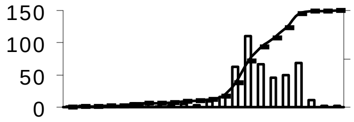
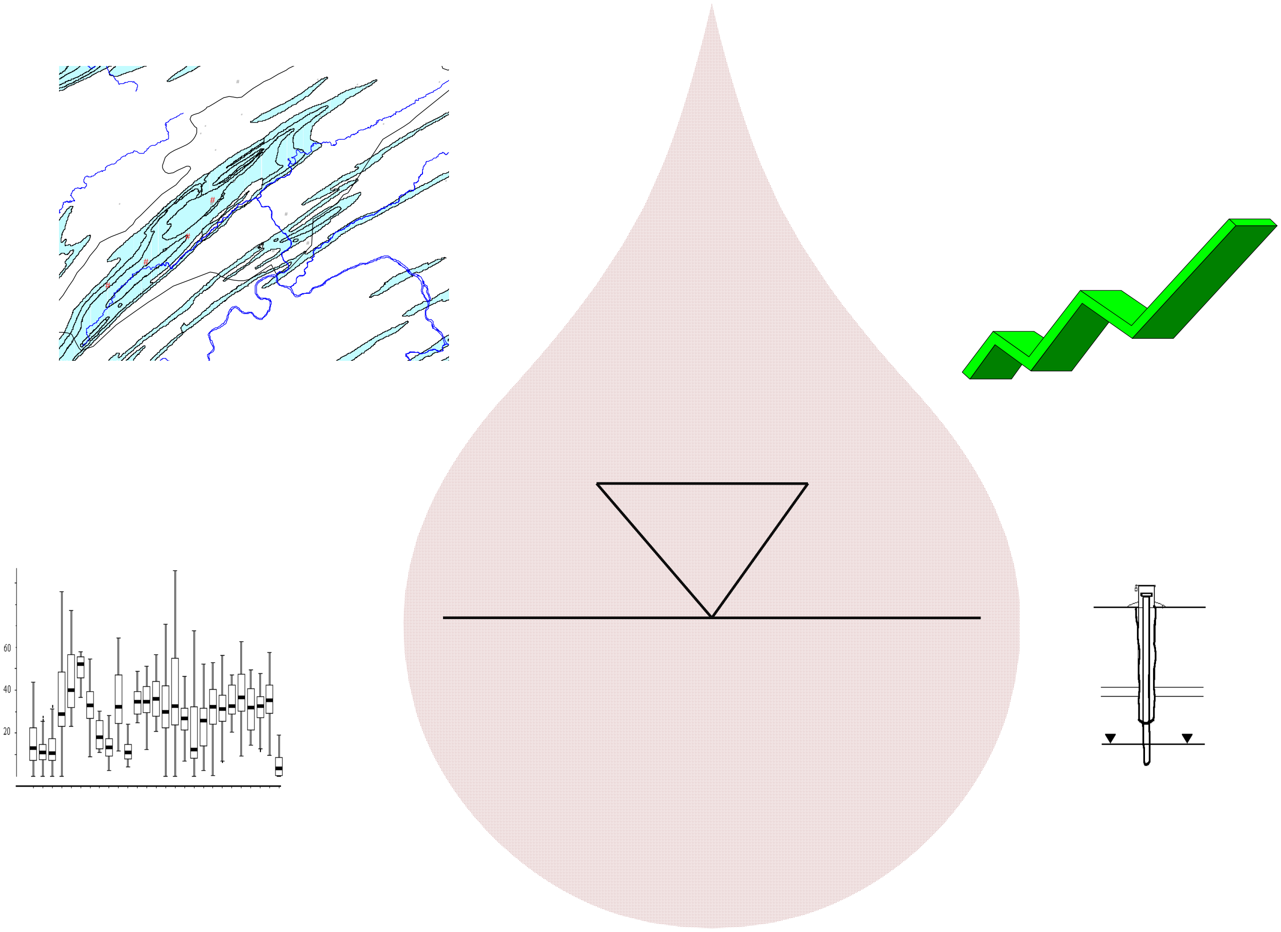
Commonwealth of Pennsylvania
Department of Environmental Protection
Bureau of Water Supply Management

Summary of Groundwater Quality Monitoring Data (1985 - 1997) from Pennsylvania's Ambient and Fixed Station Network (FSN) Monitoring Program

Selected Groundwater Basins in Southwestern, Southcentral and Southeastern Pennsylvania





Tom Ridge
Governor

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Secretary

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This manual and related information is available electronically via Internet. Access the DEP website at http://www.dep.state.pa.us (choose Information by Subject/Water Management)

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CONTENTS

APPENDIXES

EXECUTIVE SUMMARY

This report summarizes groundwater quality data collected under the Pennsylvania Department of Environmental Protection's (DEP) Fixed Station Network (FSN) and Ambient Survey groundwater monitoring program. The report covers data collected from 1985 to 1997 for selected groundwater basins, most of which are located in southcentral and southeastern Pennsylvania. Groundwater basins were selected based on a 1985 prioritization of basins. Monitoring points were typically homeowner wells or springs, and occasionally included untreated water from public water supplies and industrial wells.

Groundwater samples from 1,089 wells and springs were analyzed for 27 different analytes including basic inorganic constituents, nutrients and metals. Nearly 10,000 sample results were reviewed and compared to existing groundwater quality standards such as maximum contaminant levels. Water quality data from 940 of the monitoring points were analyzed based on lithology, land use types, and additional information such as well depth and geographic location. Land use descriptions and well depths for 149 monitoring points in the southwestern region of Pennsylvania were not collected.

Trend analysis was performed on water quality data from 475 monitoring points that were located in southcentral and southeastern Pennsylvania. The Kendall Tau nonparametric test was used to test for trends at the 95 percent confidence level.

The geographic extent of the sampling has been limited to selected basins in the southern half of the state. In general, the highest priority basins were sampled, based on the 1985 prioritization of Pennsylvania's 478 groundwater basins. The groundwater samples that were analyzed represent some of the top 100 priority basins. These basins were ranked as deserving a higher concern regarding groundwater quality.

Results indicate that groundwater quality is typically good. This is despite the sampling of high priority basins, which likely biases the data and presents a more negative picture of the overall groundwater quality of Pennsylvania. Some exceedances of drinking water standards are the result of naturally elevated concentrations of substances such as iron, total dissolved solids (TDS) and manganese or low pH. Concentrations and trends of some parameters such as nitrate, chloride and total hardness suggest that groundwater is being affected by human activities.

For pH, TDS, nitrate, iron, manganese and turbidity, 10 to 25 percent of the samples analyzed for each constituent exceeded groundwater quality (drinking water) standards. For the metals cadmium and lead, two to three percent of the samples exceeded their respective standards. For nitrite, chloride, sulfate, arsenic, barium, chromium, copper, zinc and mercury, less than one percent of the samples for each constituent exceeded an associated drinking water standard.

Groundwater quality is most obviously related to geology and land use. Other factors probably exert lesser influences that are often difficult to discern. Box plots were generated that show the range of concentrations by groundwater basin for each analyte.

The trend analyses suggest that groundwater quality is undergoing some change. Although natural shifts probably can account for some of the variation, it is most likely that human activities are affecting the groundwater quality on a regional scale. Analytes with upward trends at more than 10 percent of the 475 monitoring points that underwent trend analysis included alkalinity, TDS, nitrate, total hardness, calcium, magnesium, sodium, potassium and chloride. Analytes with downward trends at more than 10 percent of the 475 monitoring points included pH, nitrate, magnesium, chloride and sulfate.

Exact causes of the groundwater quality trends are difficult to determine. Different areas of the state are obviously under different stresses and only general inferences can be made from the data. The presence of natural shifts in groundwater quality (from precipitation trends or cycles) may have a background presence on some of the changes in groundwater chemistry. Nevertheless, notable downward trends in nitrate and sulfate at many monitoring points may be the result of the reduction in sources of nitrate from agricultural areas (fertilizers), onlot septic systems and atmospheric deposition. Increases in TDS, chloride, calcium, potassium, total hardness and sodium at many monitoring points may be the result of increased nonpoint source pollution such as road salting and sprawling paved developments and suburbs.

1. INTRODUCTION

1.1 PURPOSE OF THE REPORT

The purpose of the report is to summarize data that have been collected for selected groundwater basins under the Fixed Station Network (FSN) and Ambient Survey groundwater monitoring program. Various factors of regional groundwater quality are reviewed as geographic and temporal trends in groundwater quality are assessed. Data are compared to water quality standards and differences are examined based on land use, rock type, and well depth and flow path.

The monitoring program is an ongoing project that continues to sample groundwater basins. The data presented in this report depict groundwater quality for specific portions of the state. Appendix 1 lists the status of the groundwater basins that have been sampled since 1985.

1.2 IMPORTANCE OF GROUNDWATER IN PENNSYLVANIA

The amount of groundwater in the United States at any given moment is 20 to 30 times greater than the amount of water in all of the lakes, streams and rivers. In Pennsylvania, groundwater is extremely important. At least 28 percent of Pennsylvanians depend on self-supplied groundwater as their main supply of water for domestic needs. When community and noncommunity water systems are included in a tally of groundwater users, the percentage of Pennsylvanians that use groundwater is nearly 50 percent.

Groundwater is an important component of water in a watershed, and contributes a major portion of flow to surface streams and rivers. In times of drought, groundwater flow provides nearly all of the sustaining baseflow to streams and rivers. High quality groundwater is essential to all users, which include public water suppliers, industrial facilities, agricultural operations and domestic users.

1.3 GROUNDWATER MONITORING EFFORTS IN PENNSYLVANIA

Monitoring of groundwater quality in Pennsylvania is usually done near a permitted facility to determine the impacts of the facility on groundwater or to monitor as a safeguard for a public water supply well. In either case, the monitoring is limited to the immediate area around a permitted facility.

DEP's Bureau of Water Supply Management conducts a monitoring program of homeowner wells or springs and occasionally untreated water from public water and industrial supplies. It is the only DEP program that monitors the ambient or general background groundwater quality on a watershed basis. U.S. Environmental Protection Agency (EPA) groundwater grants support the program.

Two combined programs (Ambient Surveys and FSN monitoring) are used to monitor the general quality of groundwater. These programs are described in a DEP document (DEP, 1997a). The FSN program involves the sampling of selected groundwater basins over an extended period of time. The FSN program was designed to allow for evaluation of the groundwater resources of the state. Data collected are used to 1) determine the general background quality of the groundwater resources; 2) monitor for changes in groundwater quality; and 3) generate statistical reports and assessments of sample results and trends. FSN sampling can contribute to an understanding of long-term water quality trends, and can be used to gather information on the impact of land management practices on groundwater quality. An ambient survey is conducted the same way; however, only two groundwater samples are collected per monitoring point (over one year). Both monitoring programs were designed to provide a measure of regional (background) groundwater quality at sampling locations that are unaffected or minimally affected by obvious, specific point sources of contamination in the immediate vicinity.

