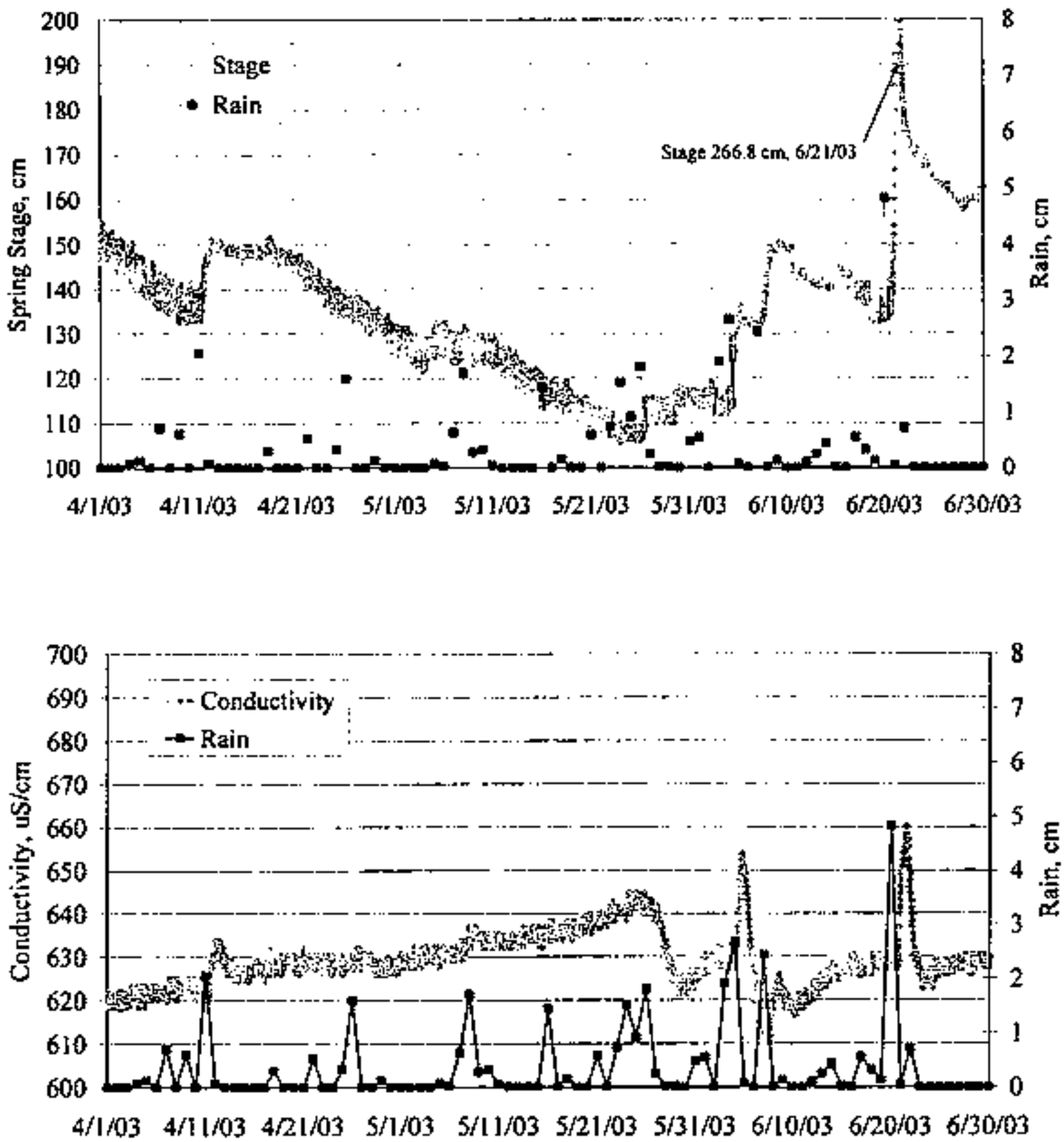
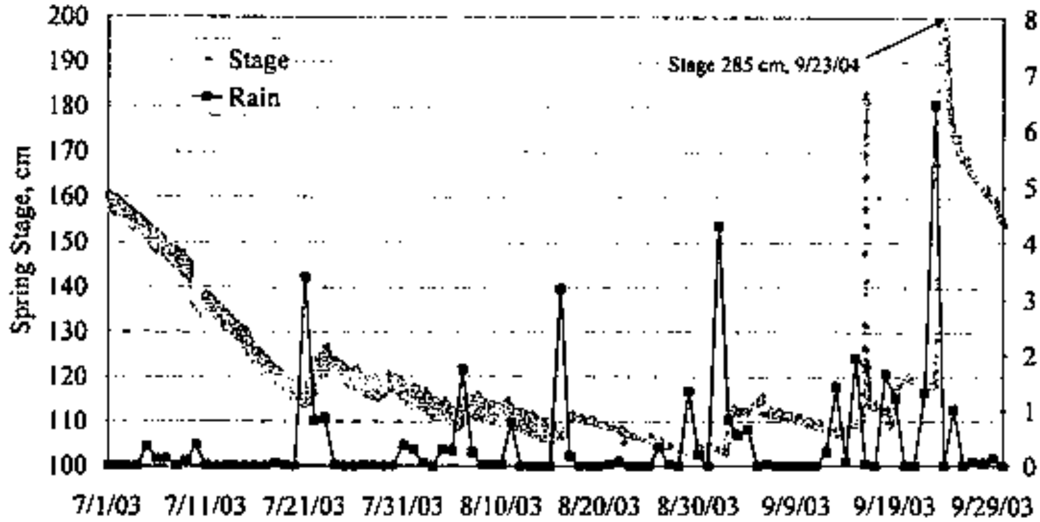


Figure 4-4. Summaries of stage and conductivity data from the Spring 2003 season. Both types of conductivity responses to storms were observed during this season. A storm on June 18, 2003 caused the stage to peak at 267 cm.

increase immediately followed by decrease to below antecedent conditions. On June 20, 2003, almost 5 cm of rain fell in one day and the conductivity rose approximately 30 μS/cm in 18 hours, followed immediately by a decrease of almost 40 μS/cm over the next 40 hours. The conductivity then recovered to antecedent conductivity, which was approximately 10 μS/cm higher than the conductivity minimum.

Summer 2003

In summer 2003 stage followed a similar trend to the previous season, with steady decrease through the first two months, and then a slight upward shift in baseflow (~ 5 cm) for the rest of the season in response to increased storm activity (Figure 4-5). The months of July and August 2003 were marked by stage decrease, except for storm events on July 18 – 21, July 31 – August 6, and August 16-17, 2003, which resulted in stage rise. The lowest stage of the season was 103 cm, on August 29 and September 1, 2003. Beginning in early September, a series of small storms caused the stage to rise to 116 cm. Two large stage increases occurred at the end of the summer season in response to storm activity. On September 15, 2003, spring stage peaked sharply at 183 cm, a 74 cm rise from antecedent stage, then decreased 71 cm within 34 hours of the peak stage. The largest storm of the entire monitoring period occurred September 23, 2003. The maximum precipitation rate was 6.45 cm/day, and the stage rose 167 cm in 16 hours. Hurricane Isabel, which arrived in southeastern Pennsylvania on September 18, 2003, only caused a slight rise in stage (8 cm from antecedent), and the precipitation rate was only 1.42 cm/day.



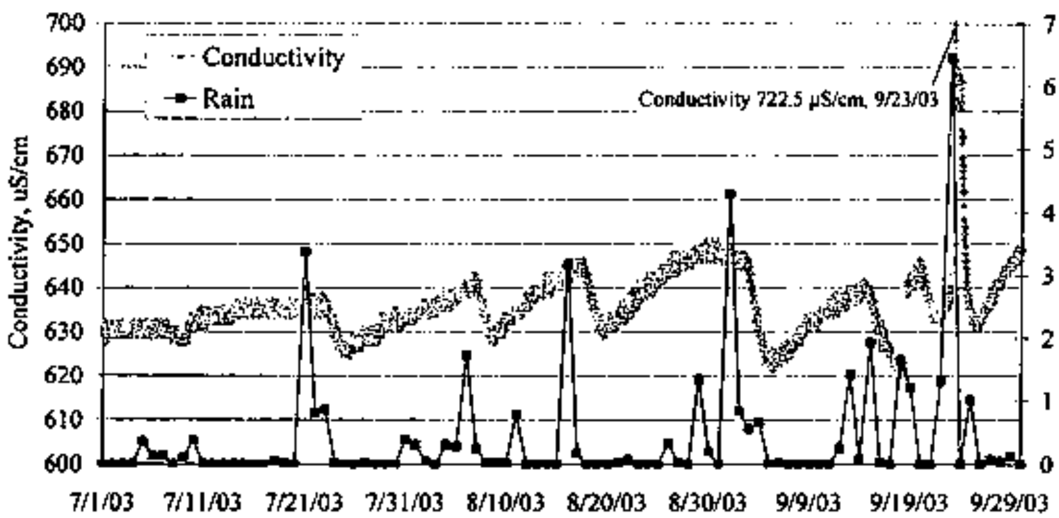


Figure 4-5. Summaries of stage and conductivity data from the Summer 2003 season. The conductivity responses seen during most of the storms in this season are thought to result from the frequent storms keeping the karst system flushed with relatively dilute water. The September 23 storm, however, had a conductivity peak of 722.5 μS/cm, and the stage rose to 284 cm, the highest observed in the monitoring period.

Summer 2003 conductivity ranged from 620 to 650 μS/cm, excluding the storm maximum on September 23, 2003. All Summer 2003 conductivity storm responses are marked by a fairly rapid decrease (7-13 uS/day) with gradual recovery (~2 uS/day) (Figure 4-5). The September 23 storm is the only summer storm of 2003 where the conductivity response includes a sharp increase followed by a decrease. As mentioned above, this storm had the most rain in any one day of entire monitoring period, and the accompanying rise in conductivity was approximately 80 μS/cm in only 2 or 3 hours. The decrease to antecedent conductivity took 3 days, and the recovery trend in conductivity continued for the rest of the month.

Fall 2003

Fall 2003 baseflow stage ranged from 115 cm to approximately 150 cm (Figure 4-6). A stormflow peak of 180 cm occurred during a flood on December 11, 2003. Stage recovery from the September 23 storm continued through October, with a short rise in response to a storm event on October 14 – 15. The seasonal low of 115 cm was reached on October 27, 2003, just before a 30-cm water level rise following a storm event which lasted from October 26 – 29, 2003. Three storm events in November caused stage increases. The first occurred on November 11 – 13, a small storm of less than 3 cm total precipitation, triggering a stage increase of 3 cm. The second storm of November 2003 occurred on November 19, when 3.45 inches of rain fell and stage rose 12 cm, and the third storm occurred on November 28, during which 2.61 cm of rain fell, resulting in a stage increase of approximately 19 cm. At least one stage increase in December 2003 was similar to those in early March 2003, when a rain event and warmer air temperature

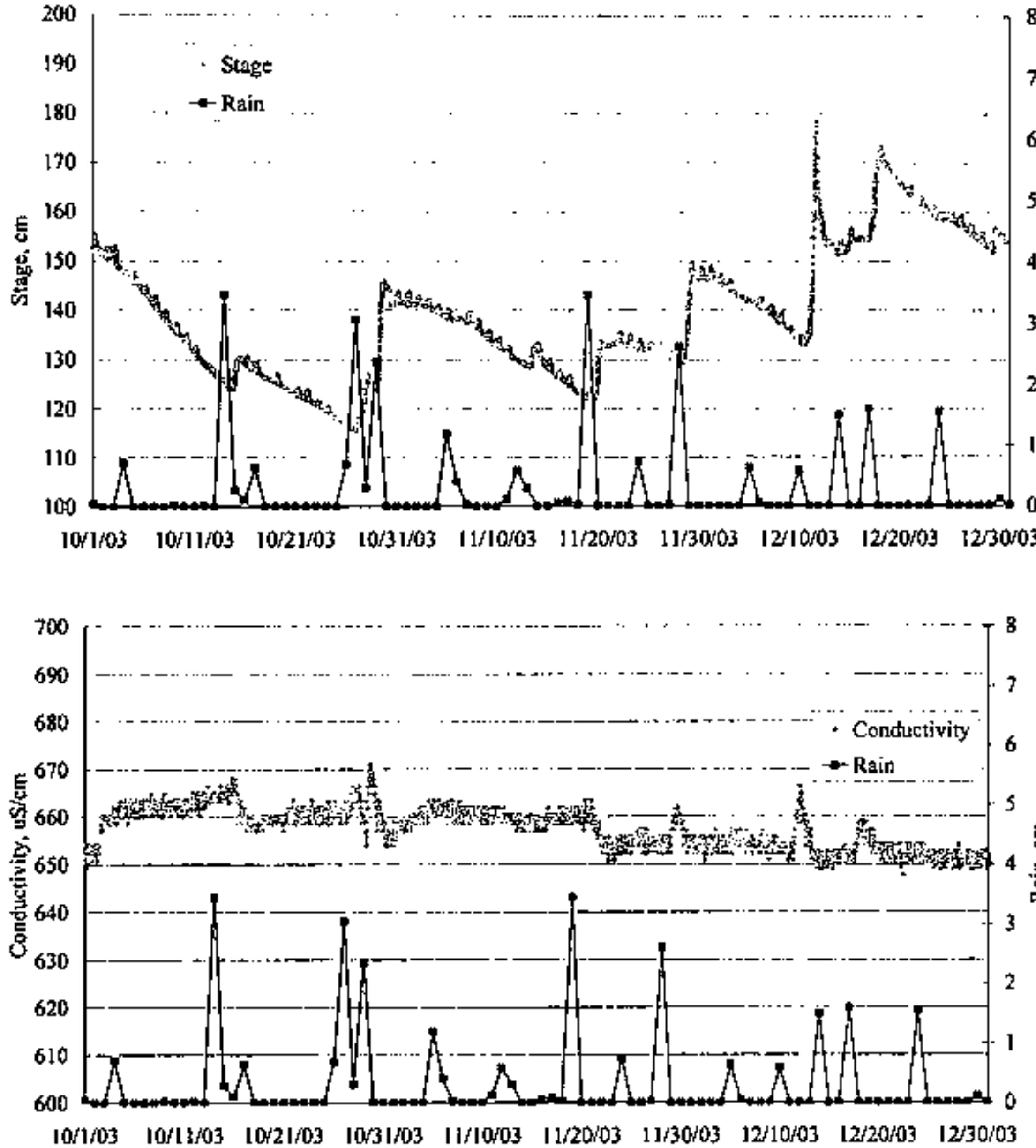


Figure 4-6. Summaries of stage and conductivity data from the Fall 2003 season. Conductivity varied little during this season, but all of the storm responses began with a rise in conductivity. The peak in stage on December 11, 2003 is the result of widespread flooding in southeastern Pennsylvania, which occurred after a temperature rise, which was accompanied by a small amount of rain and significant snowmelt.

triggered snowmelt. An abrupt temperature rise of 9°C on December 10 – 11, combined with a small amount of rain, melted the remaining snow which had fallen five days previously, causing major flooding across southeastern Pennsylvania. This flooding is reflected in the spring hydrograph, when stage rose 45 cm over 28 hours. Another smaller (4°C) temperature rise occurred on December 17, 2003, concurrent with 1.6 inches of rain, which triggered a stage increase of 18 cm.

Fall 2003 conductivity ranged from 650 to 670 μS/cm, including all storm maxima and minima (Figure 4-6). Conductivity responses to storms throughout the fall began with a small but sharp increase followed by decrease to antecedent conductivity or slightly below. All of the Fall 2003 storms had a maximum daily intensity of 2.5 cm/day or more, but the conductivity responses were more muted than previous storms during the monitoring period, which had more dramatic conductivity responses. The 3 highest conductivity rises during the Fall 2003 season were 13 μS/cm on October 29, 10 μS/cm on December 12, and 7 μS/cm on December 18.

Discussion

Conceptual Model for Storm Response in Nolte Spring

As mentioned in the Introduction, a number of stormflow models for karst springs include the displacement of "old" pre-storm water by "young" storm water entering the system. Dissolved ions, isotope ratios, and conductivity measurements have been used in these models to quantify "old" and "young" water (Dreiss, 1989; Lakey and Krothe, 1996; Desmarais and Rojstaczer, 2002). Here, conductivity is used to distinguish two different types of water, as it was the only chemical parameter in this study continuously monitored before, during, and after the storm, and has been successfully used as a marker in previous studies (Ryan and Meiman, 1996; Desmarais and Rojstaczer, 2002). In this study, however, conductivity was a qualitative tool, because I did not have endmember compositions. However, higher-conductivity water has higher TDS, possibly due to a longer period of water-rock interaction, and represents relatively older water. Water that has a lower conductivity and is more dilute has probably spent less time in the karst system and represents relatively younger water. As mentioned previously, these distinctions are qualitative, as I did not date the water. For ease of description, however, I will use the terms "older" and "younger" to refer to the types of water observed in Nolte Spring.

