Transport and Storage of Metals in Fractured and Karstic Rock Aquifers

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The objective of this project was to evaluate the movement of metals in karst aquifers including metal accumulation, release, and transport under low flow and storm conditions. Metals investigated include aluminum, arsenic, chromium, lead, and nickel. Measurements were made of variations in metal concentration from base flow to storm flow using three springs before, during, and after storm events to study metal transport and release. Sediment samples from 10 springs were analyzed for metals and characterized by bulk mineral identification. The metals were subjected to a selective extraction procedure that evaluated the form of the accumulated metal which in turn controls the availability of the metal to humans and ecological receptors. Results indicate that metals are transported as adsorbates on clays and other small particles which are mobilized during storms, leading to a peak in metal concentration coincident with the peak of the storm hydrograph. Trace metals are stored in the spring sediments mainly bound onto iron or manganese oxide coatings on the silicate grains.

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Enclosure 1

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1.0 Objectives of Research

The objective of this project is to evaluate the movement of metals in karst aquifers. Specifically, the project focuses on the carriers of metal contamination, metal accumulations and storage reservoirs, and temporal variation through storm events. Our approach had two components: determining chemical variability and transport in spring water during storm events, and evaluating the storage of metals in karst spring sediments.

The test site for these investigations was the Fort Campbell Army Base in western Kentucky and Tennessee. This site was chosen because it illustrates the principles to be tested in this investigation and also because results would be of immediate use in environmental assessments now underway at Fort Campbell. The results of ground water basin delineation and other characterization of the site were generously made available to this project. The region lies of the western Highland Rim of the Nashville Dome and is underlain by the near-horizontal limestones of the Mississippian St. Louis and Ste. Genevieve formations. The ground water drains through a series of springs to several tributaries of the Cumberland River.

2.0 Summary of Important Results

2.1 *Carbonate Chemistry*

The response of springs to storm events constitutes a useful probe of the internal structure of karst aquifers. Specifically, information can be gleaned by comparing the chemical response (chemograph) with the discharge response (hydrograph). Bulk chemical response was determined by continuous conductivity measurements for six springs at the Fort Campbell site. The chemographs lagged the hydrographs for some springs and the recession period was often longer for the chemographs than for the hydrographs. Detailed chemographs for two of the springs were determined by chemical analysis of samples collected over short time intervals during a storm event. The calcite saturation index (SI_c) and carbon dioxide partial pressure were calculated for each samples using the MINTEQ aqueous chemistry program. In both springs the CO_2 pressure increased during the chemograph recession suggesting that the input of diffuse infiltration from the soil zone is important during this period. The addition of the high P_{CO_2} water at this time causes a corresponding decrease in the calcite saturation index. The result of this correspondence is that the lowest SI_c observed during the storm event occurred during the chemograph recession and lagged behind the hydrograph recession. Hence the discharge of the most aggressive spring water lagged the period of rapid chemical change. It appears that the full chemograph, specifically changes in CO_2 pressure, reveals details on the mixing of water in the conduit system with water from fracture storage or dispersed infiltration. The full details are given in Appendix 5.1.

2.2 *Metal Transport*

Contaminated ground water often escapes conventional monitoring techniques in karst aquifers due to the localization of flow in solution conduits. An alternative approach successfully used in such locales in spring monitoring. Metal transport typically occurs in association with particulates. Hence in karst aquifers, where the transport of sediments varies with storm flow, the associated metal concentrations can be expected to vary likewise. This portion of the project was directed toward determining metal concentrations in spring discharge and how these metal concentrations vary both with discharge and with turbidity of the springs.

Aqueous samples were collected from three of the karst springs at the Fort Campbell site. The samples were collected spaced at short time intervals during and immediately after storms. Approximately 100 samples were collected in five sets over a two year period. Each sample was split into two aliquots. One was digested to reflect the "total" concentrations including any metals adsorbed onto suspended particulates. The second was filtered through a 0.45 μm filter to reflect the "dissolved" concentrations. The samples were analyzed using inductively-coupled plasma mass spectrometry. Chemographs, plots of chemical composition as a function of time, were generated using sample times, precipitation data, hydrographs, and analytical concentrations.

The chemographs for the digested samples illustrate the signatures of two separate water sources. As expected, elements resulting from limestone dissolution are elevated during base flow and are diluted during storms. During storms, iron and aluminum rich water is discharged from springs. Turbidity also increases during this period suggesting that Al can be a proxy for colloidal or particulate transport. Manganese, lead, chromium, nickel, arsenic and cadmium concentrations are elevated coincident with the arrival of storm water.

Strong correlations ($R^2 > 0.94$) exist between Al and the trace elements in the digested samples. Filtered samples contain lower concentrations of these elements with poor to no correlations between aluminum and the trace element concentrations.

The introduction of storm water strongly alters the chemistry of the karst spring by two means. Mixing of base flow water with storm water injected through sinkholes and through the thick regolith dilutes the high-carbonate chemistry present in aquifer storage. The dominance of Al-rich water, with the accompanying trace elements, is interpreted as due to the increased velocity and enhanced sediment-carrying capacity of the conduit system during storm periods. The correlation of trace metals with aluminum in the digested samples and the near-absence of trace metals in the filtered samples supports this conclusion. Complete results are given in Appendix 5.2.

2.3 *Transport of Other Contaminants*

Detailed analyses of the way in which other contaminants vary across a storm hydrograph provide an opportunity to compare the behavior of several categories of dissolved substances. Results outlined above show that the background carbonate chemistry reflects primarily the dilution of ground water in the aquifer by low carbonate storm water flushed into the conduit system and rapidly transmitted to the spring. As a result the chemograph for Ca^{2+} shows a pronounced dip either coincident with the hydrograph peak or lagging behind it. Metals, in contrast, are mainly transported as adsorbed species on particulates so peak coincident with the peak in the hydrograph when turbidity is the highest. Two additional contaminant species were investigated.

Nitrate concentrations decreased during storms with a chemograph similar to that of calcium. Early spikes in nitrate concentrations suggest that the nitrate is being stored in the epikarstic zone. The coincidence of early-storm spikes in both nitrate and calcium suggests that the nitrate-rich epikarstic water is being flushed by the influx of rain water.

Samples collected concurrently with this study by the U.S. Army contained detectable concentrations of chloroform and trichloroethene (TCE) in spring water. Although only five samples were analyzed for volatile organic compounds (VOC's) at Beaver Spring in 1999, they were collected during critical times of the storm response. The VOC concentrations were constant within 1.6 μg/L and the data suggest that a slight decrease may have occurred during the main storm. To the extent that these sparse results can be generalized, it appears that these DNAPL compounds are stored in the aquifer and are gradually released at fairly constant but low concentrations during low and moderate flow conditions.

A more extensive discussion is given in Appendix 5.3.

2.4 *Metal Storage in Spring Sediments*

In addition to evaluating water chemistry through time, we have evaluated metal accumulation and speciation in spring sediments. Sediments can act as a storage reservoir for metals, hence they may be a long-term source of exposure for receptors at the spring. Sediment samples were collected from six springs at Fort Campbell. Soil samples were also collected from Fort Campbell to provide information on the up-gradient source materials for the spring sediments.

The samples were analyzed using a sequential, selection extraction procedure modified from the BCR standard method. The procedure separates the metals into 5 operationally-defined fractions: exchangeable, carbonate, oxides, organics, and residual. To complement the extraction data, the samples were also analyzed for total organic carbon, particle size, total metals, mineralogy (by X-ray diffraction), and elemental surface chemistry (by energy dispersive x-ray spectroscopy). As expected, the preliminary data suggests that metal speciation and metal distribution between extracts varies significantly between metals. The major metals seem to have a reasonably consistent distribution between fractions regardless of the source while the trace metals vary in their distribution between sources. For example, aluminum and iron are primarily present in the residual fraction, calcium is split between exchangeable, carbonate and residual fractions, and manganese is present as an oxide. Trace metal speciation appears to be dependent on the location. For example, in Beaver Spring nickel is distributed between the exchangeable, carbonate, and organic fractions while in Gordon Spring nickel is largely residual. Chromium is almost entirely associated with the organic fraction in Beaver Spring while it is largely residual in Gordon Spring. The differences in the trace metals is likely to depend on both the source of the metal (particularly the differences between background and contaminant sources) and the sediment's physical and chemical characteristics.

Concentrations of all metals in the sediments scaled linearly with the concentrations in water samples that included suspended particulates. Concentrations of metals in filtered water samples were usually at or below the limits of detection. There was, therefore, little correlation between metals incorporated in the sediments and the concentration of metals dissolved in the ground water.

Complete experimental detail and resulting data are given in Appendix 5.4.

3.5 *Overall Conclusions*

The results summarized above can be reduced to a conceptual model for the movement of sediments and sediment-related contaminants through karst aquifers (Fig. 1). The results also lead to a series of conclusions as presented below. These conclusions are drawn from a detailed examination of the Fort Campbell karstic carbonate aquifer and therefore their range of applicability must be further investigated. In general, these conclusions are in agreement with results found from the examination of other carbonate aquifers.

i) Dispersed infiltration occurs late in the storm response and can be identified by its high CO_2 signature.

ii) Trace metal transport is enhanced during storms and occurs in association with suspended sediments.

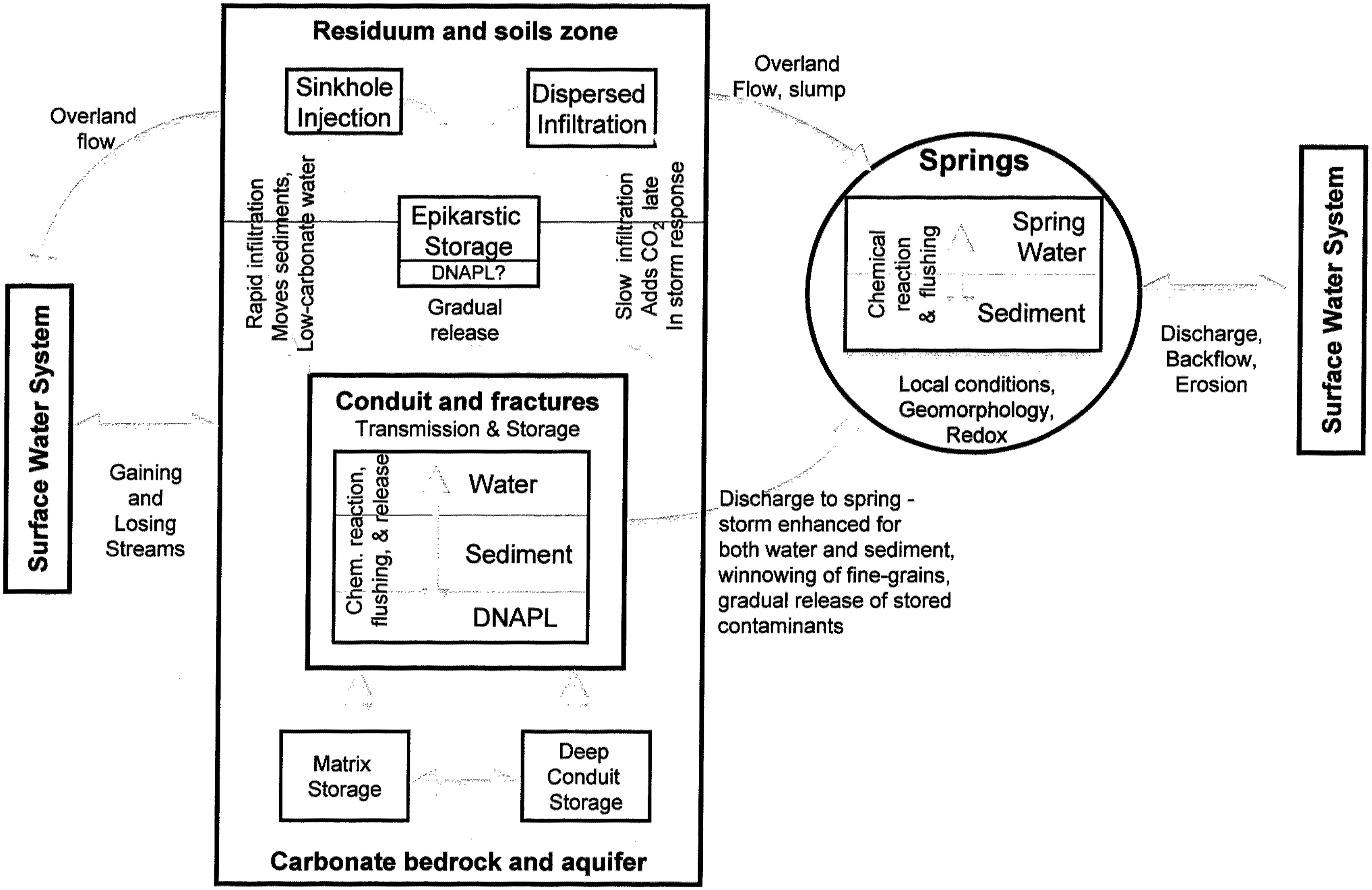
iii) The chemical variability of one type of chemical constituent in spring water cannot be used to predict the variability of other types because the controlling processes are sometimes independent.

iv) Contaminant concentrations can increase, decrease, or remain constant in spring water during storm events. The change depends on the specific constituent and how it is stored and transported through the aquifer.

v) The accumulation and speciation of metals in spring bed sediments is primarily controlled by local conditions, specifically the spring geomorphology and the presence of organic matter.

vi) On a basin-wide scale, the transport and storage of metals is controlled by physical rather than chemical processes. Chemical processes become more important on a small (e.g. individual spring) scale.

vii) Spring water is heterogeneous temporally and spring sediments are heterogeneous spatially – the two media present different types of environmental impact.


