Characterizing Storm Response in an Urban Karst Aquifer at Valley Creek, Chester County, Pennsylvania

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ABSTRACT

Karst aquifers respond more quickly to precipitation events than other types of aquifers. However, continuous monitoring and geochemical analysis can provide the necessary information to better understand aquifer recharge pathways and sources during precipitation events. From May 2005 to March 2006 continuous data and water samples were collected from four springs in the Valley Creek Watershed, Chester County Pennsylvania. The springs selected for this study are in commercial or residential land use in an urban setting. This area is underlain by carbonate units that trend east-northeast to west-southwest bounded on the north and south by crystalline igneous and metamorphic units. All springs were in the Elbrook Formation, which is a fractured dolomite unit of Upper Cambrian age.

The goal of this study was to look at the effects of urbanization in a karst setting by monitoring conductivity, water level, and temperature at several springs with different land-use and use halides to distinguish possible source of anthropogenic contamination of the groundwater. Storm response was rapid, on the order of 1-3 hours. Recovery to baseflow conditions of both conductivity and water level was usually within 3-6 hours. This was in contrast to storm response measured in a previous study in a rural setting showing 1-2 days response time from the start of the precipitation event to increases in water stage and to decreases in conductivity at the monitored sites. The water stage response was also on the order of 10-100 centimeters higher in the rural setting than in the urban setting. The maximum water stage increases at the urban springs were typically less than 10 centimeters greater than baseflow conditions, with the more commercialized springs showing only ≤ 5 cm increase. The fast response and lower water

stages at these urban springs were due to smaller capture areas for the springs compared to those in the rural settings.

Conductivity responses were small during storms similar to water level responses. The timing of the initial conductivity responses corresponded also with the timing of the initial water level responses. In general a decrease in conductivity occurred during storm responses, this indicated that recharge moves through quickly. There were slight variations in storm responses between the different springs. Overall however, each spring showed little variation from storm to storm. The consistent and fast response indicated short, fast flow paths.

Geochemical analysis of halide concentrations (chlorides and bromide) in the water samples from the commercial spring site shows contamination by road salt. High chloride concentrations (150 mg/L -280 mg/L) were measured throughout the year. The excess application of road salt during deicing periods has led to accumulation of road salt in the capture area of these springs and has become a continuous anthropogenic halide contamination source.

The urban setting thus influenced spring response by limiting the capture area and reducing infiltration. The reduced infiltration led to smaller storm response and the smaller capture area led to rapid storm response. The presence of high chloride concentrations, concluded to be contributions from road salts also was further indication of shallow, rapid flow paths in this urban setting.

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I would like to express my thanks to my family for their love and support. This is dedicated to my parents Cher, Yia, and Yee. This is for your efforts and patience. Without you I would not have had the opportunities that I have been blessed with. I can not thank you enough for your valor to walk those hundreds of miles in rain or shine through darkness and light. To all my siblings, especially Khou, Phoua, Kia, Mai Song, Lee, and Yer, thank you for cheering me on. I would also like to thank Eric Chan-Tin for his love and understanding.

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I would like to convey my thanks to Dr. Clair Welty for her background information of the Valley Creek Watershed, and for recommending springs for our study. Although I did not have the opportunity to meet Dr. Welty's students, I would also like to thank them for their hard work in tramping around and discovering or re-discovering all the springs in the Valley Creek Watershed.

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CHAPTER 1
INTRODUCTION

Karst terrains are characterized by the numerous sinkholes, sinking streams, voids and cavities, and springs. The permeabilities of karst aquifers are from enlargement of joints, fractures, and bedding plane partings due to dissolution of carbonate rocks by groundwater. The dissolution in karst areas is an ongoing process; therefore, what can be observed today is a moment in the evolution of karst (White, 1999). Karst aquifers, however, are major sources of groundwater for municipal, industrial and domestic use in many parts of the country. An estimated one third of the drinking water in the nation comes from karst aquifers; therefore, it is important to understand and protect them.

Purpose

The purpose of this study was two-fold. The first goal of this study endeavors to look at storm recharge from measurements of discharge at the spring mouth, with the added complication of an underlying karst aquifer. Tancredi (2004) previously looked at the storm response of a karst spring in a rural setting. The storm and continuous monitoring data from this study was compared with data previously to illuminate the differences and similarities of the urban and rural setting. I hypothesized that several aspects of the urban setting will be different from the rural setting spring. The first difference would be that there will be more uniform baseflow conditions for the urban springs than the rural spring because recharge areas are more restricted. Also storm responses in both conductivity and water level in the urban springs would be faster than the rural spring because flow paths are shorter. The urban springs will have higher concentrations of chloride than rural springs due to anthropogenic influences. This leads to the second goal of this study, which was to use measurements of halides to discriminate sources of possible anthropogenic contamination.

This thesis is organized as follows. Chapter 1 provides literature reviews of karst hydrogeology, karst contamination, storm response in both rural and urbanizing settings, and urban hydrology. Chapter 2 includes a description of Valley Creek Watershed, the geology, hydrology, and spring sites location and land-use practices. Chapter 3 presents the method and results of the field sampling and continuous monitoring. Chapter 4 discusses the results and interpretations. Chapter 5 includes an introduction, method and results, and interpretations of the geochemistry of halides. The conclusions are given in Chapter 6.

Karst Hydrogeology

In karst areas, surface and groundwater are being exchanged at faster rates than in a porous medium aquifer. Surface water can quickly become groundwater when it sinks into the stream bed or into swallets and groundwater quickly becomes surface water when it discharges at springs to form headwaters for surface streams. Recharge occurs in karst aquifers several ways. Allogenic recharge is when surface streams from non-carbonate rocks enter the carbonate aquifer through swallets and sinking streams. Overflow recharge is from caprock or perched aquifers that enters the carbonate aquifer through vertical shafts or fractures in the unsaturated zone. Diffuse infiltration is recharge through the soil, fractures, and matrix of the carbonate aquifer. Temporary storage in the epikarst, which is the overburden soil mantle above the carbonate bedrock, may slow the diffuse recharge water by weeks. In karst areas without epikarst, diffuse infiltration can rapidly enter the aquifer (White, 1999). Storm flow recharge is precipitation entering the aquifer through sinkholes. This is the fastest pathway for recharge to enter the karst aquifer (Ford and William, 1989).

Groundwater at karst springs could have several sources with different travel pathways. The three different end member paths are matrix-fed, fracture-fed, or conduit-fed (Figure 1-1); combinations of these three are likely in karst aquifers (Quinlan and Ewers, 1985). Chemical variability of karst spring water has been used to identify and define pathways and recharge to the aquifer (Shuster and White, 1971). In general, high chemical variability is observed in karst aquifers. Again, this is due to the direct connection of surface recharge sources to the karst aquifer. This is evidenced by relatively more diluted groundwater (a mix of older and more conductive groundwater with new recharge water) appearing at the discharge point. Commonly monitored at springs are total dissolved ions (which is related to conductivity), temperature and stage. For example, the process of "flushing" old groundwater by new recharge water is identified by chemical variability. Stage (*i.e.,* water level) may also vary abruptly (Vesper and White, 2003).

Shuster and White (1971) classified diffuse-flow and conduit-flow karst aquifers by monitoring the chemistry of 14 springs in central Pennsylvania. The coefficient of variation (CV) of Ca^{2+} and Mg^{2+} was successfully used to separate diffuse-flow springs from conduit-flow springs. Temperature was also used to support separation of conduit *vs.* diffused flow springs. Conduit-flow springs have greater seasonal variation of temperature than matrix-flow springs. Conduit-flow springs have low temperature during high spring flow. This is because of rapid flow through conduits, which doesn't allow the recharge water to equilibrate with the surrounding rocks. The temperature data are

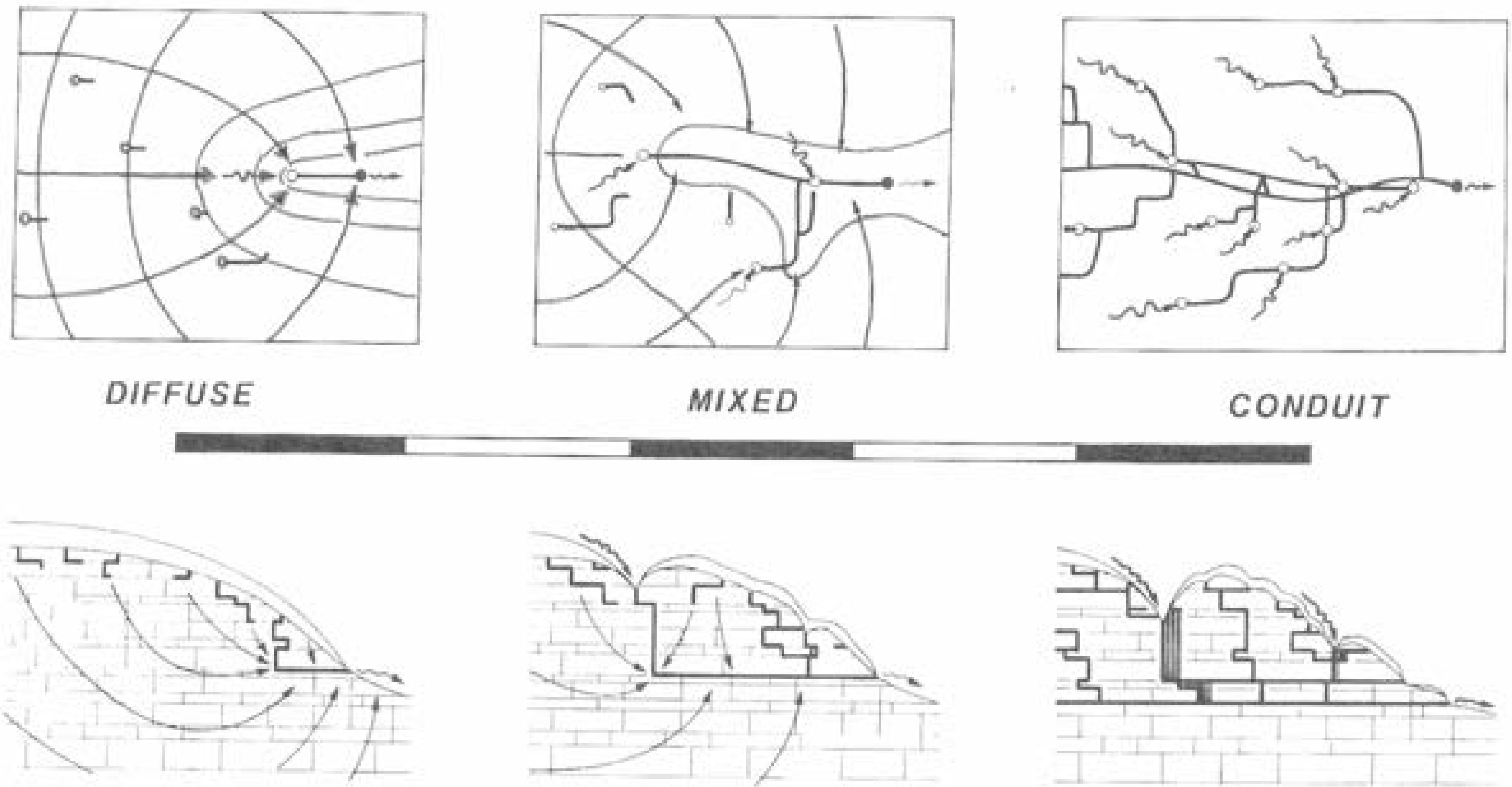


Figure 1-1. The conceptual evolution of flow paths in karst aquifer systems. The top figure show map views and the bottom figures show cross sectional views of diffused, mixed, and conduit flow paths (from Quinlan and Ewers, 1985).

supported by the saturation index of the water chemistry. Conduit-flow groundwater was more under-saturated with respect to calcite and dolomite.

Karst Contamination

The defining features of karst aquifer are open conduits. These are the low-resistance pathways for groundwater flow from recharge sources to the springs. Conduit pathways generally have localized and turbulent non-Darcian flow (White, 1999). Aquifers in these areas are more susceptible to contamination because of diminished absorption and diminished filtration of recharge water. This problem becomes more severe during storms because of the larger volume of water entering the aquifer (Hess and White, 1988). The water carries spills, leaks and drain-pipe-outfall directly into the conduit systems of karst aquifers (Loop and White, 2001).

Stephenson *et al.*, (1999) showed that a significant quantity of storm run-off enters the karst aquifer during storm events (Figure 1-2). Storm water run-off also significantly increases the flux of total dissolved solids, nutrients, bacterial matter and metals in groundwater. Total dissolved solids include dissolved organics such as leaf materials, man-made organic waste (Loop and White, 2001), and nutrients include nitrate and phosphate, which adversely effect surface water ecosystems (Carpenter *et al.*, 1998). Increased concentrations in metals (lead, zinc, cadmium, and mercury) in both the sediment and aqueous parts of groundwater have also been documented (Vesper and White 2003).

Currently, storm water run-off is monitored quarterly. Johnson *et al.* (2002) showed that for karst aquifers, continuous monitoring is preferable because karst aquifers

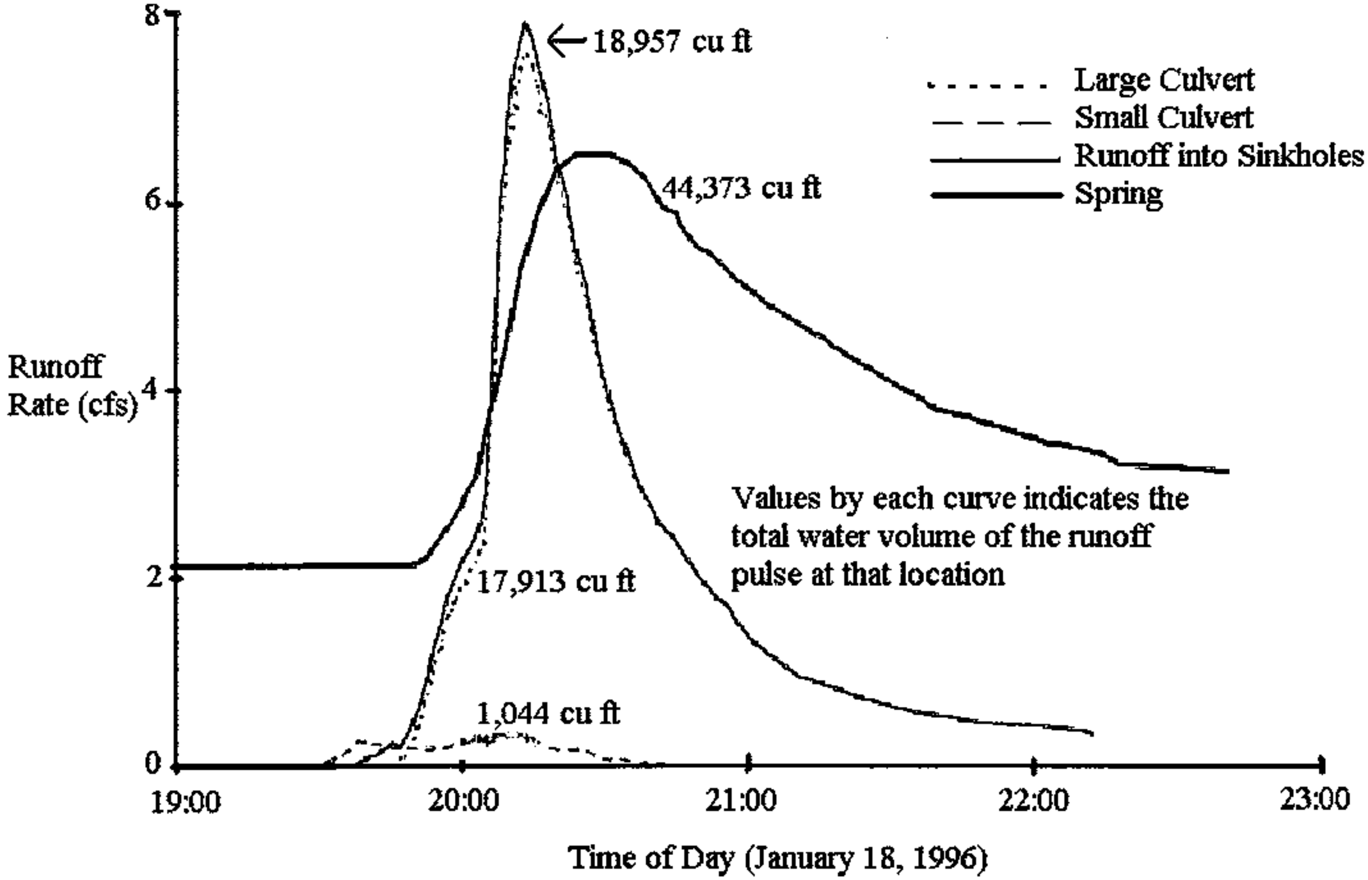


Figure 1-2. Hydrographs of storm runoff into a sinkhole and spring discharge at Holston Spring in eastern Knoxville, TN (after Stephenson *et al.*, 1999)

have fast infiltration and sudden changes in flow. Both of these characteristics are missed with the quarterly monitoring. Therefore, there is a need for more frequent monitoring of karst aquifers, especially in densely populated areas. Springs are essential to understanding the groundwater in karst terrain.

Storm Response

Monitoring springs during storm events is important because discharge at springs integrates system behavior. Specifically, storm response can give clues to recharge types and flow paths in karst systems. Scanlon and Thrailkill (1987) working in the Inner Bluegrass carbonate region of Kentucky saw that during low flow conduit-flow and diffuse-flow springs have similar chemical characteristics. Chemical reaction in the epikarst of the conduit springs influenced the chemistry before the water reached the deep conduit system. Therefore, spring water chemistry is not only a function of the conduit size, but it also reflects the recharge type and length of flow path. Only during high discharge was the recharge to conduit springs from surface run-off (storm flow) through sinkholes. Typically storm flow water is identified by lower conductivity (lower concentrations of dissolved ions) relative to the more diffused recharge water.

Hess and White (1988) found a relationship between flow rate, water temperature and specific conductance. Storm water recharge into the karst aquifer led to decreased specific conductance, which continued to decrease until a broad (2-5 day duration) minimum was reached. This was due to dilution of older groundwater, which has higher concentrations of dissolved ions from water-rock interactions, with new recharge water, which has lower concentration of ions, such as Ca^{2+}, Mg^{2+}, and HCO_3^- The recovery to pre-storm conditions was a slow gradual process, requiring two to three weeks. Hess and

White (1988) also observed that before the drop of conductance at the arrival of the new storm water, water conductivity showed an initial rise from baseflow. They hypothesized this be initial spring discharge was older groundwater driven out by the increased hydraulic head in the recharge zone before the arrival of new storm water. The shape, duration and intensity of the storm in combination with soil and aquifer conditions explain why each storm response is not an exact copy in conductance and temperature levels from the previous storm.

Desmarais and Rojstaczer (2002) saw abrupt increases in discharge at springs within 1-2 hours of the storm peak. This spike was follow by a gradual (6-10 days) decrease of spring discharge to the baseflow. The initial increase in discharge was due to storm water loading, which changes the pressure head so that groundwater quickly discharges at the mouth of the spring. The discharge increased 5-30 L/s during storm events (Figure 1-3a). The high conductivity response was correlated with the peak response in discharge (Figure 1-3b). The conductivity increased until a maximum was reached follow by gradual (2.1-2.5 days) decrease to baseflow. There appeared to be three step processes involving the response of the spring to storm water 1) flushing, 2) dilution, and 3) recovery, evidenced by the different stage discharge at the spring and the different conductivity response.

Based on conductivity, Tancredi (2004) observed two types of storm response at Nolte Spring in Lancaster County southeastern Pennsylvania. Type I storm response showed the "flushing" of old water signified by large increase in conductivity. High-intensity storm events tended to push out older groundwater as observed by Hess and White (1988). The return to baseflow conductivity level was slow, possibly because: a) it

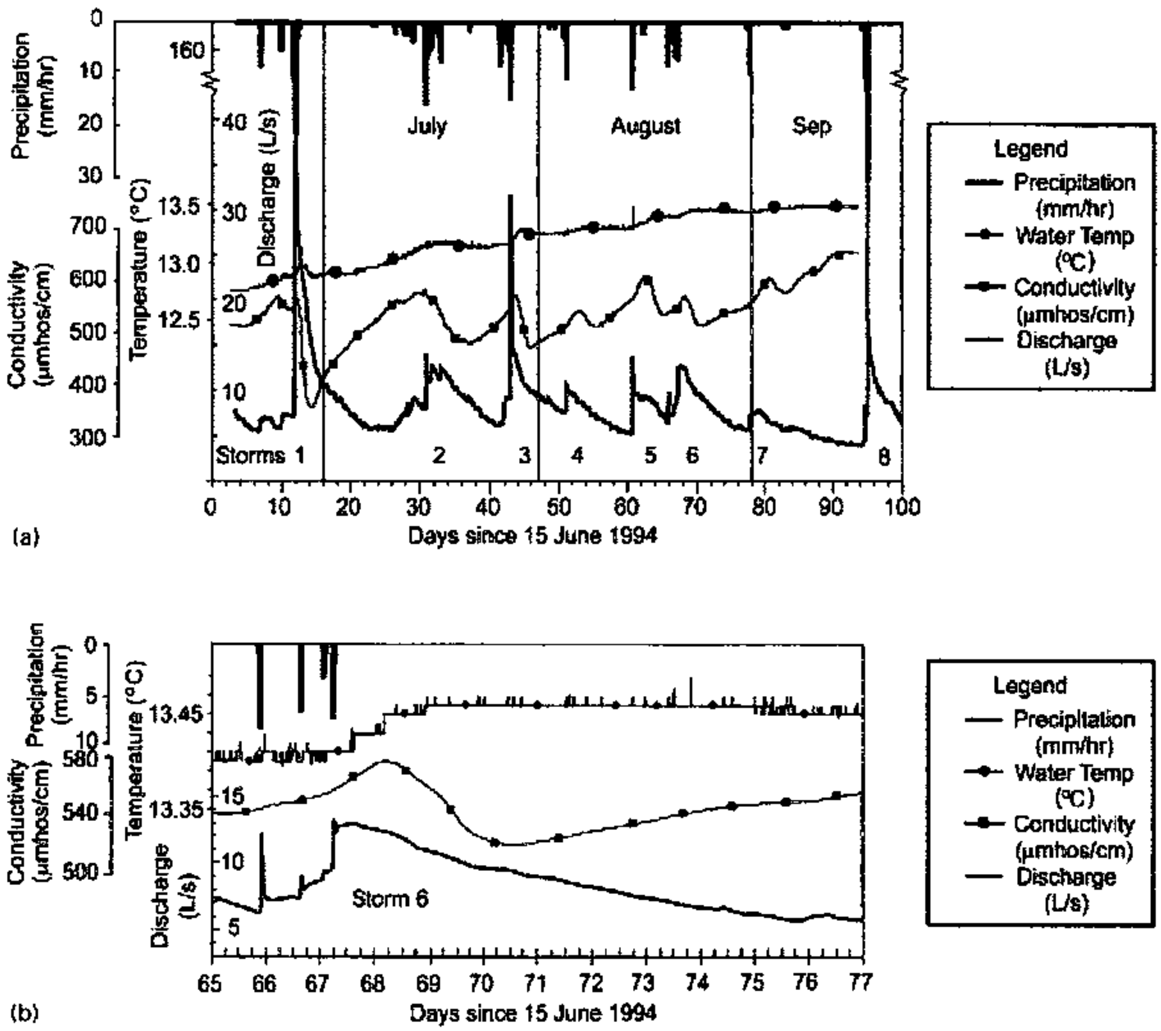


Figure 1-3. Observed discharge, conductivity, and temperature during storms for carbonate springs and wells monitored from study of storm response near Oak Ridge, Tennessee (from Desmarais & Rojstaczer, 2002).

takes time for water-rock interaction to bring the conductivity of the recharge water to normal level or b) refilling conduits with old water from smaller surrounding fractures was slow (Figure 1-4).Tancredi (2004) observed that seasons with less frequent, but more intense storms were more likely to generate point recharge (i.e. through sinkholes and conduits).

Tancredi (2004) also observed that at high stage (after a high-intensity storm event or a combination of smaller storms where the water table has risen) the total dissolved ion concentration decreased due to dilution. At these times, Type II storm response was observed. A Type II storm response showed a decrease in conductivity after the storm events. This was likely due to relatively younger pre-storm water present in the aquifer due to more frequent but lower-intensity storm events in these seasons. It is thought that the more diffused recharge; lower intensity storm events allowed for slower and diffused recharge by infiltration (Figure 1-4). The recharge water then was gradually mixed with the groundwater, and returned to pre-storm conductivity. The seasonal variability in the rural setting was concluded to be due to the epikarst response to storm events (Tancredi, 2004).

Urban Hydrology

Most of the previous discussion assumes natural infiltration (for example in rural settings). However, in urban and rapidly developing areas storm water run-off is of great concern for both groundwater and surface water quality. The fast flowing and concentrated quantity of storm run-off and contaminated surface water going through karst aquifers make them vulnerable to pollution, because in urban settings multiple

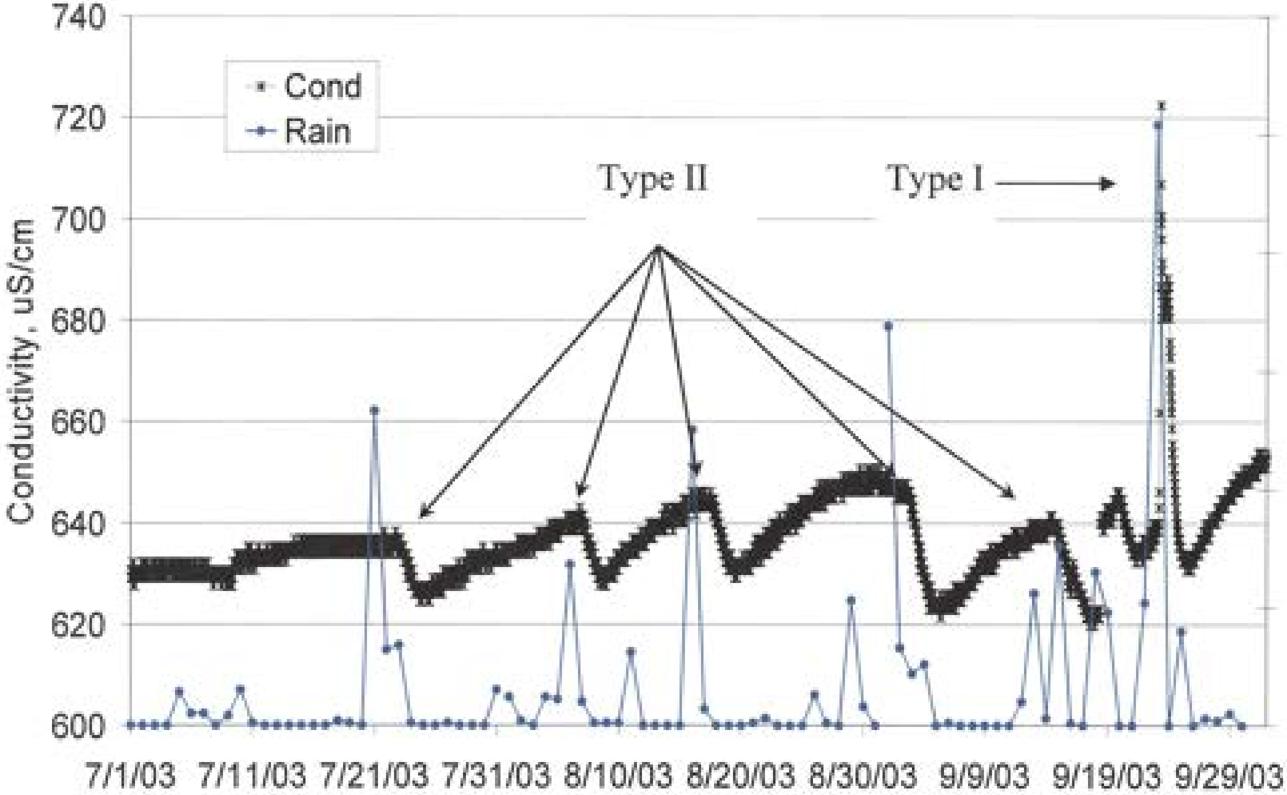


Figure 1-4. Summaries of conductivity and rainfall data from Nolte Spring summer 2003. Mostly Type II storm response, where there an initial conductivity decrease after the storm event, are present in this season. The storm on 9/22/03 showed a Type I storm response, where old groundwater flushed out by new storm water produced conductivity increases (from Tancredi, 2004)

sources of pollution are possible as water flows across impervious surfaces such as rooftops, road pavement, and paved parking lots (Stephenson *et al.*, 1999).