Storm Response Type I: Old Pre-storm Water

The sharp conductivity increase in the spring following a storm, as seen in the Summer and Fall 2002 seasons, during some storms in the Winter, Spring and Summer 2003 seasons, and in the Fall 2003 season, could indicate that older pre-storm water is being displaced from the relatively immobile zones in the spring ahead of younger storm water (Figure 4-7). The rapid decrease below the pre-storm conductivity value that follows this increase indicates dilution of the spring discharge as the storm water flows out of the spring behind the displaced pre-storm water. A possible reason for the gradual conductivity recovery back to the pre-storm conductivity value is that the lower-conductivity young water begins to interact with the rocks of the aquifer and the conductivity increases as a result of dissolution. Another possibility is that during the rapid injection of stormwater into the system, displaced pre-storm water is forced into

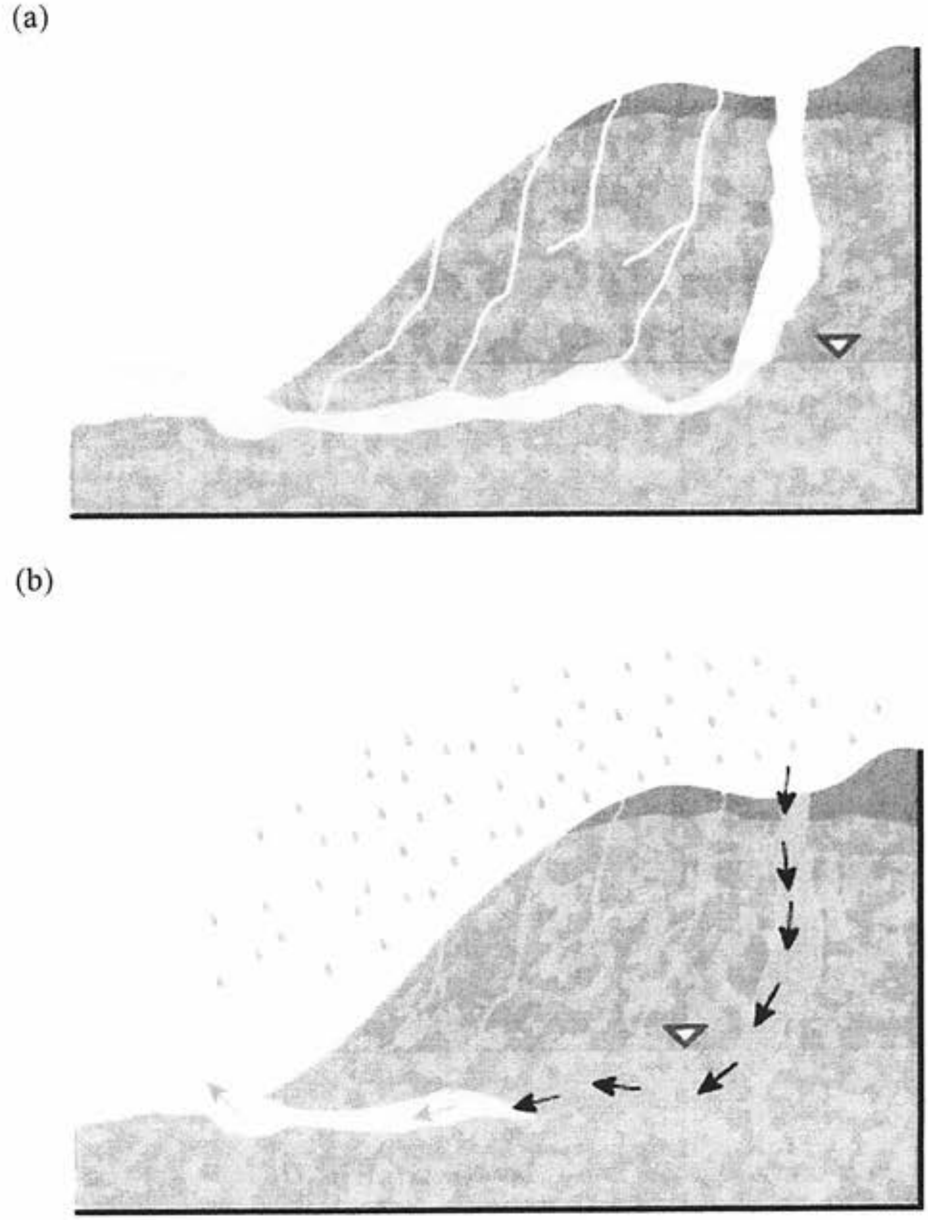


Figure 4-7. Conceptual model of Storm Response Type I. (a) Prestorm water has resided in the karst system for a relatively long period of time and is relatively older (light blue). (b) Younger and more dilute storm water (dark blue) flows rapidly into the system, displacing the prestorm water so that the conductivity initially increases in response to the storm, then decreases as the younger water reaches the spring mouth.

storage in bedding plane partings or the aquifer matrix, as well as pushed through the conduits. This type of physical behavior has been described in White (1999). After the storm, this stored water leaks back into the main fractures and conduits of the system, and mixes with the dilute stormwater, thus causing the conductivity to rise (Figure 4-8).

A special case of this type of storm response is the storm that occurred on September 26, 2002. The antecedent conductivity, 780 μS/cm, was one of the highest recorded during the monitoring period, and the conductivity peak reached during this storm is the largest observed, at 1708 μS/cm. This increase in conductivity, over 900 μS/cm, is higher than typically observed in the literature. Subsequent storms of equal or higher total rain or intensity occurred over the course of the monitoring period, but the conductivity response to those storms did not approach that which occurred on September 26, 2002. One hypothesis that has been suggested for this large rise in conductivity is that the extremely low stage may have enabled access to a more-deeply circulating system of old water of high ionic strength. The increase in ionic strength is higher than can be accounted for by carbonate rock dissolution and may have been caused by the flushing of salts that accumulated in the vadose zone during the drought by the large volume of storm water entering the aquifer. High-frequency collection of dissolved ion or isotope data over the course of this storm might explain this phenomenon more quantitatively; however, the automatic sampler did not collect during this storm because a smaller storm on September 22 filled the sampler.

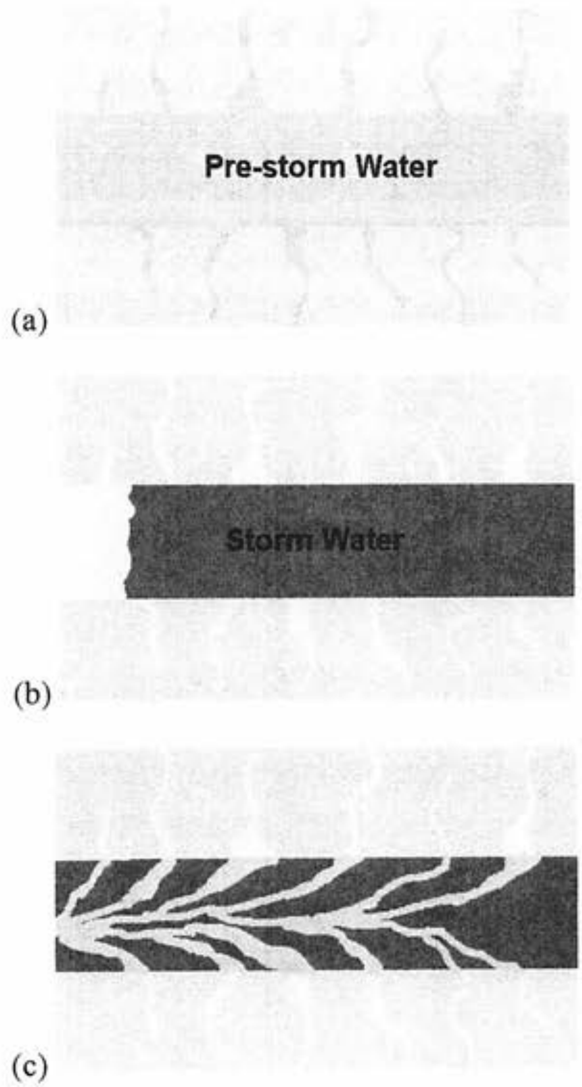


Figure 4-8. Storage and subsequent re-infiltration of prestorm water into a conduit, after White (1999). This model is analogous to bank storage in surface water systems, and is thought to cause the slow conductivity recovery observed following a Type I storm response. The prestorm water (a) is pushed into smaller fractures by the stormwater (b), and is released later into the system (c), causing the conductivity in the spring to recover to antecedent levels.

Storm Response Type II: Young Pre-storm Water

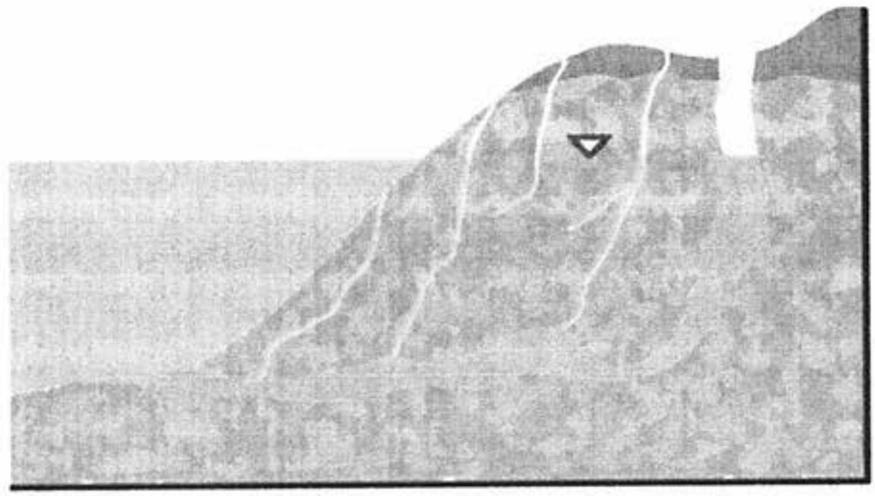
Possible explanations for those storm responses which consist of an initial decrease in conductivity, followed by a recovery to antecedent conditions, are based on the hypothesis that younger dilute water makes up most of the spring discharge during both baseflow and storm flow (Figure 4-9). This could occur after a rainy period, where the older water has either been flushed out of the spring, or is circulating in a deeper system inaccessible to storm water. If this is the case, there is no older water in the spring for incoming storm water to displace, so the relatively younger storm water mixes with the dilute pre-storm water and is discharged through the spring. The chemographs of some storms which occurred in the Winter, Spring, and Summer 2003 seasons reflect this mixing and further dilution of the relatively younger pre-storm water. Additionally, as mentioned above, the higher baseflow observed during these seasons may have precluded access to deeper-circulating water, which is thought to be the source of some of the higher conductivity peaks observed during storms in the Summer and Fall of 2002.

Conceptual Model for Precipitation and Recharge Types

Precipitation type can be described in terms of storm intensity, which I calculated as mean daily rain and highest daily rain. These parameters can then be used to describe the nature of the recharge to the karst system during a storm event, and the relationship between the type of recharge and the storm response of the spring can be examined.

I used the mean daily storm intensity to classify the storms as high intensity (>1.5 cm/day) or low intensity (< 1.5 cm/day) (Table 4-1 and 4-2). However, if the high daily intensity was greater than 2.0 cm/day, then the storm was classified as high intensity. In

(a)



(b)

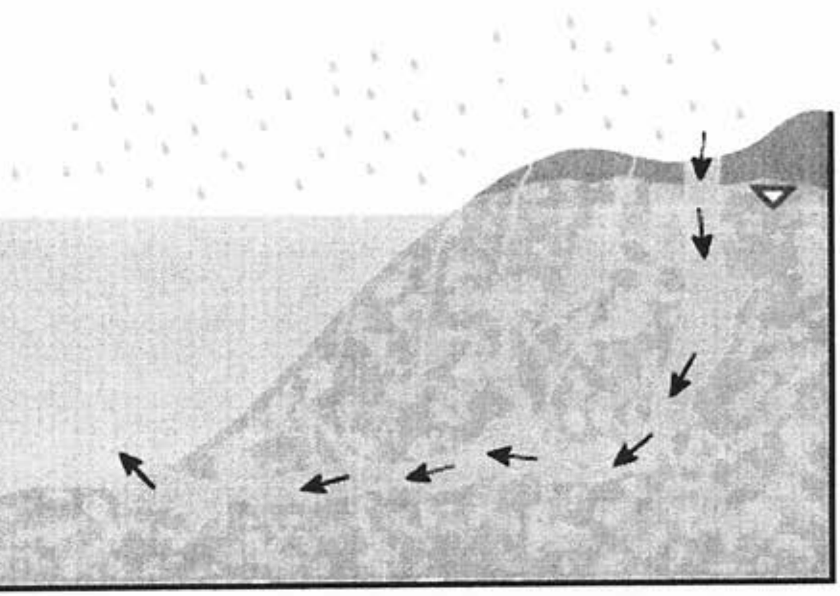


Figure 4-9. Conceptual model of Storm Reponse Type II. In (a), the prestorm water is relatively young and dilute, due to frequent rains. During storms (b), the relatively younger stormwater gradually infiltrates the karst system and dilutes the prestorm water, resulting in an initial decrease in conductivity.

Table 4-1. High Intensity/Point Recharge Events

	Storm Start	Total Rain (cm)	Duration (days)	Intensity (cm/day) Mean Daily	High Daily
E	8/23/02	2.18	3	0.73	1.85
E	10/30/02	2.72	2	1.36	1.73
	9/26/02	5.89	2	2.95	4.24
	10/11/02	5.84	2	2.92	3.25
	10/16/02	4.67	2	2.34	3.71
	11/16/02	5.03	3	1.68	4.01
	3/20/03	3.94	2	1.97	3.84
	4/7/03	3.45	4	0.86	2.06
	6/3/03	4.65	3	1.55	2.67
	6/7/03	2.44	1	2.44	2.44
	6/17/03	5.84	4	1.46	4.83
	9/22/03	7.77	2	3.89	6.45
	10/14/03	4.47	4	1.12	3.45
	10/26/03	6.40	4	1.60	3.05
	11/16/03	3.61	4	0.90	3.45
	11/27/03	2.64	2	1.32	2.62
	12/14/03	1.50	1	1.50	1.50
	12/17/03	1.60	1	1.60	1.60
	12/24/03	1.55	1	1.55	1.55

E Marked storm is an exception to the criteria for high intensity

Table 4-2. Low Intensity/Diffuse Recharge Events

	Storm Start	Total Rain (cm)	Duration (days)	Intensity (cm/day) Mean Daily	High Daily
E	2/21/03	3.94	3	1.31	3.35
	3/3/03	0.43	1	0.43	0.43
	3/6/03	1.57	2	0.79	0.91
	5/22/03	2.46	3	0.82	1.60
	7/5/03	1.12	7	0.16	0.36
E	7/18/03	5.16	7	0.74	3.38
	7/31/03	3.30	8	0.41	1.73
E	8/16/03	3.35	2	1.68	3.18
	8/26/03	8.26	10	0.83	1.35
	9/18/03	2.87	2	1.44	1.65
	9/12/03	3.71	5	0.74	1.93

E Marked storm is an exception to the criteria for low intensity determining the classification criteria I considered both the mean and high daily storm intensity so that a long, low-intensity storm with one day of high precipitation would not incorrectly be grouped as being high-intensity, or a high-intensity storm preceded by only a day or two of very small amounts of rain would not be mistaken for a low-intensity storm. For example, a storm on November 16, 2003 had a mean daily intensity of 0.90 cm/day, but a high daily intensity of 3.45 cm/day and a Type I storm response. This high daily intensity, averaged over three days, significantly lowered the mean daily intensity so that would appear to be a low-intensity storm if the high daily intensity were not considered.

There were five exceptions to the storm response behavior based on this classification (Tables 4-1 and 4-2). Two of these are storms that occurred on August 23 and October 30, 2002. These storms had mean daily intensities below 1.5 cm/day, but the conductivity initially increased after these storms. A possible explanation for these two storms is that the spring had not yet recovered from the drought, so the antecedent stage may have affected the conductivity response. The storm beginning February 21, 2003 had a mean daily intensity of 1.3 cm/day but a high daily intensity of 3.35 cm/day. A large snowfall occurred during February 15-18, however, so the February 21 storm was most likely accompanied by diffuse recharge from snowmelt, resulting in the observed conductivity decrease. A storm on July 18, 2003 lasted for 7 days and had a mean daily intensity of 0.74 cm/day, but a high daily intensity of 3.38 on the last day of the storm. The low intensity rain that preceded the high intensity day caused the conductivity response to decrease in response to this event. Another exception is a storm that occurred on August 16, 2003, for which the storm intensity was greater than 1.5 cm/day, but the conductivity in the spring initially decreased in response to this storm. Although this storm had a higher intensity than the other low intensity storms, the period preceding this storm had frequent low intensity rain, so the response of the spring was affected by antecedent weather conditions. In addition to antecedent weather conditions, local variations in precipitation may also have affected the spring response in all of these exceptions, so that the storm intensity within the spring capture zone was higher or lower than recorded at the Lancaster Airport weather station.

I believe that at Nolte Spring, the storm intensity affects the nature of the recharge to the karst aquifer. Recharge to karst systems is often defined as autogenic, where precipitation falls directly onto the karst land surface, or allogenic, where runoff from neighboring non-karst catchments enters the system through sinkholes, caves, or sinking streams (Ford and Williams, 1989) (Figure 4-10). However, the definitions of these recharge types are geologic as well as hydrologic. The capture zone for Nolte Spring is almost entirely underlain by carbonate rock and is therefore by definition an autogenic system only, but point recharge also occurs, as suggested by the presence of sinkholes and the rapid response to storms observed in the hydrograph and chemograph. To avoid contradiction with the geologic components of the definitions for autogenic and allogenic, the terms "point" and "diffuse" are used to describe recharge to the karst aquifer for Nolte Spring, based on storm intensity and conductivity response.