Surface Water System
Overland flow
Gaining and Losing Streams
Residuum and soils zone
Sinkhole Injection
Dispersed Infiltration
Rapid infiltration
Moves sediments,
Low-carbonate water
Epikarstic Storage
DNAPL?
Gradual release
Slow infiltration
Adds CO_2 late
In storm response
Conduit and fractures
Transmission & Storage
Chem. reaction, flushing, & release
Water
Sediment
DNAPL
Matrix Storage
Deep Conduit Storage
Carbonate bedrock and aquifer
Overland Flow, slump
Springs
Chemical reaction & flushing
Spring Water
Sediment
Local conditions, Geomorphology, Redox
Discharge to spring - storm enhanced for both water and sediment, winnowing of fine-grains, gradual release of stored contaminants
Discharge, Backflow, Erosion
Surface Water System

3.0 Publications and Presentations

3.1 *Manuscripts Prepared for Publications*

Vesper, Dorothy J. and William B. White. Metal transport to karst springs during storm flow: An example from Fort Campbell, Kentucky/Tennessee, U.S.A. *Journal of Hydrology* (in galley proof)

Vesper, Dorothy J. and William B. White. Comparative storm response of ground water and contaminant chemistry in a carbonate aquifer, Fort Campbell, Kentucky-Tennessee, U.S.A. *Environmental Science and Technology* (submitted).

Vesper, Dorothy J. and William B. White. Storm pulse chemographs of saturation index and carbon dioxide pressure: Implications for shifting recharge sources during storm events in karst aquifers. *Hydrogeology Journal* (submitted)

Vesper, Dorothy J. and William B. White. Spring and conduit sediments as storage reservoirs for metal contaminants. In preparation for *Environmental Geology and Water Science.*

3.2 *Papers Presented at Meetings*

Vesper, Dorothy J. and William B. White. Transport of trace contaminants to a karst spring during storm events. 11th Annual V.M. Goldschmidt Conference, Hot Springs, VA, May, 2001

Vesper, Dorothy J. and William B. White. Relation of storm chemographs to storm hydrographs: Interpretations from the karst springs at Fort Campbell, Kentucky/Tennessee. Geological Society of America, Boston, MA, November, 2001

3.3 *Other Presentations of Technical Results*

Summaries of project results were presented orally at the following meetings:

Fort Campbell Ground Water Symposium, Fort Campbell, December, 2001.

Working Session on Fracture Aquifers, Massachusetts Institute of Technology, August 1, 2002.

ARO Project Review, Vicksburg, MS, August 12-13, 2002.

4.0 Scientific Personnel

William B. White, Professor of Geochemistry, Principal Investigator

Dorothy J. Vesper, Graduate Assistant. Completed Ph.D. in Geosciences, August 2002. Thesis title: Transport and Storage of Trace Metals in a Karst Aquifer: An Example from Fort Campbell, Kentucky.

Appendix 5.1

Storm Pulse Chemographs of Saturation Index and Carbon Dioxide Pressure: Implications for Shifting Recharge Sources During Storm Events in Karst Aquifers

Manuscript submitted to Hydrogeology Journal

Storm Pulse Chemographs of Saturation Index and Carbon Dioxide Pressure: Implications for Shifting Recharge Sources During Storm Events in Karst Aquifers

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Abstract Continuous records of discharge, specific conductance, and temperature were measured through a series of storm pulses on two limestone springs at Fort Campbell, western Kentucky/Tennessee, USA. Water samples, collected at short time intervals across the same storm pulses were analyzed for calcium, magnesium, bicarbonate, total organic carbon and pH. Chemographs of calcium, calcite saturation index, and carbon dioxide partial pressure were superimposed on the storm hydrographs. Calcium concentration and specific conductance track together and dip to a minimum either coincident with the peak of the hydrograph or lag slightly behind it. The CO_2 pressure continues to rise on the recession limb of the hydrograph and as a result the saturation index decreases on the recession limb of the hydrograph. These results are interpreted as being due to dispersed infiltration through CO_2-rich soils lagging the arrival of quickflow from sinkhole recharge in the transport of storm flow to the springs. Karst spring hydrographs reflect not only the changing mix of base flow and storm flow but also a shift in source of recharge water over the course of the storm.

[179 words]

Keywords

Karst, carbonate rocks, recharge/water budget, hydrochemistry

Introduction

The chemistry of ground water in aquifers recharged by dispersed infiltration is generally determined by water-rock interactions within the aquifer. These interactions operate on long time scales so that the chemistry at any given location within the aquifer remains constant on the time scale of the seasons or the spacing between storms. In the special case of karst aquifers, the high rate of throughput means that different sources of recharge can provide chemical signals that are transmitted through the aquifer and can sometimes be detected at the springs where the ground water is discharged. Recharge sources vary on both seasonal and individual storm time scales and are reflected in spring water chemistry on corresponding time scales.

Recharge to karst aquifers is often separated into allogenic recharge and autogenic recharge. Allogenic recharge is point source recharge from sinking streams with catchments on subjacent non-karstic rocks. Autogenic recharge is derived from precipitation that falls directly on the karst land surface. It is sometime useful to separate autogenic recharge into internal runoff which is storm flow funneled directly into sinkholes, open fractures, or vertical shafts, and dispersed infiltration which is the water that percolates through overlying soils, may be temporarily stored in the epikarst, and which enters the aquifer slowly through pores and fractures in the bedrock. Allogenic recharge and most internal runoff is injected directly into the conduit system and reaches the spring rapidly. This component within the aquifer is sometimes called “quickflow”. Dispersed infiltration has a longer transit time because it moves slowly through fractures and pores before it reaches the conduit system.

The source of recharge has been cited as one of the key controlling factors in the chemical variability of spring water (Atkinson 1977; Scanlon and Thrailkill 1987; Worthington et al. 1992). Scanlon and Thrailkill (1987) used source of recharge to classify two types of springs in the Kentucky Inner Bluegrass Region. Chemically-variable springs had a higher percentage of recharge from internal runoff as defined by the sinkhole density in their catchments. Quickflow through conduit permeability and storage capacity within the aquifer are also a factor in spring chemistry variability (Field 1993; Ray and O'Dell 1993; Shuster and White 1971; Smart and Hobbs 1986; White 1999). Most conceptual models agree that chemically variable springs can be characterized by allogenic and/or internal runoff recharge, conduit-dominated transmission, and low storage capacity.

There is a very large literature on the variability of spring water chemistry as a means of characterizing karst aquifers, particularly the interpretation of plots of chemical variables as a function of time (chemographs) either on seasonal time scales or through the hydrographs of individual storms. The present paper addresses two of the less investigated chemical parameters, the CO_2 partial pressure (P_{CO2}) calculated from pH and alkalinity and the saturation index of calcite, SI_c. P_{CO2} has been used to infer source of recharge (Drake and Harmon 1973). Quickflow is derived mainly from allogenic and internal runoff water which often has a P_{CO2} only slightly higher than that of the surface atmosphere. Dispersed recharge reflects the P_{CO2} of the soil atmosphere which may be hundreds of times higher than the P_{CO2} of the surface atmosphere. Seasonal variability of P_{CO2} has been used to display the effect of growing season on karst water chemistry (e.g. Hess and White 1993; Shuster and White 1972). The present paper examines the variation in P_{CO2} over single storm events and its implication for sources of the water arriving at the spring over the course of the storm.

Physical Setting

This study is part of an investigation of springs on and near the Fort Campbell Army Base. The base is located along the Kentucky-Tennessee border approximately 65 km northwest of Nashville, TN (Fig. 1a, b). The area of the base is approximately 430 km^2. Of that, approximately 80 percent is used for ranges and is largely undeveloped. Over 30 perennial springs have been identified within approximately a 250 km^2 area around the base.

The area surrounding Fort Campbell is largely agricultural with some commercial and industrial uses. The region is located on the Western Highland Rim of the Nashville Basin and is underlain by the limestones of the Mississippian St. Louis and Ste. Genevieve formations. The Ste. Genevieve crops out in the topographically high areas and largely consists of thick-bedded limestone with thinner beds of dolomite. Discontinuous layers of chert and fossils are present. The St. Louis Formation is exposed primarily in the waterways and topographic lows to the south. It is dolomitic, argillaceous, silty, and fossiliferous. Ball chert and colonial corals are profuse in layers.

Between 0 and 30 m of unconsolidated materials are present above the limestone. This regolith consists of an upper layer of reddish brown clays and a lower layer of gravely clay (Arthur D. Little Inc. 1997). Chert nodules are commonly found at the regolith – bedrock contact.

Two springs were used for this study: Beaver Spring and Millstone Spring. Beaver Spring is located approximately 220 meters north of the Little West Fork Creek (Fig. 1c) and emanates from a horizontal opening at the base of a stepped limestone outcrop. It has a base flow between 0.5-100 L/s and an estimated ground-water basin size of 2.5 km^2. Long-term monitoring of

Beaver Spring shows that it responds to storms with a stage crest approximately 8 hours after the storm occurs.

Millstone Spring is located on private property on the west side of the West Fork of the Red River (Fig. 1c). Spring water emanates from the base of a limestone ledge which is located at the head of a steeply-incised erosional pocket valley. The spring run is approximately 7 m wide with up to 4 m of relief from the steam bed to the top of the banks. The spring run flows through the valley approximately 70 m to its confluence with the river. Baseflow discharge at Millstone Spring has been measured at values from 30 to 600 L/s. The maximum discharge is unknown. Its ground water basin is estimated to be 65 km^2.

The ground water basins for both Beaver and Millstone Springs receive mainly dispersed recharge. Storm flow is provided mainly by internal runoff into sinkholes. The contribution to storm flow by sinking streams is relatively small.

Materials and Methods

Continuous data were collected for stage, specific conductance (SC) and temperature by Ewers Water Consultants, Inc. The parameters were measured at 10-second intervals with 2-minute averaging and recorded on a digital logger. Stage was measured using a pressure transducer and temperature was measured using a platinum resistance thermometer. SC was measured using a probe designed by Ewers Water Consultants (Idstein and Ewers 1991). Discharge values were calculated using a stage-discharge rating curve.

Water samples were collected using automated sampling devices programmed to collect samples at time intervals ranging from 0.5 to 8 hours (samples were collected more frequently during the storm and less frequently afterwards). Intake valves were placed in the main spring discharge inside the cave opening. Alkalinity and pH were measured for individual samples in the field. Alkalinity was measured via titration.

Calcium concentrations were measured using a Finnegan high resolution inductively-coupled plasma mass-spectrometer (ICP-MS). All of the samples were digested with approximately 2 molar nitric acid using a method modified from SW846 Method 3015 – Microwave assisted digestion of aqueous samples and extracts (USEPA 2000). For comparison with the digested samples, aliquots of the year 2000 samples were pressure-filtered through dedicated, tortuous path, 0.45-µm PVDF cartridge filters. The filtering was conducted in the field and prior to acid preservation. As expected for a normally-distributed, dissolved analyte, the concentrations measured in the digested and filtered samples were statistically equivalent based on a paired student t-test with an α of 0.05.

Total Organic Carbon (TOC) was measured using a Shimadzu (TOC-5000) carbon analyzer equipped with an ASI-5000A liquid auto sampler. To remove the inorganic carbon content, each sample is treated with HCl and air-sparged prior to analysis.

The saturation index with respect to calcite (SI_C) and the P_{CO2} were calculated using Visual MINTEQ, Version 1.01 (Gustafsson 2000). Enhanced CO_2 values are expressed as a ratio of the calculated P_{CO2} to the atmospheric P_{CO2}.

Results

Hardness/Conductivity Chemographs

Water chemistry variability was calculated as the coefficient of variation (CV) by dividing the standard deviation by the mean. The measured parameters varied up to 25 percent over the studied storms (Table 1). The literature suggests that springs with temperature or calcium variability greater than 5 percent are flashy and are characterized by rapid recharge and transmission (Quinlan 1989; Shuster and White 1971). While the original guidelines were based on bi-weekly samples over an annual period, the high-resolution data for Beaver and Millstone Springs are reasonably consistent for temperature and specific conductance over both a single storm and a longer period.

Detailed storm data were collected for the carbonate parameters in June 1999. The rain event included 5.6 cm over a two-day period. The double peak on the hydrograph is due to the distribution of the rainfall.

The calcium concentration in spring water decreased significantly in Beaver Spring during the 1999 storm (Fig. 2). The minimum calcium concentration coincides with the maximum discharge and is interpreted to have decreased due to dilution by the lower-concentration recharge water. A similar result was obtained at Millstone Spring (Fig. 3). At Millstone Spring the maximum change in water chemistry lags slightly behind the change in discharge suggesting that recharge water must first flush the system of antecedent storage water before arriving at the spring itself. While the flow system and basin size differ for the two springs, the dilution of background carbonate chemistry is consistent at both. A strong correlation exists between calcium and SC ($R^2 = 0.93$) and thus the continuous data for SC can be used as a proxy for calcium. This is not unexpected given that calcium is the dominant cation in solution in karst waters.

Total organic carbon (TOC) increases during storm events at Beaver Spring (Fig. 2). Its maximum concentration coincides with the maximum discharge and the minimum calcium concentration. At Millstone Spring (Fig. 3) the TOC concentration is erratic but seems to lag the hydrograph peak. The most likely TOC sources are surface runoff and shallow soils and therefore the TOC is an indicator of surface input.

Chemographs for Saturation Index and CO_2 Partial Pressure

SI_C and the P_{CO2} also change over the course of storms (Fig. 4). The enhanced CO_2 ranged up to 70 times the atmospheric pressure in the 1999 storm. Both during base flow and throughout the storm, the water was undersaturated with respect to calcite with a minimum SI_C value of –0.95 during the discharge recession period. The minimum SI_C value approximately corresponds to the maximum P_{CO2} value. These changes lag behind the maximum changes in discharge, SC and calcium concentration.