The focus in urban hydrology has been on surfaces events that are consequences of the increase in impervious surfaces, such as flooding and precipitation prediction for management of the urban watersheds both in the U.S. and abroad (Smith *et al.*, 2005; Berne *et al.*, 2004; Vieux and Bedient, 2004). Other studies of urban hydrology focused on efforts to moderate the effects of urbanization on both surface and groundwater include management methodologies to increase infiltration by building infrastructures such as infiltration basins (Gobel *et al.*, 2004).

In a non-urban karst system recharge to the aquifer can either be focused at sinkholes and sinking streams or distributed through the soil zone or a combination of both. In urban hydrology the complex issue of recharge to the groundwater system had not been well studied. Possible recharge pathways in urban hydrology include not only the localized infiltration through open areas such as parks and gardens, but also along roadways where storm ditches are absent, leakage from storm drains, sewer pipes, and septic tanks (Lerner, 2002). However, to assess recharge through these man-made structures requires significant time and resources. Little research has been done and there are a lot of uncertainties due to lack of basic infrastructure data. For future urban development and suburban development there will be a need to have such aquifer information available.

CHAPTER 2
STUDY SITES

Geographic Setting

The study area is in the Valley Creek Watershed in Chester County, southeastern Pennsylvania (see Figure 2-1). The Valley Creek Watershed drainage basin covers about 60 square kilometers of land. Valley Creek and its tributaries drain into the Schuylkill River. The watershed is in the Piedmont physiographic region in southeast Pennsylvania.

The Valley Creek area is experiencing high rates of both residential and commercial development. Most of the development in the watershed is in the valley area and in the western headwater of the watershed (Steffy *et al.*, 2003). Chester County experienced a 7 % population increase from 2000-2004. The number of housing units also increased 7% within the same time period. Chester County is seventh in population in Pennsylvania. The watershed has an estimated 18 – 24 % impervious surface (Chester County Water Resource Authority, 2004). This means that the watershed close to the threshold of being an impaired watershed, which has impervious surfaces > 26%. The springs monitored for this study are in the East Whiteland and Tredyffrin Townships. Both townships are experiencing a lot of growth and were classified by the U.S. census in 2000 as urban area based on population density (Chester County Water Resource Authority, 2004).

Geologic Setting

The bedrock in the basin is mostly carbonate rock (68%) with some igneous and metamorphic rocks (32 %) (Sloto, 1990). The lowlands in the Valley Creek basin

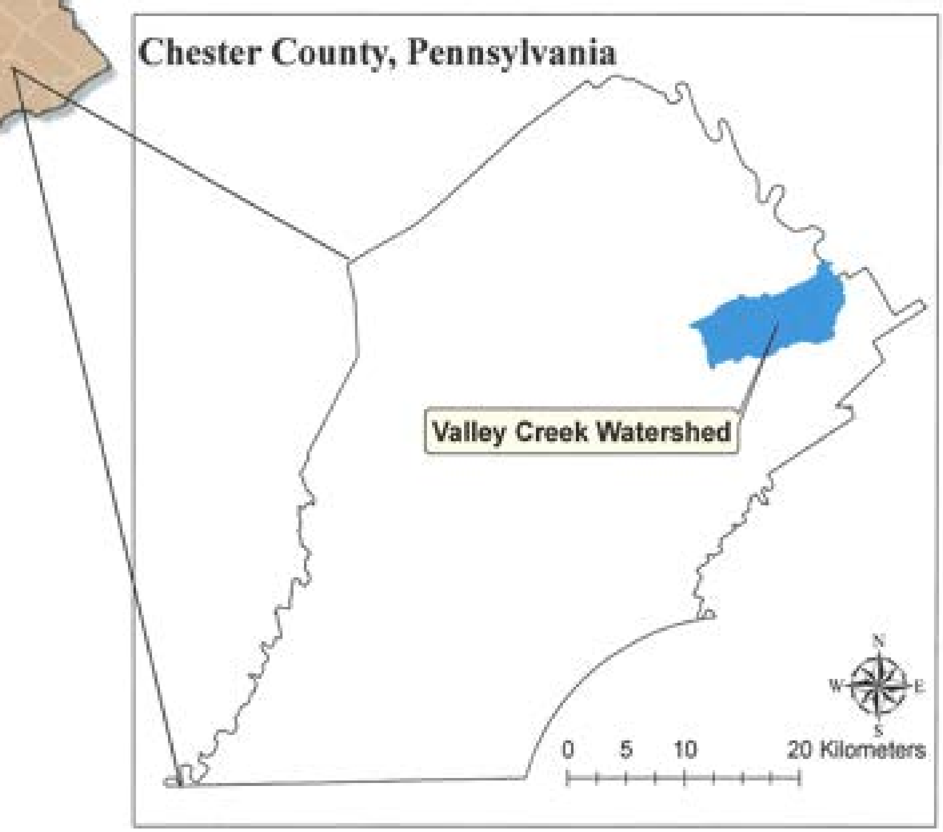


Figure 2-1. The springs are in Chester County in southeastern Pennsylvania (above). The map to the right shows Chester County with the Valley Creek Watershed outlined. The watershed is about 60 square kilometer.

are underlain by the carbonate rocks. The crystalline rocks are found in the topographic highs forming the northern and southern boundaries of the watershed. The rocks are mostly Cambrian to Ordovician in age. The main carbonate units are the Ledger Dolomite, Elbrook Formation, and Conestoga Limestone. Minor units include Vintage Dolomite and Kinzers Formation (Figure 2-2). These units are thinner and not as important water-bearing units as the other four units (Sloto, 1990).

To limit the variability between different bedrock units, all the springs selected for this study are in the Elbrook Formation, which is Middle Cambrian to Upper Cambrian in age. This unit forms low hills in the Chester Valley region (Figure 2-3). The Elbrook is approximately a 244 meters thick unit bounded by the Ledger Dolomite below and the Conestoga Limestone above. The Elbrook is a highly fractured dolomite. There are numerous millimeters to centimeter scale micro-foldings in this unit and they are defined by the thin quartz beddings. The Elbrook in Chester County appears to be more folded and metamorphosed than its equivalent in mid-south Pennsylvania and northern Maryland (Kochanov, personal communication, 2005). The most probable source of quartz is secondary fluid flow, evidenced by the fact that the thin quartz beds are present mostly along bedding planes.

Hydrogeology of Valley Creek Watershed

The Valley Creek basin, which consists mainly of the Elbrook Formation and the Ledger Dolomite, are the least productive water-bearing units in Chester County, however it is still a major public water supply and demands are increasing with rapid development of the region (Sloto, 1990). The water bearing units of Valley Creek are the carbonate rocks whose limited transmissivity is controlled by the bedding planes

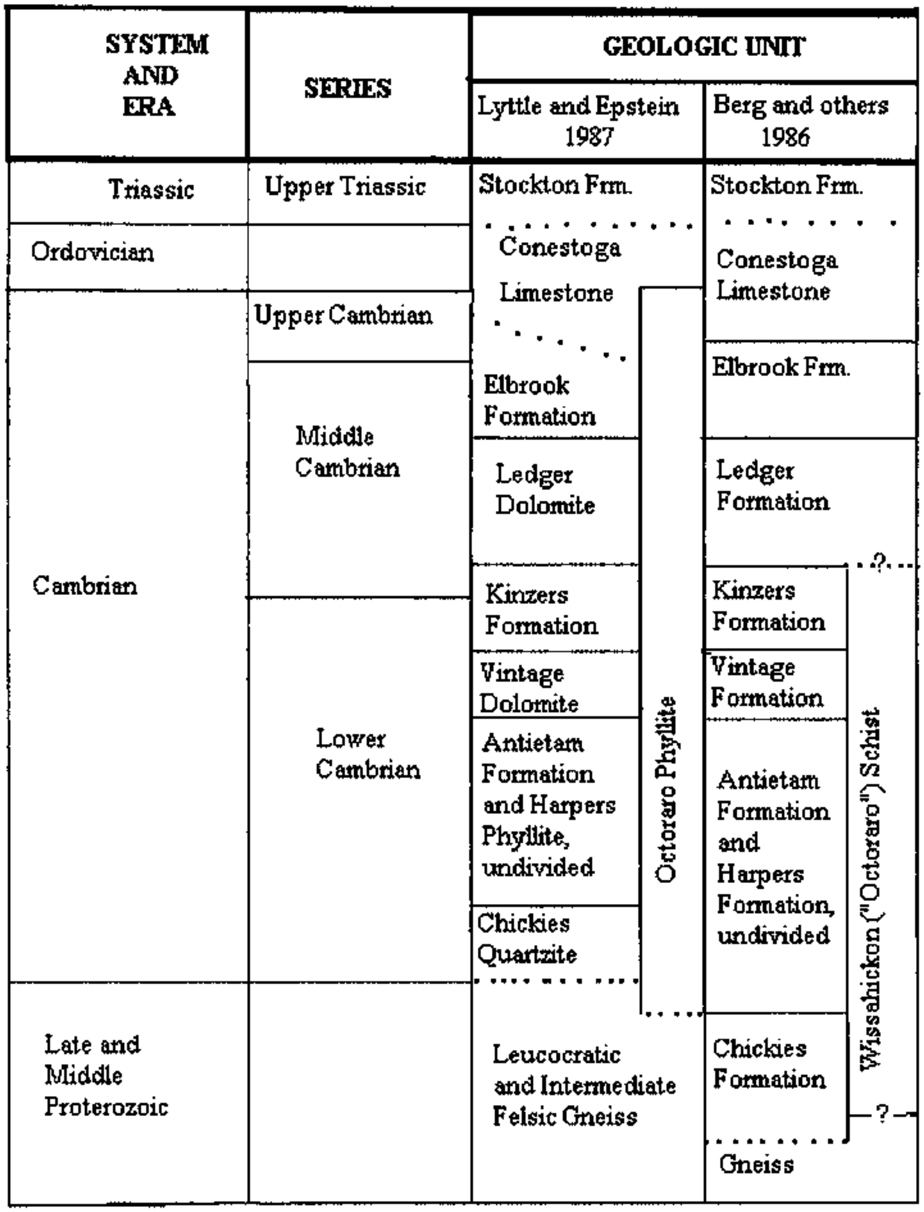


Figure 2-2. Stratigraphic column for the Malvern and Valley Forge Quadrangle (after Sloto, 1990).

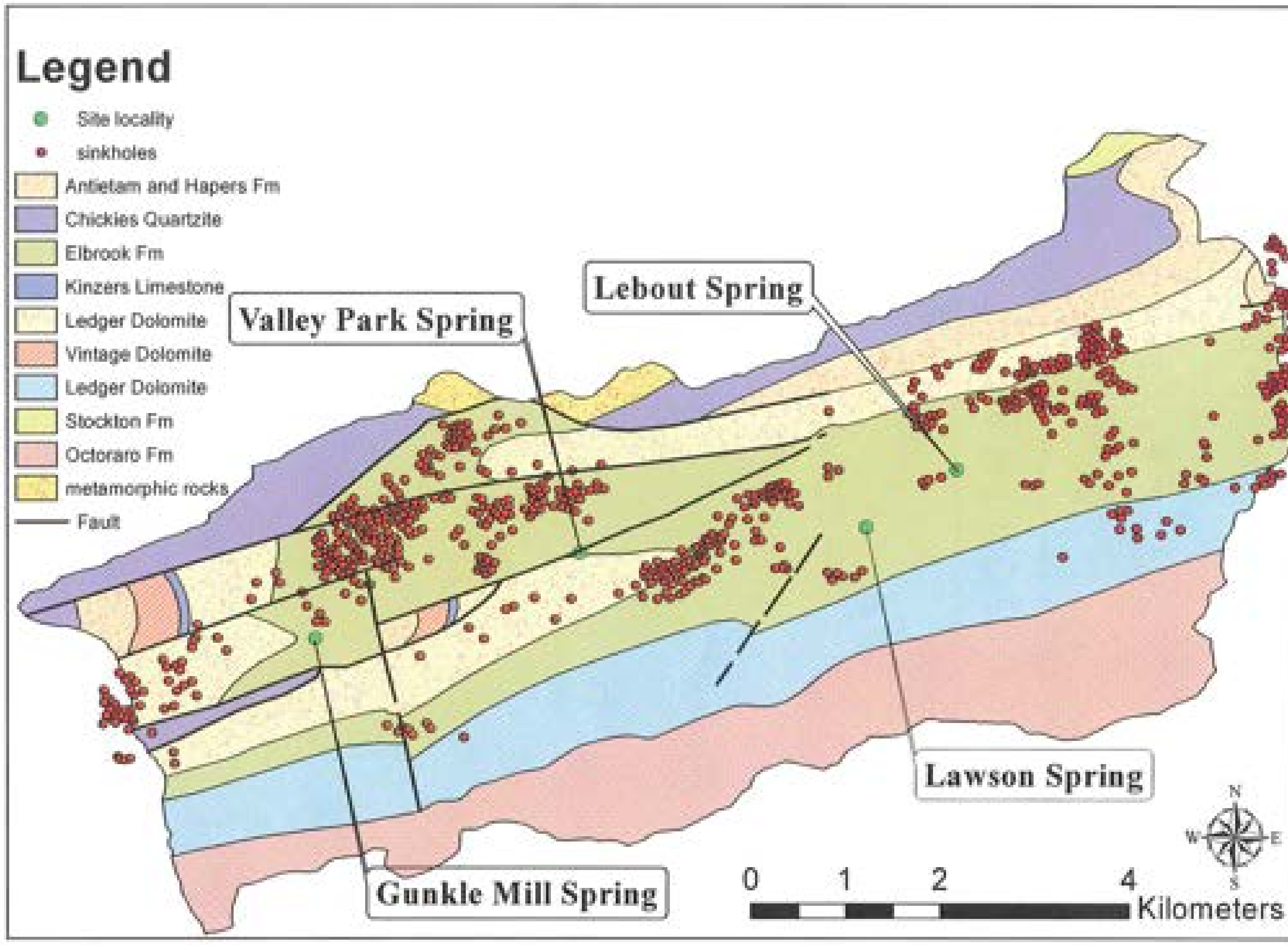


Figure 2-3. Geologic map of the Valley Creek Watershed. All springs selected for this study are from the Elbrook Formation which forms the valley of the basin. Geology data from Chester County Water Resource Authority (2005).

and fractures.

The Elbrook has abundant joints and lineations. The groundwater flows out of these fracture joints and along bedding planes. Caverns and pinnacles are common in the Elbrook due to dissolution along fractures and joints. Higher up in the Elbrook there are recumbent folds that repeats the layering in the formation. The layering is mostly of phyllitic dolomite and siliceous dolomitic layers. The recumbent fold in places doubles the thickness of the unit. The Elbrook Formation is steeply dipping by 30 to 50 degree to the south. The Elbrook also has numerous sinkholes that have been exposed and enlarged by urban development (Kochanov, personal communication, 2005).

The aquifer is phreatic (unconfined aquifer where the water table lies below the top of the aquifer); therefore, the aquifer responds rapidly to the changes in evapotranspiration and precipitation recharge events (Sloto, 1990). The groundwater flow follows the geologic structure and distribution of the fractures in the basin to discharge in Valley Creek and its tributaries (Figure 2-4). Spring discharge occurs mostly along fractures within bedrock and contacts between different rock units. For example, there are several springs along the contacts of the crystalline rock units and the carbonate rocks. The baseflow of Valley Creek and its tributaries relies on the groundwater for recharge during periods of low precipitation.

There are more than 120 springs located in the Valley Creek Watershed. These springs were discovered and/or rediscovered by Dr. Clair Welty and her students from Drexel University, Philadelphia, Pennsylvania. Results of preliminary geochemistry and physical characterizion of some of these springs were conducted by

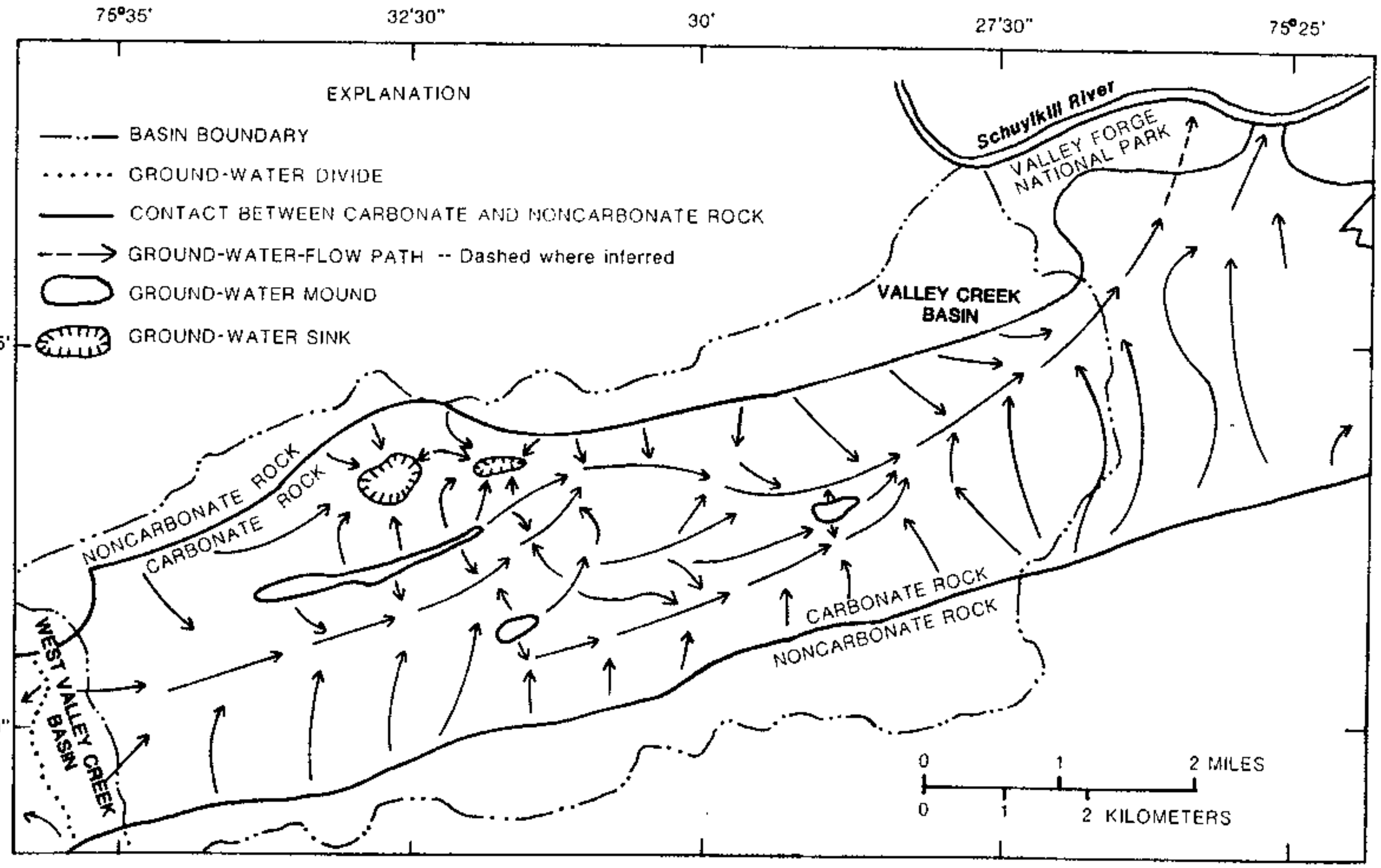


Figure 2-4. Generalized groundwater flow in the Valley Creek Watershed (from Sloto, 1990).

several studies (Steffy, 2003; McGinty, 2003). Steffy (2003) looked at the groundwater/surface interaction (mainly impervious surface coverage and that leads to temperature fluctuation) and fish biodiversity in Valley Creek and its tributaries. Fish species diversity was impacted at Valley Creek Watershed with high (>15% impervious). McGinty (2003) used semivariogram analysis to model the correlation of geologic and land use indicators of groundwater quality in the Valley Creek Watershed. McGinty (2003) did find that land-use and geology does influence the geochemistry of the water in the Valley Creek Watershed on large scale correlation.

The springs selected for my study were chosen based on high (> 0.5 L/s) and steady discharge, accessibility, and different land uses (Figure 2-5). Gunkle Mill Spring and Valley Park Spring are in the Malvern Quadrangle and Lawson Spring and Leboutillier Springs are in the Valley Forge Quadrangle. Gunkle Mill Spring is on a historical preservation site; however, the immediate area surrounding the spring house is commercialized (Figure 2-6). The spring discharge is through a conduit opening. In the spring house there are two readily visible discharge points; however, only the higher flowing discharge point was monitored. Valley Park Spring is located in the East Whiteland Township Park. The area up-gradient from the spring is highly commercialized, including an office complex (Figure 2-5 and Figure 2-7). At the top of the ridge about 0.8 kilometer uphill, outside of the recharge area is the Cedar Hollow Mine. Currently the mine is not operational; however, the groundwater in the mine is pumped to maintain trout fishing streams. The spring house contains several springs but only the largest conduit opening was monitored. Lawson Spring is in a residential area (Figure 2-5 and 2-8). This spring is on private property. The

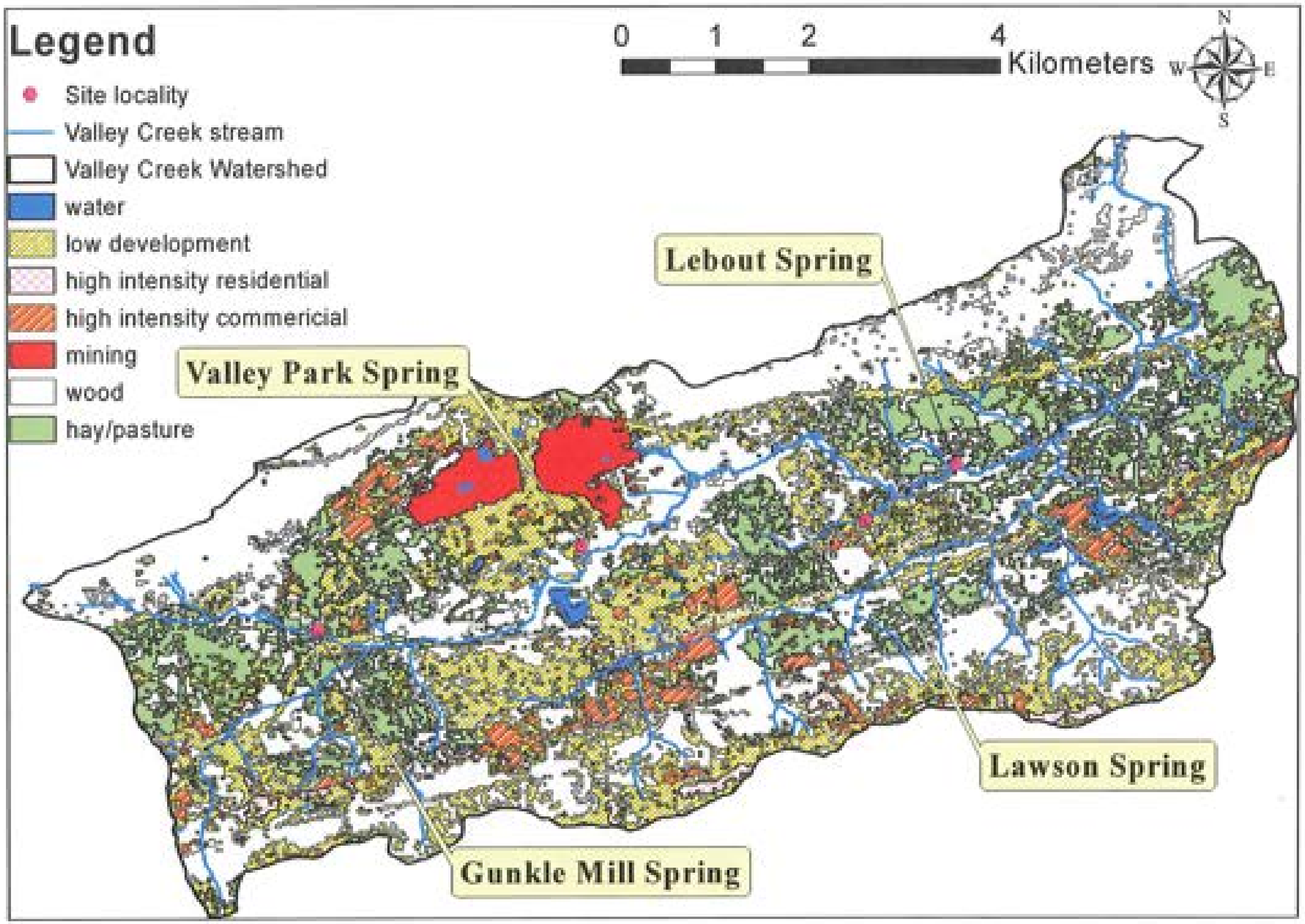


Figure 2-5. Land-use map of the Valley Creek Watershed. Most of the residential and commercial developments in this area are in the valley (center) of the watershed. Land use GIS data from Chester County Water Resources Authority (2005).

Figure 2-6. Gunkle Mill Spring is one of the two commercial land-use springs monitored for this study. The springhouse (left side) is south of the road. North of the road, up-gradient from the spring house is a large commercial office building with a large parking lot. To the east of the spring house there are several commercial office complexes.

Figure 2-7. A photo of the Valley Park Spring, another of the commercial springs included in this study. The springhouse is in the East Whiteland Township Park, Malvern, PA. Although the small area of the park is mainly open land, just up-gradient (less than 0.4 km) from the edge of the park, there are several commercial office complexes with numerous attached parking lots.

Figure 2-8. This is a photo of Lawson Spring. This spring is the most open spring because the spring house had collapsed. The land use here is mostly residential.

spring is a complex combination of several seepage springs, most likely along bedding planes. The spring house at this spring has collapsed (no roof); consequently, the monitoring equipment was installed out-of-doors. Leboutillier Spring is in an agricultural/residential area (Figure 2-5 and Figure 2-9). Although listed as agricultural by Chester County, recent development is converting the area surrounding this spring into residential land use. Inside the spring house there are several discharge points from seeps although because the stage was high at the time of the instrumentation it was difficult to isolate a distinct discharge point. Outside of the spring house there was a trough collection point; this is where the instruments were installed.

Background Characterization

Further investigations of physical and geochemical properties of the springs included capture area and coefficient of variation. Capture areas for the springs in this study were calculated based on the Rule of Thumbs (RTs), guidelines provided by the United States Environmental Protection Agency (Ginsberg and Palmer, 2002). The RT's provide methods for calculating recharge area based on discharge values of the stream in the spring basin. By using these calculated values in combination with hydrological data and geologic/structural information rough estimates of the capture area can be performed. The first step is to make spring discharge measurements. This was done by measuring: velocity of flow in spring channel, measurement of the cross sectional area of the channel (Ginsberg and Palmer, 2002). The measurements of spring velocities were conducted on March 8, 2006 (Table 2.1). This was the ideal time because the discharge should be during the high baseflow period of the spring

Figure 2-9. This is Leboutillier Spring. The land use here is in transition. Originally it was categorized as agricultural (row crop or hay pasture). However, throughout this study period the area changed from agricultural to more residential with buildings of private family homes.