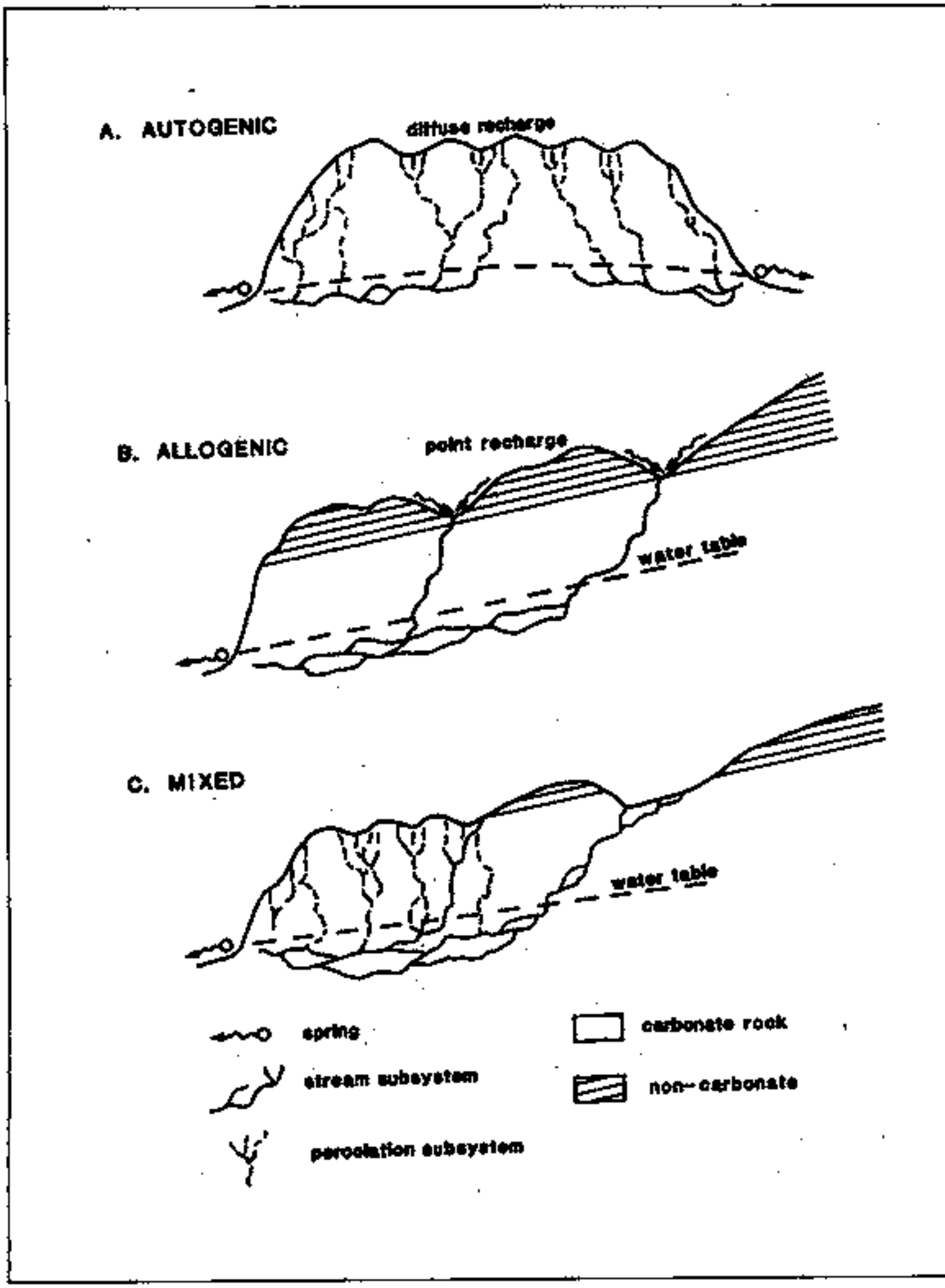


Figure 4-10. Karst recharge systems, from Ford and Williams (1989). Nolte Spring is thought to be most similar to (C), with elements of both autogenic and allogenic systems.

High Intensity Storms/Point Recharge

Storm reponses observed in the spring hydrograph and chemograph suggest that high intensity storms trigger a Type I storm response and point recharge (Table 4-1). High-intensity storms typically generate more overland flow because the infiltration capacity of the soil is quickly exceeded by the precipitation rate. This overland flow can enter the karst system rapidly through sinkholes, and is funneled directly from the surface into the conduits or fractures leading to the spring as point recharge. The Type I response observed in the chemographs of these storms indicate that point recharge storm water initially displaces the pre-event water rather than mixing with it because it is rapidly injected into the phreatic zone. Continuous monitoring data suggests that point recharge occurred during the drought in the Summer/early Fall 2002 season, at the end of the Spring 2003 season, during storms which occurred on June 4, June 7, and June 20, and throughout the Fall 2003 season.

Low Intensity Storms/Diffuse Recharge

Based on observations of the spring hydrograph and chemograph, low-intensity storms generally trigger a Type II response in the spring, which I believe is caused by diffuse recharge (Table 4-2). In the conceptual model for precipitation and recharge types (Table 4-3), low-intensity storms result in recharge that gradually infiltrates the soil layer to the bedrock interface, and flows horizontally through the epikarst until it finds a vertical fracture and then enters the karst system. Storm water from diffuse recharge events enters the karst system gradually, mixing with the pre-event water. During these events, the conductivity gradually levels off and decreases as the contribution of dilute

Table 4-3. Precipitation and Recharge Type Summary

Recharge Type	Seasons Observed	Storm Intensity	Storm Response
Diffuse	Winter 2003 Spring 2003	mean <1.5 cm/day	Type I
	Summer 2003	high <2.0 cm/day	
Point	Summer 2002 Fall 2002 Winter 2003	mean >1.5 cm/day	Type II
	Spring 2003 Summer 2003 Fall 2003	high >2.0 cm/day	

storm water to composition of the spring discharge becomes progressively larger than that of the pre-storm water and the stage recovers gradually following the storm.

The storm hydrographs and chemographs of the Summer 2003 season, as well as a Spring 2003 storm on May 25, resemble this behavior very closely. These storms are long, low-intensity storms, or multiple small storms, causing diffuse recharge. This model can also be used to explain the Type II storm response observed during the Winter 2003 season. Some of the snowmelt which contributed to the flooding occurred as discrete events, but there is constant melting at the interface between the ground surface and the bottom of the snow layer.

Summary

Both the stage and conductivity had a high degree of variability due to storms and extreme weather conditions, such as severe drought and extended periods of flooding, during the monitoring period. The lowest baseflow stage recorded occurred during the Summer 2002 season and the highest during the Winter 2003 season. The Summer and Fall 2002 data can be considered a drought end-member condition and the Winter 2003 data a flood end-member condition, with high and low conductivity, respectively.

Two types of storm responses were observed in Nolte Spring. Type I is an initial conductivity rise following a storm and a Type II response is an initial decrease in conductivity. Displacement of old water from the karst system by inflowing storm water in the initial storm response followed by more dilute water is believed to cause the Type I response. The Type II conductivity responses observed in the spring suggest that gradual mixing between the storm water and pre-storm water causes the initial decrease in conductivity.

The conceptual model for precipitation and recharge type at Nolte Spring includes high intensity storms, which result in point recharge and a Type I storm response, and low intensity storms, which result in diffuse recharge and trigger a Type II storm response in the spring. High intensity storms generate more overland flow than low intensity storms, which causes water to be transported rapidly from the surface to the karst aquifer through sinkholes and displace pre-storm water. Low intensity storms generate diffuse recharge, which infiltrates into the karst system through small fractures and mixes gradually with the pre-storm water, resulting in a Type II storm response. Point recharge occurred during the Summer/early Fall 2002, Fall 2003, and some storms during the Spring and Summer 2003 seasons. Diffuse recharge occurred during most of the storms in Winter 2003, and some storms in Spring and Summer 2003.

CHAPTER 5
GEOCHEMISTRY

Introduction

Samples collected during site visits were analyzed for major dissolved ions, including alkalinity recalculated as HCO_3^-. These samples generally reflect baseflow conditions because they were not typically collected during storms. The ion data and pH values measured in the field were plotted over the course of the monitoring period and used to calculate total dissolved solids (TDS), hardness, coefficient of variation of hardness (CV), the saturation index of calcite, SI_C, and the partial pressure of CO_2 (P_{CO2}). The variations in these parameters can be used show the response of the spring chemistry to changes in stage, recharge, or season, and to identify different flow pathways. The geochemistry results reported below have been divided into the same seasons as the continuous monitoring data.

For quality control purposes, duplicate samples and bottle blanks for ions and alkalinity were collected and analyzed, and periodically, a sample was rerun to check accuracy. A duplicate was run for approximately 20% of the dissolved ion and alkalinity samples. As described in the methods, the charge balance of all geochemical samples was calculated, and if the balance was ≥ 10%, the sample was rerun. If the balance did not improve following the rerun, the sample was not used for plots or geochemical modeling.

Five samples initially had an ion balance of ≥ 10%. Of these, two were a data entry error (which was corrected) and three were discarded. The three discarded samples, collected on October 17, 2002, October 31, 2002, and October 3, 2003, also had suspect pH and were eliminated from modeling. Because pH is an unstable parameter that is measured in-situ, reruns are not possible.

Results

TDS

TDS is the sum of all the dissolved ion concentrations in a sample, and ranged from 450.5 to 639.5 mg/L (Figure 5-1). The TDS followed a trend of general decrease through the Summer 2002, Fall 2002 and Winter 2003 seasons, from 639.5 mg/L in the sample collected on September 19, 2002 to 450.5 mg/L in the sample collected on March 7, 2003, in the Winter season. The September 19, 2002 sample was collected during a severe drought in the summer of 2002, and the March 7, 2003 sample was collected during a period of high baseflow and snowmelt.

From the Summer 2002 through Winter 2003 seasons, the inverse relationship between TDS and stage is clear (Figure 5-1). During the drought, there was very little storm water diluting the spring chemistry, and less water in the system in general, so that the ratio of dissolved material to water increased. As the spring recovered from the drought, with increased recharge, the spring chemistry was diluted and the TDS decreased. The conductivity decreased during the significant snowmelt that occurred in March 2003, when the stage was highest, and the TDS was the lowest, indicating dilute conditions. TDS data from Fall 2003 indicates a similar relationship, however it is unlikely that dilution is the reason for this pattern, as stage during the Spring and Summer 2003 seasons was higher than in 2002.

It is less clear whether a relationship between stage and TDS existed through the Spring, and Summer 2003 seasons. Following the period of dilute spring chemistry in Winter 2003, TDS was relatively stable through the Spring and most of the Summer of 2003. From the period between July 28 to September 14, 2003, the stage was less than 120 cm and the lowest since Fall 2002. Toward the end of this period, the TDS increased from 481.3 mg/L to 527.3 mg/L between September 5 and 18, 2003. This increase in the amount of dissolved material was more likely due to the greater degree of calcite undersaturation, which existed in the spring between July 28 and September 18, 2003, than the lower stage (see page 84).

Hardness and Coefficient of Variation

Although hardness is not a theoretically significant parameter, it is useful for describing the amount of precipitatable carbonate in groundwater (White, 1988). At Nolte Spring, the hardness ranged from 263.7 mg/L to 348.6 mg/L. This value is similar for other karst springs in Lancaster County (Moore, 1998). In contrast to the TDS, the hardness at Nolte Spring generally varies little over the monitoring period, because the concentrations of calcium and magnesium vary less than concentrations of some other ions, notably the alkalinity (as HCO_3^-), which varies more and consistently makes up approximately half of the total dissolved solids value. (Figures 5-2, 5-3, and 5-4).

The hardness of a spring is also useful in that the chemical variability of spring discharge can be described by the coefficient of variation of its hardness, which is calculated by dividing the standard deviation of the hardness by the mean hardness and expressing it as a percentage. The CV can be used to determine the dominant type of

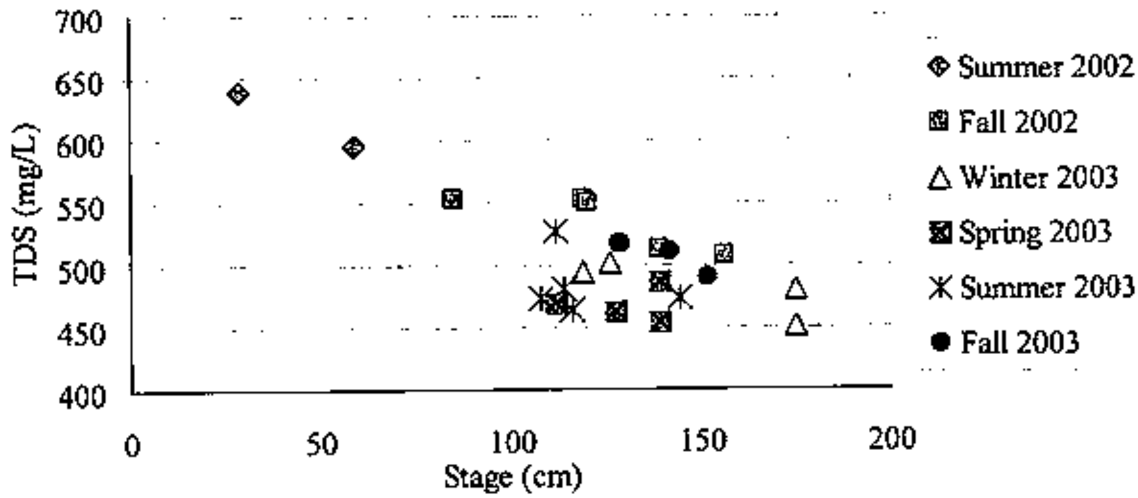


Figure 5-1. Stage vs. total dissolved solid (TDS) concentrations. An inverse relationship between TDS and stage is apparent in the Summer 2002, Fall 2002, early Winter 2003 and Fall 2003 seasons. During Spring and Summer 2003, the relationship is less clear.

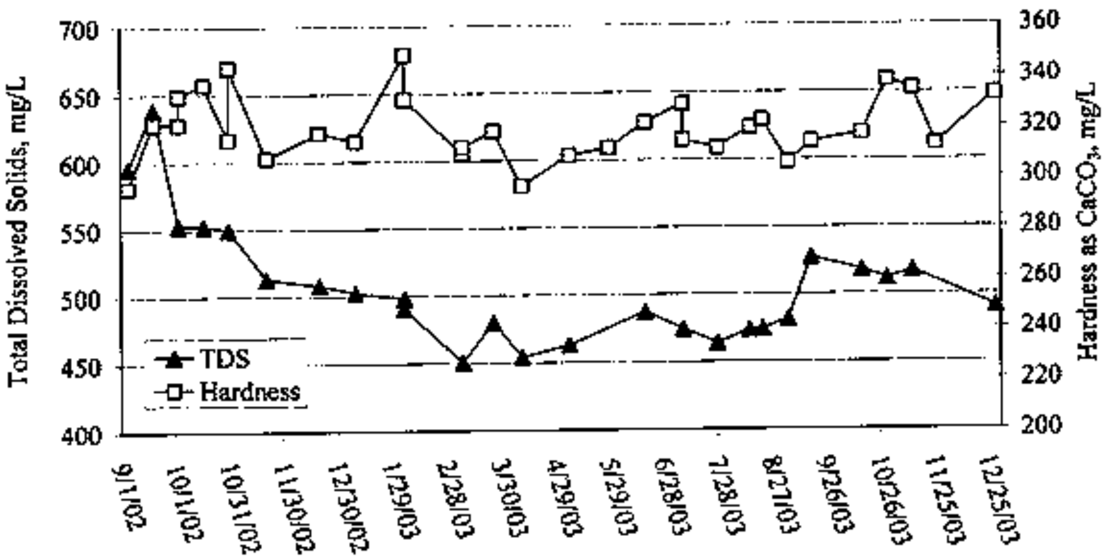


Figure 5-2. Total dissolved solids and hardness. The low hardness in the sample from July 28, 2003 is due to a low Ca^{2+} concentration. However, the ion balance is less than 5% for this sample.

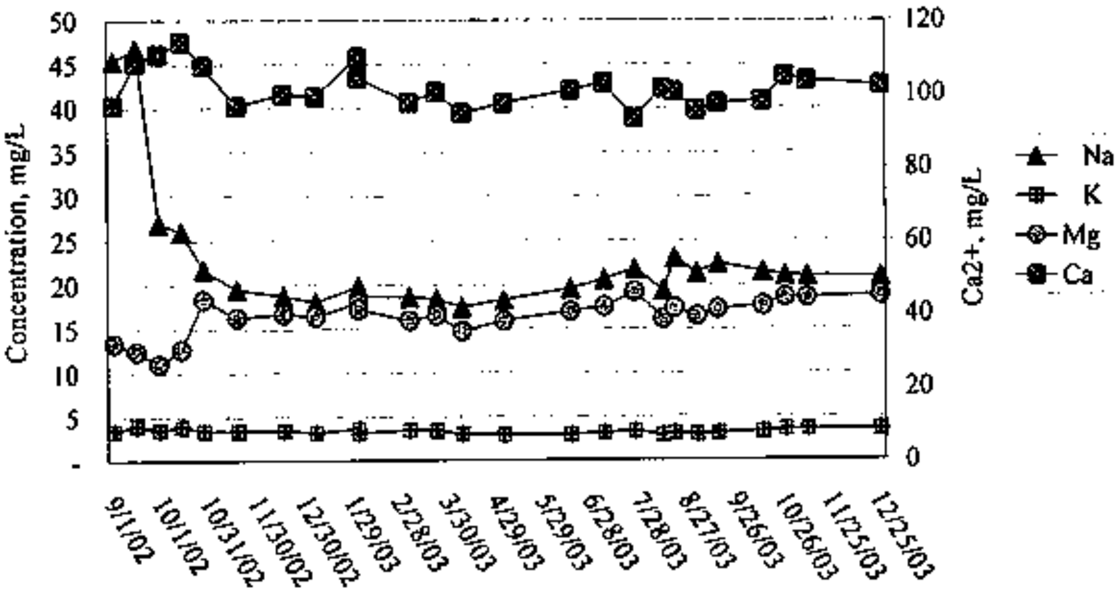


Figure 5-3. Cations concentrations. Na^{+} concentrations during the drought were approximately double the concentrations observed after the drought while Mg^{2+}, Ca^{2+} and K^{+} varied less after the drought. The decrease in Na^{+} concentrations after the September 26, 2002 storm suggest that accumulated salt may have been flushed from the spring during this storm, contributing to the observed conductivity peak of 1,708 μS/cm.