The U.S. Geological Survey and the Bureau of Topographic and Geologic Survey (Pennsylvania Geological Survey) of the Pennsylvania Department of Conservation and Natural Resources have traditionally developed reports on groundwater topics across the state. Most of these studies have been a "snapshot" of water quality, focusing on the existing water quality of an area without considering longer term trends. Nevertheless, such reports serve as invaluable sources of information on regional water quality issues. This report is intended to publish additional groundwater information collected under the ambient and FSN monitoring program, including information on long term water quality trends for some selected areas.

1.4 HISTORY OF THE FSN/AMBIENT MONITORING PROGRAM

Groundwater basins were delineated in a report by Lehigh University (Lehigh University, 1982). “Groundwater basin” was defined as a “physiographic unit containing a system of interconnected aquifers forming a significant ground-water reservoir.” Basins were delineated based on the stream map compiled by H.W. Higbee, who divided his surface water map into 104 basins having an average area of 435 square miles. The Lehigh University report concluded that the groundwater basin boundaries generally correspond to boundaries drawn on the basis of surface water movement. Local situations such as where excessive pumping occurs close to a boundary, or where mineral resource extraction activities alter local flow paths may result in areas where the surface and groundwater divides do not coincide.

From 1982 - 1985, the FSN monitoring program was designed as summarized in the 1985 *Proposal for a Ground-Water Quality Monitoring Program in Pennsylvania* (DER, 1985). In 1985, the proposal and further delineation of the groundwater basins to 478 basins were completed.

The 478 groundwater basins were prioritized based on:
- groundwater use (using state water plan reports),
- potential unmonitored sources of groundwater pollution based on county land use,
- environmental sensitivity, based on geology and groundwater quality (using the statewide TDS map from the 1980 Source Impoundment Assessment study (PADER, 1980)).

The prioritization process resulted in the high priority basins being located in the more populated, southern half of the state. Early goals for the program included the establishment of FSN monitoring for the top 50 basins in priority. Resource constraints and scarce sampling points in populated areas limited program growth.

In 1988, the Ambient Survey program was initiated to monitor additional areas (lower priority basins from priority 51 to 100 out of the 478 groundwater basins) with a limited sampling approach. To reach more areas of the state and to provide for more flexibility for DEP’s regions, the program was updated in June 1997 (DEP, 1997a).

The first samples were collected in 1985. By December 1997, 1,089 monitoring points had been sampled and their data placed on the U.S. EPA “STORET” system (Figure 1). Of these monitoring points, 649 are from FSN basins and 440 are from ambient surveys. FSN monitoring points that were established in 1985 have been sampled up to 30 times.

Monitoring in the southwest part of the state was discontinued in 1989 because of resource constraints. This area accounts for 139 FSN monitoring points and 10 monitoring points that were categorized as ambient. These monitoring points were not analyzed for trends or with regard to land use, which was not reported.

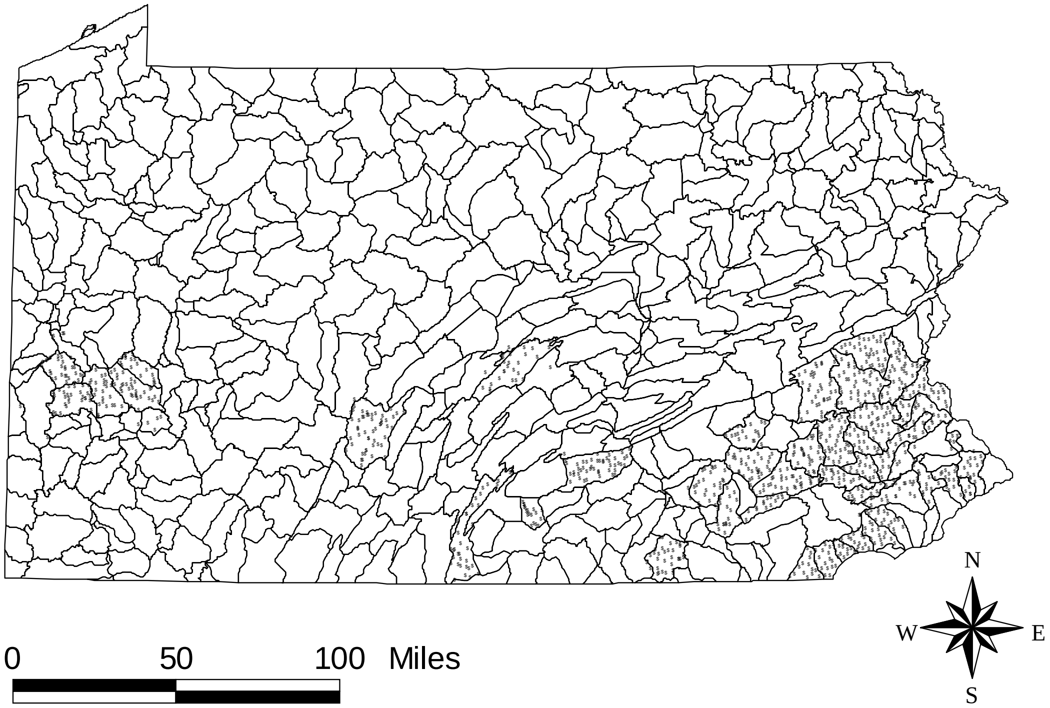
The monitoring program has included the analysis for 27 analytes per groundwater sample (except for basins in southwestern Pennsylvania, which were sampled for 24 analytes). The analytical results have been placed on the EPA STORET (STOrage and RETrieval) database.

1.5 LIMITATIONS OF THE PROGRAM

The program has historically focused on the higher priority basins. Most of the groundwater basins (especially the northern half of the state) have not been sampled. The program has recently switched emphasis to ambient surveys (limited time sampling) to cover additional areas of the state. This change has come at the expense of some of the FSN basin studies (southcentral and northeast regions), which were terminated to allow resources for the ambient surveys.

Appendix 1 lists the basins that have been sampled in the groundwater monitoring program, along with the status for each basin. Maps are included to show the location of the ambient and FSN basins. Most of the basins that have undergone trend analysis are located in the southeastern portion of the state.

Figure 1. Location of groundwater network monitoring points across Pennsylvania.



2. FACTORS OF GROUNDWATER QUALITY

Groundwater quality can be a result of a complex mix of many interrelated factors. In general, factors can usually be divided into two categories: natural and man-made. Natural variations in regional groundwater quality have been attributed to influences such as climate, soil, geologic formation, and groundwater flow path. Man-made influences are attributed to various activities such as mining and agriculture.

Groundwater quality in Pennsylvania shows wide ranges of natural quality. Table 1 lists concentration ranges in natural groundwater (Driscoll, 1986; RE Wright Associates, 1982a and 1982b). The USGS, in a study on the corrosive characteristics of groundwater, found wide ranges of natural groundwater quality that lead to widely varying levels of corrosiveness (Langland and Dugas, 1995). For example, groundwater in carbonate rocks tends to have a high pH, and elevated concentrations for total hardness, calcium, and magnesium. Groundwater in crystalline rocks such as gneiss and schist tends to have a lower pH, and lower concentrations of TDS and total hardness.

Table 1. Natural concentrations of selected constituents in groundwater.

Analyte	Natural Concentration
pH	Typically ranges from 5.5 - 8.5.
TDS	Ranges from 100 to several thousand mg/L.
Hardness	Typically less than 150 mg/L; carbonate aquifers may exceed 300 mg/L.
Nitrate	Up to 10 mg/L; greater than 3 mg/L typically indicates human activity.
Calcium	Typically range is 2 to 100 mg/L.
Sodium	Typically ranges from 10 - 100 mg/L.
Potassium	Usually less than 10 mg/L.
Chloride	Average concentration is 6 mg/L; usually less than 20 mg/L.
Sulfate	Generally 5 to 50 mg/L.
Silica	Ranges from 1 to 30 mg/L.
Iron	Typically less than 500 ug/L.
Manganese	Typically less than 200 ug/L.
Turbidity	Little natural turbidity except possibly in carbonate rocks.
Heavy metals	Typically less than 10 ug/L.

Low TDS values have been associated with mountainous, forested areas and quartzitic sandstones (DER, 1980). High TDS values have been associated with populated industrial areas and the Pennsylvania coal mining regions. Carbonate rocks typically have TDS concentrations ranging from 250 to 500 mg/L. Less commonly, TDS concentrations (and possibly turbidity in carbonate aquifers) can be naturally elevated in groundwater. Shallow groundwater with concentrations of TDS of greater than 10,000 milligrams per liter (mg/L) is rare in Pennsylvania. Naturally elevated concentrations of iron and manganese are found at some locations in Pennsylvania (Taylor and others, 1982). Such natural characteristics tend to be controlled by the geology.

Human activities often affect the groundwater quality through land use and disposal activities such as coal and other resource mining, farming, industrial operations, urban development, waste disposal, materials storage, deicing application and storage, and oil and gas development. Atmospheric deposition of some constituents may add appreciable amounts to the groundwater. The USGS (Risser and Siwiec, 1996) summarizes common contaminants in groundwater in the Lower Susquehanna Valley. The U.S. EPA (EPA, 1990 and EPA, 1994) has published detailed summaries of potential sources of groundwater contamination.

The following discussion summarizes factors that may influence the groundwater quality.

2.1 ATMOSPHERIC DEPOSITION

Groundwater ultimately begins with precipitation that infiltrates the ground to the saturated zone. Precipitation in Pennsylvania has a pH ranging from 4.0 to 4.3, which could be characterized as a dilute, aqueous solution of sulfuric and nitric acids (DEP, 1997b). More acidic water (related to lower pH) will dissolve more substances that it contacts. The buffering capacity of rocks typically raises the pH to varying degrees based on the composition of the soil and rocks.

Sulfate and nitrate are two substances that can be significantly added to the groundwater from the atmosphere. Other substances may be added to the groundwater from the atmosphere but probably at negligible concentrations. The USGS (Puckett, 1997) reported that “the deposition of nitrogen from the atmosphere can be a major source of nitrogen.…” Concentrations of sulfate and nitrate for Greene County in southwestern Pennsylvania as reported by the USGS (Stoner and others, 1987) were 3.5 mg/L and 0.39 mg/L, respectively. Mean annual concentrations of nitrate and sulfate for Pennsylvania in 1996 were 2.098 mg/L for sulfate 2.053 mg/L (DEP, 1997b). A study by the Environmental Resources Research Institute of the Pennsylvania State University (Nizeyimana and others, 1997) indicated atmospheric deposition accounted for nearly 38 percent of the contributions of nitrogen to the groundwater of the state.

DEP’s Bureau of Air Quality reported that sulfate concentrations from air deposition have declined across the state since 1983 by nearly 28 percent (DEP, 1997b). Air deposition of nitrate concentrations also have decreased by approximately eight percent across the state since 1983 (DEP, 1997b). Considering these percentages, the mean annual concentration ranges in atmospheric deposition and in groundwater, and the amount of precipitation that infiltrates to the groundwater, it is unlikely that changes in atmospheric deposition have had a significant role in the changes in groundwater quality.

