

**Analysis of Effects of Urbanization on Spring Geochemistry and Sediment
for a Karst Aquifer in Valley Creek Basin, Chester County, Pennsylvania**

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ABSTRACT

Valley Creek Basin located in eastern Chester County, southeastern Pennsylvania, is an urban karst system. Four springs within the Elbrook Formation and two springs in the Ledger Dolomite have been monitored for suspended sediment, baseflow water chemistry, and storm response. Data from previous studies at two rural sites, Nolte in Lancaster and Bushkill in Easton Pennsylvania, were used for comparison to examine the effects of urbanization on spring chemistry. The flow paths were compared using hardness coefficient of variations (CV) to differentiate between matrix and conduit dominated springs. The urban springs CV values ranged from 14.5% to 8.2%, showing a mixture between conduit and matrix flow paths. The rural sites CV values place Nolte as a matrix dominated system (5.6%) and Bushkill as distinctly conduit (17.5%). The nitrate values for the urban sites were low (< 5 mg/L) and had little variation within a 1 to 2 mg/L range. The rural sites had higher nitrate concentrations that showed seasonal variations around 10 mg/L. The difference between the urban and the rural nitrate values is most likely due to the agricultural use of fertilizers in rural areas. The calcite and dolomite average SI's were slightly undersaturated (-0.01 to -0.5), suggesting that these systems are most likely made of solutionally enlarged fractures, with mixing between conduit and matrix flow. Most of the urban log PCO_2 values averaged around -1.9, indicating that the urban springs are open systems under the influence of soil gas. The Bushkill spring's log PCO_2 averaged -2.3 indicating that it is also an open system, while Nolte spring had slightly higher log PCO_2 (around -1.5) indicating a closed

system. The suspended sediment concentrations for the urban springs have shown fairly constant low levels. The concentrations mostly range from 0.5 to 4.0 mg/L. The low suspended sediment values suggest that the karst system is not receiving a heavy load of urban sediments in the recharge area. It is believed that urbanization and increased impervious surfaces have led to a reduction of infiltrating waters, which has in turn limited the amount of sediment entering the system. Furthermore, trace metal analysis of baseflow water samples and spring mouth sediment showed low concentrations. The metal concentrations in the water samples were generally less than 10 ppb and below EPA drinking water standards. The metal concentrations in the sediment were higher than those in the water samples. Even so, two-thirds of the sites had no metal concentrations over typical background values. The low concentration of metals on the sediment suggests that there is a lack of build up of metals in the karst system. Karst aquifers are usually more vulnerable to contamination than other aquifers due to reduced filtration of infiltrating waters. However, urbanization in Valley Creek Basin's karst system has not had the effect of exposing the karst system to metal or sediment contamination, although the other geochemical indicators are typical of karst with a mixture of matrix and conduit flow paths. The lack of metal and sediment contamination appears to be related to urbanization restricting the recharge area and thus the potential flux of sediment and metals.

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CHAPTER 1 BACKGROUND

Development of Karst Systems

At the surface karst landscapes are characterized by sinkholes and disappearing streams, while below the surface features of caves and caverns are common. Karst forms in highly soluble rock, creating groundwater systems in which drainage is underground in solutionally enlarged fissures and conduits in areas underlain by carbonate rock, including limestone, dolomite, and gypsum. The solubility of carbonate rock is important to aquifer formation and will greatly affect the flow paths along which groundwater will travel. Karst is abundant and covers about 20% of the Earth's surface. Karst cavities and fissures can be greatly varied in their size, flow path or joint system configurations, and overall shape and appearance. Their features vary widely depending on several factors that help to shape them. Some of these factors are climate, volume of water seeping into the rock, geologic setting of rock, arrangement of recharge and discharge areas, and type of fracture system (Dreybrodt, 1988).

The formation of a karst aquifer is described by Dreybrodt (1988). Initially, all types of karst start as fluvial systems. A layer of carbonate rock is in sequence between two impermeable and insoluble layers of rock. Water drains from the area along the surface. Eventually a portion of the overlying rock becomes eroded away and a section of the limestone becomes exposed at the surface. Contact between the surface water and the limestone allows for

chemical interaction and additional weathering. As chemical and physical weathering of the rock continues narrow fissures are created in the carbonate rock along bedding planes or fractures. Water is able to start seeping down into these fissures and at some lower elevation a discharge area is created, which institutes a hydraulic head powered by gravity that drives the water downward through the limestone. With recharge and discharge locations set, the surface water penetrates into these primary fissures, creating a shallow water table. As time progresses, slow dissolution of the primary fissures increases the amount of water that can flow through the carbonate rock. This increased flow increases the dissolution rate, creating a positive feedback loop leading to enlargement of secondary porosity flow paths. As the dissolution of the rock progresses more effective conduit drainage is induced, creating sinkholes at the surface, which direct surface water underground. Additional erosion leads to more rock being exposed at surface, creating increased infiltration of precipitation, which creates more flow paths. This increasing permeability in the carbonate rock lowers the water table until it reaches base level.

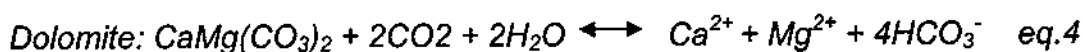
Chemistry of Karst Dissolution

The solubility product constants for calcite and dolomite are shown below.

$$\text{Calcite: } K_c = \frac{\alpha_{\text{Ca}^{2+}} \alpha_{\text{CO}_3^{2-}}}{\alpha_{\text{CaCO}_3}} = \alpha_{\text{Ca}^{2+}} \alpha_{\text{CO}_3^{2-}} \quad \text{eq.1}$$

$$\text{Dolomite: } K_d = \frac{\alpha_{Ca^{2+}} \alpha_{Mg^{2+}} \alpha_{CO_3^{2-}}^2}{\alpha_{CaMg(CO_3)_2}} = \alpha_{Ca^{2+}} \alpha_{Mg^{2+}} \alpha_{CO_3^{2-}}^2 \quad \text{eq.2}$$

These solubility product constants are a function of temperature, and calcite's solubility in pure water is about the same as quartz, around 6 ppm at 10° C (White, 1988). The presence of acid increases the solubility of the carbonate minerals, which dissolves these carbonate minerals easily. The most important acid in karst processes is carbonic acid, which is formed by the dissolution of CO₂ gas. The rate that CO₂ enters into the system is as important as the rate of water and sediment in the system, because CO₂ is an important chemical reactant in karst systems (White, 1988). Sources of CO₂ are atmosphere and biological processes in soil. In near neutral solutions reactions for dissolution of calcite and dolomite with carbonic acid are:



The water's level of acidity is given by the activity of H⁺ ion and is measured as pH. The importance of CO₂ to the dissolution of carbonate rock creates a tie between the groundwater system and the atmospheric carbon dioxide pressure. Dissolution is most active in the area above and within the zone of watertable fluctuation. This is because in this area water flows more quickly and the recharge is still acidic. Beneath the zone of water table fluctuations, dissolution slows because the water flows relatively slower and its acidity becomes neutralized. The acid neutralization occurs because as carbonic acid reacts with

the carbonate rock it produces a slightly alkaline solution, as is seen in the dissolution reactions above.

Karst Flow Paths

Dissolution of the karst creates the flow paths that the water will move along as it travels through the karst system. The two main types of flow paths are conduit and matrix flow paths (figure 1-1). While many karst systems are made up of a combination of conduit and matrix flow paths, it is important to understand these two types of pathways individually. Conduit flow paths are wider fissures, generally larger than 1 cm wide. Because of their larger size, the velocities of the water moving through are larger, around $10^{-3} \text{ cm s}^{-1}$ to 1 m s^{-1} (Dreybrodt, 1988). The water's ability to move quickly results in a short retention time, with the discharge springs showing more variability in temperature and chemistry, and quicker reaction to storm pulses. With matrix, or diffuse flow, the water travels through smaller partings of rocks joints or bedding. Moving through narrower partings causes the water to move more slowly through the system, with velocities less than $10^{-3} \text{ cm s}^{-1}$ (Dreybrodt, 1988). The slower movement gives the water a longer retention time and the water has time to equilibrate with the rock. Because of this, the water from springs that travel through more of a matrix configuration show small variations in chemistry and temperature and are close to calcite saturation. Conduit and matrix flow paths also differ in their spring's response to flood events. In the conduit system is a quick response due to the conduit being more effective in draining the system. The matrix dominated

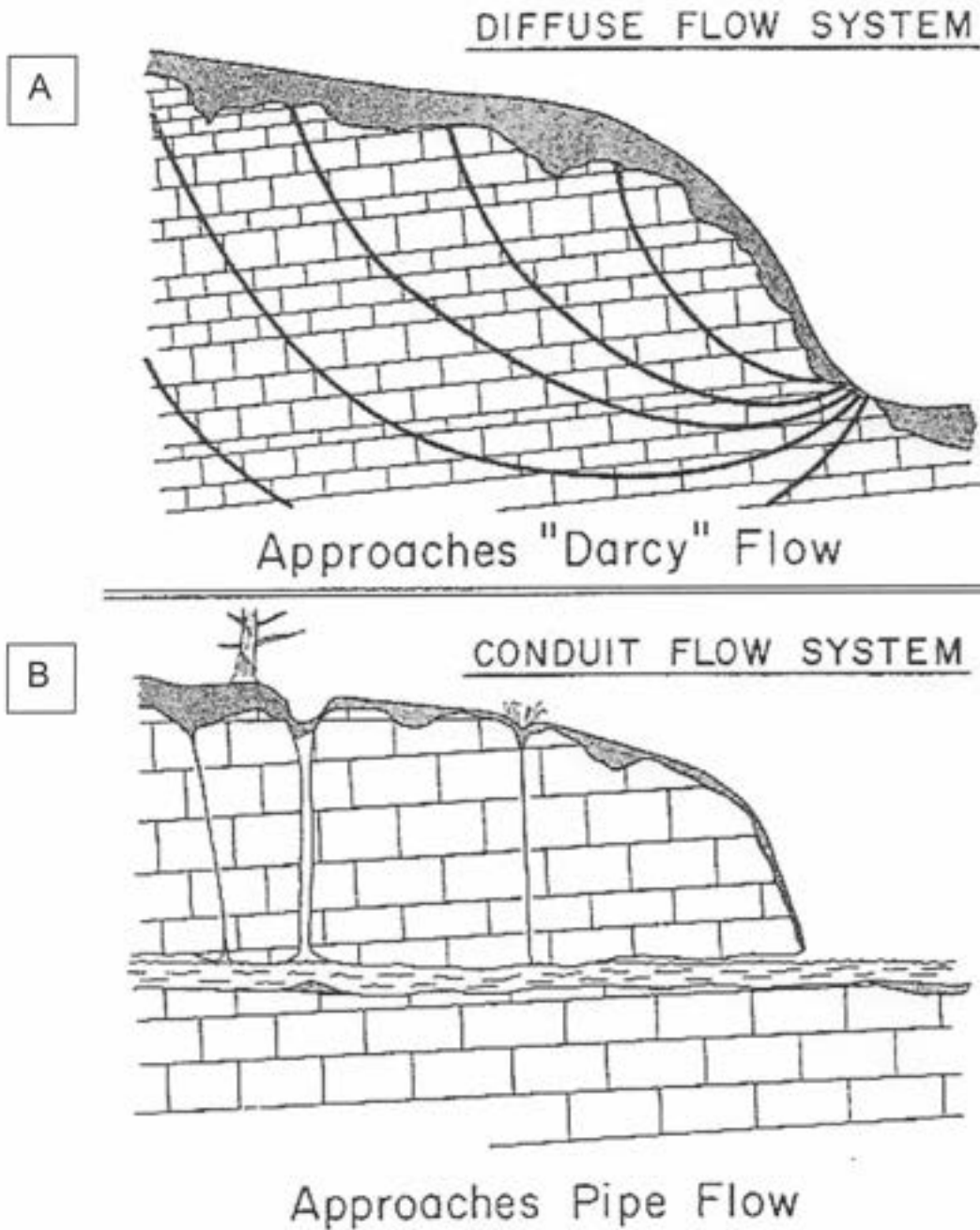


Figure 1-1. Conduit and Diffuse (Matrix) Flow Systems. From Shuster & White (1971) (A) Diffuse or Matrix dominated flow system. (B) Conduit dominated flow system.

system, in contrast, has a slow delayed response created by the flow path's resistance to flows and large storage properties.

Depending on whether the system's flow path is more matrix or more conduit dominated, there is a range of flow paths that can create various levels of surface area interaction between the water and carbonate rock. The size of the open spaces affects the amount of surface area interaction between the rock and water. At one end of the spectrum there are the matrix flow paths, which create more surface area contact and thus result in higher concentrations. At the other end of the spectrum are the conduit flow paths, which create less rock-water interaction, resulting in lower concentrations. Natural karst systems mostly fall somewhere in between these two end members. Areas with conduit flow can also experience some matrix flow. Conduit flow paths can fluctuate between the larger conduit openings and the smaller matrix fissures depending on storm events, drought, and other events that would affect the hydrologic head. Because conduit flow can vary between larger and smaller openings, these springs show more variation in dissolution constituents. For the rest of this paper, the usage of the terms conduit and matrix will refer to conduit or matrix dominated flow systems with the understanding that a combination of flow paths occurs.

Study Area

The study area discussed in this thesis is Valley Creek Basin, located in Chester County, Pennsylvania about 35 km northwest of Philadelphia (figure 1-2). Valley Creek drains a 64 km² area and the basin is approximately 12 km

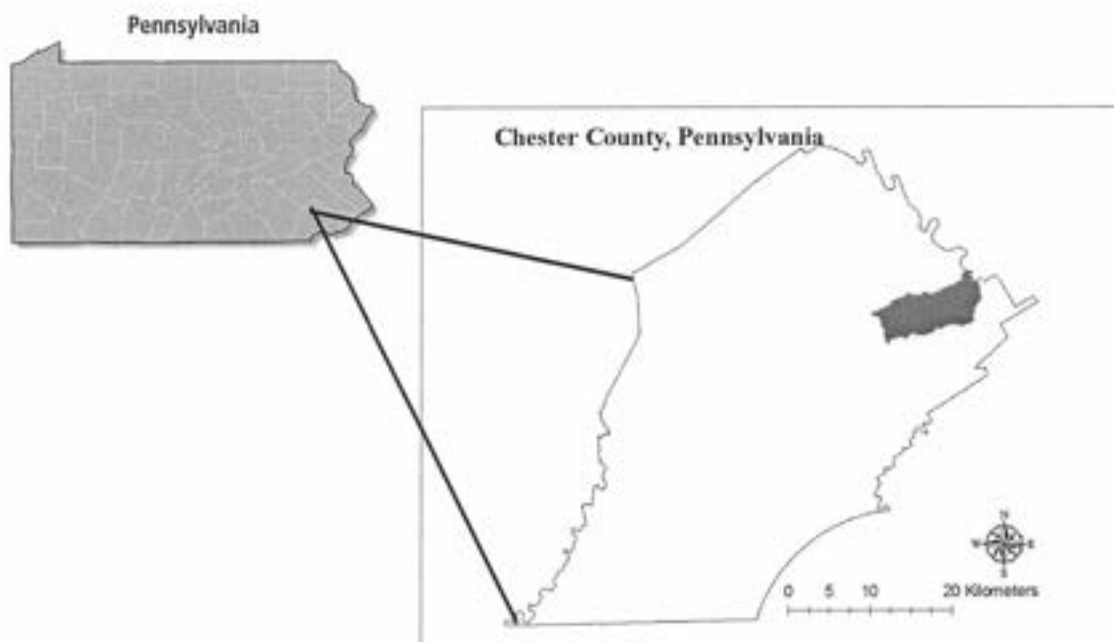


Figure 1-2. Site location, Chester County, Southeastern Pennsylvania. The site location for this study was in Chester County in Southeast Pennsylvania, within the Valley Creek Basin.

across. Valley Creek Basin contains a sequence of carbonate rocks of Cambrian and Ordovician age (figure 1-3). The basin is underlain by 68% carbonate rock. Most of the carbonate rocks are located in the center of the basin. The major formations being: Cambrian Ledger Dolomite, the Cambrian Elbrook Formation, and Cambrian and Ordovician Conestoga Limestone (figure 1-4). These rocks form Chester Valley, which runs across Chester County. Bordering the carbonate rocks in the northern area are Cambrian Chickies and Antietam Quartzite, Harpers Phyllite, and Middle Proterozoic intermediate felsic gneiss. These rocks form the North Valley Hills. To the south there is Late Proterozoic to Cambrian Phyllite that created the South Valley Hills.

Most of the groundwater flow in Valley Creek basin is local with discharge to close by streams. The water bearing zones are mostly shallow, with 50% located in the top 30 meters of the land surface and 81% within the top 60 meters (Sloto, 1990). Although effects of karstification can be seen in the region by evidence of sink holes (figure 1-3), a nearby outcrop shows the flow in this groundwater system is through enlarged fractured rock. Rather than flowing through a traditional cavernous karst system, the water travels along secondary porosity paths, such as fractures, joints, faults, parting planes, and bedding planes.

The main formation that this study focused on was the Elbrook Formation, which is composed of a gray fine crystalline dolomite with laminar partings and a siliceous dolomite interbedded with phyllitic shale. The Elbrook has an estimated thickness of 1600 m and its lower contact is gradational with the Ledger Dolomite

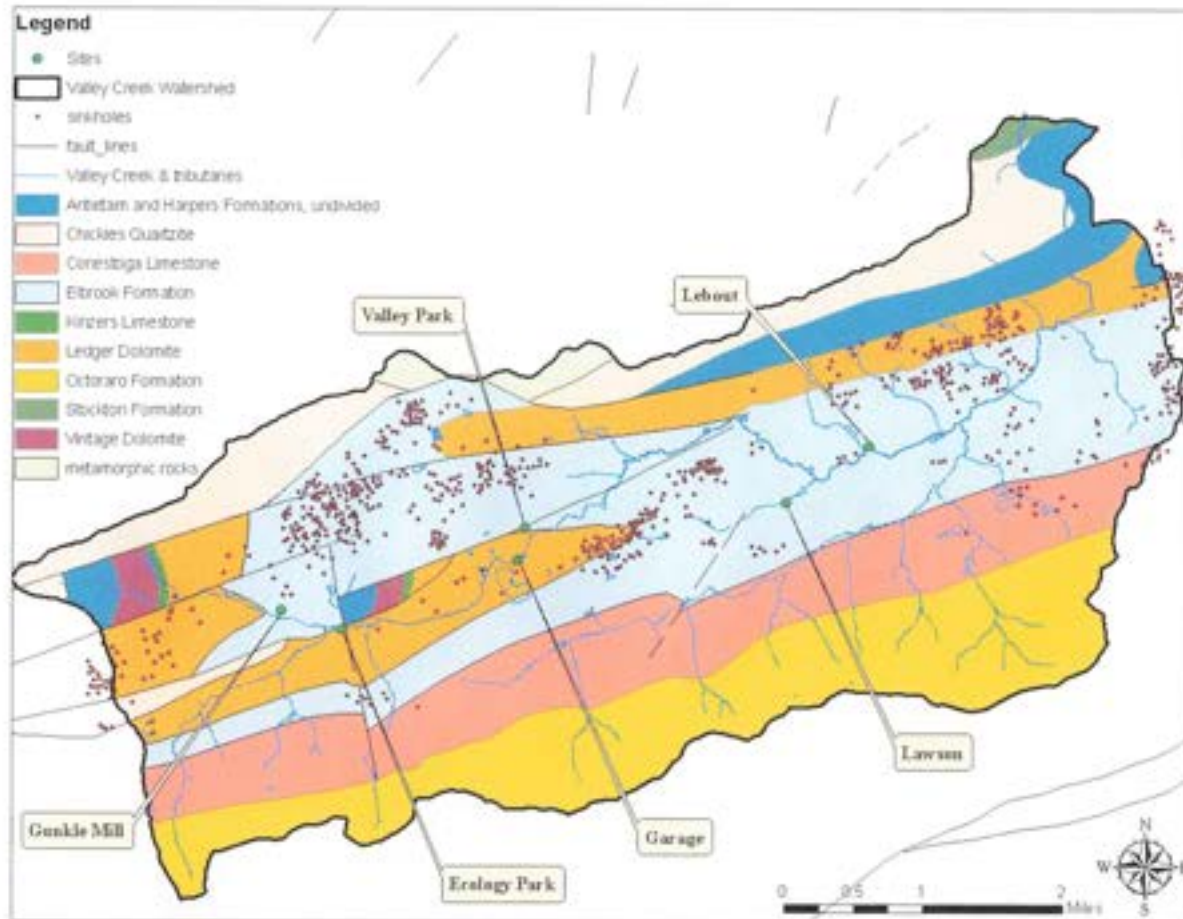


Figure 1-3. Geology of Valley Creek Basin. Gunkle, Park, Lawson, and Lebout are located in the Elbrook Formation. Eco Park and Garage are located in the Ledger Dolomite. Geology data from Chester County Water Resource Authority (2005).