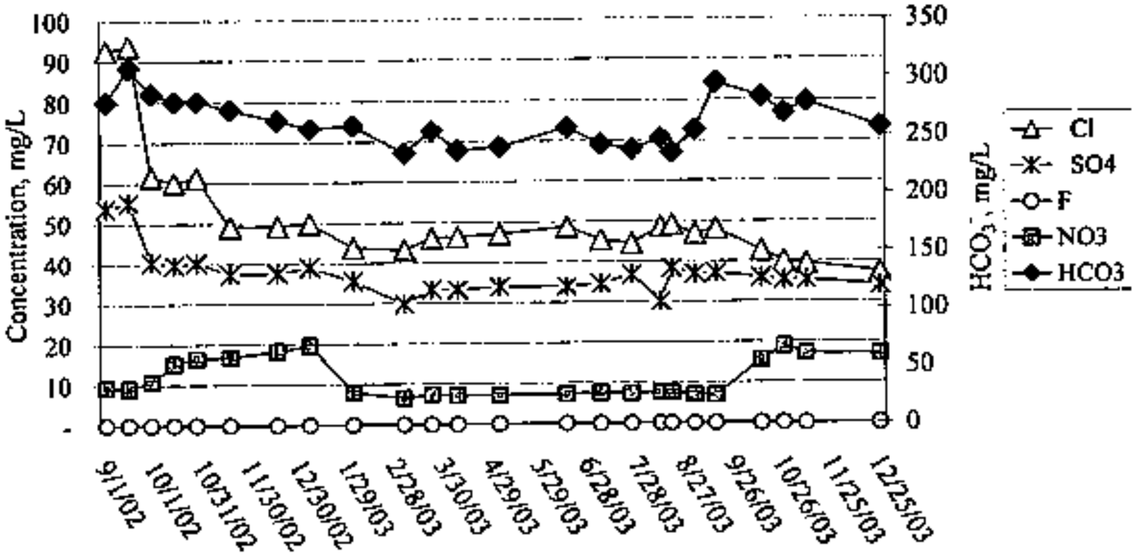


Figure 5-4. Anions concentrations. Unlike the SO_4^{2-} and Cl^-, NO_3^- concentrations increase after the drought. The NO_3^- concentration is particularly notable in the two apparently rapid shifts in early Winter 2003 and Fall 2003, which may be linked to the agricultural cycle (Mazengia et al., 2004). The decrease in Cl^- concentrations after September 26, 2002 supports the hypothesis that salt flushed by the September 26 storm caused the high conductivity peak observed at that time.

flow in a spring (Shuster and White, 1971; Wicks, 1997), where a CV greater than 5% indicates a flashy, conduit system with rapid recharge and transport rates. The CV at Nolte Spring is 5.4%, which is a low CV and indicates more stable chemistry than a conduit system. Based on this CV and geochemical variability, the karst aquifer for Nolte Spring is probably a matrix/fracture feeder system with some weakly developed conduits. Separate CVs calculated for each season did not differ significantly, which indicates that seasonality does not greatly affect this characteristic of the spring.

SI_C and P_{CO2}

SI_C ranged from –0.752 to 0.338 over the monitoring period, but only two of the samples collected at Nolte Spring had an $SI_C > 0$, which indicates that the spring was undersaturated with respect to calcite during most of the monitoring period (Figure 5-5). P_{CO2} ranged from $10^{-2.13}$ to $10^{-1.13}$ (Figure 5-6). Undersaturation in karst waters is common for both conduit and matrix/fracture flow systems, because the water typically does not reside in the system long enough to achieve equilibrium with the carbonate rock (White, 1988). However, karst systems dominated by matrix/fracture flow are generally closer to saturation than conduit systems, because the water in a matrix/fracture system has a longer residence time, and a lower water-rock ratio because it flows along smaller openings in the carbonate rock. The low SI_C values observed over the monitoring period in Nolte Spring suggests that the feeder system for the spring is composed primarily of solution-enlarged fractures and bedding plane partings rather than the small fractures that contribute to matrix flow. As indicated by the rapid response of the spring to storms,

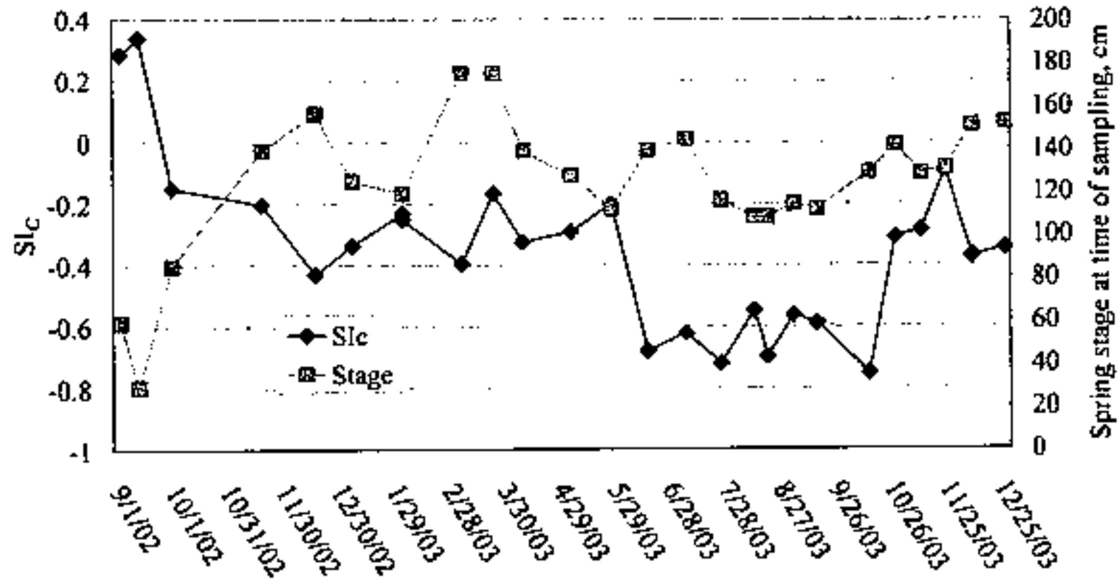


Figure 5-5. Calcite saturation index and stage at Nolte Spring. As the spring recovers from the drought in October 2002, the spring became undersaturated. During the period of high P_{CO2} during the growing season (Summer and early Fall 2003), the SI_C is the lowest of the monitoring period.

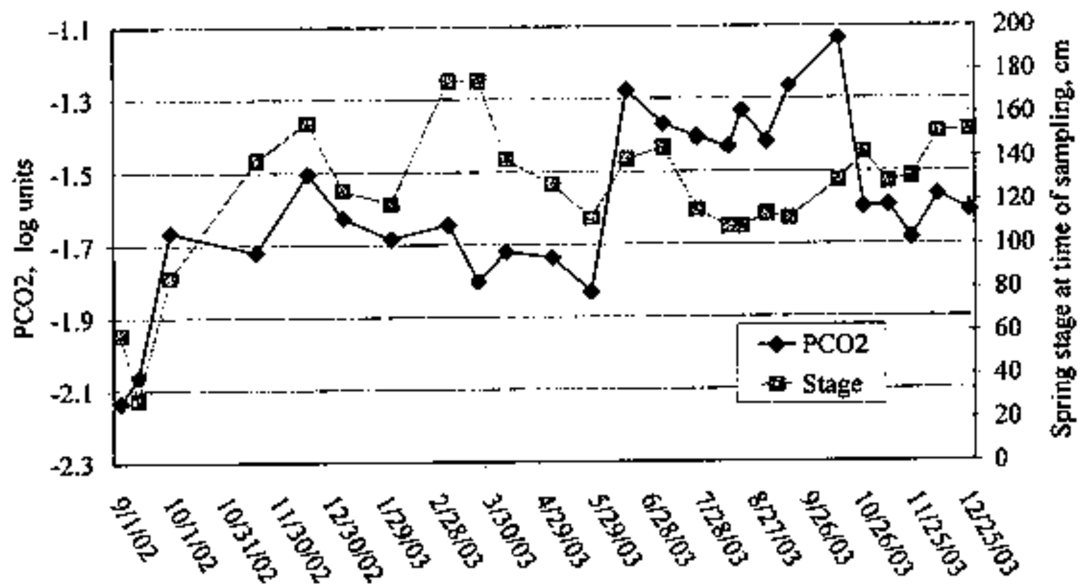


Figure 5-6. P_{CO2} and stage at Nolte Spring. The lowest P_{CO2} occurred during the drought, when plant activity and soil moisture were very low, and the lowered water table may have created a open-system conditions in the karst system, permitting outgassing of CO_2 from the groundwater. The highest P_{CO2} occurred during the Summer and early Fall of 2003, and is most likely associated with higher CO_2 production in the soil due to increased plant activity in the growing season.

there may be some larger fractures in the system, which contribute to the conduit-flow effects seen periodically.

Effects of the 2002 Drought

The two samples with $SI_C > 0$, collected on September 5 and 19, 2002, indicate that the spring water was near or at equilibrium with calcite during the drought of 2002. The SI_C of the September 5 sample was 0.284 and SI_C for the September 19 sample was 0.338, respectively. The fact that the spring was oversaturated during this time may be due to very slow groundwater flow, which allowed more time for the SI_C to increase. The P_{CO2} values in these two samples are $10^{-2.13}$ in the September 5 sample and $10^{-2.06}$ in the September 19 sample. These values are significantly lower than P_{CO2} during the rest of the monitoring period, and occur coincident with the lowest stage recorded (Figure 5-5). The low P_{CO2} values are probably due to the escape of CO_2 gas from the spring water into the soil layer and the atmosphere (Figure 5-6).

SI_C and P_{CO2} can be used to indicate whether a karst system is open or closed. White (1988) defines a closed system as one in which water enters the aquifer with a finite quantity of dissolved CO_2, which is gradually depleted through water-rock interactions along the flow path. Conversely, in an open system, the dissolved CO_2 in the groundwater is in equilibrium with the gas phase in the vadose zone, which supplies the CO_2 generated in the overlying soil. Because of the low stage during the drought, some normally phreatic (water-filled) fractures or conduits in the feeder system for Nolte Spring became open for long periods of time, effectively changing the karst system from a closed system to an open system.

Previous studies have examined the connection between elevated P_{CO_2} and the span of the growing season (Shuster and White 1972; Hess and White, 1993). During the growing season, more soil gas is generated in the O and A soil horizons and in both open and closed systems, the gas is transported to the phreatic zone by infiltrating water. Factors affecting CO_2 production in the soil include plant activity, soil temperature, soil moisture, and input of organic material. Due to the drought, the P_{CO_2} was lower in the spring because there was less plant activity and little to no soil moisture due to lack of recharge. This lack of recharge also prevented the transport of dissolved CO_2 to groundwater through infiltration. The P_{CO_2} is inversely related to the SI_C (Figure 5-7), thus the low P_{CO_2} during the drought also contributed the high SI_C observed in the samples collected during this time.

Recovery from the 2002 Drought

Although the drought status was not lifted from Lancaster County until January 2003, it is evident from the continuous monitoring data and the geochemical data that a large storm that occurred on September 26, 2002 initiated the end of the drought regionally. Dilution of the spring chemistry as a result of the large input of meteoric water to the karst system and the flushing out of water with a long residence time and high in dissolved ions is shown in the decreases in TDS and SI_C between the collection of the September 19 and October 3, 2002 samples (Figures 5-1 and 5-5). TDS decreased 86 mg/L, and the SI_C decreased from 0.33 to –0.15, a difference of 0.5 log units. These changes occurred as a large amount of dilute stormwater with very low dissolved ion content was input rapidly into the karst system and transported to the spring.

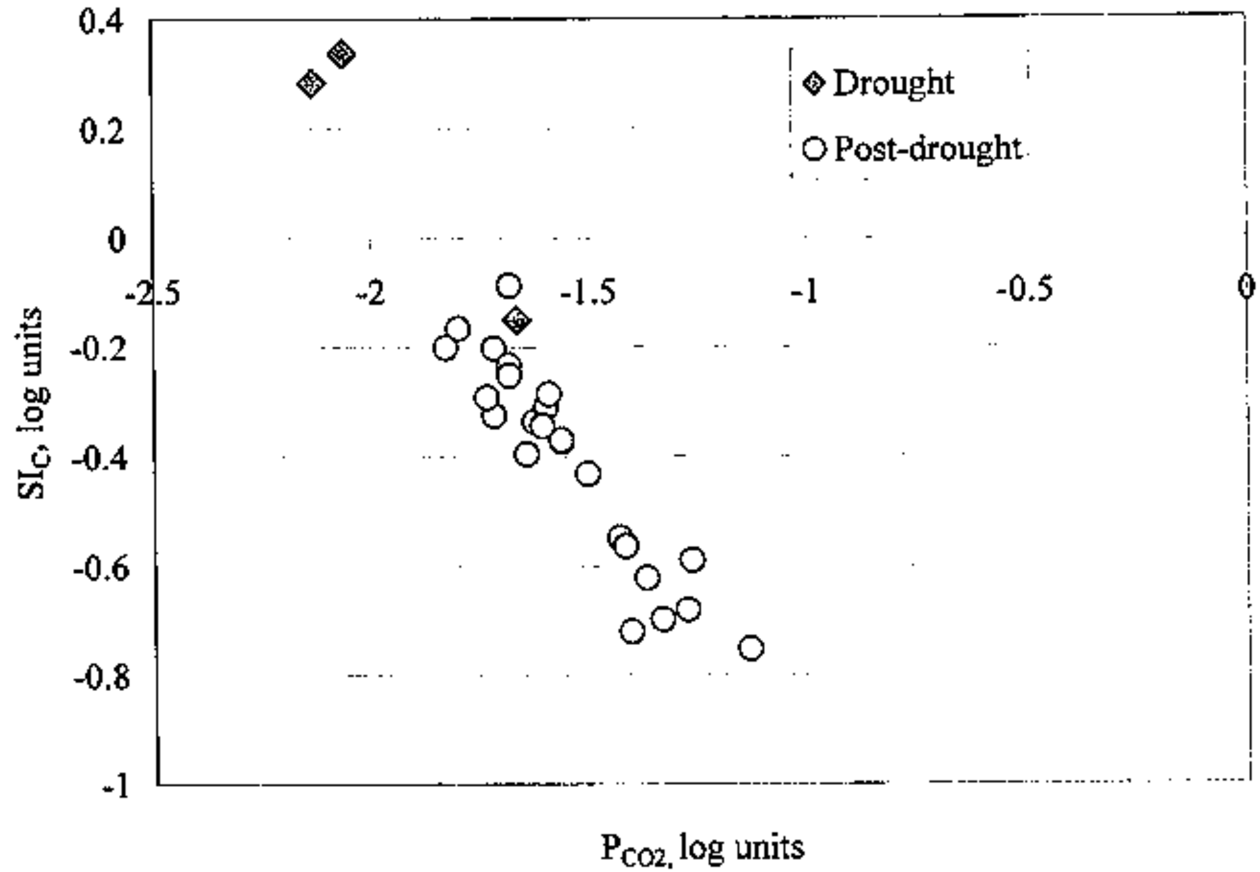


Figure 5-7. Relationship of P_{CO2} to SI_C. P_{CO2} is inversely related to SI_C, thus, when P_{CO2} was low during the drought due to the transition of the aquifer from a closed to an open system, the SI_C was close to saturation or slightly above.

The increase in P_{CO2}, from $10^{-2.06}$ in the September 19 sample to $10^{-1.66}$ in the October 3, 2002 sample indicates that the conduits, fractures, and pore spaces, which would have been open due to the lowering of the water table, were once again saturated due to the large amount of recharge from this storm, precluding the outgassing of CO_2 from the groundwater (Figure 5-6). Also, as mentioned above, the lack of recharge during the drought prevented CO_2 in soil gas from being transported to groundwater. The stormflow may have transported enough dissolved CO_2 to the groundwater to increase the P_{CO2} of the spring discharge on the order of 1.5 log units.

SI_C in all of the samples collected after the end of the drought were undersaturated, ranging from – 0.15 to – 0.33 in the samples collected between October 3, 2002, and June 18, 2003. The increased recharge following the 2002 drought resulted in more dilute water flowing through the karst system to the spring. This water was most likely discharged from the spring before it could approach equilibrium, as are most undersaturated karst waters in conduit-fed systems.

The 2003 Growing Season

The SI_C indicated a higher degree of undersaturation during the Summer and early Fall 2003 seasons, which ranged from –0.75 to –0.52 in the samples collected between July 9 and October 16, 2003 (Figure 5-5). During the Summer and early Fall 2003 seasons, the P_{CO2} ranged from $10^{-1.37}$ on July 9, 2003 to the monitoring period maximum of $10^{-1.13}$ on October 16, 2003. As mentioned above, previous studies have shown that the P_{CO2} in karst groundwater increases during the growing season as a result of increased soil gases. Since Nolte Spring is located in a primarily agricultural area, it is very likely that the high P_{CO_2} values measured during the Summer and early Fall 2003 seasons are a result of increased soil gas in the growing season. As the P_{CO_2} is inversely related to the SI_C, the SI_C decreased proportionally.

SI_C in samples collected after October 16, 2003 is slightly higher and ranges from -0.09 to -0.33 and is more similar to the SI_C during the late Fall of 2002. The mean P_{CO_2} in the same samples decreased to $10^{-1.62}$, which is more similar to the values seen in the late Fall of 2002 (Fall 2002 mean $P_{CO_2} = 10^{-1.66}$). The decrease in P_{CO_2} (and increase in SI_C) from the summer may indicate a decrease in soil gas based on the agricultural cycle.

Summary

Nolte Spring has the geochemical characteristics of both matrix/fracture and conduit flow springs. The water is unsaturated with respect to calcite most of the time, but is fairly close to equilibrium, indicating longer residence times for water in the karst system than are typically observed in larger conduit-fed springs. The hardness is relatively high, but the CV calculated for Nolte Spring indicates that it is at the upper boundary of the diffuse flow category of karst springs (Schuster and White, 1971). Examination of the CV with respect to the storm chemographs and hydrographs suggests that some solution-enlarged fractures or possibly small conduits contribute to Nolte's feeder system at least part of the time. The characterization of Nolte Spring as both a conduit and diffuse-flow spring also supports the conceptual model of a spring that is fed by a combination of both diffuse and conduit type recharge.