SI_C and P_{CO2} can be used as plotting variables for displaying spring water chemistry. The data from Fig. 4 were grouped in different segments of the hydrograph as indicated by the vertical dashed lines. These appear in the circled clusters in Fig. 5. In addition to the sample data, Fig. 5 illustrates different regimes and reactions:

- The horizontal lines indicate the calcite dissolution regimes. Calcite is at saturation (equilibrium) at SI_C equal to 0. The horizontal line below equilibrium separates the dissolution regimes into rapid and slow kinetics.
- The gray lines illustrate the reaction pathways for the degassing of CO_2 at a constant concentration of dissolved Ca^{2+}. They are calculated from the relationship (White 1997):

$$SI_C = \log \frac{a_{Ca^{+2}}}{P_{CO_2}^{1/3}} \; \frac{2^{2/3}\, K_2^{1/3}\, \gamma_{HCO_3^-}^{2/3}}{K_1^{1/3}\, K_{CO_2}^{1/3}\, K_C^{1/3}\, \gamma_{Ca^{+2}}^{2/3}}$$

Where K_1, K_2, K_C, and K_{CO2} are the respective equilibrium constants for the first and second ionization of H_2CO_3 (K_1 and K_2), the solubility product constant for calcite (K_C), and the dissolution constant for CO_2 in water (K_{CO2}). a_{Ca+2} is the activity of calcium and the γ's are the activity coefficients for the specified variables. The calculations were completed using a temperature of 15°C. The γ values were calculated initially assuming a value of one and then recalculating iteratively until a convergence of 0.001 was obtained.

Similar plots have been used to classify types of springs (White 1997) but the data presented herein suggest that temporal variation within a single spring can be greater than the variation between springs. In general, the dominant change between storm initiation and crest (groups 1 and 2) is for the SI_C to decrease while the P_{CO2} is relatively constant. The later stages of the storm (groups 3 and 4) are characterized by a concurrent decrease in SI_C and an increase in P_{CO2}.

As can be seen from the equation above, the relationship between SI_C and log [Ca] is linear for a given P_{CO2} if it is assumed that the ratio of γ_{HCO3-} to γ_{Ca+2} is relatively constant. However, the SI_C and calcium concentrations from Beaver Spring fall onto two separate lines not a single linear relationship (Fig. 6). This implies significant changes in P_{CO2} during the storm significantly alter the relationship between the other parameters. Groups 1 and 2 fall onto one line while groups 3 and 4 fall on a second line.

Discussion

A lag between the minimum conductivity and SI_C value was also reported by Desmarais and Rojstaczer (2002) for a spring on the Oak Ridge Reservation, Tennessee. Unfortunately the corresponding P_{CO2} data were not included with this dataset and therefore the role of dispersed infiltration at this spring cannot be determined.

One implication of the present results is that the most aggressive water at the spring, signified by the lowest SI_C value, does not occur during the main storm pulse but rather during the discharge recession. While the time lag may be short at Beaver Spring due to its small ground water basin, it could be considerably more in a larger basin. This suggests that the maximum rate of dissolution may also lag behind the main storm pulse rather than occurring concurrently. Recent rate equations (Dreybrodt, 1990; Palmer, 1991) show that the rate of dissolution scales with the undersaturation of dissolved Ca^{2+} with respect to calcite.

Data from Beaver Spring suggests that the timing of the SI_C minimum is controlled by the P_{CO2} values. Elevated pressures of CO_2 lag after the main recharge pulse because the dispersed infiltration is transported more slowly than is the sinkhole-controlled quickflow. In the aquifer studied, dispersed infiltration reaches the spring within a day of the storm input. While the soil/residuum is the most likely source for the elevated CO_2, another possible source is the epikarstic zone at the residuum soil interface. However, flushing of the epikarst during the storms recession would be driven by the slow infiltration of the water through the residuum. It is likely that the identification of the two recharge sources at Beaver Spring are aided by (1) the small basin size allowing for the quick-flow recharge to be rapidly discharged, and (2) the presence of a thick residuum.

The complexity of the recharge argues that spring flow cannot be defined into storm and baseflow by a two-component separation as has been done in numerous studies (Desmarais and Rojstaczer 2002; Dreiss 1989; Lakey and Krothe 1996; Talarovich and Krothe 1998). Lakey and Krothe (1996) used hydrogen and oxygen isotopes to separate baseflow and storm flow in the

Orangeville Rise spring, Indiana. However, their isotopic compositions did not fall onto a tie-line between the mixing components and therefore they concluded that a two-component mixing model does not account for the complexity of the recharge and mixing processes. Lee and Krothe (2001) used isotopic data to conduct a four-component separation of storm water, also at Orangeville Rise spring. They concluded that the epikarst contributed a significant amount of storm water (~ 50%) but that there was little contribution from soil water (~ 3%). The ground water basin for the Orangeville rise has a thick soil zone (~ 10 m) it is still considerably less than the residuum at Fort Campbell (~ 30 m) and thus may have less of a contribution.

The relationships between SI_C with calcium and CO_2 supports the conclusion that different processes control the water chemistry over the course of the storm. SI_C and P_{CO2} have been used to distinguish between types of springs (Drake and Harmon 1973; White 1997) but temporal variability can be greater than the variability between springs. Therefore classifications of this type must consider the nature of each spring as well as the hydraulic conditions at the time of chemical sampling.

While both quickflow and dispersed infiltration occur in many aquifers, karst studies frequently assume that one type of recharge dominates for a single spring. However, the low CO_2 values can only be attributed rapid recharge and the elevated CO_2 values must result from some interaction with the soil/residuum zone. Therefore the data suggest that a single recharge style does not dominate throughout all conditions in a given spring. Although the flashiness and rapid response at Beaver Spring would have suggested that it is dominated by quickflow recharge, the data indicate that recharge even in a flashy spring with a small basin is more complex than anticipated.

While most conceptual models include both recharge styles, it is also essential that they account for the temporal variability in styles. Desmarais and Rojstaczer (2002) included temporal changes in their three stage model but did not include dispersed infiltration. The conceptual model presented in Fig. 7 is drawn from numerous sources (Field 1993; Ray and O'Dell 1993; Smart and Hobbs 1986; White 1999) but modified to explicitly include dispersed infiltration and reflect changes in the water's CO_2 composition.

During periods of baseflow, the conduit system may or may not be submerged (phreatic) and obtains its water from storage (Fig. 7a). During precipitation, water is rapidly input into the system via sinkholes and vertical drains (Fig. 7b). The rapidly injected rainwater is low in CO_2 and arrives in sufficient quantity to dilute the background carbonate chemistry. The potentiometric surface may be reversed during this time causing water to be forced into storage in fractures, bedding planes and the aquifer matrix, in a manner analogous to bank storage in a river. After the storm, (Fig. 7c), the potentiometric surface reverts to its initial configuration and the bank-stored water, still low in CO_2, is released back into the conduit system. The presence of anastomoses along bedding planes in caves has been attributed to this storage-release process (White 1988). While these stages of a rainstorm have been proposed before, our data suggest that a considerable volume of high-CO_2 dispersed infiltration can occur during this third stage (C). While the exact flux is unknown, it is sufficient to alter the integrated chemistry at the discharging spring. At Beaver Spring, this implies that the chemistry of the samples in groups 1 and 2 is controlled by stage B dilution while the chemistry of samples in groups 3 and 4 is controlled by the stage C infiltration.

Understanding the different stages of recharge in karst aquifers is essential for both water quality and water quantity estimations. If the recharge from sinkholes and through a thick soil zone are temporally separated, then contaminants from surface and deep subsurface soil sources could also be expected to arrive in an aquifer at different time after a storm event. While the example spring given in this study has a basin with considerable residuum, it also responds quickly and thus would generally have been identified as a spring associated with rapid recharge. Determining recharge type is also critical for calculating water balances and modeling watershed processes.

Acknowledgments

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References

Arthur D Little Inc (1997). Hydrogeologic Report. Cambridge, MA, Prepared for the U.S. Army Environmental Center: 185 p

Atkinson TC (1977) Diffuse flow and conduit flow in limestone terrain in the Mendip Hills, Somerset (Great Britain). J Hydrol 35:93-110

Desmarais K, Rojstaczer S (2002) Inferring source waters from measurements of carbonate spring response to storms. J Hydrol 260:102-117

Drake JJ, Harmon RS (1973) Hydrochemical environments of carbonate terrains. Water Resources Res 9(4):949-957

Dreiss SJ (1989) Regional scale transport in a karst aquifer 1. Component separation of carbonate spring waters. J Hydrol 23(1):117-125

Dreybrodt W (1990) The role of dissolution kinetics in the development of karst aquifers in limestone: A model simulation of karst evolution. J Geol 98:639-655

Field MS (1993) Karst hydrology and chemical contamination. J Environ Systems 22(1):1-26

Gustafsson JP (2000) Visual MINTEQ. Stockholm, Sweden, Kungl Tekniska Hogskolan (KTH), Div Land Water Resources

Hess JW, White WB (1993) Groundwater geochemistry of the carbonate karst aquifer, southcentral Kentucky, USA. Appl Geochem 8:189-204

Idstein PJ, Ewers RO (1991) Deducing karst aquifer recharge, storage and transfer mechanisms through continuous electronic monitoring - a confirmation with tracers. Proc Third Conf Hydrogeol Ecology Monitoring and Management of Ground Water in Karst Terranes, Nashville, TN pp 431-445

Lakey B, Krothe NC (1996) Stable isotopic variation of storm discharge from a perennial karst spring, Indiana. Water Resources Res 32(3):721-731

Lee ES, Krothe NC (2001) A four-component mixing model for water in a karst terrain in south-central Indiana, USA. Using solute concentration and stable isotopes as tracers. Chem Geology 179:129-143

Palmer AN (1991) Origin and morphology of limestone caves. Geol Soc Amer Bull 103:1-21

Quinlan JF (1989) Ground-Water Monitoring in Karst Terranes: Recommended Protocols and Implicit Assumptions. Las Vegas, Nevada, U.S. Environmental Protection Agency: 79

Ray JA, O'Dell PW (1993). DIVERSITY: A new method for evaluating sensitivity of ground water to contamination. Environ Geol 22:345-352

Scanlon BR, Thrailkill J (1987) Chemical similarities among physically distinct spring types in a karst terrain. J Hydrol 89:259-279

Shuster ET, White WB (1971) Seasonal fluctuations in the chemistry of limestone springs: a possible means for characterizing carbonate aquifers. J Hydrol 14:93-128

Shuster ET, White WB (1972) Source areas and climatic effects in carbonate groundwaters determined by saturation indices and carbon dioxide pressures. Water Resources Res 8:1067-1073

Smart PL, Hobbs HO (1986) Characterization of carbonate aquifers: a conceptual base. Proc Conf Environmental Problems in Karst Terranes and Their Solutions, Bowling Green, Kentucky, National Water Well Association pp. 1-14

Talarovich SG, Krothe NC (1998) Three-component storm hydrograph separation of a karst spring contaminated by polychlorinated biphenyls in central Indiana. Environ Geosci 5(4):162-176

USEPA (2000). SW-846 Test Methods for Evaluating Solid Waste Physical/Chemical Methods. 2000

White WB (1988) Geomorphology and Hydrology of Karst Terrains. Oxford, New York

White WB (1997) Thermodynamic equilibrium, kinetics, activation barriers, and reaction mechanisms for chemical reactions in Karst Terrains. Environ Geol 30(1/2):46-58

White WB (1999) Karst hydrology: Recent developments and open questions. In: Beck BF, Pettit AJ, Herring JG (ed) Hydrogeology and engineering geology of sinkholes and karst, AA Balkema, Rotterdam, pp.3-21

Worthington SRH, Davies GJ, Quinlan JF (1992) Geochemistry of springs in temperate carbonate aquifers: Recharge type explains most of the variation. Ann Sci Univ Besancon Mem 11:341-347

Table 1. Summary of water chemistry data

Parameter	Beaver Spring					Millstone Spring				
	June 20-26, 1999 Storm					June 20-26, 1999 Storm				
	Min	Max	n	Mean	CV*	Min	Max	n	Mean	CV*
Temperature (°C)	15.5	17.0	25	16.2	3.4%	15.2	17.8	22	15.8	3.9%
Specific Conductance (µS/cm)	337	476	25	415	13%	254	461	22	364	13%
Calcium (mg/L)	45	91	25	66	25%	41	87	22	64	16%
Magnesium (mg/L)	5.3	9.9	25	7.4	24%	5.3	9.0	22	7.1	16%
Alkalinity (mg/L HCO_3^-)	153	324	16	201	22%	167	264	16	210	12%
	June-August 1999					June-July 1999				
Temperature (°C)	15.4	21.6	3177	16.1	4.8%	15.1	18.5	2092	15.9	5.6%
Specific Conductance (µS/cm)	225	510	3177	445	9.3%	180	436	2092	234	24%

* CV = Standard deviation divided by the mean

Figure Captions

Figure 1. Regional location of study area and outline of estimated ground water basin for Beaver Spring.

Figure 2. Hydrograph and chemographs for Beaver Spring, June 1999 storm.

Figure 3. Hydrograph and chemographs for Millstone Spring, June 1999 storm.

Figure 4. Variation in SI_C and P_{CO2} over a storm event, Beaver Spring, June 1999.

Figure 5. Relationship between SI_C and P_{CO2} over storm event, Beaver Spring June 1999.

Figure 6. Relationship between SI_C and Ca concentrations over storm event, Beaver Spring June 1999.