SYSTEM AND ERA	SERIES	GEOLOGIC UNIT	
		Lytle and Epstein 1987	Berg and others 1986
Triassic	Upper Triassic	Stockton Frm.	Stockton Frm.
Ordovician		Conestoga Limestone	Conestoga Limestone
Cambrian	Upper Cambrian	Elbrook Formation	Elbrook Frm.
	Middle Cambrian	Ledger Dolomite	Ledger Formation
		Kinzers Formation	Kinzers Formation
	Lower Cambrian	Vintage Dolomite	Vintage Formation
		Antietam Formation and Harpers Phyllite, undivided	Antietam Formation and Harpers Formation, undivided
		Chickies Quartzite	Chickies Formation
Late and Middle Proterozoic		Leucocratic and Intermediate Felsic Gneiss	Chickies Formation Gneiss

Octoraro Phyllite

Wissahickon ("Octoraro") Schist

Figure 1-4. Stratigraphic column for the Malvern and Valley Forge Quadrangle (after Sloto, 1990)

Formation. Four springs studied for this paper were in the Elbrook formation. Because of the Ledger Dolomite's similarity to the Elbrook, two springs within the Ledger Dolomite were added during the study to expand the data set. The Ledger Dolomite is white to gray, fine to medium grained crystalline dolomite, with fine laminates containing high magnesium content. It has an estimated thickness of 1100 m.

Land Use

Valley Creek basin, like many other suburbs, is an area that is undergoing increasing development. Over the past 30 years this development has resulted in an increase of more than 17% impervious surfaces in the watershed (Steffy and Silham, 2006). The effects of urbanization on groundwater include contamination, increased overland flow / storm response, increased public water demands, and changes in the productivity and placement of both recharge and discharge areas. Valley Creek basin's land use (figure 1-5) can be broken down into the following percentages: 3% public, 2% farms, 41% residential, 22% commercial, 6% industrial, 3% utilities, and 13% roads (McGinty, 2003 from Chester County GIS 2002).

There is variability of land use in the areas surrounding the research springs. Most of the spring locations are on small sections of preserved land, as either East Whiteland Township parks or land owned by the Natural Land Conservancy. One spring, Lawson, is located on private property. Gunkle is located at a historic mill at the corner of Conestoga and Moores Road. There is

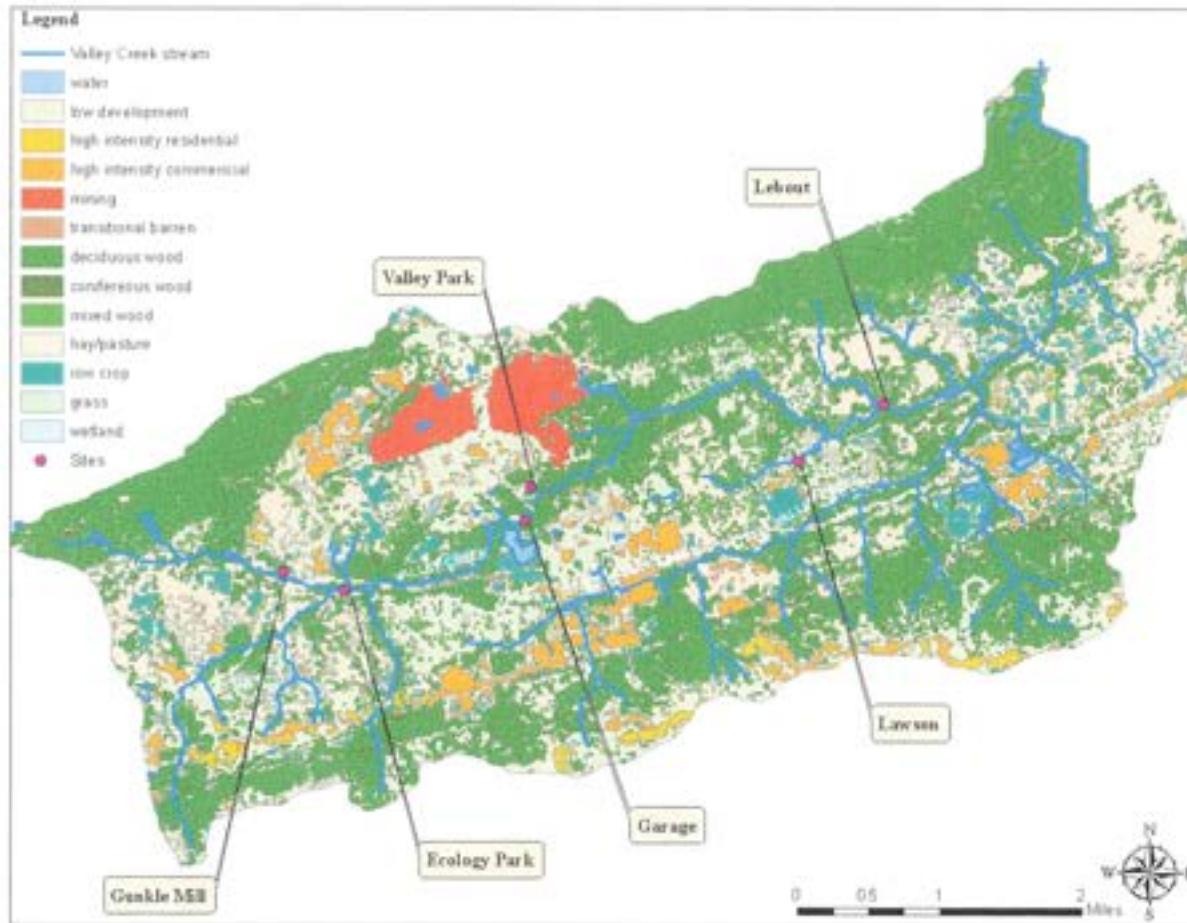


Figure 1-5. Land Use of Valley Creek Basin. Gunkle: commercial and residential. Park: quarry and commercial. Lawson: residential. Lebout: agricultural changing to residential. Eco Park: commercial and residential. Garage: commercial. Land use GIS data from Chester County Water Resource

both residential and commercial land use surrounding Gunkle. Park is located on Rt. 29 north of Rt. 202 at Valley Creek Park (East Whiteland Township Park). There is a quarry just north of this site. To the south, east, and west of the spring are commercial office parks. Lawson is located on Swedesford Road, directly west of Great Valley Presbyterian Church, in a residential area. The spring on Leboutillier Road (abbreviated as Lebout) is surrounded by old farmhouses and fields that are no longer used for agriculture. These fields are now filled with grass, but on some new houses are being built. Thus, Lebout represents an area in transition from agriculture to residential land use. Eco Park spring is at Ecology Park on Conestoga Road, just east of the Rt. 202 onramp. This location is very close to Gunkle, so Eco Park has a similar land use of commercial and residential. Garage spring is located at the bottom of a hill on Old Morehall Road, slightly southeast of Park. Garage is named after the property directly adjacent, which is a mechanic shop. The rest of the surrounding area is mainly composed of commercial offices, similar to Park.

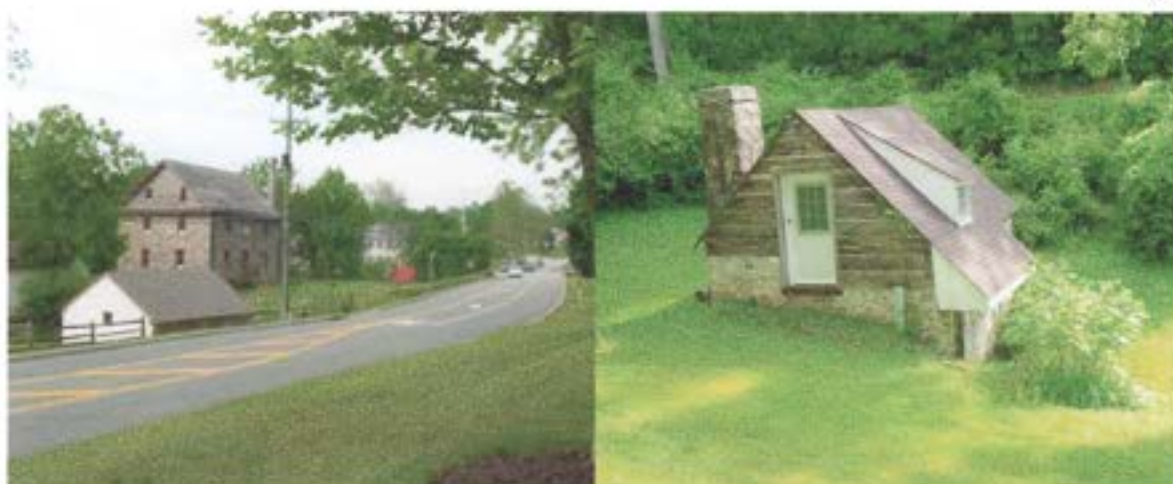
To add contrast to the data collected from the urban sites listed above, data from past studies at rural karst springs are included in this paper. The two rural site locations are Nolte in Lancaster County, PA and Bushkill in Easton, PA. Nolte's recharge area is in pastureland, which isn't surprising since 65% percent of Lancaster's land use is for pasture or cropland. Bushkill's recharge area is in a sinkhole rich location that contains an athletic field and a small farm.

Spring Descriptions

Gunkle, Park, Lawson, and Lebout springs are all located at springhouses on the Elbrook Formation. Their site locations are pictured in figure 1-6 A-D. The other two springs, Eco Park and Garage, are located within stream banks on top of the Ledger Dolomite. Their site locations are shown in figure 1-7 A & B. Gunkle, Park, Eco Park, and Garage all have similar spring mouths', they have obvious discharge points in which the location and shape of the spring mouth is easily seen. Gunkle and Park's spring mouths are situated at 5-10 cm openings within outcrops. Eco Park's spring mouth is along a bedding plane on a stream bank. Garage's spring mouth location also has a distinct opening in a stream bank, but the mouth has now shifted about two meters to the right of the spring house in which it initially resided. Lawson and Lebout's spring mouths are more diffuse and bubble up through sediment rather than at an outcrop.

Previous Work

Continuous logger data on water levels and conductivity was reported by another graduate student, Ms. Youa Yang. She concluded that there are short flow paths in Valley Creek's karst system (Yang, 2006). The evidence for the short flow paths was seen in the springs' small response to storm events. The rise in water level was minimal and the return to base flow was fast, on the order of hours rather than days (figure 1-8). The springs' water level response to storm events looked small compared to a typical groundwater spring. This muted storm response was likely due to reduced infiltration caused by impervious surfaces.



A

B



C

D

Figure 1-6. Photographs of Elbrook Formation spring sites.

(A) Gunkle Mill's spring house is the lower white building in front of the stone mill. The old mill is seen just behind it. (B) Valley Creek Park (Park) Spring House. (C) Lawson Spring House. The roof collapsed, but four stone walls are remaining. (D) Lebout Spring House.



Figure 1-7. Photographs of Ledger Dolomite Formation spring sites.

(A) Garage's spring mouth is located in the stream bank five feet to the right of the old spring house. (B) Ecology Park (Eco Park) spring mouth is also located in a stream bank to the right of the bridge (indicated by arrow).

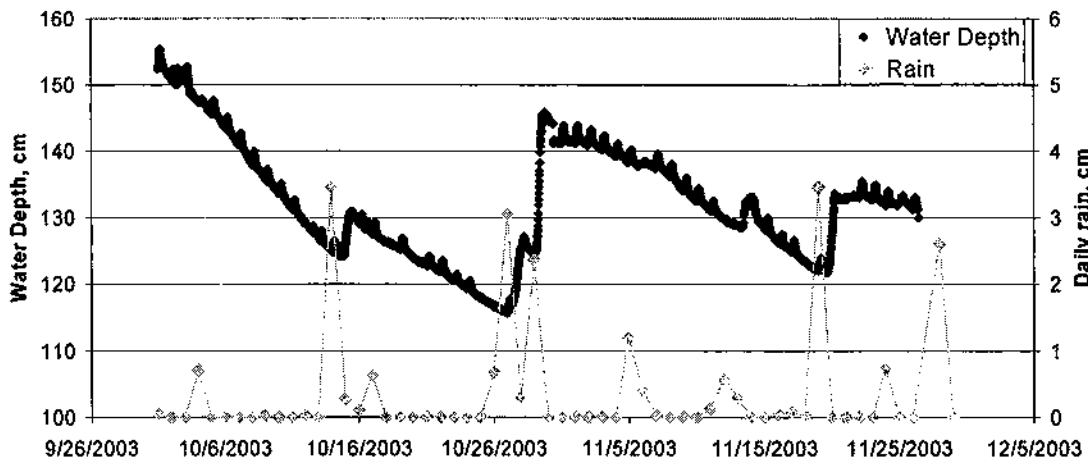
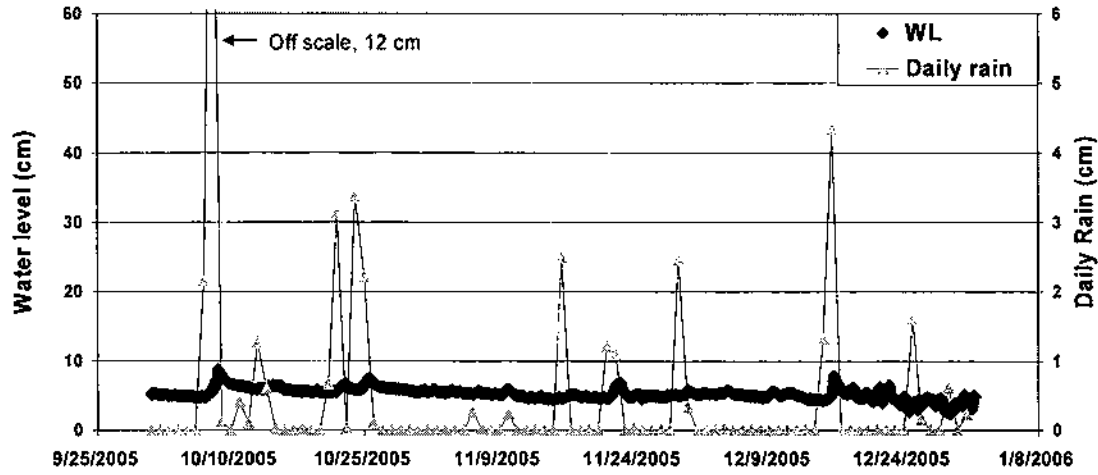


Figure 1-8. Urban and Rural Hydrographs. (A) Urban storm hydrograph for Gunkle. (B) Rural storm hydrograph for Nolte. The urban storm signal is muted due to less infiltration. (Yang, 2006)

Goals & Hypothesis

The goal of this thesis was to characterize the impact of urbanization on karst springs within the Valley Creek Basin. Geochemical data from the urban springs was compared with data previously collected at rural karst springs to determine what aspects are related to land use and which are related to spring type. Geochemical data are used to determine types of flow paths, nitrate levels, metal concentrations, and saturation indices. Coefficients of variations (CVs) for hardness and saturation indexes of calcite were used to differentiate between matrix and conduit flow paths and to interpret flow path length. Metal concentrations were analyzed in both sediment and water samples as a way to track potential urban contamination. Suspended sediment concentrations were also used as a means of tracking urban sediment contamination. The data collected were evaluated and reported to show how the urban springs are similar to the rural springs and in which ways they have been impacted by urbanization.

The hypothesis of this thesis was that urban springs would have characteristics distinct from rural springs. One possible distinction was that urbanization would result in contamination of the springs. Contaminants considered included trace metals, sediments, road salt, and nitrate. Distinctions in flow paths were also considered. Flow paths analyses included differentiating between matrix or conduit dominated flow, evaluating storm response, and inferring flow path lengths and depths.

CHAPTER 2 GEOCHEMISTRY

Methods

Field work

Site visits and field work for this research paper were conducted every three to four weeks. At each site a round of samples was collected; these included a 500 ml unfiltered suspended sediment sample, a filtered 50 ml ion sample, a filtered 125 ml alkalinity sample, and (for seven months) a filtered trace metal (ICP) sample. The trace metal samples are discussed in Chapter 4. Duplicate samples of each type were taken for each sampling round. These samples were kept cool until they were brought back to the lab and stored in a refrigerator. During these visits, data were also downloaded from Global Water loggers. Each logger was equipped with an electrical conductivity probe, a transducer (water level), and sometimes a temperature sensor. If the Global Water logger did not have temperature sensor, then a Hobo temperature sensor was used instead. The logger data were described elsewhere (Yang, 2006). In addition to these continuously measured elements, point measurements for electrical conductivity, temperature, and pH were taken using hand held meters.

Geochemical analyses

Most of the geochemistry data was gathered using a Dionex GP40 DX Land 5.1 Software ion chromatograph. The Dionex is able to analyze for either cations or anions at one time, and for this research it was calibrated to analyze

Na, Ca, Mg, K, Cl, F, NO₃, and SO₄. The ion chromatography instrument uses a column lined with either a positive or negatively charged polymer to separate the anions or cations. Since the ions in the sample are attracted to the oppositely charged polymer in the column, the higher the attraction, the longer it takes for that ion to travel through the column. A detector measured the ions at the outlet of the column. Each ion had an individual peak at its corresponding retention time, which was specific to the ion and used for identification. The area under the peak was calculated and converted into concentrations in mg/L.

