the filtering capacity of sand and gravel aquifers. Studies of river bank filtration are important for documenting the effectiveness of natural sand and gravel aquifers to filter particulates and pathogens. This point emphasizes the importance of identifying the type of contaminant being considered when an aquifer is identified as sensitive.

The other association evident in Figure 15 is that public water systems with elevated nitrate concentrations also occur in areas of thin uplands and lacustrine deposits, represented by the yellow shading. This relationship is more clearly illustrated in Figure 16, which shows an area in southwest Ohio that includes the Great Miami Aquifer and thin tills covering the carbonate aquifers in the adjacent upland areas. The ODNR Glacial Aquifer Map refers to these areas of thin till as thin upland aquifers. Numerous public water system wells (generally drilled and cased through the thin till into carbonate bedrock aquifers) with elevated nitrate values are associated with the thin upland aquifers. This subset clearly identifies a second aquifer setting that is sensitive to nitrate migration from land use practices. This setting may exhibit sensitivity to pathogen or particulate transport due to the presence of fractures or macropores in the thin till and fractures. These shallow bedrock features do not provide for effective filtration of ground water or recharge to ground water.

Public Water System Compliance Data - Statistical Analysis

Public water system compliance nitrate data were queried and compiled to determine statistical relationships to see if the sand and gravel and thin till aquifer settings are sensitive. The number of PWSs in each aquifer setting and the percentage of these PWSs having elevated nitrate concentrations were determined to further clarify the relationship between elevated nitrate concentrations and glacial aquifer settings illustrated in Figures 15 and 16. This analysis was also completed for the lithologic attributes (sand and gravel, fine grained sediment, till) identified on the ODNR Aquifer Maps. The reader is reminded that glacial deposits are not always the production aquifer for the associated public water system wells. If the public water system wells are bedrock wells, the overlying glacial materials may act as a hydrogeologic barrier, depending on the materials present. The results of this analysis on 4,136 PWSs are reported by the total thickness of the glacial deposits and are shown in Table 4 based on the aquifer setting of glacial units, and in Table 5 based on the lithology of glacial units. In several cases, the low numbers of PWSs associated with a specific thickness range reduces our confidence in the significance of the percentage presented, but generally the number of PWS included in the groups are large and provide a solid statistical basis for our conclusions.

Aquifer Map Settings

In Table 4 the **sand and gravel aquifer** settings include the buried valley, alluvial, valley fill (Ohio River), outwash/kame, and beach ridge aquifer settings. These are the aquifer settings that include coarse sands and gravels interbedded with some finer-grained deposits. The aquifer settings dominated by sands and gravels exhibit elevated nitrate concentrations (>2.0 mg/L) in 12 -13 percent of all public water systems that are located in these glacial aquifer settings. This percentage is higher than most of the other hydrogeologic categories. The percentages for all thickness groups increase for PWSs that exhibit maximum nitrate values greater than 2.0 mg/L. In most cases these wells are using the glacial aquifers as

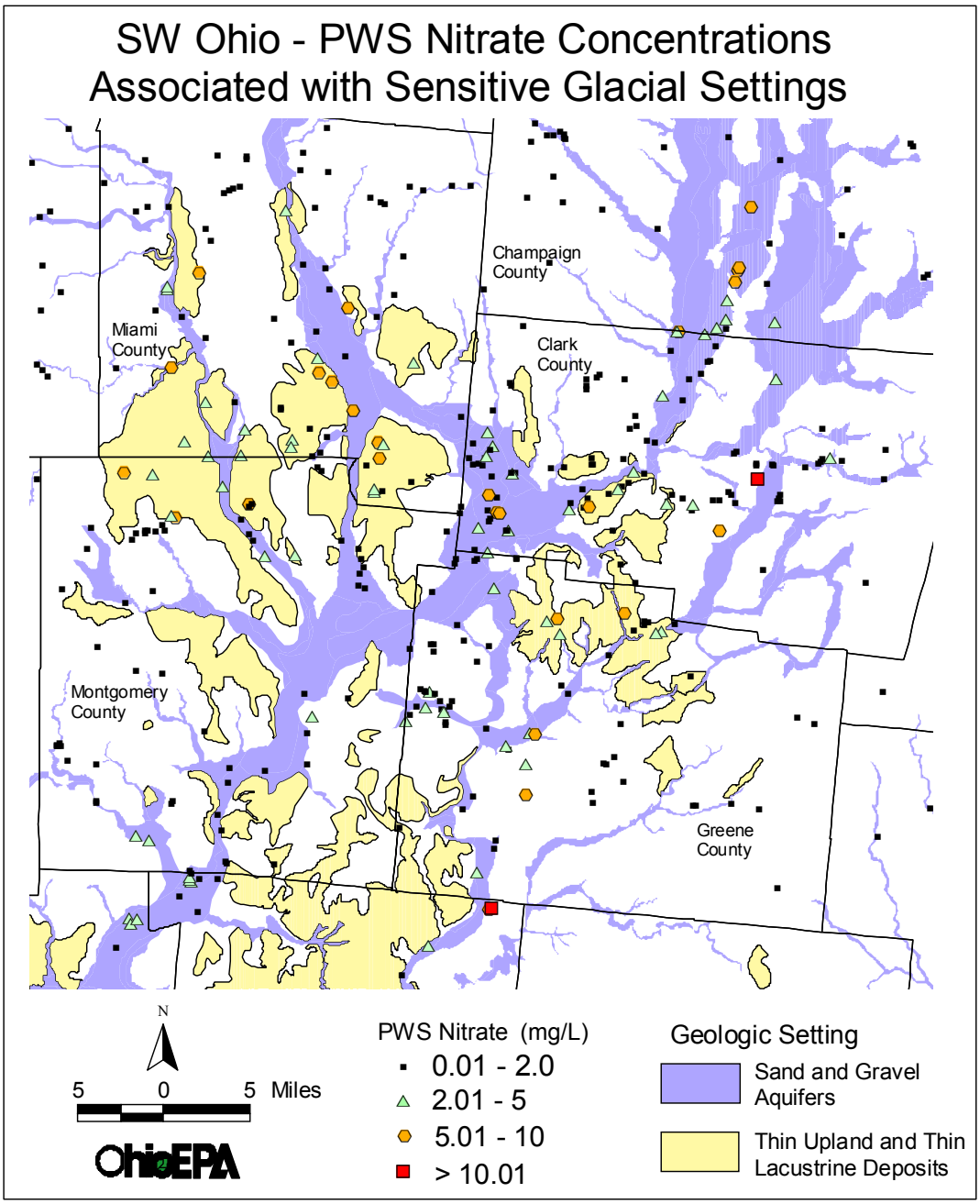


Figure 16. PWSs in SW Ohio with elevated nitrate concentrations.

the production aquifer. New PWS wells require a minimum of 25 feet of casing (OAC Chapter 3745-9), so the few PWSs included in the 0-25 foot range are almost certainly producing from bedrock aquifers below the glacial cover. This may help explain the lower percentage of wells with elevated nitrate in the 0-25 foot range.

The bedrock aquifers below **thin upland and lacustrine** deposits represent hydrogeologic settings comprised of thin glacial deposits overlying bedrock aquifers. These glacial deposits are tills or fine grain material deposited in glacial lakes. The significant drop in the percentage of PWSs with elevated nitrate from 13 percent in deposits 0-25 feet thick to 5 percent in deposits 25-100 feet thick suggests that thin till (< 25 feet) provides only limited protection from the transport of surface contaminants to shallow aquifers. The level of protection provided by the thin tills appears similar to that provided by sand and gravel aquifers. If more than 25 feet of till is present, however, the protection from surface contamination increases considerably. This thickness control suggests that the fractures and macropores in tills are more abundant in the upper 25 feet of till deposits. The small number of PWS in the >100 feet category does not allow a reliable conclusion to be drawn about this group of PWSs and requires additional data and evaluation.

The **moraine deposits** include the ground moraine, end moraine, and thick drift complex aquifer settings. Till dominates these settings and PWS wells in these settings produce water from thin sands and gravels included in the tills or from bedrock aquifers below the moraine deposits. In contrast to the sand and gravel aquifers, only 3 percent of PWSs associated with moraine deposits exhibit elevated nitrate concentrations. This suggests that tills greater than 25 feet thick provide significant protection from migration of surface contaminants compared to sand and gravel deposits and the thin tills associated with upland settings.

The **unglaciated areas** occur in southeastern Ohio. These PWSs are generally located in the upland areas and utilize sandstone aquifers. The soil and colluvium in the unglaciated areas is composed of weathered bedrock and may include some glacial loess. The thickness of the colluvium will vary by location depending on slope, bedrock lithology, intensity and duration of weathering among other factors. The aquifer map does not provide colluvium thickness, so all these wells are included together. Of the PWSs in the unglaciated areas of Ohio, 5.4 percent exhibit elevated nitrate concentrations which suggests that colluvium provides reasonable protection to the bedrock aquifers. This percentage may exaggerate the protection level since the nitrate sources are generally not as widespread in southeast Ohio as in the other parts of the state.

Aquifer Map Lithologies

Table 5 presents analysis of the Glacial Aquifer Map lithologic attributes on the same PWS data used in Table 4 for aquifer setting. The aquifer settings provided insight into the geologic processes that deposited the glacial material while the lithologic attributes reveal the linkage to the materials within the glacial deposits. Because the recharge of surface water to an aquifer is controlled by the migration of water through the soil and vadose zone, it is important to evaluate the statistics of elevated nitrate in PWSs using the lithologic information. A good correlation was expected between glacial lithology and elevated nitrate concentrations; in fact, the lithologic associations show stronger nitrate correlations than do the aquifer settings.

Table 4
Anthropogenic Effects in PWS Wells: Associations Between Nitrate Concentration and Hydrogeologic* Setting of Glacial Units

Thickness of Glacial Unit (Feet)	Number of PWS in Glacial Unit	Mean NO_3 > 2.0 Percentage of Wells	Max NO_3 > 2.0 Percentage of Wells
Sand and Gravel Aquifer Settings (Aquifer Map settings - Buried Valley, Alluvial, Valley Fill, Outwash/Kame, Beach Ridge)			
0-25	33	**9 %**	30 %
25-100	419	**12 %**	21 %
>100	887	**13 %**	20.5 %
Bedrock Aquifers Below Thin Uplands and Lacustrine Deposits (Aquifer Map settings - Thin Uplands and Lacustrine)			
0-25	677	**13%**	21 %
25-100	824	**5 %**	10 %
>100	27	**11 %**	29 %
Moraine Deposits (Aquifer Map Settings - Ground Moraine, End Moraine, Complex)			
0-25	1	**0**	0
25-100	556	**3.2 %**	6 %
>100	451	**3.3 %**	7.5 %
Unglaciated Areas (No glacial units on Aquifer Map)			
0	261	**5.4 %**	11.5 %

* Hydrogeologic settings are from ODNR Aquifer Map

The **sand and gravel lithologies** are a subset of the sand and gravel aquifer settings and include the coarser aquifer material (sand and gravel with minor fine grained material, sand and gravel with thin till included, and a few confined sand and gravel deposits). PWSs using wells in these units exhibit elevated nitrate 20 to 23 percent of the time if the glacial units are thicker than 25 feet. The few systems that are located on thin sand and gravel units (0 to 25 feet) have an even higher percentage of elevated nitrate but most of these PWSs are utilizing bedrock aquifers for water production (25 feet of casing required). Although the overlying sand and gravel does not appear to be providing effective protection to the production aquifers, the low number of PWSs in the thin sand and gravel group (9) make this conclusion uncertain.

The **fine grained lithologies** are predominantly a subset of the sand and gravel aquifer settings, but also include some lacustrine aquifer settings. These lithologies include undifferentiated fine-grained sediments, as well as fine sediments which include sand and gravel lenses. Of the PWSs with wells associated with these lithologic units, 5.5 to 7 percent have elevated nitrate concentrations. This is significantly less than the percentage of PWSs with elevated nitrate concentrations in the sand and gravel aquifers (20 to 23 percent). This indicates that fine sediments provide more protection for aquifers than sand and gravel lithologies. The low number of systems in the 0 to 25 feet thickness group (32) does not provide sufficient data for solid conclusions, but the 0 to 25 feet group has significantly more PWSs (two times) with a maximum nitrate concentration greater than 2.0 mg/L than the 25 to 100 and greater than 100 feet thick units. This suggests a greater influence of surface recharge in the thin (0 to 25 feet) glacial fine grained lithology.

The **till lithologies** encompass the majority of the 4,136 PWSs included in this analysis. The tills include all the moraine depositional settings (ground moraine, end moraine, complex) and many of the thin upland settings. A few buried valley, outwash/kame, and lacustrine setting are also included where till deposits dominate the sands and gravels, and fine grained deposits. Overall, thicker till lithologies appear to provide significant protection to production aquifers, with only about 4 percent of the associated PWSs exhibiting elevated mean nitrate concentrations. When the till cover is thin (0-25 feet), the till provides significantly less protection with 13 percent of the associated PWS exhibiting elevated nitrate levels. This is the same percentage as for aquifers below thin uplands and thin lacustrine settings. This is to be expected because the thin uplands aquifers are primarily thin tills and many of the lacustrine aquifer settings are wave cut till lithologies. The similar number of PWSs included in the 0-25 feet groups of thin uplands and lacustrine aquifer settings (677, Table 4) and the till lithologies (670, Table 5) illustrates this association.

The analyses summarized in Tables 4 and 5 provide statistical support for identifying the sand and gravel aquifers and bedrock aquifers underlying thin till as being the most geologically sensitive aquifers, as illustrated visually in Figures 15 and 16. This determination is for dissolved contaminants, based on nitrate concentration. It is important to point out that the same sensitivity may not be present when considering particulates, such as pathogens, in the sand and gravel aquifers. On the other hand, it is suspected that the shallow bedrock aquifers below thin till may demonstrate sensitivity to particulates as a result of the presence of fractures and macropores in the thin till or fractures in the bedrock.

Table 5
Anthropogenic Effects in PWS Wells: Associations Between Nitrate Concentration and Lithology* of Glacial Units

Thickness of Glacial Unit (Feet)	Number of PWS in Glacial Unit	Mean NO_3 > 2.0 Percentage of Wells	Max NO_3 > 2.0 Percentage of Wells
Sand and Gravel Lithologies (including: sand and gravel, minor fines, confined, thin till included within or over unit)			
0-25	9	**33 %**	56 %
25-100	119	**23 %**	38 %
>100	445	**20 %**	31 %
Fine Grained Lithologies (including: fine grained sediments undifferentiated, fines with minor sand and gravel lenses)			
0-25	32	**6 %**	25 %
25-100	337	**7 %**	14 %
>100	344	**5.5 %**	12 %
Till Lithologies (including: till, till with sand and gravel lenses)			
0-25	670	**13 %**	21 %
25-100	1343	**4.4 %**	9 %
>100	576	**4 %**	8 %
Unglaciated Areas (areas with no glacial units on ODNR Aquifer Map)			
0	261	**5.4 %**	11.5 %

* Lithology divisions are from ODNR Aquifer Map

The distinct difference between the percentage of PWSs with elevated nitrate levels with till thickness less than 25 feet (13 percent) and till thicknesses more than 25 feet (4 percent), suggests till thickness of more than 25 feet provides significant protection for underlying aquifers. This empirical information is relevant to questions about the extent of till fractures (Weatherington-Rice, et al, 2000). Till fractures and other macropores certainly occur in tills, but the PWS data suggests that there is a significant decrease in the transport of surface contaminants through tills that are more than 25 feet thick as compared to tills less than 25 feet thick. This observation is based on regional analysis and consequently, application to any specific site is not straight forward. Nevertheless, the empirical data on which this statement is based is relevant to helping set priorities for protecting the state's ground water resources. Statewide, aquifers that have more than 25 feet of till or fine grained glacial deposits overlying the production zone are 3-5 times less likely to exhibit elevated nitrate concentrations than sand and gravel aquifers. If till overlying a bedrock production aquifer is less than 25 feet thick, the bedrock aquifer is 1.5 times less likely to exhibit elevated nitrate than sand and gravel aquifers. The data in Tables 4 and 5 illustrate the high geologic sensitivity of Ohio's productive sand and gravel aquifers, and to a lesser degree the bedrock aquifers underlying thin till. These conclusions are not unexpected and they support the generally accepted views of hydrogeologists familiar with the distribution of contaminants and sensitive aquifers in Ohio. The significant point is that this analytical effort, using empirical data, provides significant support for opinions based on professional experience.

NITRATE TREND ANALYSIS

The long sampling history for AGWMP wells is one of the most valuable characteristics of the AGWMP data. Figure 17 shows the distribution of nitrate concentration versus time for all the AGWMP data since 1987 (about 2,950 samples). The water quality data referred to as "nitrate" throughout this section is actually nitrate plus nitrite reported as N in mg/L. A least squares fit line for this data exhibits a slightly negative slope (decreasing with time) and is dominated by the nondetect results. Overall eight out of ten nitrate analyses are below the detection limit. With the exception of two sample results in the late 1980s, this graph exhibits a general increase in the maximum concentration of nitrate detected in the AGWMP wells. The elevated nitrate concentrations generally occur in the sand and gravel aquifers, but some elevated nitrate samples are associated with bedrock aquifers (Figure 17). The fact that these high results are below the nitrate MCL of 10 mg/L is encouraging. Nevertheless, a continued increase in this trend of high nitrate concentrations suggests that some aquifers providing source water to public water systems may eventually exceed the nitrate MCL. If this occurs, it will have significant treatment and/or replacement cost consequences for public water systems utilizing the aquifers with nitrate values that exceed the MCL.

With the identification of "impacted" wells based on nitrate concentrations as discussed in AGWMP and PWS Data - Geographic Analysis sections (pages 31-35), an obvious question is how does the nitrate concentration vary through time. Figure 17 exhibits the statewide trend, but an analysis based on individual sites is more informative. To explore site specific trends, time series plots of nitrate concentrations versus time were generated for all the active AGWMP wells.

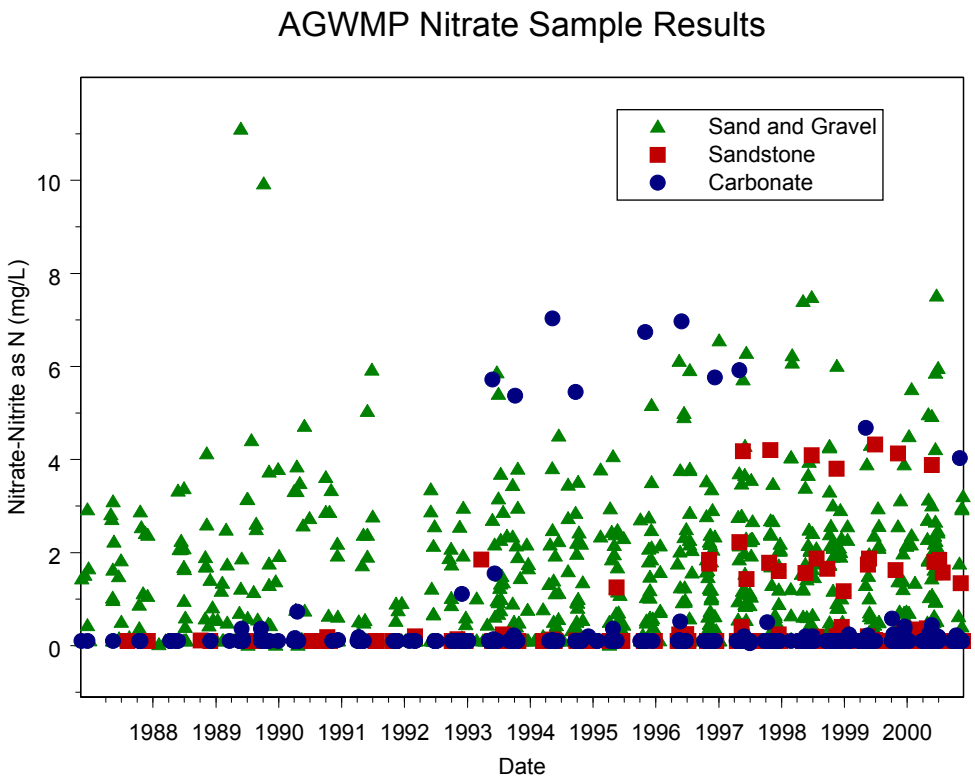


Figure 17. The complete set of AGWMP nitrate data since 1987.

Analysis of these nitrate time series plots suggested three distinct groupings of nitrate behavior for AGWMP wells. The division of nitrate behavior into three classes is interpreted to reflect hydrogeologic settings with distinct processes that affect nitrate concentration. The three classes, based on review of all individual time series, are identified as:

- Nitrate Unstable - no detections of nitrate;
- Transient - irregular, isolated detections of nitrate; and
- Nitrate Stable - detections of nitrate are common.

Each of these divisions is described in the following sections and examples of time series are provided. Physical explanations for the variability of nitrate concentration for each class are provided as hypotheses for these observational data. The empirical data represented in these time series integrate source, geology, and weather variables that influence nitrate concentration. More precisely, these variables include:

- nitrate source availability - are land use sources present;
- source timing - when is nitrate present;
- volume of recharge - weather related;

- transport pathways - geologic controls;
- rate of recharge movement;
- rate of microbial activity; and
- dominant oxidation-reduction conditions.

The nitrate concentration and variation at any site is the result of the interaction of these variables. It is striking that this multi-variant system is reduced empirically to three classes.

A note of caution is provided with regard to interpreting the AGWMP time series based on the sampling frequency. The AGWMP sites are sampled for nitrate at either a six or 18 month frequency. Each sampling event occurs randomly within a 3-4 month sampling window. Thus, the AGWMP time series are low frequency, irregular time series. This distribution limits our ability to resolve the duration and intensity of transient results below the reporting limit, which places constraints on the exactness of these graphs. The following interpretation assumes that the spikes of elevated nitrate concentration are accurate representations of the geochemical history.

Nitrate Unstable Class

This class is characterized by all of the nitrate analyses below the reporting limit, producing a graph with a flat line at the reporting concentration of 0.1 mg/L, as illustrated in Figure 18. This is the most obvious group and one that needs little explanation. Of 200 active AGWMP sites, 86 sites (43 percent) are included in this group. The absence of nitrate can be related to interaction between one or more of following factors:

- there may be limited nitrate sources in the zone of recharge;
- the pathways to transport nitrate from the surface to the production aquifer are restricted; and
- the geochemical environment in the aquifer is dominated by reduced conditions or active microbial activity resulting in nitrate conversion to nitrite, ammonia, or nitrogen gas.

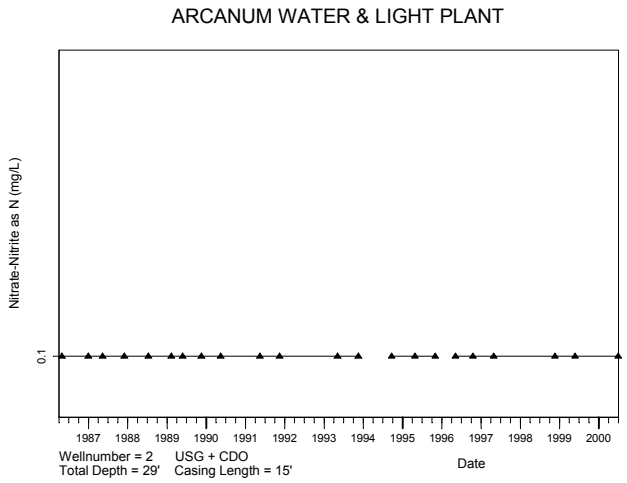


Figure 18. Example of nitrate unstable class.

The dominant factors at any site are difficult to determine. If nitrate sources are present, the balance between the volume and timing of recharge and the processes that result in denitrification are critical to the presence of nitrate in the production well. At a nitrate unstable site, it appears that no rapid influx of oxygenated recharge (with detectable nitrate) is present to disturb the generally reduced ground water environment. The shallow depth of the Arcanum well illustrated in Figure 18 (total depth = 29' and casing length = 15') suggests that a hydrogeologic barrier is present and/or there are limited nitrate sources at this site.