(Ginsberg and Palmer, 2002). The velocity measurements were carried out using floats (leaves), a stop watch, and a meter stick.

Table 2-1. Spring discharges and estimated capture areas.

Spring	Spring Discharge (L/sec)	Spring capture area (sq. km)
Gunkle Mill Spring	0.59	0.054
Valley Park Spring	1.07	0.098
Lawson Spring	14.98	1.35
Leboutillier Spring	5.10	0.47

For determination of stream discharge, daily discharge record of Valley Creek was obtained from USGS water data website (Valley Forge, Hydrologic Unit: 02040202). The average stream discharge was 595 L/s for Valley Creek. The drainage area of Valley Creek Watershed is 53.87 km^2. The recharge rate for Valley Creek is simply the stream discharge divided by the drainage area. The capture area is then determined by dividing the spring discharge by the recharge rate based on the stream discharge.

The spring with the largest discharge was Lawson Spring followed by Leboutillier Spring, Valley Park Spring, and finally Gunkle Mill Spring (Table 2.1). *In-situ* complications at each spring mean that there are a lot of uncertainties in the discharge values. Due to the complex folding of the bedrock and lack of good outcrop localities in the Elbrook Formation near the most of the spring locations, essential geologic data (*i.e.*, strike/dip) was not available. Although rough estimates given for the dip of the Elbrook Formation is about 30-50 degree dip to the south (Kochanav, personal communication, 2005). Also, because the baseflow of Valley Creek is not just from groundwater but also from the pumping at the mines (as mentioned earlier), the capture area calculations had 10-20 % uncertainties. Thus, only rough estimates of capture areas could be obtained.

The calculated capture area of each spring was plotted on topographic and land use maps. Again, because Lawson Spring had the largest discharge rate this spring had the largest calculated capture area at 1.35 km^2 (Figure 2-10). Leboutillier Spring has a capture area of 0.47km^2 (Figure 2-10). Both Gunkle Mill Spring and Valley Park Spring have capture area of ten less than either Lawson Spring or Leboutillier Spring. Valley Park had a capture area at 0.098 km^2 and Gunkle Mill Spring has the smallest capture area of 0.054 km^2 (Figure 2-11). The use of rectangles to delimit the capture areas is intended to show that they are simplified capture area estimates. The rectangles were placed so that they didn't cross stream divides and the spring was otherwise centered on the capture area. The estimated capture areas show the land-use type expected for each of the springs.

Based on the Ca^{2+} and Mg^{2+} concentrations analyzed in a geochemistry study of the springs, Gross and Toran (2006) calculated the coefficient of variation for Gunkle Mill Spring, Valley Park Spring, Lawson Spring, and Leboutillier Spring using the following equation:

$$CV\% = 100 \text{ x } \frac{\text{Std. } (2.5Ca^{2+} + 4.1Mg^{2+})}{\text{Mean } (2.5Ca^{2+} + 4.1Mg^{2+})}$$

The ratios of standard deviation (std.) to the mean normalize the variation of the major cations (Ca^{2+} and Mg^{2+}). Ca^{2+} and Mg^{2+}were measured in mg/L, therefore the coefficients provide molar proportions. CV has been used to classify springs into diffused, conduit, or mixed flow type. The coefficients of variation of the springs classified Gunkle Mill Spring and Valley Park Spring as conduit-flow springs with

CV ~19%. Lawson Spring and Leboutillier Spring were classified as mixed between matrix-flow and conduit-flow with CV ~ 11%. The coefficients of variation values observed in the springs are in the range of typical karst aquifers.

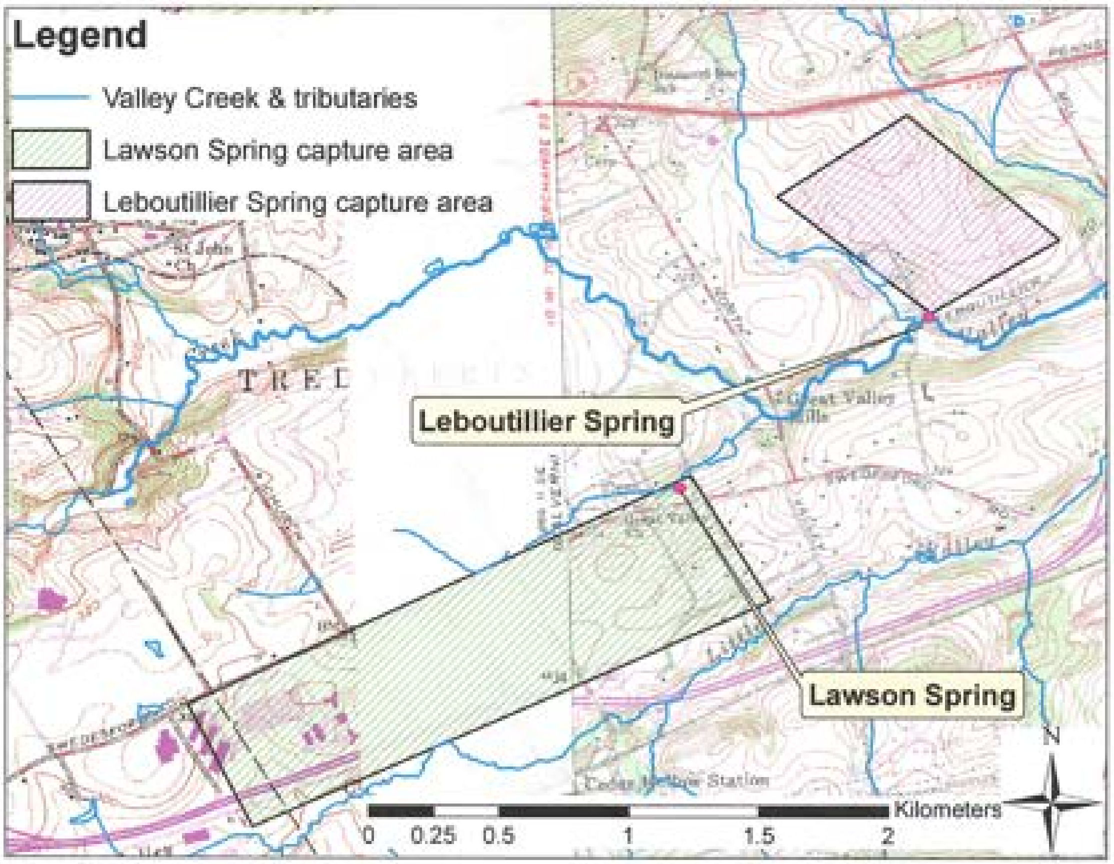


Figure 2-10. Capture area of Lawson Spring and Leboutillier Spring. These springs capture more residential areas. The location and areas for these springs were approximated according to the Rule of Thumbs method (Ginsberg and Palmer, 2002). The topographic maps were downloaded from the Pennsylvania Spatial Data Access website (March 9, 2005).

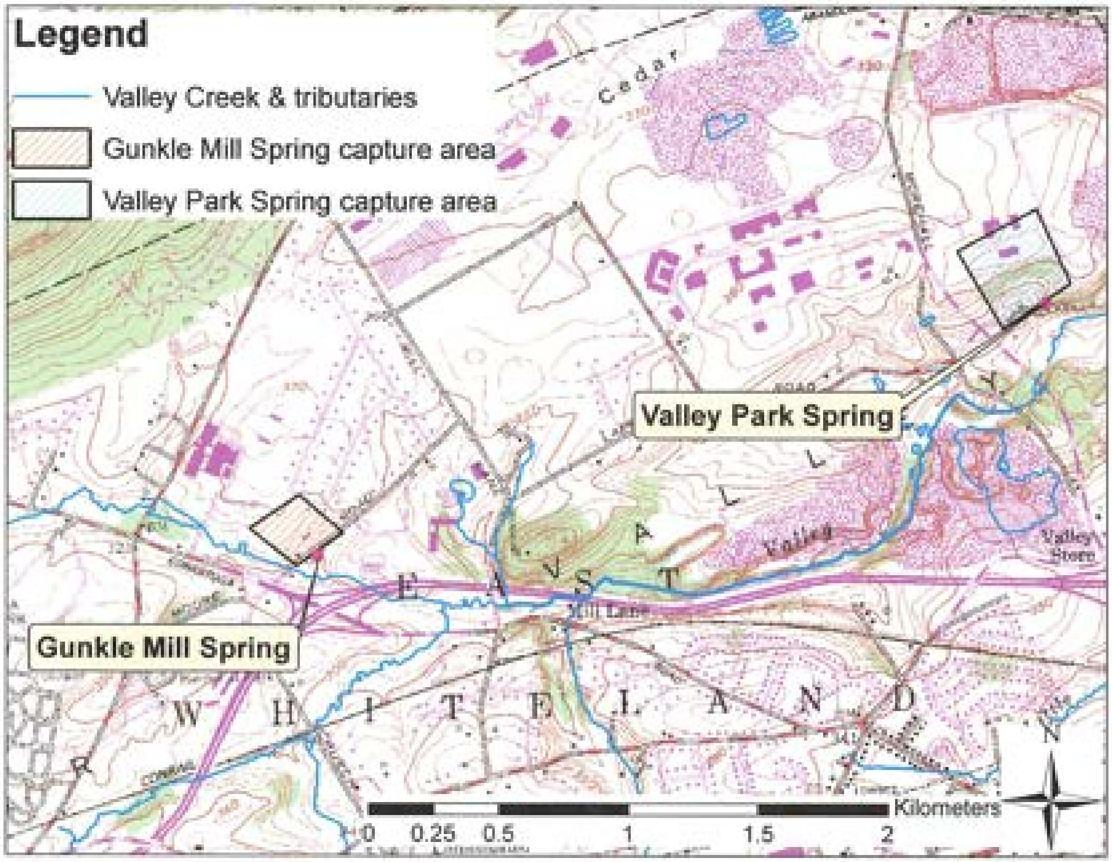


Figure 2-11. Capture area of Gunkle Mill Spring and Valley Park Spring. These springs have capture area in more commercial areas. The capture areas are smaller than the residential springs. The location and size of the areas for these springs were approximated according to the Rule of Thumbs (Ginsberg and Palmer, 2002).

CHAPTER 3
CONTINUOUS MONITORING AND STORM RESPONSE:
METHODS AND RESULTS

Introduction and Methods

The parameters monitored using continuous data logging included conductivity, water level, and temperature. These data provide high temporal resolution short and long term information about the springs that are typically missed from data collected during field visits. The conductivity was measured using a Global Water conductivity sensor (WQ301). The calibrated range of the conductivity sensor was from 0 μS/cm to 2000 μS/cm with an accuracy of 1%. The water level was measured with a Global Water pressure transducer (WL400). The transducer was calibrated to measure from 0 cm to 91 cm with an accuracy of ±0.2% from 35-70°F. The conductivity and transducer instrument were connected to multi-channel Global Water logger (GL400) with a 12V rechargeable battery. The temperature data were collected with an Onset Stowaway sensor. The temperature sensor has - 4°C to 37°C range with accuracy of ±0.2°C at 21°C. All instruments were placed close to the discharge point of each spring. The water level, conductivity, and temperature data were collected at 15 minute intervals. The logger cases were kept from direct sunlight and dry by placing them on a cement cinder block and wrapped with tarps.

Initially, one Global Water logger was installed at each spring site. At two of the sites, Gunkle Mills and Valley Park, it was possible to keep the instrumentations and loggers inside the spring houses. For the other two springs, Leboutillier and Lawson, the instrumentations were installed outside. Lawson Spring did not have a spring house and at Leboutillier Spring the discharge was more readily visible on the outside of the spring house. To better see the effects of overland flow at the spring discharge points during storms, two additional loggers were installed at Gunkle Mill Spring and at Leboutillier Spring. For Gunkle Mill Spring the extra logger was installed outside of the spring house. For Leboutillier Spring the extra logger was installed inside the spring house. These sites were selected for loggers because they have responses that differ from each other and there was access for equipment installation both inside and outside the spring houses.

In addition to continuous monitoring, monthly field visits during baseflow were also included in this study. During the field visits general maintenance of the continuous sensors and loggers, such as replacing the battery and downloading of data, were performed. Measurements of pH, water level, conductivity and temperature were made when the water samples were collected. The water level, conductivity, and temperature measurements were taken to verify the continuous monitoring data. The field data collected were plotted to discern seasonal trend in baseflow measurements of conductivity, water level, and temperature. Baseflow pH data is reported elsewhere (Gross and Toran, 2006).

Precipitation data used in during this study were downloaded from the USGS water data website (http://waterdata.usgs.gov) for stations in Chester County (USGS, 2006). Initially, the precipitation data were acquired from the East Brandywine Creek station (Hydrologic Unit: 020402205) in Downingtown, PA. However, once the Valley Creek station (Hydrologic Unit: 02040202) near Valley Forge National Park came online in August 2, 2005, the data from this station were used because the station is closer to the study sites (Figure 3-1).

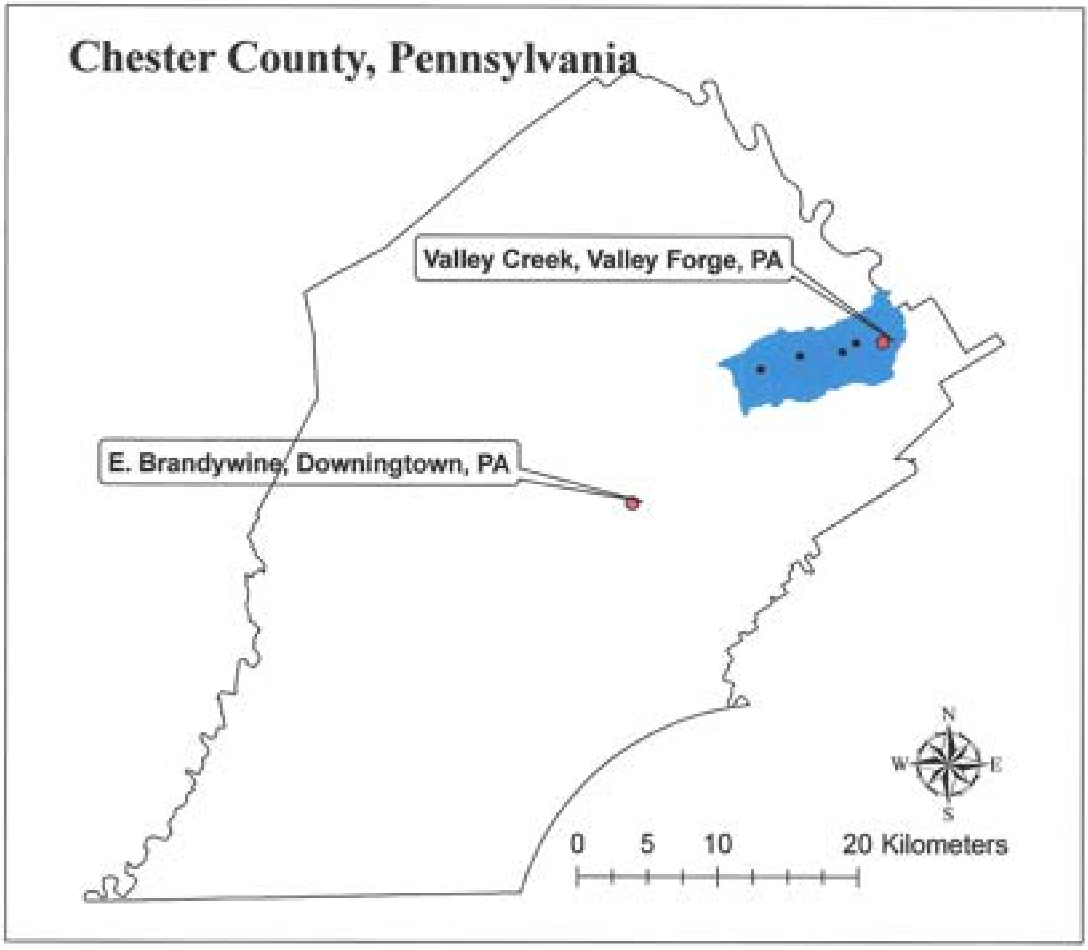


Figure 3-1. This map show the locations of the springs monitored during this study (black dots) inside the Valley Creek Watershed. The locations of the weather stations from which precipitation data were downloaded from are also shown on the map.

The pulsating nature of the water discharging from the springs caused the data to be noisy for the early part of the monitoring period. In the early part of the summer season stilling wells, constructed from PVC pipes with 3-4 horizontal slits at the base of the pipe for water flow, were installed at all sites to dampen the pulsating effect of the springs' discharge. Afterwards the storm events were more readily apparent in both conductivity and water level data.

Field Data From Site Visits

Baseflow temperature did not appear to show any seasonal trend. The baseflow spring stage showed slight seasonal trend at all the springs (Figure 3-2). The lowest baseflow spring stages measured were during the late summer and early fall. The highest spring stages were measured during the late fall, winter and spring seasons when the precipitation was lowest.

Baseflow conductivity for Leboutillier Spring, Gunkle Mill Spring, and Lawson Spring did not show any season trend. For Valley Park there was a seasonal trend (Figure 3-3). The lowest baseflow conductivity (1010 μS/cm) measured at this spring was in the early spring of 2006. The baseflow conductivity at the start of the study period was 1160 μS/cm. The conductivity increased in the summer season until a maximum conductivity of 1677 μS/cm was reached at the beginning of the fall season. The conductivity then decreased to 1060 μS/cm in the late winter of 2006.

Continuous Monitoring Results

This thesis covers the first nine months of data collection. For the purpose of data organization the data collected were divided into three month span seasons. Spring 2005 included data from the start of the study May 20, 2005 – June 30, 2005. Summer

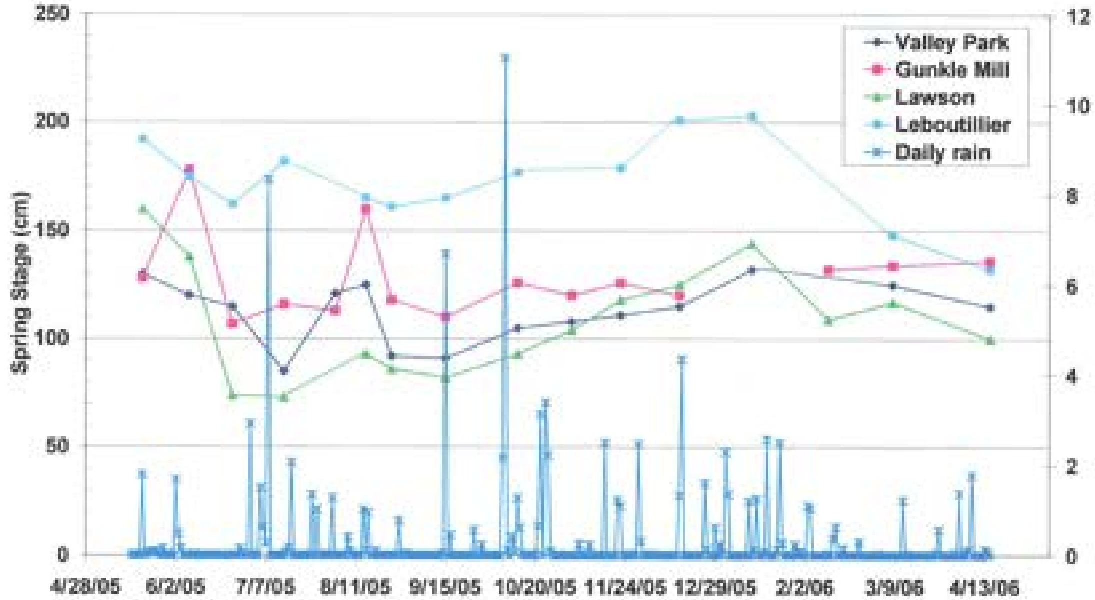


Figure 3-2. Field measurements of baseflow spring stage and precipitation throughout the study period.

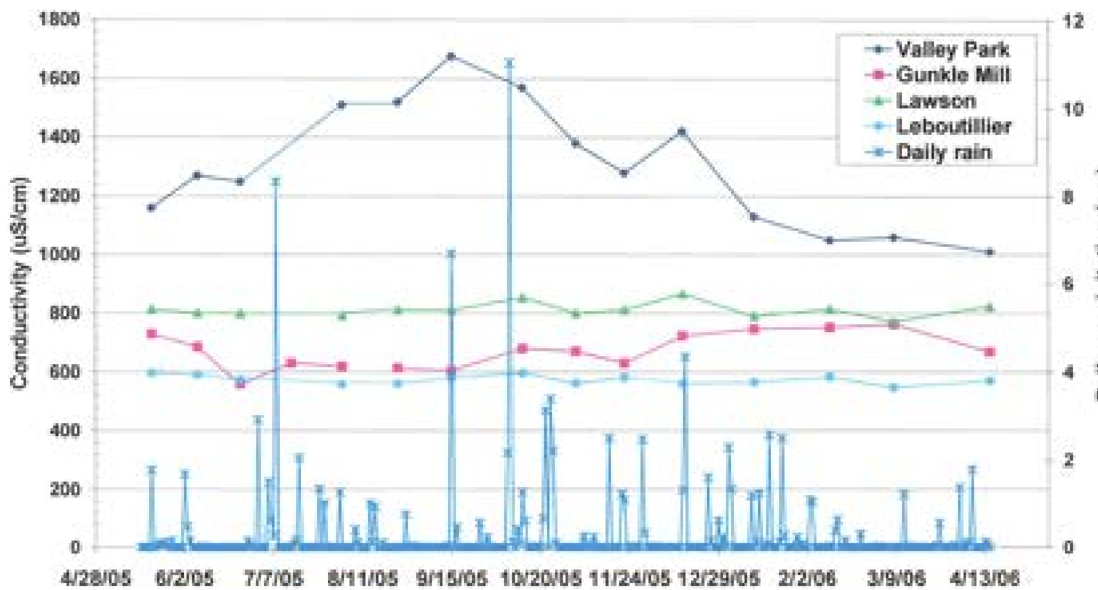


Figure 3-3. Field measurements of baseflow conductivities at all the springs and precipitation for the study period.

2005 included July 1, 2005 – September 30, 2005. Fall 2005 included October 1, 2005 – December 31, 2005. Winter 2006 included January 1, 2006 – March 31, 2006. Lawson Spring data was described first. Next Gunkle Mill Spring was described, then Leboutillier Spring and finally Valley Park Spring. Figures of the monitored data for each spring were presented as follows: spring 2005, summer 2005, fall 2005, and then winter 2006. For continuity of text description all the figures were placed at the end at the chapter. Noisy data were omitted because they were not significant for the overall description of the result and discussion. Data were considered noisy when there was large variation in conductivity (± 30 uS/cm) or water level (± 5 cm) over a1-2 hour duration

Lawson Spring had the most consistent baseflow average conductivity during the whole study period. For the spring season the average conductivity was around 720 μS/cm with variation between 710 μS/cm and 730 μS/cm (Figure 3-4). For the summer season the average conductivity slightly increased to about 745 μS/cm with variation of 740-750 μS/cm. The water level at the Lawson Spring during the spring season was about 7 cm (Figure 3-4). The logger and sensors were moved to a different location on June 24, 2005; therefore, the water level was reset. This was the location that the sensors remained for the rest of the study period. The water level was around 5 cm in the beginning of the summer season and it slowly decreased to a minimum of about 0.5 cm at the end of the summer season (Figure 3-5). The trend for the fall season was the opposite of the summer season. The base flow water level average was 2 cm and it gently increased to an average of 8 cm at the end of the season (Figure 3-6). The average water level at Lawson Spring was ~4 cm in the winter season, with the higher baseflow water level in the beginning of the season and it was steady for most of the season at 4 cm (Figure 3-7).

For the inside location at Gunkle Mill Spring the average conductivity for the spring season was 675 µS/cm. The range during base flow was between 600 µS/cm and 700 µS/cm and with a decreasing conductivity trend during the spring season. For the summer the average conductivity has decreased to 575 µS/cm with ranges between 550 and 600 µS/cm (Figure 3-8). During the summer season baseflow conductivity continued on a decreasing trend. For the fall season the average conductivity increased from the summer average to 650 µS/cm, which was near the average for the spring season. However, the range was much higher than either the spring or the summer seasons with variation between 550 µS/cm and 750 µS/cm (Figure 3-9). During the fall season the conductivity had an increasing trend. The average baseflow conductivity during the winter season increased to 760 µS/cm (Figure 3-10). The range in average was between 740 µS/cm and 780 µS/cm. At the end of the winter season the baseflow conductivity was on a decreasing trend.

The water level data for the Gunkle Mill site in the spring season was noisy, again this continued until the stilling wells were put in at all the sites. The water level during base flow averaged 5 cm for the summer season at Gunkle Mill Spring a high of ~5.5 cm and low of ~4.2 cm. For the fall season the average water level was the same as during the summer except that at the end of the season the water level was decreasing in general (Figure 3-9). The average water level during the winter season increased slightly from the summer and fall seasons to ~5.5 cm (Figure 3-10).

For part of the fall and the winter season data for the conductivity, water level, and temperature were available both inside and outside the Gunkle Mill spring house. The conductivity average was about the same as the indoor logger, around 650 µS/cm

(Figure 3-11). Due to the noisy data the range of conductivity varied between 550 to 700 μS/cm during baseflow; however, the source of the noise was unknown. The average baseflow conductivity for the winter season was about 700 μS/cm (Figure 3-12). The conductivity for the outdoor location at this spring showed a bigger variation compared with the indoor location (Figure 3-9). The outside logger was replaced to try to reduce the noise at this location during the fall season. Nonetheless, the average baseflow conductivity from the second logger was the same as the first logger at 650 μS/cm

The conductivity during baseflow was also steady at the Leboutillier outdoor site for most of the study period. The average conductivity during the spring season was the highest observed throughout the study period at ~545 μS/cm (Figure 3-13). The range of variation in conductivity for the spring season was less than ±5 μS/cm. For the summer season the average conductivity slightly decreased to ~530 μS/cm (Figure 3-14). This was also the average for the fall season (Figure 3-15). The variation in conductivity for baseflow during these two seasons was not greater than ±10 μS/cm. During the middle of the fall season the logger at Leboutillier was moved and replaced with another logger. Nevertheless, the conductivity remained steady but the average was ~450 μS/cm (Figure 3-16). This was probably lower because of calibration difference in the conductivity sensors between the different loggers since baseflow field measurements did not shift. During the winter season the average baseflow conductivity was ~485 μS/cm with variation between 480 μS/cm and 490 μS/cm (Figure 3-17).

The water level data during the spring season at Leboutillier was also noisy as with the other sites. However, the coarse average appears to be ~20 cm. The water level average for the summer season before 8/3/2005 can not be evaluated because the data was also noisy. Water level average for the summer season can only be calculated for part of the season from August 9, 2005-September 30, 2005. The baseflow water level average for the summer season was ~16.5 cm with range of 16 – 17 cm (Figure 3-14). Like the other springs (Gunkle Mill and Lawson) the water level was decreasing at the end the summer season. This decreasing trend in water level continued until the large fall storm on October 7, 2005 – October 8, 2005. The average water level for the fall season at this site was ~7 cm with variation between 5 cm to 9 cm (Figure 3-15 and Figure 3-16). Like the Lawson water level this site showed a general increasing trend during the latter part of the fall season. For the end of the fall season and the early winter seasons water level data were unavailable due to instrument failure. During the rest of the winter season the average water level was about 5.5 with variation between 4 cm to 6 cm.