The Dionex can not detect alkalinity (HCO₃), so titration was used instead. A Hach digital titrator was used to titrate 50 ml portions of each sample with of 1.600 ± 0.008 N sulfuric acid at a time to. The pH of the sample was continuously measured and recorded. At first as the acid was added to the sample, there were only small drops in pH. However, when the buffering capacity of the sample was reached, a larger drop of about 1 pH unit (10⁻¹) occurred. The data on the amount of acid added and the corresponding pH readings were entered into U.S.G.S. alkalinity calculation webpage (<http://or.water.usgs.gov/alk/>) to determine the HCO₃⁻ concentrations in mg/L.

Coefficients of Variation, Nitrates, & Geochemical Modeling

Valley Creek Basin is situated in dolomite rock. Dolomitic rocks form alkaline rich ground water, so bicarbonate (HCO₃⁻) is the dominant anion. The other two largest constituents are magnesium and calcium, which are reported together as hardness. High levels of Mg²⁺ and Ca²⁺ are typical of the dissolution

of dolomite. The value for hardness is expressed as the total concentration of Ca^{2+} and Mg^{2+} as milligrams per liter equivalent CaCO_3 (figure 2-1). It is calculated from the following equation which converts Ca^{2+} and Mg^{2+} concentrations to equivalent concentrations of CaCO_3 (Freeze and Cherry, 1979):

$$\text{Total Hardness} = 2.5(\text{Ca}^{2+}) + 4.1(\text{Mg}^{2+}) \quad \text{eq.5}$$

The groundwater's concentration of elements is greatly effected by the type of flow path that the water traveled through the aquifer. Matrix flow paths have more surface area contact between the water and carbonate rock, resulting in higher dissolution rates. More conduit based flow paths have less water-rock interaction and thus not as much dissolution of the rock. Because conduit flow can vary between the larger conduit openings and the smaller matrix fissures, these springs show more variation in dissolved ion concentrations. In this study concentrations of hardness were used to compare flow paths between the different springs.

After collecting hardness data, coefficients of variation (CVs) were calculated to compare hardness variations between different springs. CVs allow for a normalization of concentration variations at one spring, so that it can be compared to amounts of variation at other springs. This way even if two separate springs have differing average concentrations, their range of the concentrations can still be compared. CVs are calculated by dividing the standard deviation of the hardness by the mean value of the hardness and multiplying by 100, as shown on the following page.

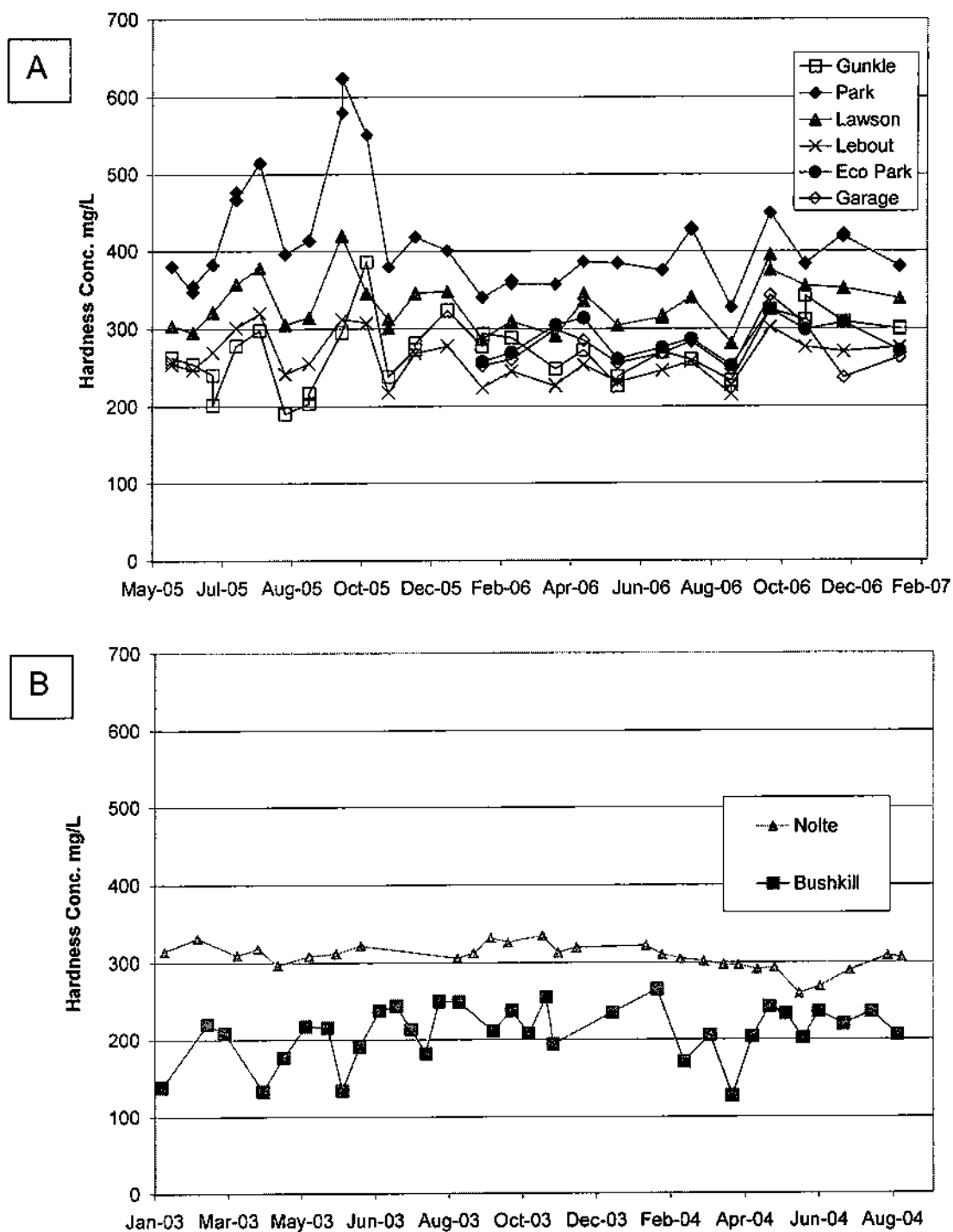


Figure 2-1, A & B. Hardness (as CaCO_3) concentration charts for urban and rural sites. (A) Urban sites show hardness variation typical of karst. (B) Rural sites plotted at the same scale for comparison. Nolte has more consistent concentration, typical of matrix flow, while Bushkill has more variation suggesting conduit flow.

$$CV = 100 \times \frac{\text{Standard Deviation of Hardness}}{\text{Mean Value of Hardness}} \quad \text{eq.6}$$

Springs that have lower CV values show less variation in their concentrations and have a more matrix based flow path. Likewise, springs with higher CV values have greater variations in their hardness concentrations, indicating more conduit flow paths. A general guideline is the very diffuse springs will have CVs below 5%, while conduit springs have CVs between 10 and 24%. (Shuster and White, 1971)

The saturation index (SI) describes quantitatively how close the carbonate waters are to equilibrium with the calcite or dolomite (White, 1988). The definition of the calcite and dolomite SI's are given below:

$$SI_c = \log \left(\frac{\alpha_{Ca^{2+}} \alpha_{CO_3^{2-}}^2}{K_c} \right) \quad \text{eq.6}$$

$$SI_d = \log \left(\frac{\alpha_{Ca^{2+}} \alpha_{Mg^{2+}} \alpha_{CO_3^{2-}}^2}{K_d} \right) \quad \text{eq.7}$$

If the water is exactly saturated with respect to the mineral, then the saturation index will equal zero. However, natural karst waters are rarely in equilibrium with their surrounding rock. When water is undersaturated with respect to the carbonate rock, then the SI value will be less than 0, and when it is supersaturated it will be greater than 0. The SI values were calculated using the PHREEQC Interactive 2.8 software (Parkhurst and Appelo, 1999).

In addition, PHREEQC was used to calculate the partial pressure of carbon dioxide in equilibrium with each water sample. The carbon dioxide partial pressure expressed in atmospheres, or P_{CO_2} , is also important to understanding the karst geochemistry. P_{CO_2} is affected by the atmospheric CO_2 levels, the CO_2 produced in the soil zone, and the amount of carbonate rock dissolved. The atmospheric concentration of CO_2 is close to 380 ppm, corresponding to a P_{CO_2} of $10^{-3.5}$ atm. Soil P_{CO_2} varies depending on biological processes, but 10^{-3} to 10^{-2} atm is common (White, 1998). In an open system, the dissolved CO_2 will interact with water and dissociate to form carbonate ions (CO_3^{2-}) and hydrogen ions (H^+) forming a mildly acidic solution.



Since pH is the negative logarithm of the activity of the hydrogen ion, in pure water the P_{CO_2} and pH should follow similar trends, but with opposite changes in value.

When carbonate rocks dissolve in a closed system, there are two competing influences on P_{CO_2} . The increase in pH will tend to lower the P_{CO_2} . However, the increase in total inorganic carbon will tend to increase the P_{CO_2} . Because the system is closed, the CO_2 cannot be out gassed. Thus, when P_{CO_2} values are higher than atmospheric or soil gas values, it is an indication that the system is closed.

Unlike the hardness or SI values, the nitrate levels found in the spring samples are not related to flow path types because their concentrations are not due to dissolution of the carbonate rock. Nitrate levels are related to land use or

intensity of nitrate application. A common source of nitrate is fertilizers that are applied to fields. Fertilizer that is not taken up by plants is washed down through the soil infiltrating into the groundwater system. At the end of a growing season the plants are no longer taking up nitrate, which increases the amount infiltrating into the groundwater system. This creates a seasonal trend with a rise in concentrations during the autumn months.

Results

Coefficient of Variation of Hardness

CV values of hardness that range from 10 to 24% indicate a conduit system, while values of less than 5% indicate a matrix system (Shuster & White, 1971). The urban springs' CVs were ranged from 14.5% to 8.2% (table 2-1). Gunkle and Garage had the highest CVs. However, their CV values still fell relatively low for the range of conduit springs. These relatively low CV values are evidence that the flow paths do not involve cavern sized conduits. Eco Park has a conduit spring opening, but the CV is lower than typical for conduit springs. It may be that the sample collection at that site (one year) was not sufficient to detect the variation. Lawson and Lebout are more diffuse springs as is evident by more dispersed discharge at the spring mouths. However, their CV values are close to conduit and range above 5%. Thus, their flow likely contains some conduit pathways.

The rural karst sites had a large difference in their CV values. Nolte spring's 5.6% is diffuse, while Bushkill spring's 17.5% is well into the conduit

	Gunkle	Park	Lawson	Lebout	Eco Park*	Garage*	Nolte **	Bushkill **
CV of Hardness	14.5	10.7	9.8	9.3	8.2	11.2	5.6	17.5
Average log PCO₂	-1.9	-1.9	-1.9	-2.1	-1.6	-1.8	-1.6	-2.3
Average SI_{Ca}	-0.3	-0.01	-0.05	-0.1	-0.4	-0.3	-0.4	-0.3
Average SI_{dol}	-0.6	-0.05	-0.1	-0.2	-1.0	-0.5	-1.3	-1.1

Table 2-1. Table of CV, log PCO₂, and SI values for urban and rural sites. May '05 – Feb '07

* Eco Park and Garage had a shorter sampling period from Feb. '06 to Feb. '07

**Nolte and Bushkill data for similar time period from 2003-2004.

range. The range of CV values for both urban and rural springs includes conduit and diffuse flow. This gives evidence that CVs are not a result of land use, but of the type of flow system.

Nitrates

While there may not have been evidence of urbanization affecting the CV values, there is distinction between the urban and rural springs' nitrate values. In the rural springs there were larger $\text{NO}_3\text{-N}$ concentrations and greater variation of the concentrations than in the urban springs. Bushkill's concentrations ranged from 1.4 to 8.2 mg/L and Nolte's concentrations ranged from 6.87 to 19.53 mg/L (figure 2-2 A). These higher concentrations relate to the agricultural land use near the springs' recharge areas. Concentrations of nitrate higher than 4 to 5 mg/L signify contamination from an outside source, such as sewage, fertilizer, or animal manure (Martin, 1997).

At the urban sites there is very little nitrate in the water and little variation in concentrations. Almost all of the concentrations were below 4 mg/L (figure 2-2 B). Generally, Gunkle and Lebout's values were between 3 and 4 mg/L; Park, Lawson, and Garage's values were between 1 and 2 mg/L; and Eco Park's concentrations were in the middle averaging 2.5 mg/L. Some of the variations within these concentrations fall in the Dionex ion chromatograph detection limit of 1 to 2 mg/L. These lower concentrations are evidence of a lack of agricultural land use in the area. Figure 2-2 B shows a slight seasonal trend rise of 0.5 to 1.5 mg/L starting in October and ending in January. The increase in nitrate

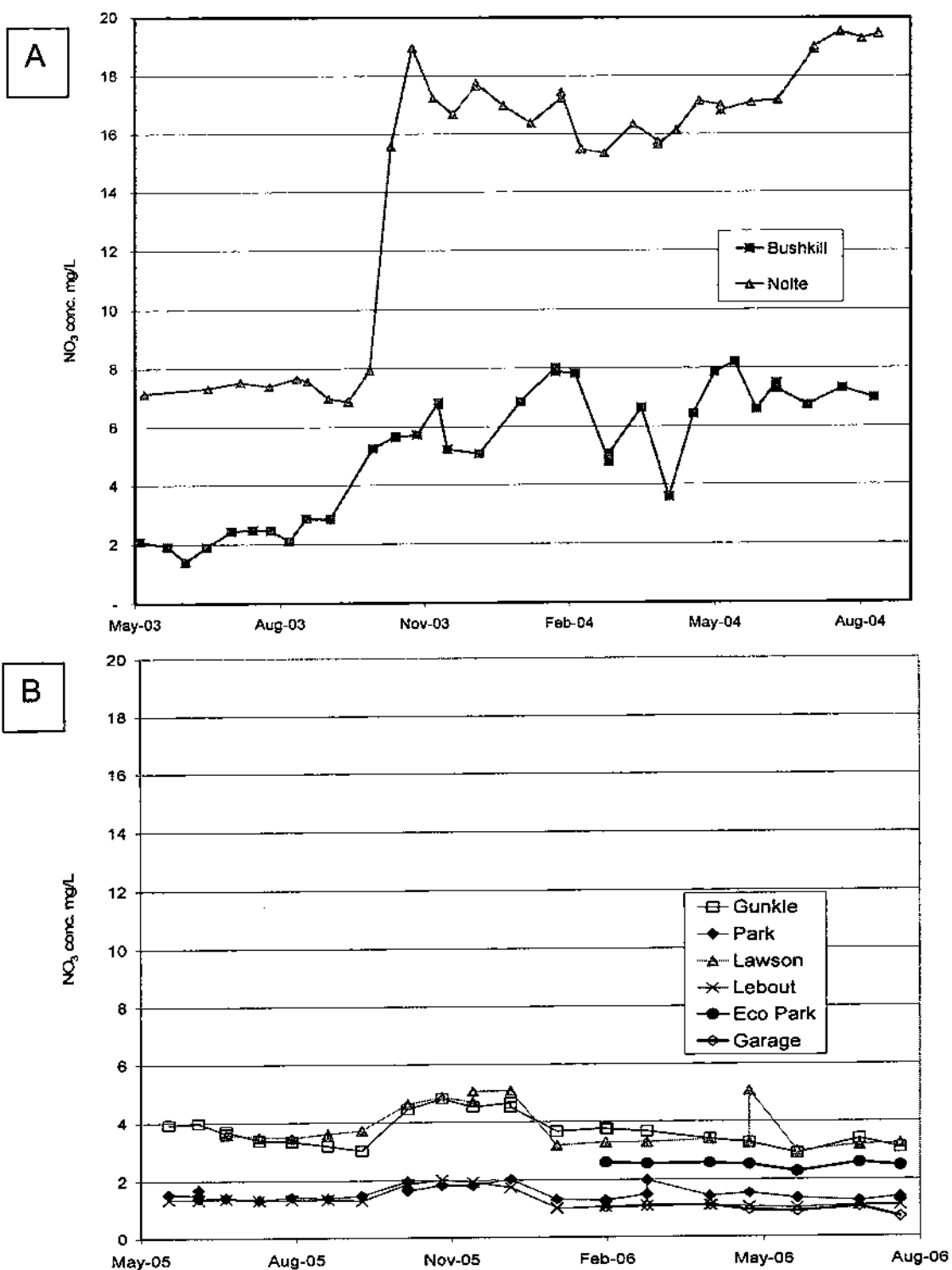


Figure 2-2, A & B. Nitrate concentrations for urban and rural sites. Both charts plotted at the same scale. (A) Rural sites have larger concentrations and a strong seasonality trend. (B) Urban sites have lower concentrations and only a slight seasonal trend.

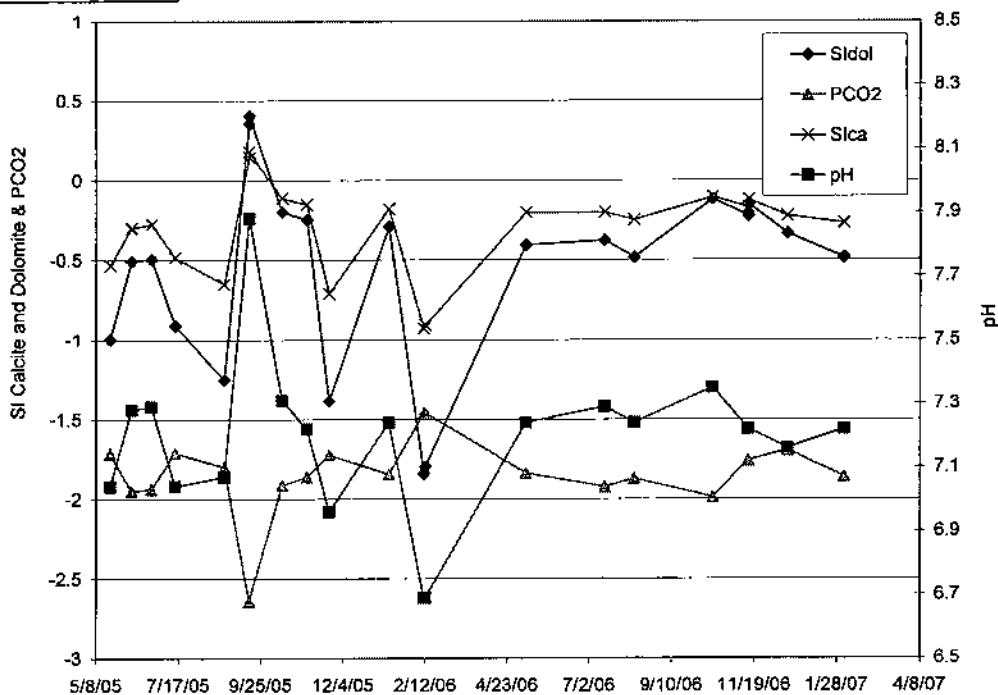
concentration could be due to lawn fertilizers washing into the system at the end of the growing season, as there are manicured lawns surrounding homes and office complexes in the area.