Transient Class

The transient class is characterized by isolated spikes of detected nitrate concentrations above a background of sample results at the nondetect concentration (0.1 mg/L). The spike is represented by a single sample with detected nitrate concentrations. Nitrate spike concentrations are low, generally between 0.2 to 0.5 mg/L and almost all of the spikes are less than 1.0 mg/L with one or two exceptions. Some sites have more than one spike at irregular intervals. Figure 19 provides examples of the graphical characteristics of this class. Fifty-six of 200 active AGWMP sites (28 percent) are included in the transient class. This subset of sites appears to receive pulses of oxygenated, nitrate-laden recharge water at irregular intervals. The AGWMP field data collection does not include direct measurements of oxygen concentration, so there is no direct confirmation of this hypothesis.

The semi-annual sampling frequency does not define the duration of spikes of detected nitrate. The anomalous spikes are less than six months long, and probably significantly shorter than six months, but how short can not be determined with the available data. The reduced nature of the ground water at these sites, indicated by the lack of nitrate, implies that the ground water is generally isolated from surface water at these wells. Elevated iron concentrations (iron is soluble in reduced environments) at the transient class wells independently supports the identification of the reduced geochemical environment. This suggests that the spikes of detected nitrate reflect major recharge events that disrupt the typical, reduced ground water geochemistry. These spikes may be more common and of longer duration than the AGWMP sampling can resolve. The long periods without spikes, however, suggest that the spikes of

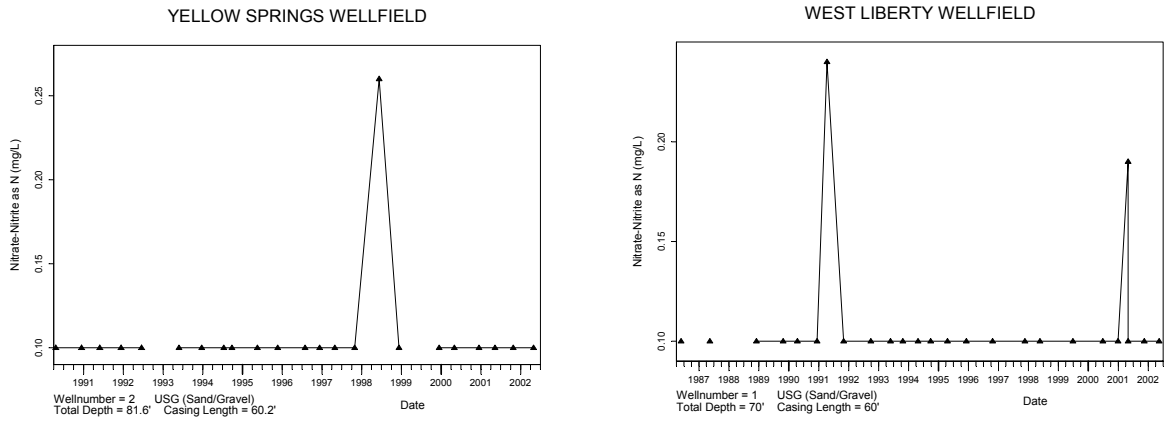


Figure 19. Examples of the nitrate transient class.

nitrate are transient events. Multiple spikes at a site indicates that the site is more frequently affected by pulses of nitrate-enriched recharge. Additional recharge spikes may be present but will be undetected in these time series if the recharge was not transporting water with elevated nitrate concentration, or if they occurred and were subsequently reduced before the next AGWMP sample.

Another important issue is the lag time between the recharge pulse and nitrate detection at the well intake or screen. There is certainly a lag time for surface recharge to be delivered to the water table. The effect of this recharge on the aquifer's ground water quality will also have a lag time depending on the well location relative to the locations of recharge and depth of the production zone relative to the water table surface. This lag in arrival time is impossible to determine on the basis of the nitrate time series data presented, but it is assumed that the typical time frame is days to weeks rather than months. Site specific analysis comparing local rainfall to nitrate time series will help to identify these lag times. More difficult to identify is the potential for horizontal recharge, which may originate close to the well location with short travel times, or may have much longer travel times with horizontal flow related to regional flow patterns.

Nitrate Stable Class

The nitrate stable class includes those sites where detections of nitrate dominate the analytical results. This group exhibits considerable variability and individual sites illustrate trends. Many of the sites exhibit multi-year decreasing nitrate trends, which was an unexpected result. The nitrate stable class includes 52 of the 200 active AGWMP sites (26 percent). Of these 52 sites, almost half (22 sites, 42 percent) exhibit decreasing nitrate concentrations and 18 sites (35 percent) exhibit increasing nitrate concentrations. The other 12 sites (23 percent) demonstrate relatively constant nitrate concentrations over time.

The AGWMP sites were evaluated to identify sites with nitrate concentrations above 2.0 mg/L (discussed in AGWMP Data - Geographic Analysis section, page 31). Over half of these 52 sites (27 sites) were identified as "impacted" using the nitrate stable criterion. The other 25 sites exhibit consistent nitrate detections but at lower concentrations. Figure 20 provides some examples of the nitrate time series for the nitrate stable group. The Coshocton and Philo time series exhibit decreasing nitrate concentrations with time. Enon has periods of increasing nitrate concentration, but the recent data has the same concentration as the 1987-1988 results suggesting a constant average concentration. Loveland exhibits an increasing nitrate concentration with a suggestion of seasonal variation.

According to our hypothesis, the frequent detection of nitrate at the nitrate stable sites suggests the dominance of oxygenated ground water due to relatively rapid movement of surface recharge to the aquifers. The variation in nitrate concentration reflects a balance between the presence of nitrate sources, movement of nitrate with recharge, and denitrification processes associated with the soil, vadose zone, and aquifer geochemical environments. The concentration of nitrate detected is generally an indication of the amount of nitrate transported from the surface with recharge minus the amount lost during transport. The nitrate concentration in ground water decreases with chemical reduction of the dissolved nitrate or the retardation of surface recharge movement resulting in loss of nitrate through absorption or denitrification processes. The slower the recharge, the more nitrate will be removed by the time it reaches the ground water. Thus, the time series trend at any site may be related to changes in land use (variation in nitrate sources or loading), the distribution of rainfall (variation in the volume of recharge), the rate of recharge through the vadose zone to the ground water system that determines the amount of absorption and denitrification (vadose zone variability and microbial population), and the capacity of the ground

water system to reduce the nitrate. The interaction of these variables within a sensitive hydrogeologic setting produces the dynamic graphs which characterize the stable nitrate class. There are hints of annual and multi-year cycles in the time series included in Figure 20, which are difficult to resolve at the current sampling rate.

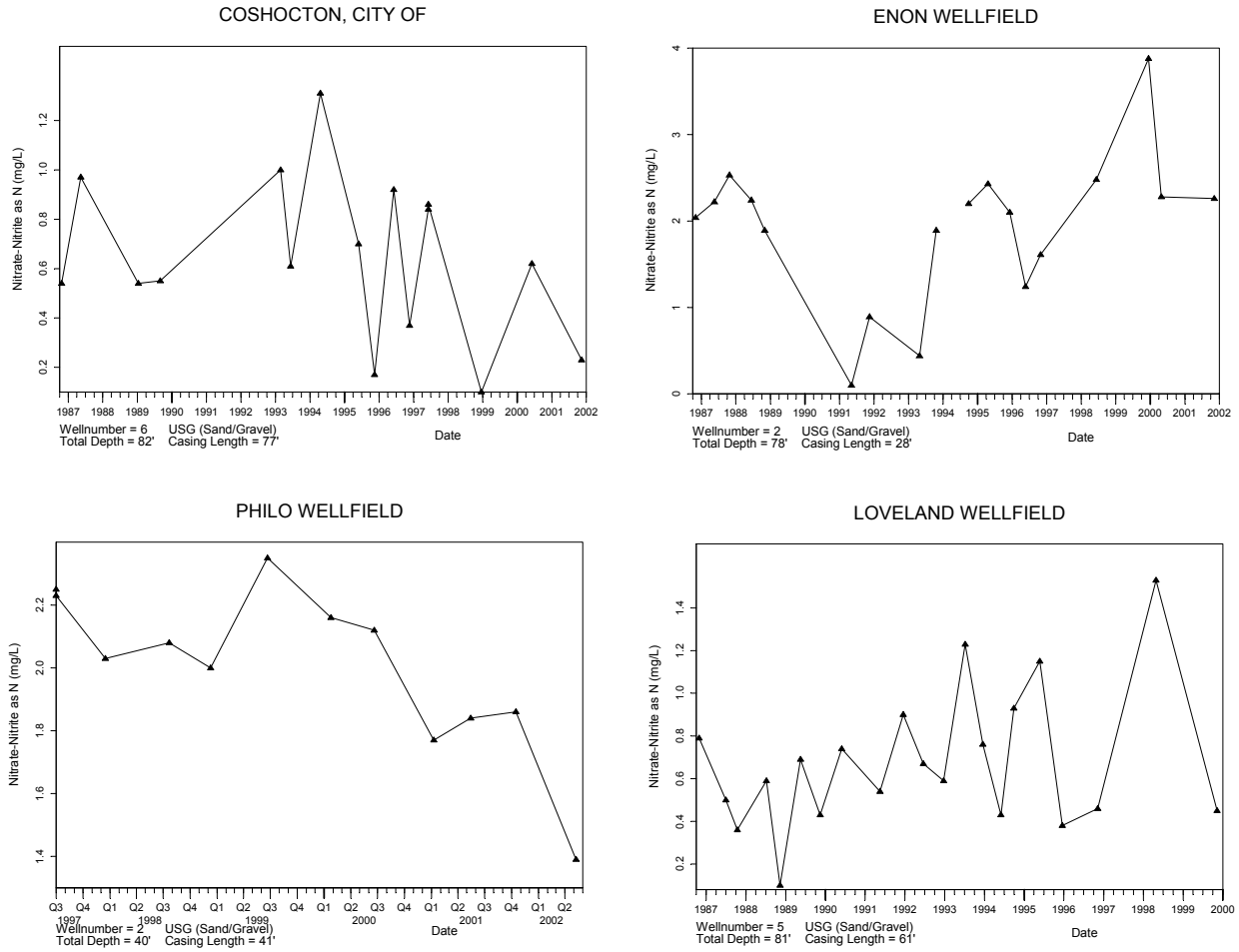


Figure 20. Examples of nitrate stable class.

It is encouraging that almost half of the time series for the "impacted" sites exhibit a decreasing concentration of nitrate with time (13 of 27 sites). Other sites, however, exhibit either stable (seven) or increasing (seven) nitrate concentrations over time. Sites with dramatic changes in nitrate concentrations over time warrant a site specific evaluation to determine if local land use practices (for example, farming practices, home septic systems, or irrigation), can be correlated with the variations in nitrate concentration. Information gained in these evaluations will be useful in targeting sensitive sites for implementation of land use planning to reduce nitrate concentration in ground water. This is a potential topic for site specific studies for the next 305(b) report.

In some cases, a site in the nitrate stable class exhibits a spike with a significantly higher concentration (5-10 times the historic nitrate concentration for the site). This geometric relationship is similar to the transient class, except that the background level is different. Figure 21 illustrates this relationship at the Oxford wellfield. The spike is interpreted to result from a recharge event that transports an unusual volume and/or concentration of nitrate to the ground water. The flux of nitrate can occur from normal volumes of recharge with very high nitrate concentration, or from a very large volume recharge event of elevated nitrate, or some combination of these two extremes. This relationship supports the pulses of the nitrate concentrations for the transient class. Future efforts will investigate the possible correlation between nitrate variability and precipitation/recharge events at selected sites to determine if a direct link can be observed.

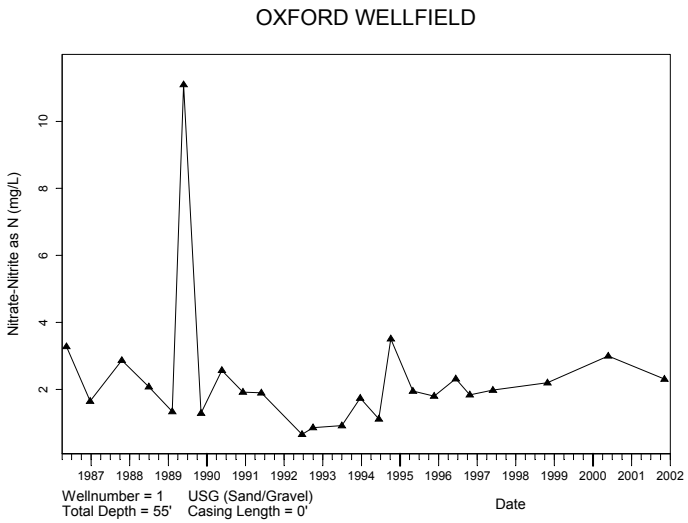
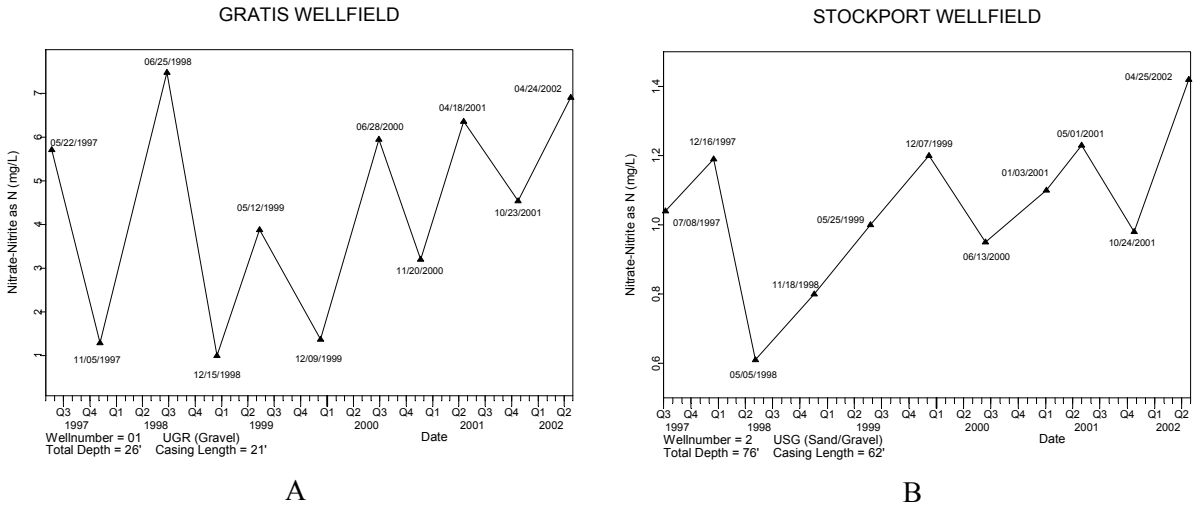


Figure 21. Nitrate stable class with spike of high nitrate.

Cyclic Variation

The time series of the nitrate stable class exhibit suggestions of cyclic variation. The semi-annual sampling period, however, does not allow the precision necessary for identifying annual or multi-year cycles. It is reasonable to expect annual variability based on the hydrogeologic cycle with recharge focused in the winter and early spring and longer cycles based on land use practices, such as crop rotation. Changes in water table elevation resulting from induced recharge, draw down from local wells, natural recharge or drought will also be components that affect these time series. Correlations with other geochemical factors, precipitation records, local water table elevation, or pumping rate data may be helpful in deducing the most important influence on nitrate variability.

It is not unusual for the nitrate time series to exhibit annual or multi-year cycles (typically spread over two-three years). Figure 22 provides two examples of the cyclic variation observed and similar relationships are present in Figure 20. It is speculated that the multi-year cycles illustrated are related to crop rotation with variable application rates of fertilizers in a corn-soybean rotation. Confirmation of this will require site specific investigation to correlate application rates and water quality impacts.



A B

Figure 22. Examples of cyclic variation in nitrate time series.

The dates of nitrate maximums in Figure 22A (Gratis) suggests a strong annual cycle in the nitrate time series. Significantly, each maximum in Figure 22A occurs between April and May. In this time frame, average precipitation volume is increasing in Ohio to a July maximum. The time series in Figure 22B (Stockport) exhibits a strong multi-year cycle. Analysis of specific sites may identify land use practices that control nitrate sources which in turn control the cyclic nature of the delivery of nitrate to ground water. Establishing a direct link to local land use practices may not be straightforward due to the many variables that influence recharge, the presence of nitrate sources, transport pathways, and geochemical conditions within the aquifer. We plan to identify several sensitive sites where data for land use, pumping, water level, and water quality are available. Initiating a shorter frequency sampling plan at selected sites will help to more clearly identify the cycles associated with groundwater and surface water interaction at sensitive sites.

Mixed Groups

Six of the 200 nitrate time series plots for active AGWMP wells were not classified because they did not fit nicely into one of the three classes described. It is logical that these represent intermediate stages between the three classes within the continuum of nitrate unstable to nitrate stable aquifers. An example that exhibits this mixed nature is presented in Figure 23. Bremen Wellfield would have been classified in the transient class if sampling had stopped in 1998. The continued sampling documents a trend of increasing nitrate concentration that places the site in the nitrate stable class. This illustrates the dynamic nature of factors that control nitrate concentrations and suggests that continued or increased nitrate input drives an increasing effect on ground water quality. Changes in land use practices that have contributed to changes in water quality require site specific investigation.

Figure 23 includes a trend of the total iron concentration at the Bremen wellfield for comparison with the nitrate concentration. The general decrease in iron concentration in concert with the increase in nitrate concentration is clearly illustrated, and provides independent confirmation of the hypothesis that the

nitrate stable class reflects a dominance of oxygenated recharge producing a geochemical environment in which nitrate is stable and free iron solubility is limited.

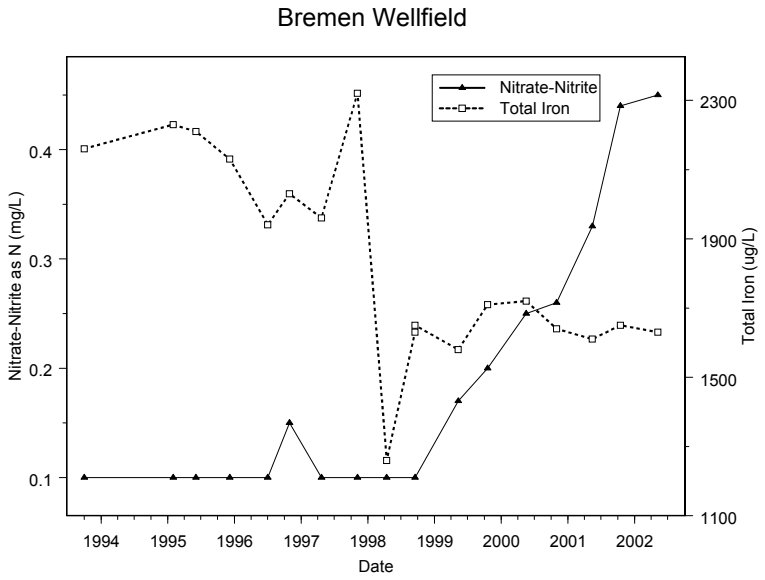


Figure 23. Example of site with mixed nitrate classes.

Well Parameter Correlations

If the nitrate class identification and the hypotheses provided for the physical explanations are accurate, these groups should correlate with well parameters that reflect hydrogeologic sensitivity. To test this association, intra-well mean nitrate concentrations are plotted against well casing lengths with sites represented by their nitrate stability class and aquifer lithology in Figure 24. The mean nitrate concentration was selected for the horizontal axis because it appears to be the best proxy to indicate nitrate sources associated with land use. Casing length was chosen for the vertical axis because it provides a simple measure of the length of the pathways from the surface to the ground water. Whether casing length, total depth, or depth of unconsolidated material is used, the relationships are generally similar.

Figure 24 clearly indicates a correlation between aquifer sensitivity, as indicated by the high and low nitrate stable group, and casing length. The lithology for each AGWMP site is indicated in Figure 24 (green - sand and gravel; red - sandstone; blue - carbonate), which illustrates that most of the sensitive wells are located in sand and gravel aquifers. A best fit line (not shown) through the nitrate stable points confirms that the higher nitrate means are associated with shorter casing lengths in production wells, but the correlation is not strong (low r^2) since the casing lengths for wells with elevated nitrate range from 25 to 75 feet for various nitrate concentrations. The visual correlation between casing length and mean nitrate concentration exhibited in Figure 24 is, however, significant, especially in light of the complex nature of the system it represents (with multiple variables: sources; pathways; hydrogeologic barriers; adsorption; redox conditions; etc.).

The lower boundary of the plotted sand and gravel sites (green symbols) suggest that across Ohio, 70 to 75 feet of casing appears to be sufficient to protect a production well in sand and gravel aquifers from the effects of nitrogen application associated with land use activity. This is not to say that every well needs to have 70 feet of casing to isolate the production zone from nitrate-enriched recharge. The insensitive sites (nitrate unstable and transient sites) occur along the vertical axis and document that many sites are not affected by nitrate detections with casing lengths much less than 70 feet. These sites are more isolated from surface recharge due to the presence of hydrogeologic barriers that restrict the downward movement of nitrate enriched recharge. The lower boundary of plotted points may be viewed as the lower bound of normal penetration of oxygenated, nitrate-enriched surface recharge in sensitive aquifers.

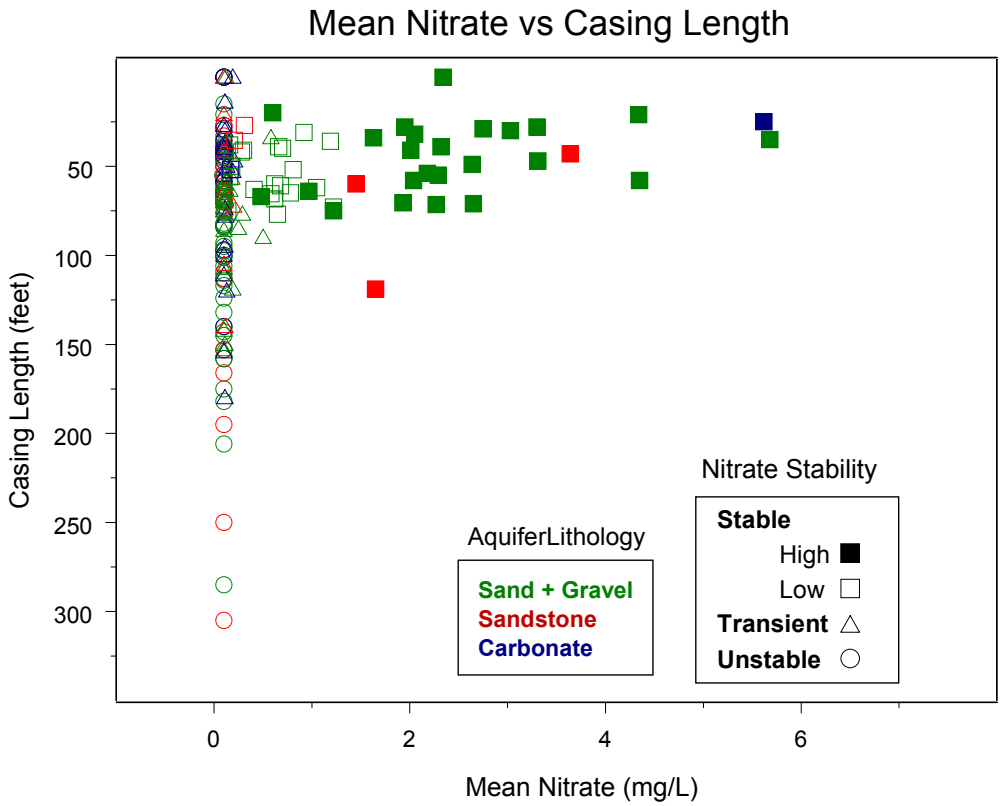


Figure 24. Mean nitrate vs. casing length for nitrate stability classes.

Most AGWMP wells are public water supply wells and consequently well construction issues should be rare. Nevertheless, poor well construction or deteriorated casing can provide short pathways for surface recharge resulting in rapid movement of recharge to production aquifers. Karst environments with solution enhanced fractures or fractured bedrock may provide pathways in which surface recharge can rapidly penetrate to great depths. These environments may result in exceptions to the casing length relationships presented in Figure 24 and may be part of the explanation for the deep sandstone well with elevated nitrate (casing length = 120 feet, mean nitrate = 1.75 mg/L).