Figure 7. Conceptual model for recharge in a karst aquifer

FIGURE 1

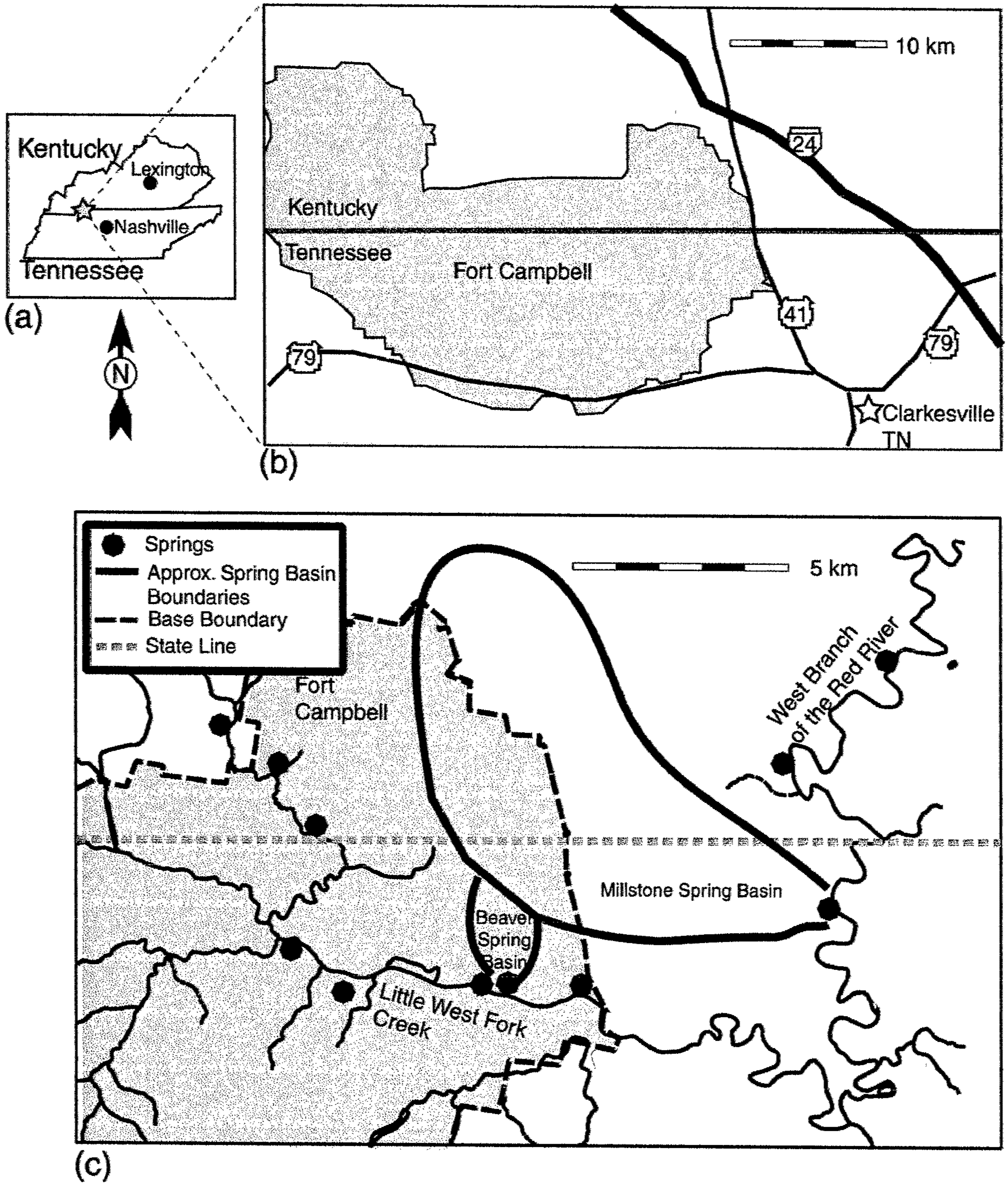
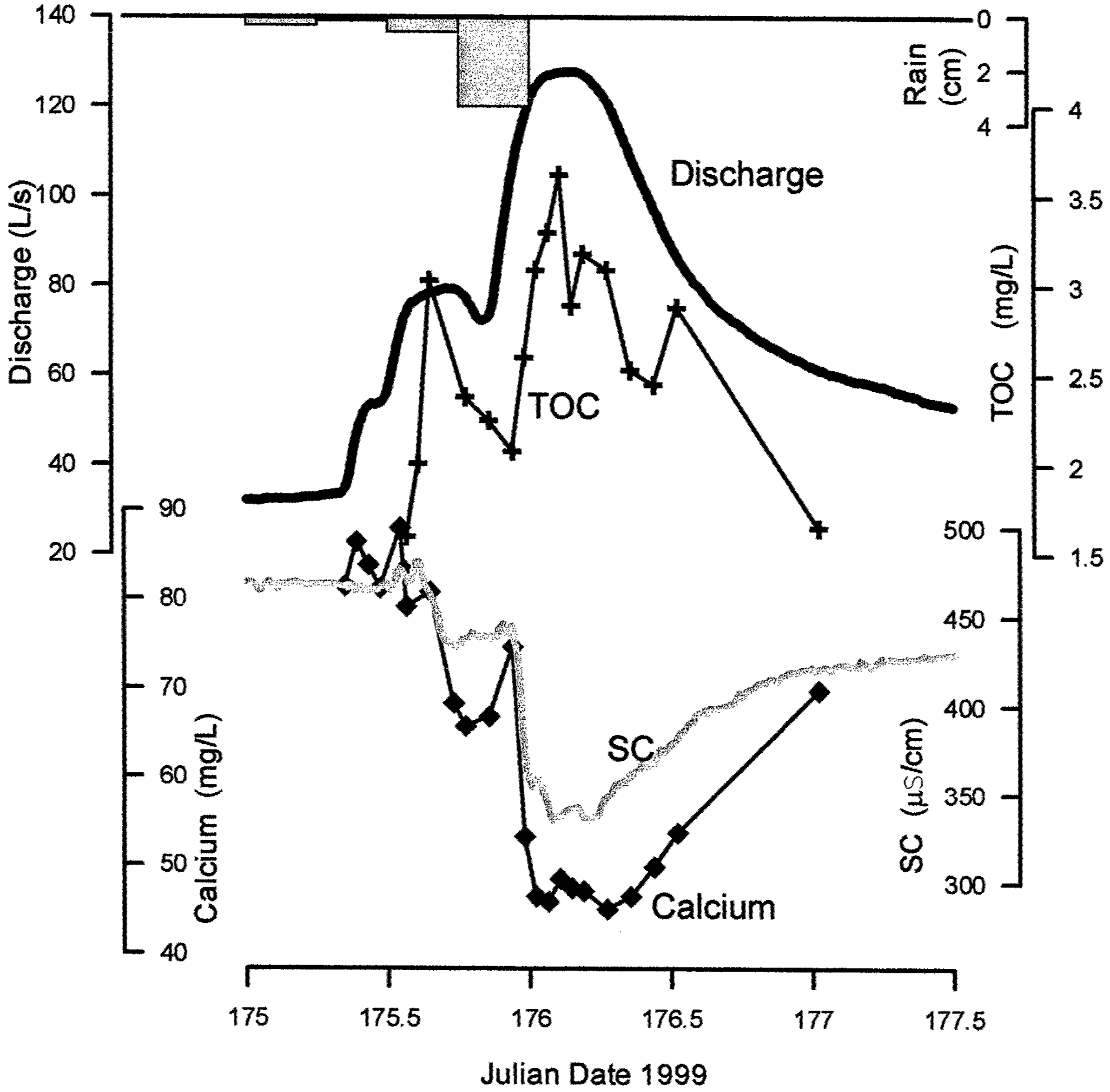
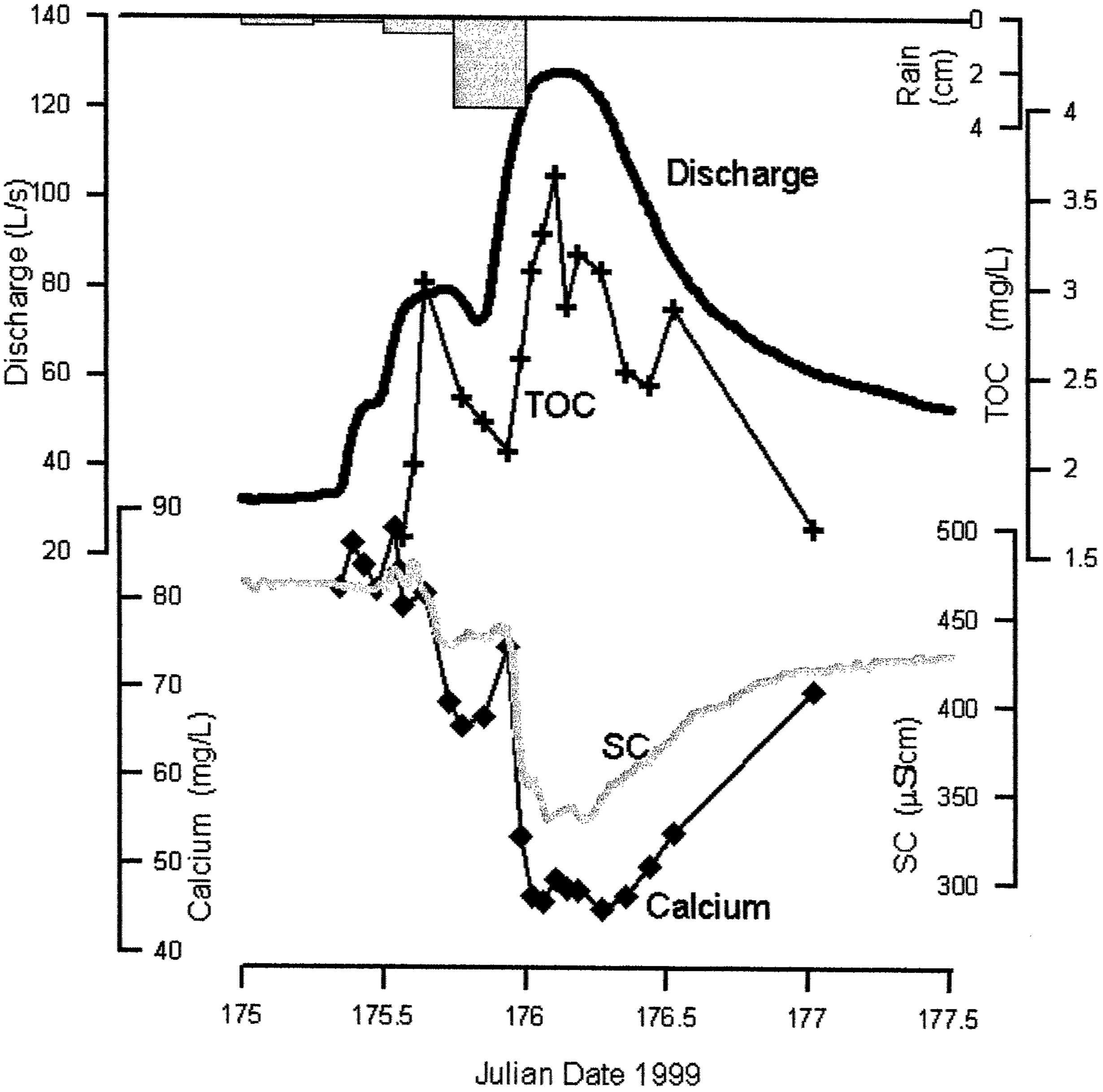

Kentucky
Lexington
Nashville
Tennessee
(a)
N
10 km
24
Kentucky
Tennessee
Fort Campbell
41
79
79
Clarkesville
TN
(b)
Springs
Approx. Spring Basin Boundaries
Base Boundary
State Line
5 km
Fort Campbell
West Branch of the Red River
Millstone Spring Basin
Beaver Spring Basin
Little West Fork Creek
(c)

FIGURE 2



Discharge (L/s)
140
120
100
80
60
40
20
Rain (cm)
0
2
4
TOC (mg/L)
4
3.5
3
2.5
2
1.5
Discharge
TOC
Calcium (mg/L)
90
80
70
60
50
40
SC (µS/cm)
500
450
400
350
300
SC
Calcium
175
175.5
176
176.5
177
177.5
Julian Date 1999

FIGURE 3



Discharge (L/s)
140
120
100
80
60
40
20
Rain (cm)
0
2
4
TOC (mg/L)
4
3.5
3
2.5
2
1.5
Discharge
TOC
Calcium (mg/L)
90
80
70
60
50
40
SC (µS/cm)
500
450
400
350
300
SC
Calcium
175
175.5
176
176.5
177
177.5
Julian Date 1999