2.2 INFILTRATION

Approximately 30 percent of precipitation enters the groundwater system. Although groundwater recharge can occur at any time of the year, on average, the most significant groundwater recharge occurs in October through November and March through April. Frozen ground in the winter and evapotranspiration by plants in the summer usually lessen recharge during these seasons.

In general, precipitation infiltrates a layer of regolith (the mantle of unconsolidated material) to fractures and joints of the bedrock. About ninety-nine percent of the Commonwealth is underlain by consolidated rocks. The main porosity components of these rocks are fractures, joints and other secondary features. Primary features of porosity (space between individual grains of rock) are generally less important in Pennsylvania. The dominance of secondary porosity features in the rocks often results in multiple groundwater bearing zones for a well. This contributes to complex geochemical characteristics of the groundwater that is sampled from a well.

The chemical weathering of soil and rock by infiltrating acidic waters largely controls the concentrations of ions in groundwater. The soil chemistry, texture, porosity and fracturing of the soil are typically related to the geology. The soil thickness and other physical characteristics can have a major effect on the groundwater vulnerability to pollution sources.

2.3 GEOLOGY

The geology of Pennsylvania is very diverse and is reflected in the large number of geologic formations. The USGS lists over 647 different geologic units for the state. Monitoring points covered in this study account for 104 different units.

“Siliciclastic” rocks (includes sandstone, siltstone, shale, and conglomerate) underlie 87 percent of the state. Carbonate rocks (limestone and dolomite) and crystalline rocks (igneous and metamorphic rocks) underlie about six percent each of the state. Less than one percent of the state is underlain by unconsolidated sediments, which include glacial or river deposits.

Using the broad categories of carbonate, crystalline, siliciclastic and unconsolidated rocks; what is the mineral composition of the rocks that groundwater encounters? This largely controls the chemistry of the groundwater. In general, the acidic water reacts with the minerals of the rocks and the major ions and trace elements are dissolved into the water. The geologic formations through which the groundwater travels relate to the amount of material dissolved in the water. Because the chemistry of the rocks is variable, groundwater quality likewise is variable as it develops an imprint of the rock it flows through.

The presence of secondary porosity will be controlled by several factors including the previous tectonic stresses of the area, the fabric of the rock and the rock’s composition. Carbonate rocks stand out as unique, because they are susceptible to varying degrees to dissolution. Limestone and dolomite may form sinkholes, solution channels, and caverns. In Pennsylvania, almost all carbonate rocks will exhibit some dissolution. Resulting flow patterns can be very complicated; flow depends on the degree of interconnection of the joints, fractures, and solution openings (small and large), the hydraulic gradient and geologic barriers.

The amount and type of fractures can affect the groundwater chemistry. Groundwater in carbonate rocks with large openings will respond quickly to precipitation events. Groundwater levels can rise very rapidly during and following precipitation. The groundwater chemistry may exhibit wide fluctuations in major ion chemistry. Also, in such an aquifer, the groundwater chemistry tends to be undersaturated with the normal constituents of carbonate rocks. There is likely to be a higher variability in the groundwater chemistry where groundwater flow is less diffuse (i.e. through solution openings). This same principle applies to a lesser degree to fractured flow in other rock types.

A rock unit that is well fractured may be thoroughly connected to the surface. In most rock types, the percentage of fractures decreases with depth. Most of the groundwater in the study basins of this report occurs in fractured rock. And most fractures typically occur less than 300 to 500 feet below the surface. The complexity of the fracture network often results in a semi-confined condition of the groundwater. Some fractures are connected to the atmosphere whereas others are not, giving the appearance of confined groundwater. Because of fracture patterns, two wells drilled adjacently to one another may encounter water at greatly varying depths and thus varying chemistries. Truly confined aquifers with specific confining units are less common.

Groundwater in carbonate rock areas has been shown to be susceptible to contaminants (Risser and Siwiec, 1996; Fishel and Lietman, 1986). However, other fractured rocks and permeable unconsolidated deposits with a high water table and a thin, permeable cover of soil can be highly susceptible to groundwater contamination.

2.4 FLOW PATH AND WELL DEPTH

Although groundwater may be present anywhere to 20,000 feet below the surface, it is most often accessed with wells less than 1,500 feet deep, and usually by wells that are less than 500 feet. Most of groundwater flow is in shallow (less than 300 feet) flow systems.

The depth to the groundwater table in Pennsylvania is typically less than 100 feet. The water table is most often a replica of the surface topography. In a study of the Lower Susquehanna Basin, the USGS (Risser and Siwiec, 1996) concluded that most of the groundwater flow is shallow through short, local flow systems. The median value for the depth to groundwater was found to be about 20 feet in a valley and 45 feet on a hill.

The location of groundwater within the flow system is an important factor in the groundwater chemistry. The residence time of groundwater will influence the quality of groundwater. Groundwater that has a longer flow path will tend to be more mineralized. For example, Wood (1980) reported that sulfate concentrations were likely related to the contact time of groundwater with rock (i.e. the flow path duration). The residence time depends mainly on the flow system and on the hydraulic nature of the rock.

Shallow wells and springs will typically intercept younger, less mineralized groundwater. A deeper well may intersect shallow and deeper zones of groundwater and therefore mix younger and older water. Regional areas of groundwater discharge may represent older, well-traveled groundwater that will contain higher concentrations of dissolved materials. This will be true especially where groundwater has traveled in a deep flow path toward the discharge point. Alternately, groundwater in a recharge area or in a very shallow, short flow path will tend to have fewer dissolved constituents.

Shallow wells are more likely to have higher concentrations of nitrates (Mueller and others, 1996). However, areas of permeable soils and rocks may allow high nitrate concentrations to exist in deep wells.

2.5 LAND USE

Human activities at and below the surface of the land have been shown in many instances to affect the groundwater quality. The monitoring points in this report were grouped into broad categories of land use: agricultural, urban, residential, residential with septic, and forest. Land use categories were assigned to monitoring points by field observation of the surrounding predominant land use.

A particular land use can place an imprint on the groundwater quality. For example, a heavily farmed region will typically provide a source of nutrients and dissolved solids into the groundwater. High nitrate concentrations have been linked with agricultural land use (Mueller and others, 1996; Ator and Ferrari, 1997). Forest areas are typically associated with low nitrate concentrations.

A dense residential area may generate contaminants by runoff from paved areas. An unsewered area with many homes on septic systems may affect the groundwater quality by adding nitrates and chloride. Other common dissolved constituents can be influenced by land use (Blickwedel and Wood, 1988). Undisturbed forest land may provide for a more steady, uncontaminated groundwater quality.

Road salts have been used to clear roads for decades; however, large amounts of salt have been increasingly used in the past decade. The increase in the use of road salt in Pennsylvania, especially during the 1990s, comes because of an increased demand for clear roads in the winter. Less anti-skid material is now used and salt is the material most commonly applied for winter maintenance of roads.

Several hundred thousand tons of road salt are typically used across Pennsylvania each year (Pennsylvania Department of Transportation, 1998). For example, the Pennsylvania Department of Transportation’s (DOT) District 6 (which includes Bucks, Chester, Delaware, Montgomery and Philadelphia counties) has applied an average of over 60,000 tons of road salt per year on state highways from 1992 to 1997 (DOT, 1998). By area, this is approximately 25 tons of salt per square mile. However, this does not include deicing for roads maintained by municipalities or airports. Areas with a high density of roads would tend to have higher amounts of salt that could reach the groundwater.

Average application rates in the northeastern United States range from about five to 20 tons per lane mile per year (Transportation Research Board, 1991). Road salting adds sodium and chloride ions to groundwater. Calcium and magnesium ions may be added from calcium magnesium acetate (although its use in Pennsylvania is limited), or from calcium chloride solutions, which are used as pre-wetting solutions for salt application. Cation exchange of sodium with ions in soil and rock such as magnesium, calcium and potassium may add these and other ions to groundwater.

The Pennsylvania Geologic Survey (McElroy, 1988) reported that coal mining has affected concentrations of sulfate, TDS and magnesium within one-quarter mile of mining operations in Fayette County in Southwestern Pennsylvania. Acid mine drainage was shown to produce groundwater that is very hard with elevated concentrations of iron, manganese, sulfate, TDS, calcium, magnesium, and zinc, and possibly lead, nickel, cadmium and chromium. Unmined areas in Fayette County were found to have little impact on groundwater quality.

Assessment of the effect of land use on groundwater quality is somewhat limited. Misclassification or changing land uses can affect any correlations. Regional trends may overshadow a specific land use surrounding a monitoring point. However, land use may produce a general effect on groundwater that can be seen in the sampling data.

3. CHANGES IN GROUNDWATER QUALITY

Changes in water quality through time further complicate the chemistry. After determining the main factors of groundwater quality, one can consider why groundwater quality might change. Pennsylvania has long been a populated, industrial and agricultural state with large areas of forest. Some factors like the geology will not appreciably change. Potentially influencing factors include changes in land use and activity, in atmospheric deposition, and natural cycles caused by the level and intensity of precipitation (Pettyjohn, 1976 and 1982). Such factors may account for some shifts in groundwater quality.

For example, what variation in groundwater quality might accompany the switch from farmland to a suburb? And how long does it generally take for a land use change to affect the groundwater quality? Answers to such questions are likely affected by site-specific features such as soil cover, depth to water, geologic formation, and the degree of disturbance of the land surface and surface hydrology. It is well known that certain settings pose greater vulnerability to groundwater contamination from human activities. A thin soil cover underlain by highly fractured, permeable rock offers little protection to the groundwater. Such areas tend to respond quickly to land use changes and stresses. For example, if a residential area replaces a farming area in a carbonate rock area with a thin soil cover, groundwater use will likely soon show characteristics of this change. One of the unintended results of this may be an improvement of the groundwater quality with respect to nitrate. On the other hand, nonpoint source pollution such as road salts, parking lot runoff, etc. may actually increase (Sloto, 1987).

Many demographic changes have occurred during the last 30 years including population growth and urban expansion into the countryside. Pennsylvania has the fourth largest highway system in the United States and these roads require winter maintenance. The increased use of deicing chemicals since the 1950s is potential source of ions like sodium, chloride, calcium and magnesium to the groundwater.

The most common changes in water quality include nitrate and chloride. Nitrate is a constituent in fertilizers, human and animal wastes, and the atmosphere (examples of sources include septic systems, animal feedlots and industrial emissions). Chloride is a constituent of human, animal and industrial wastes, and deicing operations (examples of sources include saline water zones, landfills and road salting).

Large pumping wells may alter groundwater flow paths on a local or regional scale. Changes in flow direction may be large enough to draw in groundwater with much different chemistry from other areas or deeper aquifers.