The physical hypotheses provided for the transient class behavior are consistent with the clustering of transient class sites at casing depths of 70-90 feet and low mean nitrate concentrations in Figure 24. The presence of multiple transient sites at the lower bound of data suggests that limited volumes of nitrate rich recharge do reach depths of 70-90 feet. Consequently, the nitrate rich recharge that does impact these sites arrives in pulses associated with major recharge events. Again, this same behavior will be exhibited at wells with shorter casing lengths when the site is protected/isolated by the presence of hydrogeologic barriers that restrict vertical movement of recharge.

Distribution of Elevated Nitrate Concentration

Review of the nitrate stable time series plots suggests that most of the detections of the highest nitrate concentrations occur in the spring and early summer months. AGWMP sampling has a bimodal sampling distribution (spring and fall), so any identified subset of samples with elevated nitrate needs to be compared with the AGWMP sampling distribution to determine if they are more likely to occur at a specific time of the year.

To determine if the nitrates spikes occur at specific times in the year, sample count histograms were developed for three sets of data:

- dates of samples with distinctly elevated nitrate results in the nitrate stable class;
- dates of sample results above detection limit in the transient class; and
- all of the AGWMP data.

These histograms are presented in Figure 25, one above the other so the time scale of sample counts by months coincide. The bottom histogram displays all of the active AGWMP data and clearly shows the bimodal sampling frequency for comparison with the other distributions. The middle chart represents the transient class detections which are also bimodal in distribution and do not appear significantly different from the AGWMP sampling distribution.

The upper chart includes samples with the highest nitrate concentrations. In contrast to the bimodal distribution of the transient detections, the nitrate stable class of elevated nitrate results plotted in the top panel of Figure 25 demonstrate a greater likelihood of occurring in the spring and early summer than in the fall. The controlling factors are not clear, but this distinct distribution of spikes of elevated nitrate values for state wide data in the nitrate stable class suggests a widespread nitrate source. For Ohio, the spring application of nitrogen fertilizer provides a widespread nitrogen source that is transported by erratic recharge events. For nitrate analyses in Ohio, it is generally assumed that nitrate sources are widespread as a result of agriculture practices. The more frequent detections of distinct, elevated nitrate concentrations in the period of fertilizer/manure application is consistent with this assumption, but the frequency and occurrence of recharge events will also influence this distribution.

Discussion - Nitrate Time Series

The analysis of the nitrate time series has allowed a division of the active AGWMP sites into three classes which illustrate characteristics of nitrate behavior in production aquifers. The graphic geometry of the nitrate stable class emphasizes the pulsing nature of recharge that transports nitrate from the surface to the aquifers, and is complicated by the complex nature of the nitrogen cycle in the subsurface. Longer transport pathways to greater depths of ground water restricts nitrate presence in ground water as a result of more absorption and denitrification during transport. As water moves to greater depths, it becomes more isolated from the oxygen rich atmosphere. The consumption of dissolved oxygen leads to

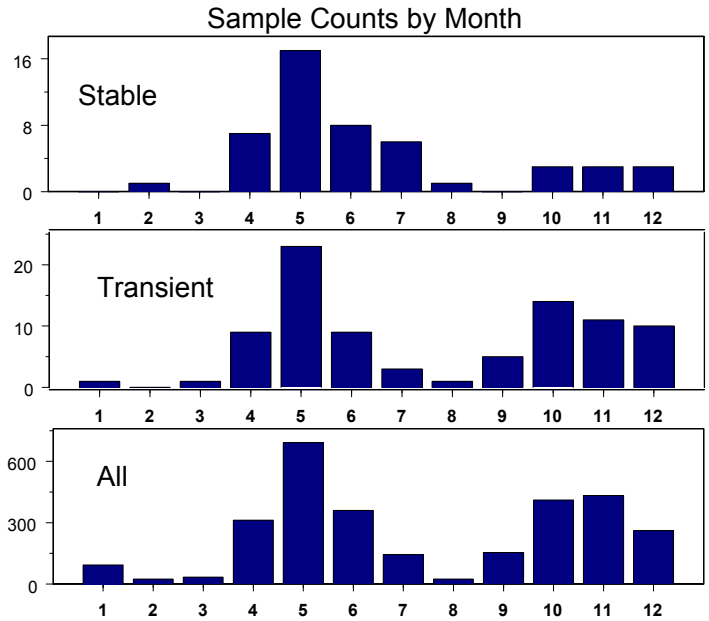


Figure 25. Sample-count histograms, by month, for distinct nitrate spikes in the nitrate stable class, detections in the transient class, and all active AGWMP data, from top to bottom.

the reduction of nitrate to nitrite as a result of microbial activity. The combination of these processes restricts the presence of nitrate to shallower ground water systems. The variability of nitrate concentrations suggest that the irregular, pulsing nature of recharge is important in controlling contaminant transport. Deeper ground water aquifers tend to be more reduced and are less likely to exhibit detections of nitrate.

Figure 26 illustrates the time series relationships in mean nitrate versus depth space and provides significant information on the surface recharge processes. The shallower, sensitive aquifers are dominated by detections of nitrate as illustrated in the nitrate stable class of time series with dramatic variation of nitrate concentration (upper right insert in Figure 26). The physical balance between nitrate source availability, volume of recharge, transport pathways, and denitrification processes during transport, results in the dynamic nitrate time series at sensitive sites. The pulses of elevated nitrate present at many sites document the dominant role that recharge plays. Heterogeneity within the vadose zone suggests that recharge is funneled or channeled into preferred pathways controlled by permeability. The random nature of rainfall and this channeling results in pulses of recharge reaching the water table. In the sensitive hydrogeologic settings represented by the nitrate stable class, ground water quality is dramatically affected by frequent pulses of recharge.

As the length of the pathways to the aquifer increase, indicated in Figure 26 by casing length, the influence of oxygenated, nitrate rich water is reduced. The irregular spikes of elevated nitrate exhibited by the transient class represents the introduction of pulses of oxygenated water by recharge events at irregular times disrupting the generally reduced nature of the deeper, less sensitive aquifers (middle inset

graph in Figure 26). Moving to depths below the transient class we see no detections of nitrate in the nitrate unstable group, reflecting the dominantly reducing characteristic of the deeper ground water due to limited input of surface water (lower left inset graph in Figure 26).

These correlations support the intuitive concept that the more isolated an aquifer is from the surface environment, the less likely the site is to be impacted by recharge events. The red line in Figure 26 emphasizes the empirical, lower boundary (greatest casing depth) of data points representing sites with nitrate detections or elevated nitrate concentrations. This boundary represents the deepest penetration of oxygenated surface recharge associated with PWS production wells in the more sensitive sand and gravel aquifers. The presence of hydrogeologic boundaries restricts this vertical movement of recharge. At any individual site, the lower boundary of the penetration of oxygenated recharge may be significantly shallower than the line indicated in Figure 26 as a result of the presence of hydrogeologic barriers that restrict vertical flow of recharge.

The AGWMP does not measure dissolved oxygen concentrations in the field, so the hypothesis of nitrate stability being controlled by oxygenated surface recharge cannot be tested directly. Supporting evidence is provided by inverse relationships exhibited by nitrate and iron concentrations (Figure 23). Another independent line of evidence in support of this hypothesis is provided by tritium data collected during a single sampling round in 1997. Figure 27 is a scatter plot illustrating tritium concentration plotted against casing length. The nitrate stability classes are represented by symbol type (nitrate concentration is proportional to symbol size) and the aquifer lithology is represented using color (the same symbols and colors as used in Figure 24 and 26). The clustering of the nitrate stable class at around 10 tritium units (T.U.) clearly suggests that the elevated nitrate concentration in ground water is closely associated to precipitation, based on the fact that Midwest U.S. rainfall has a mean 1999 tritium concentration of approximately 10 T.U. (GNIP/ISOHIS, 2000). This provides independent support for the recharge hypothesis presented to explain the nitrate stability classes in the AGWMP ground water quality data.

Another line of evidence that provides interesting support for the significance of the identified nitrate stability classes is the water sample temperature associated with each of the nitrate classes. There are many variables which influence the field temperature measurements, but these errors tend to cancel out as the data volume increases. All of the active AGWMP field temperature data are plotted in Figure 28 by month of sample date. The lines connecting the monthly stacks of data are loess regression lines (a locally weighted, non-parametric polynomial regression; Cleveland, 1979). Each of the nitrate classes were individually regressed, providing a measure of central tendency for each class (number of samples in each class are indicated in the legend). The loess lines illustrate the central tendency for each class and the distinct differences between the nitrate stability classes. The more open or sensitive aquifer settings exhibit warmer temperatures (blue data set and line). Mean ground water temperature = 14.31^{o} C for the nitrate stable class; 13.37^{o} C for the transient class; and 13.08^{o} C for the nitrate unstable class. The fact that a breakout based on the nitrate stability classes yields distinct temperature regressions suggests that the classes have a physical meaning consistent with the hypotheses proposed.

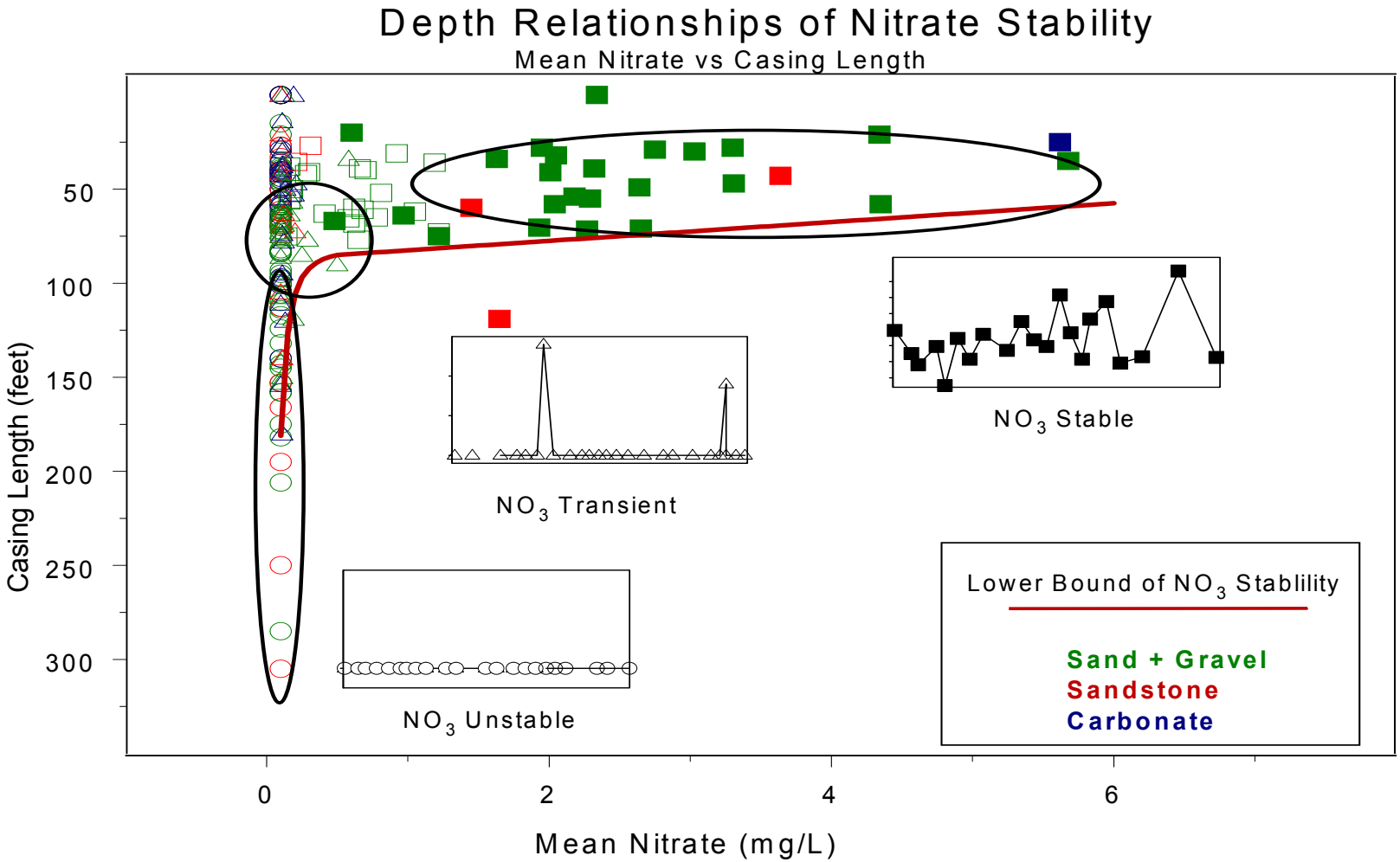


Figure 26. Summary of the depth relationships of the nitrate stability classes.

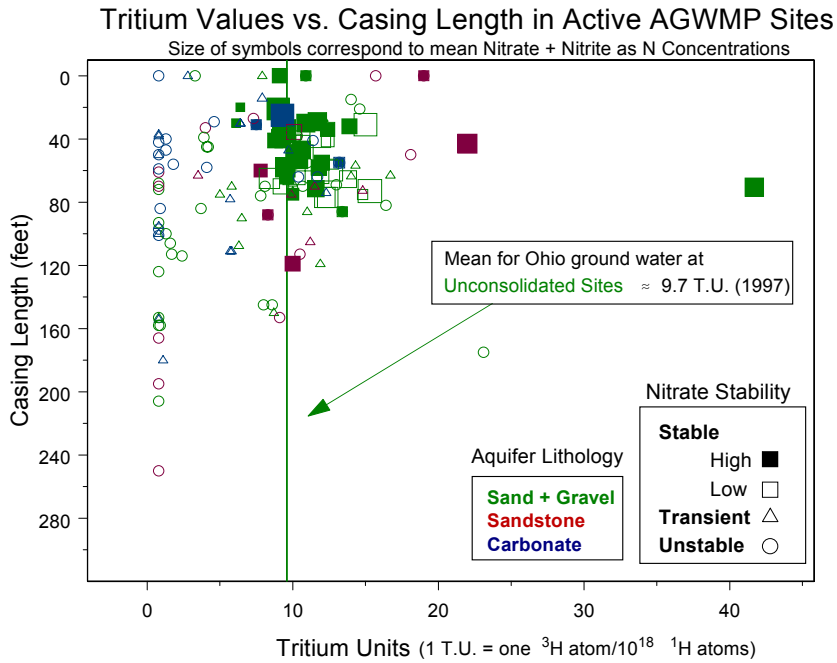


Figure 27. Tritium concentrations plotted against casing length illustrating the association between precipitation and elevated nitrate concentrations.

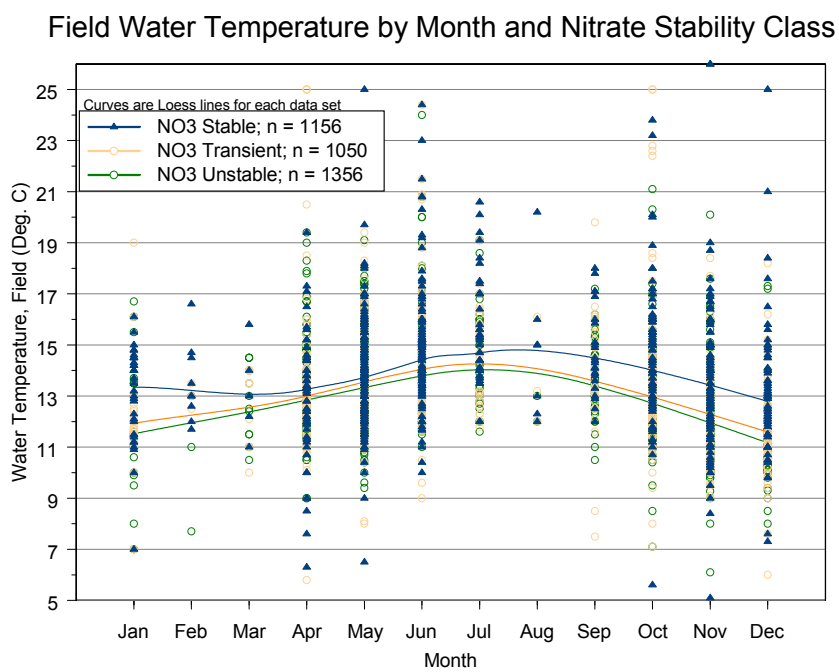


Figure 28. Temperature regression curves for the nitrate stability classes.

Conclusions

This nitrate analysis identifies the sand and gravel aquifers as the most sensitive aquifers to dissolved components, such as nitrate. Bedrock aquifers overlain with thin till are also identified as sensitive using the PWS compliance data. This analysis used till less than 25 feet thick as the thin till category based on the ODNR Glacial Aquifer Map. Table 5 documents significant differences between the presence of elevated nitrate in areas of thin till as compared to areas of thicker till for PWS production wells. These two hydrogeologic settings are the most sensitive based on general geologic knowledge, PWS compliance data, and AGWMP water quality data.

The nitrate time series analysis suggests that wells with more than 75 feet of casing will generally not exhibit elevated nitrate concentrations. It is important to point out that the trade off for setting casing to 75 feet to assure the presence of water low in nitrate is the potential for elevated levels of dissolved iron and the possible presence of arsenic in the water. Managing nitrate sources on the surface to reduce the transport of nitrate into sensitive aquifers is clearly the favored management approach to protect an aquifer and to ensure the most cost effective use of farm nutrients.

Ground Water - Surface Water Interaction

The efforts to identify sensitive aquifers and to evaluate the nitrate time series provide interesting insight into ground water - surface water interaction. The hydrologic cycle requires a close association between surface water and ground water. All water quality professionals recognize this, however, most water quality efforts focus on ground water or surface water independently with simple acknowledgment that the two resources are connected. The rapid flow rates of surface water relative to ground water flow rates makes it difficult to analyze these resources together. This is an active area of research as hydrogeologists develop new tools and approaches to study this critical hydrologic linkage.

Sensitive aquifers are areas with high recharge rates in combination with low vadose-zone residence time that produce local plumbing systems that allow rapid transport of surface water into the ground water resource. The nitrate trend analysis documents that recharge transports surface contaminants along with oxygenated surface water and that this process has significant effects on the ground water quality as reflected in the nitrate stable class. These active recharge processes create a dynamic system in which pulses of recharge disrupt or dominate the stable ground water environment. This dynamic environment is the hydrogeologic setting of sensitive aquifers, and it is clear that sensitive aquifers respond to land use activities. In contrast to the historical perception of an aquifer as "slow moving and unchanging" we now understand that some aquifers respond quickly to input from the surface. This reactivity of the sensitive aquifers emphasizes that studies to evaluate surface water - ground water interaction need to focus on the these areas. **The time scales of surface water and ground water processes converge in sensitive aquifers.**

The sensitive aquifers are clearly the aquifers most affected by land use activity. Consequently, AGWMP staff have started to evaluate land use around the AGWMP wells. This initial effort is summarized in the next section.

LAND USE/LAND COVER AND THEIR RELATIONSHIP TO AGWMP SITES

As AGWMP wells associated with sensitive aquifers are identified, understanding the land use patterns around the wells becomes important. Evaluating the potential impact of surface land use activity on ground water quality is the focus of this section. The interrelationship between land use/land cover and water quality and water quantity is a complex one. Different land uses (industrial, residential, agricultural, etc.) certainly influence ground water quality. At the same time, however, the quality and quantity of ground water also influence the choice of land uses we make at any given site. The interactive nature of these relationships is illustrated in Figure 29. Land use choices and activities have a direct impact on water resources, while water quality and quantity greatly influence the siting of land use activities. Land use is in part determined by environmental factors such as soil characteristics, climate, topography, and vegetation. To best manage and protect environmental resources, a good understanding of these relationships and their ramifications is needed.

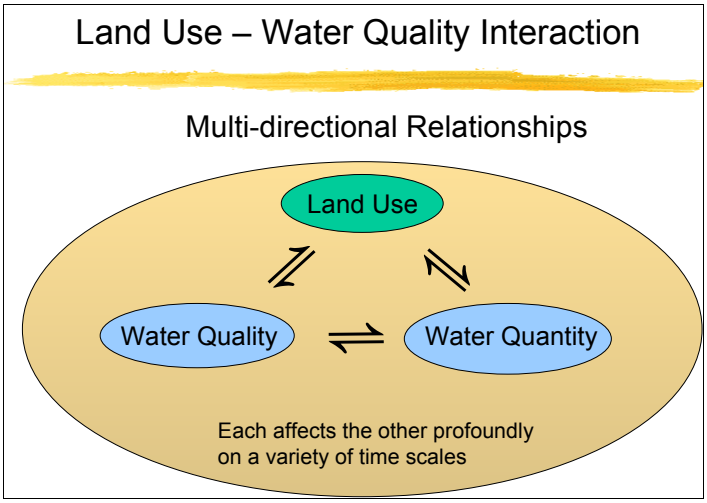


Figure 29. Multi-directional relations between land use and ground water is illustrated.

The land use analyses presented here with regard to AGWMP sites are preliminary. They represent our first endeavor to incorporate water quality data with known land use/land cover information. The main goal of this section is to uncover relationships which naturally exist between the land use/land cover of a given site and the site's subsurface water quality. The water quality at any given site is an integrated "signal" composed of components of soil, weather, aquifer matrix, existing ground water, recharge quality and intensity, subsurface residence time, and land use practices. Often, we might not expect to be able to clearly or easily discern a land use practice from a site's water quality, particularly if a single land use practice is not dominant. More often than not, this is because of the signal's complexity, not the lack of impact the land use has had on water quality. At other sites, we may find that the existing land use practices express themselves quite clearly in the ground water. In practice, mixed sets of results are found, but it is expected that the more sensitive sites will exhibit quicker and stronger responses to a given water quality stressor.

Land use and water quality impacts can be evaluated as impacts resulting from current land use as documented in the percentage of land use/land cover class (e.g., agricultural, residential/urban, forested) by area. An alternative is to relate water quality to land use changes over a period of time as recorded in land use coverages from different times. The preliminary analysis presented here focuses on analysis based on a single land use coverage. To investigate the relationship between land use and ground water quality at AGWMP sites, the National Land Cover Data (Vogelmann, et al, 2001) for Ohio was used.

The NLCD is a digital representation of continuous land use/land cover for the contiguous United States generated from 30-meter resolution Landsat thematic mapper (TM) satellite imagery data. The main classifications used in the NLCD are urban, agricultural, forested, and water, some of which contain several subclasses. The imagery was acquired by the Multi-Resolution Land Characterization Consortium (MRLC), a partnership of federal agencies that produce or use land cover data. Information provided here on the NLCD data for Ohio is summarized from the NLCD Web site: http://landcover.usgs.gov/. The general process used to create the NLCD data coverage for Ohio, and definitions for each land use/land cover classification is provided in Appendix II.

Water Quality Indicators

Water quality indicators are those ground water quality parameters used to assess the influence of a given land use/land cover percentage. The most common water quality indicator used in this analysis is nitrate-N (NO_2-NO_3 as N). This is in part due to the wide spread use of inorganic nitrate fertilizers and organic nitrate sources (sludge and manure application) as well as nitrogen input from septic systems and other waste water disposal across the state of Ohio. Consequently, we use nitrate as a tool to identify sensitive aquifers in Ohio. Although nitrate-N may exist in background ground water samples and is a component of rain, its presence is indicative of human influence at the surface when found in elevated concentrations. While the exact threshold for an "elevated" concentration is somewhat arbitrary, AGWMP uses the value of 2 mg/L or greater nitrate-N as indicating human influence (See AGWMP Data – Geographic Analysis section). Other useful water quality indicators for land use study are fecal coliform, ammonia-N, dissolved oxygen, orthophosphate, chloride, boron, and a number of organic compounds, including volatile organic compounds, pesticides, and herbicides. Some radiogenic compounds may also be useful in certain situations.