FIGURE 4

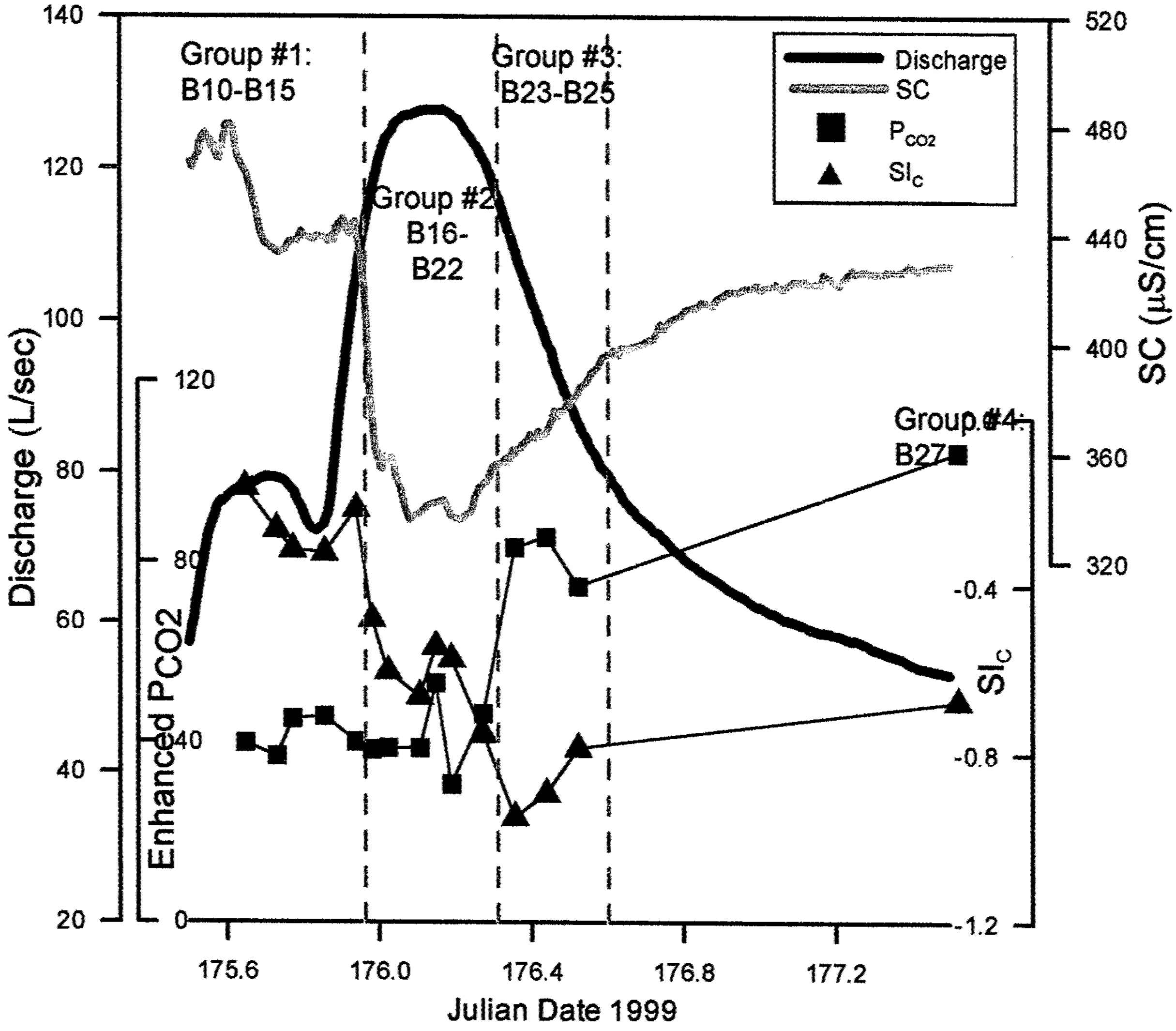

Group #1:
B10-B15
Group #2
B16-
B22
Group #3:
B23-B25
Group #4:
B27
Discharge
SC
P_{CO2}
SI_C
Discharge (L/sec)
Enhanced PCO2
SC (µS/cm)
SI_C
Julian Date 1999
140
120
100
80
60
40
20
0
40
80
120
520
480
440
400
360
320
-0.4
-0.8
-1.2
175.6
176.0
176.4
176.8
177.2

FIGURE 5.

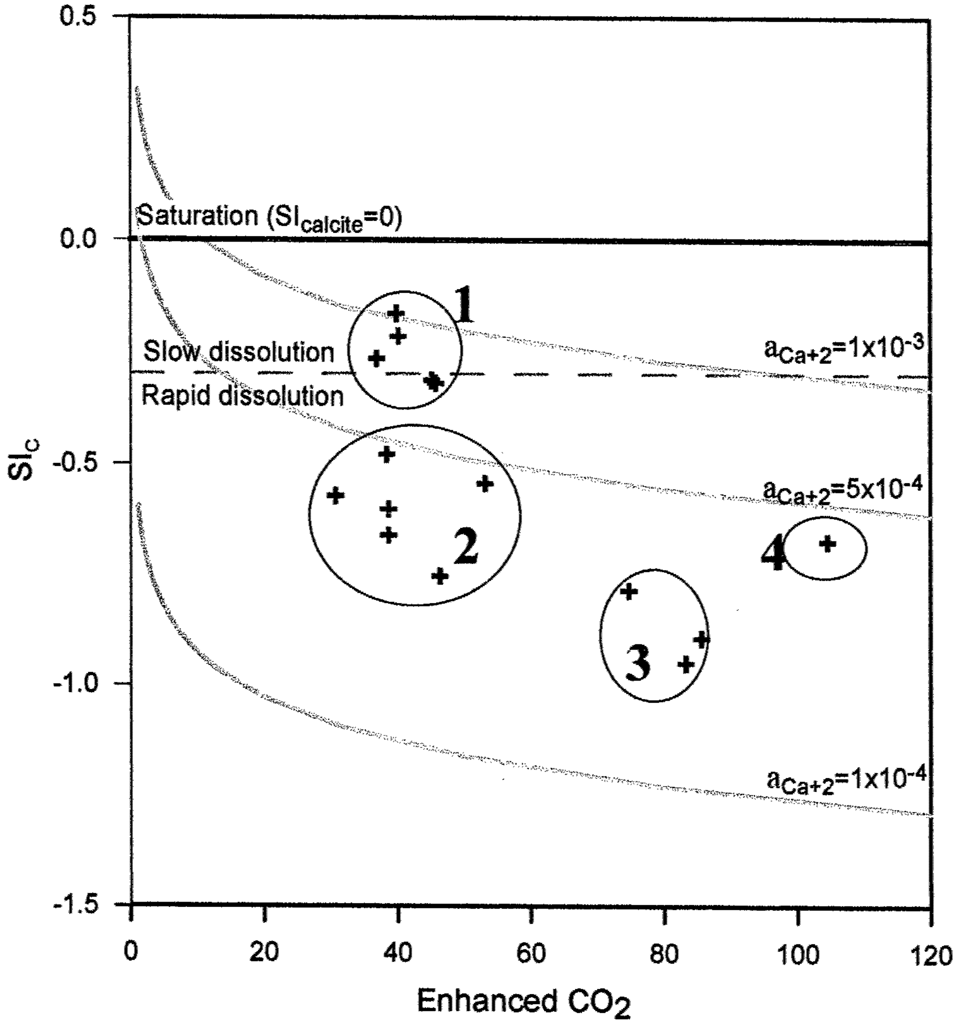

0.5
0.0
-0.5
-1.0
-1.5
SIc
0
20
40
60
80
100
120
Enhanced CO2
Saturation (SIcalcite=0)
Slow dissolution
Rapid dissolution
aCa+2=1x10-3
aCa+2=5x10-4
aCa+2=1x10-4
1
2
3
4

FIGURE 6

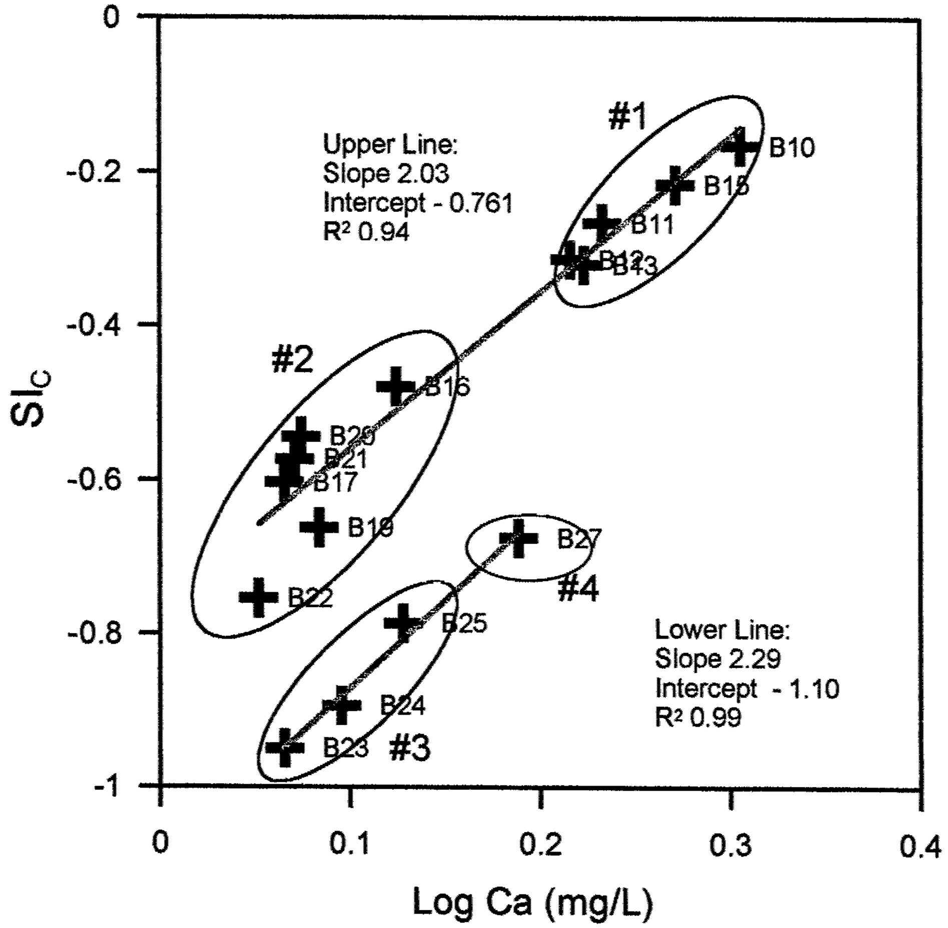
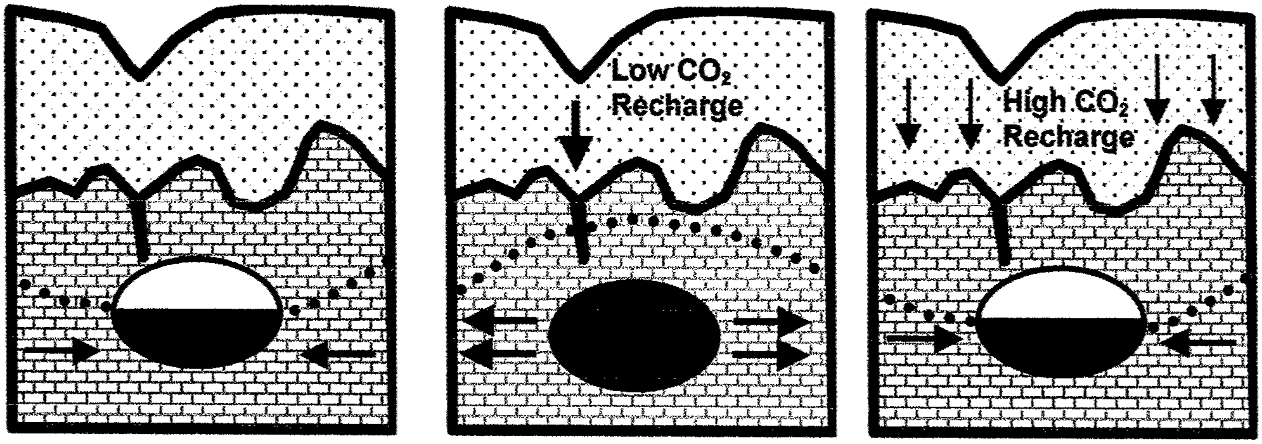

0
-0.2
-0.4
-0.6
-0.8
-1
SI_C
0
0.1
0.2
0.3
0.4
Log Ca (mg/L)
#1
#2
#3
#4
B10
B15
B11
B12
B13
B16
B20
B21
B17
B19
B22
B27
B25
B24
B23
Upper Line:
Slope 2.03
Intercept - 0.761
R² 0.94
Lower Line:
Slope 2.29
Intercept - 1.10
R² 0.99

FIGURE 7



Appendix 5.2

Metal Transport to Karst Springs During Storm Flow: An Example from Fort Campbell, Kentucky/Tennessee, U.S.A.

Paper accepted for publication by Journal of Hydrology

Metal Transport to Karst Springs During Storm Flow; An Example from Fort Campbell, Kentucky/Tennessee, U.S.A.

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Abstract

Low levels of heavy metals were investigated in a series of springs discharging from the Mississippian limestone aquifer underlying the Fort Campbell Army Base in western Kentucky/Tennessee. Springs were sampled at short time intervals through periods of storm discharge. Unfiltered samples were digested and analyzed by inductively-coupled plasma mass spectrometry. Metals detected at the μg/L level included As, Cd, Cr, Ni and Pb. Metal concentrations exhibited a pronounced maximum coincident with the peak of the storm hydrograph in contrast to carbonate species (Ca, Mg) which dipped to a minimum at the peak of the storm hydrograph. Metal concentrations track with aluminum and iron suggested that the metal transport is mainly by adsorption onto suspended particulates which are mobilized during storm flow.

Keywords: karst hydrology, geochemistry, ground water, metals, springs, sediment transport

1.0 Introduction

The water chemistry in some karst springs, like that in surface water, is known to vary considerably over storm events. The change may be short-lived, but high-flow conditions have the ability to transport increased amounts of sediments and higher concentrations of contaminants and/or nutrients in both surface water (Hjulström, 1939; Leopold and Maddock, 1953; Gibbs, 1973; Sandén et al., 1997) and in karst settings (Ryan and Meiman, 1996; Atteia and Kozel, 1997; McCarthy and Shevenell, 1998; Mahler and Lynch, 1999; Mahler et al., 2000; Shevenell and McCarthy, 2002). Sorption of contaminants and metals onto solids is a common phenomena in natural systems, and coupled sediment transport may account for acute increases in trace metals and organic contaminants with high sorption affinities (Allan, 1979; Hart, 1982; Jenne and Zachara, 1987; Horowitz, 1991; Warren and Zimmerman, 1993).

The water chemistry variability in karst springs differs from the variability seen in most surface water, because karst ground water also reflects the chemistry of the carbonate aquifer. Changes in the background carbonate-derived parameters (calcium, magnesium and alkalinity) have been used for many years to probe the physical hydrogeology of karst aquifers (Pitty, 1968; Shuster and White, 1971; Ternan, 1972; Jacobson and Langmuir, 1974). The extent to which water quality is affected by rain storms is a function of numerous aquifer properties including recharge type; permeabilities of, and interconnection between, the matrix, fractures and conduits; basin relief; and lithologic, stratigraphic and structural controls (White, 1999). These properties provide a conceptual framework for karst basins and springs. How close any given spring may be to the end-members on the chemical continuum (highly consistent vs. highly variable) depends on the combination of those properties.