4. OVERVIEW OF MONITORING POINTS

During the design of a groundwater basin, the DEP hydrogeologist divides the basin into wedges of probable groundwater flow using topographic maps. Monitoring points for each wedge are chosen to be representative of the geology and land use of each wedge. The selection of a monitoring point also considers other factors such as well construction, well depth and groundwater flow directions. Monitoring points with obvious point sources of contamination are avoided. A DEP guidance document (DEP, 1997a) details the procedures used to select monitoring points, which are typically homeowner wells or springs.

The sampling program has generated 1,089 monitoring points with groundwater quality information. Of the 1,089 monitoring points, 178 are springs. The main focus of this report is on the 940 monitoring points in southcentral and southeast Pennsylvania. This includes 430 ambient and 510 FSN types. Monitoring points collected in the southwest region are included in the discussion of groundwater quality in comparison to standards.

By DEP region, Table 2 shows the geographical distribution of the type of the 1,089 monitoring points. The monitoring points are also categorized by lithology (Table 3). The 940 monitoring points in southcentral and southeastern Pennsylvania are grouped into land use types (Table 4). Table 5 shows the distribution of monitoring points by rock type for the 940 monitoring points. Table 6 includes the categorization of rock type for each groundwater basin.

Table 2. Categorization of monitoring points by DEP region.

DEP Region	Total	FSN	Ambient
Northeast (Wilkes-Barre)	112	112	0
Southcentral (Harrisburg)	433	166	267
Southeast (Conshohocken)	395	232	163
Southwest (Pittsburgh)	149	139	10
Total	1,089	649	440

Table 3. Categorization of the monitoring points by rock type.

Rock Type	Number	Percentage
Carbonate (limestone and dolomite)	272	25.0
Siliciclastic (sandstone, siltstone, conglomerate)	574	52.7
Crystalline (slate, schist, gneiss, granitic rocks)	232	21.3
Unconsolidated sediments (alluvial deposits)	11	1.0
Total	1,089	

Table 4. Categorization of the 940 basin monitoring points by land use.

Land Use Type	Number	Percentage
Agriculture (includes orchards, pasture, feedlots, etc.)	313	33.3
Forest	205	21.8
Residential (includes golf courses)	155	16.5
Residential with septic	216	23.0

Urban (includes commercial services, industrial)	28	3.0
Unreported	23	2.4

Table 5. Categorization of the 940 basin monitoring points by rock type.

Rock Type	Number	Percentage
Carbonate (limestone and dolomite)	272	28.9
Siliciclastic (sandstone, siltstone, conglomerate)	436	46.4
Crystalline (slate, schist, gneiss, granitic rocks)	232	24.7

Forty-six established groundwater basins are represented by the 1,089 monitoring points; 20 are ambient basins, 26 are FSN basins. For the 940 monitoring points, 20 ambient and 22 FSN basins are represented.

For this report, broad land use categories were used that include those listed in Table 4. Some specific land uses were lumped into these categories because they were reported only a few times. Golf courses were included under “residential.” The reported land uses of “commercial services,” “industrial” and “barren land” were included in the “urban” category. “Orchards,” “mushroom,” feedlot and “pasture” were included in the “agriculture” category. Land use data were not reported for the monitoring points in the Southwest DEP region.

Table 6. Categorization of the 1,089 basin monitoring points by rock type.

Basin	34	35	36	37	38	39	44	45	49	51	53	55	56	57	58	59	60	61	62	63
carbonate	26	11	27	2	0	0	0	1	11	3	13	0	0	0	6	1	0	0	0	0
crystalline	1	0	1	11	6	2	6	0	3	6	0	9	10	2	16	16	2	1	0	0
siliciclastic	9	24	13	12	13	6	10	5	27	19	6	2	10	14	17	21	12	22	8	2
unconsolidated	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Basin	64	65	68	69	71	74	75	77	78	153	154	176	180	190	192	193	194	198
carbonate	11	5	0	0	0	0	0	0	0	13	23	11	2	16	17	13	16	0
crystalline	2	2	17	17	14	13	16	8	6	0	0	0	26	2	0	1	1	15
siliciclastic	10	7	0	0	0	0	0	5	2	5	24	15	4	2	1	19	16	0
unconsolidated	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Basin	261	278	303	382	383	384	477	478	others	Total
carbonate	14	12	18	0	0	0	0	0	0	272
crystalline	0	0	0	0	0	0	0	0	0	232
siliciclastic	40	18	16	20	31	17	34	28	11	574
unconsolidated	0	0	0	5	3	1	0	2	0	11

5. ANALYTES

Groundwater samples were analyzed by the DEP Bureau of Laboratories for 27 analytes as shown in Table 7. Data analysis results of the 27 analytes may be compared to any applicable groundwater standards (Safe Drinking Water Act drinking water standards or the Land Recycling and Environmental Remediation Standards Act, known as Act 2 of 1995, remediation standards) as listed in Table 7.

To keep sample analysis at a reasonable cost, organic constituents (except for total organic carbon (TOC)) and the bacteriological quality of the groundwater were not sampled. The TOC analysis serves as a screening tool for volatile organic compounds that might be present.
Groundwater samples are collected using program quality assurance/quality control guidelines. The quality assurance work plan is described in a DEP document (DEP, 1998).

Table 7. Analytes of the monitoring program.

Analyte	Abbreviation	Units	Standard	Comments
1. pH	pH	pH units	6.5-8.5 (s)	CO_3, HCO_3, OH, PO, Si raise pH; Acids, salts, CO_2 lowers pH.
2. Total Alkalinity ($CaCO_3$)	Alk	mg/L	None	Increased alkalinity often evident if pH > 7.
3. Total Filterable Residue	TDS	mg/L	500 (s)	>1000 mg/L may cause corrosion; >2500 mg/L changes Act 2 cleanup standard value
4. Total Ammonia Nitrogen	NH_3-N	mg/L	None	Typically adsorbs to soil particles.
5. Total Nitrite Nitrogen	NO_2-N	mg/L	1 (m) 1 (a)	Very limited concentrations in natural waters because it is highly reactive.
6. Total Nitrate Nitrogen	NO_3-N	mg/L	10 (m) 10 (a)	Oxidized form of N; natural ranges of 0.1-10 mg/L. Subject to seasonality.
7. Total Phosphorus	P	mg/L	None	Normal concentrations in natural water average a few tenths of a mg/L.
8. Total Organic Carbon	TOC	mg/L	None	General indicator of organic contamination.
9. Total Hardness ($CaCO_3$)	TH	mg/L	None	USGS classification of hardness (mg/L): <60, soft water; 61-120, moderately hard; 121-180, hard; > 180 mg/L, very hard.
10. Total Calcium	Ca	mg/L	None	Combines with SO4, HCO3 to form scale.
11. Total Magnesium	Mg	mg/L	None	Combines with SO4, HCO3 to form scale.
12. Total Sodium	Na	mg/L	None 20 (gl)	Typically in groundwater at 10-100 mg/L.
13. Total Potassium	K	mg/L	None	Concentrations seldom reach 20 mg/L; brines may exceed 100 mg/L.
14. Total Chloride	Cl	mg/L	250 (s)	> 500 mg/L gives a salty taste.

			250 (as)	Elevated values may be from sewage or industrial sources. Subject to seasonality.
15. Total Sulfate	SO_4	mg/L	250 (s) 500 (a)	Sources: oxidized pyrite and gypsum; igneous, metamorphic rocks; typically <100 mg/L.
16. Total Silica	SiO_2	mg/L	None	1-30 mg/L concentrations common; >1000 mg/L possible in brines.
17. Total Arsenic	As	ug/L	50 (m) 50 (a)	Associated with metal sulfides, clay minerals, and organic deposits. Eastern U.S. coals average 10 ppm. (pec).
18. Total Barium	Ba	ug/L	2000 (m) 2000 (a)	Barite is source of Ba; most barite vein deposits associated with limestone; range is 0.7-900 ug/L. (pec).
19. Total Cadmium	Cd	ug/L	5 (m) 5 (a)	Diverse sources: zinc sulfide ore; limestone; metamorphosed sedimentary rocks. (pec).
20. Total Chromium	Cr	ug/L	100 (m) 100 (a)	Rarely in trivalent form in potable water; range is 3-40 ug/L. (pec).
21. Total Copper	Cu	ug/L	1000 (s, a) 1300 (al)	Water with 1000 - 2000 ug/L imparts an objectionable taste. (pec).
22. Total Iron	Fe	ug/L	300 (s) 300 (as)	More than 0.1 mg/L may precipitate on exposure. 1-5 mg/L is common. (pec).
23. Total Lead	Pb	ug/L	15 (al) 5 (a)	Natural water seldom has values > 5ug/L. (pec).
24. Total Manganese	Mn	ug/L	50 (s) 50 (as)	Similar in behavior to Fe; values >.05 mg/L may precipitate upon oxidation; concentrations may reach 2-3 mg/L. (pec).
25. Total Zinc	Zn	ug/L	5000 (s) 2000 (a)	Range is .06-7 mg/L. May be associated with Pb and Cd because of galvanized iron and brass plumbing. (pec).

Analyte	Abbreviation	Units	Standard	Comments
26. Total Mercury	Hg	ug/L	2 (m) 2 (a)	Even though Hg is rare, its volatility tends to cause a wide dispersion. (pec).

27. Turbidity (laboratory)	Turb	NTU	0.5-1.0 (ps)	Caused by suspended and colloidal matter.

(a) Act 2 cleanup standard: medium specific concentration in “use” aquifer.
(as) Act 2 secondary contaminant cleanup standard: medium specific concentration.
(m) U.S. EPA Maximum Contaminant Level (MCL) for public drinking water supplies.
(s) U.S. EPA Secondary Maximum Contaminant Level (SMCL) for public drinking water supplies.
(al) U.S. EPA Action Level for public drinking water supplies.
(gl) U.S. EPA guidance level for public drinking water supplies.
(pec) Act 2 constituent of potential ecological concern.
(ps) U.S. EPA performance standard.

6. DATA SUMMARIES

6.1 SUMMARY STATISTICS

Groundwater basin locations are shown in the maps of Appendix 1. Appendix 2 summarizes the data by groundwater basin. The water quality data shown in Appendix 2 are the averages of monitoring point medians for the basins. Forty-six basins are listed. “Less than detected" values were used as real numbers in the calculation of these statistics. This obviously provides for some bias in the statistics. Table 8 shows the percentage of nondetects, which were calculated using approximately 500 more samples than the number used for the exceedance tables that follow in the report and appendixes. These approximate percentages should be considered when reviewing the data statistics, especially for the metals.

Table 8. Percentage of nondetects by analyte.