The development of usable land use/land cover data with respect to AGWMP sites presented here comprises a three-step process. The first step involved generating a 1,000- foot diameter buffer around each active AGWMP well bore using ArcMap® GIS (Figure 30). The 1,000-foot diameter buffer comprises eighty-one 30-meter grid rasters, for a total land area of about 18 acres. This buffer size was chosen to best represent the area around the well in terms of land use. In the future, it may be practical to use the source water protection area (SWAP area - five year time-of-travel) but all the SWAP areas are not yet completed. This area is meant to encompass most general capture zones and draw-down areas, but is not so large that the land use would have little relation to the area that contributes water to the well. The second step was to overlay the NLCD coverage over the well-area buffers and then extract the coded land use information to a new coverage. This is illustrated for well # 17 at the Middletown Wellfield in southwest Ohio in Figure 31, in which the 1,000-foot diameter buffer is overlain on the NLCD data set.

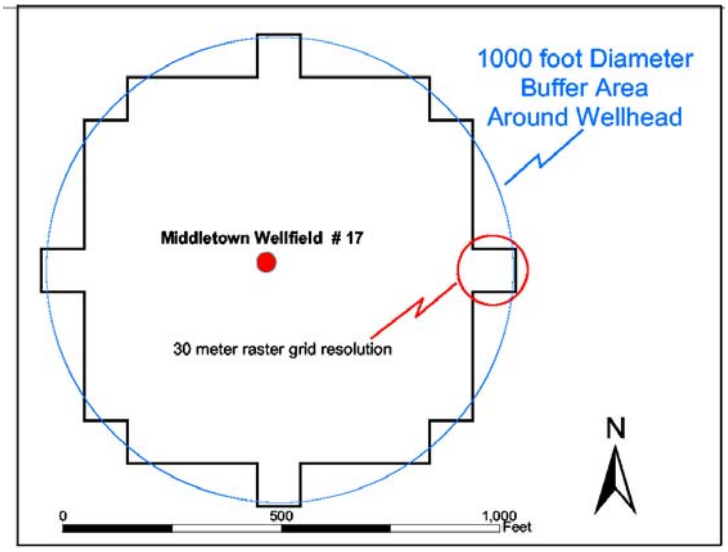


Figure 30. Generation of 1,000 foot buffer around well 17.

Note the river (open water) running across the upper third of the buffer zone in Figure 31. The choice of buffer size in Figure 31 appears to be large enough to encompass numerous land use categories when present. The third and final step involved converting these extracted land use values data to percentages making the data available for comparison with other sites. One method of displaying the single site information is shown in Figure 32, a pie chart for the same well discussed above.

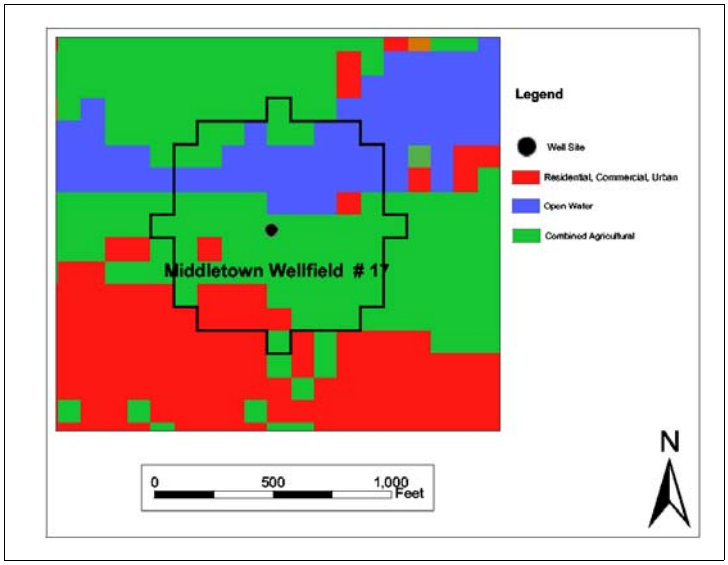


Figure 31. Buffer zone overlain upon NLCD data coverage for Middletown #17, southwest Ohio.

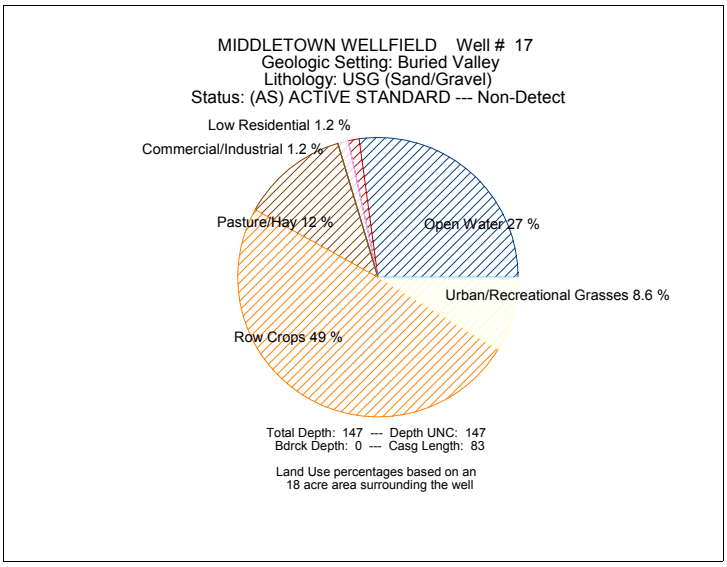


Figure 32. Pie chart indicating extracted land use/land cover percentages for Middletown # 17.

The object of the data extraction step outlined above is to create a database file of quantitative measures of land use for the AGWMP sites, allowing locations to be compared side by side, or within groups. For the example site Middletown # 17, as indicated in Figure 32, about half of the 18 acres surrounding the well is in row crops, a third in open water, and the bulk of the remaining area split between the Urban/Recreational Grasses and Pasture/Hay classes. Review of Figure 31 with these percentages in mind indicates that Figure 32 correctly represents the information in the NLCD data coverage. The level to which the NLCD data coverage accurately represents conditions at any given site is more complicated. The single largest source of potential error is misclassification in the initial processing of the Landsat TM data. Other possible errors include land use changes since the TM data were acquired, and misalignment of the NLCD data coverage with other coverages used. Overall, the NLCD appears to have enough utility to outweigh these potential sources of error.

Table 6 lists the mean land use percentages extracted from the NLCD coverage for 198 AGWMP sites, broken down by aquifer lithology. Of the 15 NLCD land use categories, four have little or no data at the AGWMP sites: Bare Rock/Sand/Clay; Quarries/Strip Mines/Gravel Pits; Transitional; and Grasslands/Herbaceous. Of the remaining 11 land use/land cover categories, the Open Water class has about even coverage between the sandstone and unconsolidated sites (4-5 percent), but is barely represented at carbonate bedrock sites (0.5 percent). Deciduous forest cover is most prevalent at sandstone (23 percent) and unconsolidated wellhead areas (15 percent), and is much less represented in the agricultural west of Ohio (carbonate sites, 4.8 percent). Evergreen and Mixed Forest covers have low percentages across all three major aquifer types. The Woody Wetlands category is also poorly represented for AGWMP sites. The remaining six categories comprise the bulk of the land use representation for all AGWMP wellhead areas, and involve two of the most important classes of land use for modern Ohio – namely urban and agricultural.

Table 6

Mean Land Use Percentages by Aquifer Type at AGWMP Sites.			
	Aquifer Lithology		
Land Use Class	Limestone	Sandstone	Unconsolidated
Open Water	0.5	4.0	5.0
Low Intensity Residential	19.5	10.4	15.2
High Intensity Residential	4.5	1.8	2.0
Comm./Industr./Trans.	9.6	1.9	5.1
Urban/Recreational Grasses	7.0	2.0	7.4
Bare Rock/Sand/Clay	0.0	0.0	0.0
Quarries/Strip Mines/Gravel Pits	0.0	0.0	0.0
Transitional	0.2	0.0	0.0
Deciduous Forest	4.5	22.9	15.2
Evergreen Forest	0.0	3.8	1.1
Mixed Forest	0.0	1.5	0.1
Grasslands/Herbaceous	0.0	0.0	0.0
Pasture/Hay	18.2	40.0	25.2
Row Crops	35.8	9.2	20.9
Woody Wetlands	0.0	2.7	1.9

Light shading = urban components; dark shading = agricultural components

From Table 6, it is clear that the major agricultural classes Pasture/Hay and Row Crop are highly significant for all three aquifer types. In addition, the statistics for the categories which form an urbanized land use are also considerable. Because of the relative importance of these two land use classes, urban and agricultural, it was decided to test if two composite classes, composed of the individual urban and agricultural components, would be useful to analyze large-scale correlations between land use class and ground water chemistry. The individual classes which were used to produce the composite land use categories are highlighted in Table 6 (light background = urban components, dark background = agricultural components), and the summary statistics are presented in Table 7.

Table 7

Combined Land Use Percentages by Aquifer Type at AGWMP Sites.			
	Aquifer Lithology		
Combined Land Use Class	Limestone	Sandstone	Unconsolidated
Urban	40.6	16.1	29.7
Agricultural	55.0	49.2	46.1
Total	**95.6**	**65.3**	**75.8**

From Table 7, it is clear that the combined classes comprise the bulk of land use/land cover at AGWMP sites as identified from the NLCD data coverage. This is most evident for the carbonate sites, for which the two combined classes total almost 96 percent of the well head areas. The sandstone and

unconsolidated sites total 65.3 and 75.8 percent, respectively. The bulk of their remainders is in the Deciduous Forest class, which, when combined with the new categories, brings their totals to 88.2 percent and 91 percent, respectively.

To illustrate the new combined urban and agricultural categories, they were plotted against one another for each of the 198 AGWMP sites, as illustrated in Figure 33. Symbols are used to identify the aquifer types for each site in Figure 33. From this graphic, it is clear that the AGWMP wells exhibit a wide range of percentages of both major land use categories, but also that there are a number of sites for which the two indices are low. Also of note is that the sites with a high agricultural index (>70 percent) *and* a low urban index are dominantly eastern Ohio sandstone wellfields. Conversely, the sites with high urban indices and low agricultural percentages tend to be either unconsolidated or carbonate sites. This would imply that eastern Ohio PWSs in the AGWMP tend to locate their wellfields, on average, farther away from urban centers than do other PWSs, or that the urban centers are smaller in SE Ohio.

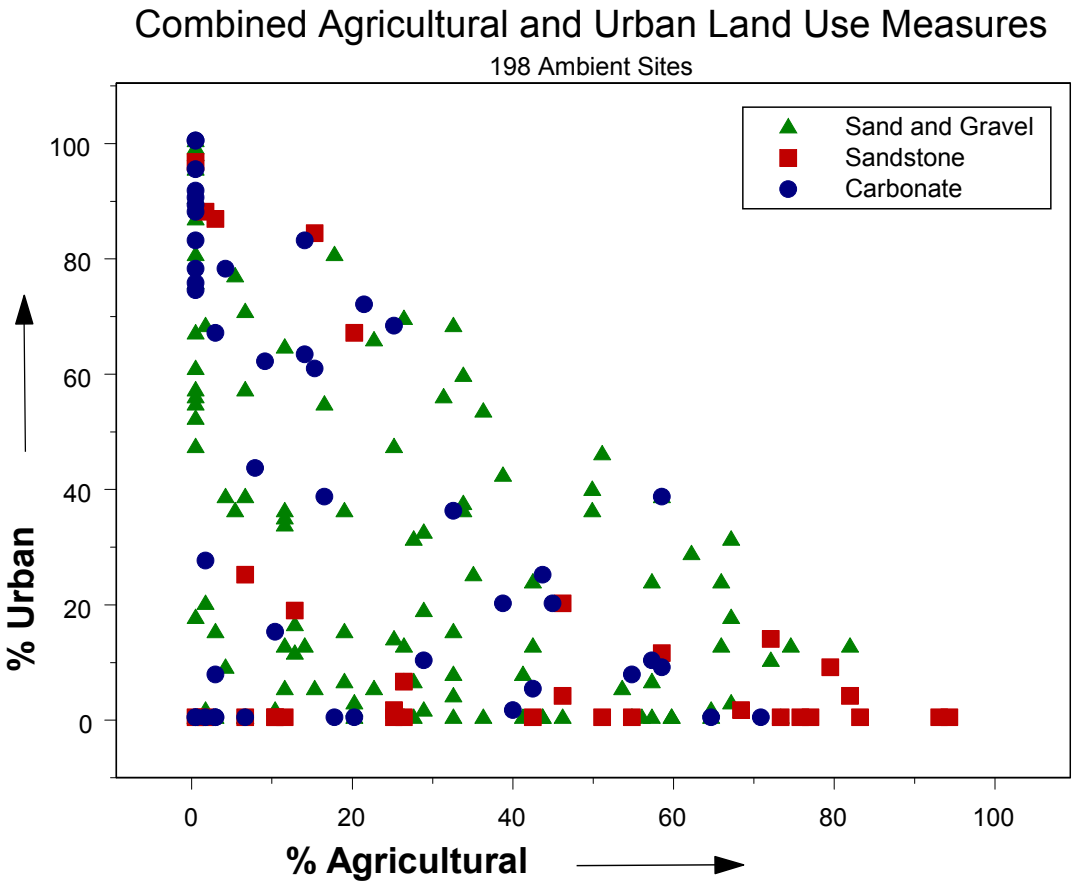


Figure 33. Agricultural and urban land use indices as a function of aquifer type.

Using the nitrate stability scheme developed previously in the Nitrate Trend Analysis section (page 41), the presence of patterns within the combined land use classes based on each site's nitrate data can be evaluated. To facilitate this effort, the graphic in Figure 33 was split into four panes plotting AGWMP sites using the four nitrate stability classes (Figure 34). Each pane is drawn using the same x and y axes as in Figure 33 (combined agricultural and urban indices). The nitrate stability class is given in the orange bar above the individual panes. The nitrate unstable class, shown in the lower left pane, mimics the whole data set (Figure 33), indicating that non-detect sites occur across all aquifer types and major land use classes. The next grouping, the nitrate transients (lower right pane, Figure 34) is somewhat sparser than the unstable group, with the first indication of a high-urban group and a high-agricultural group. The bulk of the AGWMP bedrock sites occur in the lower two panes (nitrate unstable and nitrate transient) which illustrates the generally low sensitivity of bedrock aquifers.

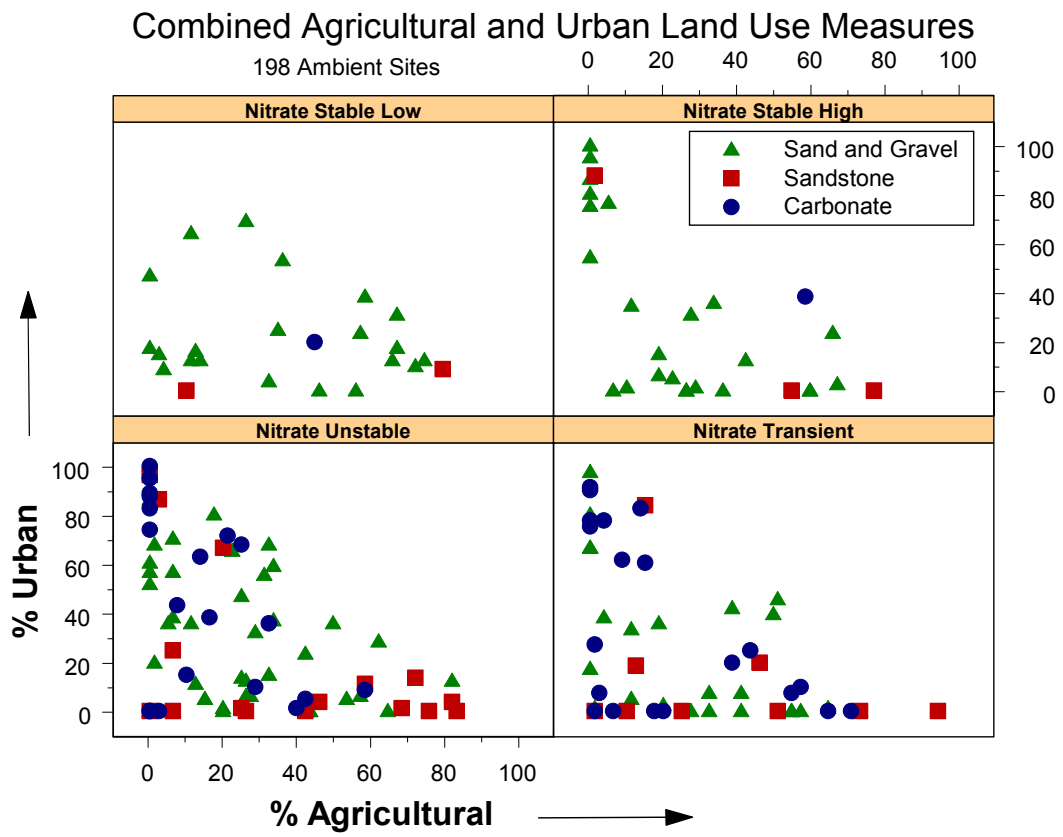


Figure 34. Nitrate stability classes in agricultural-urban land use space.

The upper left pane contains the Nitrate Stable Low grouping, in which each site had numerous detections, but the mean nitrate concentration was below 2 mg/L N. This pane shows a mixed grouping, with perhaps an indication of more agricultural influence than urban. The last group, the Nitrate Stable High (upper right pane) indicates a clear set of two groups, one being high urban index sites, and the other moderate to high agricultural index sites.

To further investigate the connection between land use and nitrate concentrations in raw ground water, the mean nitrate concentrations from each AGWMP site was imposed as a relative symbol size on the plot of urban versus agricultural land use in Figure 35. Two distinct groupings are again identified in this graphic. The first is a high-urban, low agricultural set dominated by the unconsolidated aquifer type. These are wellfields in which urban sources of nitrate may be dominant, like septic systems in unsewered developments, fertilizer application in parks or residential areas, or overflow of combined sewer operations. The second grouping consists of low to high agricultural index sites (10-70 percent), combined with a low to moderate urban index (0-40 percent). This is a more mixed grouping, presumably dominated by mineralized nitrate input from agricultural fertilizers, sludge and/or manure waste management activities, or land application operations. It is interesting to note that ground water from those sandstone sites with the highest agricultural indices are relatively unimpacted by nitrate detections.

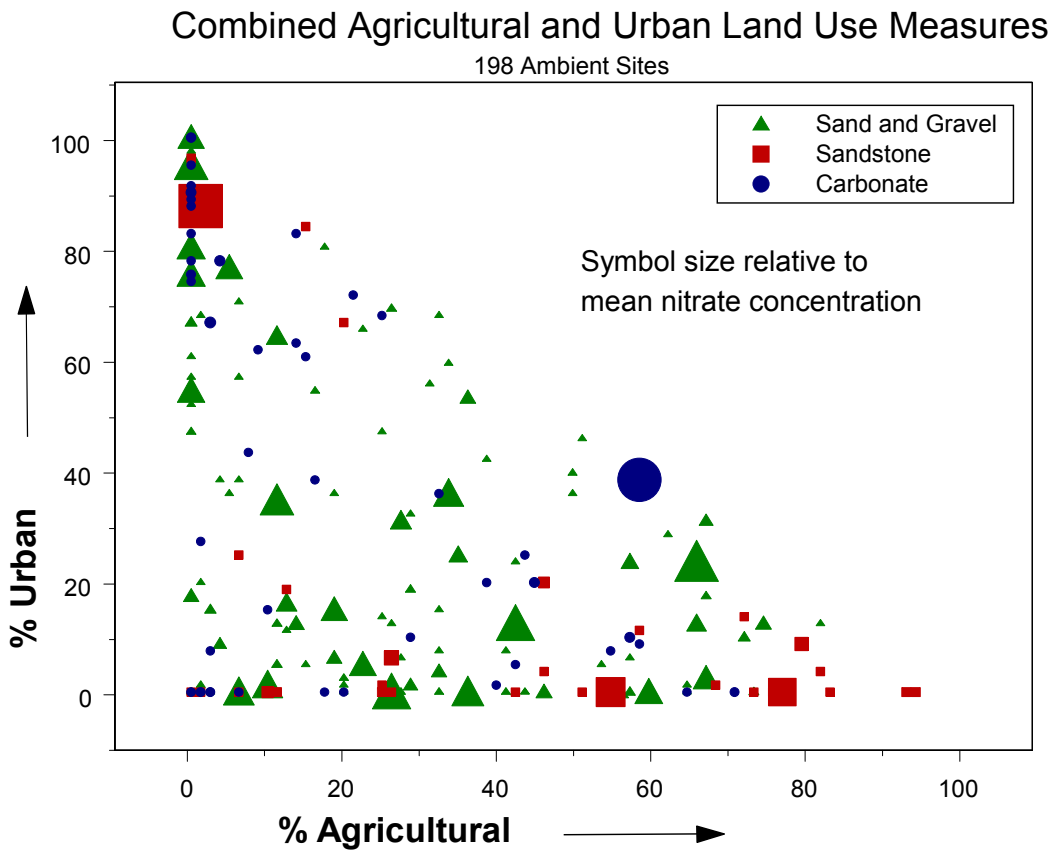


Figure 35. Mean nitrate concentration for AGWMP sites in agricultural vs. urban space.

The two groupings of mean nitrate concentrations (high urban and high agricultural) were separated by looking at the influence of the land use class Urban Recreational Grasses. In Figure 36, the data from Figure 35 is broken out into two sub-groups: 0 to 30 percent Urban Recreational Grasses in the bottom panel, and 31 to 80 percent Urban Recreational Grasses in the upper panel. The upper panel clearly sorts out the high-nitrate/high total urban sites from the other high nitrate sites. This suggests a significant correlation between elevated nitrate concentrations in urban settings, and the presence of the Urban Recreational Grasses land use class. This land use class is made up of vegetation (primarily grasses) planted in developed settings for recreation, erosion control, or aesthetic purposes. Examples include parks, lawns, golf courses, airport grasses, and industrial site grasses. Potential nitrate contributions from this type of land cover have typically been considered low. These preliminary results, however, indicate a relationship between the urban grasses land class and elevated nitrate concentrations in PWS ground water. Consequently, it is important that wellhead protection strategies for areas with significant urban grass components utilize best management practices designed to minimize impact to ground water.

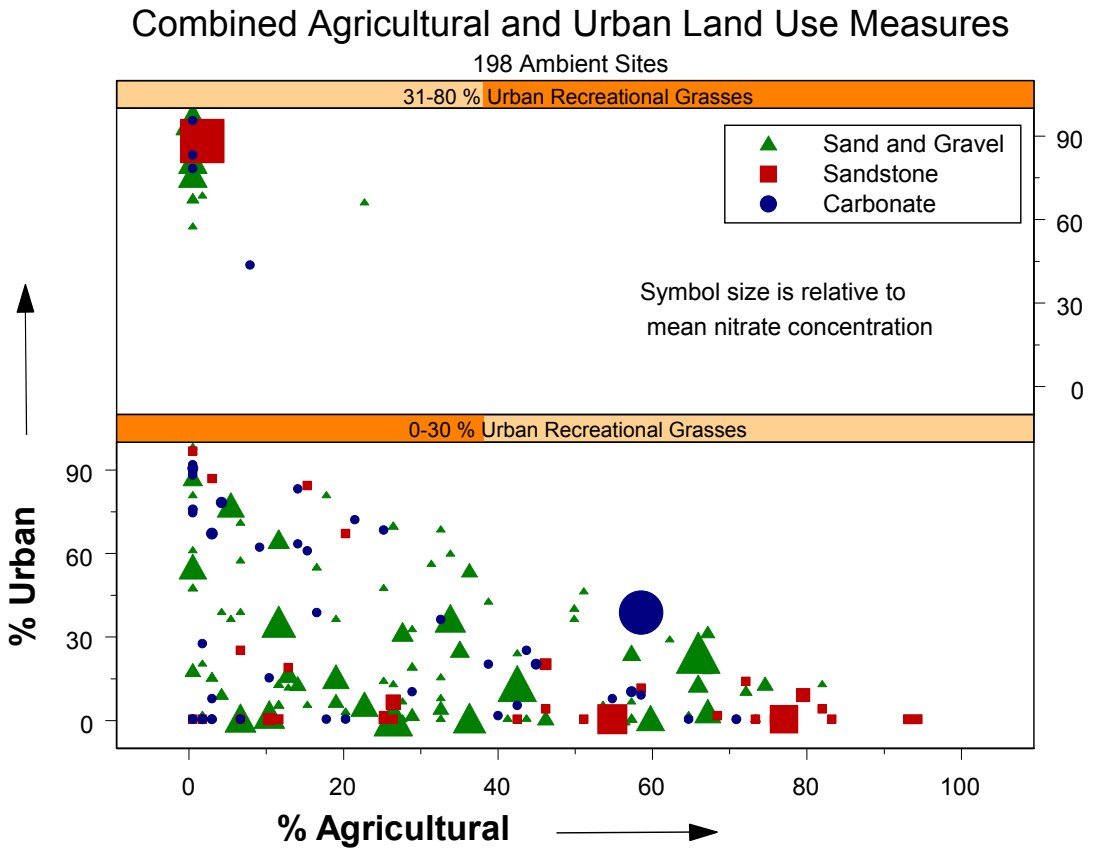


Figure 36. Mean nitrate concentrations on subgroups of urban recreational grasses land use.