The contaminant and sediment chemistry of karst springs is less well understood than the background carbonate chemistry. Studies have shown that the timing and form of contaminant transport depends on the species chemical form, source type, and the aquifer geometry (Ewers et al., 1992; Crawford and Ulmer, 1994; Ryan and Meiman, 1996; Currens, 1997; McCarthy and Shevenell, 1998; Talarovich and Krothe, 1998; Loop and White, 2001). The transport of chemical species sorbed to solids is further complicated by the increase in suspended sediment transport, and changes in sediment composition, during storms (Atteia and Kozel, 1997; Mahler and Lynch, 1999; Mahler et al., 1999).

Springs are of particular interest to the karst hydrologist because they provide the only practical means of monitoring water chemistry throughout a ground water basin (Quinlan, 1989). Conventional monitoring techniques used in granular aquifers, such as wells, are rarely fully representative of water chemistry or hydraulics in karst aquifers due to the physical heterogeneity and localization of flow caused by carbonate dissolution. Furthermore, because springs are the transition zone between ground water and surface water, they are a common location at which humans and ecosystems may contact contaminated ground water. Therefore monitoring spring quality is essential to evaluate the impact of ground water contamination and the interaction between ground and surface waters. Given the chemical variability of many springs, it is essential that time-based monitoring be conducted over storm events.

2.0 Study Area Description

This study is an investigation of springs on and near the Fort Campbell Army Base. The base is located along the Kentucky-Tennessee border approximately 65 km northwest of Nashville, Tennessee (Figure 1a). Fort Campbell encompasses approximately 430 km^2 (Figure

1b), of which nearly 80 percent is used for military ranges and is largely undeveloped. Over 30 perennial springs have been identified within an area of approximately 250 km^2 around the base.

The area surrounding Fort Campbell is largely agricultural with some commercial and industrial uses. The metals detected during this study are naturally present in the background and thus may originate from either natural and anthropogenic sources; the distinction cannot be made based on the data collected. The region is located on the Western Highland Rim of the Nashville Basin and is underlain by the limestones of the Mississippian St. Louis and Ste. Genevieve formations (Klemic, 1966a, b). The Ste. Genevieve is found in the topographically high areas and largely consists of thick-bedded limestone with thinner beds of dolomite. Discontinuous layers of chert and fossils are present. The St. Louis Formation outcrops primarily in the waterways and topographic lows to the south. It is thin to thick bedded, dolomitic, argillaceous, silty, and fossiliferous. Ball chert and colonial corals are profuse in some layers.

Between 0 and 30 m of unconsolidated materials are present above the limestone. This regolith consists of an upper layer of reddish brown clays and a lower layer of gravely clay (Arthur D. Little Inc., 1997). Chert nodules are commonly found at the regolith – rock contact.

Beaver and Millstone Springs (Table 1, Figure 1c) are falling (gravity) springs with variable water chemistry. Hydrographs from Beaver and Millstone Springs crest soon after a rainstorm (12 to 24 hrs, respectively). The spring basins have similar geology, recharge types (both sinkhole input and soil infiltration), topography, and potential contaminant sources. Single-point sinking streams (allogenic recharge) are not common in this area, although the Little West Fork Creek and its tributaries are dry in some reaches during late summer and fall (Figure 1c).

3.0 Methods

3.1 Water Samples

Water samples were collected from the springs during short time intervals over storm events in June 1999 and June 2000. The samples were collected in pre-cleaned HDPE bottles at intervals ranging from 0.5 hour to 12 hours; closely-spaced intervals were used initially and when the springs were undergoing rapid changes and widely-spaced intervals were used as the springs neared baseflow conditions. The samples were collected using automated samplers programmed to begin sample collection with stage increase.

Data collected concurrently with the water samples include precipitation, stage, specific conductance (SC), temperature, turbidity, pH and alkalinity. The precipitation data for 6-hour intervals were obtained from the Fort Campbell Army Airfield. Stage, SC and temperature data were collected by Ewers Water Consultants, Inc. The parameters were measured at 10-second intervals with 2-minute averaging and recorded on a Campbell Scientific, Inc. digital micrologger. Stage was measured using a Druck pressure transducer with a 0.03 cm resolution. The pressure values were converted into absolute stage readings using the surveyed elevations of staff gages at the springs. Temperature was measured using an Omega Engineering, Inc. platinum resistance thermometer with a 0.01 degree C resolution. SC was measured using a probe designed by Ewers Water Consultants (Idstein and Ewers, 1991). Turbidity was measured using either a LaMotte 2020 Turbidimeter or a HF Scientific, Inc. DRT-15 turbidimeter; and pH was measured using a Horiba Water Quality Checker U-10. Alkalinity was measured using a digital titrator in accordance with standard methods (Thomas and Lynch, 1960; American Public Health Association, 2000). The samples were kept cold until laboratory analysis. Samples for metal analyses were preserved with ultratrace nitric acid.

The samples were microwave digested in Teflon-lined vessels with 2 molar nitric acid (USEPA, 2000). For comparison with the digested samples, aliquots of the year 2000 samples were pressure-filtered through dedicated, tortuous path, 0.45-µm PVDF cartridge filters. The filtering was conducted in the field and prior to acid preservation. All samples were analyzed using a Finnegan high resolution inductively-coupled plasma mass-spectrometer (ICP-MS). Detection limits varied by metal and sample. Data quality was assessed via digestion-process blanks, filter blanks, and replicate analyses (Vesper, 2002). The combined error was greatest for the metals with the lowest concentrations but still smaller than the variability over the storm event.

Filtering presents several problems including cross-contamination, poor separation of size fractions due to exclusion and blocking, and an arbitrary distinction between "solid" and "dissolved" (Horowitz et al., 1992, 1996). We acknowledge the problems and have attempted to maintain consistency by using tortuous-path filters for the water samples and by collecting filter blanks for quality control. Because colloids range in size across the 0.45-µm pore size, they are not clearly separated using this approach. Therefore we will refer to the sample aliquots as digested and filtered; and the material removed as "sediment." Although colloid transport is important in granular aquifers (McCarthy and Zachara, 1989), karst aquifers are able to transport larger particles and so all sizes of sediments are relevant and of interest. The sediment considered in this study is solely suspended sediment. This study does not account for any bed load sediment movement.

Each sample has been identified as belonging to either baseflow or storm conditions. Baseflow samples are identified as those samples collected when no rain had occurred and the continuously monitored parameters (stage, temperature, SC) were relatively constant. Storm samples include those samples collected any time from the initial stage change until the SC reached a minimum. Samples that did not clearly fall into either regime (including those from the minimum SC back to baseflow) were not included in the baseflow-storm analysis. Although the criteria and identification was somewhat arbitrary, it provided a means of differentiating between the two periods.

3.2 *Filter Residues*

Aliquots of the water samples were also filtered through flat membrane filters so that the suspended sediment could be examined. During 1999, the water samples were cascade filtered through 5-µm and 0.45-µm filters to limit clogging. During 2000 the water samples were less turbid and only the 0.45-µm filters were used.

The residues on the filters were analyzed using x-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS). The XRD data were collected using a Sintag PAD X with Cu K_α radiation, over a 2θ from 5 to 85 degrees, at 4 degrees/minute. The SEM/EDX analyses were conducted using a Hitachi S-3500N variable pressure SEM equipped with a tungsten filament for generating the electron beam. Images were collected under low-vacuum (40 Pascal) with a 20 kV beam, a 15 mm working distance, and a Robinson detector for backscatter electrons. Spectral analysis was conducted using a PGT Energy Dispersive X-ray Analysis System. The spectra were quantified using a calibration file set to the 20 kV beam.

SEM/EDX data were collected on the filter residues by comparing numerous (3-5) frames at a consistent magnification (600x) and conducting a "quantification" of the resulting atomic spectrum. The proportion of silicate and carbonate materials on the filter was addressed by calculating the Si:Ca ratio for each frame, based on atomic percentages of those elements, and averaging between the frames.

4.0 Results and Discussion

4.1 Precipitation and Overall Spring Response

The precipitation events and the antecedent moisture conditions were considerably different for the two storms sampled. In 1999, the sampled storm produced 5.6 cm of rain between June 24th and 25th (Julian Date[1], JD 174-175). Prior to this storm, there had been no rain for 8 days and only 3.8 cm of rain in the past 30 days. The 2000 storm was preceded by a much larger rain event. The sampled storm was 2 cm on June 17th and 18th (JD 169-170). Approximately 20 days before the sampled storm there was a large (14 cm), multiday storm period. The recession from the large earlier storm was still evident on the hydrographs of Millstone Spring at the time of the sampled storm. In the 30 days prior to the sampled storm, there was approximately 18 cm of precipitation.

Given the pre-sampling water conditions in 1999 and 2000, it can be expected that the springs will respond differently. VanSickle and Beschta (1983) suggest that sediments are generated during dry conditions and then are gradually removed during wet periods until the initial supply of sediments is depleted. Barton Spring, in Austin Texas, appears to have cycles similar to that predicted for streams (Mahler and Lynch, 1999). In our study, the amount of rain in 1999 and 2000 was sufficiently different so that the precipitation volume alone may suffice to cause the different spring responses during the two time periods. However, it does not discount the possibility that the dry-wet sediment supply cycle has considerable impact on the sediment transport.

The spring water, during all conditions, can be classified as calcium-bicarbonate water (Vesper, 2002), although both major and trace metals were consistently detected (Table 2). The concentrations were measured in triplicate. Elements present at high concentrations typically had 2 to 3 percent error; elements present near the limit of detection had up to 20 to 30 percent error. Although the trace elements had high analytical error, the exact concentration values are less important than the trends through time and relationships between elements.

4.2 Digested Water Samples

Al, Fe, Mn and the trace element concentrations generally approximate a lognormal distribution. This distribution is also consistent for the full data set, the baseflow data, and the storm event data. The one exception is Si, which does not fit well into either a normal or lognormal distribution. This agrees with data from Currens (1997), who conducted a statistical study of over 500 samples from Pleasant Grove Spring in Kentucky and found that dissolved constituent concentrations were typically normally distributed (i.e., nitrate) while sediment-bound constituent concentrations were typically lognormally distributed (i.e., Triazine).

The changes in chemical concentrations through time, or chemographs, are best illustrated by the 1999 data (Figure 2). As expected, SC is dominated by the Ca concentrations and thus the Ca chemograph mimics the SC data. Similar chemograph patterns, with high background concentrations diluted by event water, are also exhibited by Mg and alkalinity although they are not shown. This agrees with earlier studies showing that in variable-chemistry springs the elements associated with carbonate dissolution are high during baseflow conditions (when the aquifer discharges storage water) and are diluted during storm events (Ashton, 1966; Hess and White, 1988; White, 1988).

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[1] Julian Dates begin at 1 for January 1 and continue consecutively through a single year.

The other cations measured in this study generally increase in concentration during storm events coincident with the SC minimum (Figure 2a). The Al concentration is interpreted as a proxy for soil minerals and its increase signifies the transport of sediment and particulate material. Al was chosen in preference to turbidity because it can be more accurately measured. An increase in sediment transport, coincident with the rise in stage, has been observed for other karst springs (Ryan and Meiman, 1996; Atteia and Kozel, 1997; Mahler and Lynch, 1999). Atteia and Kozel (1997) suggested that increased turbidity in their spring was due to entrainment of sediments within the conduit system during periods of high-velocity. A more likely explanation for Fort Campbell is that the sediments are from overland flow, introduced by sinkholes, or flushed from surface soils. This distinction can be made at Millstone Spring because the Ca and Al changes are coincident with each other but lag behind the stage change. If mobilization of internal sediments controls transport, then the Al concentration peak could be expected to coincide with an increase in stage while the Ca decrease lags. However, the Al peak lags stage and is coincident with the Ca dip, signifying that the surface recharge controls the sediment transport.

Input of surface soils has been identified as an important factor in sediment transport in other karst systems. Mahler and Lynch (1999) identified the sediments discharged at Barton Spring, Texas, as either allochthonous sediments that originate at the surface and or as autochthonous sediments that originate within the aquifer itself. They concluded that the sediments transported to Barton Spring are primarily allochthonous in origin based on the presence of organic matter. Ryan and Meiman (1996) also concluded that the turbidity in Big Spring, near Mammoth Cave National Park, Kentucky, was from a (allochthonous) surface source. Their conclusion was based on the coincident arrival of turbidity along with dyes injected in a distal sinking stream, and that the turbidity pulse was shorter than the hydrologic pulse. If the turbidity source was in-aquifer sediments, then the turbidity and hydrologic pulses should have been comparable in duration. The dye and turbidity pulses lagged the hydrologic pulse which was attributed to the distance from the source area to the spring combined with a phreatic flow regime. Although the time frame is shorter, a similar relationship was observed between sediment transport and hydrologic response at Millstone Spring.

The trace element chemographs generally mimic the Al and Fe chemographs, suggesting that their transport is coupled. The strength of the relationship is further supported by linear regression analyses between Al and the trace elements in the digested samples (Table 3). Both the chemographs and the correlations suggest the presence of two different water populations: storage water characterized by high Ca concentrations (poorly or negatively correlated with Al) and event water characterized by elevated Al, Fe, Mn and trace element concentrations. The proportion of each water population in the mixture varies temporally. To better determine if the storm style impacted the Al-trace element relationship, we conducted multiple regression analyses using a general linear model to test if the slopes of the regressions for 1999 and 2000 data were statistically different. The analysis indicated that the slope of the linear relationship between Al with As, Cd, Cr, Fe, Mn, Ni, Pb and Si is consistent for both years at Beaver Spring. The same elements, with the exception of Si, also had a consistent relationship in 1999 and 2000 at Millstone Spring. The multiple regression analysis is further supported by the high R^2 values obtained from the combined 1999 and 2000 datasets (Table 3). The consistency of the relationship over both years and between springs is particularly interesting given the large differences in the range of concentrations between the two years. This suggests that, even if the magnitude of sediment transport is a function of supply and depletion, the chemical relationship between the sediment-associated elements is consistent. Hence the major metal concentrations can be used to predict the trace metal concentrations in future storms regardless of the storm size.