Also evident in the water chemistry of Nolte Spring are the effects of the 2002 drought and subsequent recovery on the spring, as seen in the TDS, SI_C, and P_{CO_2} data.

TDS and SI_C are higher during the drought than at any other time during the monitoring period, due to the increased ratio of dissolved ions to water, and the P_{CO2} is the lowest of the monitoring period due to lower plant activity, soil moisture, and recharge. Rapid changes in these three parameters can be seen following the September 26, 2002 storm, a large recharge event which initiated recovery from the drought in Nolte Spring and the surrounding area. The spring chemistry became more dilute, and the P_{CO2} increase indicates that the karst system for Nolte Spring may have changed from an open to a closed system. Effects of the growing season in the Summer and early Fall 2003 seasons on the spring chemistry could be seen in the P_{CO2} and SI_C. The increased CO_2 in the soil, as a result of increased plant activity and recharge, was transported to the groundwater. The increased CO_2 input to the groundwater caused the P_{CO2} to increase and the SI_C to decrease.

CHAPTER 6
SEDIMENT

Introduction

The sediment results presented in this chapter are grouped into the filtering results and SEM/EDS results, with a discussion of each immediately following. Samples were collected during site visits and by the automatic sampler during storm events. The seasonal divisions used for the continuous monitoring and geochemistry data have been applied to both.

Filtering Results

Seasonal Samples

Filtering results from the samples collected during site visits were used to chart the long-term variability in sediment concentrations over the monitoring period, and to determine if there was a seasonal pattern. The suspended sediment concentrations from the samples collected during the site visits ranged from 0 to 75 mg/L. The 75 mg/L sample, collected on July 9, 2003, is likely anomalous as it is almost double the concentration of the next highest sample collected on September 18, 2003 (Figure 6-1). The high sediment content of the July 9 sample is due to a large amount of calcite on the filter, which is discussed later in this chapter.

Samples collected during the Summer and early Fall 2002 seasons and the Summer 2003 season generally had the highest suspended sediment concentrations (Figure 6-1). However, it is unlikely that the occurrence of high sediment concentrations at this time of year is a seasonal or stage effect (Figure 6-2) because hydrologic and geochemical conditions during Summer 2002 were different from those during Summer

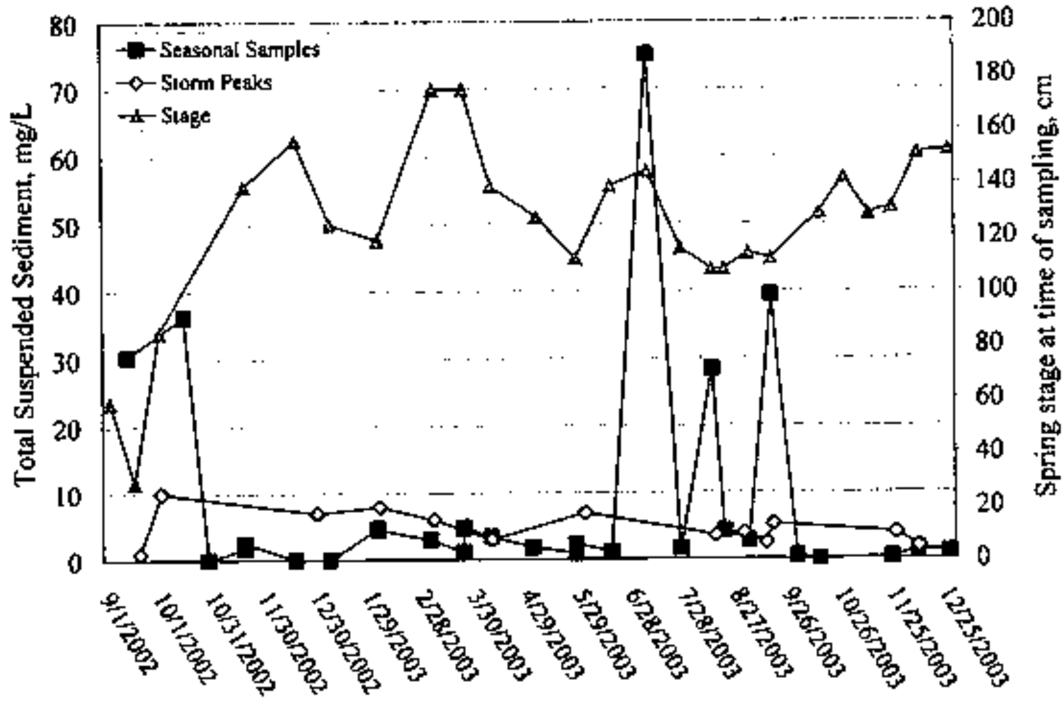


Figure 6-1. Total suspended sediment concentrations and stage variations for seasonal and storm peak samples from Nolte Spring. The highest sediment concentrations were observed in the seasonal samples during the Summer and early Fall 2002 and the Summer 2003 seasons. Storm peak sediment concentrations were often lower than the seasonal samples collected close to the same time as the storm.

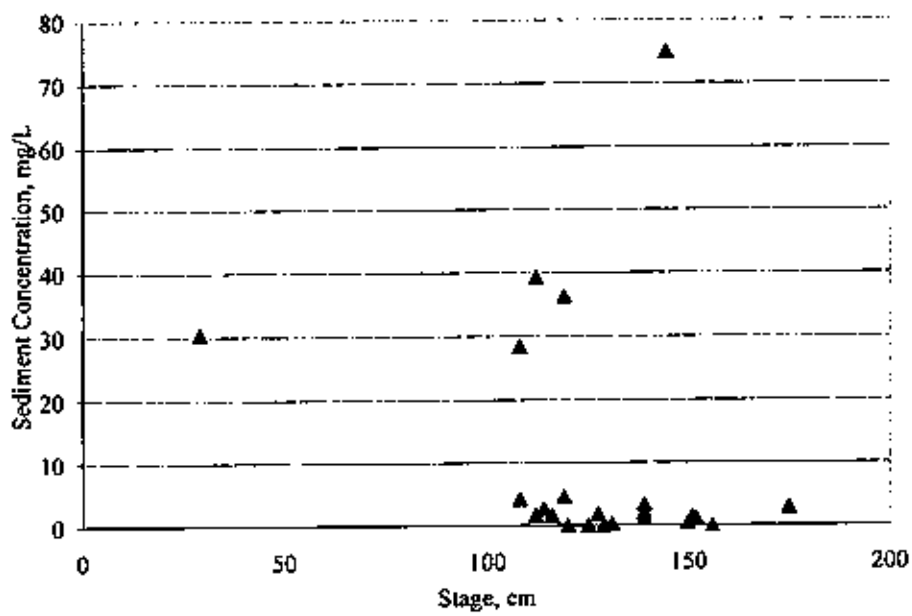


Figure 6-2. Relationship of sediment concentration to stage. Sediment concentration does not appear to be determined by stage.

2003. The mineralogy of these samples and the geochemical data from the seasons in which they were collected suggests that two diverse geochemical environments in the spring may have lead to the high sediment concentrations and the type of sediment discharged. The conductivity, TDS, SI_C and P_{CO2} data showed that during the Summer 2002, the spring had higher conductivity and TDS, with, slightly saturated discharge and low P_{CO2}, while the Summer 2003 had lower conductivity and TDS, the discharge was undersaturated, and P_{CO2} was high (Figure 6-3). The relationship between sediment mineralogy and the geochemical conditions in the spring is discussed in a later section of this chapter.

Storm Samples

The samples collected by the automatic sampler during storms were analyzed with the intention of charting the variability in sediment over a single storm, and to determine if the total amount of sediment discharged during storms varied from storm to storm. Out of 31 precipitation events observed in the stage, conductivity, and precipitation record over the 17-month monitoring period, the automatic sampler collected samples from 13 storms. When a small storm occurred, with a larger storm immediately following, the automatic sampler activated during the smaller storm, so that the sampler did not sample during many of the larger storms. Only one storm during the two-week interval between site visits could be collected by the sampler.

Sediment concentrations, particularly storm sediment concentrations, were lower than expected (Figure 6-1). The peak sediment concentration observed during storms ranged from 0 to 10 mg/L (Figure 6-1), and the concentration of suspended sediment in the storm samples was typically lower than suspended sediment in the samples collected during site visits close to the time of the storm. For example, the September 22 storm, which occurred when the stage was the lowest of the monitoring period and the baseflow sediment concentration was one of the highest, had the lowest peak sediment concentration of the storm collected by the automatic sampler. Sediment concentrations in karst aquifers are often higher during storm pulses (Ryan and Meiman, 1996), so it is possible that the storm sediment results may have been biased by the automatic method of sample collection. However, when I visited Nolte Spring during a storm on December 11, 2003, I observed that the spring discharge was clear, and the sediment concentration of the sample I collected was 1.4 mg/L, which suggests that discharge from Nolte Spring may have a lower sediment concentration during storms. A possible reason for lower storm sediment concentrations at Nolte Spring is the absence of areas in the karst aquifer where sediment would accumulate and be flushed by the storm pulse. These areas would be similar to sumps in a cave passage or shallow conduits where perched conditions exist between storms, but it is unlikely that the karst aquifer for Nolte Spring is large enough for these features to have developed.

Although the sediment concentrations in the storm samples were lower than those collected during site visits, the sediment flux through the spring was probably higher, as suggested by values estimated for Nolte Spring (Figure 6-4). The sediment flux was calculated by multiplying the peak sediment concentration by the peak discharge of the storm, with the assumption that peak sediment flux coincides with peak discharge.

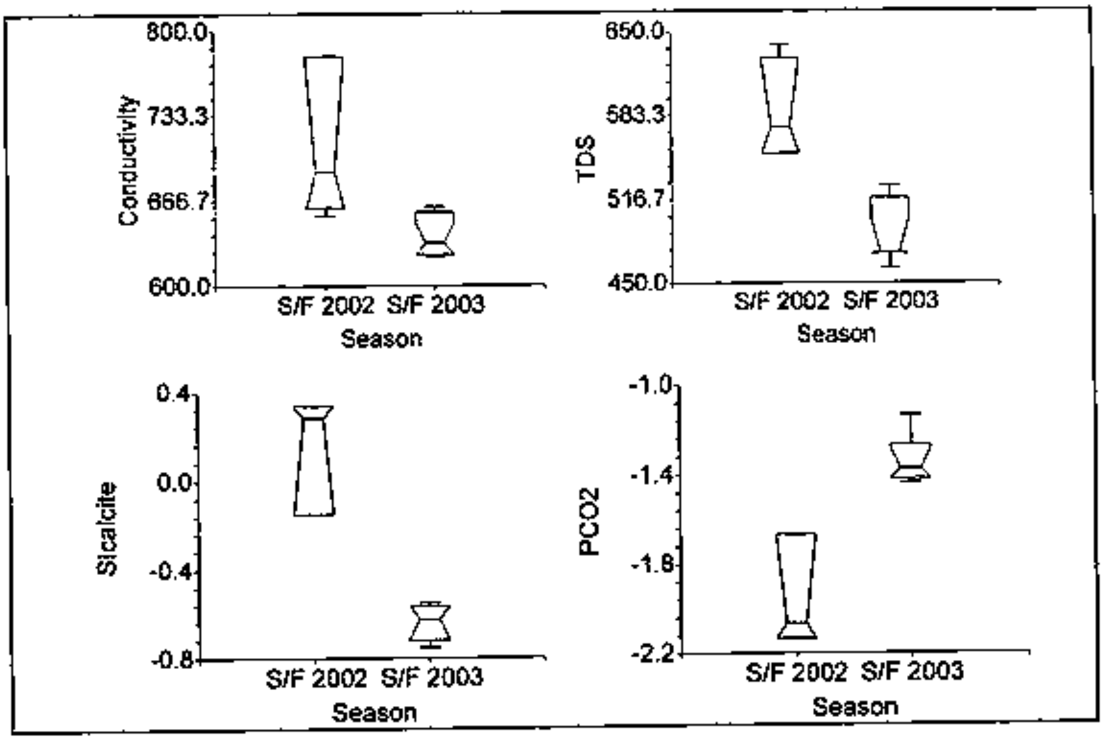


Figure 6-3. Box plots of conductivity, TDS, SI_C and P_{CO2} for Summer/early Fall 2002 and Summer/early Fall 2003. Calcite was observed in both of these seasons, but geochemical parameters of Summer 2002 were different from Summer of 2003.

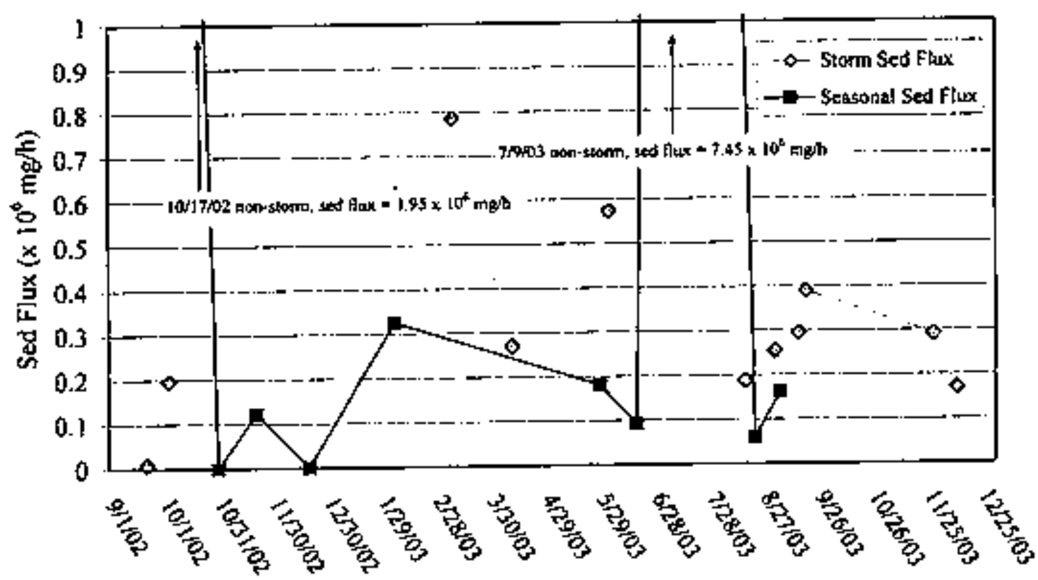


Figure 6-4. Seasonal sediment flux and estimated storm flux values. With the exception of two outliers, the storm sediment flux estimated from stage and discharge data is generally higher than the sediment flux calculated for the samples collected during site visits.

Discharge values were obtained by qualitatively fitting the peak stage of each storm to the corrected stage-discharge curve constructed for the spring (see Chapter 3, Figure 3-2). Except for two outliers, the sediment flux values for storms are typically higher than non-storm values, which indicates that the storm sediment concentrations are lower simply because there is more water, and more sediment is actually being discharged than during non-storm periods.

One of the initial tasks of this study was to examine the variations in suspended sediment over the course of a single storm. Unfortunately, suspended sediment often varied within or near the estimated noise range of ±1mg/L during a storm, making it difficult to hypothesize about the variations over an individual storm. These low concentrations also made it difficult to use particle size distribution and X-ray diffraction for characterization.

SEM Results

Scanning electron microscopy (SEM) was used to examine sediment morphologies and energy-dispersive spectroscopy (EDS) was used for qualitative elemental analysis and identification of mineral grains for selected seasonal and storm samples. Samples with both low and high suspended sediment concentrations were analyzed, but a more solid interpretation of general mineralogy could be made from the samples with the highest sediment concentrations. These samples often had a more uniform mineralogy, which made an estimate of bulk composition easier.

Mineralogy

Both seasonal and storm sediment samples for each season appear to have similar mineralogy (Figures 6-5 and 6-6). Although there is little evidence for seasonality, samples collected during the Summer/early Fall of both 2002 and 2003 had a dominant mineralogy of calcite (Figure 6-5). During the rest of the year, the mineralogy of the sediment was dominantly siliciclastics, such as clay and silt, or a mix of calcite and siliciclastics.

Samples composed mostly of calcite were easier to identify than those that were mostly siliciclastics, or a mixture of siliciclastics and calcite. The uniformity of the mineralogy in the calcite samples was often visible with 60X magnification or less (Figure 6-7). Under very high magnification (up to 1800X) and with the aid of EDS, the predominance of calcite is clear (Figure 6-8). Additionally, sediment concentrations of the calcite samples were generally higher than those of the siliciclastic samples (Figure 6-5).

It was more difficult to assign mineralogies to the two other sediment types observed in samples from Nolte Spring, one of which was a mixture of siliciclastics and calcite, and the other a siliciclastics only. In these samples, it was either hard to distinguish individual particles (Figure 6-9), or there were often only a few small particles on the sample, from which a determination of overall composition had to be made (Figure 6-10).