Analyte	N	Percentage	Analyte	N	Percentage	Analyte	N	Percentage
pH	10,419	0.0%	Ca	10,419	0.3%	Cd	7,239	97.7%
Alk	10,390	0.0%	Mg	10,418	0.5%	Cr	7,245	99.4%
TDS	10,402	0.3%	Na	10,418	0.1%	Cu	7,238	33.3%
NH_3	10,407	72.5%	K	10,419	3.7%	Fe	10,417	19.7%
NO_2	10,417	80.6%	Cl	10,419	0.2%	Pb	7,246	76.1%
NO_3	10,422	10.5%	SO_4	10,419	10.5%	Mn	5,498	67.5%
P	5,492	27.5%	Si	5,472	0.1%	Zn	7,238	38.6%
TOC	7,244	82.3%	As	7,243	93.7%	Hg	7,139	98.6%
TH	10,417	2.6%	Ba	7,242	12.5%	Turb	10,410	75.0%

Box plots (Appendix 3) were generated for the 27 analytes by basin. All monitoring points and samples by basin are included for each box, which depicts the 25th through 75th percentiles of data. Box plots can be compared to the information in Table 6, which summarizes a basin’s monitoring points by rock types. The box plots mix data from whatever rock types are included within a groundwater basin.

6.2 SUMMARY BY LAND USE

Table 9 summarizes the data from the 940 monitoring points by land use for specific lithologies. The monitoring points are categorized by lithology, and then by reported land use. Concentrations shown are averaged median values from each monitoring point.

Table 9. Averaged median values for the different land uses by rock type.

Carbonate rocks	Count	pH	Alk	TDS	NH_3	NO_2	NO_3	TH	Ca	Mg	Na	K	Cl
Land Use		pH	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Agricultural	151	7.5	216	468	0.037	0.009	7.33	251	72.7	21.8	17.9	3.06	24
Forest	21	7.0	112	210	0.021	0.004	2.20	128	33.6	13.5	5.4	1.68	9
Residential	57	7.5	197	357	0.076	0.004	4.15	228	62.6	21.4	14.1	3.05	22
Residential w. septic	23	7.5	187	358	0.025	0.004	3.67	208	57.5	18.9	34.0	1.84	45
Unreported	8	7.5	241	427	0.036	0.004	7.00	289	91.1	24.9	12.6	1.96	21
Urban	12	7.6	192	394	0.023	0.004	3.85	185	56.0	18.8	43.9	1.92	50
Average	272	7.4	191	369	0.036	0.005	4.70	215	62.3	19.9	21.3	2.25	29

Siliciclastic rocks	Count	pH	Alk	TDS	NH_3	NO_2	NO_3	TH	Ca	Mg	Na	K	Cl
Land Use		pH	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Agricultural	115	7.1	106	285	0.031	0.030	4.18	140	42.2	10.2	18.0	1.22	22
Forest	112	6.6	62	181	0.029	0.009	1.11	92	26.8	6.8	9.7	1.03	12
Residential	62	7.2	140	287	0.053	0.006	2.90	160	46.4	14.4	18.1	1.61	25
Residential w. septic	126	7.2	120	268	0.034	0.006	3.05	140	39.0	13.2	16.8	1.22	23
Unreported	10	7.2	123	280	0.028	0.004	2.14	155	44.9	13.7	12.6	1.27	29
Urban	11	7.3	148	313	0.037	0.007	2.20	192	58.0	14.2	19.1	1.56	36
Average	436	7.1	116.5	269	0.035	0.010	2.60	146.5	42.9	12.1	15.7	1.3	25

Crystalline rocks	Count	pH	Alk	TDS	NH_3	NO_2	NO_3	TH	Ca	Mg	Na	K	Cl
Land Use		pH	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Agricultural	47	6.5	38	188	0.043	0.019	6.27	72	18.6	6.7	8.9	1.75	14
Forest	72	6.6	52	204	0.023	0.005	2.56	94	26.9	7.4	8.3	1.61	13
Residential	36	6.4	57	217	0.021	0.004	4.01	98	22.4	10.1	12.1	1.81	30
Residential w. septic	67	6.8	55	305	0.022	0.005	3.84	91	22.8	9.2	11.5	1.88	24
Unreported	5	6.4	39	155	0.022	0.004	3.20	60	14.6	5.4	6.9	1.92	12
Urban	5	7.0	88	327	0.048	0.004	1.67	180	46.4	12.7	20.1	3.84	67
Average	232	6.6	55	233	0.030	0.007	3.59	99	25.3	8.6	11.3	2.14	27

Carbonate rocks	Count	SO_4	SiO_2	As	Ba	Cr	Cu	Fe	Pb	Mn	Zn	Turb
Land Use		mg/l	mg/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ntu
Agricultural	151	44	8.08	4.0	50	50	24	204	5.8	15	96	3.6
Forest	21	28	12.42	4.0	39	49	28	89	3.3	15	30	1.4
Residential	57	42	9.21	4.1	55	118	56	249	4.1	28	86	2.7
Residential w. septic	23	37	12.10	4.4	38	50	27	166	5.1	24	93	2.5
Unreported	8	52	8.72	4.0	36	50	33	237	4.0	11	73	4.8
Urban	12	39	8.03	4.0	39	50	32	108	4.2	11	127	1.4
Average	272	40	9.76	4.1	43	61	33	176	4.4	17	84	2.7

Siliciclastic rocks	Count	SO_4	SiO_2	As	Ba	Cr	Cu	Fe	Pb	Mn	Zn	Turb
Land Use		mg/l	mg/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ntu
Agricultural	115	41	14.66	4.3	103	51	36	202	5.2	73	80	2.7
Forest	112	40	13.56	4.4	72	50	44	494	3.5	70	251	4.0
Residential	62	34	15.27	4.3	212	50	39	738	4.2	30	40	3.9
Residential w. septic	126	32	18.64	4.7	161	51	45	170	4.3	30	114	1.9
Unreported	10	35	23.30	5.6	62	50	80	123	4.9	48	214	1.2
Urban	11	50	17.66	4.2	214	230	208	97	4.5	12	31	1.0
Average	436	39	17.18	4.6	137	80	75	304	4.4	44	122	2.5

Crystalline rocks	Count	SO_4	SiO_2	**As**	Ba	Cr	Cu	Fe	Pb	Mn	Zn	Turb
Land Use		mg/l	mg/l	**ug/l**	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ntu
Agricultural	47	24	16.86	**4.0**	53	50	123	606	11.4	53	44	6.5
Forest	72	42	21.86	**4.3**	41	50	66	456	3.9	23	25	4.4
Residential	36	24	17.66	**4.0**	54	50	82	45	3.6	14	89	1.0
Residential w. septic	67	27	23.90	**4.0**	36	50	81	449	5.9	32	50	3.9
Unreported	5	20	23.11	**4.0**	73	50	71	225	3.0	24	13	1.7
Urban	5	36	22.30	**4.2**	126	52	20	6292	9.4	185	93	14.8
Average	232	29	20.95	**4.1**	64	50	74	1346	6.2	55	52	5.4

This table can be used to compare average concentrations for monitoring points of a particular land use in a particular rock type. For example, nitrate concentrations are highest for each of the three rock types in agriculture land use; however, the highest average concentration is in the carbonate rock and agriculture section. Average values for each rock type are given in the last row of each section. “Count” indicates the number of monitoring points used for that category.

6.3 SUMMARY BY ROCK FORMATION

The data were summarized using the median values and reported geologic formations for each monitoring point (Appendix 4). The 1,089 monitoring points represent 104 different geologic formations. Sixteen formations were represented by only one monitoring point per formation. The Conemaugh Group of southwestern Pennsylvania had 127 monitoring points. The values shown in Appendix 4 are averaged median values that were calculated from all samples. “Less than detected" values were used as real values in the calculation of these statistics. Table 9 also summarizes different rock categories for selected parameters.

6.4 SUMMARY BY WELL DEPTH AND FLOW PATH

Average values were calculated based on the well depth for selected analytes. Table 10 shows averaged median values for wells categorized by depth. Shallow wells less than 75 feet deep and springs were compared to wells deeper than 250 feet. The main differences between the categories are iron and turbidity, which had higher concentrations in the shallower wells for all three lithology types. Carbonate rocks exhibited little difference between shallow and deeper wells for analytes other than iron and turbidity. Shallow wells in crystalline rocks and siliciclastic rocks tended to have lower pH and lesser concentrations of alkalinity, total hardness, calcium, sulfate and TDS.

Except for monitoring points in carbonate rocks (which did not show much difference between shallow and deeper wells), the data in Table 10 seem to support the idea that deeper wells will tap older, more mineralized groundwater. However, calculation of correlation coefficients (r) for well depth versus the 27 analytes did not reveal significant correlations. A correlation coefficient of 1 indicates a direct relationship between two variables. The highest correlation coefficient was 0.56 for pH in crystalline rocks, which indicates a very weak correlation (100 - r^2 equals the variability that is not explained by the correlation. In this case, approximately 70 percent of the variability is unexplained for an r value of 0.55). The monitoring points were categorized by rock type to determine any specific correlation. No significant correlation with well depth could be found.

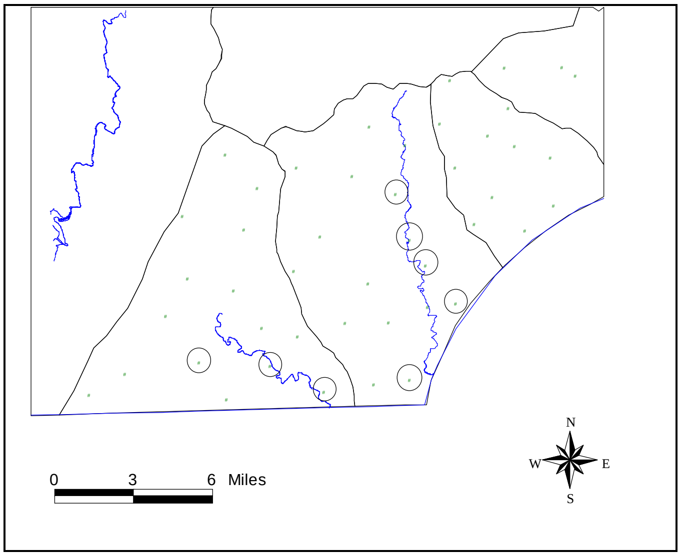
Table 10. Data for selected analytes by well depth and lithology.

<75 ft or spring)		pH	Alk	TDS	NO3	TH	Ca	Mg	Na	K	Cl	SO4	Fe	Turb
Lithology	Count	pH	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	ug/L	ntu
carbonate	72	7.4	183	347	5.4	213	67.0	16.1	8.9	2.4	18	33	413	6.4
crystalline	60	6.4	33	159	4.6	63	14.7	6.8	7.7	1.5	13	21	907	9.0
siliciclastic	121	6.7	84	240	1.8	105	30.7	7.6	17.5	1.5	15	41	536	4.0
>250 ft		pH	Alk	TDS	NO3	TH	Ca	Mg	Na	K	Cl	SO4	Fe	Turb
Lithology	Count	pH	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	ug/L	ntu
carbonate	54	7.5	201	380	5.4	241	64.3	23.5	16.2	2.3	22	46	62	1.2
crystalline	21	7.3	93	309	2.1	150	49.2	9.9	11.5	1.5	13	69	170	1.8
siliciclastic	60	7.3	121	277	2.7	157	44.8	12.3	15.0	1.0	20	39	187	1.9

Flow path may have a bearing on the concentration of ions in the groundwater. Two areas were used to test this idea. Monitoring points in recharge areas were selected against monitoring points in discharge areas of a basin. This approach assumes that the groundwater in discharge areas has traveled farther and has picked up more dissolved minerals. Two groups of monitoring points were selected from Basins 75 and 198, which are located in Chester County. Figures 2 and 3 show the locations of monitoring points in discharge and recharge areas. Data from these two groups are shown in Table 11. All monitoring points were situated in crystalline rocks.