The amount of variability through time was quantified using the coefficients of variation (COV) for each storm event. Values for digested-sample COVs for a single event range from less than 5% to greater than 170% depending upon the element, the spring, and the year (Table 2). Ca has the lowest COV for each time-series; Al and Fe typically have the highest COVs. The 1999 event generally produced higher COVs than did the 2000 event presumably due to the different in storm size and antecedent moisture conditions. In past studies, the COV of carbonate parameters has been used to define the spring type (Shuster and White, 1971) or the ground water travel time (Ternan, 1972). However, the data reported in this study indicate that the Ca COV is not a good indicator for the variability of sediment transport. This can be attributed to the different controlling factors. The Ca concentration is largely controlled by carbonate dissolution and dilution while the Al concentration depends on source materials and ground water discharge. Therefore, using the variability of carbonate parameters at a spring over time is a poor choice for predicting the magnitude of sediment, and potentially contaminant, transport.

The time variation was also addressed via a statistical comparison of the mean baseflow and mean storm concentrations, for each element and each storm. Although the concentration increase during storms may seem obvious for some elements such as Al and Mn, it is less clear for carbonate-derived parameters, and for the trace elements having low concentrations in both baseflow and storm conditions, such as Pb and Cd (Table 4). For the later elements, the baseflow and storm mean values were compared via a 2-sample t-test with a 0.05 level of significance (data log transformed as necessary). The statistical comparison confirmed the initial conclusion that the carbonate-derived parameters decreased during storm conditions, while the other parameters increased during storm conditions. The one exception was that the baseflow and storm Cd concentrations in Beaver Spring were not statistically different. It should be noted, that although this analysis is useful for comparing mean concentrations, the definition of storm and baseflow samples is not exact and that the calculation does account for clear data trends observable on the chemographs.

4.3 Comparison of digested and filtered water samples

The year 2000 filtered samples were analyzed for comparison with the digested samples (Table 2). The purpose of filtering aliquots of the 2000 samples was for comparison with the digested sample concentration.

The filtered sample concentrations are nearly always less than the digested sample concentrations for Al, As, Cd, Cr, Fe, Mn, Ni, Pb and Si. The only exceptions to this are the trace metals present near the level of detection. For most of the elements the difference was at least one order-of-magnitude. For four elements, the concentrations were closer (As, Cd, Cr, and Ni) and so the concentrations were compared via paired t-tests to determine significance. Based on a 0.05 level of significance, the mean digested and filtered sample concentrations are equivalent at both springs for As and at Beaver Spring for Cd and Si. The As and Cd comparisons are based on a limited number of sample pairs (at most 3). The digested and filtered sample Si concentrations are closer than for most metals presumably because of the high solubility of Si. In general, the strong linear correlations between Al and the trace elements, observed for the digested samples, are not present in the filtered samples. The only statistically significant correlations for the filtered samples (at $\alpha = 0.05$) were between Al with Cd ($R^2 = 0.77$) and Mn

(R^2=0.78) at Millstone Spring, 2000. No significant correlations were found in the Beaver Spring data but it should be noted that this is a much smaller data set (4 to 6 samples).

The chemographs of the filtered samples generally lack the trends visible in the chemographs of their associated digested samples (Figure 3). This is clearly true for the major metals. Some trace metals may appear to have slight trends however the changes are within the background noise of the post-storm baseflow samples. The lack of trends is likely because the trace elements are removed with the sediments in the filtering process.

The focus of this study is primarily sediment and total metal transport therefore no attempt was made to clearly distinguish between the particulate and colloidal contributions to the total metal concentrations. The filtered samples contain some colloids while the digested samples contain both larger particulate matter as well as colloids larger than the 0.45 μm filter.

Based on data from Atteia and Kozel (1997), the number of large particles discharged at a karst spring is related to flow velocity while the number of small particles is related to water chemistry (pH and temperature). They concluded that a 5 μm breakpoint distinguished between particulates which are controlled by physical processes and colloids which are controlled by coagulation processes. Using total Al concentrations in digested samples as a proxy for large particulates, we also found a strong relationship between particulate transport and flow velocity (stage) (Figure 4a). However, we found that the large particulates are not entirely independent of pH, as was found by Atteia and Kozel (1997). When digested sample Al concentrations from Beaver Spring 1999 are plotted against pH, the data fall largely within three main groups (Figure 4b). The first two groups are associated with specific times in the storm while the third group includes samples from near-baseflow conditions (Figures 4b and 4c). The relationship between Al concentrations and pH cannot be considered independent of discharge because the spring water chemistry is itself a function of discharge. These data suggest that the identification of particulates and colloids by their dependence on discharge and pH is not exact because it does not account for the relationship between water chemistry and discharge.

Similar analyses were conducted for the Millstone Spring 2000 data. The total digested Al concentrations were exponentially related to discharge (stage). However, no clear relationships could be identified between (1) digested sample Al concentrations and pH, (2) filtered sample Al concentrations and stage, or (3) filtered sample Al concentrations and pH. If colloids account for the metal concentrations in the filtered samples, their transport should be associated with changes in chemistry. However, no clear relationship was observed.

4.4 Filter residue analysis

The filter residues were examined to see if they confirm the conclusions made based on the water data. The XRD analysis of filter residues suggested that the Beaver and Millstone Spring suspended sediments are a combination of goethite, opal and quartz. However, many of the filters had insufficient solids to produce a strong pattern, and therefore mineral identification was not exact. The SEM/EDX analysis showed that the sediments are heterogeneous both through time and on individual filters. During baseflow conditions individual grains of calcite, quartz and aluminosilicates can be seen on a fibrous filter (Figure 5a). During the main storm response the filter is coated with aluminosilicate materials while individual grains of quartz and aluminosilicates are visible (Figure 5b). Although nearly all of the filters contained silicate and aluminum silicate minerals, calcite rhombs can be observed in the baseflow samples. Changes in the type of suspended sediments can be seen on the filters collected over the storm event. The Si:Al atomic ratio was generally lower during baseflow conditions and higher during the storm itself. Beaver Spring can be used to illustrate the integration of the water chemistry and filter residue Si:Ca ratios (Figure 6). The filter residue observations are in agreement with earlier work, (Atteia and Kozel, 1997; Mahler and Lynch, 1999), indicating that the sediment composition transported to a karst spring varies over the course of a storm. In some studies the sediment composition change has been attributed to sources from different geologic formations (McCarthy and Shevenell, 1998) or regions within the same formation (Mahler and Lynch, 1999). A similar division can be made at Fort Campbell; periods of internal aquifer erosion occur between storms when autochthonous sediments are discharged at springs. The calcite rhombs and grains visible in the baseflow filter samples signify these periods. Periods of surface erosion occur during storms when allochthonous sediments, namely clays and silts, are flushed from the surface, transported through the aquifer, and discharged at springs. The aqueous data further support this division. Chemical compositions consistent with surface infiltration and soil flushing (low Ca, high Al) coincide with the increased discharge of sediments, namely the clays and silicates. Chemical compositions consistent with aquifer storage discharge (high Ca, low Al) coincide with the presence of calcite rhombs in spring sediments.

Fe was detected in the spectra for many of the filters and Mn was detected occasionally. Neither metal was detected at a constant spectral ratio with Al or Si suggesting that they may be present only as coatings on the aluminosilicate and quartz grains. Both Fe and Mn are commonly found as coatings in natural systems and are able to scavenge trace metals (Jenne, 1968; Singh and Subramanian, 1984; Kay et al., 2001). Hence the presence of the metal oxides provide one possible mechanism by which the trace metals can be associated with the transported sediment. While other mechanisms, such as incorporation into the mineral matrices must also occur, the association of trace metals with Mn-oxides has been well demonstrated in other karst settings (White et al., 1985).

5.0 Conclusions

The results of this study demonstrate that trace contaminant metals are transported in karst aquifers during storm events in association with sediments. A closer look at the data indicates the following conclusions can be made:

1. The chemistry of trace metals is highly variable temporally in some karst springs. The trace metal transport can be linked to sediment transport and is enhanced during storm periods.
2. Although different storms may produce different magnitudes of flow and chemical responses in a given spring, the relationship between the sediment proxy (Al) and the trace metals (As, Cd, Cr, Pb, Ni) remains consistent. This relationship allows researchers to anticipate periods of elevated trace element concentration based on the proxy concentration.
3. The lag between the maximum Al and Ca changes in concentration with respect to the hydrograph suggests that the discharge of suspended sediments appears to be controlled by allochthonous surface erosion rather than mobilization of sediments already within the aquifer.
4. Variation in carbonate parameters through storms, often used to assess the physical hydrogeology of karst aquifers, may be useful for indicating the timing of sediment transport, but is a poor indicator of the magnitude of variability in sediments and contaminants.

The significance of this study is to confirm that trace metals are transported to karst springs over short time intervals during storms and may contribute to acute water quality problems. Given the rapid changes in water quality, monitoring must be conducted on closely-spaced time scales and interpreted within a hydrologic context. If spring water metal concentrations are necessary for regulatory or risk assessment purposes, then the concentrations should be time-weighted or separated into mean concentrations by baseflow and storm populations. Grab sample concentrations, or samples collected without associated hydrologic data, cannot be assumed to represent environmental conditions at all karst springs.

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7.0 References

Allan, R.J., 1979. Sediment-Related Fluvial Transmission of Contaminants: Some Advances by 1979, Environment Canada, Regina, Saskatchewan.

American Public Health Association, 2000. 2320 Alkalinity. In: L.S. Clesceri, A.E. Greenberg and R.R. Trussell (Editors), Standard Methods for the Examination of Water and

Wastewater, Seventeenth Edition. American Public Health Association, Washington, pp. 35-39.

Arthur D. Little Inc., 1997. Hydrogeologic Report, Prepared for the U.S. Army Environmental Center, Cambridge, MA.

Ashton, K., 1966. The analysis of flow data from karst drainage systems. Transactions Cave Research Group, Great Britain, 7: 161-203.

Atteia, O. and Kozel, R., 1997. Particle size distributions in water from a karstic aquifer: from particles to colloids. Journal of Hydrology, 201: 102-119.

Crawford, N.C. and Ulmer, C.S., 1994. Hydrogeologic investigations of contaminant movement in karst aquifers in the vicinity of a train derailment near Lewisburg, Tennessee. Environmental Geology, 21: 41-52.

Currens, J.C., 1997. A sampling plan for conduit-flow karst springs: Minimizing sampling cost and maximizing statistical utility. Sixth Multidisciplinary Conference on Sinkholes and the Engineering and Environmental Impacts of Karst. Springfield, Missouri, pp. 193-198.

Ewers, R.O., Duda, A.J., Estes, E.K., Idstein, P.J. and Johnson, K.M., 1992. The transmission of light hydrocarbon contaminants in limestone (karst) aquifers. Third Conference on Hydrogeology, Ecology, Monitoring and Management of Ground Waters in Karst Terranes. Nashville, TN, pp. 287-304.

Gibbs, R.J., 1973. Mechanisms of trace metal transport in rivers. Science, 180: 71-73.

Hart, B.T., 1982. Uptake of trace metals by sediments and suspended particulates: a review. Hydrobiologia, 91: 299-313.

Hess, J.W. and White, W.B., 1988. Storm response of the karstic carbonate aquifer of southcentral Kentucky. Journal of Hydrology, 99: 235-252.

Hjulström, F., 1939. Transportation of detritus by moving water. In: P. Trask (Editor), Recent marine sediments: A Symposium. Am. Assoc. Petroleum Geologists, Tulsa, OK, pp. 5-31.

Horowitz, A.J., 1991. A Primer on Sediment-Trace Element Chemistry, Second Edition. Lewis Publishers, Inc., Chelsea, Michigan, 136 pp.

Horowitz, A.J., Elrick, K.A. and Colberg, M.R., 1992. The effect of membrane filtration artifacts on dissolved trace element concentrations. Water Research, 26(6): 753-763.

Horowitz, A.J. et al., 1996. Problems associated with using filtration to define dissolved trace element concentrations in natural water samples. Environmental Science and Technology, 30: 954-963.

Idstein, P.J. and Ewers, R.O., 1991. Deducing karst aquifer recharge, storage and transfer mechanisms through continuous electronic monitoring - a confirmation with tracers. Third Conference on Hydrogeology, Ecology, Monitoring and Management of Ground Water in Karst Terranes. Nashville, TN, pp. 431-444.

Jacobson, R.L. and Langmuir, D., 1974. Controls on the quality variations of some carbonate spring waters. Journal of Hydrology, 23: 247-265.

Jenne, E.A., 1968. Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides, Trace Inorganics in Water. Advances in Chemistry Series 73. American Chemical Society, Washington, D.C., pp. 337-387.

Jenne, E.A. and Zachara, J.M., 1987. Factors influencing the sorption of metals (Ch 8). In: K.L. Dickson, A.W. Maki and W.A. Brungs (Editors), Fate and Effects of Sediment-Bound Chemicals. Pergamon Press, New York, pp. 83-98.

Kay, J.T., Conklin, M.H., Fuller, C.C. and O'Day, P.A., 2001. Processes of nickel and cobalt uptake by a manganese oxide forming sediment in Pinal Creek, Globe Mining District, Arizona. Environmental Science and Technology, 35(24): 4719-4725.