A predominance of calcite was observed in the sediment samples from the same time of year during both 2002 and 2003 (Figure 6-5 and 6-6). However, as mentioned in

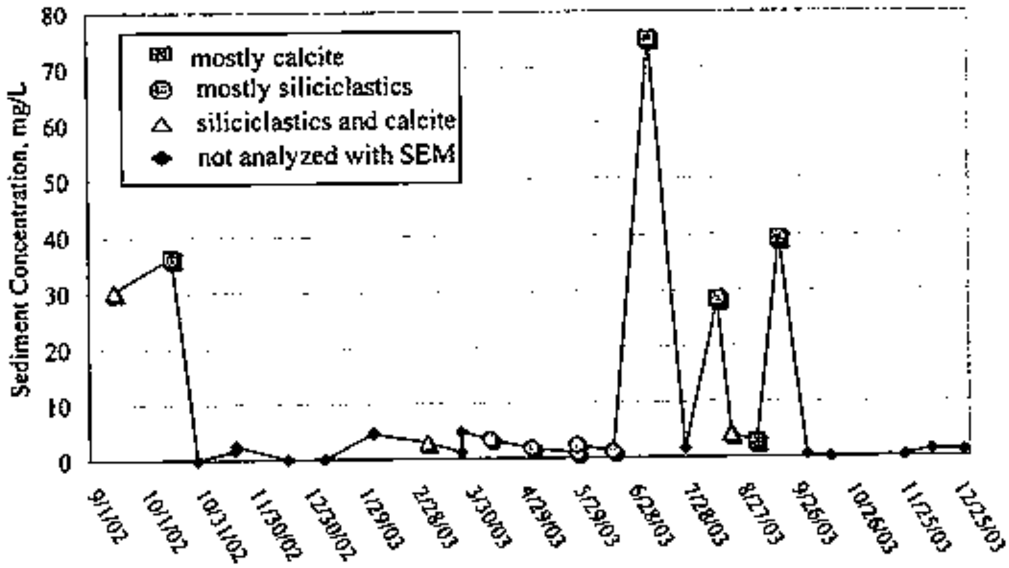


Figure 6-5. Sediment concentration and mineralogy for seasonal samples. Data points marked with a symbol for mineralogy were analyzed with SEM/EDS. Calcite was observed mostly in the samples from the Summer/early Fall seasons of 2002 and 2003, whereas siliciclastics were mostly observed during the Winter and Spring 2003 seasons.

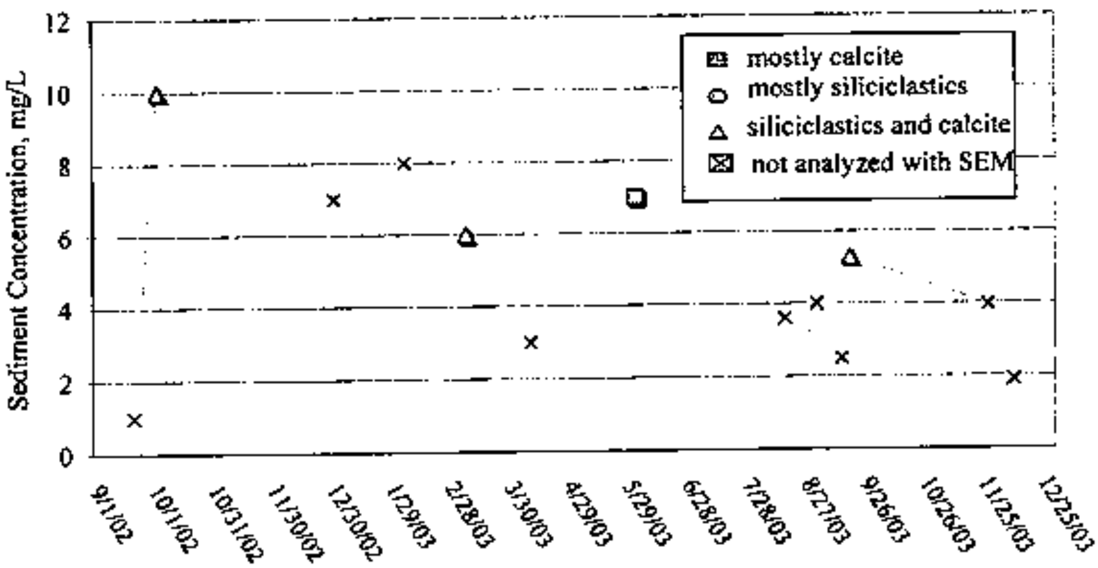


Figure 6-6. Sediment concentration and mineralogy for storm peaks. Data points marked with a symbol for mineralogy were analyzed with SEM/EDS. Except for the mineralogy of sediment collected during a storm on June 3, 2003, the storm sediment mineralogy closely follows the seasonal mineralogy.

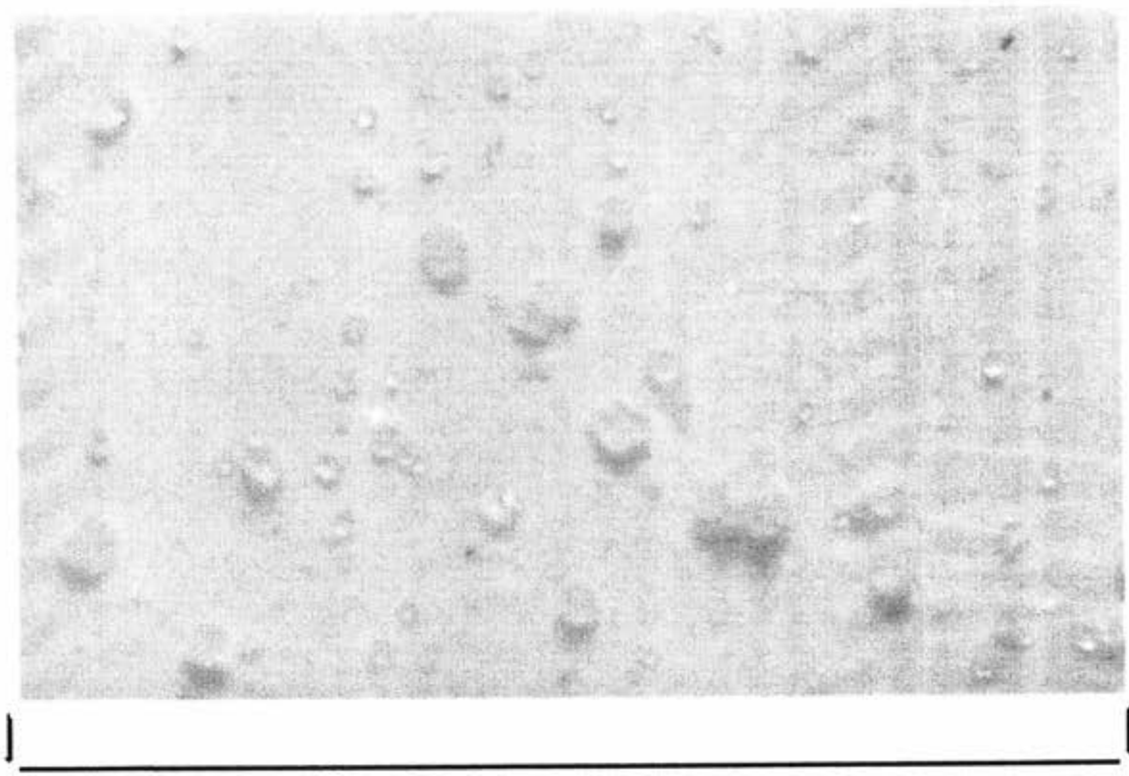


Figure 6-7. Photograph of calcite particles from the sample collected on July 9, 2003 at low magnification (60X). Even at low magnification, the uniformity of the mineralogy is apparent in the calcite samples.

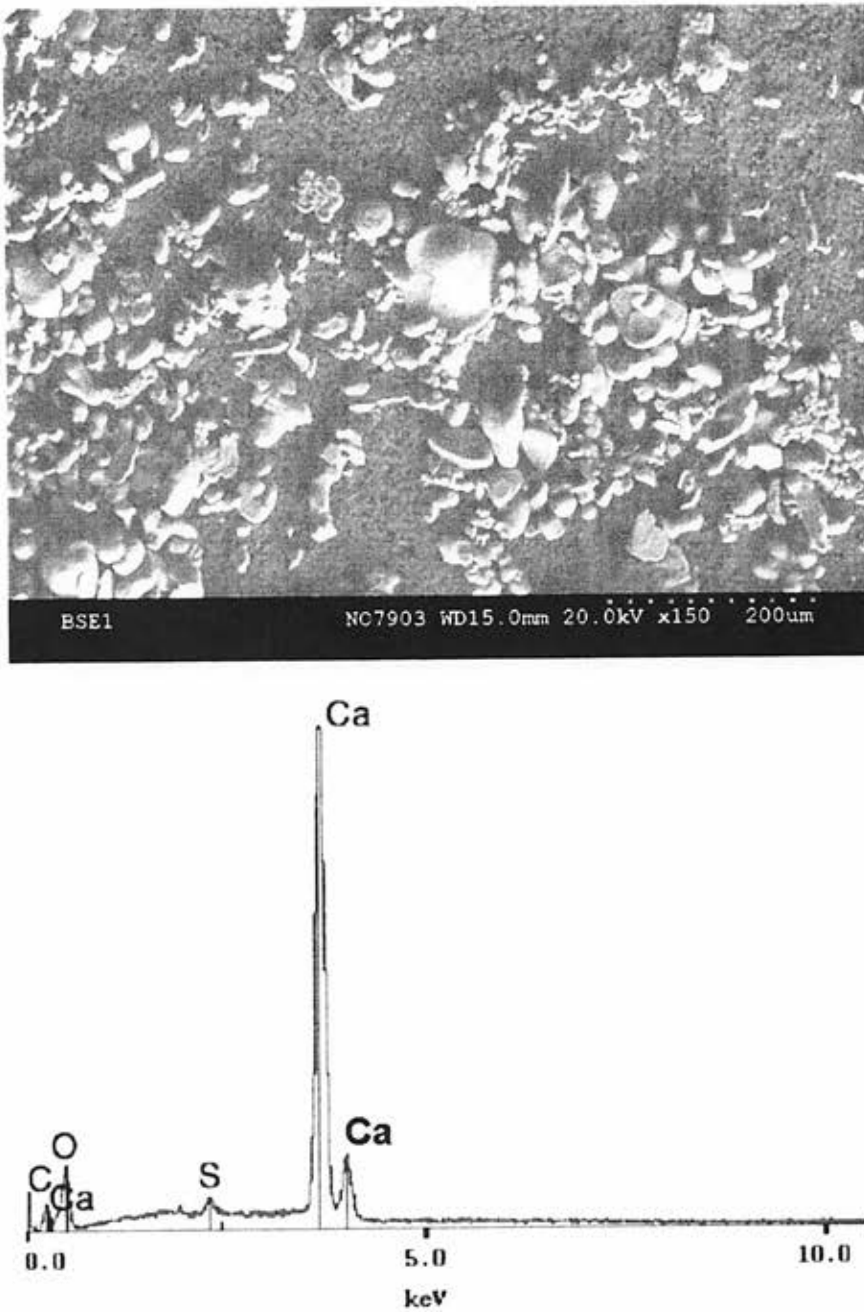
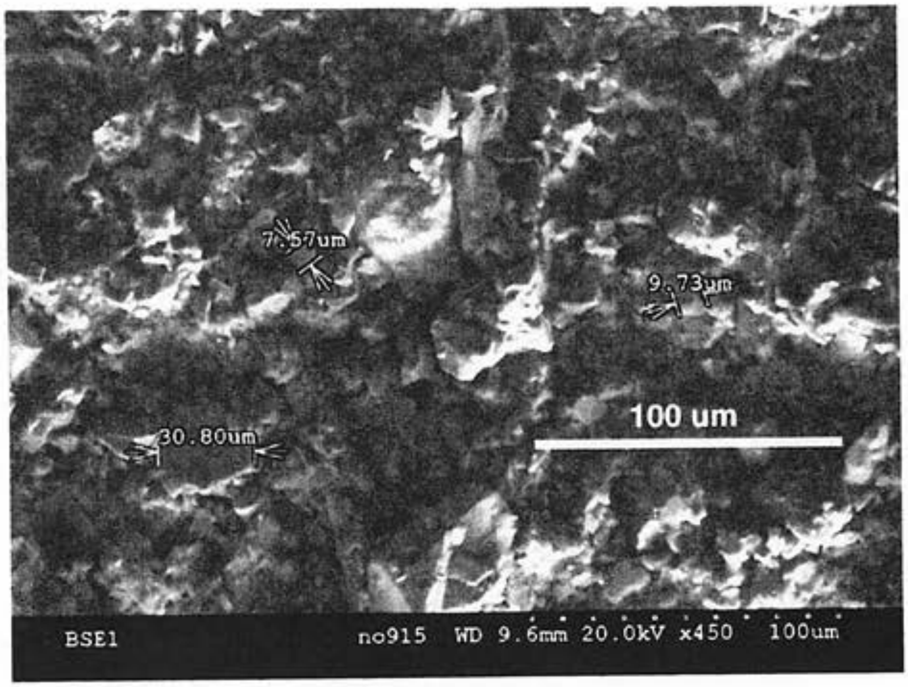


Figure 6-8. SEM photograph and EDS spectrum of the sample collected on July 9, 2003 from Nolte Spring. This sample had the highest sediment concentration of the monitoring period, and the EDS spectrum over the area shown in the photograph has a high calcium peak, indicating that most of the particles in the photograph are composed of calcite. The reason for the small sulfur peak has not yet been determined, but may be from the presence of a sulfate mineral in the sample or the result of contamination from the sample preparation area of the SEM laboratory.



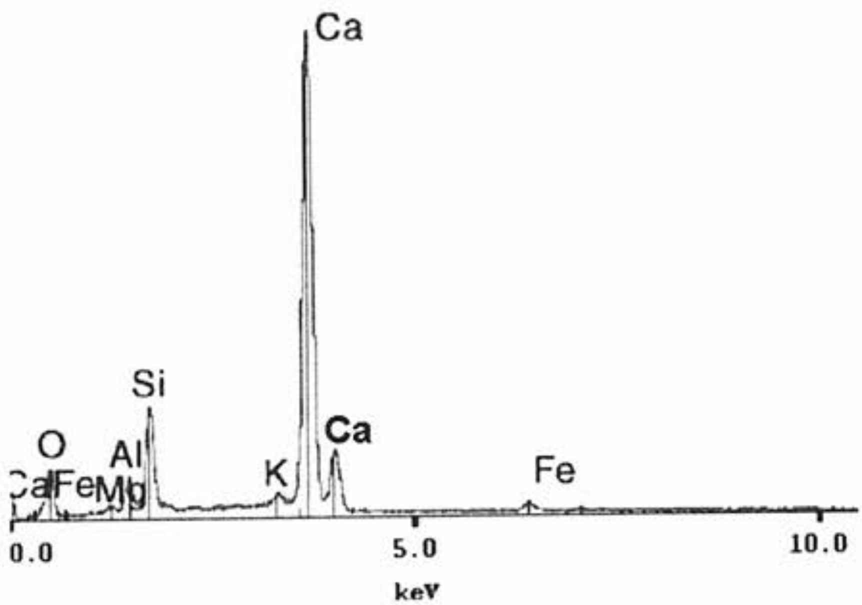


Figure 6-9. SEM photograph and EDS spectrum of a sample classified as a mixture of calcite and clay. This sample was collected on September 15, 2003. The EDS spectrum is for the area shown in the photograph. XRD indicated the presence of quartz, calcite, muscovite, and chlorite on this sample.

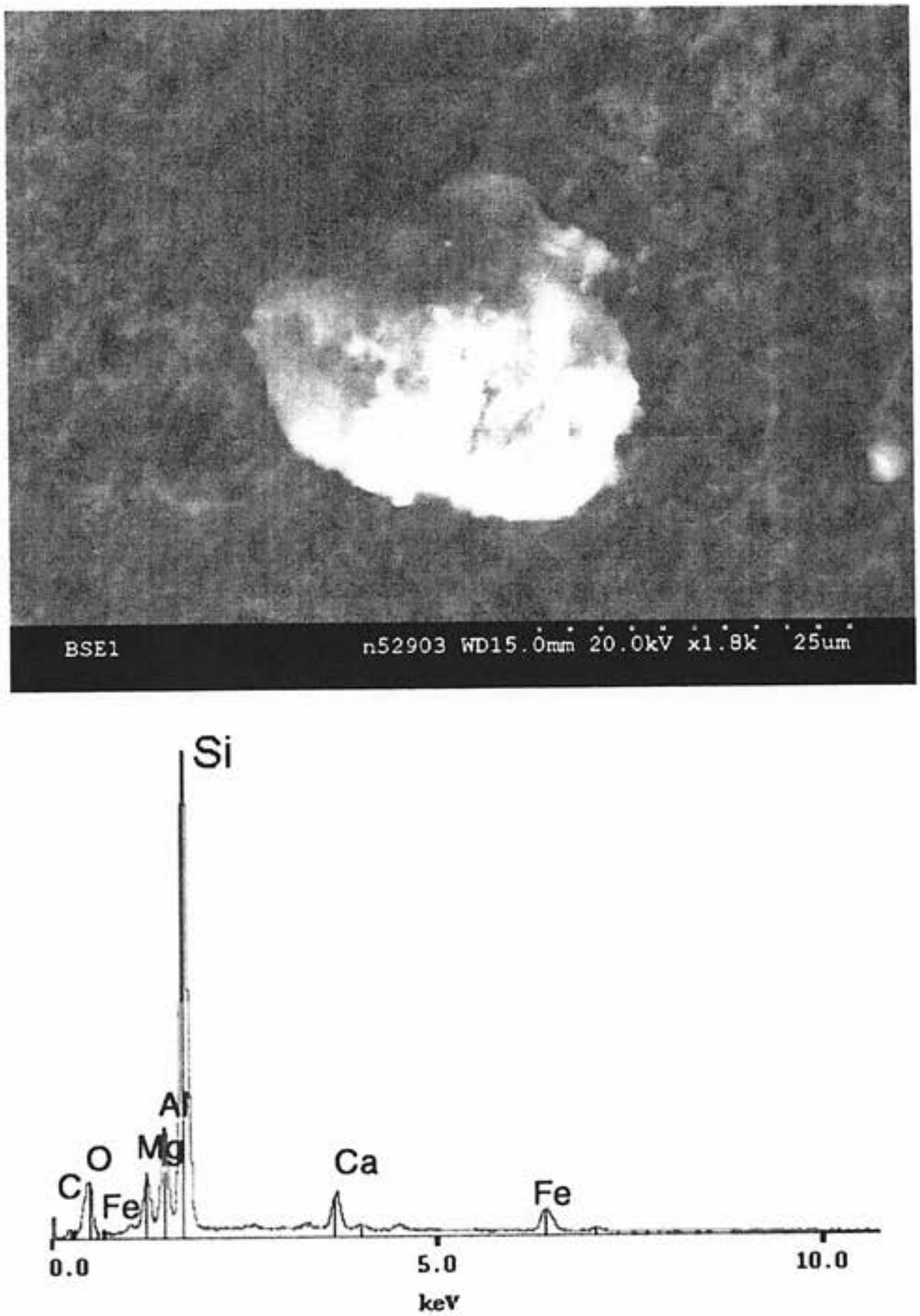


Figure 6-10. SEM photograph and EDS spectrum of a siliciclastic particle. The sample in which this particle was observed was collected on May 29, 2003 and classified as mostly siliciclastics. The samples composed mostly of siliciclastics generally had small amounts of sediment, so XRD was not able to identify the mineralogy of the grains in these samples.

a previous paragraph, there was little evidence observed for the influence of seasonal change on the variations in mineralogy of the sediment discharged from Nolte Spring. The hydrologic conditions during the two periods in which calcite was observed were different. The Summer/early Fall 2002 seasons were extremely dry, whereas the Summer 2003 season had frequent precipitation and a significantly higher stage. Additionally, the geochemical conditions in the spring during the drought of 2002 were very different from those during the Summer of 2003. More samples would have to be collected and analyzed for mineralogy before a direct connection between stage and the presence of calcite could be established, but stage does seem to affect the groundwater geochemistry at Nolte Spring, as discussed in Chapter 5.