Leboutillier Spring was the second spring site that an additional logger installed at two different locations. This site originally had the instruments installed outside of the spring house. On November 22, 2005 water level and temperature sensors were installed on the inside of the spring house closer to a diffused spring discharge point. Conductivity data for the inside location started on December 4, 2005. The conductivity average was ~455 μS/cm with small variation between 450 μS/cm and 460 μS/cm (Figure 3-16). The average baseflow conductivity during the winter season was ~505 μS/cm with variation between 500 μS/cm and 510 μS/cm (Figure 3-17). The water level here had an average of ~38 cm for the monitored part of the fall season (Figure 3-16). Like the outdoor water level data the average baseflow water level here showed a general decreasing trend. Water level data for the winter season was not available due to instrument failure.

The average conductivity at Park during the spring, summer and fall season was higher than at any of the other springs. In the spring season the Valley Park spring had an average conductivity of ~1150 μS/cm (Figure 3-18). For the summer season the average increased to 1300 μS/cm for the first half of the season; thereafter, the data were noisy and unreadable (Figure 3-19). For the fall season the conductivity data became more complex. The conductivity would slowly decrease after a storm event then between dry periods the data were noisy again (Figure 3-20). At beginning of the fall season the average conductivity was around 1100 μS/cm; at the end of the fall season the conductivity was reading ~750 μS/cm. The decreasing trend was not as smooth as those observed at the other springs. This was probably due to instrument degradation more than an actual trend based on high conductivity in field measurements (consistently above 1000 μS/cm). For the winter season the average baseflow conductivity was ~1090 μS/cm with variation between 1040 μS/cm and 1140. The baseflow conductivity during the winter showed an increasing trend (Figure 3-21).

Water level at Valley Park Spring before July 20, 2005 was too noisy to evaluate. Once the stilling wells were installed on 8/3/05 this site showed a decreasing water level trend for the summer season (Figure 3-19). The fall season showed an increasing water level trend (Figure 3-20). The average water level was ~7.5 cm. The water level at the beginning of the fall season was ~6 cm and it increased to ~9 cm at the end of the season. The baseflow average water level during the winter season was ~11 cm with variation between 10 cm and 11.5 cm (Figure 3-21). Perhaps more focused groundwater recharge caused larger water level variation during baseflow.

Temperature during baseflow did not have significant seasonal trends. Each spring varied less than 0.5 °C during baseflow. The temperatures for all four springs during the spring season were similar (between 12 -13 °C). In summer 2005 all the springs show slight increase in baseflow temperature (Figure 3-23). The biggest temperature change was at Valley Park Spring, which had about 0.8 °C increase. In fall 2005 the average baseflow temperature of Valley Park Spring, Gunkle Mill Spring, and Lawson Spring were steady (Figure 3-24). The average baseflow temperature of Leboutillier Spring slightly decreased again to below that of Lawson Spring, almost mirror image of spring 2005 (Figure 3-24). For winter 2006 the baseflow temperatures at Lawson Spring and Gunkle Mill Spring were steady at 12.2 °C and 12.9°C, respectively (Figure 3-25). Baseflow temperature at Valley Park Spring had a decreasing trend from 12.7 °C to 12.3 °C. Baseflow temperature at Leboutillier Spring also decreased during the winter season with average at 12.7 °C in the beginning of the season and it decreased to 11.6 °C.

Storm Response Data

There were 32 storms total that occurred during the monitoring period. A storm was defined as a precipitation event with >0.5 cm of total rainfall (Table 3-1). The storms ranged in size from 0.5 to 13.1 cm of total rainfall. Storm intensity was defined as the total rainfall over the total hours of duration of the storm. A high intensity storm is defined here as ≥1 cm/hour and a low intensity as <1 cm/hour. However, plots of water level increases during storms at the springs versus storm intensity did not show any significant correlation (Figure 3-26). All of the storm figures were zoomed in view of the

Table 3-1. Summary of all storms in this study period.

Storm Start Date	Total Rain (cm)	Duration (hours)	Intensity (cm/hour)
6/3/2005	2.29	51.75	0.044
7/1/2005	2.92	0.5	5.840
7/5/2005	1.21	11.5	0.105
7/7/2005	8.59	14	0.614
7/15/2005	2.31	49	0.047
7/25/2005	1.35	6.5	0.208
7/27/2005	1.02	5	0.204
8/2/2005	1.27	0.75	1.693
8/8/2005	0.51	15.25	0.033
8/14/2005	1.07	1	1.070
8/16/2005	0.94	4.5	0.209
8/28/2005	0.76	6	0.127
9/14/2005	6.73	9.75	0.690
9/17/2005	0.46	3.75	0.123
9/26/2005	0.56	5.25	0.107
10/7/2005	13.08	37.5	0.349
10/22/2005	3.12	22.75	0.137
10/25/2005	5.59	23.75	0.235
11/16/2005	2.49	7	0.356
11/21/2005	2.31	19.25	0.120
11/29/2005	2.79	9	0.310
12/15/2005	5.66	8.75	0.647
12/25/2005	1.75	18	0.097
12/29/2005	0.61	10.75	0.057
1/2/2006	3.63	18.75	0.194
1/11/2006	1.19	3.25	0.366
1/14/2006	1.24	9.00	0.138
1/17/2006	2.64	15.75	0.168
1/22/2006	2.59	9.00	0.288
2/3/2006	2.13	22.50	0.095
2/13/2006	1.6	23.75	0.067
3/12/2006	1.22	10.00	0.122
3/26/2006	0.61	13.00	0.047
Rainfall average	2.61		

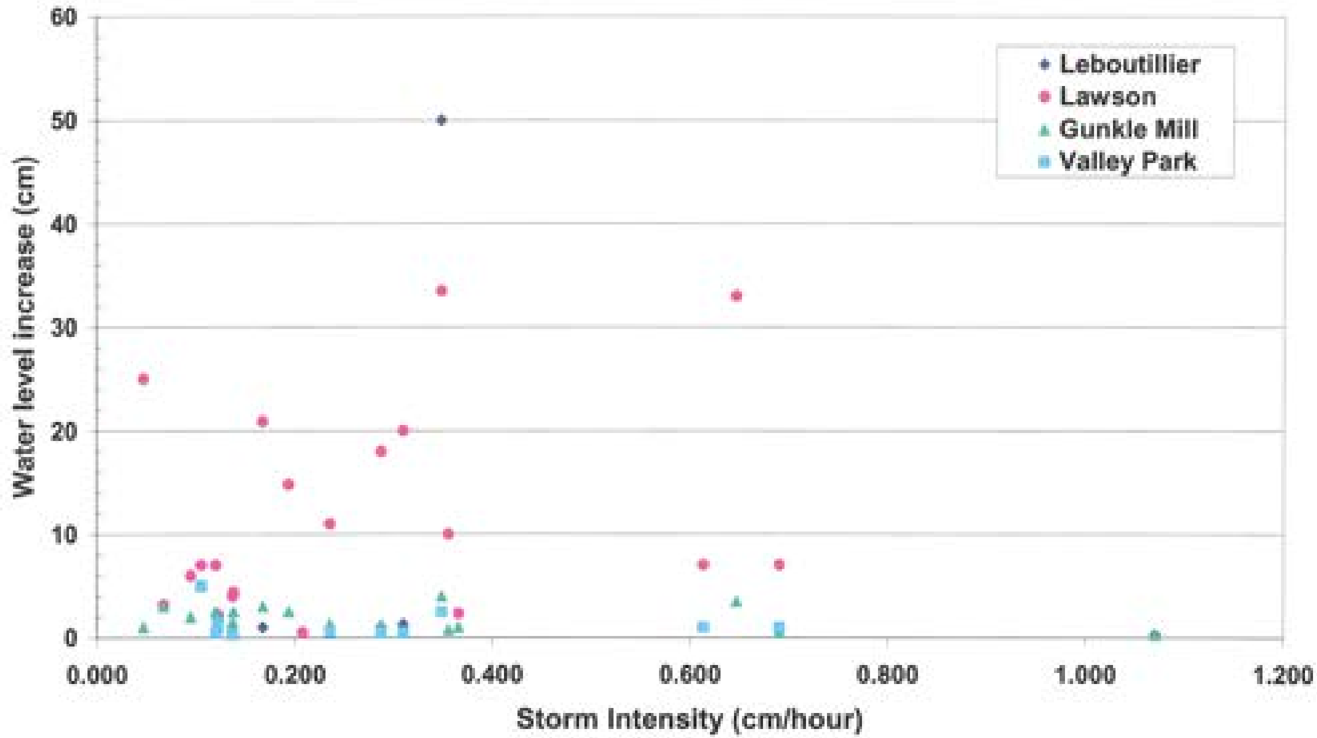


Figure 3-26. Plot of storm intensity *vs*. the water level increase measured for storms during the monitored period

continuous monitoring figures. As with the continuous monitoring figures, the storm figures were also placed at the end of the chapter.

Gunkle Mill Spring showed responses in conductivity and water level for 18 storms (Tables 3-2, 3-3 and 3-4). Storms with high intensity such as July 1, 2005 and August 2, 2005 and one slightly lower intensity storm on September 14, 2005, did not show any response in either conductivity or water level at Gunkle Mill Spring. The biggest response in conductivity for Gunkle Mill Spring was during the October 7, 2005 storm. The conductivity increased 150 μS/cm. This storm also produced the highest water level (~4 cm) response at this spring. All storms, despite size or intensity, produced water levels that were 4 cm or less at Gunkle Mill Spring. Of the 18 storms that produced responses at Gunkle Mill Spring ten storms had conductivity increases. The conductivity increase ranged from 10 -150 μS/cm. Five storms (October 25, 2005, November 29, 2005, January 2, 2006, January 17, 2006, and January 22, 2006) had an initial conductivity decrease then a conductivity increase before returning to baseflow conductivity (Tables 3-3 and 3-4). These storm usually have low initial decreases (5-20 μS/cm) followed by just slightly bigger conductivity increases (10-55 μS/cm). Only three of the 18 storm responses observed at Gunkle Mill Spring have only a conductivity decrease. These storms occurred on July 15, 2005, August 14, 2005, and January 14, 06. The largest conductivity decrease (~35 μS/cm) observed at Gunkle Mill Spring was during the 7/17/05 storm. The water level increase during this storm was ~1 cm.

Gunkle Mill Spring had two monitoring locations during the later part of the fall 2005 season. Data for the outdoor location started at Gunkle Mill Spring on December 4, 2005. The storm on December 15, 2005 produced a conductivity increase of 85 μS/cm

Table 3-2. Summer 2005 storm conductivity and water responses. N/A's mean that there was no logger present at the site. X's mean that the data was noisy.

	Gunkle		Lawson		Lebout		Valley Park	
Storm date	ΔCond.	ΔWL	ΔCond.	ΔWL	ΔCond.	ΔWL	ΔCond.	ΔWL
7/5-7/8	+80	X	-55	+7	-61	X	-17	+5
7/17	-35	+1	-120	+25	-40	X	-15	+1
7/25-7/27	X	X	-50	+0.5	+47	X	X	X
8/14/05	+25	0.25	-8	+0.5	-5	+0.3	X	X
9/14-9/15	0	0.5	-27	+7	-15	X	-15	+1

Table 3-3. Fall 2005 storm conductivity and water level responses.

	Gunkle Inside		Gunkle Outside		Lawson		Lebout Outside		Lebout Inside		Valley Park	
Storm date	ΔCond.	ΔWL	ΔCond.	ΔWL	ΔCond	ΔWL	ΔCond.	ΔWL	ΔCond.	ΔWL	ΔCond.	ΔWL
10/7	+150	+4	N/A	N/A	-270	+33.5	+440	+50	N/A	N/A	-60	+2.5
10/22	+15	+1.5	N/A	N/A	X	+4	+8	+0.4	N/A	N/A	X	+0.3
10/25	-8, +33	+1.3	N/A	N/A	-20	+11	+3	+0.5	N/A	N/A	X	+0.6
11/16	-11	+0.75	N/A	N/A	-30	+10	X	X	N/A	N/A	X	X
11/21	-12	+2.5	N/A	N/A	-11	+7	X	X	N/A	N/A	X	+0.5
11/29	-6, +20	+0.6	N/A	N/A	-47	+20	X	+1.3	N/A	N/A	X	+0.5
12/15	+120	3.5	+85	+3.3	-430	+33	-95	X	-30	+25	X	X

Table 3-4. Winter 2006 storm conductivity and water level responses. N/A's mean that there was no logger present at the site and X's mean that the data was noisy.

	Gunkle Inside		Gunkle Outside		Lawson		Lebout Outside		Lebout Inside		Valley Park	
Storm date	ΔCond.	ΔWL	ΔCond.	ΔWL	ΔCond.	ΔWL	ΔCond.	ΔWL	ΔCond.	ΔWL	ΔCond.	ΔWL
1/2/06	-12, +55	+2.5	X	+2	-35	+14.8	+10	X	+10	X	X	X
1/11/06	X	+1	-20	+0.5	X	+2.3	X	X	X	X	X	X
1/14/06	-10	+2.5	+80	+1	-10	+4.4	X	X	X	X	X	X
1/17/06	-15, +20	+3	-80	+1.2	-23	+20.9	+5	+1	+10	X	X	X
1/22/06	-20, +13	1.2	-35	+1.4	-22	+18	+5	+1	+20	X	-10	+0.5
2/3/06	+10	+2	N/A	N/A	X	+6	X	X	X	X	X	X
2/13/06	+85	+3	N/A	N/A	X	+3.2	+25	X	+20	X	+25	X
3/12/06	+10	+1	N/A	N/A	-21	+2.2	X	X	+5	X	+10	+1.5

and the water level increased ~3.3 cm for the outdoor location (Table 3-3). The water level response was comparable to the indoor monitored location, which had a water level increase of 3.5 cm. The conductivity response was somewhat less for the outdoor location than for the indoor location, which had an increase of 120 μS/cm. This large increase was probably due to snowmelt and road salt associated with this storm event.

At Lawson Spring all storm responses showed decreases in conductivity from baseflow condition. The range of conductivity responses to storms were from 10 - 430 μS/cm. The largest conductivity decrease at this spring was ~430 μS/cm during the December 15, 2005 storm. The water level response for this storm was 33 cm, which was the second highest water level increase at this spring. The water level responses to storms range from 0.5 cm – 33.5 cm above baseflow water level. The largest water level response for Lawson Spring was recorded during a fall 2005 storm on October 7, 2005 at 33.5 cm above the baseflow water level. This storm had a conductivity decrease of ~270 μS/cm. The lowest water level response recorded was 0.5 cm above baseflow water level for the summer 2005 storm (July 15, 2005- July 17, 2005). Although this storm had a small water level response the conductivity decrease was significant at ~50 μS/cm.

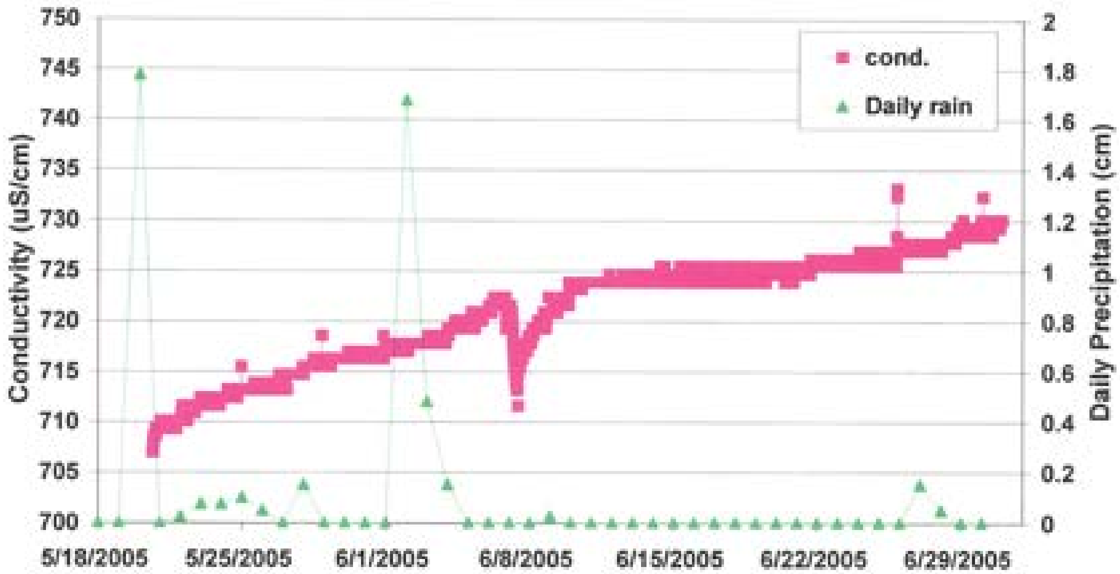
Valley Park Spring was not responsive to storms. There were seven storms for which both conductivity and water level showed responses Valley Park Spring. When Valley Park Spring did show responses, both the conductivity and water level showed small responses. The range of water level storm response for Valley Park Spring was between (0.3 – 5 cm). The largest water level storm response (~ 5 cm) occurred during the July 5, 2005-July 8, 2005 storm. The conductivity for this storm was a decrease of ~17 μS/cm. The conductivity mostly showed conductivity decreases (10-60 μS/cm) during storms. The largest conductivity storm response was during the October 7, 2005 storm, where there was a decrease of ~60 μS/cm. For this particular storm the water level increase was 2.5 cm, which was the second highest water level response at Valley Park Spring. There were two cases of slight conductivity increases in response to storms (February 13, 2006 and March 12, 2006); however, the increases were small, 25 μS/cm and 10 μS/cm respectively. For these two storms only the March 12, 2006 showed significant water level response of ~1.5 increase from baseflow condition.

Leboutillier Spring was more responsive to storms then Valley Park Spring. Leboutillier showed conductivity responses to 12 storms (Tables 3-2, 3-3, and 3-4). Most of the conductivity responses at Leboutillier Spring were increases. The conductivity increases ranged were from 5-440 μS/cm. The largest conductivity increase (~440 μS/cm) occurred during the October 7, 2005 storm. The water level response during this storm, which rose 50 cm above baseflow water level, was also the highest water level response at this spring throughout the monitored period (Figure 3-27). Several storms October 22, 2005, October 25, 2005, January 17, 2006, and January 22, 2006 had conductivity increases of ~5 μS/cm. Four of the 12 storms showed conductivity decreases. Three of the four storms were in the summer 2005 season, and one storm was from the fall 2005. The conductivity decreases during storm responses ranged from 15 – 95 μS/cm. The largest conductivity decrease for Leboutillier Spring was observed during the December 15, 2005 storm (Figure 3-28). The conductivity during this storm decreased ~95 μS/cm. The smallest conductivity decrease for Leboutillier Spring was during the 9/14/05 storm.

Leboutillier Spring also had additional location for the later part of the fall 2005 season. The storm on December 15, 2005 produced a water level increase of 25 cm for the Leboutillier Spring inside location. A conductivity decrease of ~30 was also observed at this location during that storm. Significant aspects about the storm responses for these two locations were their magnitude of conductivity response and the timing of the response (Figure 3-28). The inside location had a conductivity decrease that was about one third of the outdoor location. The timing of the peak conductivity decrease for the indoor and outdoor differs by about 2 hours.

Summary

This chapter described baseflow and storm responses at all four springs. The data were presented as plots and summarized in tables. The following chapter provides an interpretation of how the responses relate to the hydrologic conditions in an urban setting.



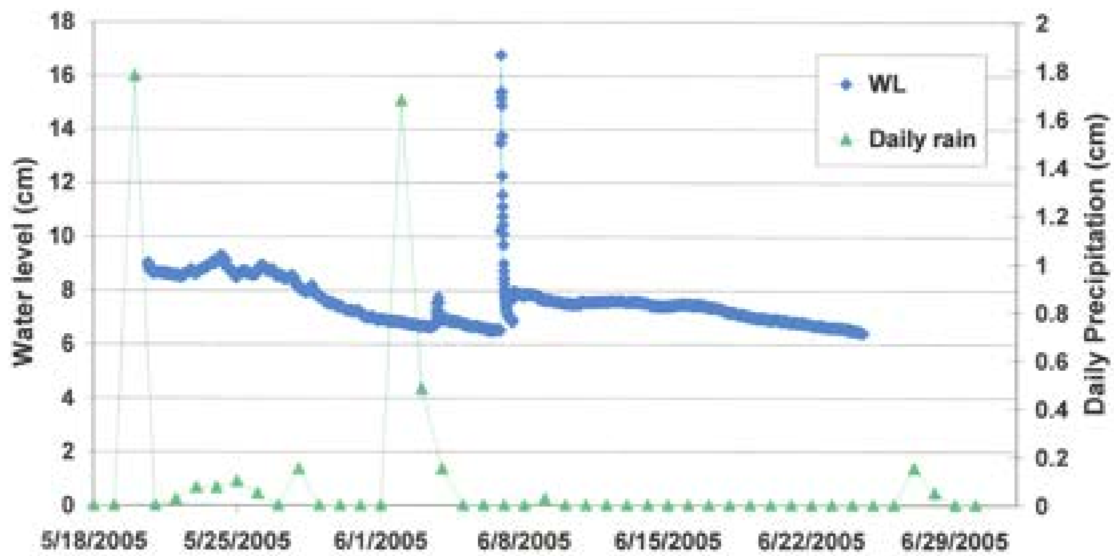
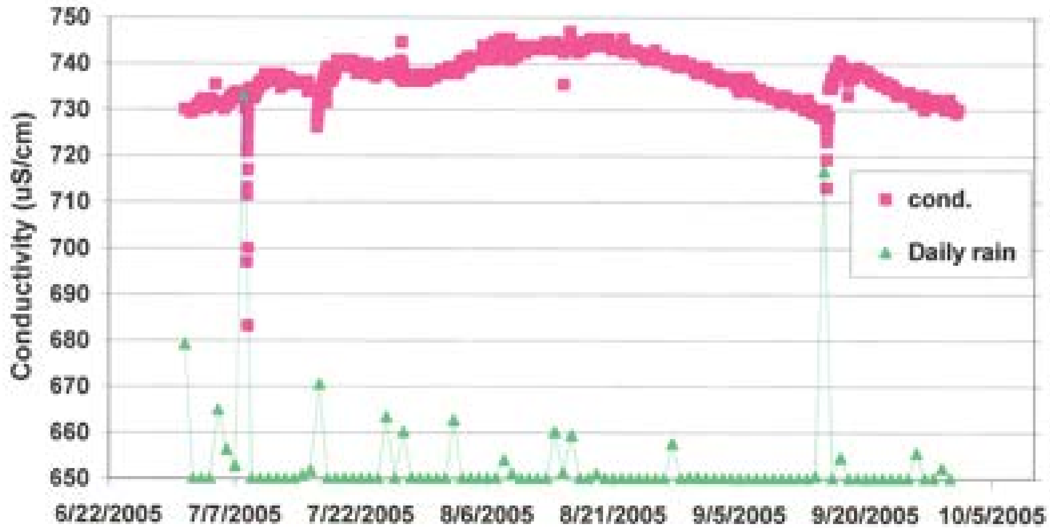


Figure 3-4. Summaries of conductivity, water level and precipitation for the Lawson Spring during the spring season of 2005.



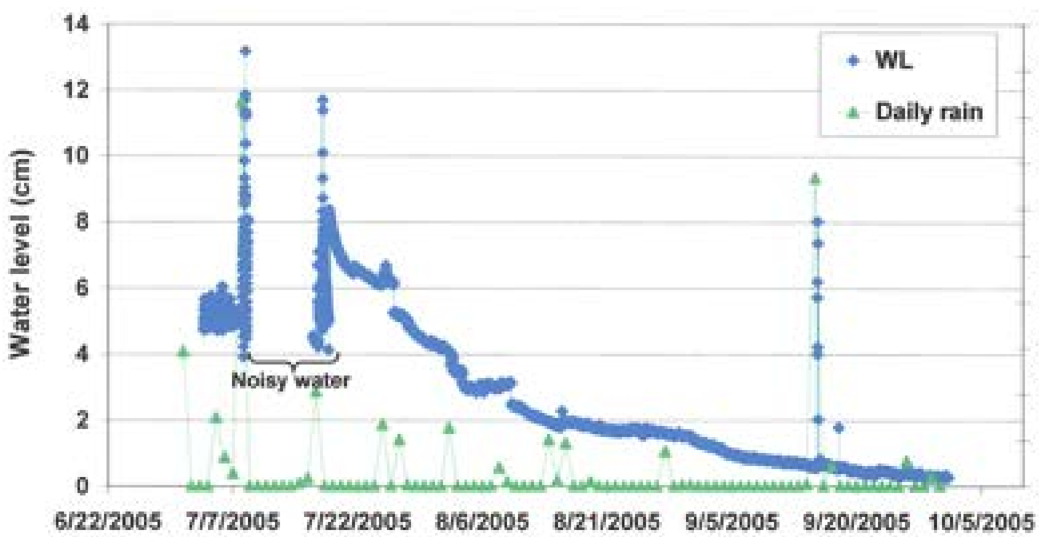
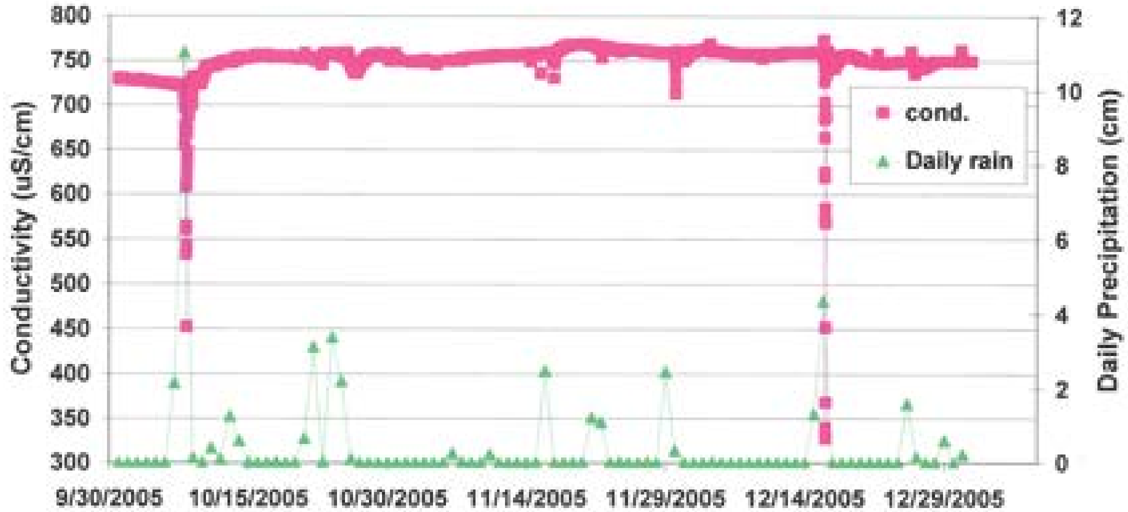


Figure 3-5. Summaries of conductivity, water level and precipitation for the Lawson spring during the summer of 2005.