Saturation Index & Carbon Dioxide Partial Pressure

The SI and PCO_2 values varied from site to site (figure 2-3 to 2-6). Most of the PCO_2 values at the urban sites were fairly low, with the log PCO_2 averaging -1.9 (table 2-1). The rural Bushkill spring has the lowest log PCO_2 averaging -2.3. These are indicative of open systems in contact with soil gas. The other rural spring Nolte had slightly higher log PCO_2 (-1.6) suggesting discharge from a closed system. This suggests that the urban system and Bushkill have short, shallow, predominantly conduit flow paths; while Nolte has a longer, deeper flow path (figure 2-7, will be new figure). Bushkill and the urban springs' short, shallow conduit flow paths would allow for greater out gassing of the groundwater, while Nolte's systems' longer, deeper flow paths would allow the CO_2 to build up in the system.

Gunkle's calcite and dolomite SIs were undersaturated for most of the year (figure 2-3 A). Most of the values vary between -0.7 to -0.1 for the SI_{ca} and it averages -0.3. The SI_{dol} mostly ranges between -1.4 to -0.2 and its average is -0.6, so Gunkle spring's water is not greatly undersaturated. Gunkle's log PCO_2 is fairly steady around -1.8, except for a dip to -2.6 also on 9/15/05. Park's SI values also vary (figure 2-3 B). Most of the SI values are between -0.2 and 0.2 with an average of 0.01 for the calcite and between -0.4 and 0.6 with an average

A: Gunkle



B: Park

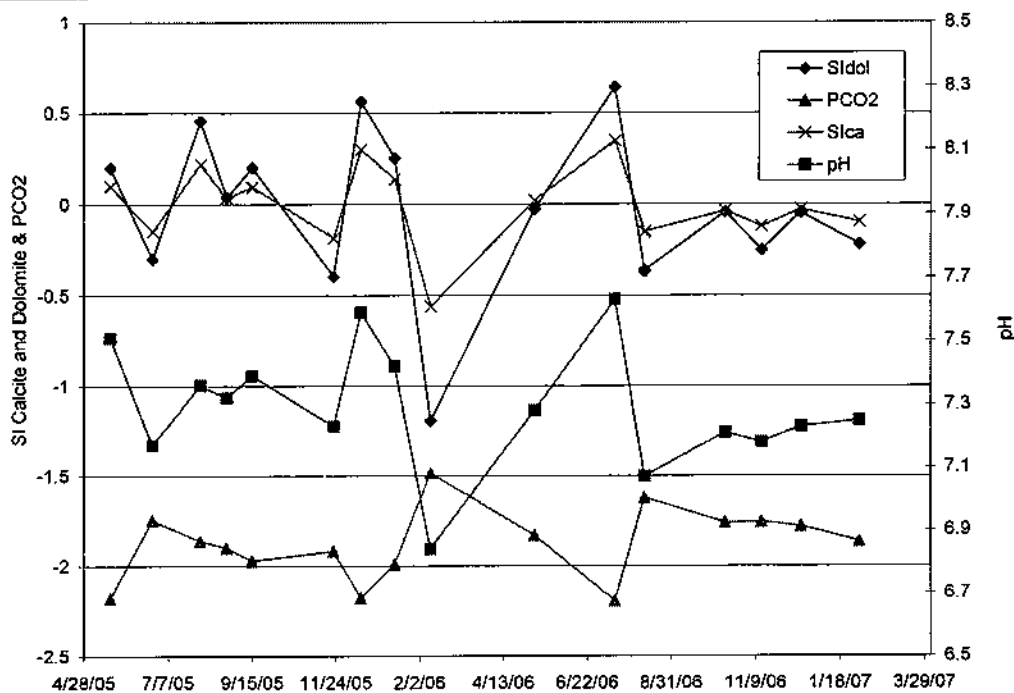
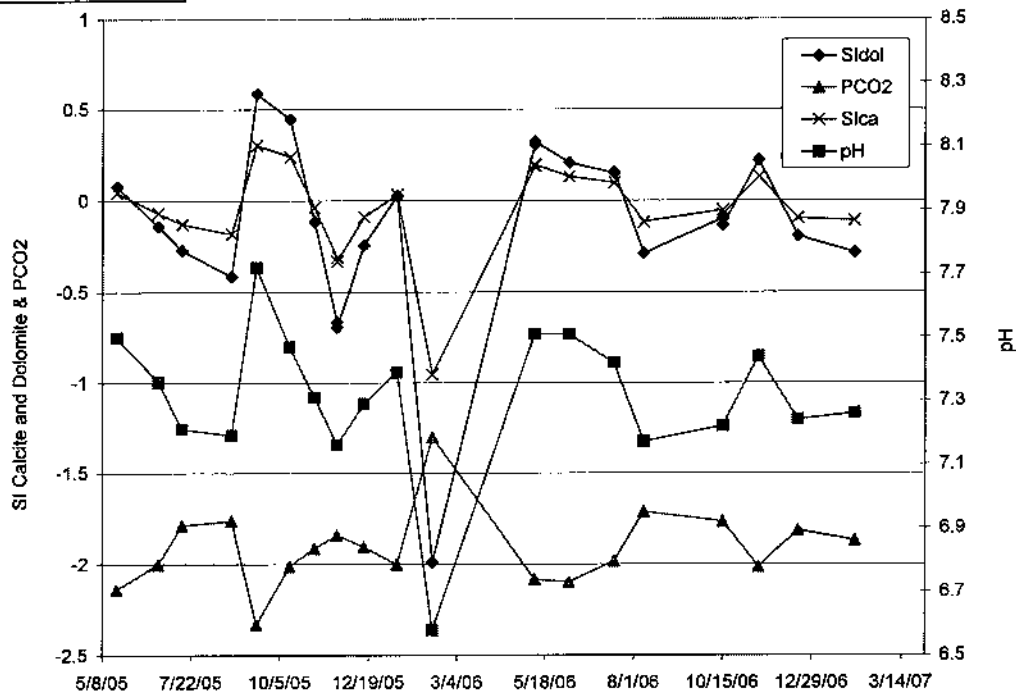


Figure 2-3, A & B. SI calcite (Slca), SI dolomite (Sldol), PCO₂, & pH charts for Gunkle and Park. (A) Gunkle (B) Park

A: Lawson



B: Lebout

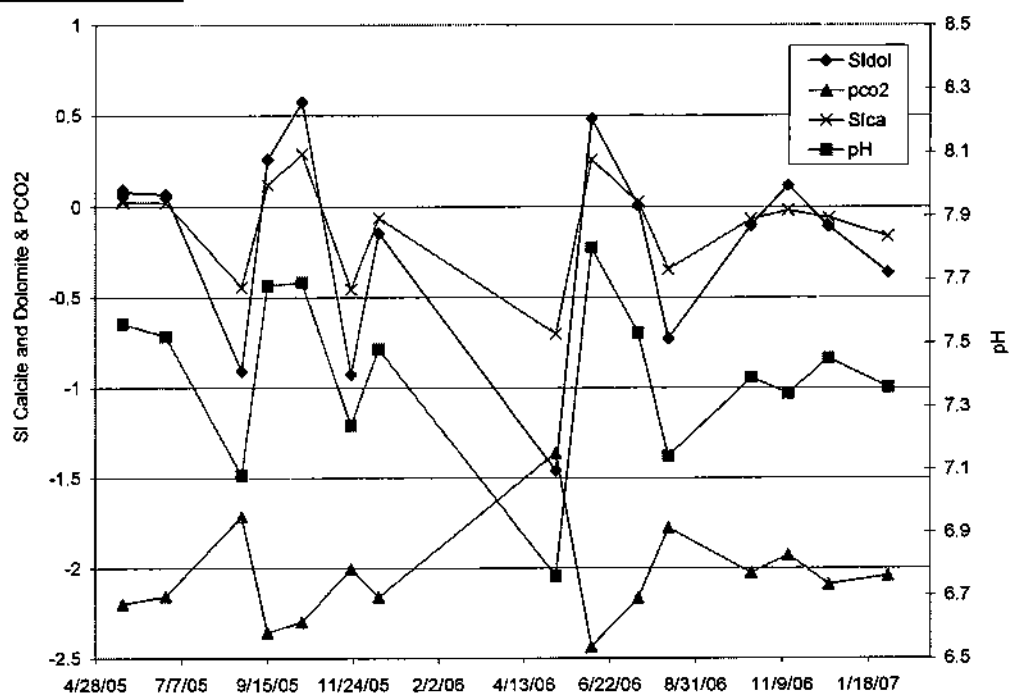
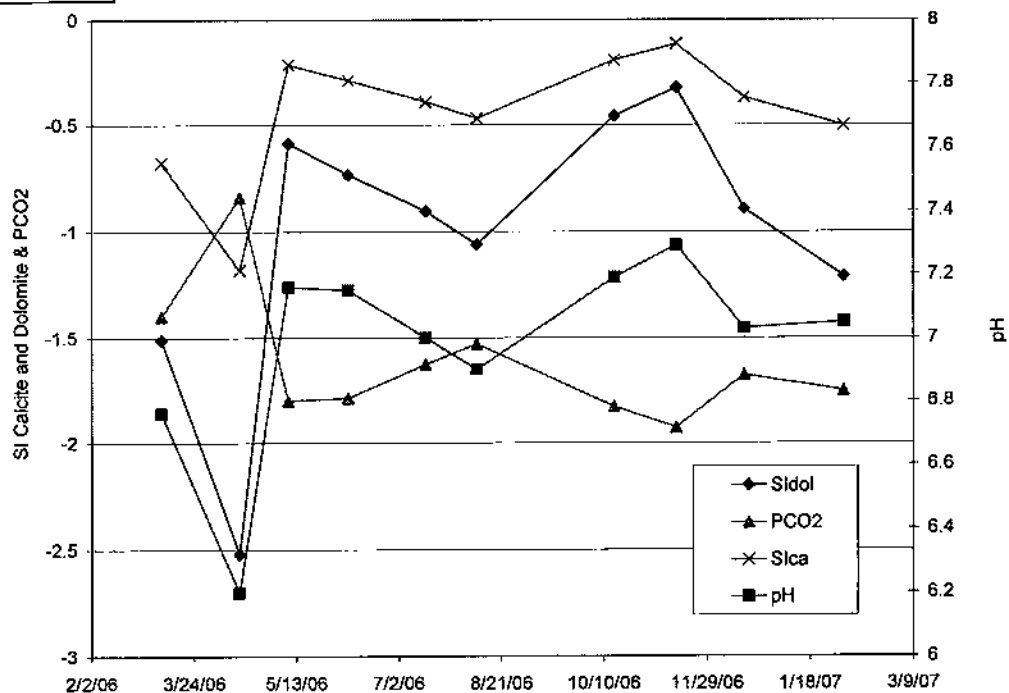


Figure 2-4, A & B. SI calcite (Sica), SI dolomite (Sldol), PCO₂, & pH charts for Lawson and Lebout. (A) Lawson (B) Lebout

A: Eco Park



B: Garage

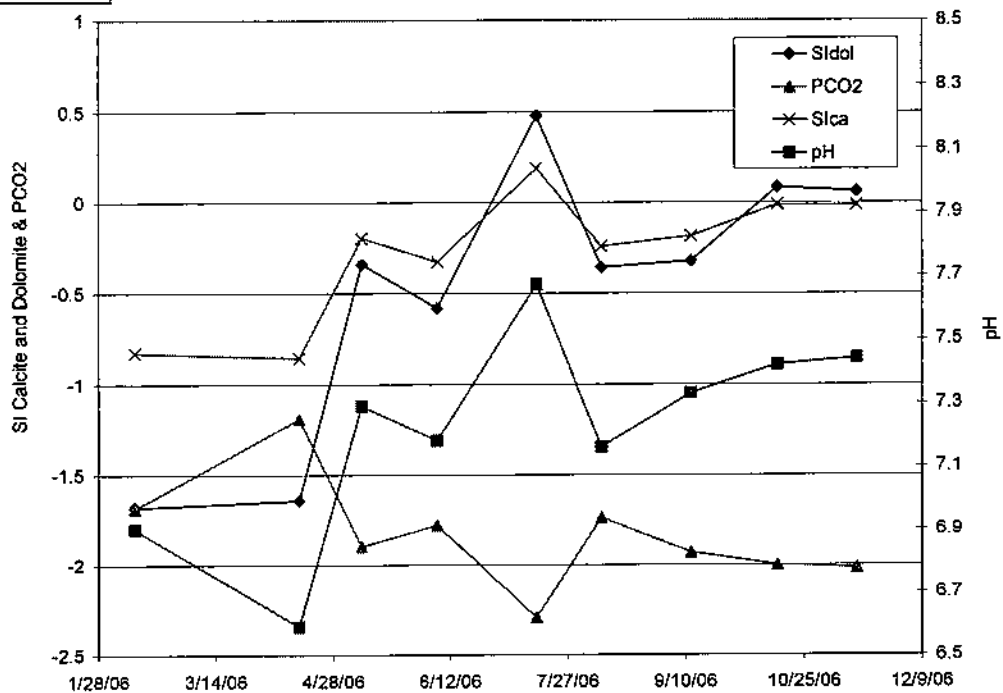
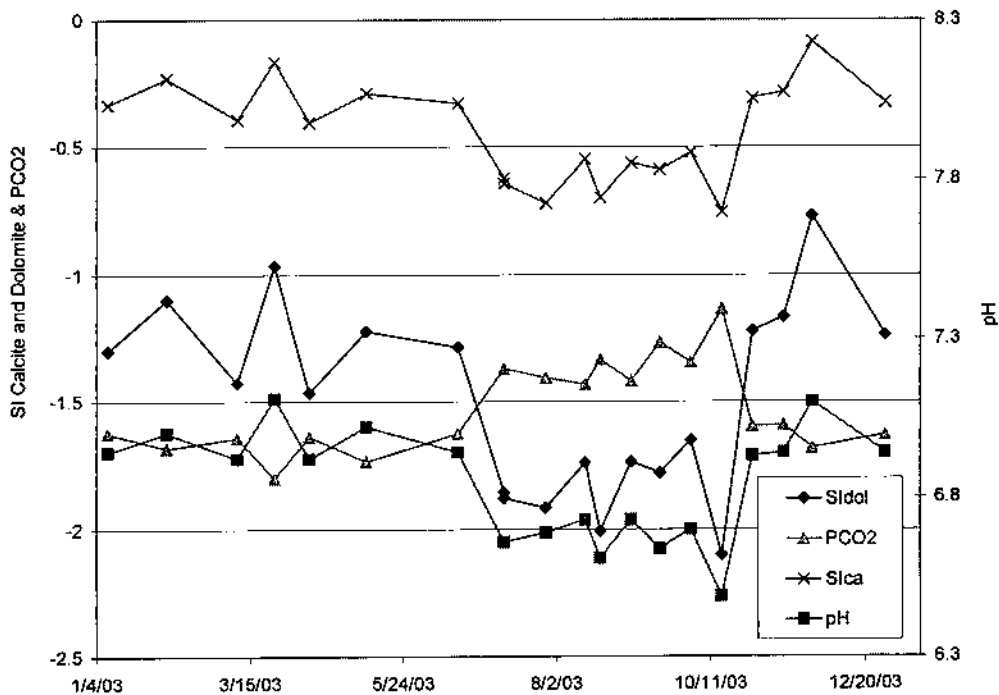


Figure 2-5, A & B. SI calcite (SIca), SI dolomite (SIdol), PCO₂, & pH charts for Eco Park and Garage. (A) Eco Park (B) Garage

A: Nolte



B: Bushkill

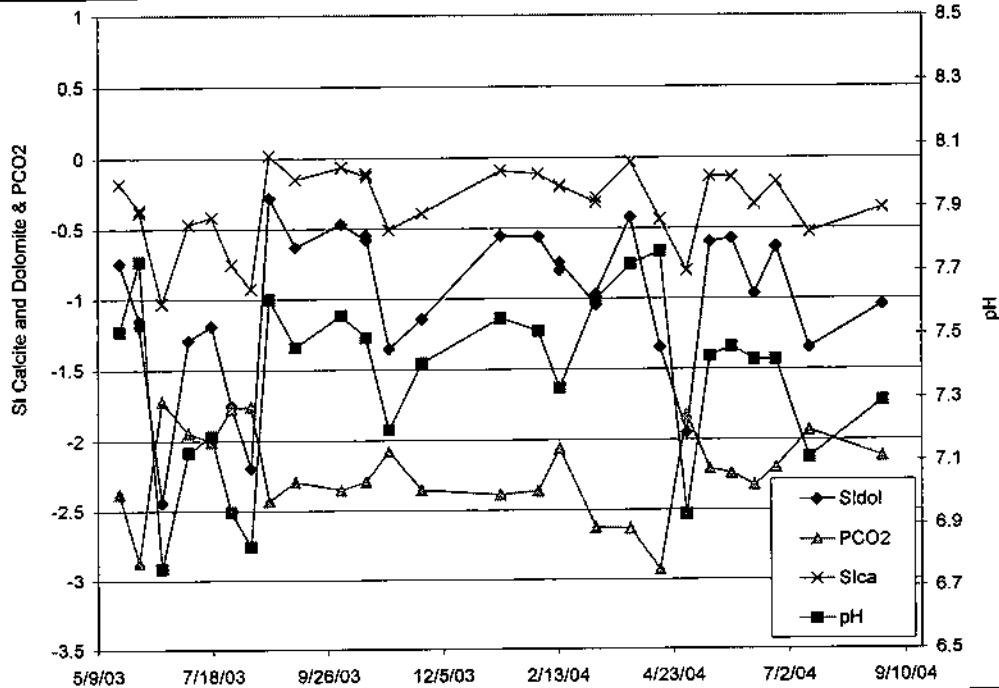
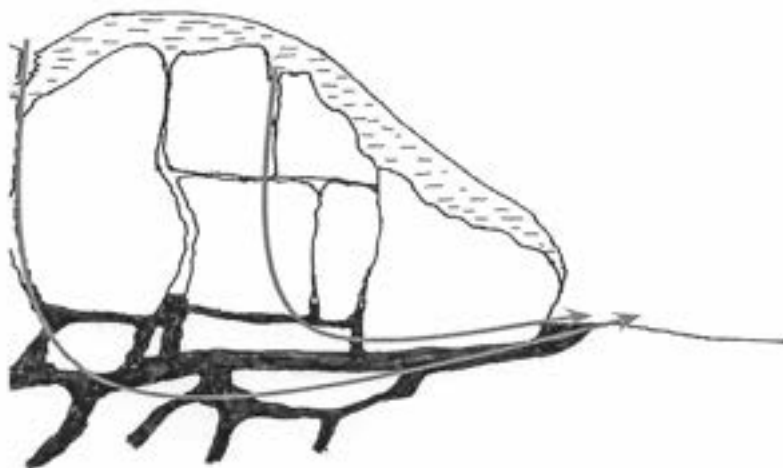


Figure 2-6, A & B. SI calcite (Slca), SI dolomite (Sldol), PCO₂, & pH charts for Nolte and Bushkill. (A) Nolte (B) Bushkill

A



B

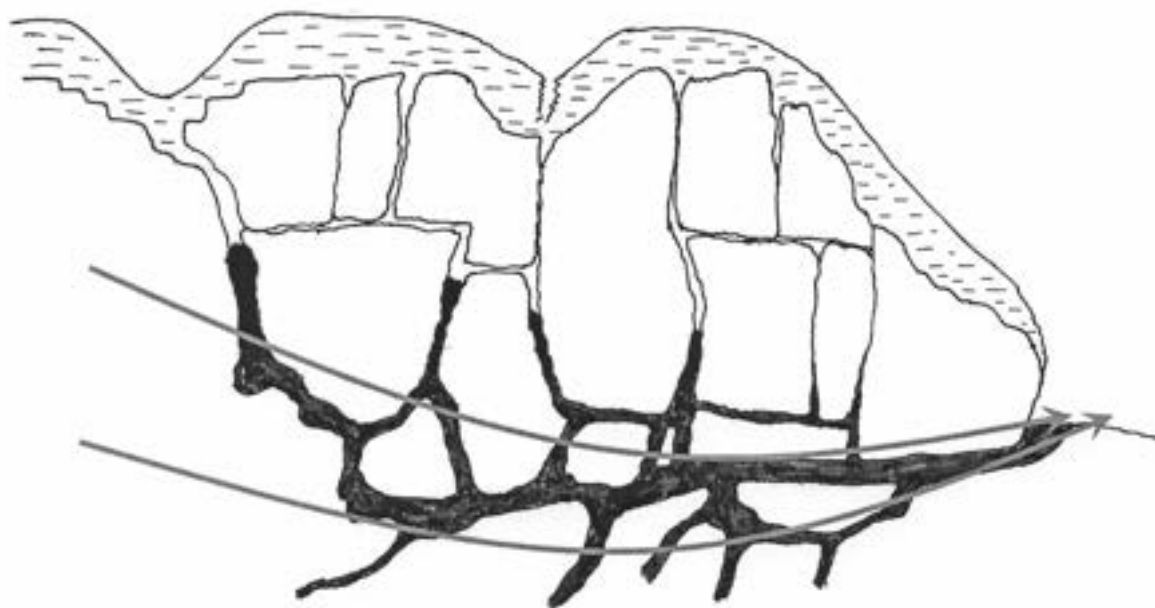


Figure 2-7. Comparison of short, shallow and deep, long flow paths in karst systems. (A) Short, shallow flow paths allow for out gassing found in open systems. (B) Long, deep flow paths limit out gassing (except at the water table) causing higher CO_2 concentrations found in closed systems.