Conclusions

Development of a land use data file for AGWMP sites, and introductory analysis of site percentages has proved useful in the interpretation of ground water quality data. These preliminary steps led to the generation of individual wellfield statistics, which may be utilized by ground water staff to gain a more holistic view of how the surface and subsurface interact. By mid-2003, a new set of land use/land cover data coverages are expected, funded through a 319 grant, which will allow updated wellfield statistics to be run. From these new coverages, we can estimate levels of changes in land use, in addition to having access to more recent and more accurate land use percentages.

The association of urban recreational grasses with elevated nitrate values was a surprising finding, because this land use is encouraged in wellhead protection areas as better than other alternatives. Golf courses, parks, and other urban grass settings are recognized for their contribution to stabilizing recharge areas, erosion control, and maintaining strict controls on pesticide usage, but management of urban grasses do require application of fertilizers and other chemicals. The interesting point is that these Urban Recreational Grasses, as a grouping, contain some of the highest mean nitrate concentrations, suggesting a relationship between this land use class and the observed ground water chemistry. These values are still well below the nitrate MCL of 10 mg/L, but the results emphasize the importance of applying best management practices to all activities in wellhead protection areas. Given this information, the potential for contributions to nitrate loading in urban grass-land settings should be evaluated on a site specific basis.

ARSENIC IN OHIO'S PUBLIC WATER SYSTEMS

Due to its toxicity, arsenic is an unacceptable impurity in the water served to customers by public water systems (PWSs). In 1975, U.S. EPA set the Primary Drinking Water Standard (maximum contaminant level, MCL) at 0.05 mg/L (50 ug/L or 50 parts per billion), and recently re-evaluated this standard, recommending that it be reduced to 10 ug/L. This new rule will be phased in so that compliance for all public water supplies (both community and non-community) will be required by 2006. The objective of this section is to summarize information gathered from various Ohio EPA databases and to provide an overview on the occurrence and distribution of ground water arsenic in Ohio's PWSs.

Arsenic (As) is a relatively common element (metalloid) that occurs in air, water, soil, and all living tissues. It ranks 20th in abundance in the earth's crust, 14th in seawater, and 12th in the human body (NAS, 1977). Because arsenic is commonly found in many geologic materials, and total dissolved arsenic is less mobile in streams and river waters, ground water tends to contain more total dissolved arsenic than does surface water. As a result, PWSs that rely on ground water as a water source are more likely to have arsenic in their finished (treated) water than are PWSs that use surface water as a source. Evidence suggests that most of the arsenic found in Ohio's PWSs ground water comes from natural sources.

Arsenic Distribution in Ground Water

Because ground water contains, on average, more arsenic than surface water, and since most small PWSs use ground water, the smaller systems tend to have more problems with arsenic in their finished water. This situation is illustrated in Figure 37, in which mean arsenic concentration in finished water (y-axis, log scale) is plotted against the average water production of the PWS (x-axis, log scale, where the PWSs average water production in gallons per day is used as a proxy of PWS size).

The data used to generate Figure 37 is from Ohio EPA's compliance data base covering the years 1990-1999. The average arsenic concentrations presented are thus decadal averages in the cases where that length of data are available. The compliance data set was queried to exclude older Reporting Limits (RLs) of 10.0 ug/L and 20.0 ug/L which would skew the results. Clearly visible in Figure 37 are the more recent RLs of 3 ug/L, 4 ug/L and 5 ug/L. The display in Figure 37 also breaks out the three types of public water system categories in Ohio; the number of individual system types queried is noted in the legend. These systems are the : 1) Community (COMM); 2) Non-Transient, Non-Community (NTNC); and 3) Transient Non-Community (TNC).

The data illustrated in Figure 37 indicate that 268 of the 2,543 systems (10.5 percent) for which data are available have mean arsenic concentrations greater than the proposed MCL of 10 ug/L. The comparison of these data to the MCL for arsenic is done only to illustrate the scope of the problem; actual MCL calculations are based on yearly averages of PWS compliance data. Ohio EPA anticipates that approximately 150 PWS that will exceed the proposed MCL of 10 ug/L for arsenic. Figure 37 indicates that the TNCs and NTNCs (diamond with lines and open circles, respectively) in Ohio tend to be more susceptible to elevated arsenic in ground water than are the larger COMMs (solid squares). Additionally, the largest COMMs have lower mean arsenic values than do the smaller COMMs. Observations noted regarding Figure 37 are:

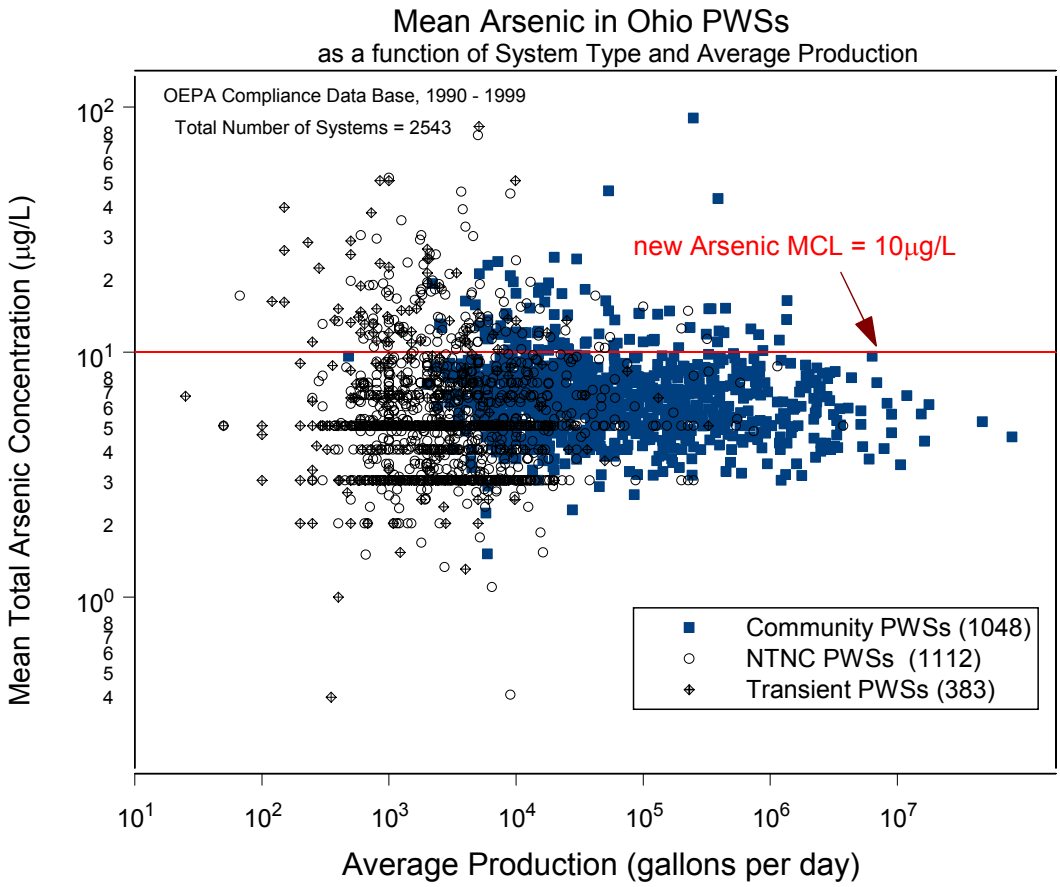


Figure 37. Average arsenic concentrations in Ohio PWSs as a function of average production and system type.

- COMMs tend to have more complex treatment systems; in some cases these treatments may specifically target arsenic;
- COMMs as a whole draw their water with high pump rates inducing recharge, leading to generally higher levels of oxygenation;
- The smaller system wells generally have a lower "yield," contributing to a longer residence time for water in the subsurface and a probable lower oxygen content, which, in certain cases, may favor the mobilization of arsenic;
- COMMs may often draw water from multiple aquifers, possibly diluting a strong arsenic signal with a weaker one; and
- TNCs are not required to routinely sample for arsenic. Arsenic data from a TNC is usually a single analysis from a required new well sample.

The distribution of arsenic in ground water across Ohio is variable and complex, but can be summarized by identifying several important control mechanisms. These controls are inferred from the compliance data set described above, as well as from the Ambient Ground Water Monitoring Network database (AGWMP), in which measurements of raw ground water are made semi-annually at selected PWSs. Arsenic measurements on raw and treated ground water samples from Ohio PWSs reveal only limited differences between these two groups. The mean arsenic concentration for these combined data sets is 5.59 ug/L and the median is 5.0 ug/L, indicating a positive skew due to the concentration of data near the detection limits. This data set is illustrated in Figure 38 as a box plot, showing the 25th and 75th percentiles (see box plot explanation on page 16), the outliers in the data set, and the old and new MCLs of 50 ug/L and 10 ug/L, respectively. These means are log-normally distributed, with a minimum value of 0.2 ug/L (a single, older sample with a lower detection limit) and a maximum value of 94 ug/L.

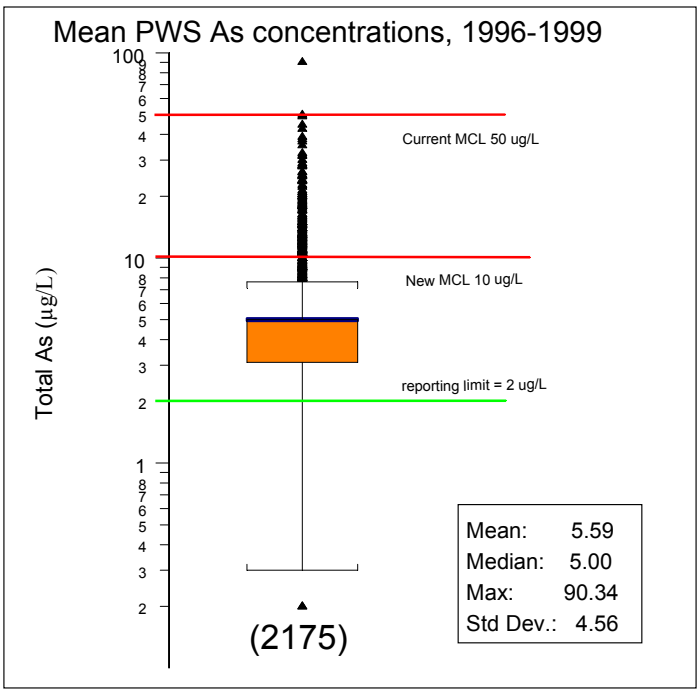


Figure 38. Box plot of arsenic means for 2175 PWSs in Ohio.

The spatial distribution of mean arsenic measurements across Ohio for the AGWMP and PWS wells indicates that elevated concentrations are found more commonly in wells developed in the sand and gravel unit aquifers. Also, waters with elevated arsenic concentrations are apparently associated with the deeper portions of these buried valley settings. These relationships are presented in more detail in the Ohio EPA publication "Ohio's Ground Water Quality, 2000 305(b) Report,", which is available by request to the Division of Drinking and Ground Waters, (614) 644-2752, or in PDF format on the Ohio EPA Web site at the URL: http://www.epa.state.oh.us/ddagw/pdu/gw_305b.html .

Geochemical Controls of Aqueous Arsenic Concentration

If arsenic is present in a local aquifer, redox reactions can control aqueous arsenic concentrations by their effects on arsenic speciation, and hence, arsenic adsorption and desorption. Reduction of arsenate (arsenic V) to arsenite (arsenic III) can promote arsenic mobility since arsenite is generally less strongly adsorbed than arsenate. Redox reactions involving either aqueous or adsorbed arsenic can affect arsenic mobility.

The relationship between arsenic, ground water, and aquifer solids is thought to be controlled mainly by the redox potential of the ground water and its effect on the dissolution of arsenic-bearing iron and manganese hydroxide minerals. If oxidizing (aerobic) conditions prevail in an aquifer, such as in a shallow setting relatively close in time and space to recharge waters, the waters will be less likely to dissolve the arsenic-bearing coatings. Arsenic is found to increase with depth within the sand and gravel aquifers of the AGWMP, suggesting a relationship between depth and redox potential. Most reducing ground water environments are found at depth, which is a function of their separation from atmospheric contact (a shallow confined system may be an exception).

Because water-rock interaction typically consumes H+, the pH of ground water tends to increase with residence time, which, in turn, increases along ground water flow paths, particularly on a regional scale. As a result of the pH dependence of arsenic adsorption, changes in ground water pH can promote adsorption or desorption of arsenic. Because iron-oxide surfaces can hold large amounts of adsorbed arsenate, geochemical evolution of ground water to high (alkaline) pH can induce desorption of arsenic sufficient to result in exceedence of the U.S. EPA current MCL in some environments.

A review of PWS and AGWMP data sets further uncovers several significant relationships regarding arsenic, nitrates, and free iron (Fe^{2+}) concentrations. These relationships reveal themselves as two apparent end-member modes, the first triggering significant arsenic mobilization in ground water while the second appears to inhibit the dissolution of arsenic in ground water.

In the mobilization mode, arsenic dissolved in ground water is found to have a strong inverse relationship with the detection of dissolved nitrogen species (NO_2 + NO_3 as N), that is, the detection of nitrogen species seldom accompanies the detection of dissolved arsenic. This finding suggests that if nitrogen is not detected, arsenic may be found. The empirical association between nitrogen and arsenic is thought to be related to the fact that nitrogen is reduced (consumed reductively) before the iron and manganese hydroxides are reduced, with subsequent release of arsenic to the ground water. The mobilized arsenic end-member for an Ohio PWS is illustrated in time series in Figure 39, where arsenic (left y-axis) and iron (right y-axis) are detected and move in concert with each other, while the nitrogen species NO_2 + NO_3 as N, and ammonia as N (left y-axis) are reported at nondetect levels.

A striking feature of Figure 39 is the strong positive co-variance found between dissolved iron and arsenic concentrations. This distinct relationship is thought to result from the cycling between dissolution and subsequent precipitation of the metal hydroxides and the accompanying adsorption/ desorption of arsenic. This cycling may have several controlling factors, including pumping rates, seasonal and natural variability in recharge rates, induced infiltration, etc. Many of these factors affect the water table elevation at any given point, and may become more or less important as other factors evolve over time. The three obvious cycles peaks observed in Figure 39 are not annual, but biennial (peaks at June 1995, April 1997, and May 1999), and thus may have a drought component as well.

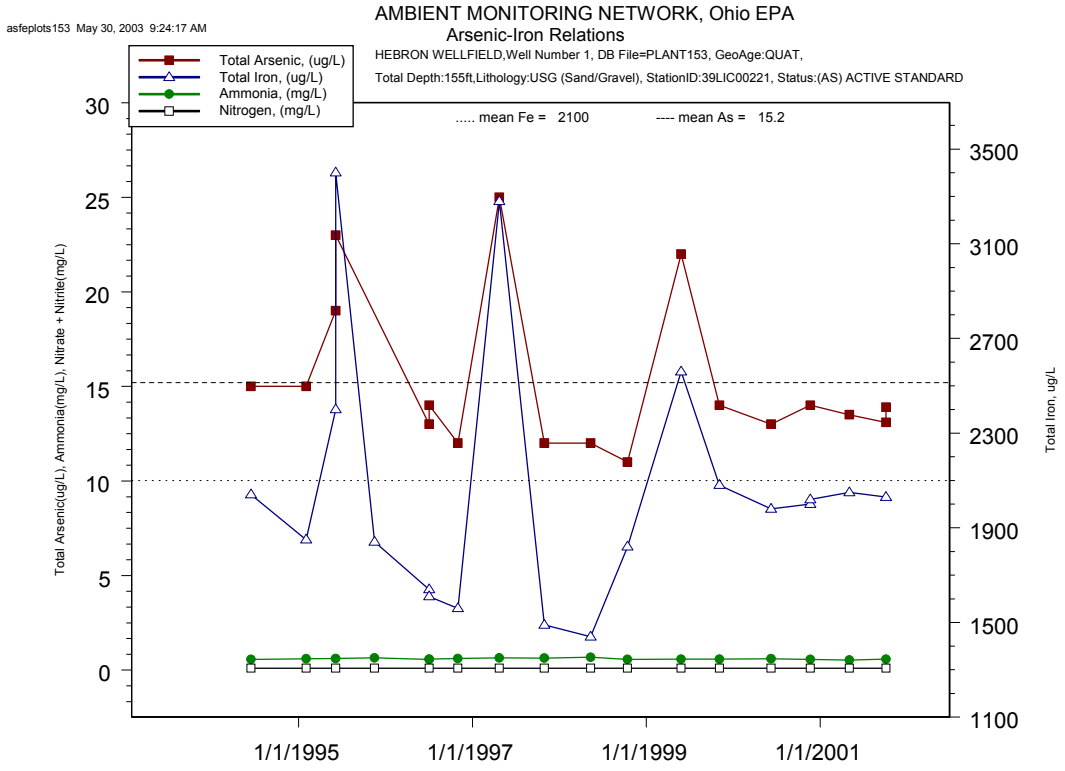


Figure 39. Graphs of the mobile arsenic end-member with nondetect nitrogen values.

In the inhibiting mode, when nitrates are found at detectible concentrations, both dissolved iron and dissolved arsenic are commonly found below the detection limit or at very low levels. Iron may often be detected by itself (without arsenic) in this mode. In this scenario, the potential of mobilizing arsenic to ground water is very low because under aerobic conditions, nitrates, the metal hydroxides and their adsorbed arsenic loads are stable. This end-member mode is illustrated in Figure 40, showing arsenic, iron, ammonia, and nitrates in an Ohio PWS well estimated to penetrate an aerobic aquifer in which both total arsenic and total iron are at nondetect concentrations.

An additional empirical relationship emerges from looking at associations between dissolved iron and arsenic in the AGWMP data base (Figure 41). It appears that a mean minimum of 700 ug/L dissolved iron in raw ground water is required before arsenic concentrations rise above the 10 ug/L level (the new MCL). This association is revealed when dissolved iron is plotted against dissolved arsenic concentrations for AGWMP ground waters, as illustrated in Figure 41. Arsenic occurs together with iron below the apparent 700 ug/L Fe limit, but only at lower concentrations. We can also see from Figure 41 the higher incidence of elevated arsenic concentrations in the sand and gravel aquifers (solid diamonds) compared to the sandstone (open circles) and carbonate (open squares) systems.

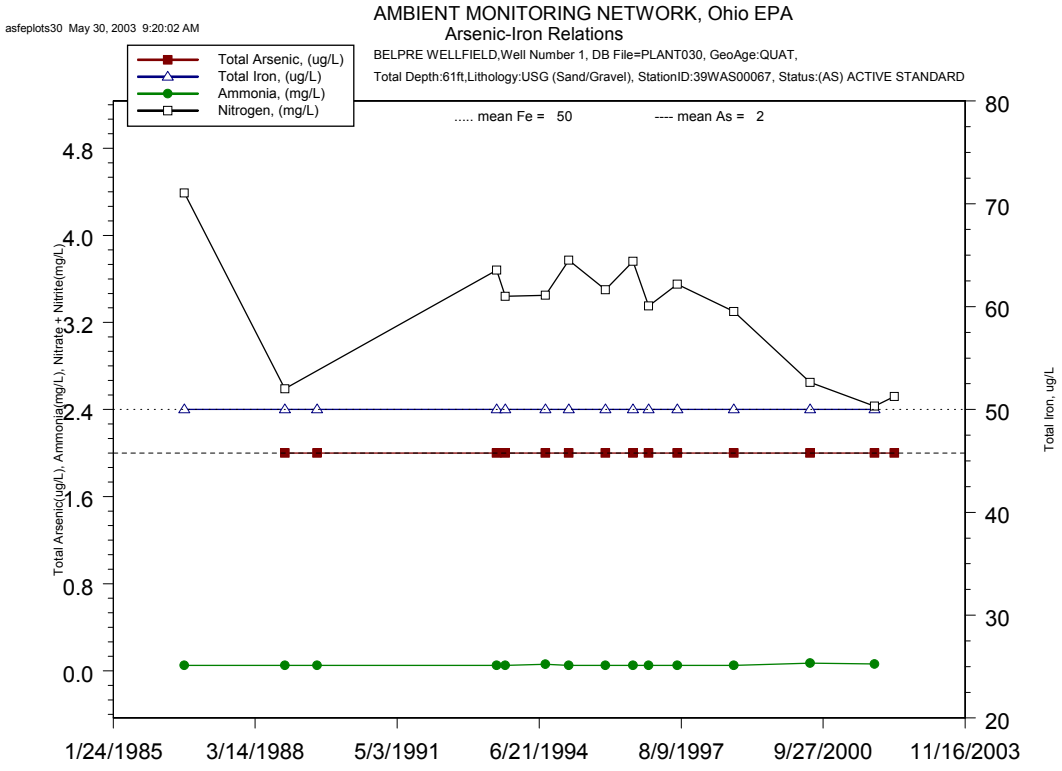


Figure 40. Graphic representation of the inhibited arsenic end-member mode.

The two empirical relationships outlined above (the two end-member nitrate-arsenic and the 700 ug/L iron-arsenic limit) allow an estimate of the potential for significant arsenic impact to ground water to be made, as well as estimate the current redox potential in the aquifer. When raw ground water has an iron concentration greater that 700 ug/L; **and** $NO_2 + NO_3$ (as N) concentration very near to, or at the detection limit, a greater potential for elevated ground water arsenic concentrations exists. This, of course, assumes the availability of arsenic in the geologic material, although evidence suggests that arsenic is present in most, if not all aquifer materials in Ohio. For the above situation, we can estimate that at a minimum, mildly reducing conditions exist within the aquifer, based on the iron, nitrate, and arsenic concentrations. Alternatively, oxidizing conditions may be inferred from the existence of detectible nitrates, coupled with the absence of dissolved total arsenic and iron. These observations provide indirect evidence of aquifer redox conditions which controls the mobilization of arsenic in ground water. They are presented here as a general guidance for using existing water quality data to indicate the presence of possible problems with arsenic impact to ground water. These guidelines are no substitute for field measurements of redox potential, or for site specific analyses for arsenic.