Figure 2. Monitoring points (circled) located
located
in discharge areas of basins 75 and 198.
198.

Figure 3. Monitoring points (circled)
in recharge areas of basins 75 and



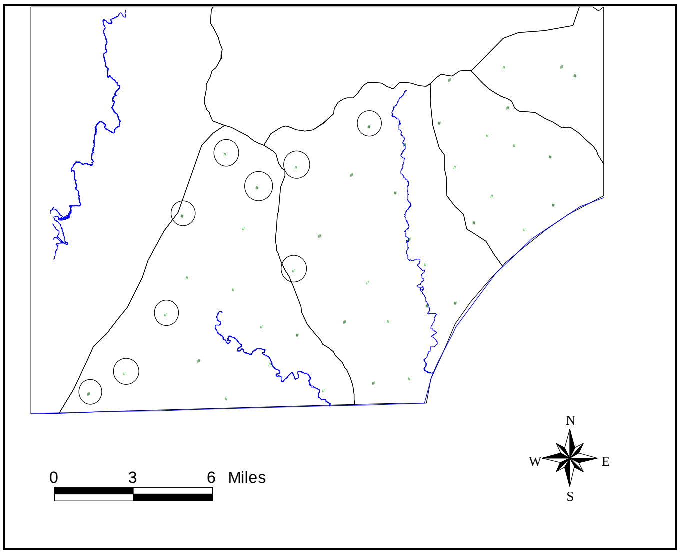


Table 11. Averaged median values for selected analytes and monitoring points by recharge and discharge areas of groundwater basins 75 and 198.

Area	Count	pH	Alk	TDS	NO_3	TH	Ca	Mg	Na	K	Cl	SO_4	Fe	Mn	Turb
		pH	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	ug/L	ug/L	ntu
Recharge	9	6.3	25	129	5.8	48	10.0	5.5	7.5	2.3	14	14	172	39	1.9
Discharge	8	6.7	70	286	4.9	111	26.2	10.6	10.7	2.6	16	40	281	15	3.1

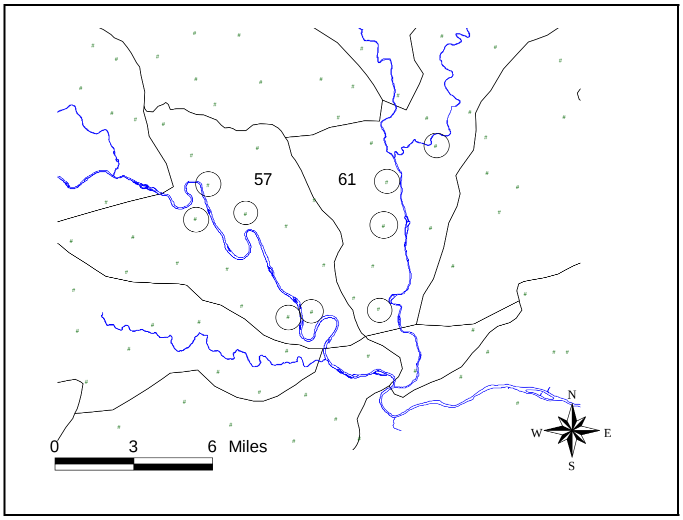
Another area was selected to briefly analyze this hypothesis. Basins 57 and 61 are located in Chester and Montgomery counties. The discharge and recharge groups of monitoring points are shown in Figures 4 and 5. All monitoring points were located in Triassic sandstone and shales. Data from the two groups are shown in Table 12.

For both locations, the data suggest that the discharge areas have more mineralized groundwater. Although there are not major differences, the two discharge areas seem to have a higher pH, and higher concentrations of TDS, alkalinity, total hardness, calcium, magnesium and sulfate. This may be a reflection of a longer residence time as assumed from the position of the monitoring points in the groundwater basin.

Figure 4. Monitoring points (circled) located
located
in discharge areas of basins 57 and 61.

Figure 5. Monitoring points (circled)

in recharge areas of basins 57
and 61.



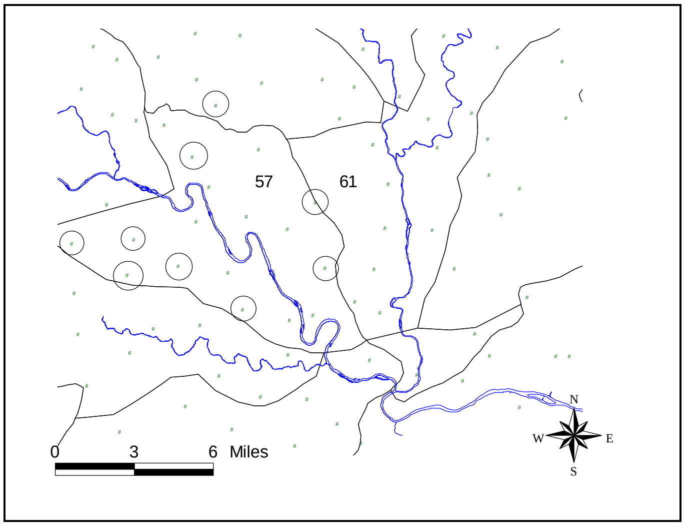


Table 12. Averaged median values for selected analytes and monitoring points by recharge and discharge areas of groundwater basins 57 and 61.

Area	Count	pH pH	Alk mg/L	TDS mg/L	NO_3 mg/L	TH mg/L	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Cl mg/L	SO_4 mg/L	Fe ug/L	Mn ug/L	Turb ntu
Recharge	9	6.6	99	206	3.3	110	33.3	10.1	13.1	0.9	17	26	139	21	2.2
Discharge	9	7.2	127	260	4.7	152	43.1	12.7	15.1	1.0	16	36	31	10	1.0

R.E. Wright Associates (1982a and 1982b) also attempted to quantify such relationships in their study of groundwater in the Delaware River Basin. Their study could not find any strong correlations between well depth and groundwater quality, or between position in the groundwater flow system and mineral content. They attributed the lack of correlation to the fact that deeper wells typically will draw in shallow groundwater also. For example, a well may have a major water-bearing zone at 50 feet and then be completed to 300 feet, without encountering any more major fractures. Depths of water bearing zones are not often identified, which further complicates any assessment of groundwater quality and well depth. Also, the number of factors that can influence the groundwater is high. The mixing of older and younger water may be one specific cause of the small differences between shallow and deep wells, and regarding a well's position in the groundwater flow system.

6.5 COMPARISON WITH GROUNDWATER STANDARDS

As shown in Table 7, 17 of the 27 analytes have associated public drinking water or remediation standards. Results of the sampling were compared to standards such as the Maximum Contaminant Level (MCL) and Secondary Maximum Contaminant Level (SMCL) values of the Safe Drinking Water Act. Although the contaminant levels apply to public drinking water supplies, the comparison was performed as a means to assess the groundwater quality. The results are based on individual monitoring point samples collected from 1985 to 1997 (Table 13).

All 39 exceedances of the mercury MCL (2 ug/L) occurred over a nine-month period in 1992 in the Southeast region. Only two of the samples were above 4.0 ug/L. Laboratory or sampling error or contamination is possible.

Table 13. Comparison of analyte concentrations with public drinking water standards.

Analyte	Standard	Number of Samples	Exceedances	Percentage
pH	>8.5	9935	91	0.9
pH	<6.5	9935	1742	17.5
TDS	>500 mg/L	9918	1240	12.5
Nitrite	>1.0 mg/L	9933	9	0.09
Nitrate	>10 mg/L	9937	998	10.0
Chloride	> 250 mg/L	9935	34	0.3
Sulfate	> 250 mg/L	9935	59	0.6
Arsenic	> 50 ug/L	6759	2	0.03
Barium	> 2000 ug/L	6758	3	0.04
Cadmium	> 10 ug/L	6757	161	2.4
Chromium	> 100 ug/L	6761	19	0.3
Copper	> 1000 ug/L	6754	29	0.4
Iron	> 300 ug/L	9933	1455	14.6
Lead	> 15 ug/L	6762	210	3.1
Manganese	> 50 ug/L	5014	650	13.0
Zinc	> 5000 ug/L	6754	18	0.3
Mercury	> 2 ug/L	6756	39	0.6
Turbidity	> 1 NTU	9925	2464	24.8

Median analyte concentrations for each monitoring point by rock type and land use type were compared to the water quality standards. The six analytes with over 10 percent exceedances of samples were reviewed (Tables 14 and 15). Because land use was not reported for the monitoring points in the southwestern region, Table 15 is based on the 940 monitoring points.

The percentages of exceedances should be compared to the second column, which gives the overall percentage of rock type or land use for the monitoring points analyzed. For example, even though carbonate rocks account for 25 percent of the monitoring points, they compose nearly 55 percent of the exceedances for nitrate.

Table 14. Percentage of selected analyte medians that exceed the standard out of 1,089 monitoring points by rock type.

Rock Type	Percent of rock type	pH	TDS	NO_3	Fe	Turb	Mn
Total Exceedances→		221	106	84	186	329	126
Carbonate	25.0	4.1	43.4	54.8	14.0	21.0	11.9
Crystalline	21.3	48.9	9.4	25.0	23.1	21.3	27.0

Siliciclastic	52.7	47.0	43.4	20.2	61.8	57.1	61.1
Unconsolidated	1.0	0	3.8	0	1.1	0.6	0

Table 15. Percentage of analyte medians that exceeds the standard out of 940 monitoring points by land use.

Land Use	Percent of land use	pH	TDS	NO_3	Fe	Turb	Mn
Total Exceedances		215	79	83	143	263	118
Agricultural	33.3	21.4	52.6	78.3	32.1	33.8	34.8
Forest	21.8	45.6	12.8	2.4	24.5	26.2	26.3
Residential	16.5	14.4	9.0	3.6	10.5	10.7	9.3
Residential with septic	23.0	15.4	18.0	12.1	25.9	23.2	24.6
Unreported	3.0	2.3	3.8	0	2.1	2.7	2.5
Urban	2.4	0.9	3.8	3.6	4.9	3.4	2.5

Some of the six analytes that commonly exceeded the MCL or SMCL levels can be associated with land use or rock type. The association of high nitrate values with carbonate rocks (nearly 55 percent of the exceedances) and agricultural land use (78 percent of the exceedances) is evident. Forest land use and crystalline rocks account for a disproportionate share of the exceedances of the pH SMCL. TDS concentrations that exceed the SMCL are more likely in agricultural land use and carbonate rock terrain. Other associations are less obvious although siliciclastic lithologies seem to have a higher portion of exceedances than might be expected for manganese, iron, and turbidity. Out of these six analytes, nitrate is the parameter with exceedances that are most attributed to human factors. High levels of iron, manganese, and turbidity and low pH levels are most likely the result of dominating natural groundwater conditions. TDS concentrations seem to be affected where the aquifer is more vulnerable to land activities, especially agricultural operations over carbonate rocks.