-0.05 for the dolomite. This alteration between positive and negative values shows Park shifting between undersaturation and supersaturation, but on average it is close to equilibrium. Most of Park's PCO_2 values are between -1.6 and -2.2 with an average of -1.9. Lawson also experiences shifting between under and supersaturation (figure 2-4 A). With the exception of 2/11/06, most SI_{ca} values range from -0.03 to 0.3 with an average of -0.05 and the SI_{dol} ranged from -0.7 to 0.6 with an average of -0.1. This shows that Lawson's is very close to equilibrium. The log PCO_2 mostly ranged from -2.1 to -1.7 and averaged about -1.9, which is typical of some interaction with the soil for a shallow flow system. Lebout is similar to Park in that its SI values have a wide range of varying between undersaturated and supersaturated, where about half the values lay in either zone (figure 2-4 B). Most of Lebout's SI_{ca} concentrations ranged from -0.5 to 0.3 and the average was -0.1. Most of Lebout's SI_{dol} range was from -0.9 to 0.6, with -0.2 as the average. Lebout's PCO_2 varied a little bit, but averaged at -2.1.

There was twelve months of data for the sites in the Ledger Dolomite (Eco Park and Garage). Eco Park water samples were consistently undersaturated with respect to calcite and dolomite (figure 2-5 A). Their SI_{ca} mostly ranged from -0.7 to -0.2 and averaged -0.4. Eco Park's SI_{dol} ranged from -1.2 to -0.5 and averaged at -1.0. With the exception of one outlier on 4/15/06, all of the SI measurement fell between -0.2 and -1 and the PCO_2 fell between -1.5 and -1.8 (average of -1.6). Garage was also mostly undersaturated (figure 2-5 B). The SI_{ca} values ranged more widely than Eco Parks, spanning from -0.9 to 0.2 and its

average was -0.3. The SI_{dol} ranged from -1.7 to 0.5 and averaged -0.5. Garage's PCO_2 were all between -1.2 and -2.3 and they averaged -1.8.

As for the rural sites, Nolte's PCO_2 and SI_{ca} had a seasonal trend (figure 2-6 A). Nolte's PCO_2 showed higher values starting in June and ending in October. The high log PCO_2 was -1.2 and the low was -1.8 with an average of -1.6. Due to increase of PCO_2 during the growing season the SI_{ca} averaged around -0.6, while during the non-growing season it was higher and averaged around -0.3, with an overall average of -0.4. Nolte's SI_{dol} had a slightly lower range from -0.8 to -2.0 with an average of -1.3. Bushkill's SI_{ca} were undersaturated and generally ranged from -0.1 to -0.8 with an average of -0.3 (figure 2-6 B). Bushkill's SI_{dol} mostly ranged between -2.0 to -0.5, with an average of -1.1. The PCO_2 was lower than Nolte's and ranged from -2.9 to -1.7 with an average of -2.3.

The average SI and PCO_2 values calculated for the urban springs are not very different from those calculated at the rural springs (figures 2-3 to 2-6). There also isn't a particular spring type that has more variability. This shows that the urban springs and rural springs still have similarities. Although flow paths in the urban system are believed to be shorter due to the fast storm response (Yang, 2006), both the rural and urban springs seem to experience conduit and matrix flow. Both the urban and rural systems have geochemical variation of hardness concentrations typical of karst springs fluctuating between matrix and conduit path ways. However, the open system PCO_2 in most of the urban springs may indicate a shallower flow path than in Nolte spring.

The urban system contains two springs that are close to saturation (Lebout and Park). Neither of these springs are at the low end for CV, which would indicate more matrix flow. Park has a conduit opening and Lebout has a diffuse opening. Although the urban flow paths are believed to be shorter than the rural flow paths, the flow is slow enough to provide time for the water to equilibrate with the rock. The urban karst system seems to have less recharge, which may limit flushing in the urban system compared to the rural. The limited flushing may lead to slower flow paths, giving more time for equilibration.

CHAPTER 3 SEDIMENT

Sediment in the Environment

Sediment in karst systems is categorized by source area.

Sediments that are generated by dissolution processes within the karst system are autochthonous. Sediments that come from outside the carbonate terrain are allochthonous. Allochthonous sediments were transported to or are present in the karst system's recharge area and then taken into the system by infiltrating waters.

An excessive amount of sediment is considered a contaminant.

Construction sites in urbanizing areas can generate large amounts of sediment runoff during storm events. The sediment itself can be a contaminant, clouding the waters and clogging wells. Sediments have also been linked to transportation of other contaminants. Mahler et al. (1999) stated "Mobile particulates play a fundamental role in determining water quality; sediment is itself a contaminant, and also profoundly affects the transport and fate of other contaminants". And Vesper and White (2003) have also stated "The flux of sediment serves to transport metals through karst aquifers attached to fine-grained suspended sediments". Because metals will sorb onto sediment surfaces in much greater concentrations than the quantity remaining dissolved in the water, study of sediment transport is especially important in urbanizing or

industrial areas that are susceptible to metal contamination. A review of trace metals in Valley Creek Basin will be discussed in the following chapter.

Methods

Suspended sediment samples were collected for the urban and the rural sites to determine the total suspended solids (TSS). During site visits, unfiltered 500 mL water samples were collected. While collecting the sample it was important not to disturb the bedload sediment around the spring mouth. Disturbing the bedload sediment would increase the TSS concentration artificially. Several of the spring sites, including Gunkle, Park, and Lebout, had troughs within their springhouses. The water from the spring would flow in these troughs that surrounded the springhouse floor, which resulted in the build up of a layer of bedload sediment. To reduce the chance of disturbing this bedload sediment, the suspended sediment sample was usually the first sample collected at each site and any movement within the trough was done with great care.

In the lab each suspended sediment sample was filtered through two separate filters using a Millipore vacuum system. The first filter was a 5.0 μm pore size to remove most of the sediment, then a 0.45 μm filter was used to separate the remaining suspended sediment from the dissolved solids. These filters were weighted before and after the filtration process to determine the weight of the particles on them. The weight of the filtered sediment on the 5.0 and 0.45 μm filters were added together for each sample. The sample bottles

were also weighed twice, once when they were filled and then again after the sample was poured out, to determine the weight of water filtered. The total suspended sediment weight was then divided by the water weight to determine the suspended sediment concentration in mg/L.

The suspended sediment sample collection at Garage and Eco Park was more difficult than at the other spring locations. Garage and Eco Parks' spring mouths are located in stream banks that erode easily. During each site visit their spring mouths had to be dug out from soil that collected around them. This digging disturbed the bank soil, and even after waiting for the springs' flow to clear, some particles of bank soil were found to contaminate the suspended sediment samples. Due to the presence of bank soil, data on Garage and Eco Park suspended sediment samples were not included here.

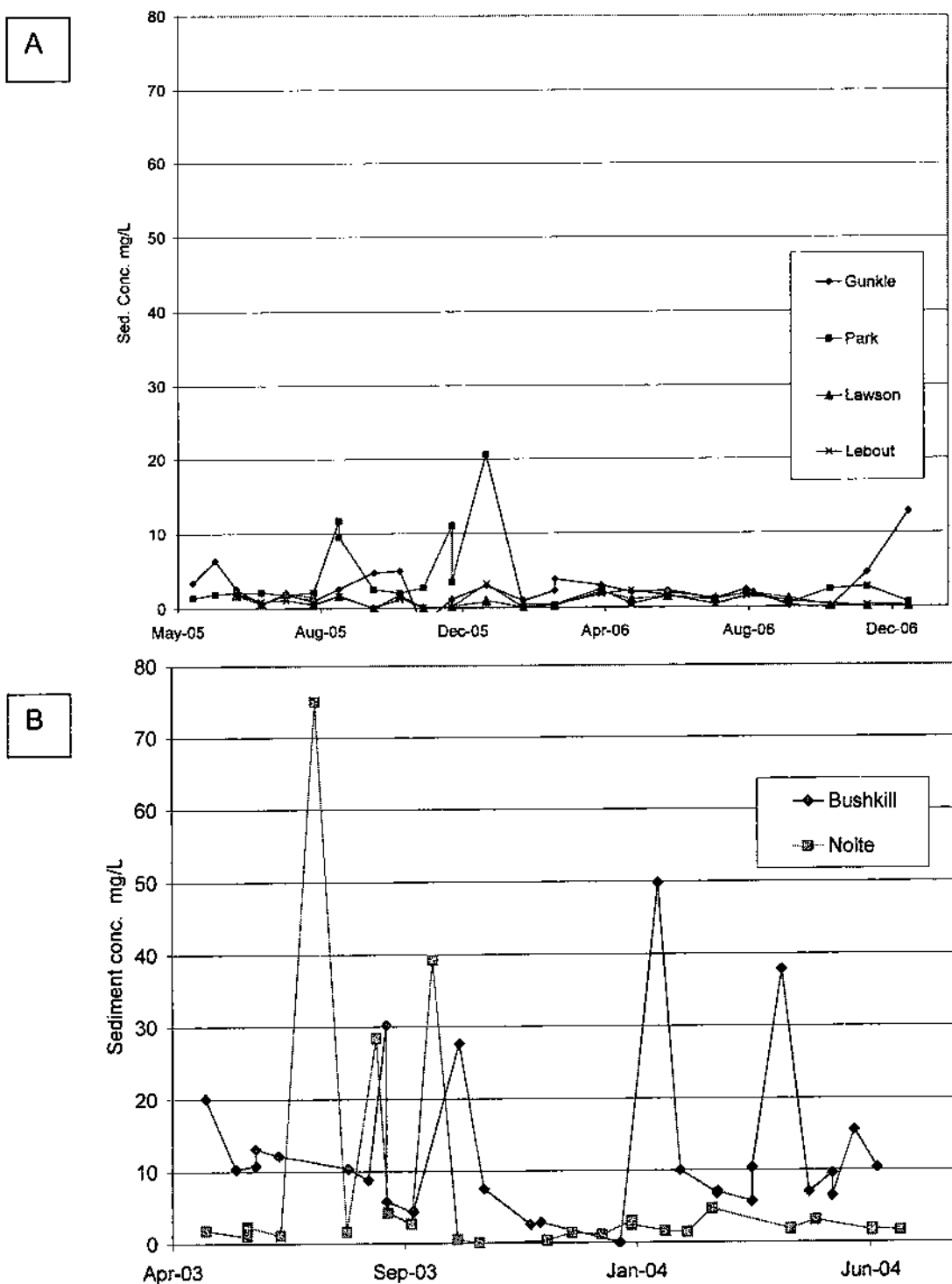
ISCO automatic storm samplers were also set up at Gunkle, Park, Lawson, and Lebout to sample storm flow sediment concentrations. ISCO samples collect up to 24 samples at a timed interval (every 45 minutes for this study). The use of these samplers proved to be problematic due to the springs' lack of water level response during storm events. The ISCO setup includes a sensor that would determine when water level rose (due to a storm event) and that would trigger a round of sampling. Because the springs' rise in water level was minimal, the ISCO's sensor rarely triggered, and there would not be any samples of the storm flow. This made it difficult to compare base flow and storm flow suspended sediments.

After the sampling for this research paper was completed the suspended sediment samples were analyzed to determine the sediments' mineralogy. The filter papers that had been used to separate the sediment from the water were placed under a light microscope to magnify the grains. Lebout was chosen as a representative site in which a majority of samples were analyzed to determine the overall trends in mineralogy. Then selected samples from each of the other sites were analyzed for comparison. After the samples were examined under the light microscope, a quarter of the filter paper was cut off and a drop or two of 68-71% trace metal grade nitric acid was applied. This acid test was used to determine the presence of carbonate minerals, which would fizz as when reacted with the acid.

Results

Suspended sediment in baseflow samples

The urban spring locations had very low suspended sediment concentrations (figure 3-1 A). The concentrations were generally lower than 4 mg/L and almost all were about 2 mg/L or less. The small amount of variation seen was usually within 1 to 2 mg/L, which is the sensitivity range for the suspended sediment analyses. Sometimes higher concentrations were seen at Park spring, such as 20 mg/L on 1/12/06. However, the conduit opening at Park created turbulent water at the spring mouth. The turbulent water may have



mobilized bed sediments and is the most likely cause of the occasional higher urban sediment concentrations.

The rural springs had much more variation in their suspended sediment concentrations (figure 3-1 B). At times sediment values were low, similar to the urban springs, but sometimes they would have high peaks ranging between 28 and 50 mg/L. Nolte had a peak of 79 mg/L on 7/9/03.

A possible reason for the low sediment concentrations at the urban sites could be because the conduits are too narrow to allow the sediment to pass. If the urban systems' flow paths are narrow, the water's velocity would be slower; and according to Stoke's Law that would make it difficult to transport suspended sediment. Narrow passageways would also indicate small intersections, which could further limit the volume of suspended sediment flowing through the system.

However, there are geochemical data supporting the presence of conduit flow, so there are larger passage ways in which sediment could be transported. As stated in the previous chapter on geochemistry, some of the urban springs' flow paths are believed to be conduit dominated, particularly Gunkle, Park, Garage, and Eco Park. These springs have CV values within the conduit range (excluding Eco Park), suggesting that there are larger passageways within the urban karst. Their spring mouths are also distinctly conduit, so there is no obvious physical feature that would limit sediment transport within the system.

Also, inside each urban springhouse there is a layer of sediment covering the trough floors. The sediment layer is approximately 5 cm thick and it formed

by accumulation of suspended sediment being discharged at the springs.

When the water discharges from a spring, it leaves a narrow passageway, and then spreads out into a larger trough within the springhouse. Moving from a narrow passage into a wider trough increases the area and allows the water's velocity to slow. Slowing the velocity results in sediment particles settling out of the water and accumulating on the trough floor. Because of this accumulation of sediment, it is common for springhouse troughs to be periodically dredged.

Although it is not possible to determine the last date at which these springhouses were dredged, the volume of sediment collected in the troughs is evidence that the volume of sediment flow was likely much larger in the past for this urban karst system. If suspended sediment levels had always been as low as they are now, it would have been difficult to build up the present amount of bedload sediment.

While the data from the urban springs has shown consistently low suspended sediment levels, as previously mentioned, the rural springs have had periods of high and periods of low sediment flow. The variation could be a result of the rural springs having larger recharge areas. Due to the larger area in which water is infiltrating, it would be easier for larger volumes of water and sediment to enter the rural systems. The recharge area is related to the spring's discharge rate. The urban discharge rates range from 0.6 L/sec for Gunkle to 15 L/sec at Lawson, with an average of 5.4 L/sec (Yang, 2006). They are smaller than the rural springs discharge rates, for example, Nolte discharge rate is 25 L/sec (Tancredi, 2004). Because of the smaller discharge rates, and hence smaller

recharge areas, the urban system is less likely to have the same volume of sediment entering as the rural system. Bedload sediment layers found in the spring house troughs indicate that in the past there was greater suspended sediment discharge at the urban springs. There are certainly greater sediment flows found at the rural springs. An explanation for the change in sediment flow is that urbanization and increased impervious surfaces have limited the sediment being recharged into the system. Steffy and Kilham's (2006) study on the effects of urbanization and land use on fish communities in Valley Creek watershed determined, "As the amount of impervious surfaces increased to more than 17% in the Valley Creek watershed, the warm water coming off these surfaces became greater than the groundwater input (to the streams)." This shows that precipitation has been rerouted, which limits its infiltration. Much of the precipitation has been directed into storm drains and surface water systems. For example, storm pipes have been identified near both the Park and Gunkle springs and during the study period, a retention basin was installed in Valley Creek Park to capture storm water. By restricting the infiltration of water, urbanization has had the effect of reducing the influx of sediment into the karst system. Thus only a small volume of sediment is being discharged at the springs, because there is only a small volume of sediment entering the system at the recharge area.

Suspended sediment in storm flow samples

Collecting storm flow data proved to be difficult due to the springs' lack of response. However, two storm events were able to trigger ISCO sampling, once at Park on 6/29/05 and then again at Lebout on 5/14/06. The suspended sediment collected during these storms would initially start as a slightly higher concentration, 7.1 mg/L at Park and 5.6 mg/L at Lebout. However, the concentrations would drop back to base flow conditions within two hours (figure 3-2 A & B). Thus, sediment concentrations in storm samples were only slightly higher than baseflow and only for a brief period.

Sediment mineralogy

The mineralogy of the suspended sediment from the springs is not the same as the dolomitic karst system that it traveled through. At all four Elbrook springs most of the suspended sediment consisted of silt-size silicate grains. The silicates included angular quartz grains and weathered mica flakes. Sometimes the quartz and mica would appear as individual grains, but about 15% of the silicate grains were formed into aggregates. There was also some organic matter, which generally composed 5 to 15% of the total sample. The presence of carbonate minerals was tested for by applying drops of acid to the filter papers containing the sediment samples. Almost all of the samples had no reaction at all. Lebout's 9/15/05 and Park's 4/15/06 samples did show a slight reaction, however only minor amounts of carbonate were present. Also, based on Lebout samples, there was no temporal variation in sediment composition.