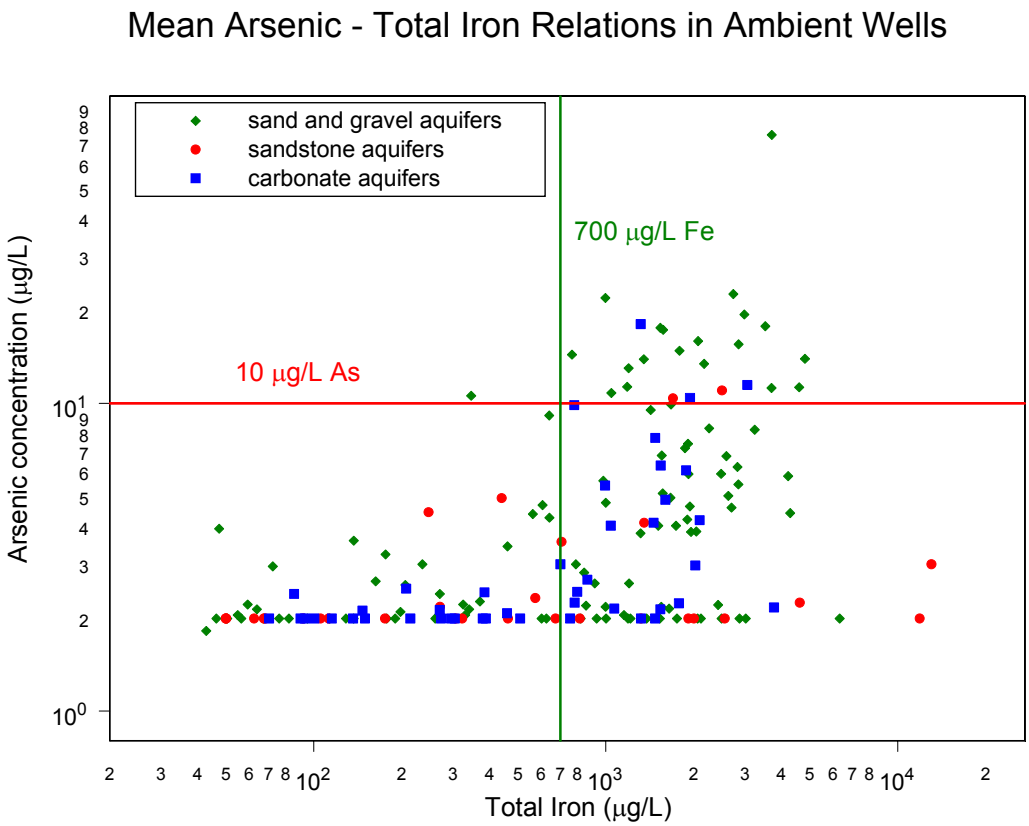


Figure 41. Log-log plot of arsenic-iron concentrations in AGWMP wells showing the apparent 700 ug/L Fe limit below which waters rarely exceed the potential MCL of 10 ug/L.

The inverse arsenic-nitrate relationship is illustrated in Figure 42, using mean AGWMP data. This graph clearly shows, with a few exceptions, arsenic in ground water is rarely accompanied with detections of nitrate. This provides further evidence of the control that redox conditions impose on the ground water regime. The relationship shown in Figure 42 is not a causal one; it exists because the mildly reducing conditions typically found in ground water allow the readily available dissolved oxygen and nitrates to be consumed reductively. The order of reduction is codified in the "natural attenuation" sequence: O_2 > NO_3 > Mn oxides > Fe oxides > SO_4 > methane. After the nitrates are consumed, the metal oxides may be reduced through microbial reduction reactions, releasing the available arsenic to ground water. This is the most common arsenic release mechanism found in Ohio's ground waters.

The predominance of elevated arsenic in Ohio's sand and gravel systems, as opposed to the carbonate and sandstone aquifers, is also evident in Figure 42. There are a few wells in which the strong inverse relationship between arsenic and nitrates does not hold, as illustrated by those stations in Figure 42 with both detectible nitrates and arsenic. It is believed that these represent either stations in which the nitrate load is very high, or possibly stations in which the release of arsenic occurs through an oxygenating environment, such as through dissolution of pyrite. In this case, the existing nitrates would be naturally stable. These stations are clearly in the minority, as seen in Figure 42.

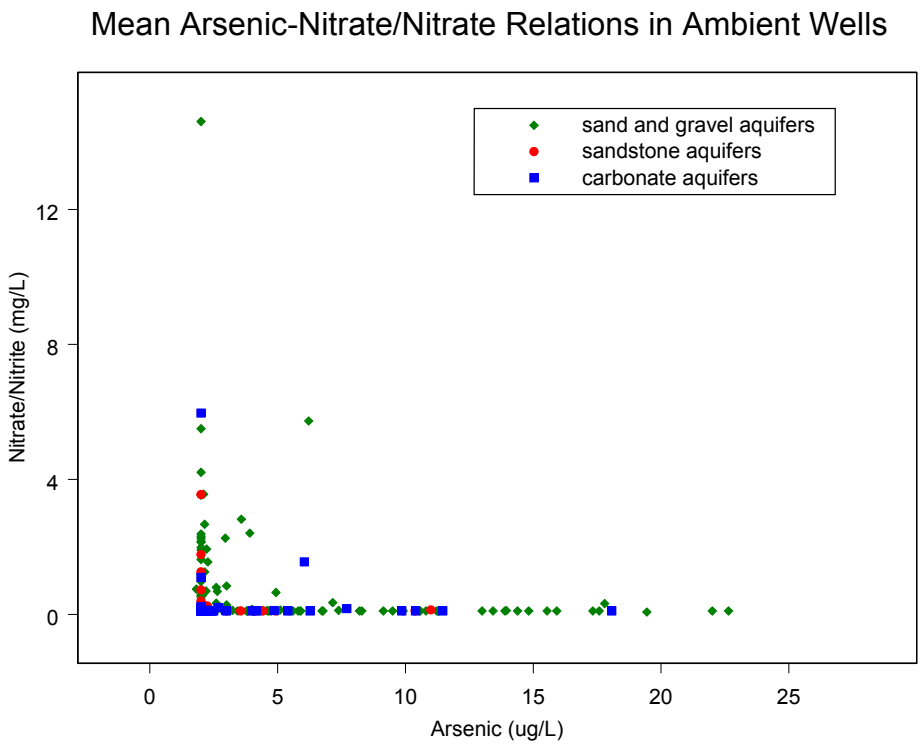


Figure 42. Arsenic versus Nitrate-Nitrite (as N) in Ambient Monitoring System wells.

Arsenic Sources for Ohio Ground Water

If arsenic is present in the local aquifers, the origin of the arsenic is thought to be from mobile arsenate, (the +5 valence form) in surface water passing though the young, yet unconsolidated sediments as they were buried and lithified. Arsenic is strongly adsorbed onto metal hydroxide minerals and deposited as secondary coatings that cement the aquifer matrix. The arsenic may also co-precipitate with these iron and manganese coatings as they are formed. If reducing conditions then occur within the saturated zone, microbial degradation of organic matter will often lead to a series of reductive reactions, first consuming the available dissolved oxygen, followed by the reduction of any nitrates present. Arsenic may then be released through subsequent reduction of the Fe and Mn-oxide cements bearing this element as a trace contaminant.

A second source of naturally occurring arsenic which may impact ground water is arsenic-bearing sulfide minerals such as arsenopyrite. Although pyrites are found in the coal seams and beds of eastern Ohio, they would need to be oxidized to mobilize the arsenic. Since the overwhelming number of cases indicates that reducing conditions are present where arsenic is being mobilized, little evidence exists which points to arsenic-bearing pyrites as an arsenic source to ground water in Ohio. In addition, the oxidation of pyrites would release significant amounts of sulfate to ground water, with a consequent decrease in bicarbonate ion concentration, neither of which are observed. It is possible that an earlier oxygenation of pyrite generated the Fe and Mn hydroxide minerals with associated arsenic that are discussed in the previous paragraph.

Pump Rate Control of Arsenic Concentration

The relationship between arsenic levels and pumping rates for individual wells is not well understood at this time, but the relationships described here suggest that the higher the well yield (e.g., sustained pump rate or total daily production), the less likely a system is to encounter elevated arsenic levels in ground water (trend exhibited in Figure 37). This may be the case because a system under high pumping pressure is less likely to retain a reduced character over time. High-yield wells are set in permeable zones and have the potential to be "refreshed" with oxygenated recharge in several ways: constant pumping (bringing in foreign water), or significant draw-down in the well. The data presented here suggest also that the occurrence of arsenic is correlated with low-yield wells (low pump rate or intermittent pumping). This idea is supported by data from the Ohio Department of Health, in which the occurrence of high arsenic concentrations in raw well water appears greater in small (low-yield), privately-owned wells than in larger, public water supply wells. Perhaps the low-flow condition of a smaller well allows the ground water to more fully equilibrate with its reducing environment, with the resulting reduction of iron oxy-hydroxides inhibiting the release of arsenic. Needless to say, this pump rate related geochemical control for arsenic is only relevant when arsenic is present in the local aquifer.

CONCLUSIONS AND FUTURE FOCUS

The water quality analysis presented in this report illustrates the progress that Ohio EPA, Division of Drinking and Ground Waters, has made during the last reporting period. We continue to work to increase the quality of the AGWMP data, to incorporate improvements in the data management tools and to improve our data analysis, as discussed in the Ambient Water Quality section. We are proud of this progress. More importantly, this progress sets the stage for utilizing ground water quality data in support of DDAGW programs, including:

- listing and cataloging ground water resources impacted from land use activities;
- increasing our understanding of the ground water resources of Ohio;
- continuing to identify sensitive aquifers;
- supporting effective implementation of new SDWA rules;
- incorporating SWAP sensitivity analyses into our water quality analysis; and
- transferring the AGWMP data into STORET.

The Ambient Network Data Summary (Table 3) provides an updated summary of ground water chemistry that can be used to help identify ground water that exhibits impact from human activity or reveals significant natural variability. These summary data can also be used to help evaluate site specific data. The 2002 305(b) Report presents all the inorganic AGWMP data in Appendix I as box plots for each parameter listed in Table 3, in order to illustrate the distribution of individual data points. AGWMP data collection and efforts to identify significantly impacted wells will continue.

Efforts to identify areas of anthropogenetic impacts to water quality (Sensitive Aquifers section) and to characterize natural variation within each aquifer type (Arsenic in Ohio's PWSs section) will continue. The identification of impacted ground water and understanding of sensitive aquifers can be used to set broad priorities for ground water protection efforts and/or compliance activities. Once areas of impact are identified and confirmed, they can be targeted as priority areas for implementation of best management practices to protect the ground water through 319 grant funds.

Our ability to focus protection efforts on sensitive aquifers or public water systems with the greatest potential for impact becomes critical under the weight of numerous SDWA rules and finite resources. The option or requirement to target implementation to areas of more vulnerable public water systems (UIC Class 5 Well Rule and Ground Water Rule) illustrates another need for evaluating and identifying sensitive aquifers and ground water protection areas. In the next reporting period, significant effort will be directed at identifying sensitive PWSs for implementation of the SDWA Ground Water Rule, which will be final in 2003. The Nitrate Trend Analysis section of this report provides a useful tool to help evaluate vulnerability of specific sites that have a history of detects in ground water nitrate monitoring. Particulates, such as pathogens, and dissolved material, such as nitrate, will behave differently in sensitive aquifers and this is one of the issues that needs to be evaluated for the Ground Water Rule. In addition, the locations of PWSs identified as under the influence of surface water need to be compared with the distribution of sensitive aquifers. The results of PWS bacterial sampling needs to be integrated with efforts to identify aquifers sensitive to pathogens.

Compiling all sites in Ohio with documented or confirmed releases of contaminants to ground water from regulated sites and nonpoint sources is another priority activity. This database of documented impacts will help to identify locations with multiple ground water impacts and/or releases to help direct priorities for ground protections efforts and to identify activities that would benefit from implementation of best management practices. This effort will also contribute to the identification of sensitive aquifers, and improve our reporting capabilities for 305(b) reports.

Another benefit of identifying sensitive aquifers is that these are the aquifers where the recharge is the most rapid and consequently the ground water-surface water interaction is most active. We plan to identify several areas with rapid recharge and initiate a short term sampling program to monitor temporal geochemical variation associated with seasonality. This effort will lead directly to a better understanding of the local ground water-surface water interaction, and to a larger understanding of the nature of the sensitivity of water resources in Ohio. The intent is to include a sensitive SWAP area in the short-term sampling program, and to investigate how some new environmental tracers, such as the N and O isotopes of nitrate, may allow tracing nitrogen impact to specific contaminant sources.

The continued collection and analysis of water quality data and supporting hydrogeologic setting data will increase our understanding of the geochemical controls of natural water quality, as documented by the oxidation and reduction controls for the arsenic distribution. The arsenic summary begins to illustrate how water quality data can be used to identify production settings in the state where there are likely to be a greater concentrations of arsenic in the source water. There are many variables to consider, but these analyses point to water quality characteristics that should allow the agency to set criteria for prioritizing wells or areas of concern. The local geochemistry and composition of the portion of the aquifer providing water to the a well is the ultimate control, so decisions will always need to be based on site specific data.

SWAP assessments for the community PWSs will be completed in 2003. These assessments include evaluation of susceptibility based on geology, water quality impacts, and the presence of contaminant sources. This effort provides an independent approach to confirm identification of sensitive aquifers. In addition, the SWAP assessment process provides electronic access to site-specific and regional data useful for analyzing water quality data associated with public water supplies, including locational information, hydrogeologic setting information, well construction data, and aquifer hydrologic parameters. This information increases the opportunity to establish detailed associations between geologic parameters or land use data and water quality data. Land use/land cover analysis can be enhanced with these improved data to help to identify or confirm cause and effect relationships between potential sources of contamination and the resulting ground water contamination in public water systems. Documenting examples of ground water contamination and associated land use activities has great potential for identifying and prioritizing areas for implementation of best management practices. Improved land use coverages are also being generated for Ohio using 319 funds, which will be used for land use analysis.

Efforts to transfer AGWMP data to STORET are underway. This effort avoids the expense of rewriting the Ground Water Quality Characterization database data entry and editing modules, but the transfer is not a small undertaking. STORET will improve our capabilities of sharing the water quality data with the public.

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APPENDICES

Appendix I - Box and Whisker Plots of Inorganic AGWMP Data . . . . . A 2

Appendix II - NLCD Data Coverage for Ohio . . . . . A 13

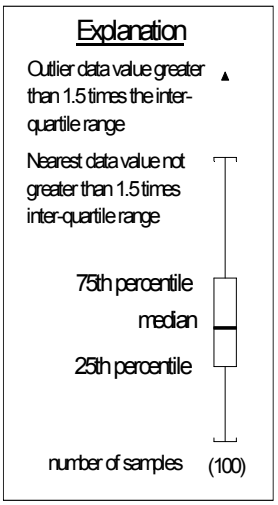
Appendix III - U. S. EPA 305(b) Tables . . . . . A 16

APPENDIX I
Box and Whisker Plots of Inorganic AGWMP Data

Table 3, pages 20-21 provides a summary of the aquifer geochemistry for the major aquifers in Ohio by providing values for the mean, median, maximum, minimum, etc. In order to provide a more complete view of the AGWMP data behind these summary values, Appendix I was generated. Appendix I provides a graphical view, in box and whisker plot format, of the entire inorganic data set of the Ambient Ground Water Monitoring Program. An explanation of the box and whisker plot graphic is provided in the box below.

All of the box plots are generated using the Major Aquifer breakout (carbonate, sandstone, and sand and gravel) as presented in Table 3. In addition, the box plots are presented in the same order and groupings as in Table 3: Field Parameters, Major Constituents, Trace Constituents, and Nutrients. The number of samples used to construct each box plot can be read directly from Table 3 by scrolling down to the parameter and Aquifer Type of interest, and then across to column seven (Number of Samples).

In some cases, the Y-axis is presented in log scale to enhance readability of the plots.
Box plots which appear without "boxes" (common in Trace Elements section) have too little data variability to generate 25th and 75th percentiles of the distribution (the upper and lower box bounds). In these cases, the boxes appear collapsed to the most common data point, typically the MDL. These collapsed boxes generally occur when the "Percent Censored" column of Table 3 is greater than 75 percent, indicating that the bulk of the data set was reported below the detection limit. In a few cases (chromium, copper, lead, and nickel), the AGWMP includes some low level data, so some data points are present below the normal detection limit.



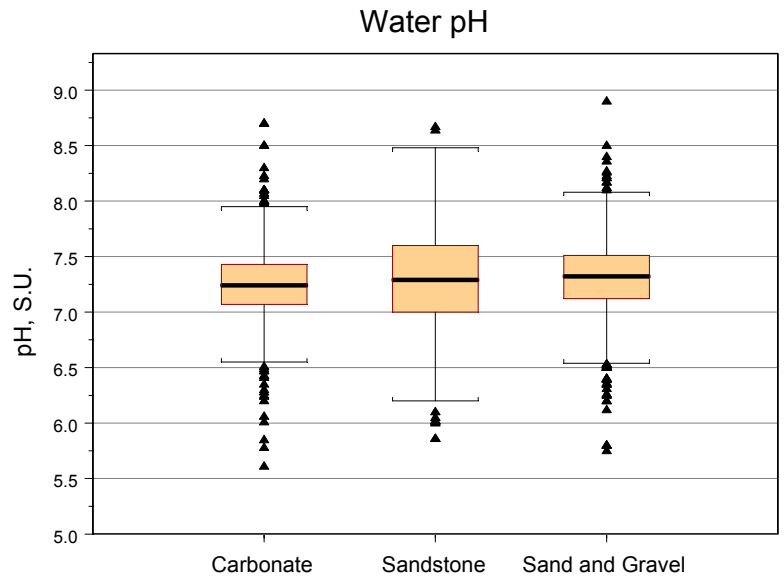
Box and Whisker Plots

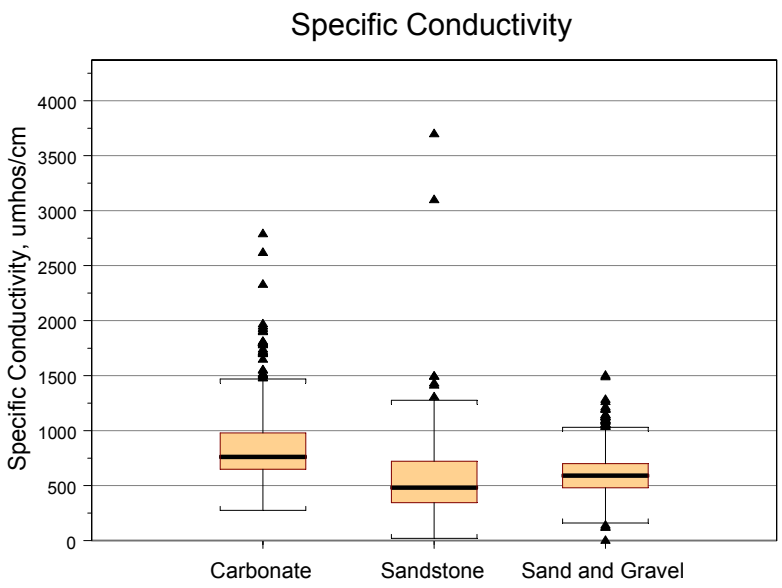
Box and Whisker Plots are an efficient graphical method for viewing how a data sets' individual points are distributed. The "box" itself outlines the range of half the data (the 25th to 75th percentiles, also called the Inter-Quartile Range, or IQR). The median, or 50th percentile, is indicated by a horizontal bar inside the box.

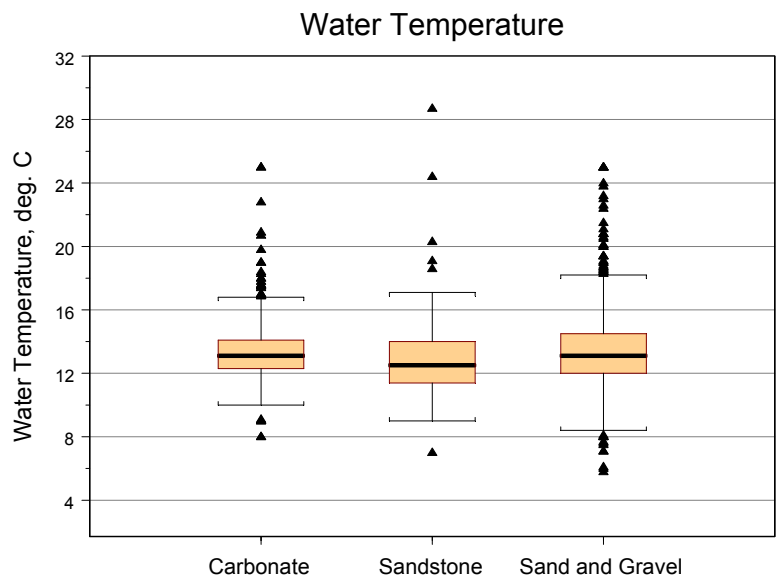
Two whiskers (vertical lines extending from the box) indicate the distance to the largest and smallest data points not defined as outliers. Outliers are defined as data points which exceed 1.5* IQR, and are identified by individual points above or below the whisker caps.

If the median is located mid-way between the top and bottom of the box, the data are normally distributed. Otherwise, an asymmetrical distribution exists.