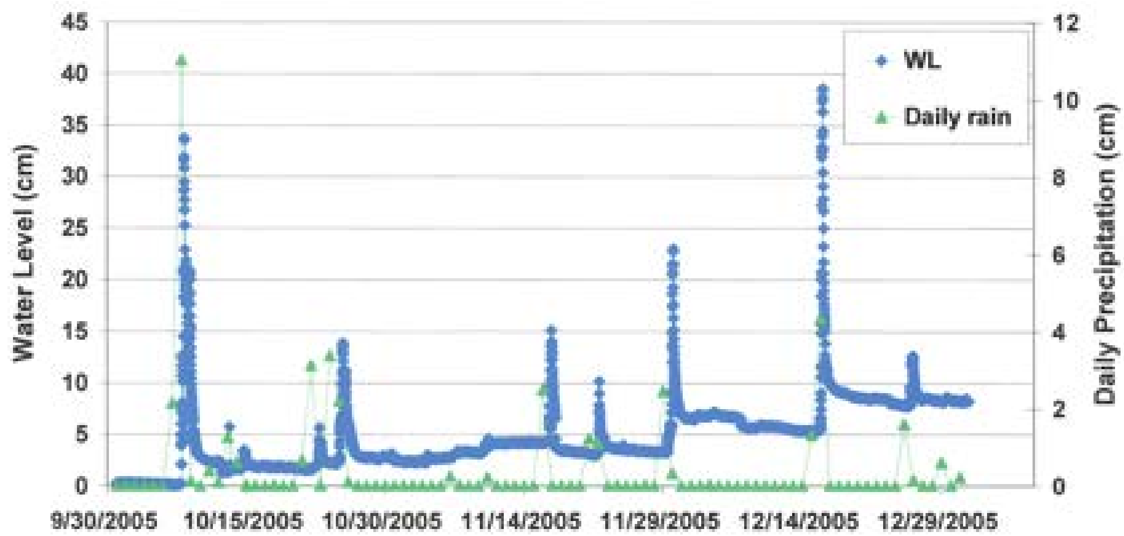
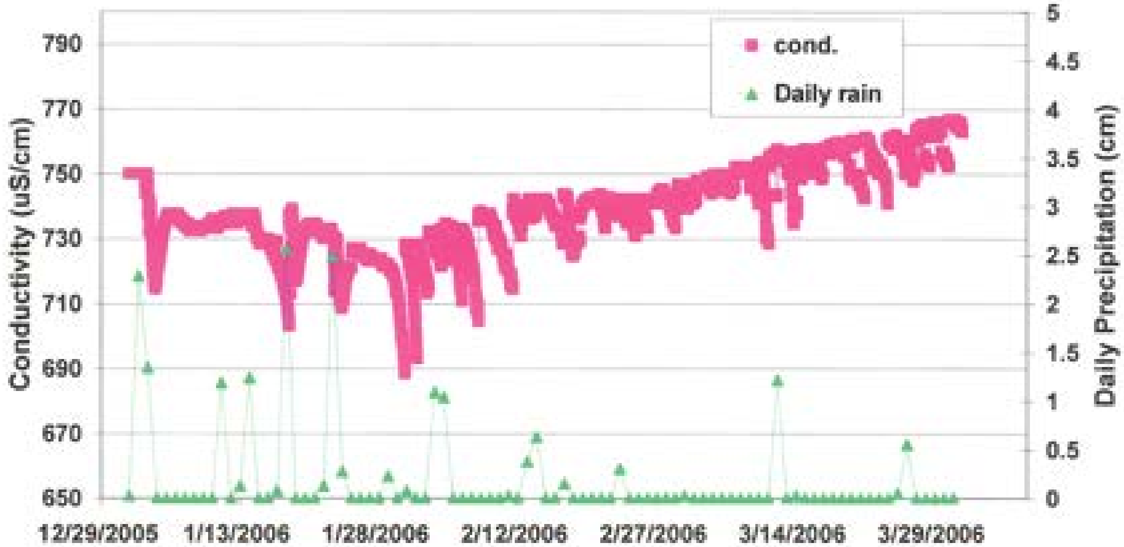


Figure 3-6. Summaries of conductivity, water level and precipitation for the Lawson spring during the fall of 2005.



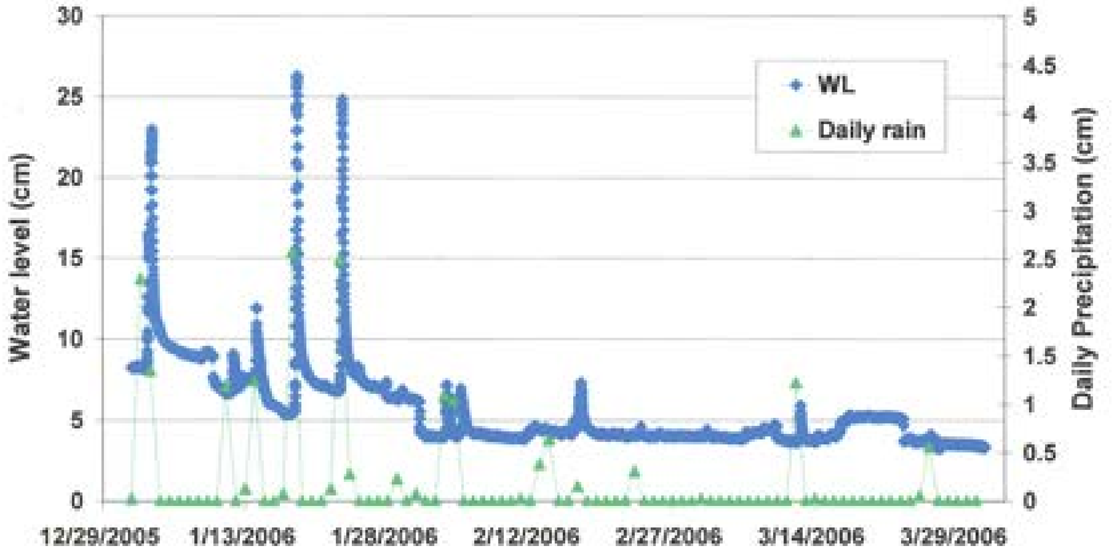
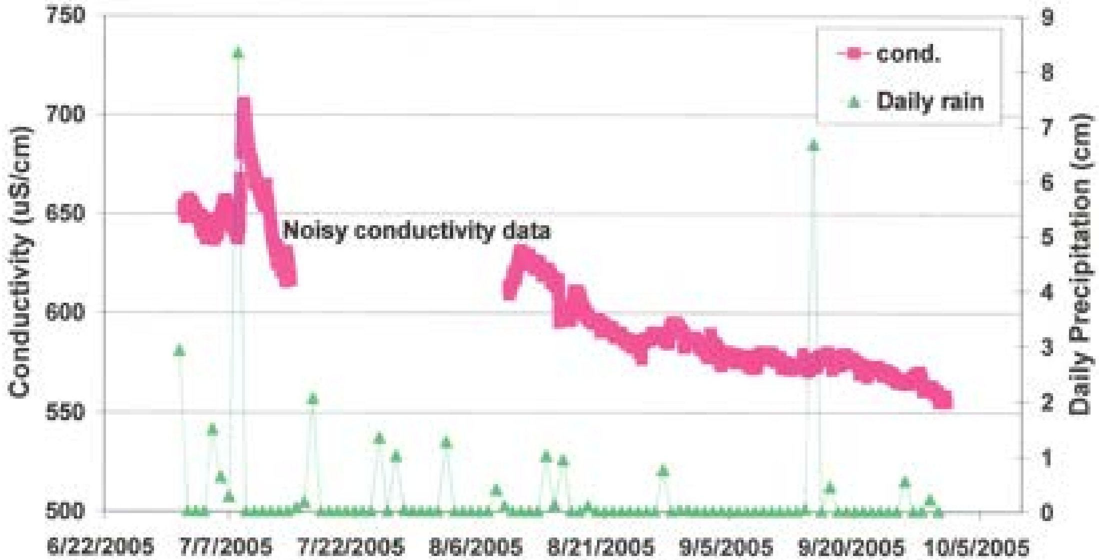


Figure 3-7. Summaries of conductivity, water level and precipitation for Lawson Spring during the winter season of 2006. There is a period (February to March 2006) of low level noise in the conductivity data here.



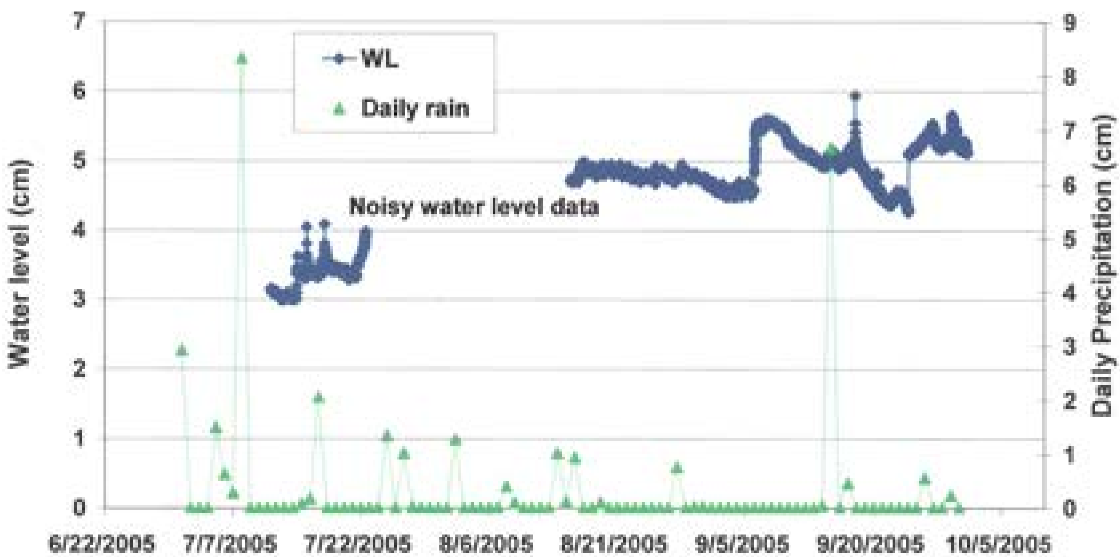


Figure 3-8. Summaries of conductivity, water level and precipitation for the Gunkle Mill Spring during the summer season of 2005.

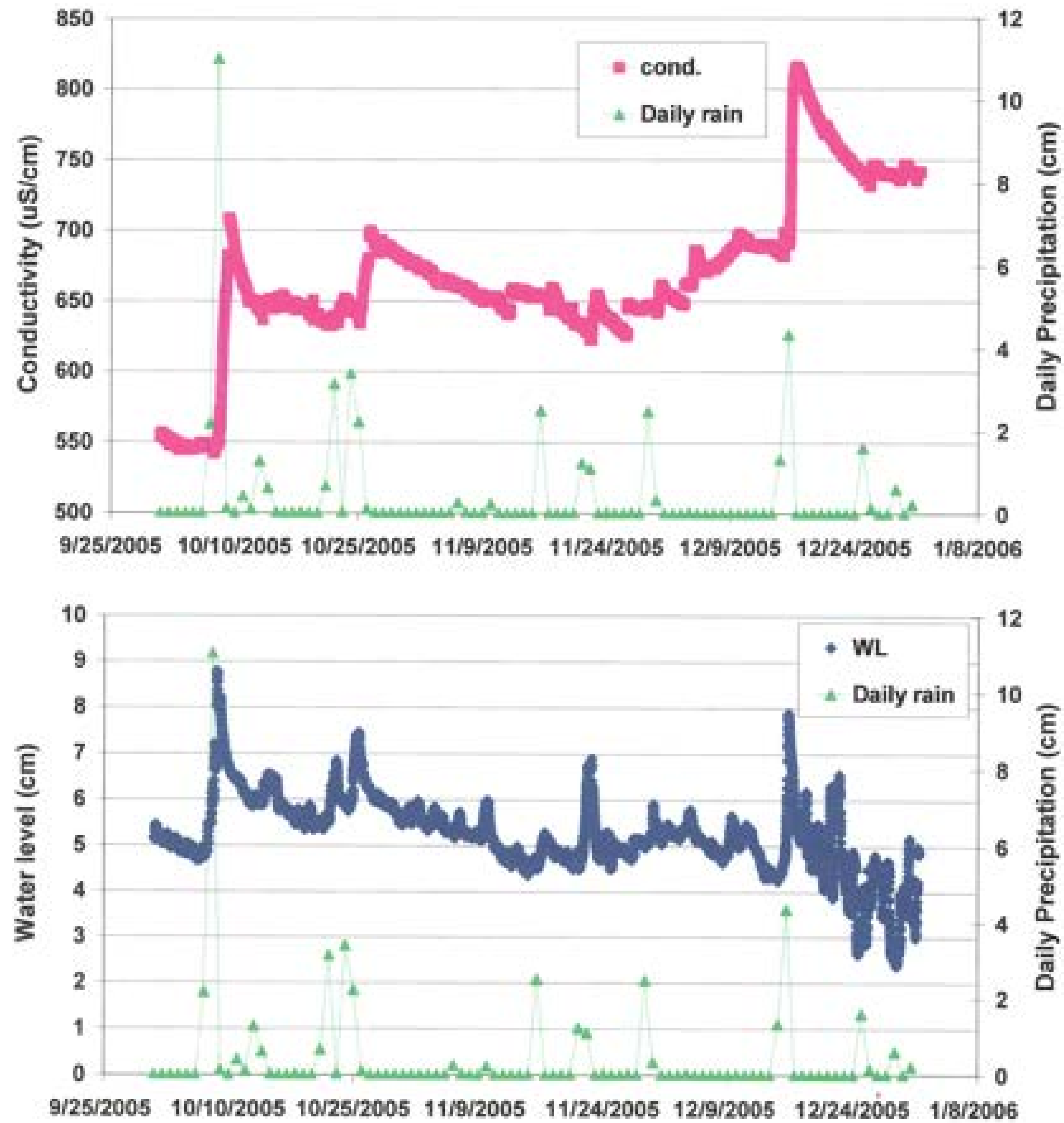


Figure 3-9. Summaries of the conductivity, water level and precipitation at the Gunkle Mill Spring during fall 2005.

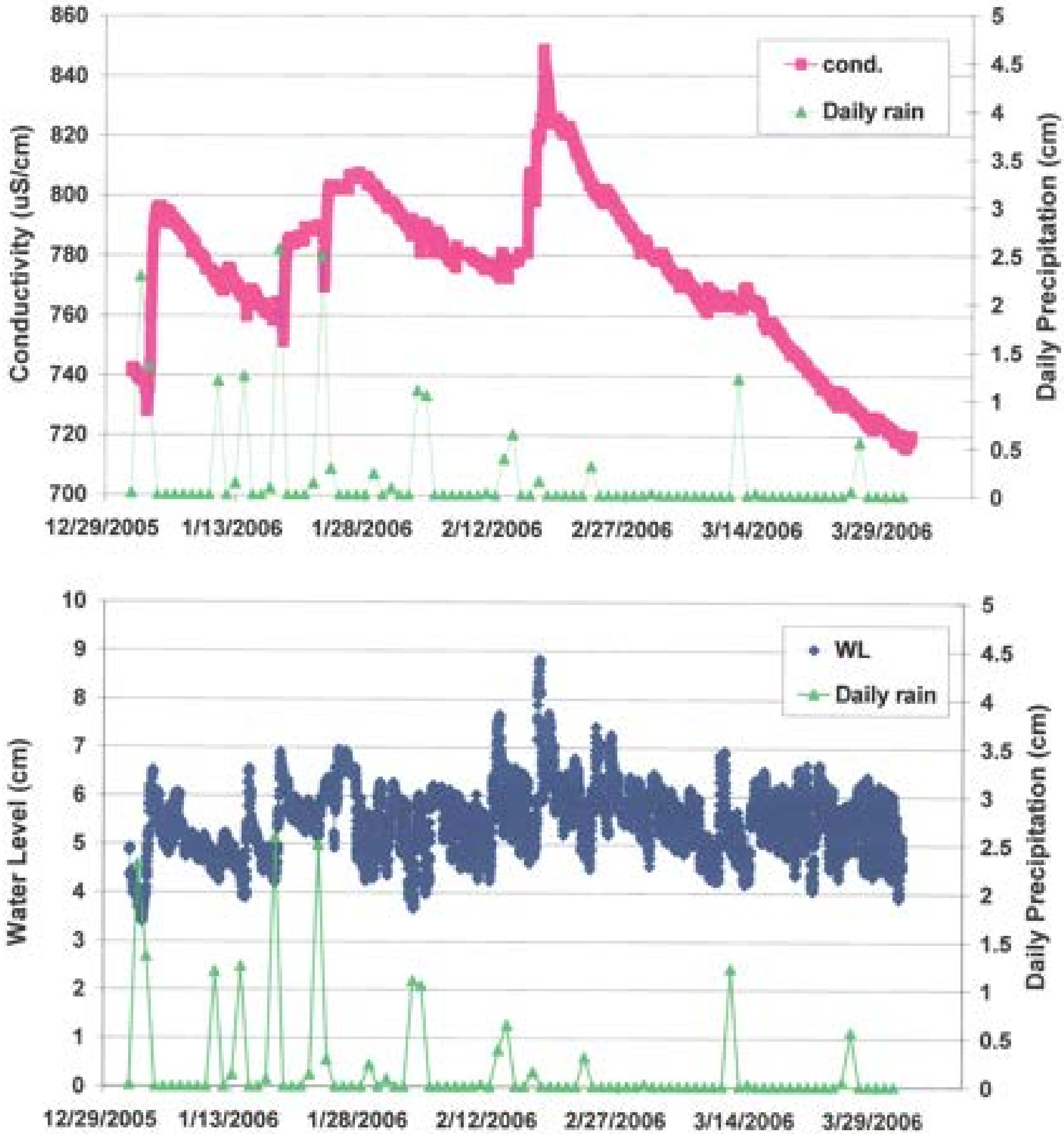


Figure 3-10. Summaries of the conductivity water level, and precipitation at the Gunkle Mill Spring inside the spring house for the winter season of 2006. There is low level noise in the water level data from March 15, 2006 to March 31, 2006.

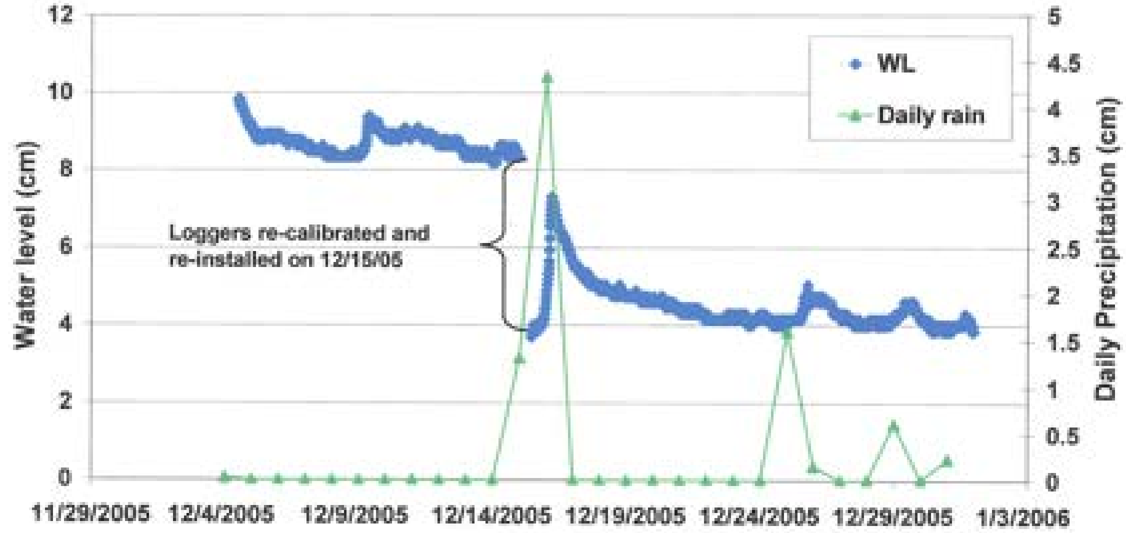


Figure 3-11. Summaries of the water level and precipitation at the Gunkle Mill Spring outside the spring house for the latter part of fall 2005.

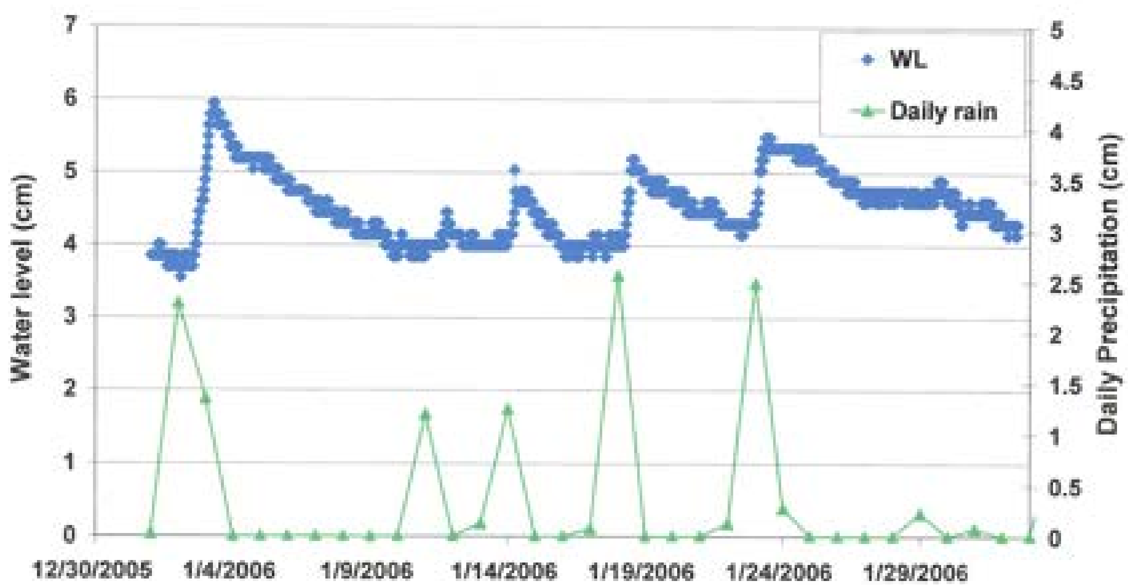


Figure 3-12. Summaries of the water level and precipitation at the Gunkle Mill Spring outside the spring house for the winter season of 2006.

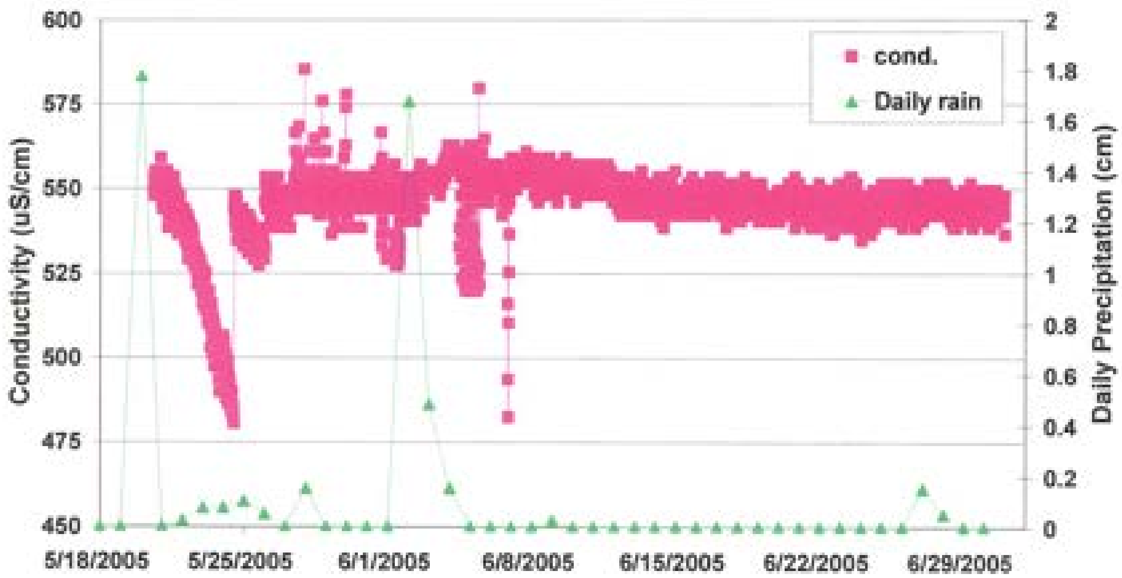


Figure 3-13. Summaries of conductivity and precipitation for the Leboutillier Spring during the spring of 2005. The water level data were noisy for this entire period and are not shown.

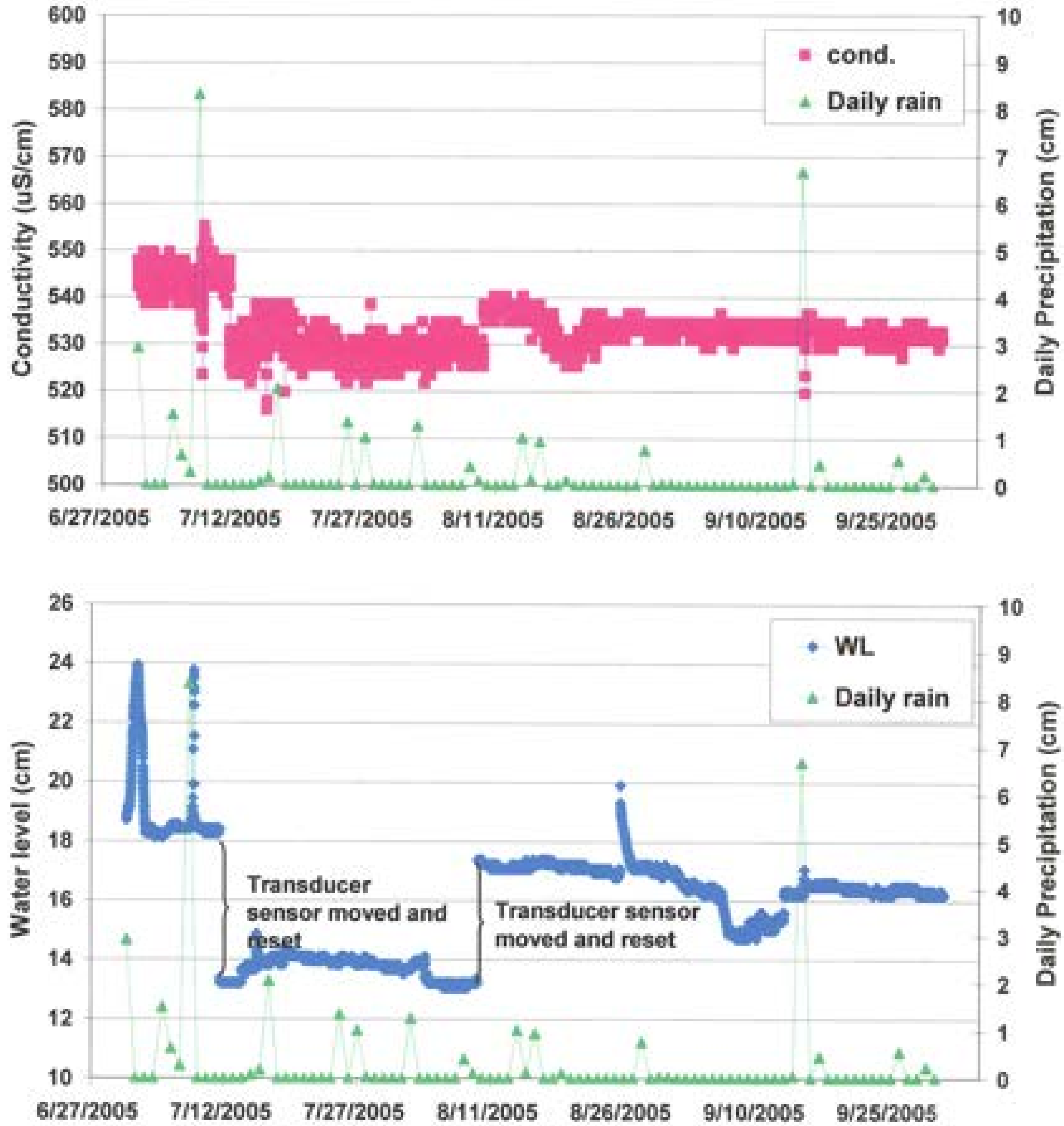
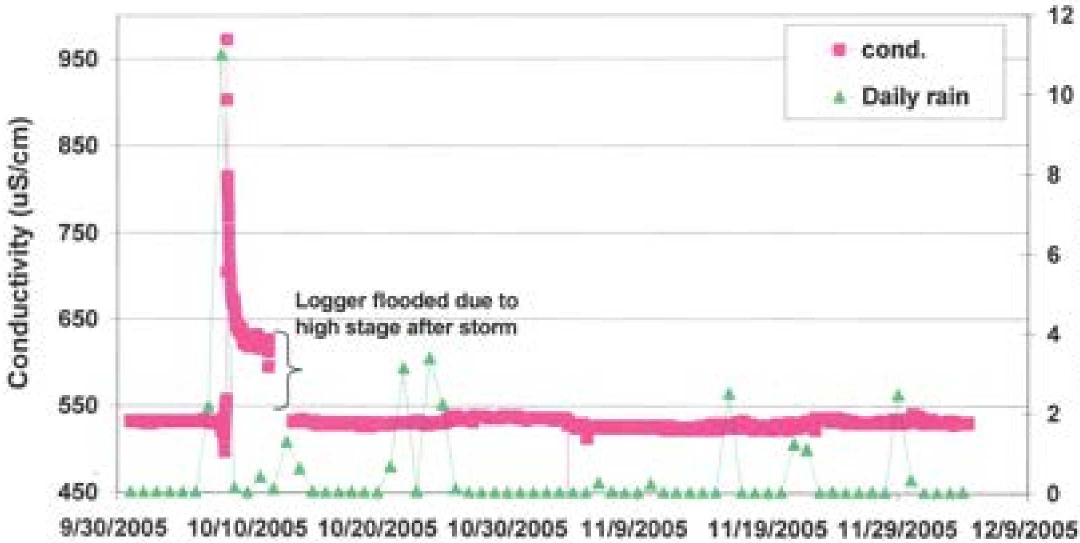


Figure 3-14. Summaries of conductivity, water level and precipitation for the Leboutillier Spring during the summer of 2005. There is low level of noise in the conductivity data for the entire season here.