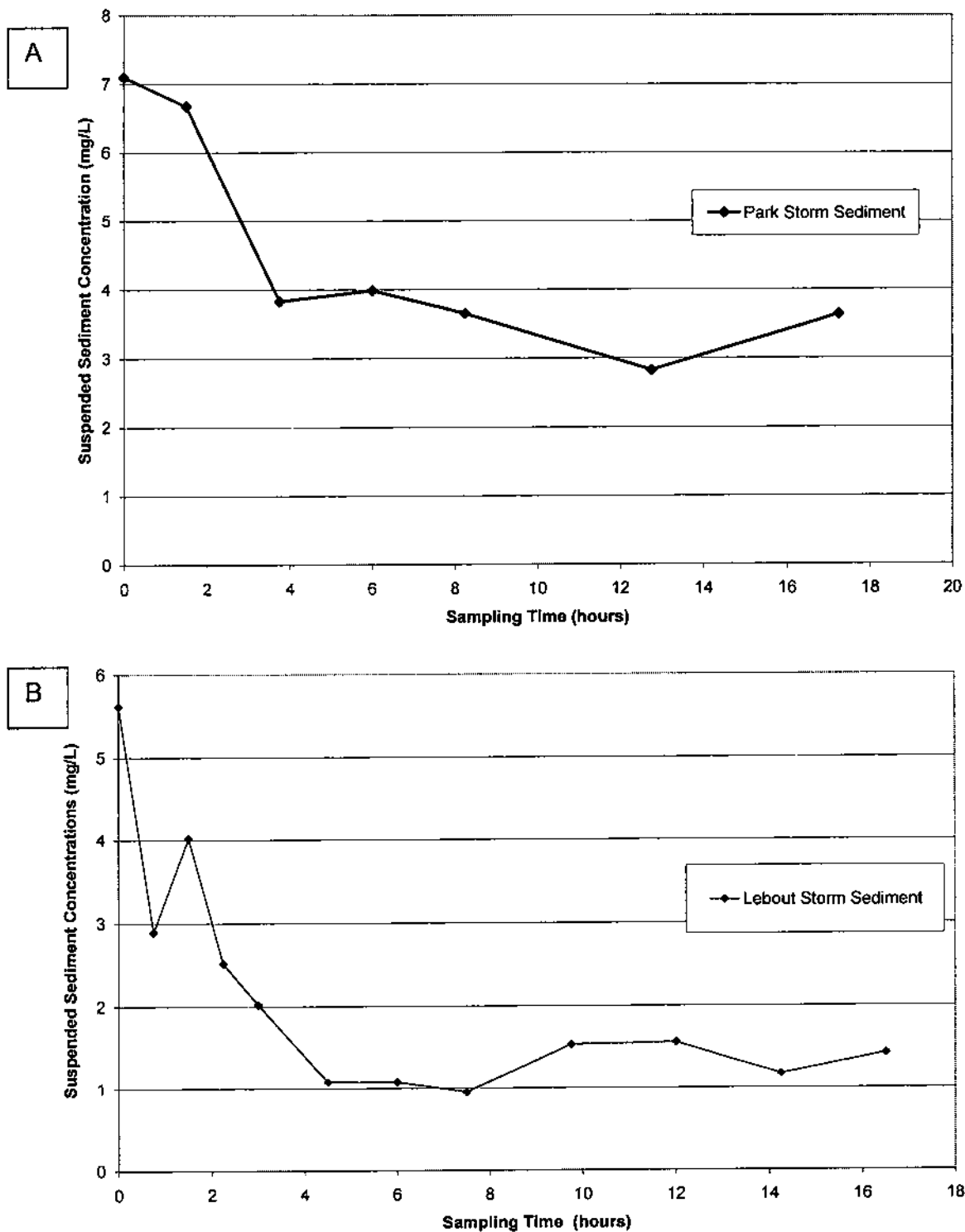


Figure 3-2 A & B. Urban storm flow suspended sediment charts. (A) Storm sediment at Park on 6/29/05. (B) Storm sediment at Lebout on 5/14/06. Both sites initially had slightly higher concentrations, but within two hours the concentrations dropped back to their typical baseflow values.

The mineralogy of the bedload sediment collected at the spring mouths was similar to the suspended sediment, but it was generally coarser. Clay-size pieces were evident from the sieving in preparation for the sediment digestion. However, sand and silt were the most prominent sediment size in the remaining sediment, based on visual inspection. Gravel was also common among the outside springs. Quartz was a major component at all of the sites, as well as mica. Carbonates were also present, as all the samples reacted with trace metal grade nitric acid. The largest difference between the urban springs and Bushkill (the rural spring) was that Bushkill is located along side a stream. Thus, its collection of sediment also contained rounded river stones that may have washed in from the stream.

The presence of silicate minerals and the lack of carbonate minerals indicate that the suspended sediment in this karst system is allochthonous in origin. Also, in some of the Park samples pieces of insects' exoskeletons were found. It is apparent that these materials were not generated from within the system, but were carried in by infiltrating waters or mobilization of soil in the recharge area.

CHAPTER 4 TRACE METALS

Trace Metals in the Environment

Metals in the environment can occur naturally or can be evidence of anthropogenic activity. Iron and manganese are found commonly in sedimentary rocks and comprise most of the natural background levels of metals (Vesper et al. 2001). Sources of metals found in residential or urban areas include lead from automobiles (particularly lead in gasoline before 1986), lead based paint chips, and atmospheric deposition of mercury. Iron, copper, and zinc are found in dust from tires and break linings, while cadmium, copper, zinc, and nickel are found in commercial fertilizers.

Naturally Occurring Metals in Rock

Naturally occurring metals can be found in all rocks of the earth's crust. The type and concentration of the metals can vary widely depending on the type of rock. For sedimentary rocks the concentrations are generally lower than for igneous, and close to or a little less than concentrations found in metamorphic rocks. However, shales (particularly black shales) may have high concentrations. Aubert and Pinta (1977) classified trace metals naturally occurring in rocks. They state that the amount of Co in limestone is between 1 to 5 mg/kg, sometimes as low as 0.1 to 0.3 mg/kg. Carbonate rocks have some of the lowest Zn levels of all rock types at 20 mg/kg. The amount of Cu found in limestone ranges from 3 to 10-15 mg/kg and the average concentration of Pb for

limestone is 7 to 10 mg/kg. Fitzpatrick et al. (1995) provided carbonate rock metal ranges similar to Aubert and Pinta. They also stated that carbonate rock in the United States have As concentrations ranging from 0.7 to 2.5 mg/kg, Cd concentrations around 0.04 mg/kg, Cr ranges of 3 to 29 mg/kg, and Ni ranges from 2 to 16 mg/kg.

High levels of metals can indicate contamination, especially in urban areas. Common products and equipment people use contain metals and so use of these items expose the environment to metal contamination. A large source of these metals comes from transportation. Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn contaminations are associated with automobiles. They are emitted to the environment through gasoline, exhaust, motor oil and grease, antifreeze, undercoating, brake linings, rubber, asphalt, concrete, diesel oil, and engine wear. Sources of Sn in the environment include bronze and tin cans. Urbanized areas have more people using more of the commodities containing metal, such as cars, which increases the release of metals to the environmental. Anthropogenic metal contamination can also be a problem in some rural areas. Some pesticides used in agriculture contain As. Thus, the application of these chemicals to crop fields has allowed for exposure of As to the environment.

Sediments within a karst system can be used as environmental indicators of metal contamination. The sediments incorporate contaminant concentrations over time and so are able to give a better long-term picture of urbanization effects than water samples alone (Gutierrez et al. 2004). For instance, metals

adsorb onto sediment surfaces, so sediment transport and storage are related to metal cycling in a hydrologic system (Vesper and White, 2003). To bypass analytical issues concerning variation of total dissolved solids (with precipitation) and possible low ion concentrations, sediments are used as a media to test for metals in the environment and to assess environmental quality (Gutierrez et al. 2004).

Sediment quality guidelines (SQGs) for concentration of metals have been determined using various approaches depending on the intended application. Each approach had its own pros and cons, but in an effort to assimilate the guidelines consensus-based SQGs were developed. MacDonald et al. (2000) developed the consensus-based SQGs by calculating the geometric mean of previously determined SQG values that fell into two main categories. The first category was threshold effect concentrations (TEC) where sediments are considered clean or only slightly polluted and below which no adverse affects are expected for most sediment dwelling organisms. The second category was labeled probable effect concentrations (PEC), where metal concentrations higher than the PEC values are expected to cause adverse effects on sediment dwelling organisms. These TEC and PEC values were intended for assessing sediment quality conditions in freshwater ecosystems.

The predictive ability of the consensus-based SQGs was tested by using 347 sediment samples, which were collected at fourteen fresh water locations in the United States. These sites were selected to ensure the data collected was

from quality sources that would be useful for evaluating sediment quality conditions in fresh water ecosystems. MacDonald et al. (2000) were able to measure the concentrations of metals, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and organochlorine pesticides. Then the sediments' concentrations were compared with the consensus-based SQG values to determine if the sediments were considered non-toxic (below TEC value) or toxic (above PEC value). Afterward the responses of lower aquatic life-forms (e.g. mayfly, midge, daphnid, amphido, oligochaete, and bacterial luminescence) were tested to evaluate the consensus-based SQG predictability. The TEC values ability to determine which sediments were non-toxic ranged between 72% for Cr and 82.3% for Cu. The predictive ability for most of the PEC values was better. The lowest percentage was for As at 76.9%, but the other metals ranged from 89.6% for Pb to 91.8% for Cu.

Background levels of metals in water systems are difficult to determine due to anthropogenic alteration of systems before sampling records existed. However, the EPA has set certain drinking water standards to ensure the health and safety of the public as part of the Safe Drinking Water Act (SDWA) (EPA Drinking Water Standards, 2003). Stream water quality analysis in the Delaware River Basin found that two-thirds of small urban streams exceed these standards (Fischer et al. 2004). While natural levels may exist above these standards, they are a good comparison to determine the health of the system. In their assessment of water quality in the Illinois River basin for the U.S.G.S., Fitzpatrick

et al. (1995) also used EPA drinking water standards as a baseline measurement for metal concentration in water. Thus, it is these EPA standards that will be used as a comparison for the trace metal concentrations.

The TEC and PEC values that MacDonald et al. (2000) developed were compared with the medians of non-urban indicator sites used by the United States Geological Survey's National Water Quality Assessment Program (NAWQA). The NAWQA metal concentration ranges for nonurban sites matched MacDonald et al.'s TEC values, although the NAWQA Cu concentrations were a bit higher (Rice, 1999).

Methods

For this study trace metal analyses were performed on base flow water samples collected over nine months and on bedload sediments samples collected during a one time sampling. The water samples were collected every three to four weeks during normal sampling rounds. Suspended solids were first removed from the water samples using a 0.45 um pore-sized filter. The samples were then stored in plastic bottles that had been acid-washed using a solution of diluted trace grade nitric acid. Before the samples were added to the bottles, two additional drops of nitric acid were added to stabilize the samples. Then the samples were kept refrigerated until their analysis.

The sediment samples had to be collected from bedload sediment because of low to absent concentrations of suspended sediment being

discharged by the springs. At all the urban springs and at Bushkill bedload samples were gathered from around the spring mouth. At Park a second sediment sample was taken from a trough within the spring house. At Lawson samples were taken from inside the springhouse, outside the spring house, and from a second spring discharging from underneath the main house. At Lebout sediment samples were taken from inside and outside the springhouse. The sediment samples were initially stored in plastic sandwich bags and then transferred to glass jars.

After the sediment samples were collected, they were dried and then shaken through a 1/256 inch plastic sieve to separate the clay size particles. The clay-size particles were then digested using hydrogen peroxide (H_2O_2) and nitric acid (HNO_3) to remove metals. However, the digestion process did not remove metals from the structure of the silicate/clays, but from adsorbed matter such as carbonates, organics, hydrous ferric oxides, and maybe sulfides (marcasite). The digestion process transferred the sediments' metal concentration into a solution that could be analyzed as described below. The bedload sediment leftover from each site after the sieving was examined under a light microscope to determine the grain size and mineralogy, same as the suspended sediment samples.

The water and digested sediment samples analyzed using an inductively coupled plasma – optical emissions spectrometer (ICP-OES) at Franklin and Marshall College in Lancaster, PA. The ICP-OES can measure concentrations of

trace metals in liquid solutions. The liquid sample is sprayed into argon plasma, which excites the dissolved metals. Once the metals are excited they emit a characteristic radiation. The radiation passes through a grating monochromator to separate the wavelengths. These wavelengths are then detected with photomultiplier tubes. Different metals emit different wavelengths of radiation, so the wavelengths can be used as an identification of the element, and the radiation intensity can be used to determine its concentration. ICP-OES measure elements in the concentration range of 1 ppb (part-per-billion) to 1000 ppm (parts-per-million) or more. The metals that were analyzed for the urban and rural sediments were Cr, Co, Ni, Cu, Zn, As, Cd, Sn, and Pb.

Results

Over all, the data suggested that the concentrations of metals in the water are very low, mostly less than 10 ppb (table 4-1). Slightly less than half the water analyses were considered above detection (larger than 0.1 ppb). That means that only 49.7% (143 out of 288) of the water sample analyses had metal concentrations large enough to be accurately measured. The EPA has set the maximum allowable concentration of As in drinking water to be 50 ppb. All of the water samples were well below this value with the highest being 6 ppb. The amount of copper can be 1300 ppb, but the highest concentration in the water samples was 1 ppb. The highest allowable lead concentration has been set by the EPA at 15 ppb, where as the highest our water samples had was 7 ppb. Zinc

Water Conc. ppb	Cr	Co	Ni	Cu	Zn	As	Cd	Sn	Pb	
Gunkle	5/20/2005	2		4	1	26	5		3	3
	6/7/2005			3		1	5		3	
	6/24/2005	1		2					8	
	7/14/2005	2				0.6			10	
	8/3/2005			2				4	9	
	8/25/2005	1							9	
	9/15/2005	1					0.6		7	
	10/13/2005	2	0.6			0.3		16	14	
11/22/2005	2							18		
Park	5/20/2005	2		1	1	13	6		3	2
	6/24/2005	3							7	7
	7/14/2005	2							7	5
	8/3/2005	1		1			1	4	5	
	9/15/2005	2	0.6						10	
	10/13/2005	2					1	7	15	
10/13/2005	2	0.5	1			4	7	13	6	
Lawson	5/20/2005	2	1	1		10			2	
	6/24/2005	2	0.6						7	
	7/14/2005	2		1			2		10	
	8/3/2005			2				5	7	
	9/15/2005	2		2				6	14	
	10/13/2005	2							15	
	10/13/2005	2							10	
8/3/2005 House	1						13	5	2	
Lebout	5/20/2005	2				11			3	3
	6/24/2005	2					2		4	
	7/14/2005	2		3					6	
	7/14/2005	1		2			4		3	
	8/3/2005	1		2				5	8	
	9/15/2005	1		1				2	12	
	10/13/2005	1		2				27	13	
	10/13/2005	2		3				15	12	

Table 4-1. Water metal concentration table (ppb). The water metal concentrations were very low, mostly less than 10 ppb.

Below detection = 

recommended highest concentration is 5000 ppb, but it is not legally enforced. However, the largest Zn concentration found was 26 ppb and the rest of the samples were below 13 ppb or non-detect. These low metal concentrations show that there is not a toxicological problem with the springs' water. The EPA does not have drinking water standards for Co, Ni, and Sn. Concentrations of these metals in the springs' water were all around the same order of magnitude as the other metals, suggesting that they do not pose a toxicological problem.

As expected, the metal concentrations in the sediment were higher than those in the water samples. Even so, two-thirds of the sites had no metal concentrations over the SQGs consensus-based TEC values. These sites include Park, outside the Lawson spring house, inside at Lebout, and the rural site Bushkill (table 4-2). However there were some instances in which sediment metal concentrations exceeded TEC or PEC recommendations. The Cd concentration at Lawson's house was 1.6 mg/kg, which is a little higher than the TEC value of 0.99 mg/kg, but well below the PEC value of 4.98 mg/kg. The Cu concentration at Gunkle was 54.8 mg/kg and inside the Lawson spring house the concentration was 34.8 mg/kg. Both values exceed the TEC value of 31.6 mg/kg, but were well below the PEC value of 149 mg/kg. The Zn concentration at Gunkle was 190.7 mg/kg and at Lebout it was 127.7 mg/kg, both exceeding the 121 mg/kg TEC value. At the Lawson's house the Zn's concentration of 801.3 mg/kg was well above the PEC value of 459 ppm. The Pb concentration at Gunkle was 114.9 mg/kg, well above the TEC value 35.8 mg/kg. The Pb

Sediment Conc. mg/kg	Cr	Co	Ni	Cu	Zn	As	Cd	Sn	Pb
TEC	43.4	X	22.7	31.6	121	9.79	0.99	X	35.8
PEC	111	X	48.6	149	459	33	4.98	X	128
GUNKLE	19	82.8	20	54.8	190.7		0.5	2.6	114.9
PARK SPRING MOUTH	12.3	64.5	13.3	9.5	27.4			2.7	2.9
PARK TROUGH	9.2	61.6	11.6	17.8	19		0.1		
LAWSONS HOUSE	15.6	137.6	11.7	22.7	801.3		1.6	3.8	135.4
LAWSONS SPRING OUTSIDE	5.1	49.6	7.6	7.9	33.4		0.1		
LAWSONS SPRING OUTSIDE	5.3	48.1	7.4	5.9	33.1		0.1		
(return) LAWSONS SPRING INSIDE	8.5	59.4	16.1	34.8	45.9		0.6		
LEBOUT OUTSIDE	17.8	95.6	12.6	15.5	127.7				260.5
LEBOUT INSIDE	9.1	68.1	10.4	9.9	17.4				
BUSHKILL	17.4	98.7	18.8	21.6	86.9		0.2		24.1

Above TEC values	
Above PEC values	

Table 4-2. Sediment metal concentration table (mg/kg). The sediment metal concentrations were compared with MacDonald et al. consensus-based SQGs values. Two-thirds of the springs had no metal concentrations over the TEC values, and 96% of the metal concentrations were below the PEC values. Blank = below detection
X = not available in reference article

concentration at Lawson's house was 135.4 mg/kg and outside at Lebout it was 260.5 mg/kg, placing both of them above the PEC value of 128 mg/kg.

With the exception of one slightly high concentration inside Lawson's roofless springhouse, most of the sediment metal concentration TEC exceedances are found at Gunkle, Lawson's main house, and outside at Lebout. Thus, other than at Gunkle, the high sediment metal concentrations are located at outside spring sources. At Lawson's the spring that flows out from under the main house is surrounded by structures over 200 years old. It is possible that metals concentrations could be due to old piping containing Zn and Pb, which would no longer be used in modern day. At Lebout the inside concentrations are all low, however the outside has high Zn and Pb. The main difference between the inside and outside environment is that the outside experiences overland flow. Lebout's location is next to a road, at the bottom of a hill, and just slightly elevated from a stream. During storm events, overland flow from the surrounding land and roadways would easily find its way to the trough outside the springhouse.