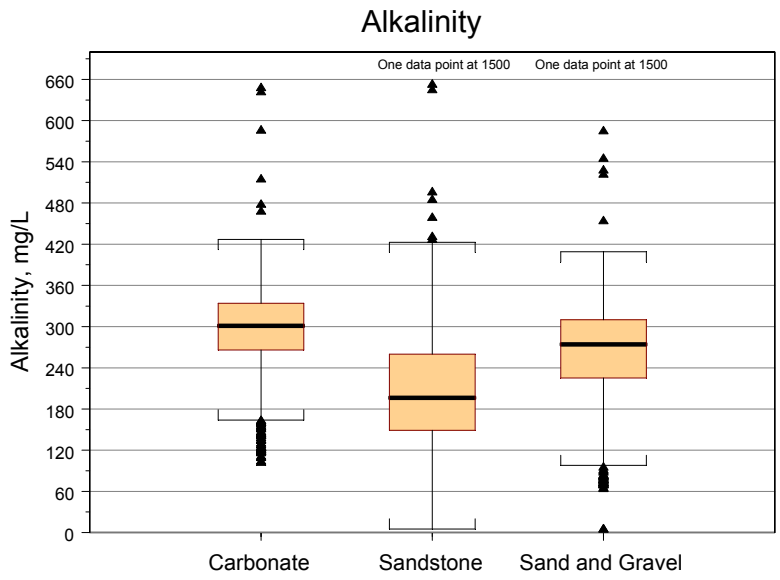
Field Parameters

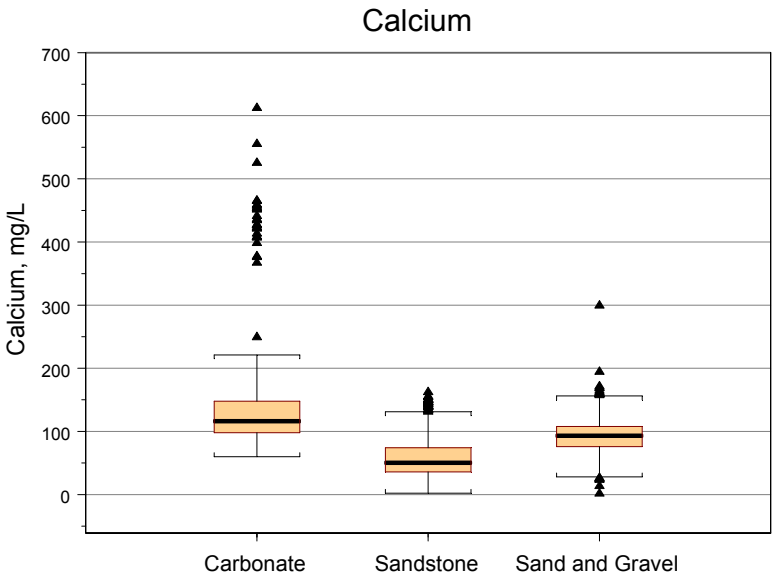


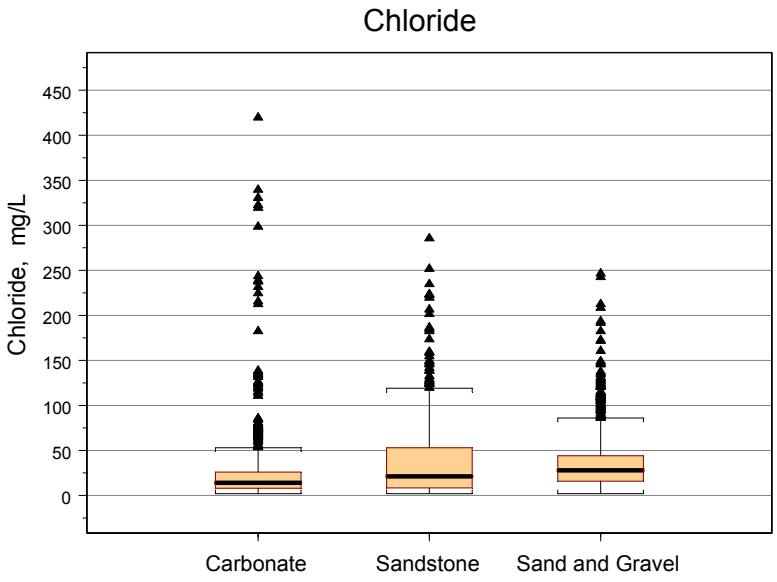


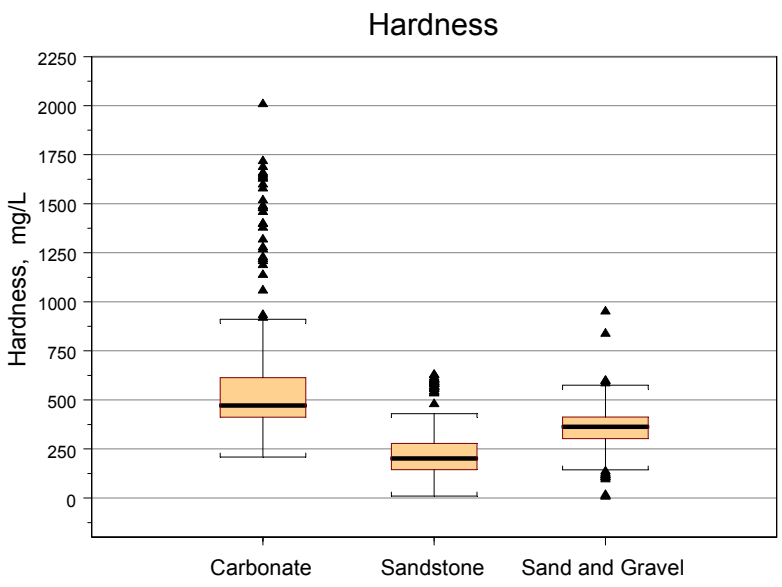


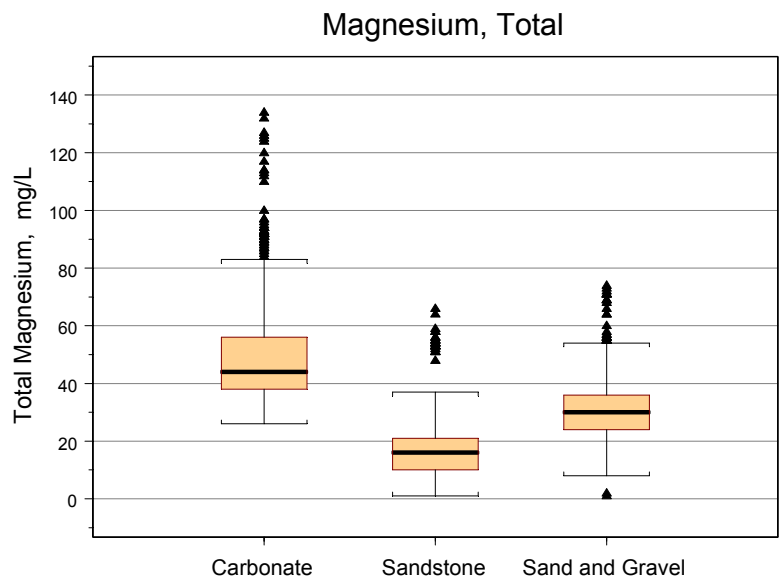
Major Constituents

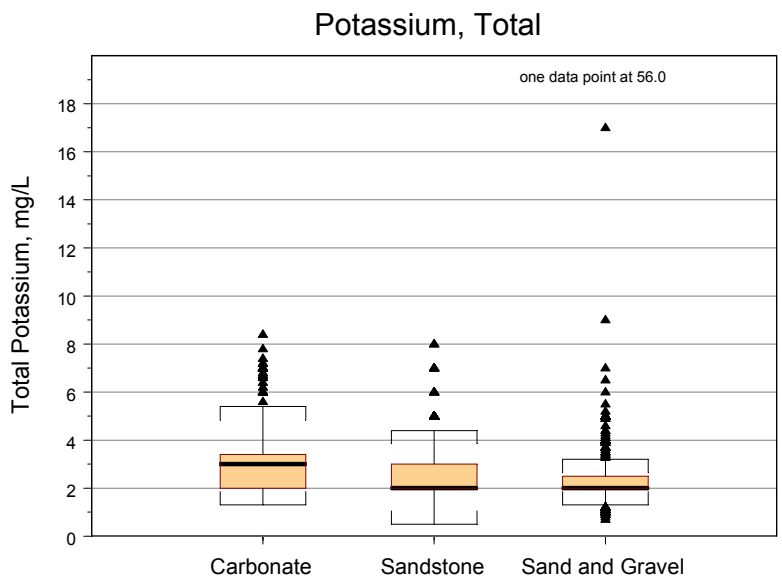


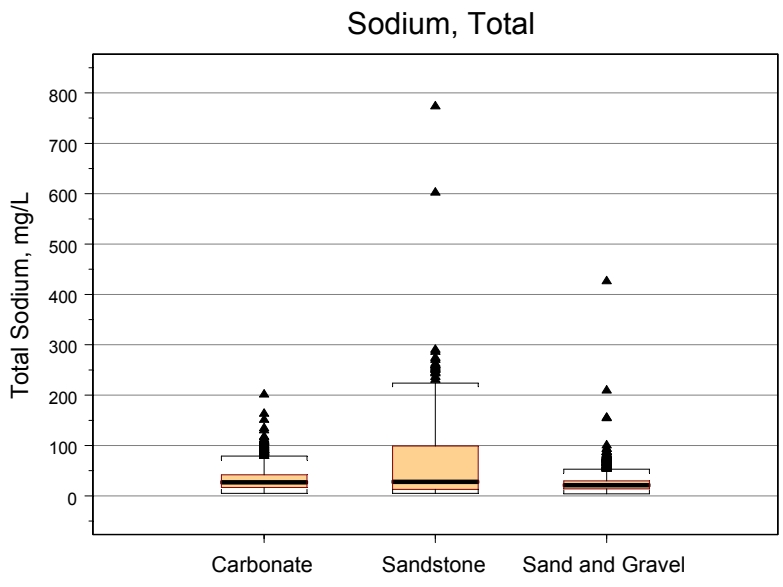


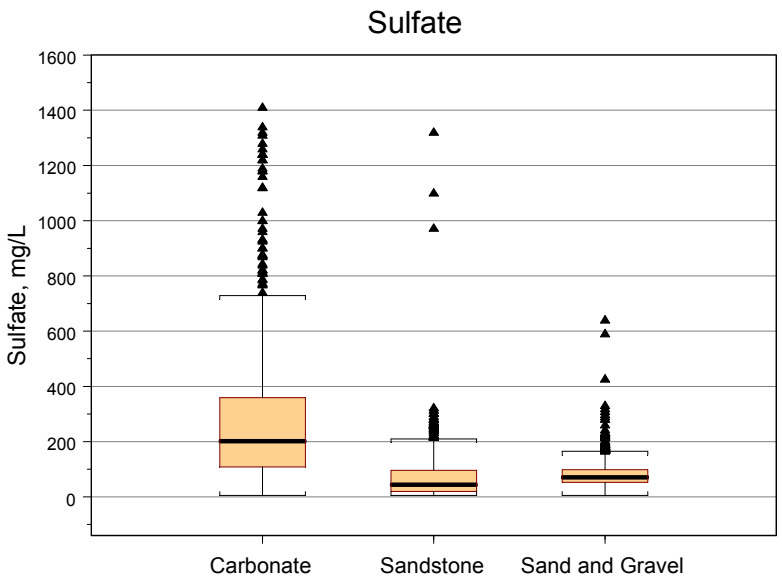


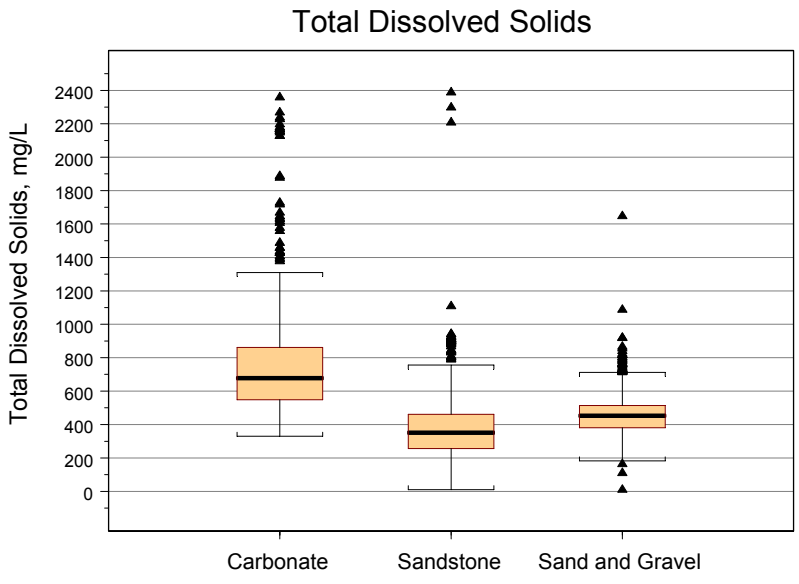

Hardness
Hardness, mg/L
2250
2000
1750
1500
1250
1000
750
500
250
0
Carbonate
Sandstone
Sand and Gravel


Magnesium, Total
Total Magnesium, mg/L
140
120
100
80
60
40
20
0
Carbonate
Sandstone
Sand and Gravel

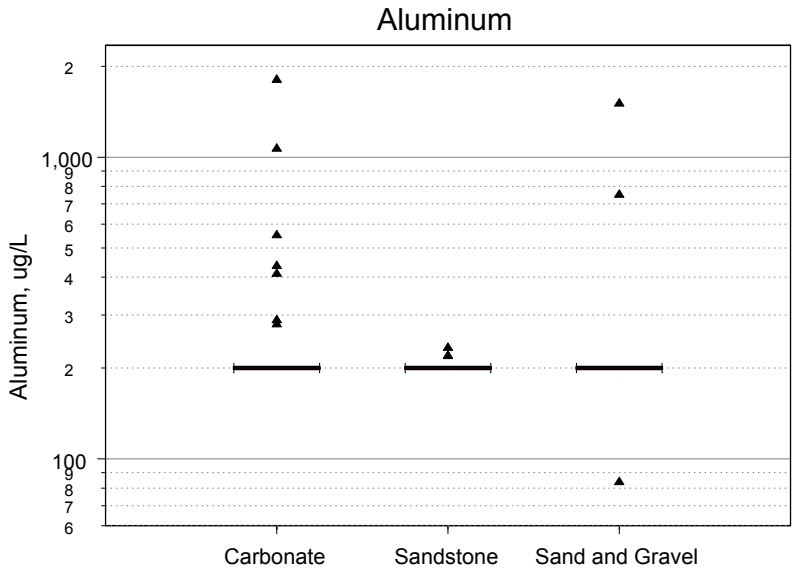

Potassium, Total
one data point at 56.0
Total Potassium, mg/L
18
16
14
12
10
8
6
4
2
0
Carbonate
Sandstone
Sand and Gravel

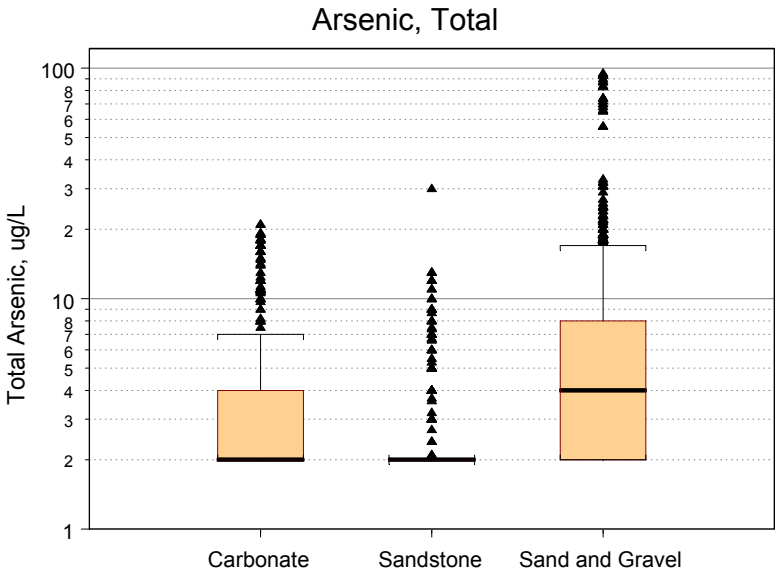

Sodium, Total
Total Sodium, mg/L
800
700
600
500
400
300
200
100
0
Carbonate
Sandstone
Sand and Gravel

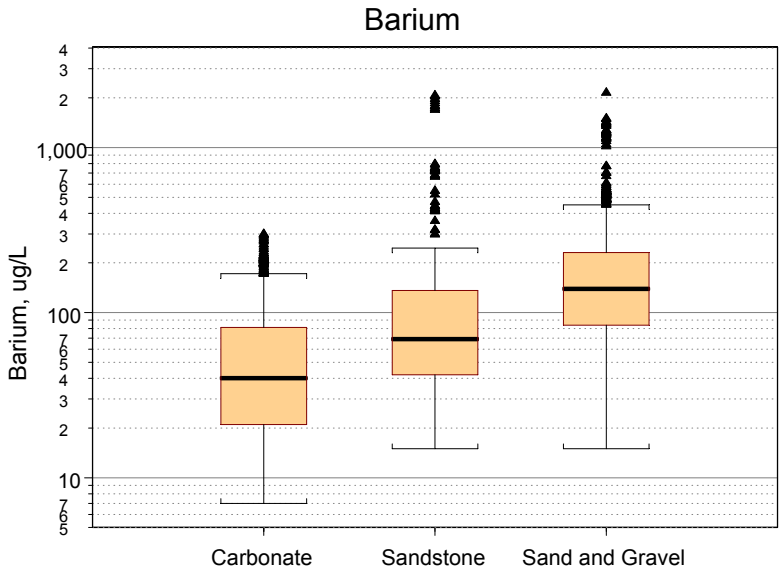

Sulfate
Sulfate, mg/L
1600
1400
1200
1000
800
600
400
200
0
Carbonate
Sandstone
Sand and Gravel

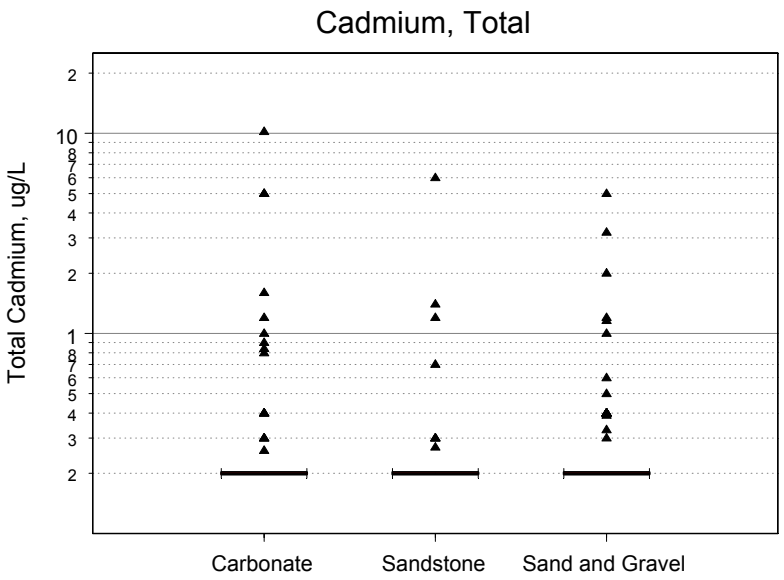

Total Dissolved Solids
Total Dissolved Solids, mg/L
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
Carbonate
Sandstone
Sand and Gravel