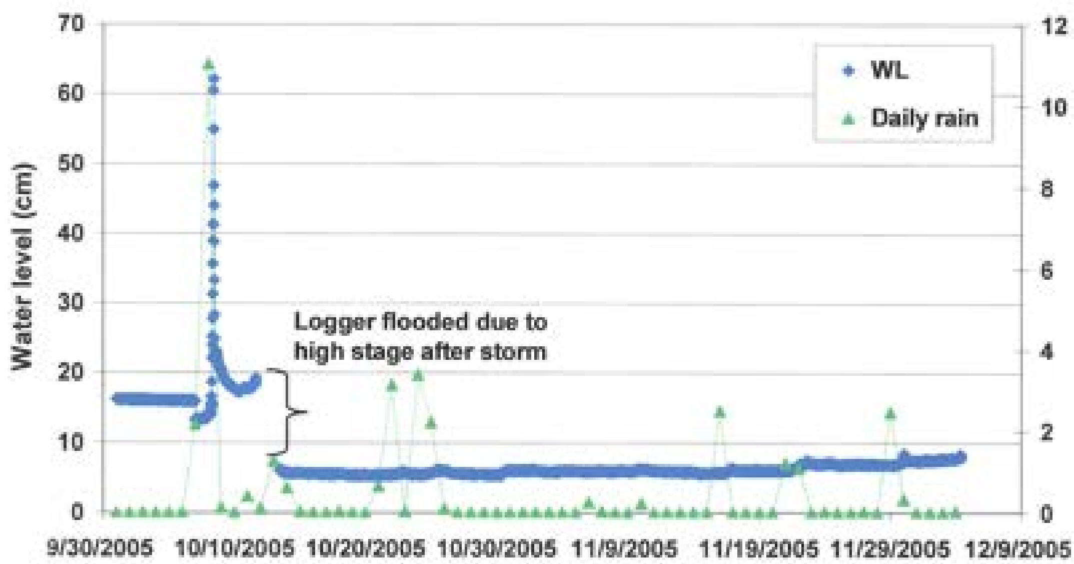
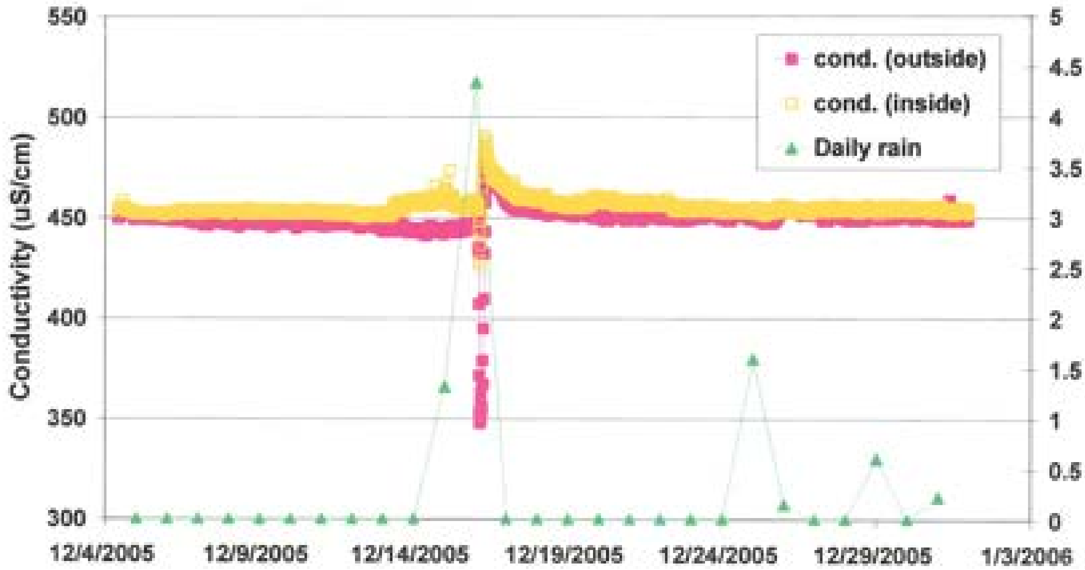


Figure 3-15. Summaries of conductivity, water level and precipitation for the Leboutillier Spring during the fall of 2005.



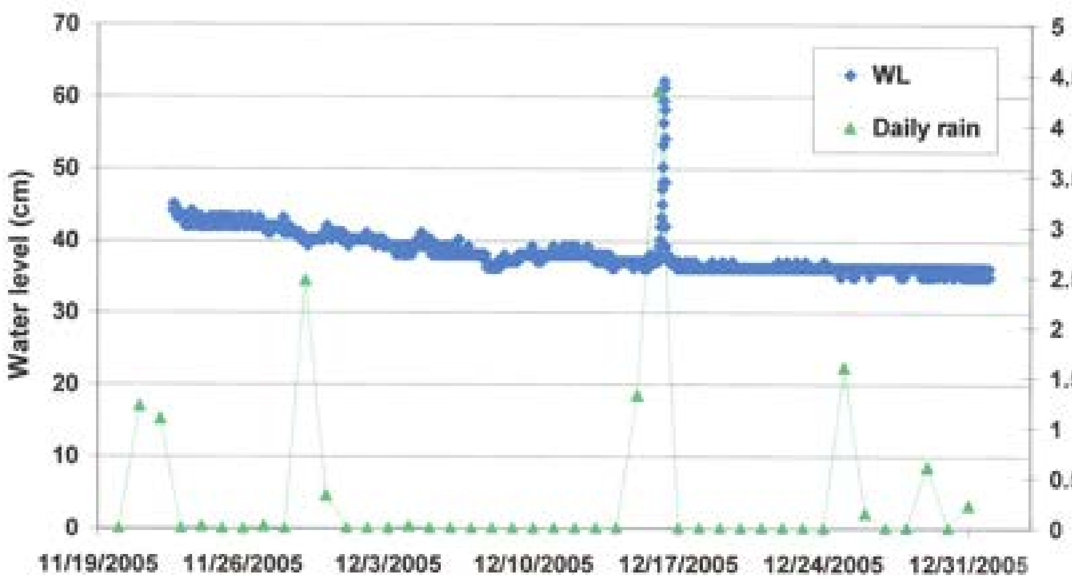
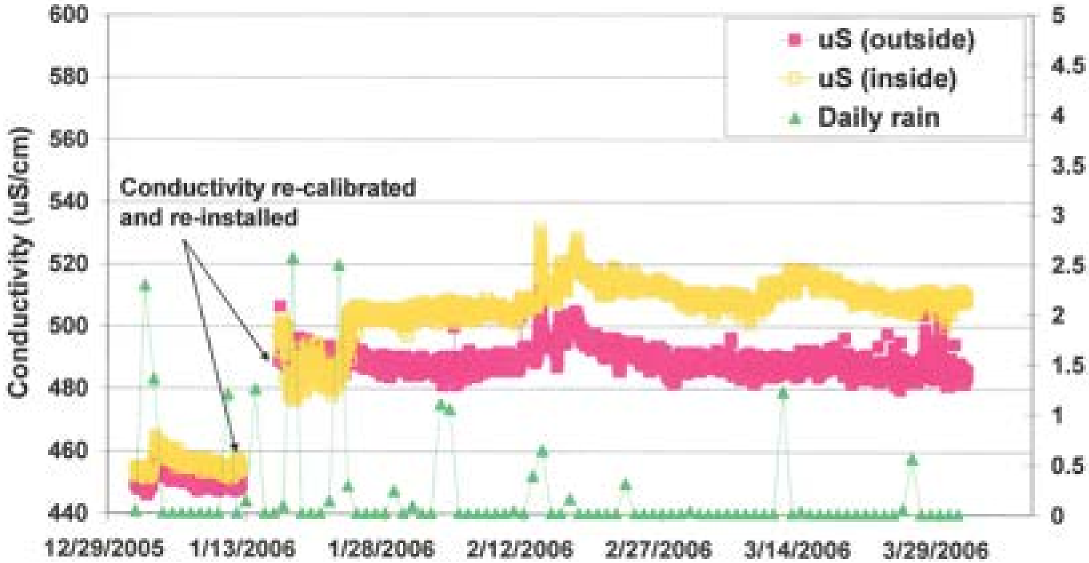


Figure 3-16. Summaries of the conductivity water level and precipitation for Leboutillier Spring during the later part of the fall season (12/4/05 – 12/31/05) with a new logger. Only water level data for the inside logger was available due to the transducer failure for the outside location.



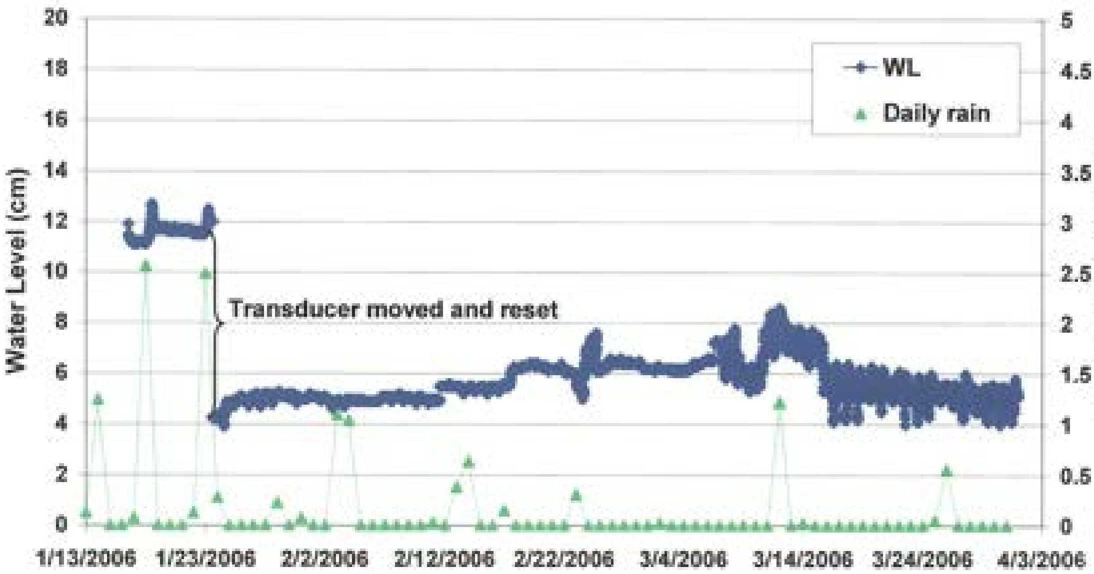


Figure 3-17. Summaries of the conductivity (outside and inside), water level (outside) and precipitation for Leboutillier Spring during the winter season of 2006.

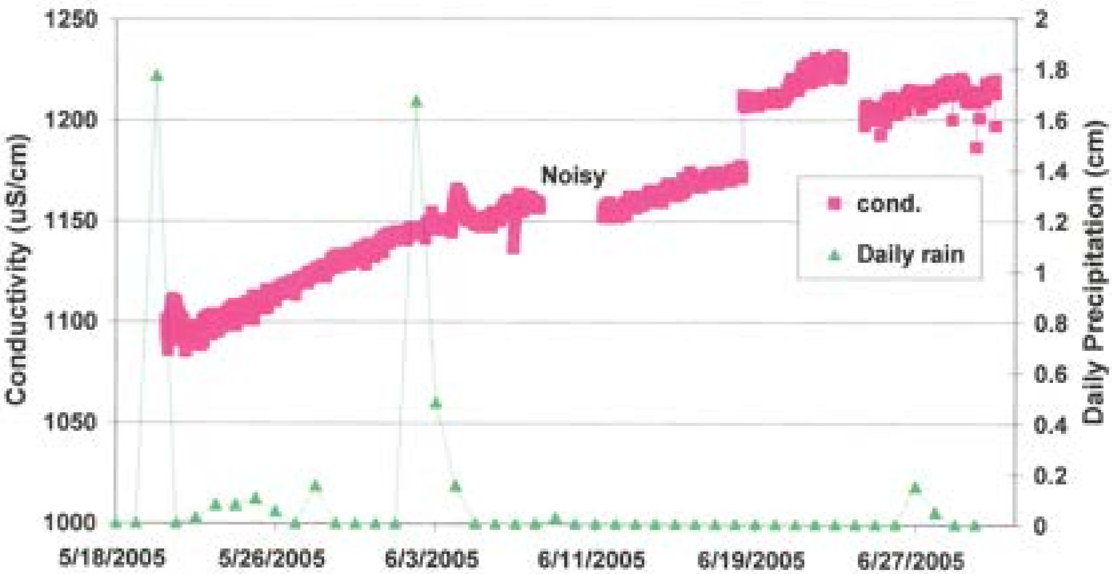


Figure 3-18. Summaries of conductivity, water level and precipitation for the Valley Park Spring during the spring of 2005. Water level was noisy for the entire period and are not shown here.

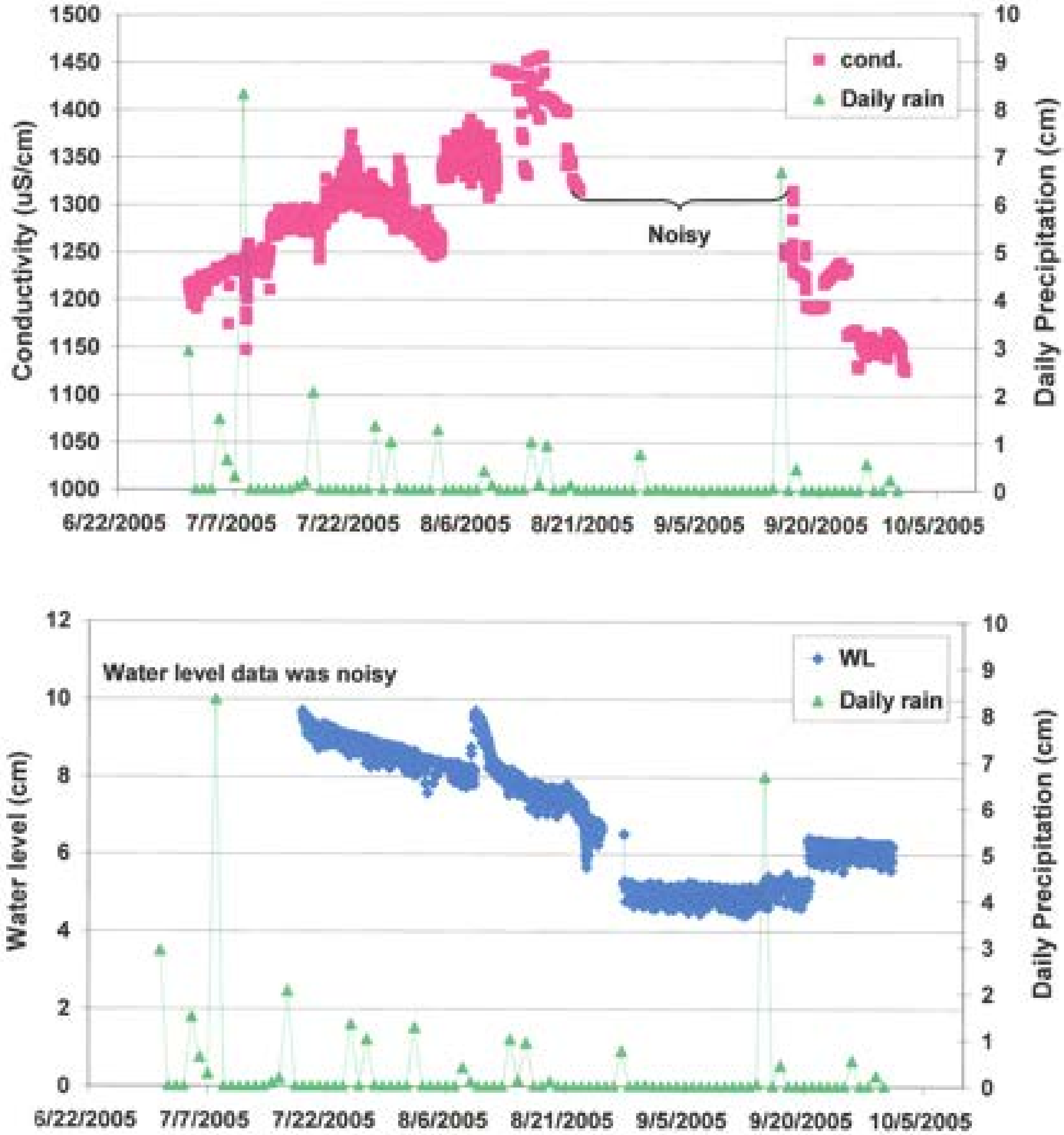


Figure 3-19. Summaries of conductivity, water level and precipitation for the Valley Park Spring during the summer of 2005.

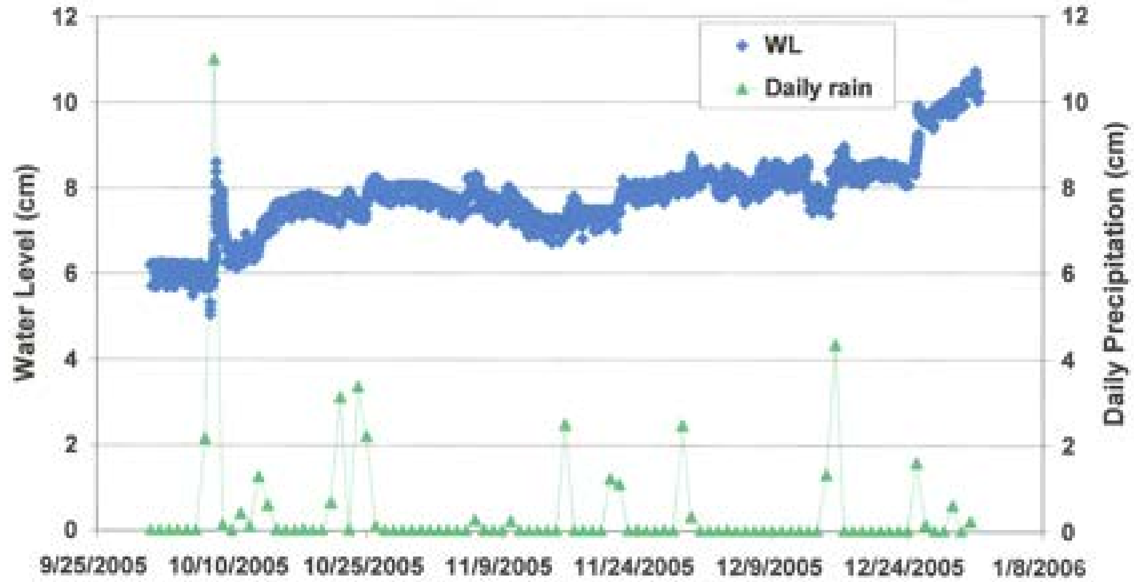
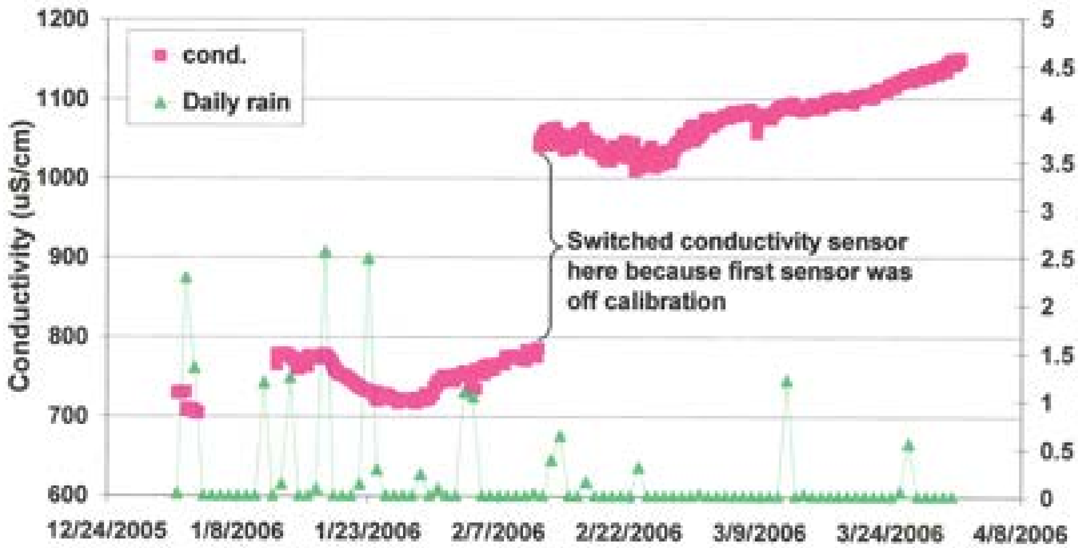


Figure 3-20. Summaries of the water level and precipitation for Valley Park Spring during the fall season of 2005. Conductivity data was noisy due to sensor failure and are not shown.



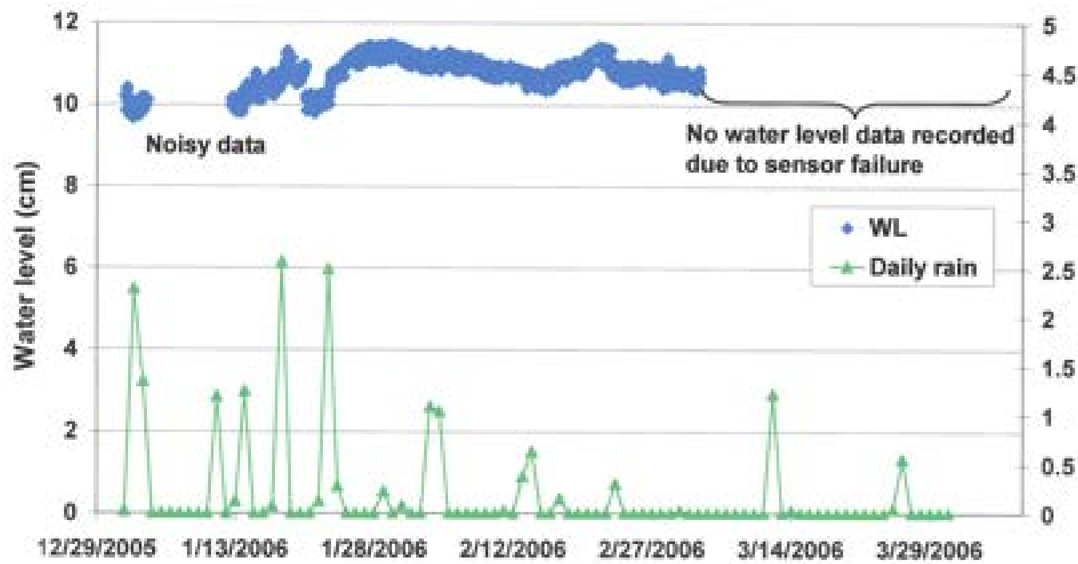


Figure 3-21. Summaries of the conductivity, water level and precipitation for Valley Park Spring during the winter season of 2006.

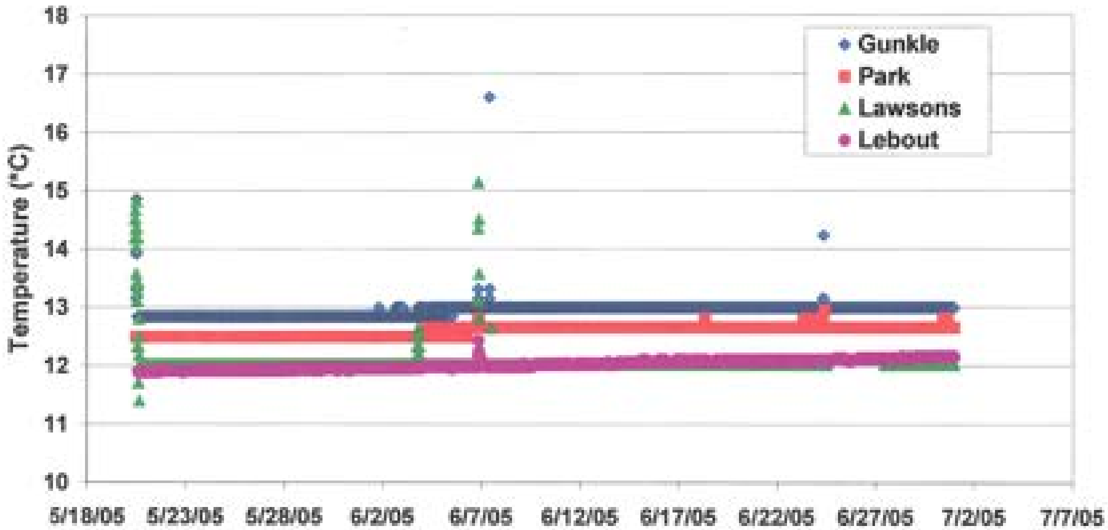


Figure 3-22. Summary of the temperature data for all springs monitored in this study during the spring 2005 season. Temperature response to storms occurred for the first storm (6/3/05) of the monitored period.

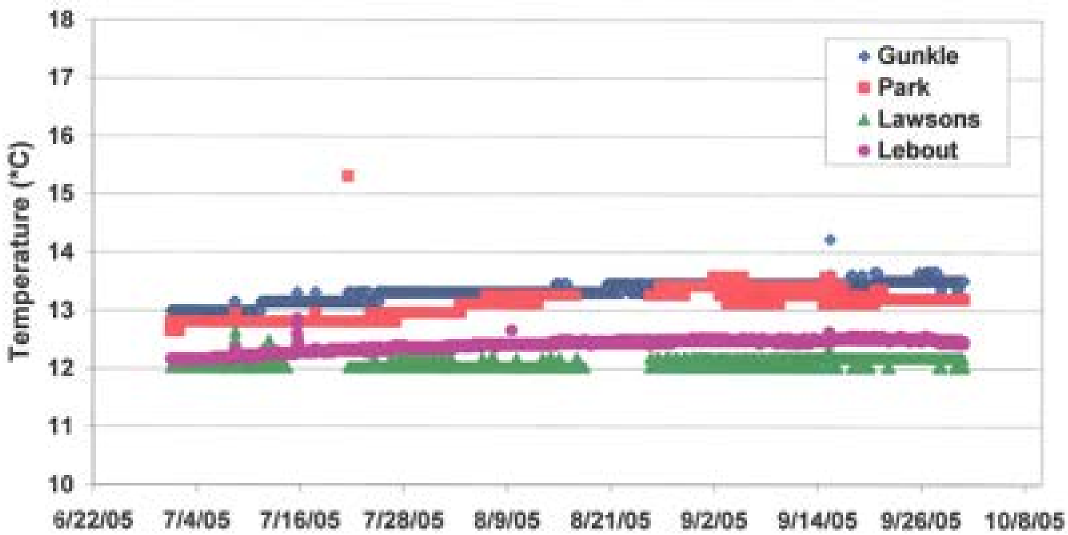


Figure 3-23. Summary of the temperature data for all springs monitored in this study during the summer 2005 season. There were slight temperature responses to several storms during this season (mainly 7/7/05 and 7/17/05 storms).