Although there are high metal concentrations found at some sites, other sites were found to have all low metal concentrations. Samples from Park, outside Lawson's springhouse, inside at Lebout, and the rural site Bushkill had no metal concentrations over the SQGs consensus-based TEC values. In addition, 95% (60 out of 63 metal analyses) of the metal concentrations were below the SQGs consensus-based PEC values. These low concentrations show

that most of the sediments' metal concentrations are too low to impair organisms, so there is no contamination concern. They also show that there is not a large difference between the metal concentrations at the urban sites and those found at the rural sites. Analysis of sediments in urban stream beds through out the Delaware River Basin found rates of metal TEC exceedances ranging from 48% and 100% of the time (Fischer et al. 2004). The low concentration of metals in the Valley Creek sediment suggests that there is a lack of build up of metals in the karst system, indicating that urbanization in Valley Creek Basin has not had the effect of exposing the karst system to metal contamination.

The sediment and water metal concentrations were compared by creating plots with the water concentrations on the y-axis and the sediment concentrations on the x-axis (figure 4-1). The plots of Cr, Co, Ni, and Pb are used for this paper because they have the least non-detects. Since metals tend to accumulate on the sediment the plots were created with water metal concentrations in ppb and the sediment in mg/kg (also ppm). If metal concentrations in the karst system were due to urban contamination, then these metals would be brought into the system by infiltrating waters. Since metals prefer to adsorb onto clay size particles rather than stay dissolved in the water, these metals would collect on the surface of sediment particles. This sorption isotherm would create equilibrium between the sediment and water metal

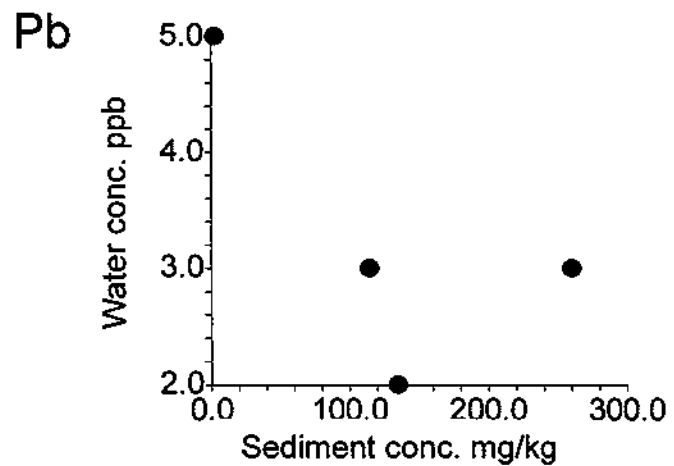
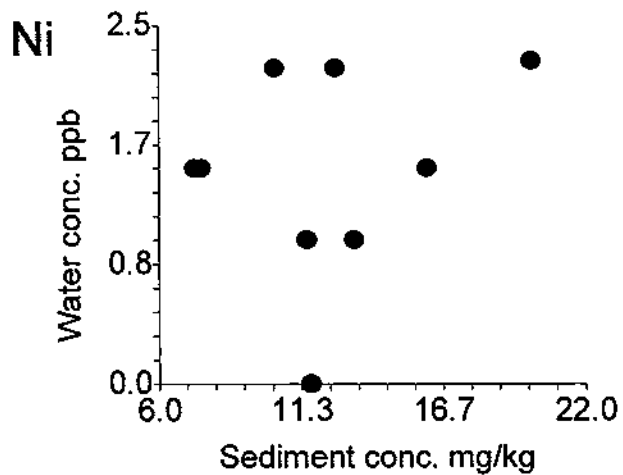
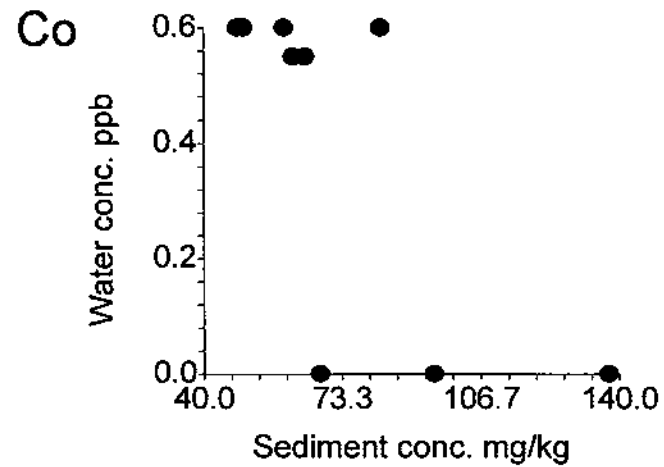
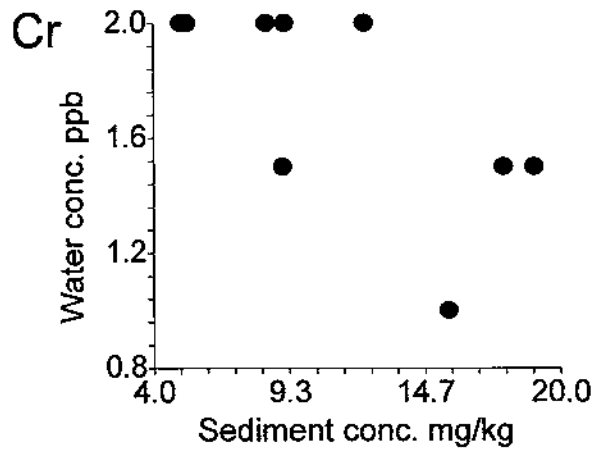


Figure 4-1. Sediment & Water Correlation Charts. These charts compare sediment metal concentrations (mg/kg) to water metal concentrations (ppb). The water and sediment concentrations are not in equilibrium and often have a negative correlation, showing that the metals are not a contamination issue.

concentrations. Equilibrium would create a straight line on the comparison charts, with low sediment concentrations matching with low water concentrations and high sediment concentrations matching with high water concentrations. The Cr, Co, Ni and Pb charts (figure 4-1) show that the sediment and water metal concentrations do not have a straight line plot, so they are not in equilibrium. Thus, the water is receiving its metal concentrations from the sediment and the source of the metal is the weathering of the sediment and not the water. This indicates that the groundwater has not had metal contamination and that the metals do not appear to be from urban contamination.

CHAPTER 5 CONCLUSIONS

Geochemistry

The geochemical data gathered shows evidence of both conduit and matrix dominated flow paths within the urban and rural karst systems (Table 2-1). The CV values placed Gunkle and Garage as the most predominantly conduit urban springs. However, Park and Eco Park also exhibit characteristics of conduit dominated flow paths, particularly with the distinct openings of their spring mouths. Lawson and Lebout have more diffuse discharge at their spring mouths, but their CV values are higher than those found in purely matrix flow systems. It is likely that their flow contains some conduit pathways. The two rural karst sites had a large difference in their CV values, with Nolte being diffuse and Bushkill being well into the conduit range. This gives evidence that CVs are not a result of land use, but of the type of flow system.

The SI and PCO_2 values for the urban springs and for the rural springs have similar average values (figures 2-3 to 2-6). Neither the urban nor the rural springs show more variability. This indicates that the urban springs and rural springs still have similarities in their flow paths. The log PCO_2 values for the urban springs were fairly low and averaging around -1.9. The rural Bushkill spring log PCO_2 was lower and averaged -2.3. These are indicative of open systems in contact with soil gas and suggests shallow flow paths. The other rural spring Nolte had slightly higher PCO_2 averages (-1.6) suggesting a more closed system with deeper flow paths (figure 2-7).

Lebout and Park in the urban system are close to saturation with respect to calcite. Although the urban flow paths are believed to be shorter than the rural (Yang, 2006), the flow is slow enough to provide time for the water to equilibrate with the rock. A reduced amount of recharge in the urban karst system may limit flushing in the urban system compared to the rural. The limited flushing may lead to slower flow paths, giving more time for equilibration.

A difference in the chemical signature between the urban and rural sites was the variation in their nitrate values. At the urban sites there is very little nitrate in the water and little variation in concentrations. The rural sites showed a large increase of NO_3 concentrations at the end of the growing season. The higher values in the rural springs clearly indicate an affect of agricultural land use in the area. While the urban springs also showed a rise at the end of the growing season, it was very slight and likely due to the presence of lawn fertilizers.

Sediment

The mineralogy of the suspended sediment from the urban springs is not similar to the dolomitic karst system from which it was discharged. At all four Elbrook springs most of the suspended sediment consisted of silt-size silicate grains. The silicates included angular quartz grains and weathered mica flakes. This mineralogy indicates an allocthonous source for the sediment.

The suspended sediment data from the urban springs has consistently low levels, while the rural springs fluctuated between periods of high and periods of low sediment flow. The variation could be a result of the rural springs having

larger recharge areas. Having a larger area would make it easier for larger volumes of water and sediment to infiltrate into the rural systems. The recharge areas are related to the springs discharge rates. The urban discharge rates range from 0.6 L/sec for Gunkle to 15 L/sec at Lawson (Yang, 2006) and they are smaller than the rural springs discharge rates. Because the urban discharge rates are smaller than the rural, it would be difficult to have the same volume of sediment entering the urban karst system and the flow rates may not be high enough to mobilize stored sediments.

However, bedload sediment layers found in the spring house troughs indicate that in the past there was greater suspended sediment discharge at the urban springs. An explanation for the change in sediment flow is that urbanization and increased impervious surfaces have limited the sediment being recharged into the system. Much of the precipitation has been directed into storm drains and surface water systems. This is evident by storm pipes identified near Park, Gunkle, and Garage springs and by a retention basin in Valley Creek Park. By restricting the infiltration of water, urbanization has had the effect of reducing the influx of sediment into the karst system. Thus only a small volume of sediment is being discharged at the springs, because there is only a small volume of sediment entering the system at the recharge area.

Trace Metals

For the water metal data the concentrations of metals were very low, mostly less than 10 ppb (table 5-1). Slightly less than half the water analyses

were even considered above detection (larger than 0.1 ppb). These low metal concentrations suggest that there is not a metal contamination problem with the springs' water.

Sediment metal concentration exceedances were found at some sites, but other sites were found to have all low metal concentrations. Park, outside Lawson's springhouse, inside at Lebout, and the rural site Bushkill had no metal concentrations over the SQGs consensus-based TEC values. Furthermore, 95% (60 out of 63 metal analyses) of the metal concentrations were below the SQGs consensus-based PEC values. There is not a large difference between the metal concentrations at the urban sites and those found at the rural sites. The low concentration of metals on the sediment suggests that there is a lack of build up of metals in the urban or rural karst systems. Urbanization in Valley Creek Basin has not had the effect of exposing the karst system to metal contamination.

The water and sediment comparison charts of Cr, Co, Ni, and Pb (figure 4-1) show that the sediment and water metal concentrations do not have a straight line plot, meaning they are not in equilibrium. This indicates that the water is receiving its metal concentrations from the sediment and the source of the metal is the weathering of the sediment and not the water. This indicates that the groundwater has not had metal contamination and supports further evidence that the metals do not appear to be from urban contamination.

Effects of Urbanization

The main impact of urbanization in Valley Creek Basin seems to have been to restrict the recharge area and thus the potential flux of sediment and contaminants. The urban springs' response to storm events was minimal, especially when compared to the rural data sets (Yang, 2006). The urban baseflow flow rates were also lower than the baseflow rates found at the rural sites (Yang, 2006).

Urbanization has increased impervious surfaces, such as roads and parking lots. The impervious surfaces increase the amount of overland flow. Rather than having a large percentage of precipitation becoming part of the groundwater system, it drains off over the land and becomes part of the surface water system. This diversion has reduced the amount of sediment and other contaminants washing into the groundwater system. Thus, metal concentrations at the springs are low because metal infiltration has been reduced. Likewise, only low levels of sediment are being discharged at the springs, because only low levels are washing into the system.

Although contaminant levels have not increased due to urbanization, the springs may be at risk for future contamination. The lack of flushing means that the system will not cleanse itself if contamination occurs, and the short flow paths make the karst system vulnerable to spills and leaks.

REFERENCES

- Aubert, H., and Pinta, M. (1977) Trace Elements in Soils: Developments in Soil Science 7. Elsevier Scientific Publishing Company, Amsterdam.
- Chester County Water Resource Authority, 2005. GIS Files for Valley Creek Watershed. September 29, 2005.
- Dreybrodt, Wolfgang. (1988) Processes in Karst Systems: Physics, Chemistry, and Geology. Springer-Verlag Berlin Heidelberg, Germany.
- EPA Drinking Water Standards. (2003) List of Drinking Water Contaminants & their MCLS.
<http://www.epa.gov/safewater/contaminants/index.html#listmcl>
- Fischer, Jeffrey M., Riva-Murray, Karen, Hickman, R. Edward, Chichester, Douglas C., Brightbill, Robin A., Romanok, Kristin M., Bilger, Michael D. (2004) Water quality in the Delaware River basin; Pennsylvania, New Jersey, New York, and Delaware, 1998-2001. U. S. Geological Survey Circular Report no. 1227
- Fitzpatrick, Faith A., Scudder, Barbara C., Crawford, J. Kent, Schmidt, Arthur R., Sieverling, Jennifer B., Colman, John A., Crawford, Charles G., Sullivan, Daniel J. (1995) Water-quality assessment of the upper Illinois River basin in Illinois, Indiana, and Wisconsin; major and trace elements in water, sediment, and biota, 1978-90 Water-Resources Investigations - U. S. Geological Survey Report no. 95-4045
- Freeze, R. Allan, and Cherry, John A. (1979) Groundwater. Prentice Hall, Inc., Upper Saddle River.
- Gutierrez, M., Neill, H., and Grand, R.V. (2004) Metals in sediments of springs and cave streams as environmental indicators in karst areas. Environmental Geology. 46, p. 1079-1085.
- MacDonald, D. D., Ingersoll, C. G., and Berger, T. A. (2000) Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems. Archives of Environmental Contamination and Toxicology, 39, p. 20-31.
- Mahler, B.J., Lynch, L., and Dennett, P.C. (1999) Mobile sediment in an urbanizing karst aquifer: implications of contaminant transport. Environmental Geology, vol. 39 no. 1, p. 25-38.

- Martin, Harris. (1997). Interpretation of Water Chemistry Data from a Florida Underwater Cave for Determination of Possible Groundwater Pollution. <http://www.gue.com/Research/Karst/qienj.htm>. Copyright 1998-2006 GUE.com
- McGintly, Angela Lea. (2003) Geostatistical Analysis of the Impacts of Urbanization on Spring Water Quality in Valley Creek Watershed, Chester County, Pennsylvania. Masters Thesis from Drexel University. Philadelphia, Pennsylvania.
- Parkhurst, D.L. and Appelo, C.A.J. (1999) User's guide to PHREEQC (version 2); a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U. S. Geological Survey Water-Resources Investigations 99-4259, 312 pp.\
- Rice, K.C. (1999) Trace-element concentrations in streambed sediment across the conterminous United States: Environmental Science and Technology, vol. 33 no. 15, p. 2499-2504.
- Shuster, Evan T., and White, William B. (1971) Seasonal Fluctuations in the Chemistry of Limestone Springs: A Possible Means for Characterizing Carbonate Aquifers. Journal of Hydrology, 14, p. 93-128.
- Sloto, Ronald A. (1990) Geohydrology and Simulation of Ground-water flow in the Carbonate Rocks of the Valley Creek Basin, Eastern Chester County, Pennsylvania. U.S. Geological Survey: Water-Resources Investigations Report 89-4169. Harrisburg, Pennsylvania.
- Steffy, Luanne Y., and Kilham, Susan S. (2006) Effects of urbanization and land use on fish communities in Valley Creek watershed, Chester County, Pennsylvania. Urban Ecosystems, 9, p. 119-133.
- Tancredi, J. H. (2004) Variation in Sediment and Geochemistry as Evidence of Changes in Flowpath to a Karst Spring in Southeastern Pennsylvania. Masters Thesis from Temple University. Philadelphia, Pennsylvania. 128 pages
- (<http://or.water.usgs.gov/alk/>) United States Geological Survey. Oregon Water Science Center. Alkalinity Calculator.
- Vesper, Dorothy J., Loop, Caroline M., and White, William B. (2001) Contaminant transport in karst aquifers. Theoretical and Applied Karstology, 13-14, p. 101-111.

Vesper, D. J., and White, W. B. (2003) Spring and conduit sediments as storage reservoirs for heavy metals in karst aquifers. *Environmental Geology*, 45, p. 481-493.

White, William B. (1988) *Geomorphology and Hydrology of Karst Terrains*. Oxford University Press, Inc. New York, NY.