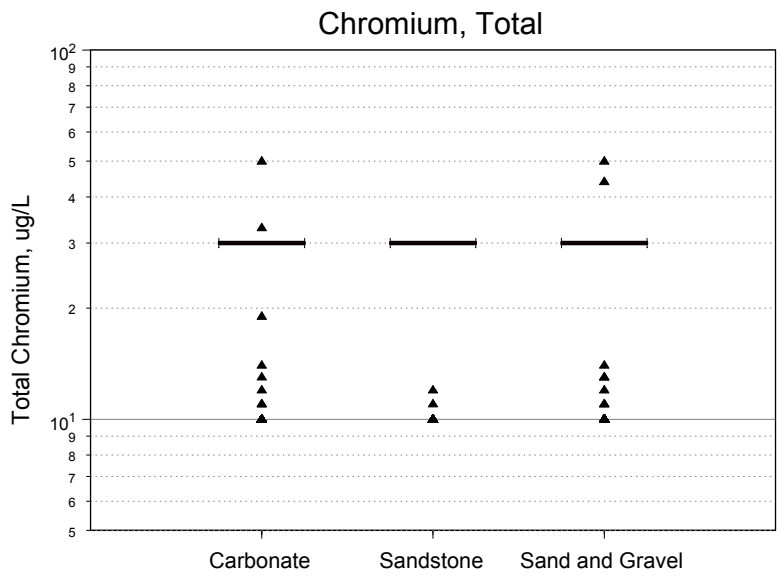
Trace Constituents

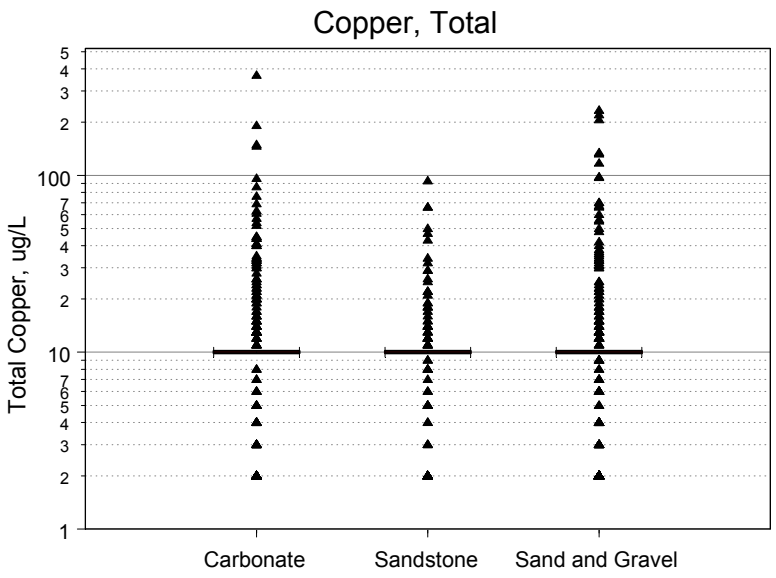


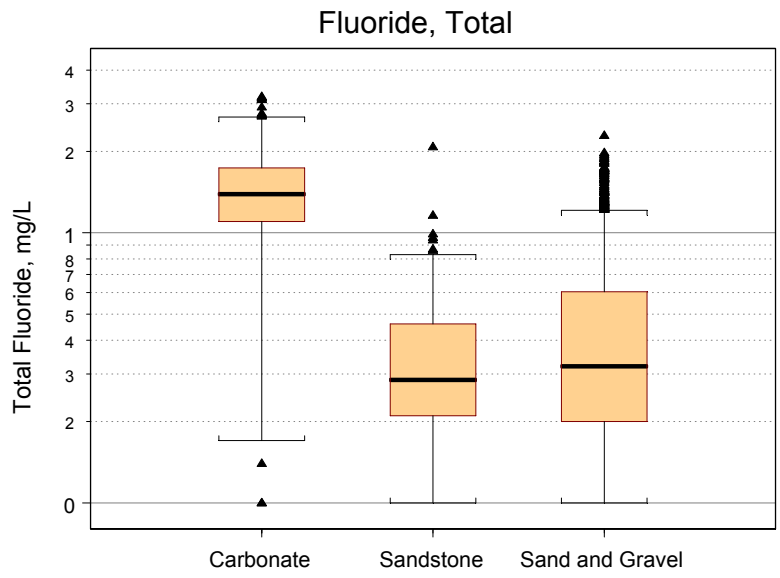


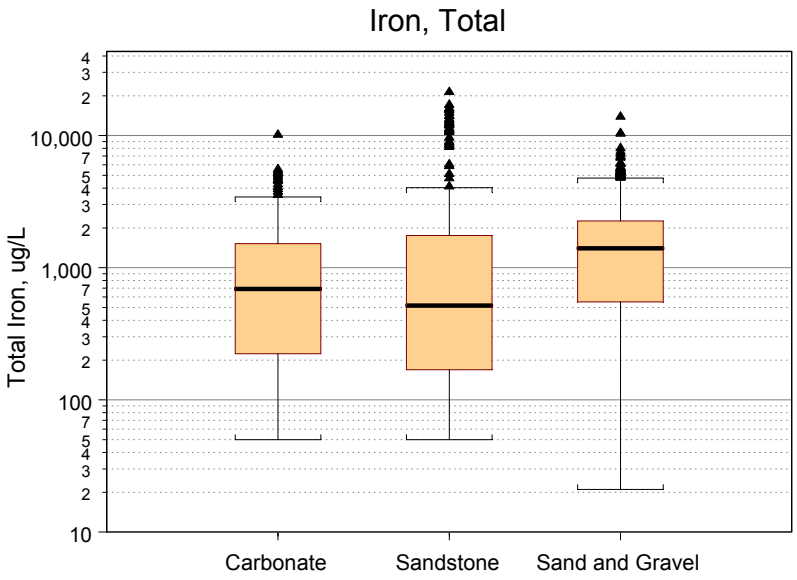


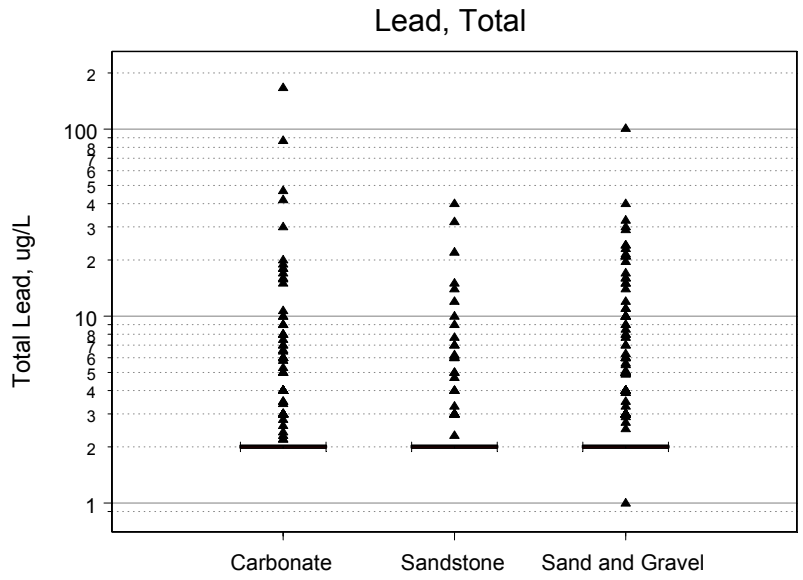

Cadmium, Total
Total Cadmium, ug/L
Carbonate
Sandstone
Sand and Gravel

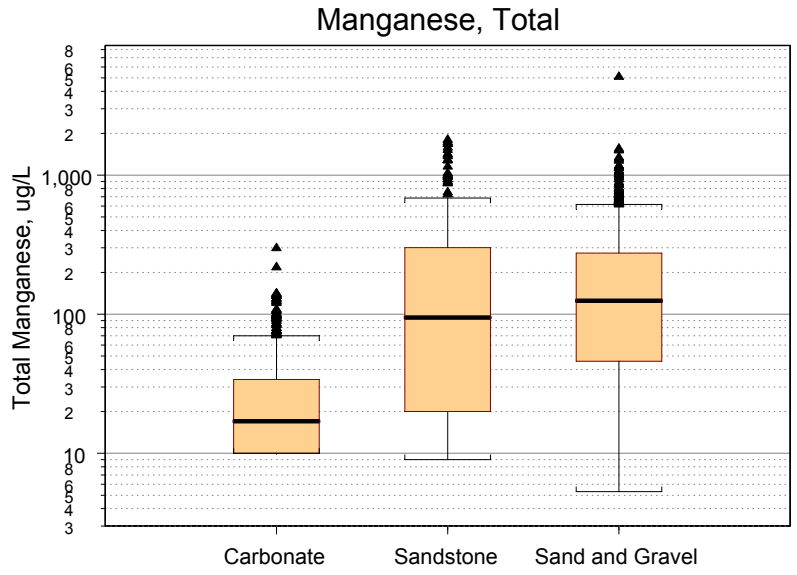

Chromium, Total
Total Chromium, ug/L
Carbonate
Sandstone
Sand and Gravel

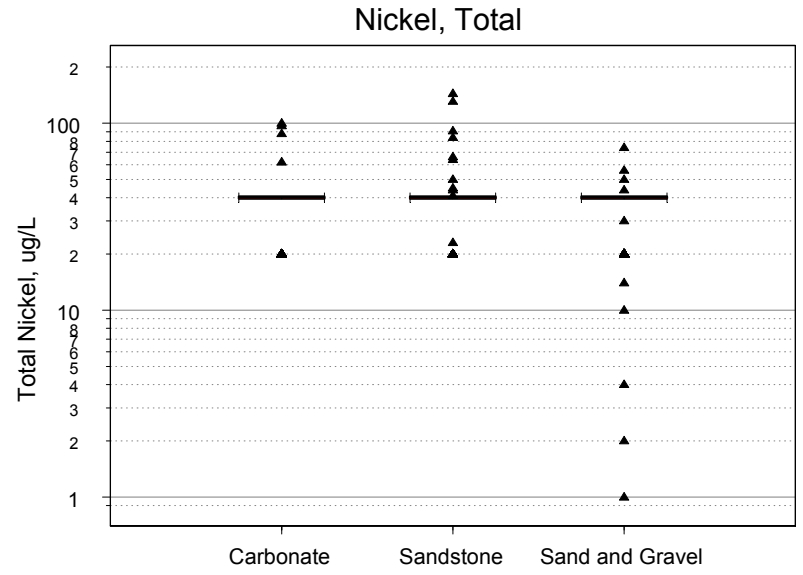

Copper, Total
Total Copper, ug/L
Carbonate
Sandstone
Sand and Gravel

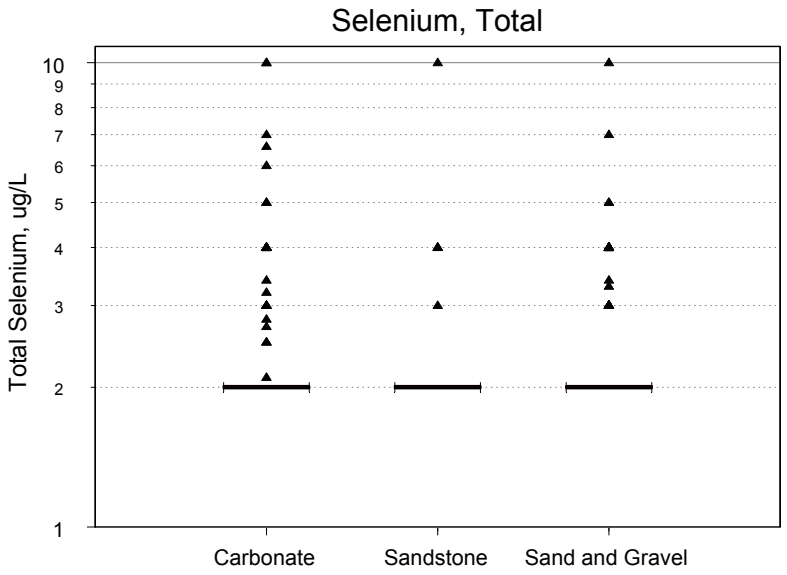

Fluoride, Total
Total Fluoride, mg/L
Carbonate
Sandstone
Sand and Gravel

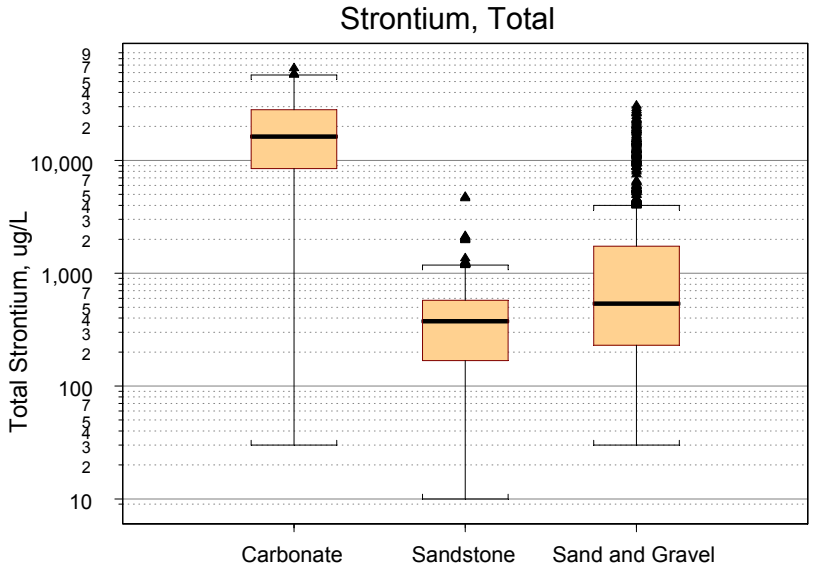

Iron, Total
Total Iron, ug/L
10,000
1,000
100
10
Carbonate
Sandstone
Sand and Gravel

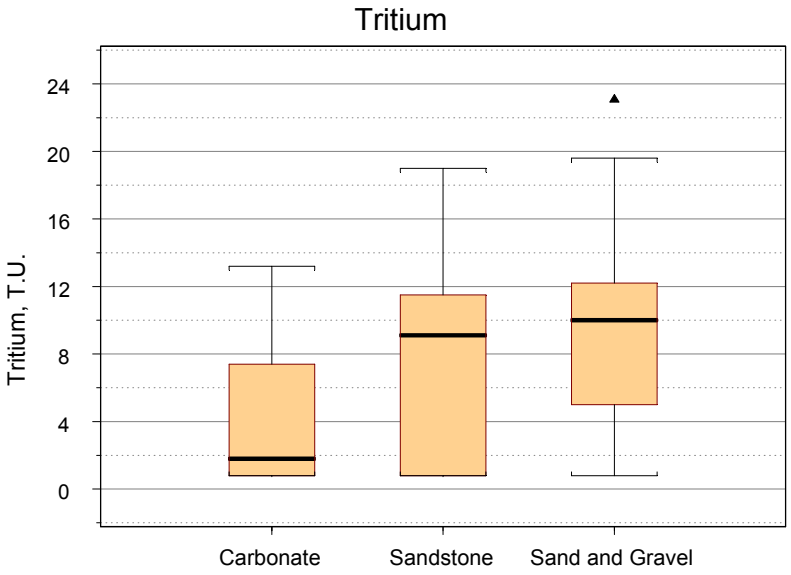

Lead, Total
Total Lead, ug/L
100
10
1
Carbonate
Sandstone
Sand and Gravel

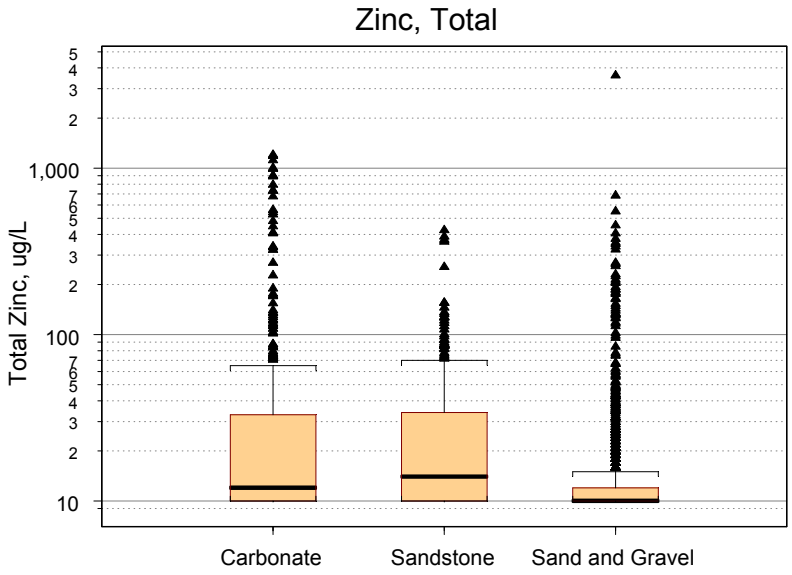

Manganese, Total
Total Manganese, ug/L
1,000
100
10
Carbonate
Sandstone
Sand and Gravel


Nickel, Total
Total Nickel, ug/L
100
10
1
Carbonate
Sandstone
Sand and Gravel

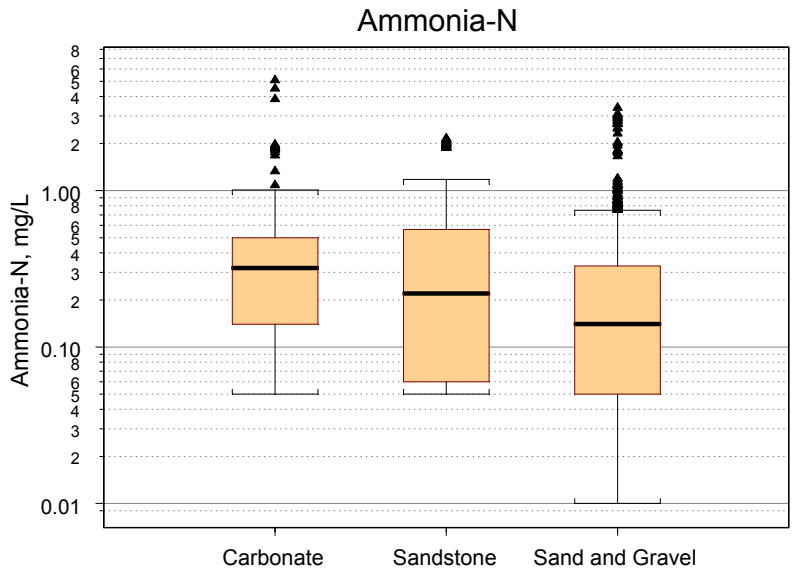

Selenium, Total
Total Selenium, ug/L
10
9
8
7
6
5
4
3
2
1
Carbonate
Sandstone
Sand and Gravel

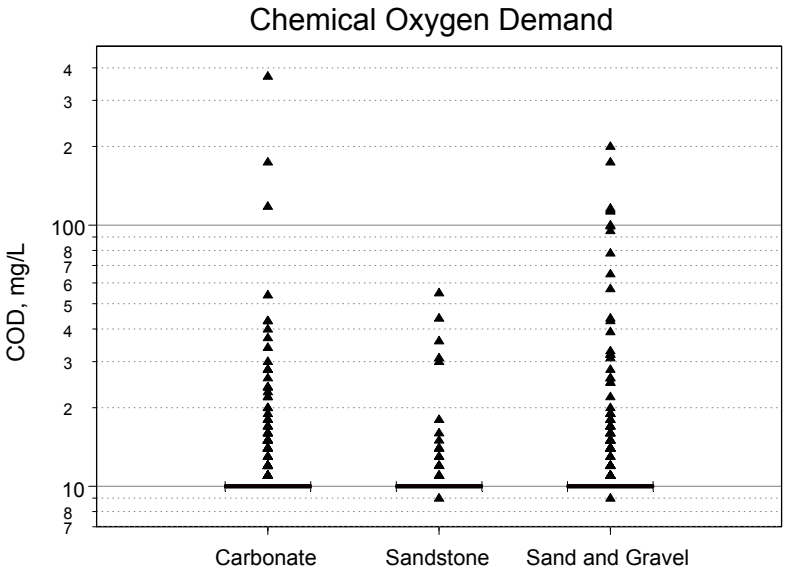

Strontium, Total
Total Strontium, ug/L
10,000
1,000
100
10
Carbonate
Sandstone
Sand and Gravel

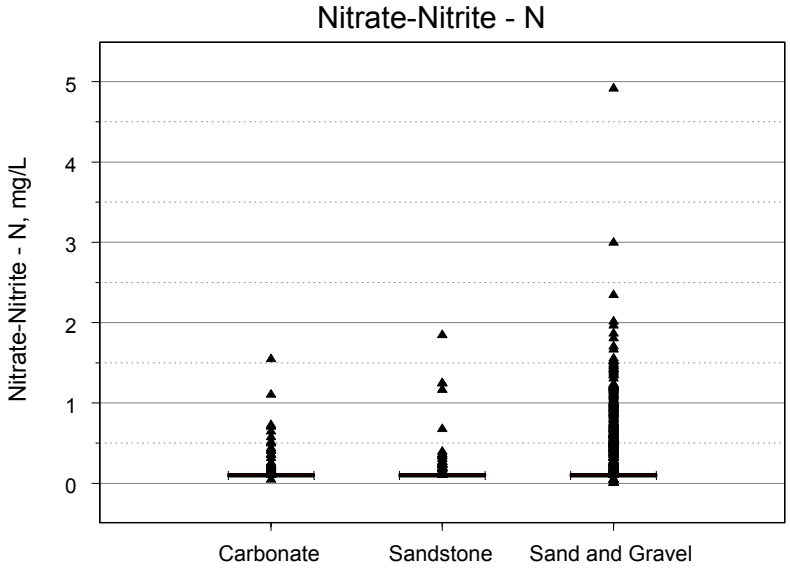

Tritium
Tritium, T.U.
24
20
16
12
8
4
0
Carbonate
Sandstone
Sand and Gravel

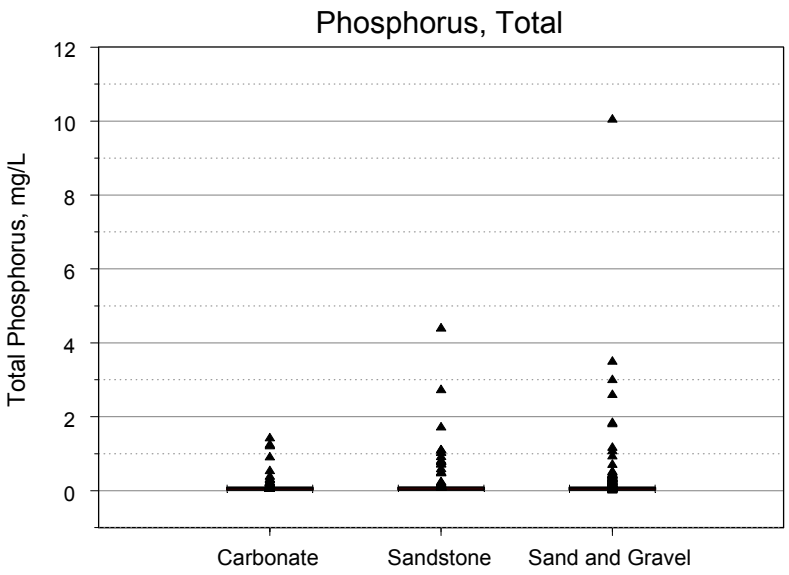

Zinc, Total
Total Zinc, ug/L
1,000
100
10
Carbonate
Sandstone
Sand and Gravel

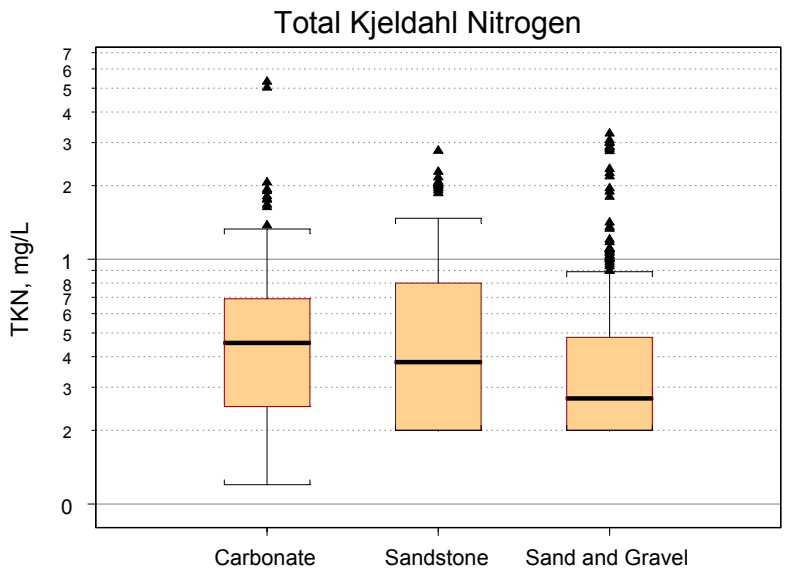
Nutrients

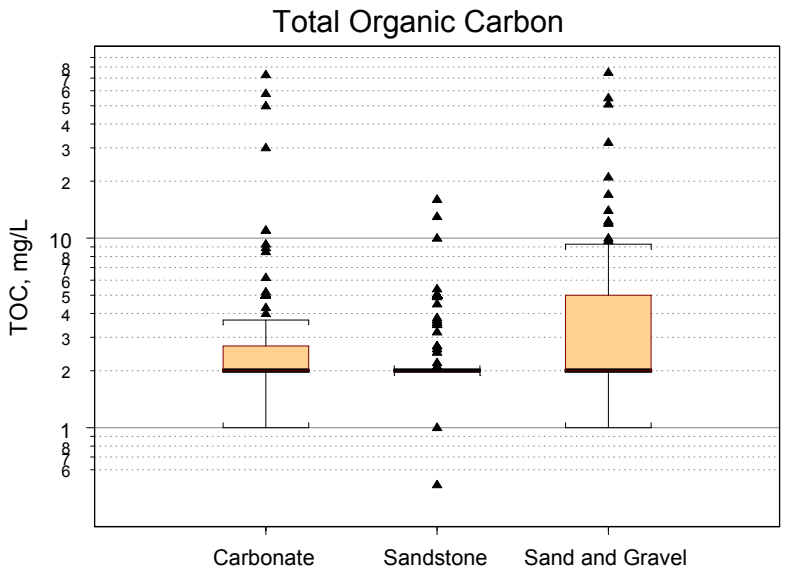

Ammonia-N
Ammonia-N, mg/L
1.00
0.10
0.01
Carbonate
Sandstone
Sand and Gravel


Chemical Oxygen Demand
COD, mg/L
100
10
Carbonate
Sandstone
Sand and Gravel


Nitrate-Nitrite - N
Nitrate-Nitrite - N, mg/L
5
4
3
2
1
0
Carbonate
Sandstone
Sand and Gravel


Phosphorus, Total
Total Phosphorus, mg/L
12
10
8
6
4
2
0
Carbonate
Sandstone
Sand and Gravel


Total Kjeldahl Nitrogen
TKN, mg/L
7
6
5
4
3
2
1
8
7
6
5
4
3
2
0
Carbonate
Sandstone
Sand and Gravel


Total Organic Carbon
TOC, mg/L
8
7
6
5
4
3
2
10
8
7
6
5
4
3
2
1
8
7
6
Carbonate
Sandstone
Sand and Gravel

Appendix II
NLCD Data Coverage for Ohio

The NLCD is a digital representation of continuous land use/land cover for the coterminous United States generated from 30-meter resolution Landsat thematic mapper (TM) satellite imagery data. The main classifications used in the NLCD are urban, agricultural, forested, and water, some of which contain several subclasses. The imagery was acquired by the Multi-Resolution Land Characterization Consortium (MRLC), a partnership of federal agencies that produce or use land cover data. Information provided here on the NLCD data for Ohio is summarized from the NLCD Web site: http://landcover.usgs.gov/.

The NLCD data coverages were generated through spectral mosaics and clusters of the TM data, followed by interpretation and labeling using aerial photos, and finally incorporating ancillary data sets to augment and refine the basic classification. To complete the analysis, a variety of accuracy assessments are performed to determine the number and magnitude of mis-classification errors. The data sources used for this coverage are listed below:

Base data set:
- Leaves-off Landsat TM data, nominal-1992 acquisitions.

Other ancillary data layers include:
- Leaves-on TM;
- Aerial Photos
- USGS 3-arc second Digital Terrain Elevation Data (DTED) and derived slope, aspect and shaded relief;
- Bureau of the Census population and housing density data;
- USGS land use and land cover (LUDA);
- National Wetlands Inventory (NWI) ;
- STATSGO soils information ;
- Ohio Wetland Inventory (OWI) data.

NLCD Land Cover Classification System

The NLCD Land Cover Classification System consists of 16 categories defining the main classes of agricultural, residential, commercial, and natural land covers (forested, wetland, grassland, open water, etc.) The 16 classes are listed in Table A-1.

Table A-1

NLCD Land Use/Land Cover Classification	
NLCD Land Cover Type	**Description**
Open Water	All areas of open water; typically 25 percent or greater cover of water (per pixel).
Low Intensity Residential	Includes areas with a mixture of constructed materials and vegetation. Constructed materials account for 30 to 80 percent of the cover. Vegetation may account for 20 to 70 percent of the cover. These areas most commonly include single-family housing units. Population densities will be lower than in high intensity residential areas.
High Intensity Residential	Includes highly developed areas where people reside in high numbers. Examples include apartment complexes and row houses. Vegetation accounts for less than 20 percent of the cover. Constructed materials account for 80 to100 percent of the cover
Commercial/Industrial/Transportation	Includes infrastructure (e.g. roads, railroads, etc.) and all highly developed areas not classified as High Intensity Residential.
Bare Rock/Sand/Clay	Perennially barren areas of bedrock, desert pavement, scarps, talus, slides, volcanic material, glacial debris, beaches, and other accumulations of earthen material.
Quarries/Strip Mines/Gravel Pits	Areas of extractive mining activities with significant surface expression.
Transitional	Areas of sparse vegetative cover (less than 25 percent of cover) that are dynamically changing from one land cover to another, often because of land use activities. Examples include forest clearcuts, a transition phase between forest and agricultural land, the temporary clearing of vegetation, and changes due to natural causes (e.g. fire, flood, etc.).
Deciduous Forest	Areas dominated by trees where 75 percent or more of the tree species shed foliage simultaneously in response to seasonal change.
Evergreen Forest	Areas dominated by trees where 75 percent or more of the tree species maintain their leaves all year. Canopy is never without green foliage.

Mixed Forest	Areas dominated by trees where neither deciduous nor evergreen species represent more than 75 percent of the cover present.
Grasslands/Herbaceous	Areas dominated by upland grasses and forbs. In rare cases, herbaceous cover is less than 25 percent, but exceeds the combined cover of the woody species present. These areas are not subject to intensive management, but they are often utilized for grazing.
Pasture/Hay	Areas of grasses, legumes, or grass-legume mixtures planted for livestock grazing or the production of seed or hay crops.
Row Crops	Areas used for the production of crops, such as corn, soybeans, vegetables, tobacco, and cotton.
Urban/Recreational Grasses	Vegetation (primarily grasses) planted in developed settings for recreation, erosion control, or aesthetic purposes. Examples include parks, lawns, golf courses, airport grasses, and industrial site grasses.
Woody Wetlands	Areas where forest or shrubland vegetation accounts for 25-100 percent of the cover and the soil or substrate is periodically saturated with or covered with water.
Urban/Recreational Grasses	Areas where perennial herbaceous vegetation accounts for 75 to 100 percent of the cover and the soil or substrate is periodically saturated with or covered with water.

Appendix III
U.S. EPA 305(b) Tables

The U.S. EPA 305(b) tables (Major Sources Of Ground Water Contamination, Ground Water Protection Programs, Ground Water Contamination Summary, Aquifer Monitoring Data) were not updated for the 2002 305(b) Report. The reader is referred to the 2000 305(b) Report Appendix for the most current tabulation of these tables. This report is available on the Web at:
http://www.epa.state.oh.us/ddagw/pdu/305b2k.pdf