The P_{CO2} and SI_C data from Nolte Spring was divided into three groups: low P_{CO2}/high SI_C, intermediate P_{CO2}/SI_C, and high P_{CO2}/low SI_C. Low P_{CO2}/high SI_C was observed during the drought of 2002, intermediate P_{CO2}/SI_C was observed during the mid Fall 2002 to Spring 2003, and high P_{CO2}/low SI_C occurred during the growing season in the Summer and early Fall of 2003 (as discussed in Chapter 5). There is some evidence that geochemistry in the spring, specifically the P_{CO2} and SI_C plays a role in the mineralogies of the sediment observed in Nolte Spring. Only the low P_{CO2}/high SI_C and high P_{CO2}/low SI_C groups will be discussed, because calcite was observed mostly in the samples collected during these two geochemical groups during the drought of 2002 and growing season of 2003, respectively. The mineralogy observed during the period of intermediate SI_C/P_{CO2} was mainly clay and other siliciclastics, which was expected. There are several exceptions, such as a storm sample from June 3, 2003 and samples from late Fall 2002. The presence of calcite is noteworthy, as its presence was not expected in Nolte Spring, given the fact that the spring is undersaturated with respect to calcite most of the time.

Calcite During the 2002 Drought

One scenario for the existence of calcite in the spring during the 2002 drought might be precipitation of calcite in the spring mouth, although it is less likely since the SI_C observed is close to equilibrium. The model for calcite precipitation in caves presented by White (1988) includes CO_2 degassing from infiltrating waters, which have acquired CO_2 from the soil ($P_{CO2} \sim 10^{-1}$) and have higher CO_2 pressure than the atmosphere of the cave ($P_{CO2} \sim 10^{-2.5}$) (Figure 6-11). In the case of Nolte Spring, the low stage during the drought of 2002 may have caused the larger fractures and the conduits that are usually phreatic to drain, allowing dissolved CO_2 in the groundwater to escape into the air-filled spaces and lowering the P_{CO2}, which would in turn cause the SI_C to increase (Figure 6-12) and drive the precipitation reaction for calcite. Although calcite precipitation is kinetically inhibited, I have observed calcium carbonate crust growing on the water level sensor for the automatic sampler that developed between site visits (two to four weeks). Based on these observations, I believe that calcite could have precipitated within the time frame of the drought

Another possible explanation is that the calcite was precipitated in another part of the spring's feeder system, where more saturated conditions prevailed. The variations in sediment mineralogy observed in Nolte Spring suggest that there may be multiple sources for sediment in the spring's karst system, since the spring's storm chemographs provide

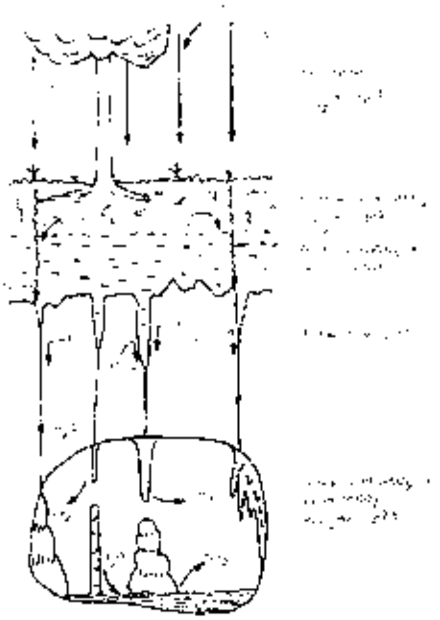


Figure 6-11. Model of calcite deposition in caves, from White (1988). Calcite precipitation may have occurred in a similar manner at Nolte Spring during the Summer and Fall 2002 seasons and the Summer 2003 season, based on P_{CO2} and SI_C data.

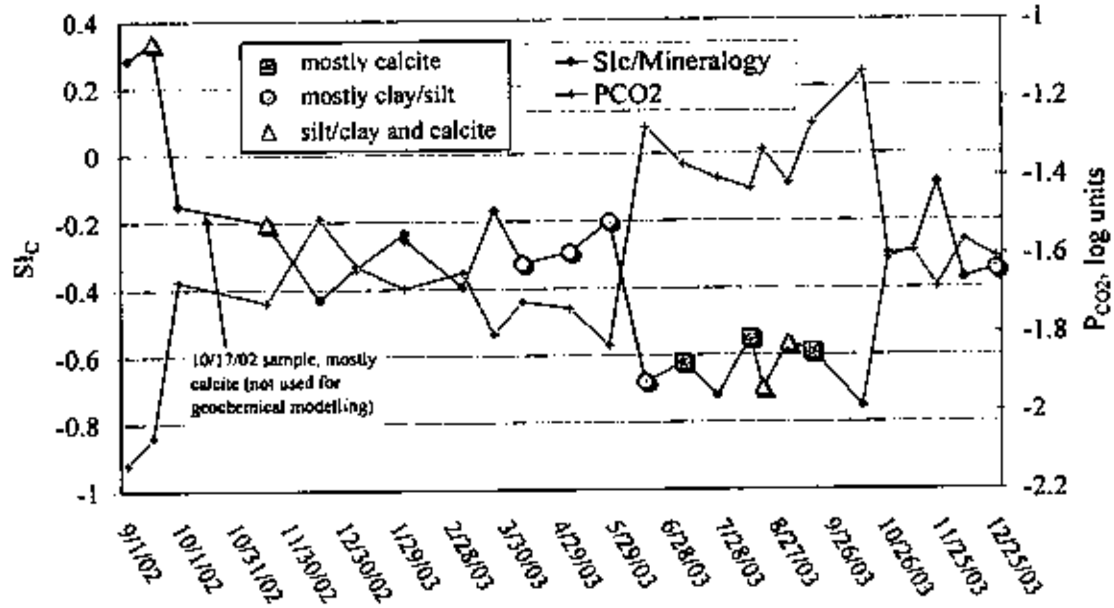


Figure 6-12. Geochemistry and mineralogy. Mineralogy of samples collected concurrent with the geochemistry samples are marked on the SI_C data points. The presence of calcite in the spring when SI_C is high and P_{CO2} is low is attributed to calcite precipitation, whereas the presence of calcite when P_{CO2} is high and SI_C is low is attributed to plucking of speleogenic calcite particles from the wall rock by water flowing through the aquifer.

evidence of mixing between different groundwater circulation systems (see Chapter 4, Figure 4-1). As discussed in Chapter 3, the capture zone calculated for the spring is not very large, but the SI_C at the spring mouth was at saturation during the drought, so it is possible that more saturated conditions exist in an area of the spring's feeder system further from the spring.

Some calcite morphologies observed during the drought suggest that vadose growth at the soil/bedrock interface may also be a possibility for the presence of calcite in the spring (see page 104). Although the overlying soils are generally well-leached, there is carbonate available at the soil-bedrock interface from which calcite could precipitate. The lack of moisture during the drought may have caused supersaturated conditions sufficient for calcite to form, become disarticulated and be transported into the aquifer by storm water.

Calcite in the 2003 Growing Season

However, calcite precipitation in the spring mouth cannot be the reason for the calcite observed during the Summer and early Fall 2003 seasons. The SI_C analyzed during Summer/early Fall 2003 is the lowest of the entire monitoring period, ranging from –0.75 to –0.52 in the samples collected between July 9, 2003 to October 16, 2003, whereas SI_C ranges from –0.43 to 0.33 during the rest of the monitoring period (Figure 6-12). P_{CO_2} is the highest of the monitoring period, ranging up to an order of magnitude higher than the P_{CO_2} measured one year earlier, during the drought. These conditions would cause the water in the spring to be aggressive toward calcite. The reactions for calcite dissolution and bicarbonate equilibrium are

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \qquad \text{(eq.1)}$$

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \qquad \text{(eq. 2)}$$

During the 2003 growing season, CO_2 was accumulating in the karst aquifer, instead of outgassing. This drove eqs. 1 and 2 to the right, which would decrease the pH and cause calcite dissolution.

A possibility for the calcite observed in the spring in Summer/early Fall 2003 is that speleogenic calcite precipitated at an earlier time may have been dislodged from the wall rock of the karst system and transported to the spring by flowing water. The transport time to the spring may have been faster than the time required for dissolution of these dislodged particles by the water. Thus, calcite was observed in the spring discharge, even though the spring discharge was undersaturated with respect to calcite. Additionally, because the capture zone for the spring is relatively small, the sediment probably does not travel very far from its source area to the spring mouth.

Sediment Morphology

Additional clues to the existence of calcite are found in the morphologies of the sediments analyzed with SEM/EDS (Figure 6-13). Intact and weathered rhombs, needle-like clusters, and various other morphologies were observed, particularly on the samples with a high sediment concentration. Some of these morphologies indicate precipitation of calcite at the spring mouth or in the epikarst as a possible mechanism, while others suggest that speleogenic grains growing in conduits or larger fractures may have been dislodged from the wall rock and transported by flowing water.

White, W.B., 1999, Karst hydrology: recent developments and open questions, *in* Beck, Pettit & Herring, Ed., Hydrogeology and Engineering Geology of Sinkholes and Karst: Rotterdam, Netherlands, Balkema, p. 3-21.

Wicks, C.M., 1997, Origins of groundwater in a fluviokarst basin: Bonne Femme Basin in Central Missouri, USA: Hydrogeology Journal, v. 5, no. 3, p. 89-96.

Poth, C.W., 1977 Summary, ground-water resources of Lancaster County, Pennsylvania: Harrisburg, Pennsylvania: Pennsylvania Geological Survey, 80 p.

Ryan, M., and Meiman, J., 1996, An examination of short-term variations in water quality at a karst spring in Kentucky: Groundwater v. 34, no. 1, p. 23-30.

Scholle, P.A. and Ulmer-Scholle, D.S., A color guide to the petrography of carbonate rocks: grains, textures, porosity, diagenesis: American Association of Petroleum Geologists Memoir 77, 474 p.

Schuster, E.T. and White, W.B., 1971, Seasonal fluctuations in the chemistry of limestone springs: a possible means for characterizing carbonate aquifers: Journal of Hydrology, v. 14, no. 1971, p. 93-128.

Smart, C.C., 1988, Artificial tracer techniques for the determination of the structure of conduit aquifers: Groundwater v. 26, no. 4, p. 445-453.

Toran, L., 1982, Isotopes in groundwater investigations: Groundwater, v. 20, no. 6, p. 740-745.

Vesper, D.J., and White, W.B., 2003, Storm pulse chemographs of saturation index and carbon dioxide pressure: implications for shifting recharge sources during storm events in the karst aquifer at Fort Campbell, Kentucky/Tennessee, USA: Journal of Hydrology, in press.

Welton, J.E., SEM Petrology Atlas: Tulsa, Oklahoma, The American Association of Petroleum Geologists, 237 p.

White, W.B., 1988, Geomorphology and hydrology of karst terrains: New York, Oxford University Press, 464 p.

Kochanov, W.E., 1990, Sinkholes and karst-related features of Lancaster County, Pennsylvania: *in* Open File Report 90-01, Commonwealth of Pennsylvania, Department of Natural Resources, Bureau of Topographic and Geologic Survey, scale 1: 24 000, 8 sheets.

Lakey, B., and Krothe, N.C., 1996, Stable isotopic variation of storm discharge from a perennial karst spring, Indiana: Water Resources Research, v. 32, no. 3, p. 721-731.

Mahler et al, B.J., Lynch, L., and Bennett, P.C., 1999, Mobile sediment in an urbanizing karst aquifer: implications for contaminant transport: Environmental Geology, v. 39, no. 1, p. 25-38.

Mazengia, T., Toran, L., and Tancredi, J., 2004. Seasonal variation of nitrates in a karst spring, Nolte, Pennsylvania. Geological Society of American Northeast-Southeast Regional Meeting, Tysons Corner, VA, March 25-27.

Meisler, A., and Becher, A.E., 1971, Hydrogeology of the carbonate rocks of the Lancaster 15-minute Quadrangle, southeastern Pennsylvania: Harrisburg, Pennsylvania, Department of Internal Affairs, Topographic and Geologic Survey, 149 p.

Moore, M., 1998, Pennsylvania Ground-Water Information System, Harrisburg, Pennsylvania, Pennsylvania Department of Conservation and Natural Resources, Bureau of and Topographic and Geologic Survey.

Parkhurst, D.L., 2002, PHREEQC Interactive (Version 2.6): Denver, Colorado, United States Geological Survey, Branch of Information Services.

Ford, D., and Williams, P., 1989, Karst geomorphology and hydrology: London, Unwin Hyman Ltd., 601 p.

Freeze, R.A., and Cherry, J.A., 1979, Groundwater: Englewood Cliffs, New Jersey, Prentice Hall, 604 p.

Ginsberg, M., and Palmer, A., 2002, Delineation of source-water protection areas in karst aquifers of the Ridge and Valley and Appalachian Plateaus physiographic provinces: rules of thumb for estimating the capture zones of springs and wells: Washington, DC, United States Environmental Protection Agency, EPA Document 816-R-02-015, 41 p.

González, L.A., Carpenter, S.J., and Lohmann, K.C. Inorganic calcite morphology: roles of fluid chemistry and fluid flow: Journal of Sedimentary Petrology, v. 62, no. 3, p. 382-399.

Hess, J.W., and White, W.B., 1993, Groundwater geochemistry of the carbonate karst aquifer, south-central Kentucky, USA: Applied Geochemistry, v. 8, no. 189, p. 189-204.

Jenkins, S. A., 1999, Factors causing sinkhole development in Northampton County, Pennsylvania [M.S. thesis]: Philadelphia, Temple University, 75 p.

Jonas, A.I. and Stose, G.W., 1926, Geology and Mineral Resources of the New Holland Quadrangle: Harrisburg, Pennsylvania, Department of forests and waters, Topographic and geologic survey, 40 p.

Katz, B.G., Coplen, T.B., Bullen, T.D., and Davis, J.H., 1997, Use of chemical and isotopic tracers to characterize the interactions between ground water and surface water in mantled karst: Groundwater, v. 25, no. 6, p. 1014-1028.

REFERENCES CITED

Atteia, O., and Kozel, R., 1997, Particle size distributions in waters from a karstic aquifer: from particles to colloids: Journal of Hydrology: v. 201, no. 1997, p. 102-119.

Berg, T.M., and Dodge, C.M., compilers, 1981, Atlas of preliminary geologic quadrangle maps of Pennsylvania: Pennsylvania Geological Survey, Issue 61, scale 1:62,500, 623 sheets, 12 p. text.

Desmarais, K., and Rojstaczer, S., 2002, Inferring source waters from measurements of carbonate spring response to storms: Journal of Hydrology: v. 260, no. 2002, p. 118-134.

Dreiss, S.J., 1989, Regional scale transport in a karst aquifer: 1. component separation of spring hydrographs: Water Resources Research: v. 25 no. 1, p.117-125.

Drever, J.I., 1997, The geochemistry of natural waters, 3rd ed.: Upper Saddle River, New Jersey, Prentice-Hall, 436 p.

Farmer, J.J., and Williams, S.D., 2001, Seasonal and short-term variability in chlorinated solvent concentrations in two karst springs in Middle Tennessee: implications for sampling design [Electronic version], *in* Proceedings, USGS Water-Resources Investigations Report 01-4011,U.S.Geological Survey Karst Interest Group, St. Petersburg, Fla., 2001, E.L. Kuniansky, Ed., p. 141-149.

FitzPatrick, E.A., Soil microscopy and micromorphology: Chichester, England, John Wiley and Sons Ltd., 304 p.

Additionally, the nature of the storm event should be considered. The conductivity responses suggest that point recharge events caused by high-intensity storms will most likely result in an increase in contaminant concentrations from baseflow values, while diffuse recharge events caused by snowmelt and low intensity storms will most likely result in a decrease from baseflow concentrations. Although Nolte Spring typically had low sediment concentrations during storms, a large point recharge event would be more likely to result in a higher sediment discharge than a diffuse recharge event. A variety of storm events should be sampled to characterize sediment transport and the behavior of karst springs.

study could be used to test the influence of recharge events on whether the spring behaves as a fracture or a conduit system.

The existence of calcite in the spring should also be studied further. More sampling and SEM/EDS analysis of sediment could be conducted through the Summer 2004 to see if calcite is observed again during the growing season, and if the geochemical conditions during this season are similar to those seen in Summer 2003. A more detailed morphological and geochemical study of the calcite observed in existing samples would also be beneficial in determining the origins of this calcite and mechanisms for transport to the spring.