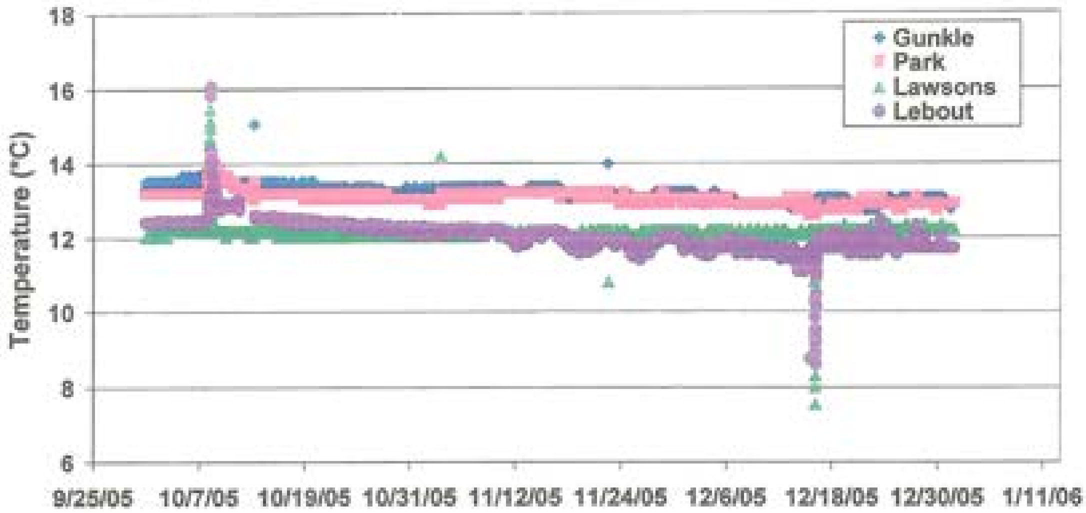


Figure 3-24. Summary of the temperature data for all springs monitored in this study during the fall 2005 season. The only significant storm temperature responses were for the 10/7/05 and 12/15/05 storms.

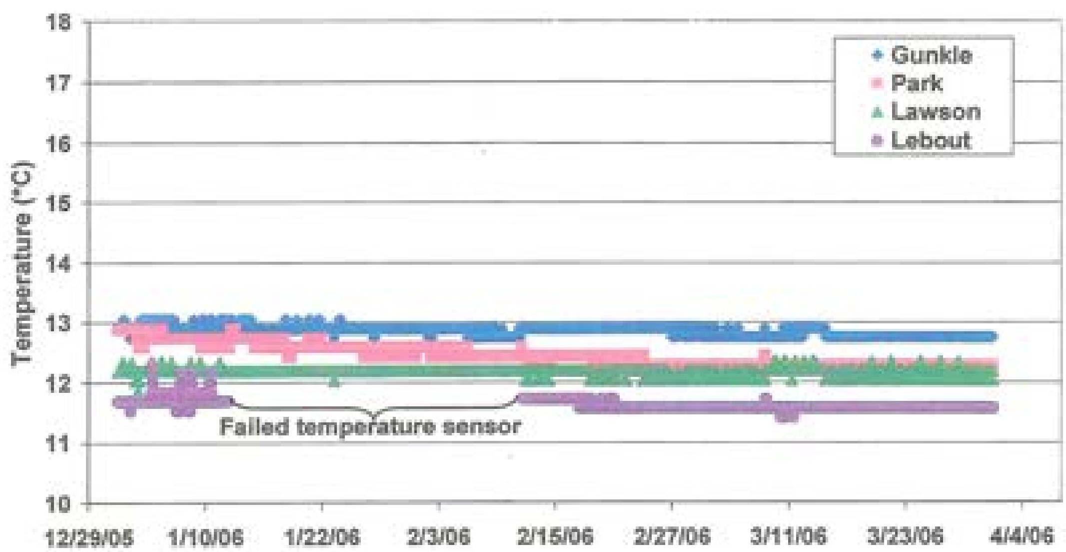


Figure 3-25. Summary of the temperature data for all springs monitored in this study during the winter 2006 season.

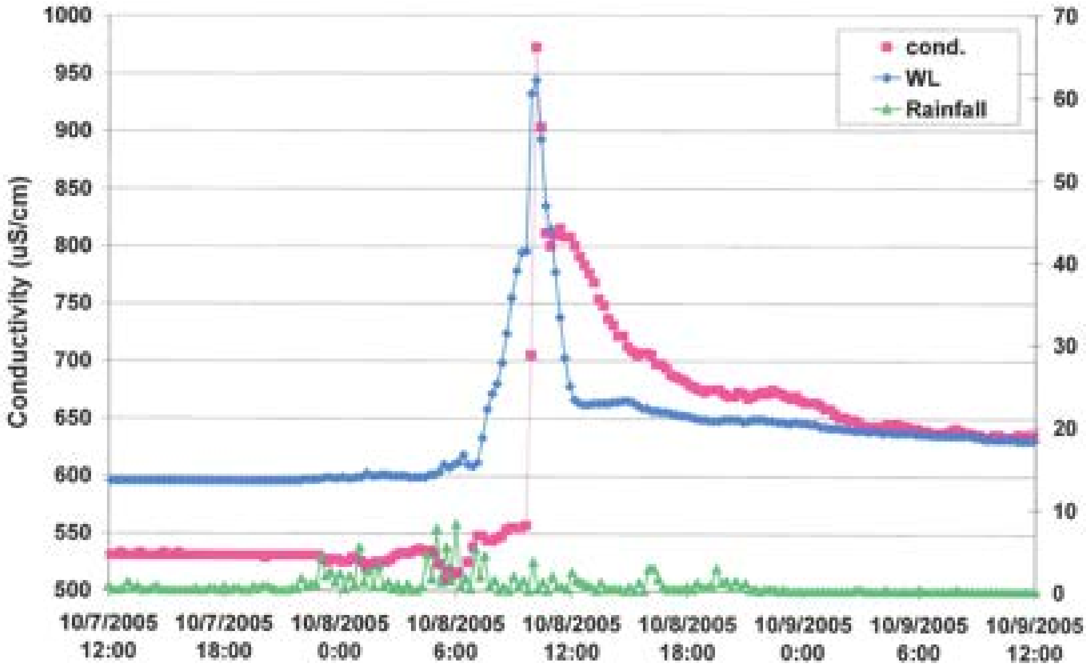


Figure 3-27. Storm response at Leboutillier Spring during the10/7/05 storm. The conductivity increased 285 μS/cm and the water level increased 50 cm.

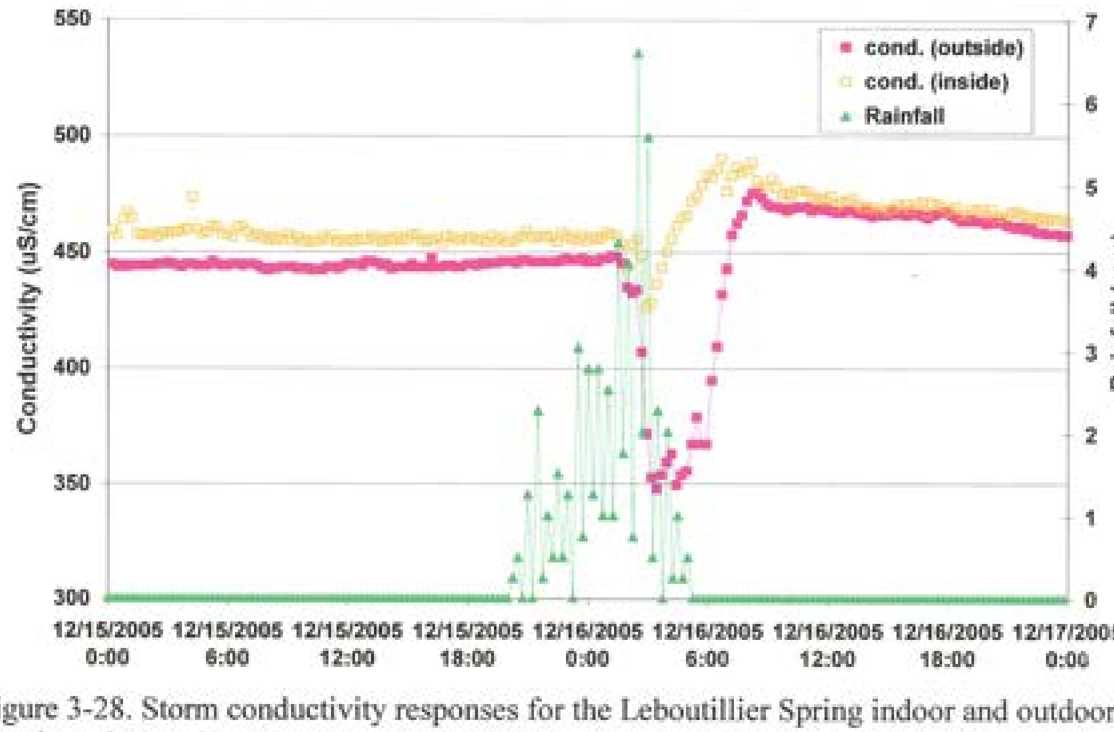


Figure 3-28. Storm conductivity responses for the Leboutillier Spring indoor and outdoor locations during the 12/15/05 storm. The inside location showed a faster response time.

CHAPTER 4
CONTINUOUS MONITORING AND STORM RESPONSE: INTERPRETATIONS

Baseflow

Baseflow data provide information on seasonal variation. Flow paths can potentially vary from season to season. Relatively constant parameters would suggest little variation, whereas variations suggest multiple flow paths occur. The baseflow water level varied only a few centimeters (1-5 cm) over different seasons for all these springs; therefore, discharge was nearly constant.

The lowest baseflow spring stages were recorded in the end of the summer to the beginning of the fall season during field visits. This correlated to the general climate regime of the area. Generally the lowest amounts of precipitation for the northeast area occurred in the summer and the fall seasons, consequently the recharge into the groundwater system would be at minima. The general decrease in water level in the summer at all the springs and the general increase of water level at the Valley Park Spring, Lawson Spring and Leboutillier Spring in the latter part of the fall season to the winter season could be attributed to the precipitation pattern. The smallest amounts of precipitation were during the latter part of the spring and most of the summer. In the fall and winter seasons there were more precipitation events and the total precipitation for each storm event had increased. Also, the evapo-transpiration rate was at its lowest during these seasons. The combination of increased precipitation and decreased evapo-transpiration was the probable cause of the water level increase from the lows at the start of the season to the higher overall water level average at the end of the season.

The baseflow conductivity varied only ± 20 μS/cm for Leboutillier Spring and ±10 μS/cm for Lawson Spring over different seasons. The steady baseflow conductivities for these two springs are likely related to their flow type. In karst system less variation is typical of more matrix-mixed flow type system. The CV% of these springs (both around 11%) supports a mixed flow type (which has CV= 8-11%). The baseflow conductivity at Gunkle Mill Spring varied ± 75 μS/cm. The baseflow conductivity at Valley Park Spring varied ± 100-150 μS/cm. The greater variation at Gunkle Mill Spring and Valley Park Spring is typical of conduit flow; again this is supported by high CV% (~19%) calculated for these two springs. These two springs discharge from visible conduits in contrast to the two springs with lower CVs, which have more diffused discharge. The baseflow conductivity maximum observed at Valley Park Spring correlated with the minimum baseflow spring stage at Valley Park Spring. This suggests that the spring discharge showed little dilution of the groundwater by the recharge water during this period. The largest variation in conductivity was observed in the rural spring. Nolte Spring had seasonal variations of >150 μS/cm (Tancredi, 2004). This probably represents a combination of short and long flow paths for Nolte Spring depending on the recharge patterns.

The relatively constant baseflow temperatures are typical of groundwater discharge and indicate that storage time in the karst aquifer was long enough to reach temperature equilibrium. In general, the relative constant baseflow parameters for the urban springs suggest little variation in flow paths during different seasons. Probably shorter flow paths provide less opportunity for variation.

Storm Responses

Storm response data provide information on recharge to the aquifer, specifically for this study, the effects of urbanization on recharge of a karst system. The magnitude and timing of the water level rises and conductivity during storms will give clues about the flow paths. The variations in storm responses observed at these springs can be differentiated based on the land-use surrounding the springs.

All of the springs showed an increased in temperature if there was any temperature response to storms during the summer and early fall season (Figure 3-23 and 3-24). Whereas during the late fall and winter seasons there were negative temperature responses during storms (Figure 3-24 and 3-25). This was likely due to the weather (air temperature) at the time of the storm. In the spring, summer and early fall the air temperature was higher than the groundwater temperature, thus precipitation during these seasons would be warmer. Whereas during the late fall and winter the air temperature would be about that of the groundwater or lower, thus precipitation would be cooler and if the storm water quickly recharged the aquifer (as evidenced by the rapid water level increases and changes in conductivity) the spring discharge would be cooler than the baseflow temperature. The temperature response in storms is typical of both urban and rural karst systems, and will not be discussed further.

In general, the Lawson site had higher water level increases than any other sites accompanied by conductivity decreases during storms (Tables 3-2, 3-3, and 3-4). This site is the most "open" site. As mentioned in the site description this spring lacks protection of a spring house and the instrumentations were installed out-of-doors; therefore, it is probable that it is more readily affected by overland flow, especially during large storms. Dilution of the groundwater by both new storm water recharge and overland flow was evidenced by 1) consistent higher increases in water level and 2) larger decreases in conductivities compared with the other springs monitored in this study.

The Gunkle Mill Spring generally showed an increase in conductivity during storms and the water level rise was quite small even during larger storms. For small storms there was rapid small increase in water level with an initial small decrease in conductivity followed by larger increase conductivity for small storms. During large storms (October 7, 2005 – October 8, 2005 and December 15, 2005 – December 16, 2005) the storm water quickly recharges the aquifer, which moves the older groundwater out, evidenced by the rapid water level rise and high conductivity response (Figure 4-1 and Figure 4-2). This response suggests the Gunkle Mill Spring has contribution from a deeper flow path and during storm recharge water flushed older groundwater out of the system. Gunkle Mill Spring had a somewhat longer time to return to baseflow conditions (2-3 days), further suggesting it has longer flow paths than the other urban spring in this study.

Leboutillier Spring showed both decreased and increased conductivity responses for different storms. The water levels vary with the size of the storm. For the smaller storms there were smaller increases in water level. The variation in water level response was hypothesized to be the influence of overland flow to the spring. There was less water level increase when there was more infiltration of the storm water depending on the antecedent conditions and storm intensity. In storms where either the soil was over-saturated or large volume overcame the saturation rate of the soils, overland flow

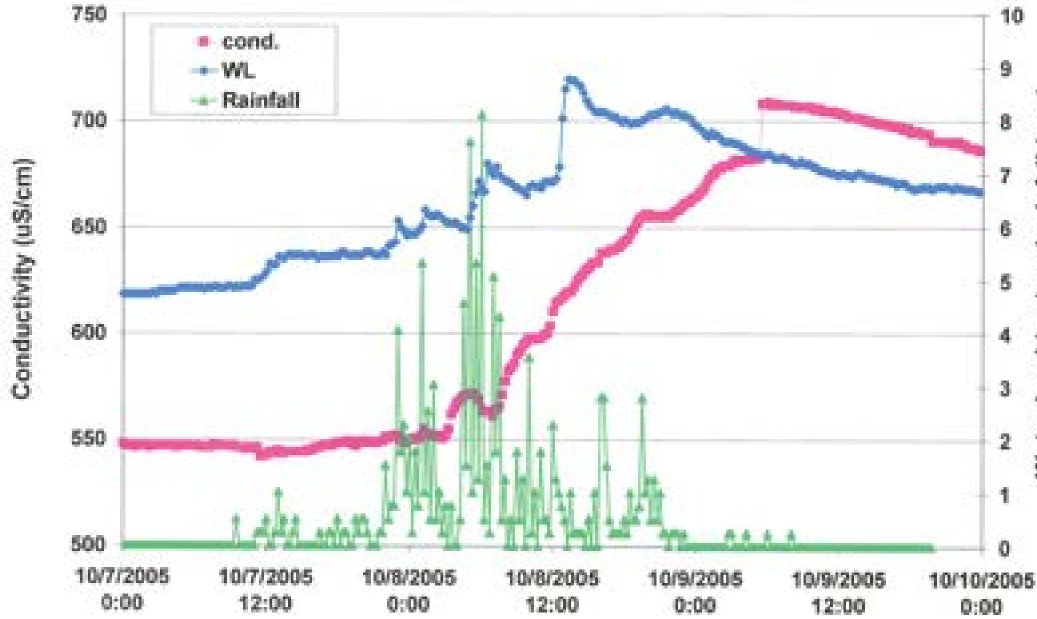


Figure 4-1. Storm response at Gunkle Mill Spring during the 10/7/05 storm. The water level response was small (~2 cm). The conductivity increased ~150 μS/cm during this storm.

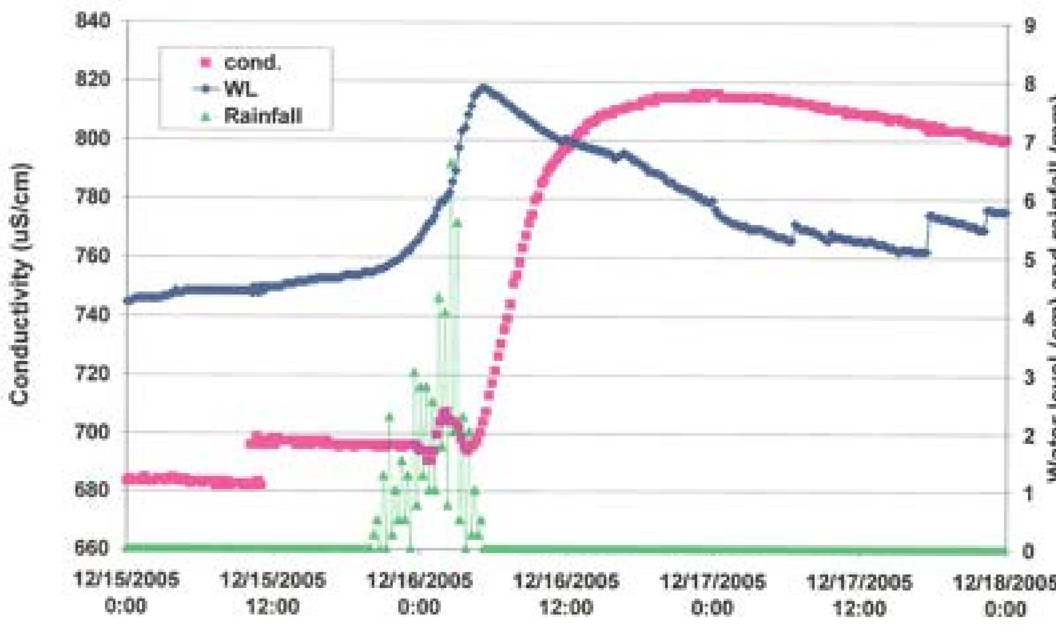


Figure 4-2. Storm response at Gunkle Mill Spring during the storm on 12/15/05. The water level increased 3.5 cm and the conductivity increased 120 μS/cm .

significantly added to the water level of the outdoor spring discharge point. The influence of overland flow can be further supported by the magnitude of the conductivity response for the outdoor location versus the indoor location. As shown in Figure 3-28 the outdoor location had a conductivity decrease three times bigger than the indoor location. Thus, the more "open" spring discharge showed overland contribution. The indoor spring location having no overland flow influence responded quicker (2 hours) to the storm event and it also returned to baseflow sooner.

The largest storm response at this site was to the October 7, 2005 and October 8, 2005 storm, with a water level increase of ~ 50 cm and a conductivity increase of 440 μS/cm (Figure 3-27). The increase in conductivity was either due to 1) sediment washing into the spring from a construction site ~100 meter up gradient from the spring, or 2) the intensity of the storm pushed older groundwater out as observed at Gunkle Mill Spring during most storms. A combination of the two may have occurred since the conductivity increase was the highest observed at any time during this study, but contributions can not be distinguished with the data available.

Valley Park Spring showed consistently lower water level rise (highest water level rise was only ~ 5 cm) and small decreases in conductivity (maximum ~60 μS/cm) during storms. The baseflow conductivity at this spring was also always higher in comparison to the other springs, with averages of 1150 μS/cm and 1250 μS/cm (Figure 3-18 to Figure 3-21). Thus with any addition of rain water in the aquifer only slightly diluted the groundwater, which is the likely cause for the small decreases in conductivity. The small water level increases during both large and small storms suggest that the groundwater here does not get significant recharge during storm events. The large coverage (18-24 %) of impervious surfaces in the capture area of Valley Park Spring likely reduces recharge.

These variations show that for the more open land use (residential and residential/agricultural) there is more infiltration of storm water compared with the commercialized springs. Therefore, the conductivity and water level response show bigger changes during storms at the more open land-use springs. There were also more predictable responses in conductivity and water level changes for these open springs compared with the commercial spring sites. The water level responses were smaller at the commercialized springs because less volume of storm water can be added to the aquifer due to less infiltration. A good example of this would be the December 15, 2005 storm. The water level rise for the indoor Leboutillier Spring, which has residential/agricultural land use, was ~20 cm greater than the water level response at both Gunkle Mill Spring and Valley Park Spring, which are commercialized (see Figures 3-27, 4-2, and 4-3).

The springs in this study have different responses compared with other karst springs. Comparisons between Nolte Spring (Tancredi, 2004), a rural setting karst spring, and SS-5 in Bear Creek Valley (Desmarais and Rojstaczer, 2002), a less developed land use setting than the springs in this study, demonstrated the differences in storm responses. The first difference between the springs in this study and Nolte Spring and SS-5 was the delayed return to baseflow condition after a storm event in both water level and conductivity.

For the SS-5 spring the peak water level rises at the spring occurred 1-2 hours after the peak of the storm, which was similar in timing to the responses observed in the springs in this study. However, at the non-urban springs the return to baseflow water

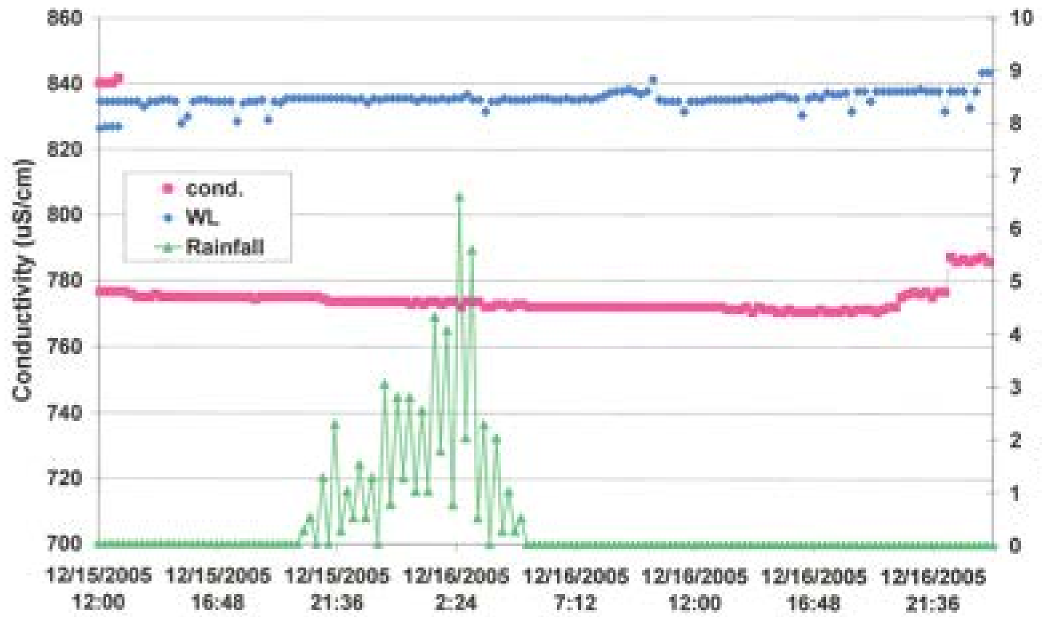


Figure 4-3. Storm response at Valley Park Spring for the 12/15/05 storm. No response in conductivity or water level was apparent.

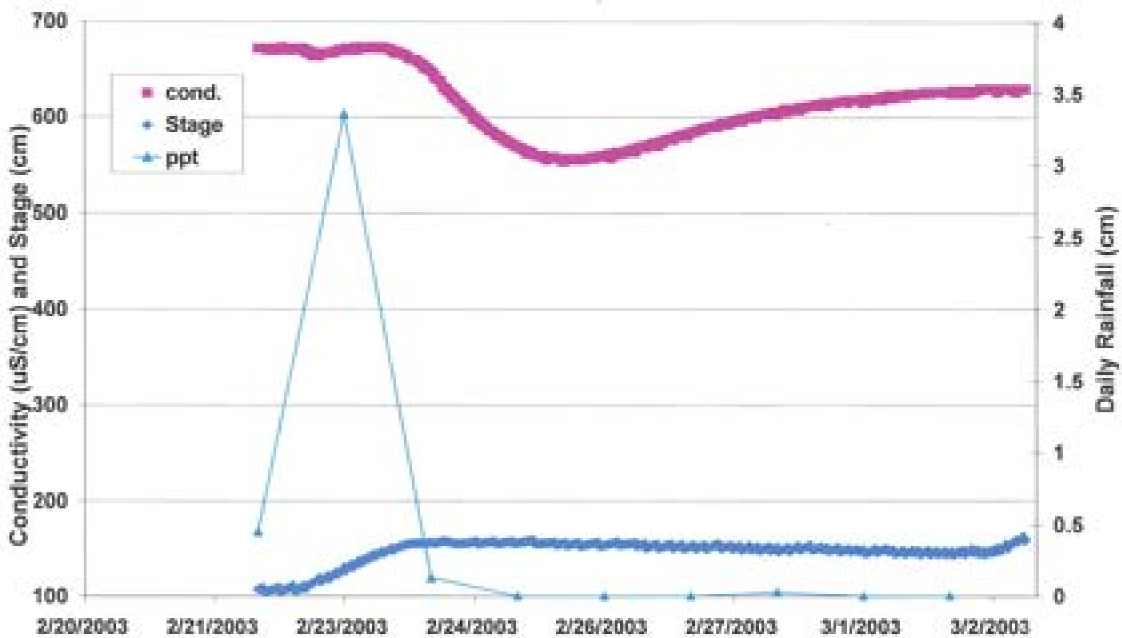


Figure 4-4. Storm response at Nolte Spring during a small storm on 2/23/03 (3.5 cm total rainfall). The peak conductivity response occurred two days after the storm event. The water level increased 50 cm.

For the commercial sites large storms produced water level increases of 0.5-5 cm and small storms increases of 0.25 – 1 cm (Figure 4-6). None of the storms produced water level rises as large as observed at Nolte Spring. Even within the study area differences in response were observed based on the degree of development.