The association of carbonate rock and agricultural land use with high TDS and nitrate concentrations is the most significant result of the data. This conclusion regarding nitrate is shared with other investigations (Puckett, 1997). Although TDS concentrations can be naturally elevated in carbonate rocks, agricultural activities likely contribute to the levels of TDS in groundwater.

6.6 TREND ANALYSIS

The Kendall Tau rank correlation test was used to test for trends in groundwater quality over time. This is a nonparametric procedure to assess the presence of a trend. The 95 percent confidence level (significance level of .05) was used with the calculated Kendall Tau correlation coefficients. Trend analysis was performed on monitoring points using SAS™ statistical software. Analyses were not performed for total organic carbon, arsenic, cadmium, chromium, lead, manganese or mercury.

This section is based on the 475 monitoring points that underwent trend analysis. Most of these monitoring points are located in southeastern Pennsylvania (east of the Susquehanna River). One basin is located in southcentral Pennsylvania (Blair County). These monitoring points are from 18 groundwater basins and have been sampled up to 30 times. Table 16 shows the categorization of the 475 monitoring points by land use type. Table 17 categorizes the monitoring points by rock type.

Table 16. Categorization of the 475 basin monitoring points by land use.

Land Use Type	Number	Percentage
Agricultural (includes orchards, pasture, feedlots, etc.)	140	29.5
Forest	117	24.6
Residential (includes golf courses)	97	20.4
Residential with septic	92	19.4
Urban (includes commercial services, industrial)	12	2.5
Unreported	17	3.6

Table 17. Categorization of the 475 basin monitoring points by rock type.

Rock Type	Number	Percentage
Carbonate (limestone and dolomite)	157	33.0
Crystalline (slate, schist, gneiss, granitic rocks)	92	19.4
Siliciclastic (siltstone, conglomerate, claystone)	226	47.6

Table 18 summarizes the trend analyses for 20 analytes. The percentage of trends that are upward is listed in the first row. For example, out of 86 trends detected for TDS, 91.9 percent of those trends are upward. The table indicates that over 16 percent of the monitoring points for TDS show upward trends (fourth row). Table 19 summarizes the trends by basin. The percentage of trends that are upward per basin is based on the analytes for each monitoring point of the basin.

Table 18. Summary of trends.

Trend	pH	Alk	TDS	NH_3	NO_2
% Up	14.6%	62.6%	91.9%	26.7%	54.5%
Up	13	77	79	8	18
Down	76	46	7	22	15
% overall UP	2.7%	16.2%	16.6%	1.7%	3.8%
% overall DOWN	16.0%	9.7%	1.5%	4.6%	3.2%
	NO_3	P	TH	Ca	Mg
% Up	40.1%	25.0%	74.0%	81.1%	49.5%
Up	61	4	91	116	50
Down	91	12	32	27	51
% overall UP	12.8%	0.8%	19.2%	24.4%	10.5%
% overall DOWN	19.2%	2.5%	6.7%	5.7%	10.7%
Trend	Na	K	Cl	SO_4	Si

% Up	84.9%	90.3%	73.3%	21.9%	13.8%
Up	146	93	132	23	4
Down	26	10	48	82	25
% overall UP	30.7%	19.6%	27.8%	4.8%	0.8%
% overall DOWN	5.5%	2.1%	10.1%	17.3%	5.3%
Trend	Ba	Cu	Fe	Zn	Turb
% Up	64.4%	41.1%	40.6%	38.7%	50.0%
Up	38	23	26	24	15
Down	21	33	38	38	15
% overall UP	8.0%	4.8%	5.5%	5.1%	3.2%
% overall DOWN	4.4%	6.9%	8.0%	8.0%	3.2%

Table 19. Summary of trends by basin.

Groundwater Basin	Number of Monitoring Points	Trends Upward	Trends Downward	Percent of Trends That Are Upward
34	36	101	78	56.4
35	35	93	72	56.4
36	41	109	51	68.1
44	16	17	32	34.7
58	39	19	80	19.2
59	37	10	23	30.3
61	22	20	31	39.2
64	23	73	39	65.2
65	14	52	21	71.2
68	16	7	10	41.2
69	14	5	2	71.4
77	12	30	16	65.2
78	8	36	8	81.8
176	25	102	40	71.8
190	20	56	47	54.4
193	33	102	45	69.4
194	32	112	49	69.6
261	52	97	71	57.7

Caution must be exercised when interpreting the results of groundwater trends. The presence of a trend does not necessarily equate to improving or declining groundwater quality on a regional basis. Although FSN monitoring points were selected to be representative of the groundwater basin, the total number of monitoring points nevertheless represents a small portion of the groundwater of a basin. Trends at one monitoring point may not be reflected at other nearby monitoring points. However, the dominance of upward trends of an analyte may be evidence that human activities are affecting the groundwater quality. On the other hand, comparison of actual values may show that concentrations are generally quite low and changes have been minor.

Exact causes of trends are difficult to determine and some presumptions must be made. The first assumption is that the major trends represent widespread changes in the groundwater quality. Groundwater quality shifts are most likely related to an aquifer's vulnerability to changes (see Section 6.6.4 on vulnerability). Some areas are prone to variations in groundwater quality.

Notable downward trends were found for sulfate and nitrate. Upward trends that were considered to be significant (more than 10 percent of the monitoring points) were detected for alkalinity, nitrate, total hardness, calcium, magnesium, sodium, potassium, and chloride. As noted in Section 2.1, downward trends in atmospheric deposition of sulfate and nitrate have been evident since 1983. However, the minor reductions for groundwater are unlikely to have had much of an impact on sulfate and nitrate concentrations.

6.6.1 Trends and Land Use

The increases and decreases in nitrogen and sulfate may be related to changing demographics and nitrogen distribution in the environment. Increased use of community sewers and conversion of farm land to residential areas has been occurring in Pennsylvania. The number of farms in Pennsylvania decreased nearly 20 percent from 1982 to 1992 (to less than 45,000 farms) while the average size of farms continued to grow. The application rate of animal manure in agricultural areas may affect the nitrate levels in groundwater. Areas that contain an increased number of animals per acre may have increased nitrate concentrations in groundwater. Sulfate is an ingredient in many fertilizers, and the downward trends in sulfate concentrations may have similar causes as decreases in nitrate levels.

The increase in concentrations of dissolved minerals such as calcium, magnesium, sodium, potassium and chloride may be related to the increased use of road salts, and urban expansion and development. Average salt usage on state highways in Pennsylvania over the last five years is near 700,000 tons. This is an increase over reported amounts from 1989 of approximately 400,000 tons (Transportation Research Board, 1991). An area with a high density of roads and vulnerable hydrogeology could be affected by road salting. The most likely zone to be affected is immediately adjacent and downgradient of a road. For example, if 50 percent of the salt infiltrates the top 100 feet of an aquifer (assuming 10 percent porosity), and 10 tons of salt are added in a mile of highway (in a zone 100 feet wide), chloride concentrations may rise by 15 to 20 mg/L.

Sloto (1987) compared land uses with wells that showed increases of sodium and chloride. He assumed that sewered areas have a denser population and a denser network of roads, which would have more road salt applied per unit area than the less populated, unsewered areas. Using these criteria, the percentages of FSN monitoring points by land use (urban and residential versus forest and residential with onlot septic systems) were compared with monitoring points showing upward trends in sodium and chloride. The percentage of monitoring points with urban and residential (sewered) land uses and upward trends in chloride and sodium was 38 percent and 32 percent, respectively. However, monitoring points with these land uses account for just 24 percent of the 475 monitoring points that underwent trend analysis. This suggests that road salting is affecting the groundwater quality in parts of the more developed areas of the FSN basins. By contrast, monitoring points with forest land use and residential with septic land use accounted for just 32 percent and 29 percent of the upward trends in chloride and sodium, respectively. However, these land uses accounted for 44 percent of the monitoring points that underwent trend analysis.

When the residential and urban land uses together are compared with the trends, several attributes are apparent (Table 20). Urban and residential land uses represent about 23 percent of the monitoring points. However, monitoring points with these land uses account for over 30 percent of the monitoring points with upward trends in alkalinity, TDS, calcium, magnesium and sodium, and over 35 percent of the monitoring points with upward trends in total hardness and chloride. Also, the monitoring points with urban and residential land uses have over 30 percent of the downward trends in nitrate. In other words, these land uses seem to have a disproportionate share of these trends. The decreases in nitrate concentrations might be expected for such land uses that have been converted from farm use or have constructed sewer systems in recent years. However, such decreases cannot be assumed for land use changes because of the numerous factors that may be involved.

Table 20. Percentage of monitoring points with trends by land use.

Analyte trend	Overall percentage	pH down	Alk up	TDS up	NO_3 up	NO_3 down	TH up	Ca up
Agricultural	29.5	31.6	32.5	38.0	41.0	33.3	33.0	31.0
Forest	24.6	15.8	19.5	11.4	26.2	15.6	14.3	20.7
Residential	20.4	23.7	29.9	27.8	16.4	24.4	33.0	27.6
Residential w septic	19.4	19.7	13.0	19.0	14.8	17.8	16.5	14.7
Unreported	3.6	5.3	1.3	0.0	1.6	2.2	0.0	0.9
Urban	2.5	3.9	3.9	3.8	0.0	6.7	3.3	5.2
Trend	**Overall percentage**	**Mg down**	**Mg up**	**Na up**	**K up**	**Cl up**	**Cl down**	**SO_4 down**
Agricultural	29.5	43.1	26.0	39.0	39.8	29.5	43.8	34.1
Forest	24.6	11.8	18.0	15.8	22.6	10.6	18.8	25.6
Residential	20.4	19.6	28.0	26.7	16.1	32.6	14.6	17.1
Residential w septic	19.4	13.7	22.0	13.0	19.4	20.5	12.5	15.9
Unreported	3.6	5.9	0.0	0.7	1.1	1.5	4.2	2.4
Urban	2.5	5.9	6.0	4.8	1.1	5.3	6.3	4.9

6.6.2 Trends and Rock Type

A similar analysis can be made using the basic rock types (Table 21). Monitoring points in carbonate rock account for just 33 percent of the monitoring points that underwent trend analysis. Upward trends in chloride and sodium in carbonate rock accounted for 43 percent and 54 percent, respectively, of the monitoring points. The presence of carbonate rocks typically increases the vulnerability of an aquifer to contamination. The higher percentage of trends for chloride and sodium in carbonate rocks suggests that its presence may contribute to potential groundwater contamination by road salts (assuming that road salting is the major source of the increases in sodium and chloride).

Table 21. Percentage of monitoring points with trends by rock type.