Yang, Youa. (2006) *Characterizing Storm Response in an Urban Karst Aquifer at Valley Creek, Chester County, Pennsylvania*. Masters Thesis from Temple University. Philadelphia, Pennsylvania. 98 pages

**APPENDIX A
GEOCHEMISTRY DATA**

Gunkle									
Date Collected	Na	K	Mg	Ca	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄	HCO ₃
	-----mg/L-----								
5/20/05	24.4	3.0	36.2	45.7	0.1	52.5	3.9	16.8	258.3
6/7/05	22.9	3.2	35.4	43.9	0.1	47.6	4.0	16.1	258.2
6/24/05	17.7	2.8	32.5	43.0	0.1	42.1	3.6	15.1	273.1
7/14/05	21.6	3.3	37.5	49.8	0.1	40.2	3.4	14.0	258.4
8/3/05	22.7	3.6	40.4	52.9	0.1	38.7	3.4	13.9	259.6
8/25/05	15.5	2.3	25.2	34.9	0.1	35.6	3.2	13.1	221.5
9/15/05	15.9	2.8	27.6	36.2	0.1	33.9	3.0	12.1	209.0
9/15/05	16.0	3.1	29.0	39.4	0.1	34.0	3.0	12.1	209.0
10/13/05	25.3	3.5	38.4	55.2	0.1	46.4	4.5	15.8	304.8
11/3/05	32.5	4.7	51.6	69.8	0.2	46.1	4.8	16.8	281.5
11/22/05	20.4	3.0	31.4	43.9	0.1	45.9	4.5	17.0	209.2
12/15/05	28.8	3.6	36.4	49.5	0.2	54.4	4.7	17.2	221.3
12/15/05	29.4	3.8	37.4	51.2	0.1	55.5	4.5	17.2	221.3
1/12/06	31.9	4.3	44.1	57.1	0.1	62.5	3.7	20.0	305.4
2/11/06	25.2	3.6	36.2	51.5	0.1	63.3	3.8	20.7	209.1
2/11/06	26.9	3.8	38.4	54.4	0.1	63.3	3.8	20.7	209.1
3/8/06	26.5	3.7	37.4	54.0	0.1	63.2	3.7	20.1	307.4
4/15/06	21.0	3.2	32.4	46.0	0.2	54.8	3.4	17.6	307.4
5/9/06	22.1	3.1	34.7	52.1	0.1	52.3	3.3	17.9	307.6
6/7/06	18.4	2.6	29.5	42.0	0.2	47.2	2.9	18.9	283.0
6/7/06	19.4	2.8	30.8	44.8	0.2	47.3	2.9	18.7	283.0
7/15/06	24.1	3.2	35.1	50.3	0.2	55.7	3.4	19.7	282.8
8/9/06	21.6	3.3	33.2	49.7	0.2	46.6	3.1	17.5	282.5
9/12/06	20.8	2.7	30.1	43.9	0.2	49.8	3.6	25.5	331.0
10/15/06	20.6	3.8	45.3	55.8	0.1	47.8	3.4	23.1	282.8
11/14/06	23.9	3.2	44.4	51.9	0.2	57.9	4.1	18.9	356.2
11/14/06	26.1	4.1	47.5	59.0	0.2	58.8	4.2	19.1	356.2

12/17/06	22.8	4.2	43.6	52.1	0.1	47.4	3.9	17.5	356.7
2/3/07	21.3	3.4	40.8	53.0	0.1	57.8	4.3	23.5	282.5
2/3/07	21.3	3.4	40.8	53.4	0.1	57.9	4.3	23.7	282.5

Park									
Date Collected	Na	K	Mg	Ca	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄	HCO ₃
	-----mg/L-----								
5/20/05	70.5	2.9	48.7	72.1	0.2	189.7	1.5	25.6	270.3
6/7/05	76.7	3.1	44.7	65.5	0.2	161.4	1.5	26.2	282.7
6/7/05	79.0	3.2	45.9	66.6	0.2	153.9	1.7	29.0	282.7
6/24/05	81.7	3.1	48.6	73.2	0.2	222.3	1.4	26.6	331.9
7/14/05	110.5	3.8	60.3	91.7	0.2	215.1	1.3	25.6	332.0
7/14/05	112.2	3.7	60.1	88.2	0.2	212.8	1.3	25.8	332.0
8/3/05	130.2	4.0	66.5	96.8	0.3	266.2	1.4	27.3	331.9
8/25/05	99.0	3.6	48.3	79.2	0.2	277.8	1.4	27.7	405.7
9/15/05	119.3	4.0	52.7	79.0	0.2	224.6	1.5	28.3	332.0
10/13/05	162.5	5.4	71.8	114.3	0.8	266.6	2.0	32.5	363.0
10/13/05	175.3	5.8	77.5	122.4	0.3	265.6	1.7	32.5	363.0
11/3/05	131.7	4.9	68.8	107.5	2.7	212.0	1.8	29.2	334.5
11/22/05	108.0	3.8	46.7	75.2	0.2	234.7	1.8	28.7	258.2
12/15/05	124.2	4.3	51.5	82.7	0.1	237.2	2.0	30.2	331.9
1/12/06	90.3	3.7	49.5	79.0	0.2	192.7	1.3	27.5	337.4
2/11/06	61.8	2.9	40.5	69.5	0.2	159.0	1.3	25.8	284.0
3/8/06	66.4	3.1	43.2	73.7	0.2	167.2	1.5	30.2	356.1
3/8/06	66.2	3.1	42.9	72.6	0.2	179.4	2.0	32.8	356.1
4/15/06	79.0	3.2	43.1	72.1	0.2	218.0	1.4	29.3	356.6
5/9/06	85.1	4.0	45.4	79.8	0.3	216.6	1.5	29.1	356.5
6/7/06	92.7	3.2	46.1	78.0	0.3	240.8	1.4	31.9	356.8
7/15/06	71.1	3.0	44.9	76.3	0.2	178.9	1.3	28.6	344.4
8/9/06	106.8	3.9	50.3	88.2	0.2	237.3	1.4	29.9	355.4
8/9/06	107.7	3.8	50.8	88.5	0.2	218.4	1.3	27.7	355.4
9/12/06	62.4	2.5	39.3	66.4	0.1	161.4	1.4	38.7	341.3
10/15/06	77.2	3.4	59.1	82.7	0.1	188.5	1.3	36.8	356.6
11/14/06	47.7	2.8	48.4	74.0	0.1	121.8	1.4	24.0	331.9
12/17/06	71.1	4.1	54.4	79.3	0.1	149.7	1.6	23.5	356.5
12/17/06	70.1	4.0	53.9	79.1	0.1	159.8	1.7	25.0	356.5
2/3/07	56.4	2.7	47.5	74.1	0.2	167.6	1.6	30.5	307.2

Lawson									
Date Collected	Na	K	Mg	Ca	F	Cl	NO3	SO4	HCO3
	-----mg/L-----								
5/20/05	28.0	1.9	38.9	57.7	0.1	59.2	8.1	24.4	285.9
6/7/05	30.4	2.1	38.2	55.5	0.1	38.9	3.7	25.4	307.1
6/24/05	31.5	2.1	41.0	61.5	0.1	64.3	3.6	25.2	282.9
7/14/05	35.9	2.3	45.6	68.1	0.1	65.9	3.5	25.2	332.1
8/3/05	39.8	2.4	48.9	70.9	0.1	67.6	3.5	25.5	332.1
8/25/05	29.7	2.0	37.2	61.0	0.1	66.5	3.6	25.6	331.9
9/15/05	31.3	2.1	40.0	60.4	0.1	62.8	3.7	24.4	307.5
10/13/05	42.0	2.7	51.9	82.8	0.0	85.8	4.7	29.1	363.0
11/3/05	33.8	2.3	42.3	69.0	0.2	66.4	4.9	28.8	308.6
11/22/05	34.7	2.2	38.5	61.9	0.0	68.5	4.7	29.0	258.5
11/22/05	34.8	2.1	37.4	59.0	0.0	68.1	5.1	29.0	258.5
12/15/05	37.8	2.5	42.4	68.8	0.1	65.5	5.1	28.9	307.4
1/12/06	36.0	2.5	42.7	69.2	0.1	66.5	3.2	27.5	303.8
2/11/06	28.4	1.9	34.2	58.7	0.1	67.1	3.3	27.9	234.9
3/8/06	30.8	2.2	36.8	63.6	0.1	70.3	3.3	28.1	331.9
4/15/06	30.9	2.0	35.2	58.8	0.0	77.7	3.4	27.9	332.1
5/9/06	35.2	2.0	39.7	69.2	0.1	76.1	3.3	28.8	332.3
5/9/06	36.2	2.1	40.7	71.4	0.0	68.1	5.1	40.2	332.3
6/7/06	34.4	1.9	36.5	61.9	0.1	75.6	3.0	31.1	320.0
7/15/06	34.6	2.1	37.2	65.0	0.1	74.6	3.2	29.5	332.2
7/15/06	34.9	2.1	37.6	65.2	0.1	74.8	3.2	29.7	332.2
8/9/06	38.8	2.3	40.6	69.7	0.1	77.9	3.3	30.0	356.0
9/12/06	31.6	1.8	33.4	57.9	0.2	67.5	3.4	37.0	330.9
10/15/06	31.7	2.4	51.0	74.3	0.1	67.8	3.3	35.3	356.7
10/15/06	30.8	2.2	49.0	69.9	0.1	68.0	3.4	35.5	356.7
11/14/06	26.0	2.3	43.6	70.6	0.2	55.1	3.5	24.5	332.0
12/17/06	30.1	2.7	45.2	66.7	0.1	55.7	3.4	23.5	331.7
2/3/07	26.9	2.3	41.0	68.3	0.1	70.7	3.9	31.9	307.3

Lebout									
Date Collected	Na	K	Mg	Ca	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄	HCO ₃
	-----mg/L-----								
5/20/05	11.2	2.9	34.0	47.7	0.1	18.6	1.4	17.6	282.5
5/20/05	11.6	2.8	33.7	46.3	0.1	18.6	1.4	17.6	282.5
6/7/05	11.7	3.3	33.1	44.9	0.1	18.2	1.4	17.8	258.2
6/24/05	10.9	3.1	35.3	50.0	0.1	17.4	1.4	17.5	282.9
7/14/05	12.8	3.6	39.8	55.2	0.1	17.0	1.3	17.2	258.3
8/3/05	13.6	3.8	42.4	58.4	0.1	17.1	1.3	17.3	282.7
8/25/05	10.1	3.0	30.5	46.7	0.1	17.1	1.4	17.4	282.8
9/15/05	11.5	3.3	33.4	47.4	0.1	17.3	1.3	16.9	258.0
10/13/05	13.6	3.8	39.8	59.7	0.0	24.0	1.9	19.3	304.9
11/3/05	12.8	3.7	39.0	59.1	0.1	21.7	2.0	19.1	281.4
11/22/05	10.9	2.9	27.6	41.7	0.1	20.7	1.9	19.1	209.1
12/15/05	13.1	3.6	34.3	51.0	0.1	21.4	1.8	19.0	259.3
1/12/06	13.9	3.7	35.4	52.9	0.1	21.1	1.0	18.7	271.7
1/12/06	14.2	3.7	35.6	52.9	0.1	20.5	1.0	18.2	271.7
2/11/06	10.6	2.8	27.6	44.3	0.1	20.7	1.1	19.1	172.0
3/8/06	11.6	3.2	30.3	48.5	0.1	21.2	1.1	18.9	307.4
4/15/06	10.5	2.9	28.1	44.3	0.1	21.5	1.1	18.4	284.0
4/15/06	10.5	2.9	28.3	44.7	0.1	21.4	1.1	20.1	284.0
5/9/06	12.2	2.9	30.9	50.7	0.1	21.0	1.1	18.9	307.2
6/7/06	11.3	2.8	28.5	45.7	0.1	20.8	1.0	20.9	283.0
7/15/06	11.7	3.0	30.1	49.2	0.1	21.9	1.1	20.4	282.9
8/9/06	12.6	3.3	31.6	51.3	0.1	21.3	1.1	20.4	281.3
9/12/06	11.3	2.7	26.6	42.6	0.1	21.2	1.2	26.4	301.0
9/12/06	11.5	2.8	27.7	45.6	0.2	21.2	1.2	26.0	301.0
10/15/06	10.2	3.5	40.0	55.2	0.1	19.9	1.1	24.9	282.7
11/14/06	11.2	3.9	36.2	51.1	0.1	20.4	1.2	17.4	282.5
12/17/06	10.7	3.7	35.7	49.8	0.1	17.7	1.2	17.2	282.6
2/3/07	9.9	3.5	34.7	53.5	1.6	21.9	1.4	22.3	258.0

Eco Park										
Date Collected	Na	K	Mg	Ca	F ⁻	Br ⁻	Cl ⁻	NO ₃ ⁻	SO ₄	HCO ₃
	-----mg/L-----									
2/11/06	39.3	2.3	27.4	58.1	0.0	1.6	87.3	2.6	34.8	282.4
3/8/06	40.9	2.5	28.9	60.4	0.0	1.5	85.8	2.6	34.5	282.8
4/15/06	48.3	2.7	32.2	69.1	0.0	1.6	88.2	2.6	33.7	282.9
5/9/06	50.2	2.7	33.1	71.1	0.0	1.4	88.0	2.5	35.0	283.8
6/7/06	42.7	2.2	27.5	59.2	0.1	1.3	82.4	2.3	36.3	282.9
7/15/06	45.4	2.5	29.1	62.6	0.1	1.5	87.9	2.6	36.7	282.6
8/9/06	47.3	2.7	30.1	65.5	0.0	1.5	85.9	2.5	36.0	280.5
9/12/06	42.8	2.6	26.2	58.0	0.1	1.4	79.0	2.7	44.2	306.3
10/15/06	39.6	2.6	37.6	68.4	0.1	1.4	76.5	2.5	42.0	282.7
11/14/06	38.7	3.0	33.9	63.8	0.1	1.1	73.3	1.1	30.7	282.3
12/17/06	36.4	2.7	33.6	68.2	0.0	1.2	69.9	2.7	30.5	281.5
2/3/07	34.3	2.1	30.2	59.1	0.0	1.6	83.8	3.0	38.9	257.8

Garage										
Date Collected	Na	K	Mg	Ca	F ⁻	Cl ⁻	Br ⁻	NO ₃ ⁻	SO ₄	HCO ₃
	-----mg/L-----									
2/11/06	74.5	6.8	33.3	46.3	0.0	147.0	1.0	1.1	31.9	208.5
3/8/06	83.8	6.5	34.8	47.1	0.1	171.8	1.2	1.1	31.2	282.3
4/15/06	108.8	7.8	39.9	54.3	0.0	177.4	1.1	1.1	30.2	307.3
5/9/06	98.8	6.9	38.1	51.6	0.0	160.9	1.1	1.0	31.1	307.1
6/7/06	85.2	6.4	34.2	46.1	0.1	134.0	0.8	0.9	32.2	307.3
7/15/06	81.8	6.7	35.4	49.3	0.0	132.0	1.0	1.1	32.3	282.5
8/9/06	89.0	7.3	37.6	51.9	0.2	136.5	1.0	0.7	30.8	305.3
9/12/06	72.0	6.1	32.5	45.7	0.0	116.0	1.0	0.7	37.9	305.5
10/15/06	77.5	8.5	49.3	56.4	0.1	125.0	1.0	0.5	34.2	332.8
11/14/06	67.5	8.2	43.0	51.9	0.0	111.8	0.8	1.2	31.9	331.2
12/17/06	66.7	7.4	39.2	30.7	0.0	117.4	0.8	0.9	24.7	305.6
2/3/07	64.4	5.7	36.6	45.2	0.0	145.9	1.2	1.2	34.6	257.6

**APPENDIX B
FIELD DATA**

Gunkle			
	pH	Temp ©	Cond
5/20/2005	7.04	13	730
6/7/2005	7.28	13.7	685
6/24/2005	7.29	13.3	559
6/24/2005	7.29	13.3	559
7/14/2005	7.04	13.7	631
8/3/2005	7.45	15.8	619
8/25/2005	7.07	13.8	613
9/15/2005	7.88	13.7	605
9/15/2005	7.88	13.7	605
10/13/2005	7.31	13.6	680
11/3/2005	7.22	13.6	670
11/22/2005	6.96	13.1	630
12/15/2005	7.34	12.4	722
12/15/2005	7.34	12.4	722
1/12/2006	7.24	13.4	746
2/11/2006	6.69	12.7	751
2/12/2006	6.69	12.7	751
3/8/2006	6.29	12.8	763
4/15/2006		13.5	668
5/9/2006	7.24	13.3	686
6/7/2006	6.5	13.5	650
6/7/2006	6.5	13.5	650
7/15/2006	7.29	13.5	680
8/9/2006	7.24	13.8	634
9/12/2006	7.07	13.7	686
10/15/2006	7.35	13.6	686
11/14/2006	7.22	13.7	780
11/14/2006	7.22	13.7	780
12/17/2006	7.16	13.9	708
2/3/2007	7.22	12.6	714
2/3/2007	7.22	12.6	714

Park			
	pH	Temp ©	Cond
5/20/2005	7.51	12.8	175
6/7/2005	8.4	12.9	1270
6/7/2005	8.4	12.9	1270
6/24/2005	7.17	13.1	1250- 1270
7/14/05	7.26	-	-
7/14/05	7.26	-	-
8/3/05	7.36	13.4	1510
8/25/05	7.32	13.7	1520
9/15/2005	7.39	13.4	1660
10/13/2005	7.43	13.6	1570
10/13/2005	7.43	13.6	1570
11/3/2005	7.43	13.5	1380
11/22/2005	7.23	13.2	1280
12/15/2005	7.59	12.6	1420
1/12/2006	7.42	13.2	1130
2/11/2006	6.84	12.3	1050
3/8/2006	6.43	12.4	1060
3/8/2006	6.43	12.4	1060
4/15/2006		13	1010
5/9/2006	7.28	12.9	1180
6/7/2006	7.43	13	1116
7/15/2006	7.63	13.2	1180
8/9/2006	7.07	13.1	1295
8/9/2006	7.07	13.1	1295
9/12/2006	7.1	13	1124
10/15/2006	7.21	13.1	1268
11/14/2006	7.18	13	1061
12/17/2006	7.23	12.9	1090
12/17/2006	7.23	12.9	1090
2/3/2007	7.25	12.5	1045

Lawson			
	pH	Temp ©	Cond
5/20/2005	7.5	12.3	813
6/7/2005	-	12.4	801
6/24/2005	7.36	12.9	799
7/14/2005	7.21	12.1	-
8/3/2005	7.86	13.8	793
8/25/2005	7.19	12.4	811
9/15/2005	7.72	12.1	810
10/13/2005	7.47	12.5	853
11/3/2005	7.31	13	800
11/22/2005	7.16	12.3	811
11/22/2005	7.16	12.3	811
12/15/2005	7.29	11.2	865
1/12/2006	7.39	12.8	790
2/11/2006	6.58	11.7	813
3/8/2006	7.25	12.5	772
4/15/2006	6.9	12.8	823
5/9/2006	7.51	12.8	802
5/9/2006	7.51	12.8	802
6/7/2006	7.51	12.9	835
7/15/2006	7.42	14.3	785
7/15/2006	7.42	14.3	785
8/9/2006	7.17	13.1	782
9/12/2006	7.08	12.7	809
10/15/2006	7.22	12.7	818
10/15/2006	7.22	12.7	818
11/14/2006	7.44	12.8	858
12/17/2006	7.24	12.6	791
2/3/2007	7.26	11.9	799

Lebout	pH	Temp ©	Cond
5/20/2005	7.56	12.5	597
5/20/2005	7.56	12.5	597
6/7/2005	-	12.2	591
6/7/2005	-	12.2	591
6/24/2005	7.52	12.9	574
7/14/2005	7.38	12.5	-
8/3/2005	7.38	12.5	558
8/25/2005	7.08	12.5	560
9/15/2005	7.68	12.7	850
10/13/2005	7.69	13	596
11/3/2005	7.62	13.3	561
11/22/2005	7.24	12.3	581
12/15/2005	7.48	11.7	560
1/12/2006	7.39	12.3	565
1/12/2006	7.39	12.3	565
2/11/2006	6.56	11.3	582
3/8/2006	5.94	11.4	547
4/15/2006	7.36	12.8	823
4/16/2006	7.36	12.8	823
5/9/2006	6.76	12.2	573
6/7/2006	7.8	12.5	543
7/15/2006	7.53	12.7	567
8/9/2006	7.14	12.9	564
9/12/2006	8.18	13	565
9/12/2006	8.18	13	565
10/15/2006	7.39	13.1	550
11/14/2006	7.34	21.7	587
12/17/2006	7.45	12.1	553
2/3/2007	7.36	11.8	551

Eco Park			
	pH	Temp ©	Cond
2/11/2006	7.19	10.5	830
3/8/2006	6.76	12.5	766
4/15/2006	6.2	12.9	735
5/9/2006	7.16	12.8	770
6/7/2006	7.15	13.1	790
7/15/2006	7	15	757
8/9/2006	6.9	15.4	763
9/12/2006	6.39	14.5	770
10/15/2006	7.19	13.6	787
11/14/2006	7.29	13.4	760
12/17/2006	7.03	11.9	753
2/3/2007	7.05	8.2	840

Garage			
	pH	Temp ©	Cond
2/11/2006	6.9	9.9	933
3/8/2006	6.54	11.4	881
4/15/2006	6.59	14.6	920
5/9/2006	7.29	13.3	910
6/7/2006	7.18	14.4	948
7/15/2006	7.67	17	870
8/9/2006	7.16	18.6	811
9/12/2006	7.33	14.1	879
10/15/2006	7.42	12.4	919
11/14/2006	7.44	12.8	858
12/17/2006	7.49	11.5	628
2/3/2007	7.5	8.8	906