Summary

The urban springs have certain characteristic typical of karst systems such as the range of CV% (11- 19%), and conductivity (500-1400 μS/cm). However, urbanization has influenced storm response and seasonal variability. Storm response was more rapid (on order of hours) than rural karst springs (on order of days), which suggest short flow paths for the urban springs. Low variability from season to season suggests the flow paths are relatively constant, which may be the result of more restricted recharge area due to urbanization.

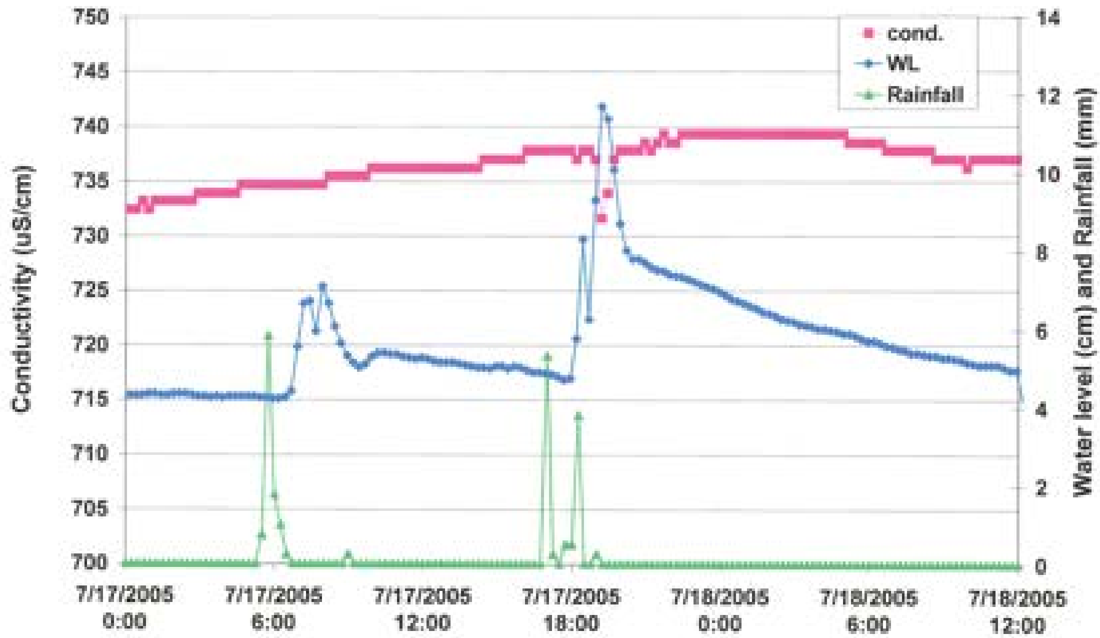


Figure 4-5. Storm response in conductivity and water level at Lawson Spring on 7/17/05. The storm response in water level was much higher at this more open spring than that of the commercialized springs.

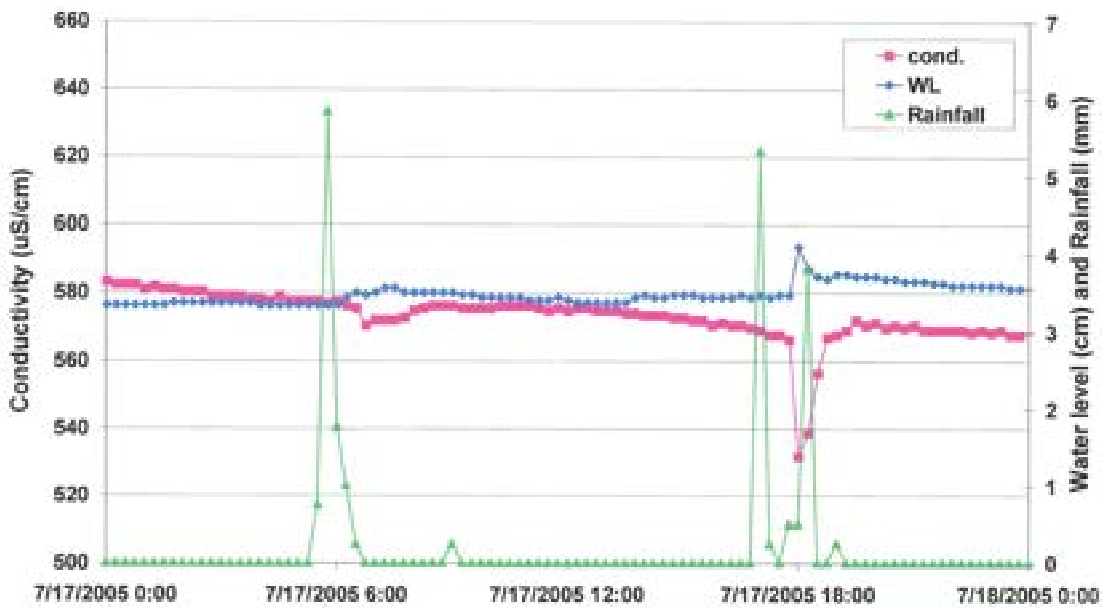


Figure 4-6. Storm response at Gunkle Mill Spring on 7/17/05. The total rainfall for this about was 2.3 cm which is considered a small storm. The response of this more commercialized spring can be compared with residential (more open) land-use spring as shown in Figure 4-5.

CHAPTER 5
GEOCHEMISTRY OF HALIDES

Introduction

The focus of the geochemical study was to discriminate sources of anthropogenic halide contamination in groundwater by measuring chloride (Cl^-), bromide (Br^-) and total nitrogen (N). High concentrations of Na^+ and Cl^- are major problems in groundwater and surface water quality, especially in urban and developing regions. Although high concentrations of Na^+ and Cl^- can easily be identified in surface and groundwater, it is harder to establish the source of contamination. Panno *et al.* (2006) looked at several end-members to characterize and discriminate possible sources of halide contamination.

Possible anthropogenic-related sources analyzed by Panno *et al.* (2006) include road-deicers, landfill leachate, agricultural, septic, and animal waste. Meteoric water, soil water, pristine groundwater, basin brine, and seawater also have background (natural) concentrations of Na^+, Cl^-, Br^- and total N. These natural concentrations are more enriched in Na^+ relative to Cl^-. Meteoric water (rain and snow melt) have the lowest concentration of Na^+ and Cl^-. For the soil water and uncontaminated groundwater Panno *et al.* (2006) hypothesized the sources of Na^+ to be interaction of water with Na-rich rock and clay. These natural sources rank from meteoric water, soil water, and then groundwater for lowest to highest concentration levels of Na^+ and Cl^-. For anthropogenic affected sources, different ion concentrations are related to different sources with some overlap, probably due to mixing of end-member sources (Figure 5-1). For -surface water and groundwater affected by road salt, the Na^+ and Cl^- concentrations depended on the proximity to sources.

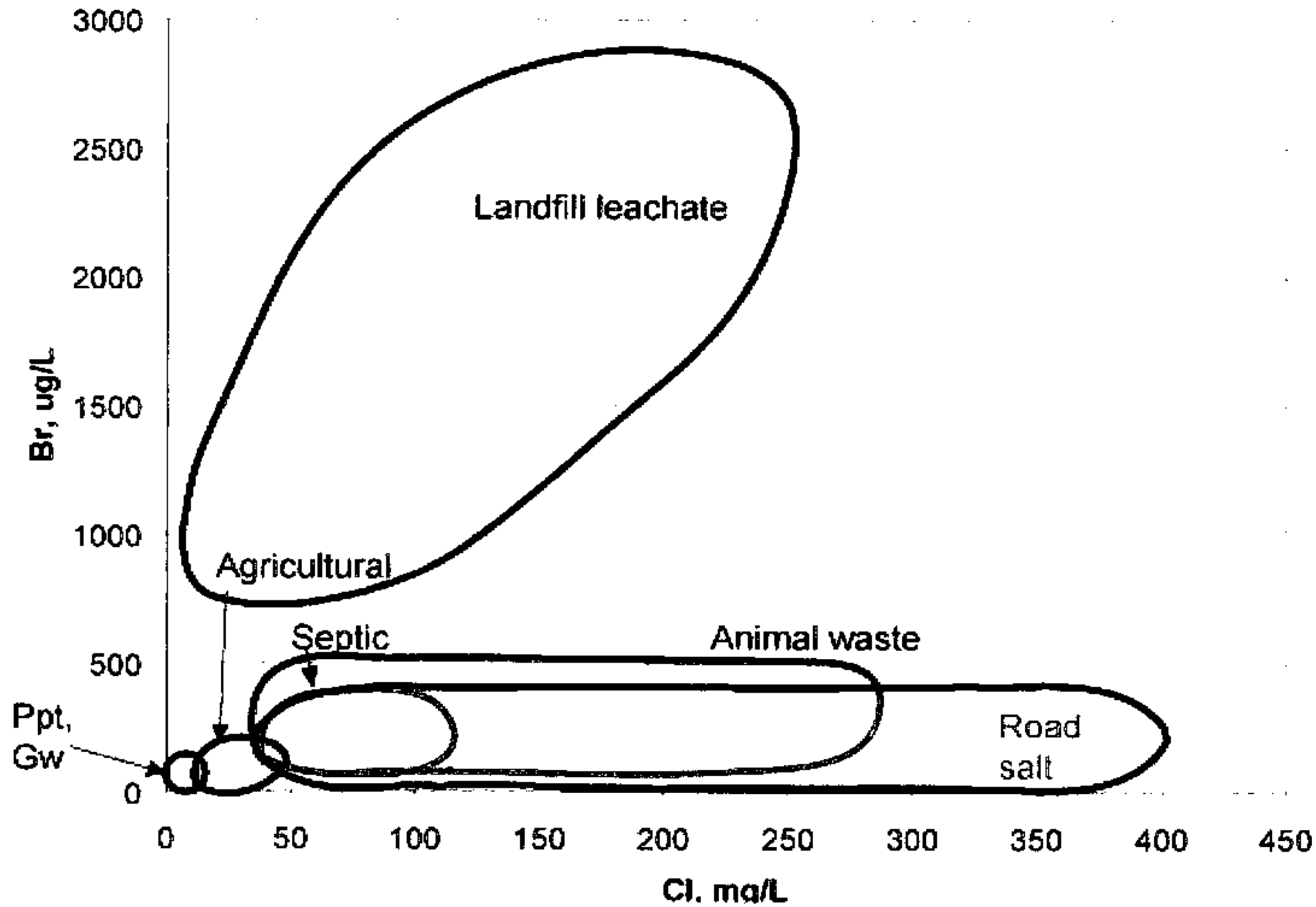


Figure 5-1. Graph of Cl versus Br to discriminate the different sources of halides. The springs in this study ranged from 16 mg/L to 280 mg/L in chloride and less than 250 μg/L bromide. All end member data for this plot are from Panno *et al.*, (2006).

The ranking of bromide concentration levels for the anthropogenically influenced sources of Na^+ and Cl^--affected water was road salt, septic, animal waste, and then landfill leachate from low to high concentration level. Panno *et al.* (2006) used total N to separate the septic and animal waste affected water from those affected by road salts. Bromide was used to differentiate septic from animal waste, which is enriched in Br^- and I^-. Landfill leachate-affected water, which is enriched in I^- relative to Na^+, was separated using Br^- concentration and I/Na ratio.

Panno *et al.* (2006) determined the threshold for anthropogenically-influenced groundwater to have a Cl^- concentration of 15 mg/L or higher. Again, rock-water interaction will also increase the concentration of Na^+ in already contaminated groundwater, although it is also determined to have the same threshold value as Cl^-. Many of the anthropogenic-related sources have very high concentrations of Na^+ and Cl^- (although not to the extent of basin brine or seawater). Br^- concentrations ranged from 500-2700 μg/L in animal waste, septic landfill leachate, and basin brine affected water. Whereas uncontaminated surface and groundwater, road salt-affected water, and agricultural-affected water have low Br concentration (4-60 μg/L); therefore, Cl/Br ratio can readily be used to distinguish these anthropogenic sources. Although many of the values for the end-members overlapped, it was still possible to discriminate these sources using the halide ions ratios in combination with total nitrogen or iodide.

Methods

Baseflow water samples were collected for laboratory analysis of major ions. These monthly baseflow samples were collected using a hand pump with a 0.45 μm filter.

The samples were placed in an ice cooler and transported to Temple University and stored in a refrigerator until analysis.

Concentrations of chloride, bromide, and total nitrogen (NO_3^- - N and NH_4^+ - N) were measured using the Dionex (DX 500) Chromatography System with a ED40 Electrochemical Detector. The accuracy of calibration was 5 percent. For bromide measurements standards of bromide solutions were prepared at concentrations of 50µg/L, 100µg/L, 250µg/L, and 500µg/L. The Dionex ion chromatograph was tested and it was determined that it could detect bromide concentrations $\geq$250 µg/L. For the purpose of this study the 250µg/L limit was acceptable because the cut off for landfill leachate and basin brine was >500µg/L. In this study, only the halides and nitrogen data are reported. Further geochemical interpretation is part of another thesis project (Gross and Toran, 2006).

Results

The chloride concentration data were plotted for each site to show the variation within and between the various monitored springs (Figure 5-2). Leboutillier Spring showed the lowest concentrations in chloride, with an average of 19 mg/L.
The chloride variation was also the smallest at this spring with a minimum of 17 mg/L and a maximum of 24 mg/L. Gunkle Mill Spring had the next lowest concentrations with an average of 48 mg/L. The variation in chloride concentrations for Gunkle Mill Spring was about ±15 mg/L with minimum concentration of 34 mg/L and maximum concentrations of 63 mg/L. Lawson Spring had concentrations that were slightly higher, an average of 65 mg/L, higher than both Leboutillier Spring and

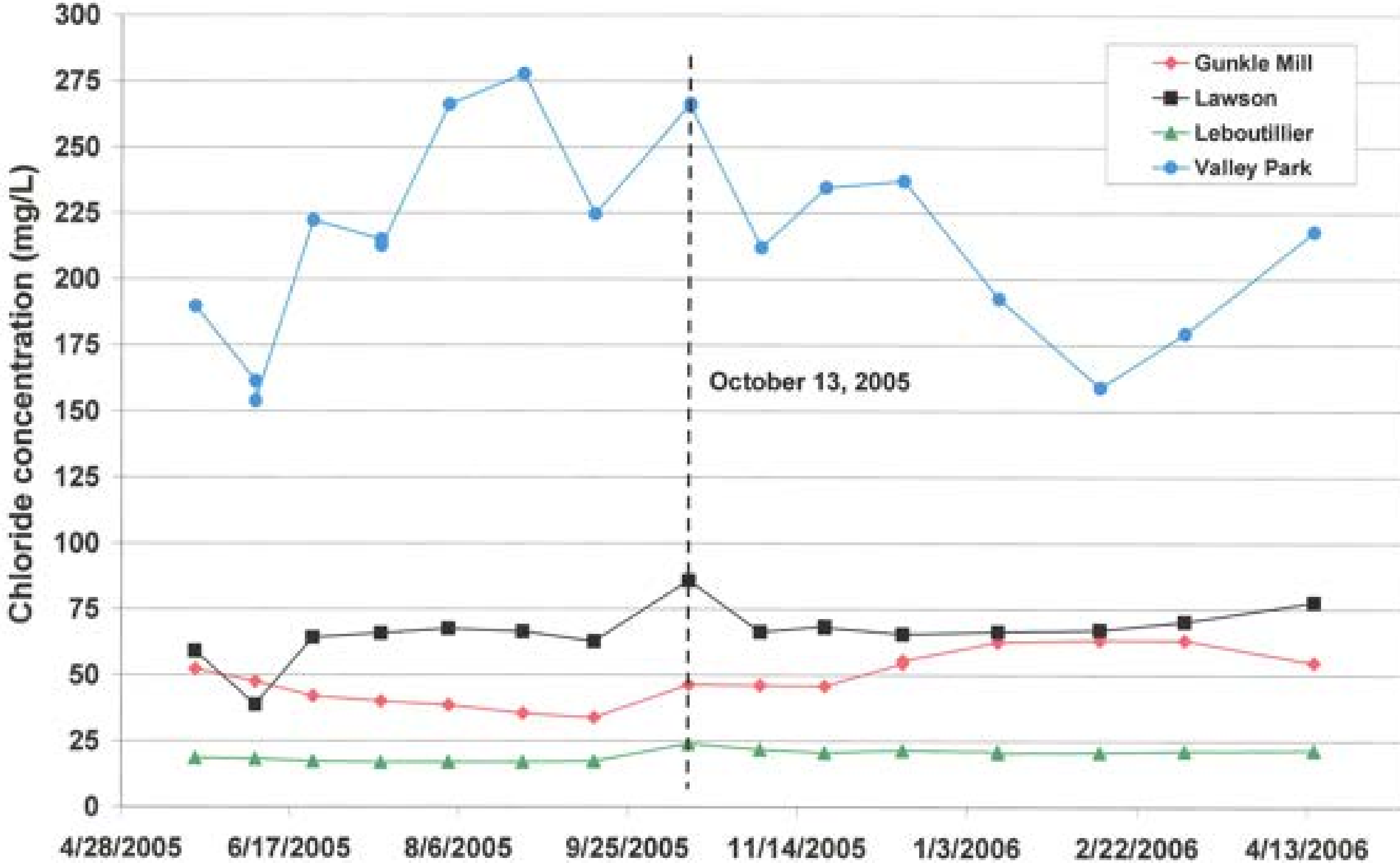


Figure 5-2. Show the plot of the variation of chloride concentrations at all the monitored springs during the study period. The highest chloride concentrations were found at Valley Park Spring, which also had the biggest variations. A large storm on October 7, 2005 increased the chloride concentrations at all four springs.

Gunkle Mill Spring. There was a greater variation of chloride concentration for the Lawson spring with a minimum of 39 mg/L and a maximum of 86 mg/L. Valley Park spring had the highest concentrations of chloride and the greatest variability. The average was 218 mg/L for Valley Park, with minimum of 154 mg/L and maximum of 278 mg/L.

Bromide concentrations were below the 250 μg/L detection limit. All samples, whether they showed high concentrations of chloride (Valley Park Spring and Lawson Spring) or low concentrations of chloride (Leboutillier Spring and Gunkle Mill Spring), showed non-detectable concentrations of Br^-.

Total nitrogen concentrations were nearly always in the form of $NO_3 - N$ with only low level concentrations of $NH_4 - N$ on one date each at Gunkle Mill Spring, Leboutillier Spring, and Lawson Spring. The NO_3 –N (and total N) were 5 mg/L or less at all sites (and 2 mg/L or less at Valley Park Spring).

Discussion and Summary

The chloride concentrations measured at the Leboutillier spring were very close to that of background level. The chloride concentrations at this spring were very steady except after the large storm in the early fall 2005 season. It increased about 15 mg/L after the storm then returned to background concentrations. Panno *et al.* (2006) have "pristine" groundwater at or below 15 mg/L of chloride. Anything significantly (> 5 mg/L) above that can be attributed to anthropogenic contamination by halides. It is evident that at the Valley Park spring the groundwater is contaminated with chloride. At Gunkle Mill Spring and Lawson Spring the chloride concentrations are also higher than background concentrations, but 2-3 times lower than chloride concentrations at the Valley Park Spring. At Gunkle Mill Spring there appears to be a seasonal correlation. The concentrations decreased during the late spring and summer as expected when there are no de-icing activities going on. After the large storm in the beginning of the fall season, chloride increased at all of the springs, but the concentration of chloride at Gunkle Mill spring returned to a steady level until after the first snow storm in the middle of December 2005. The chloride concentrations at the Lawson spring showed a nearly flat pattern that is similar to the Leboutillier spring, although the absolute concentrations were about two times higher.

Most of the samples from the springs in this study had higher chloride concentrations than expected of background "pristine" samples. So background sources can be eliminated except for Leboutillier Spring. By measuring the chloride and bromide concentrations, it was possible to discriminate the source of the chloride (after Panno *et al.*, 2006). The Dionex chromatograph did not detect any measurable concentrations of bromide in any of the samples tested from all of the springs. The low Br^- concentration eliminates both landfills and sea water brines as sources of high chloride. Although absolute concentrations of Br^- for the sea water brines was not available in the Panno *et al.*, (2006) review, the Br/Cl ratios show they would plot similarly to landfill-affected water.

All the high chloride samples also had low concentrations of NO_3^- - N; samples from all springs had concentration ≤ 5 mg/L. These concentrations do not indicate that a significant portion of the chloride would come from agricultural or septic sources. Panno *et al.* (2006) suggest 10 mg/L total N indicates significant influence by agricultural or septic sources.

This led to the determination that the chloride source at all of the springs that have greater than background concentrations was road salt-affected water (Figure 4-1). Furthermore, because 1) the variability of the chloride concentration does not follow any seasonal trend and 2) it actually decreased in the winter season, it can not be solely attributed to one time contamination by road salt during winter storm deicing period. Also because the conductivity at Valley Park Spring was high during baseflow all year round, a continuous source of road salt contamination must be assumed.

The increases in chloride during the late summer and fall could be in theory due to older, more chloride-rich groundwater discharging at the springs. However, the quick storm responses at all of these springs suggest that the pre-storm water was not from long, deep flow paths. The more likely explanation was that the drainage areas of these springs have pockets of re-precipitated road salts. This was confirmed by the chloride concentrations that were measured soon after the large storm on October 7-8, 2005. After the storm all the springs showed increases concentrations. October was too early for de-icing activities related to snow storms. The source of chloride during that time could only be pockets of re-precipitated road salts.

Two modes of transportation can be proposed for the chloride entering the aquifer system. The first model is that the large volume of storm water was enough to re-dissolve the chloride source (road salt) in the unsaturated zone and flush it through the aquifer. Assuming short flow path, supported by fast storm response time observed in the continuous conductivity data, it can be understood that the hand sample collected at the spring only caught the tail end of the peak chloride concentration washed into the springs after the occurrence of the storm because the storm occurred on October 7-8, 2005 and the hand samples were collected on October 13, 2005. The second model for getting the chloride to the aquifer would be that the storm water was able to quickly recharge the aquifer and raise the groundwater table enough that it dissolved the pockets of precipitated road salt, which were at or near the ground surface. In this case the chloride concentrations might increase slightly later then the peak of the storm. However, since water level rise is suppressed in the urban system and the observed conductivity increase was rapid, dissolution during recharge seems more likely.

The road salt in and around Valley Park Spring became a continuous contamination source because it accumulated on ground surfaces, soils, and in sinkholes, eventually entering the groundwater during storms. At Valley Park it is easier to store and re-dissolve the chloride from road salt applied during de-icing periods because it has higher land and hydraulic gradient than the other spring localities. There are also more pavement and major roads within the capture area of this spring. US 29, a major road in the watershed, is less than 0.25 mi to the east of Valley Creek Spring. Road salts are generously applied during winter storms. Based on the groundwater flow directions constructed by Sloto (1990), Valley Park Spring discharge would have storm water flow off the parking lots from the commercial complex up gradient topographically and hydraulically from the spring.

A geologic rationalization for higher concentrations of chloride at Valley Park would be that it is less than 30 meter down gradient from a major fault that runs in a general southwest to northeast direction (Figure 2-3). In this location the geologic fault, which is well within the capture area of the spring, serves as a conduit for contaminate transport from up gradient in the Valley Creek Watershed. The combination of land use and geologic structural setting is unique to this spring compared to other springs in this study.

Although this geochemical study was able to isolate and measure only one aspect of the wide range of possible anthropogenic contamination of a sensitive karst aquifer system, it is very relevant to future studies of other karst systems undergoing urbanization. The mobilization of road salts in all seasons point out the implications of the shallow flow paths possible contaminants can take in karst aquifer systems. Springs in areas of high development can be sensitive indictors of the overall health of the broader aquifer system. The Valley Creek watershed will continue to experience urbanization, which may lead to further enlargement of conduits and sinkholes developing in the area. The addition of commercial and residential developments will also lead to increase the number of possible sources for chloride and other contamination to enter the karst aquifer system.

CHAPTER 6
CONCLUSIONS

This study found short and rapid flow paths in these karst springs. The evidence for the flow path is based on storm response, baseflow monitoring, and geochemistry of halides.

Reduced Capture Area

The chemical and physical responses of the springs were influenced by the land-use in their capture areas. All four springs showed small seasonal variation in water level (< 5 cm). The conductivity ranged from 450-1470 μS/cm for theses springs. Valley Park Spring, which was in a more commercial area, exhibited higher conductivity (1000-1470 μS/cm) than the other two less developed land use springs (Leboutillier Spring and Lawson Spring). Valley Park also showed greater variation in conductivity (chemical composition) during baseflow, which indicates anthropogenic influences.

The fast storm responses in conductivity and water level observed at these urban karst springs indicate the effects of urbanization. The increased impervious surfaces, which were results of buildings and paved parking lots, decrease the overall recharge area by limiting infiltration. Thus, the impervious surfaces decreased recharge into the aquifer. The recharge water that actually enters the aquifer has shorter flow paths due to shrinkage of recharge area.

Water conductivity responses during storms were typically 1-3 hours after the peak of the storm events and return to baseflow conditions were took about 3-6 hours. Storm water level responses were also rapid. In addition the water level responses during storms at these urban springs were generally about or less than 0.1 of the water level responses observed in karst springs with less-developed land-use capture areas. The different storm responses based on land-use around the springs in this study also demonstrate the effects of urbanization. Gunkle Mill Spring and Valley Park Spring are the most developed of the urban springs in this study. These two springs showed consistently lower water level responses than the residential area springs. During large storms the commercialized springs (Gunkle Mill Spring and Valley Park Spring) showed water level maximum of ≤ 5 cm, whereas the residential springs (Lawson Spring and Leboutillier Spring) showed water level increases of 20-50 cm. These small water level responses evidently confirm decreased recharge areas for these urban springs.

Variation in storm response can indicate alternate flow paths in karst system. For the most part responses in these urban springs were similar from storm to storm, further supporting the conceptual model of short flow paths. Lawson Spring had conductivity decreases for all storms. This showed dilution of the groundwater by storm recharge and also overland flow, since this spring was open. Gunkle Mill Spring had conductivity increases for most storm events. This spring showed flushing of older groundwater during storms. Leboutillier had both increases and decreases for different storm events. This spring showed some seasonal conductivity responses to storms. Most of the storms in the summer season decreased the conductivity. Most of the storms in the fall and winter seasons showed increases in conductivity. The seasonality observed at Leboutillier Spring may correspond to a larger capture area. Valley Park Spring mostly showed conductivity decreases during storm events. Again, similar to Lawson Spring this spring had dilution of groundwater by quick flow storm recharge.

Shallow Flow Pathways

High concentrations ($\geq$ 30 mg/L) of chloride were found at three of the urban springs. The threshold for natural chloride concentration is 15mg/L. The chloride contamination at is road salt as determined by Cl versus Br discrimination plot of geochemical data.

Year round high concentrations of chloride at these springs showed shallow flow paths. The highest concentrations of chloride were measured in the late summer and early winter, where de-icing activities related to winter snow were least likely. This implies that the road salt present in the capture area is a continuous source of contamination. The increased concentration of chloride after storms showed 1) re-dissolving of the stored road salts and 2) shallow flow pathways during storm events.

Valley Park Spring has the highest road salt contamination because the spring capture area has the most highly commercialized land use. There is a major highway next to the spring and a lot of paved parking lots and roadways in the recharge area. This increases the volume of road salt applications during de-icing. Geology (faults and sinkholes) also increases the likelihood of concentrations of anthropogenic contaminations from further up gradient in the watershed.

Summary

An in-depth study of the conductivity, water level, and temperature and halide geochemistry was conducted in relation to the influence of urbanization on four karst springs. Different land uses in an urban setting showed slight variation in storm flow path lengths. This was evidenced by storm recharge patterns (increases and decreases in conductivity and small water level rises) and road salt contamination. All of the springs had shorter flow paths and faster responses than comparable non-urban karst springs.

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