Implications

Results from the seasonal and storm monitoring show that rapid changes in water chemistry and sediment concentration can occur in Nolte Spring. Many of these changes, including conductivity, dissolved ions, SI_C and P_{CO2} were observed to occur over an interval between a few hours and two weeks, based on the frequency of data collection. While most groundwater monitoring plans are based on quarterly or monthly sampling, the importance of high-frequency, flow-dependent sampling of karst aquifers is now recognized. Based on my findings at Nolte Spring, I would suggest a minimum of bi-weekly sampling during baseflow. Storm sampling should be initiated within 1 to 2 hours of the beginning of precipitation, and should be continued on an hourly basis for at least the first 12 hours. During periods of drought, significant water quality changes should be expected, as observed during the September 26, 2002 storm, so increased levels of contaminants should be expected during storms.

information on the sources of the discharge during storm events. Another area of study that would help identify different sources and pathways in the karst system for Nolte Spring would be isotope analysis during storms and over seasons, possibly with some samples from nearby wells and of meteoric water. Using this information, a hydrograph separation could be performed. Although sediment concentrations in the spring were low, further geochemical modeling and analysis combined with more quantitative methods of mineral identification could be performed to determine the reason for the presence of calcite in the spring at certain times during the monitoring period. Another attempt at continuous turbidity monitoring would be worthwhile, in addition to more storm sediment sampling.

Using the results of the capture zone delineation, a tracer test could be performed as a quantitative check. The collection of more accurate velocity measurements is planned for Spring/Summer 2004, which will help to develop a better estimate of the capture zone area. An in-depth study of the sinkholes within the estimated boundaries of the capture zone, and slightly outside those boundaries, would help identify possible injection sites, and there are at least three or four springs in the same valley as Nolte which could be monitored.

More studies could also be based on existing data for the spring. A time-series analysis of the stage, conductivity, and dissolved cation responses to storms is currently in progress. The recession curves in the conductivity, stage, and ion data for the spring would also be a beneficial study. The conceptual model for the site developed by this while another pathway is the source of the calcite. Further study is needed before either of these possibilities can be identified as the dominant mechanism for the changes in sediment type observed in the spring.

Pathway and Karst System Permeability

An additional finding of this study was that the pathways to Nolte Spring may change because the permeability of the karst system transitions from matrix/fracture to conduit. In other words, the spring has some characteristics of a matrix/fracture system and some of a conduit system. Only small amounts of sediment were observed in the spring during most of the monitoring period, however, so the conduits are probably not well-developed. The CV was relatively low, indicative of matrix/fracture flow. However, the CV value of 5.4% was at the high end of values typical for matrix/fracture flow, and the individual hardness values were relatively low, which may be evidence for the presence of larger fractures or small conduits in the karst system for the spring. Additionally, the response time of the spring to storm events is relatively rapid, a characteristic of conduit systems. The SI_C calculated from the dissolved ions analyzed in samples from Nolte Spring suggests that the spring water was undersaturated for most of the monitoring period, which is also a characteristic of fast-flowing, conduit springs.

Recommendations for Further Study

An important element of any further study at Nolte Spring would be a more quantitative definition of the "old" and "young" water as defined by the variations in conductivity over long periods of time and during storms. Collection and analysis of samples for dissolved ions, pH and alkalinity during storms could provide important

Higher concentrations of suspended sediment were observed during the drought, but the sediment flux was the lowest of the monitoring period, indicating that the ratio of sediment to water was higher during the drought, but there was less sediment being discharged from the spring. During the flood end-member, sediment concentrations were lower, but the flux was the highest of the monitoring period, except for two exceptionally high sediment fluxes, recorded in samples from October 17, 2002, and July 9, 2003.

The mineralogy of the sediment was mostly during the drought of 2002 and the growing season of 2003, whereas sediment collected during the flood period consisted mostly of siliciclastics, with few calcite particles. The presence of calcite during both the Summer/early Fall of 2002 and the Summer/early Fall of 2003 suggests that two different sets of geochemical conditions lead to the same sediment mineralogy. Some of the calcite morphologies observed in the drought of 2002 suggest precipitation of calcite then transport to the spring mouth whereas those observed in the growing season of 2003 suggest the dislodging of particles from the carbonate wall rock.

The variation in sediment mineralogy over the study period may be the result of different pathways in the aquifer or different flow regimes active in the same pathways. Different flow velocities in the aquifer would result in the transport of cohesive, as opposed to unconsolidated particles. In other words, a higher flow velocity is required for the mobilization of cohesive particles lining the conduits and fractures of the aquifer, whereas a lower flow velocity is sufficient to transport translocated material from the soil already entrained in storm water from the surface. Conversely, there may be one pathway to the spring which the source of the siliciclastics transported to the spring, period of time. During the flood end-member, which occurred during the Winter 2003 season, the conductivity was the lowest observed during the monitoring period. If the high conductivity during the drought is in fact due to the longer time period over which water-rock interactions occurred, then the lower conductivity during the flood suggests more dilute water due to higher flow rates, which were observed in the discharge from the spring during February 2003, and estimated from the stage-discharge curve constructed from measurements taken throughout the monitoring period.

The effects of the drought are also evident in the TDS concentrations in samples collected during visits to Nolte Spring between September 5 and October 3, 2002. As discussed in Chapter 5, TDS in these samples was the highest observed during the study period. Recovery from the drought was observed as a decrease in TDS after October 3. The sample with the lowest observed TDS was collected on the same day as the highest field-measured stage, on March 9, 2003.

Changes in pathway were also observed in the variability of SI_C and P_{CO2}. High SI_C and low P_{CO2} was observed during the drought, suggesting that the draining of phreatic conduits and the lack of recharge during this time resulted in calcite saturation and outgassing of CO_2 from groundwater. During the growing season in the Summer/early Fall of 2003, which had frequent low-intensity rain, low SI_C and high P_{CO2} were observed. The geochemical data from this time suggest that increased plant activity and recharge lead to these conditions, so the conduits and fractures were full and recharge was flowing into the aquifer through diffuse pathways in the soil and fractures in the carbonate matrix.

conductivity. The stage recovery after storms interpreted as point recharge was also more rapid.

The conductivity peak of 1,708 μS/cm on September 26, 2002, a high-intensity/point recharge storm, was the highest observed during the monitoring period. This conductivity cannot be accounted for by carbonate chemistry alone, and may have been caused by the flushing of salts accumulated during the drought from the vadose zone by point recharge entering the aquifer, which is suggested by the decrease in dissolved Na^+ and Cl^- observed between September 19 and October 3, 2002.

Low-intensity (mean ≤1.5 cm/day or high daily ≤ 2 cm/day) storms typically resulted in diffuse recharge that gradually infiltrated the soil layer to the bedrock interface, and eventually the karst system. During diffuse recharge events, the stage rose gradually, and the conductivity appeared to decrease then gradually recover. This response suggests that dilute storm water made up a larger portion of the spring discharge than the pre-storm water.

Pathway and Variations in Geochemistry and Sediment

Changes in the pathways through which the water travels also appeared to affect the nature of chemical variability and sediment concentration of the spring discharge. Evidence for this relationship was observed during the drought and flood end-members of baseflow conditions. During the drought of 2002, baseflow conductivity was the highest recorded. In addition to the hypothesis of a deeper circulation system, the high conductivity may also have resulted from the low-flow conditions in the spring, which enabled water-rock interactions in the carbonate aquifers to take place over a longer layers is another possible reason for the low P_{CO_2} in the spring discharge, due to less plant activity and less recharge. As recharge increased, transport of CO_2 to groundwater increased, and the vadose pathways became filled again, initiating the transition from an open to a closed system. SI_C was at or near equilibrium during the drought, and progressively decreased to undersaturated conditions as P_{CO_2} increased during the recovery from the drought.

An intermediate SI_C and P_{CO_2} were observed in late February and early March 2003 during the highest recorded stage. At this time higher pathways were activated, and fewer conduits were open. The lowest observed SI_C and highest observed P_{CO_2} occurred during the Summer of 2003. These changes in SI_C and P_{CO_2} are a result of the frequent rain and increased plant activity in the growing season, rather than a change in antecedent stage or pathway.

Storm Intensity/Recharge Type and Pathway

Storm intensity and recharge type play an important role in the type of storm response observed. In the conceptual model described in Chapter 4, high-intensity storms (mean $\geq$1.5 cm/day or high daily $\geq$2 cm/day) generated more overland flow and point recharge, which entered the karst system rapidly through sinkholes and was funneled directly into the conduits and fractures leading to the spring. Storm water from point recharge events thus reached the phreatic zone in greater volume and velocity. Chemographs of these storms suggest that point recharge storm water initially displaced the pre-event water rather than mixing with it, resulting initially in a rapid increase in

CHAPTER 7

CONCLUSIONS

Introduction

My hypothesis had two components: that the pathways through which baseflow and stormflow groundwater travels in a karst aquifer to a spring vary during storms and between seasons; and that these pathways affect the chemistry and sediment concentration in the discharge. Evidence for both has been found in variations in storm response based on recharge type, in sediment mineralogy and morphology, and in geochemical parameters such as SI_C and P_{CO2}.

Baseflow Pathways

The low baseflow stage and high baseflow conductivity observed during the drought in the Summer and early Fall of 2002 suggests that there may have been different groundwater flow pathways to the spring at this time. As discussed in Chapter 5, due to the significant lowering of the water table, many of the shallow pathways in the karst system for Nolte Spring may have been abandoned. Deeper or slower pathways may have contributed more to the discharge in Nolte Spring resulting in the higher conductivity observed during this time.

Changes in pathway can also be seen in the variations in P_{CO2} and SI_C during the drought and subsequent recovery. As discussed in Chapter 5, the low P_{CO2} values observed during the drought suggest an open system, where outgassing of CO_2 from the groundwater occurred as some normally phreatic fractures and conduits were drained as a result of the lowering water table. Decreased transport of CO_2 from the overlying soil

Summary

In summary, sediment concentrations and mineralogy in Nolte Spring varied throughout the monitoring period. Sediment concentrations in the Summer and Fall seasons were typically higher than those in the Winter and Spring, but geochemical data suggests that the geochemistry of the spring influenced the sediment concentration and mineralogy rather than seasons. Data from storm samples was less conclusive due to low sediment concentrations, but the sediment flux estimated for storms appears to be higher in the peak discharge from each storm than during baseflow.

The variation in mineralogy of the storm samples is generally similar to that of the samples collected during site visits. The results of the SEM/EDS analysis performed on the storm and seasonal samples indicate a large amount of morphologically variable calcite in some samples, which was unexpected due to the low saturation index of calcite measured over most of the monitoring period. Outgassing of CO_2, calcite saturated conditions in an area of the karst system other than the spring mouth, precipitation in the vadose zone, and dislodging of carbonate particles from the wall rock of the aquifer are possible explanations for the presence of calcite in the discharge from Nolte Spring.

communication, August 2002). A suspended sediment sample collected on July 9, 2003 contained equant crystals and nodules, as well as shell- or lichen-shaped particles, some of which were chipped or looked like they had been broken off of a larger area (Figure 6-13). A calcite rhomb with a chipped edge and dissolution pits was observed in a storm sample from June 3, 2003 (Figure 6-13), one of the few samples from the period of intermediate SI_C and P_{CO2} in which calcite was observed. The stormflow from this point recharge event may have mobilized this particle off of the conduit floor.

Because the geochemical data from Summer 2003 suggests that dissolution of calcite was occurring in the spring, the sediment morphologies observed during this time should reflect a larger amount of weathered and pitted particles than sediment from the period where precipitation is more likely. However, I also observed weathered and pitted calcite particles during the high SI_C/low P_{CO2} period, sometimes in the same sample as the more intact particles. There did not appear to be more weathered particles in these samples than in the samples collected during times of higher SI_C, but the method for determining dominant mineralogy and morphology using SEM/EDS was qualitative. A more systematic analysis, similar to point-counting of thin sections, might yield more definitive interpretation of the sediment samples.

Samples rich in clay tended to clump, causing most of the clay-rich particles to be concentrated on the 5.0 μm Millipore™ filter. The pores of the filter quickly became blocked, so that particles smaller than 5.0 μm were also retained. The accumulation of particles both larger and smaller than 5.0 μm on the filter precluded the use of different-sized filters to estimate particle size distribution in a sample.

The unweathered rhombs, clusters of needle-like crystals, popcorn structures and nodules of calcite observed in some of the samples suggest they may have precipitated, either from supersaturated water in a fracture or in the vadose zone (González et al., 1992; FitzPatrick, 1993; Scholle and Ulmer-Scholle, 2003). The prisms in the sample collected on October 17, 2002 (Figure 6-13) appear to be joined at the base, as if they have grown together. Although the aspect ratio of the crystals' long and short axes is 3:1, which is too low to be termed acicular, or needle-like, the fabric of the calcite prisms is similar to that of acicular calcite, which forms in the vadose zone of arid or semi-arid climates (FitzPatrick, 1993; Scholle and Ulmer-Scholle, 2003). In the same sample, I observed another prismatic crystal of calcite, composed of many layers, which may indicate rapid growth (Dennis O. Terry, Temple University, Department of Geology, personal communication, April 2004). The crystals in this sample may have precipitated in a drained fracture during the drought, in the soil, or the soil/bedrock interface. Under typical conditions, these areas are saturated with water, but may have become undersaturated during the drought, enabling the growth of crystals. A sample collected on September 18, 2003 (Figure 6-13) has a popcorn texture, which may indicate precipitation during the condensation of water (González et al., 1992).

Other calcite morphologies, such as rhombs with dissolution pits, flakes, and other chipped or etched grains indicate that these may have been speleogenic particles dislodged from the wall rock and transported to the spring. XRD analysis of rock samples collected indicated that the rocks around the spring mouth contain both finely and coarsely crystalline limestone with some dolomite (W.B. White, personal

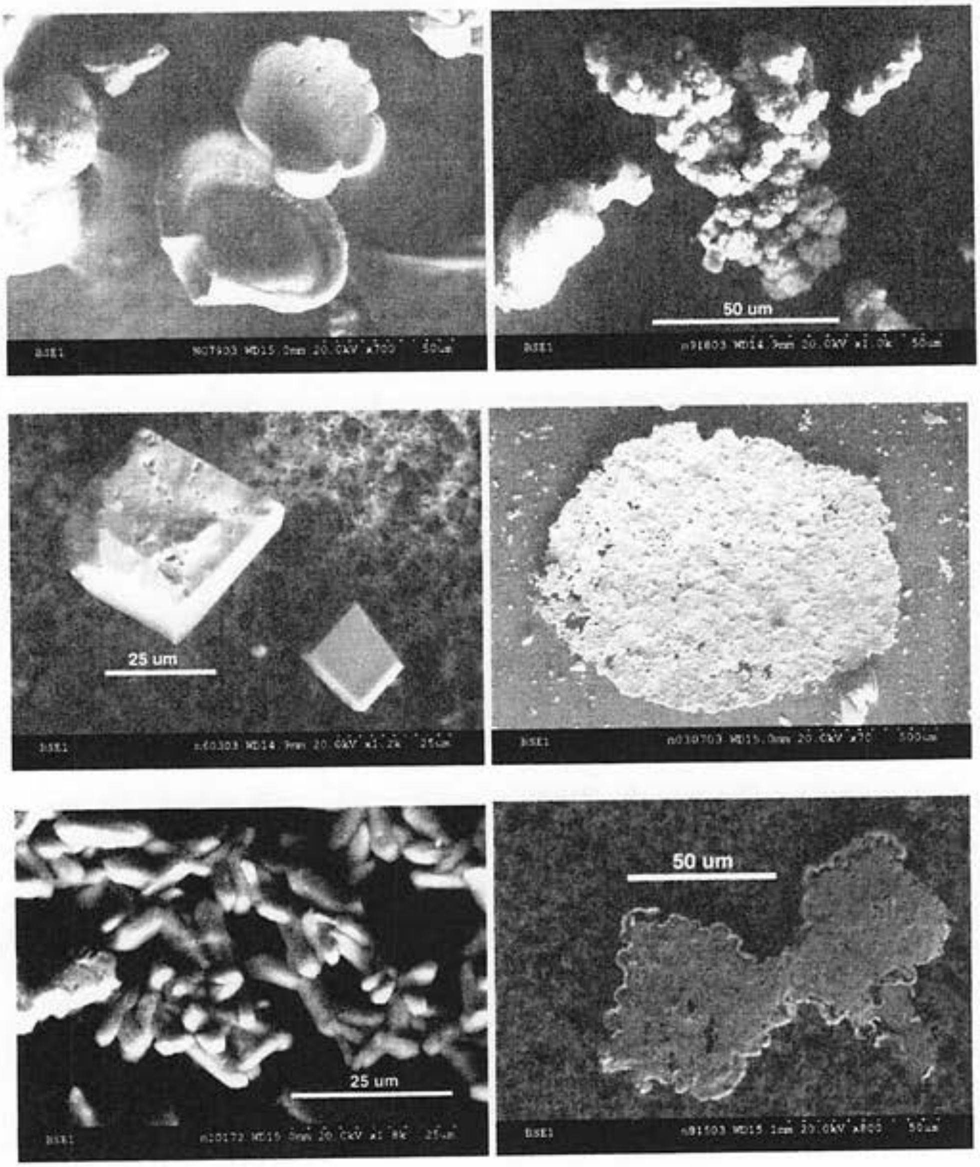


Figure 6-13. Morphologies of calcite observed with SEM. Clockwise, from top left: samples collected on July 9, 2003, September 18, 2003, March 7, 2003 (storm sample), August 15, 2003, October 17, 2003, and June 3, 2003 (storm sample). The morphology of the July 9, 2003 sample suggest that speleogenic calcite particles may have been ripped from the wall rock of the aquifer and transported to Nolte Spring. The prismatic calcite grains in the October 17, 2002 sample appear to have grown together.