Analyte trend	Overall percentage	pH Downward	Alk Upward	TDS Upward	NO_3 Upward	NO_3 Downward	TH Upward	Ca Upward
Carbonate	33.0	38.2	49.4	38.0	32.8	46.7	39.6	38.8
Crystalline	19.4	25.0	3.9	15.2	14.8	8.9	12.1	9.5
Siliciclastic	47.6	36.8	46.8	46.8	52.5	44.4	48.4	51.7

Analyte trend	Overall percentage	Mg Downward	Mg Upward	Na Upward	K Upward	Cl Upward	Cl Downward	SO_4 Downward
Carbonate	33.0	45.1	28.0	54.1	33.3	43.2	47.9	41.5
Crystalline	19.4	11.8	18.0	6.2	3.2	12.1	8.3	15.9
Siliciclastic	47.6	43.1	54.0	39.7	63.4	44.7	43.8	42.7

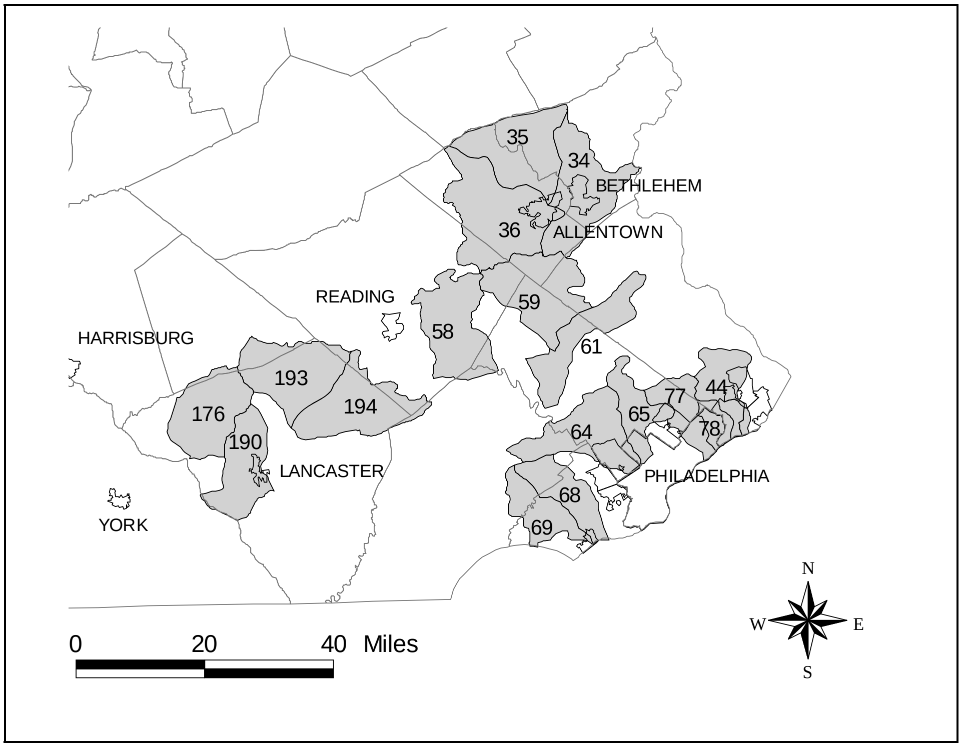
6.6.3 Trends and Geography

The latitude and longitude (and all other data) were used to generate a point dataset coverage in ARC/INFO. Geographic relationships could be assessed by comparing sampling data and monitoring point characteristics. Only the analytes that have trends at more than 10 percent of the monitoring points are reviewed. These analytes are assumed to be the ones that may be shifting in concentration on a regional scale.

For the most part, the relationship between geography and the trends is unclear. Defining regional trends in groundwater quality is difficult for several reasons. The many interrelated factors regarding groundwater quality do not favor the dominance of any particular factor to control trends. Also, FSN basins account for approximately half of the area in the southeast, so that there are gaps in the data.

Selected analyte trends by percentage of a basin’s monitoring points are shown in Appendix 5. The maps in Appendix 5 focus on 17 FSN basins in Southeast Pennsylvania (Figure 6). Twelve prominent trends are displayed to compare basins. These maps also can to be used as a general gauge of trends in these basins. Basins 58, 59, and 61 have had less than six years of sampling. This may not have been sufficient time to have captured many water quality trends.

Figure 6. Location of FSN basins in Southeast Pennsylvania.



Maps 1-4 in Appendix 5 show the analytes with prominent downward trends in the FSN basins. Downward trends in nitrate (Map 4) are widespread. Three basins have between 29 and 44 percent of the monitoring points per basin with downward trends in nitrate. Maps 5-12 in Appendix 5 show the analytes with prominent upward trends in the FSN basins. Widespread upward trends in chloride and sodium are displayed by basin. Eleven basins have greater than 20 percent of monitoring points with upward trends in chloride. Nine basins have at least 20 percent of the monitoring points with upward trends in sodium.

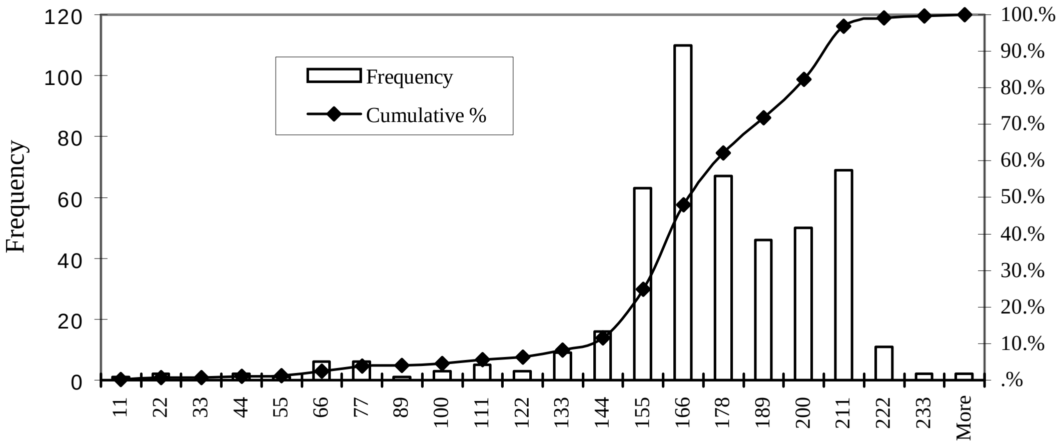
6.6.4 Vulnerability

As noted in Section 2.3, groundwater in carbonate rocks has been understood to have an increased vulnerability to contamination sources. Carbonate rocks may have more inherent shifts in groundwater quality because of this vulnerability. Land use has also been shown to be a factor in the vulnerability of groundwater to certain contaminants. Monitoring points with at least four upward or four downward trends accounted for 156 monitoring points. Over 44 percent were from monitoring points with a carbonate rock type (compared to 33 percent of the monitoring points with trend analysis data). Nearly 39 percent of these monitoring points had an agricultural land use (compared to 29.5 percent of the monitoring points by land use). Forty-eight percent of the monitoring points with greater than three downward trends had an agricultural land use. Only 34 percent of the monitoring points with greater than three upward trends had an agricultural land use. This information suggests that land use and rock type affects the presence of trends. Note that nearly half of carbonate rock monitoring points have an agricultural land use. This may cause some of the overlap in the data regarding trends.

The vulnerability of groundwater to surface contaminants is actually related to many factors. DEP through the Pennsylvania State University completed a vulnerability assessment for groundwater (Petersen and others, 1996). The DRASTIC methodology was used to develop an ARC/INFO coverage for 100-meter by 100-meter cells across the state. In calculating a DRASTIC score, the DRASTIC model considers the depth to groundwater, aquifer recharge and media, soil permeability, topography, effects of the unsaturated zone and the hydraulic conductivity (EPA, 1987).

The DRASTIC scores for each monitoring point location that underwent trend analysis were compared with the data on trends. The scores ranged from 11 to 244. The median DRASTIC score was 168; 90 percent of the data is between 140 and 203. Figure 7 shows a histogram for the DRASTIC scores of the 475 monitoring points that underwent trend analysis.

Figure 7. Histogram of DRASTIC values for monitoring point locations.



DRASTIC scores for monitoring points with few trends (less than two) were compared to those with more trends (more than four). Because the DRASTIC scores are a measure of vulnerability, monitoring point locations with high drastic scores might be expected to have more changes in groundwater quality. This presumes that there are stresses available to the groundwater quality that could cause shifts in chemical concentrations. Table 22 shows DRASTIC scores compared to selected trends.

Table 22. Comparison of DRASTIC scores and trends.

Condition of Selected Monitoring Points	Number of Monitoring Points	DRASTIC Score
Total trends = 0	64	153
Total trends less than 2	126	159
No trends in TH, Ca, Na, K, and Cl	154	160
Total trends greater than 7	56	173
Total upward trends greater than 5	50	176

Total trends greater than 4	168	176
Upward trends in Na and NO_3	29	183
Upward trends in TH, Ca, Na, K, and Cl	12	187

The information in Table 22 suggests that number of trends is related to the vulnerability of the aquifer to groundwater contamination. Other factors are probably at work including the presence of stresses to groundwater, duration of the sampling period, and the physical characteristics of each well. DRASTIC scores infer some connection to the occurrence of trends in groundwater quality, but do not explain exact causes of trends.

7. CONCLUSIONS

Because the monitoring points that underwent trend analysis represent only a small portion of the state, caution must be taken when interpreting the information on trends. Natural groundwater quality cycles may be occurring. In addition, an upward trend may have little overall effect on groundwater quality. It is obvious from reviewing the data that the concentrations of some analytes are apparently increasing while others are decreasing. This may be evidence for somewhat random and local changes in groundwater quality. Distinct geographical trends were difficult to discern; however, some land use types and rock types seem prone to certain changes in groundwater quality.

The interrelationship between the land use and rock type and its effect on groundwater trends is probably related to the vulnerability of certain settings to human activities. In addition, many of the groundwater factors are interrelated. Land uses and population trends are related to the geology and physiography. The groundwater quality is related to the geology and land uses. Additional factors such as variable geology and groundwater flow paths, changing land uses, and constantly changing precipitation rates and occurrences provide further complexities to understanding the groundwater chemistry.

Despite these uncertainties, several general conclusions can be made. Groundwater quality is essentially good. Many of the exceedances of drinking water quality standards are likely natural in origin, especially pH, iron, TDS, manganese and turbidity. Some exceedances, especially nitrate and to a lesser extent TDS, are caused by human activities. Overall downward trends in sulfate and nitrate are notable and may be related in changes in land use and reductions in atmospheric deposition. Notable upward trends (15 to 30 percent of monitoring points that underwent trend analysis) have occurred for chloride, potassium, sodium, calcium, total hardness, TDS and alkalinity. Although exact causes of such trends are unclear, they may be related to an increase in non-point source pollution from changing land uses and the more extensive use of road salts. Most changes represent only minor variations in concentration.

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