Klemic, H., 1966a. Geologic Map of the Hammacksville Quadrangle, Kentucky. Map GQ-540, U.S. Geological Survey.

Klemic, H., 1966b. Geologic Map of the Oak Grove Quadrangle, Kentucky. Map GQ-565, U.S. Geological Survey.

Leopold, L.B. and Maddock, T.J., 1953. The Hydraulic Geometry of Stream Channels and Some Physiographic Implications. USGS Professional Paper 252, U.S. Geological Survey, Washington.

Loop, C.M. and White, W.B., 2001. A conceptual model for DNAPL transport in karst ground water basins. Ground Water, 39(1): 119-127.

Mahler, B.J. and Lynch, F.L., 1999. Muddy waters: temporal variation in sediment discharging from a karst spring. Journal of Hydrology, 214: 165-178.

Mahler, B.J., Lynch, L. and Bennett, P.C., 1999. Mobile sediment in an urbanizing karst aquifer: implications for contaminant transport. Environmental Geology, 39(1): 25-38.

Mahler, B.J., Personné, J.C., Lods, G.F. and Drogue, C., 2000. Transport of free and particulate-associated bacteria in karst. Journal of Hydrology, 238: 179-193.

McCarthy, J.F. and Shevenell, L., 1998. Processes controlling colloid composition in a fractured and karstic aquifer in eastern Tennessee, USA. Journal of Hydrology, 206(3-4): 191-218.

McCarthy, J.F. and Zachara, J.M., 1989. Subsurface transport of contaminants. Environmental Science and Technology, 23(5): 496-502.

Pitty, A.F., 1968. Calcium carbonate content of karst water in relation to flow-through time. Nature, 217: 939-940.

Quinlan, J.F., 1989. Ground-Water Monitoring in Karst Terranes: Recommended Protocols and Implicit Assumptions. EPA 600/X-89/050, U.S. Environmental Protection Agency, Las Vegas, Nevada.

Ryan, M. and Meiman, J., 1996. An examination of short-term variations in water quality in a karst spring in Kentucky. Ground Water, 34(1): 23-30.

Sandén, P., Karlsson, S., Düker, A., Ledin, A. and Lundman, L., 1997. Variations in hydrochemistry, trace metal concentration and transport during a rain storm event in a small catchment. Journal of Geochemical Exploration, 58: 145-155.

Shevenell, L. and McCarthy, J.F., 2002. Effects of precipitation events on colloids in a karst aquifer. Journal of Hydrology, 255: 50-68.

Shuster, 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, 14: 93-128.

Singh, S.K. and Subramanian, V., 1984. Hydrous Fe and Mn oxides - Scavengers of heavy metals in the aquatic environment. CRC Critical Reviews in Environmental Control, 14(1): 33-90.

Talarovich, S.G. and Krothe, N.C., 1998. Three-component storm hydrograph separation of a karst spring contaminated by polychlorinated biphenyls in central Indiana. Environmental Geosciences, 5(4): 162-176.

Ternan, J.L., 1972. Comments on the use of a calcium hardness variability index in the study of carbonate aquifers: with reference to the central Pennines, England. Journal of Hydrology, 16: 317-321.

Thomas, J.F.J. and Lynch, J.J., 1960. Determination of carbonate alkalinity in natural waters. Journal American Water Works Association, 52(2): 259-268.

USEPA, 2000. SW-846 Test Methods for Evaluating Solid Waste Physical/Chemical Methods.

VanSickle, J. and Beschta, R.L., 1983. Supply-based models of suspended sediment transport in streams. Water Resources Research, 19(3): 768-778.

Vesper, D.J., 2002. Transport and Storage of Trace Metals in a Karst Aquifer. An Example from Fort Campbell, Kentucky, Doctoral Dissertation, Pennsylvania State University, University Park, PA.

Warren, L.A. and Zimmerman, A.P., 1993. Trace metal-suspended particulate matter associations in a fluvial system: physical and chemical influences. In: S.S. Rao (Editor), Particulate Matter and Aquatic Contaminants. Lewis Publishers, Boca Raton, pp. 127-155.

White, W.B., 1988. Geomorphology and Hydrology of Karst Terrains. Oxford University Press, New York, 464 pp.

White, W.B., 1999. Conceptual models for karstic aquifers. Karst Modeling. Charlottesville, Virginia, pp. 11-16.

White, W.B., Scheetz, B.E., Atkinson, S.D., Ibberson, D. and Chess, C.A., 1985. Mineralogy of Rohrer's Cave, Lancaster County, Pennsylvania. NSS Bulletin, 47: 17-27.

Table 1. Springs Included in Study

Spring Name, Longitude, Latitude	Approx. Mean Baseflow[a] (L/s)	Approx. Basin Area[b] (km^2)	Time-Series Samples Collected[c]	Physical Description
Beaver Spring 87 27 15.39 W 36 36 37.73 N	2-3	1	1999 (D) 2000 (D, F)	Flows from base of stepped-limestone outcrop; Flows 120 m into Little West Fork Creek.
Millstone Spring 87 21 59.58 W 36 37 39.60 N	140	65	1999 (D) 2000 (D, F)	Flows from base of rock outcrop located in large erosional depression; Flows 100 m into the West Branch of the Red River.

a. Baseflow data collected late-summer and fall.
b. Basin areas estimated from normalized baseflow analysis and dye trace studies.
c. D: digested samples; F: filtered samples

Table 2. Summary of Statistics for Each Time Series (Concentrations in µg/L unless noted otherwise)

Storm	Statistic	SC µS/cm	Turb. NTU	Al Dig	Al Filt	As Dig	As Filt	Ca Dig	Ca Filt	Cd Dig	Cd Filt	Cr Dig	Cr Filt	Fe Dig	Fe Filt	Mn Dig	Mn Filt	Ni Dig	Ni Filt	Pb Dig	Pb Filt	Si Dig	Si Filt
Beaver Spring 1999	Number	25	19	25	---	25	---	25	---	25	---	25	---	25	---	25	---	25	---	25	---	25	---
	Maximum	476	156	15,100	---	3.25	---	91,400	---	0.49	---	21.0	---	7760	---	132	---	15.4	---	7.45	---	18,900	---
	Minimum	337	2.70	123	---	0.23	---	45,100	---	0.11	---	1.46	---	63.1	---	2.78	---	1.76	---	0.57	---	2,800	---
	Mean	415	68.0	4,280	---	1.19	---	65,900	---	0.21	---	7.39	---	2,200	---	36.2	---	5.95	---	2.73	---	7,400	---
	Std. Dev.	53	53.9	5,030	---	0.98	---	16,200	---	0.10	---	6.49	---	2,590	---	40.8	---	4.54	---	2.19	---	5,400	---
	COV (%)	13	79	118	---	82	---	25	---	51	---	88	---	118	---	113	---	76	---	80	---	73	---
Beaver Spring 2000	Number	---	---	6	4	4	2	6	6	6	6	6	6	6	3	6	6	6	4	4	0	6	6
	Maximum	---	---	2,650	20.8	0.71	0.30	84,700	91,000	0.14	0.11	4.04	1.21	1,390	35.2	22.0	2.60	2.88	0.78	2.43	---	5,580	3,700
	Minimum	---	---	64.8	9.07	0.23	0.26	74,500	78,400	0.09	0.09	1.50	0.94	37.0	11.8	2.02	0.82	0.82	0.63	0.71	---	2,910	3,030
	Mean	---	---	740	13.8	0.42	0.28	80,100	85,000	0.11	0.10	2.19	1.07	385	19.6	8.84	1.38	1.74	0.70	1.40	---	3,700	3,400
	Std. Dev.	---	---	1,000	4.99	0.21	0.03	3,600	4,100	0.02	0.01	0.99	0.10	522	13.5	7.78	0.67	0.72	0.07	0.73	---	1,000	243
	COV (%)	---	---	135	36	49	12	4.5	4.8	19	6.7	45	9.4	136	69	88	49	41	11	52	---	27	7.1
Millstone Spring 1999	Number	22	15	22	---	20	---	22	---	21	---	22	---	22	---	22	---	14	---	22	---	22	---
	Maximum	461	589	33,500	---	6.16	---	86,600	---	0.56	---	43.4	---	18,300	---	461	---	35.8	---	17.4	---	38,900	---
	Minimum	254	4.40	54.0	---	0.27	---	40,900	---	0.06	---	1.48	---	26.9	---	4.62	---	1.38	---	0.52	---	3,220	---
	Mean	364	105	5,000	---	1.19	---	64,300	---	0.16	---	7.77	---	2,750	---	73.7	---	9.25	---	3.02	---	8,500	---
	Std. Dev.	46.8	165	8,650	---	1.56	---	10,300	---	0.14	---	10.8	---	4,740	---	123	---	10.2	---	4.12	---	9,500	---
	COV (%)	13	157	173	---	130	---	16	---	86	---	139	---	172	---	167	---	110	---	136	---	112	---
Millstone Spring 2000	Number	18	17	18	10	17	3	18	18	16	16	18	18	18	11	18	18	10	8	18	0	18	18
	Maximum	419	33.0	3,240	24.0	0.77	0.40	74,900	87,200	0.17	0.08	5.60	2.11	1,730	20.2	70.7	5.58	5.56	2.56	2.07	---	6,960	3,710
	Minimum	373	3.60	183	8.50	0.26	0.23	62,700	58,100	0.06	0.04	1.61	0.74	107	7.84	6.73	0.94	0.64	0.42	0.26	---	3,210	2,460
	Mean	400	12.3	920	15.5	0.42	0.31	69,400	68,300	0.09	0.06	2.53	1.08	496	12.4	20.0	2.16	2.21	1.11	0.94	---	4,300	2,920
	Std. Dev.	10.7	8.22	870	5.03	0.13	0.09	3,300	8,800	0.03	0.01	1.08	0.32	456	3.93	16.3	1.20	1.51	0.73	0.54	---	1,030	407
	COV (%)	2.7	67	95	32	32	28	4.8	13	27	20	43	29	92	32	81	56	68	66	58	---	24	14

SC=Specific Conductance; Turb=Turbidity; Filt=Filtered; Dig=Digested; COV=Coefficient of Variation

Table 3. R^2 Values for Al vs. Various Elements for the Digested Water Samples

		Turbidity	As	Ca	Cd	Cr	Fe	Mn	Ni	Pb	Si
Beaver Spring	1999	0.98 (19)	0.98 (25)	-0.73 (25)	0.66 (25)	0.95 (25)	0.99 (25)	0.99 (25)	0.94 (25)	0.94 (25)	0.99 (25)
	2000	--- (0)	0.99 (4)	--- (6)	0.86[a] (6)	0.99 (6)	0.99 (6)	0.94 (6)	--- (6)	0.99[a] (4)	0.98 (6)
	Both years	0.98	0.98	-0.76	0.70	0.96	0.99	0.99	0.94	0.95	0.99
Millstone Spring	1999	0.99 (15)	0.99 (20)	-0.52[a] (22)	0.95 (21)	0.99 (22)	0.99 (22)	0.99 (22)	0.97 (14)	0.97 (22)	0.99 (22)
	2000	0.89 (17)	0.99 (17)	--- (18)	0.83 (18)	0.99 (18)	0.99 (18)	0.92 (18)	0.91 (10)	0.58[a] (18)	0.96 (18)
	Both years	0.99	0.99	-0.55	0.95	0.99	0.99	0.99	0.98	0.97	0.99
All data	Both years	0.97	0.99	-0.58	0.82	0.98	0.99	0.96	0.96	0.97	0.99

Notes: (n) denotes the number of samples used for the calculation; [a] indicates correlations that are statistically significant at $\alpha=0.05$ but not at $\alpha=0.01$; all other values shown are statistically significant within a=0.01; --- indicates values with insufficient data or which are not statistically significant.

Table 4. Comparison of Baseflow and Storm Concentrations (μg/L) for Digested Spring Water Samples, 1999 data

Spring	Condition		Al	As	Ca	Cd	Cr	Fe	Mg	Mn	Ni	Pb	Si
Beaver	Baseflow	n	4	4	4	4	4	4	4	4	4	4	4
Spring		mean	191	0.53	8,700	0.24	1.80	101	8,740	4.15	4.48	1.79	3190
1999		median	158	0.35	8,901	0.22	1.88	85.6	8,900	3.80	4.66	1.45	3290
		Stdev	91.0	0.44	1,400	0.13	0.24	48.2	1,360	1.17	2.12	1.46	265
	Storm	n	19	19	19	19	19	19	19	19	19	19	19
		mean	5,290	1.34	7,300	0.21	8.86	2,710	7,270	44.2	6.58	3.05	8,470
		median	2,180	0.77	6,700	0.17	4.18	1,090	6,700	22.5	3.82	1.91	5,380
		Stdev	5,360	1.06	1,800	0.10	6.78	2,760	1,790	43.7	4.98	2.37	5,770
Millstone	Baseflow	n	5	3	5	4	5	5	5	5	1	5	5
Spring		mean	270	0.29	7,391	0.07	1.75	150	7,390	8.76	---	0.57	3460
1999		median	324	0.28	7,060	0.07	1.74	185	7,060	8.06	---	0.57	3410
		Stdev	190	0.02	945	0.01	0.20	105	945	4.28	---	0.03	202
	Storm	n	14	14	14	14	14	14	14	14	12	14	14
		mean	7,600	1.56	7,090	0.19	11.1	4,180	7,090	110	10.4	4.34	11,200
		median	4,830	1.01	6,830	0.13	7.44	2,550	6,830	69.8	6.86	2.92	8,070
		Stdev	10,000	1.74	1,300	0.16	12.5	5,500	1,310	144	10.6	4.72	11,100

Figure captions

Figures 1a, 1b and 1c. Research site: (a) regional location with state capitals, (b) local area, (c) approximate location of springs used in the study (Vesper, 2002).

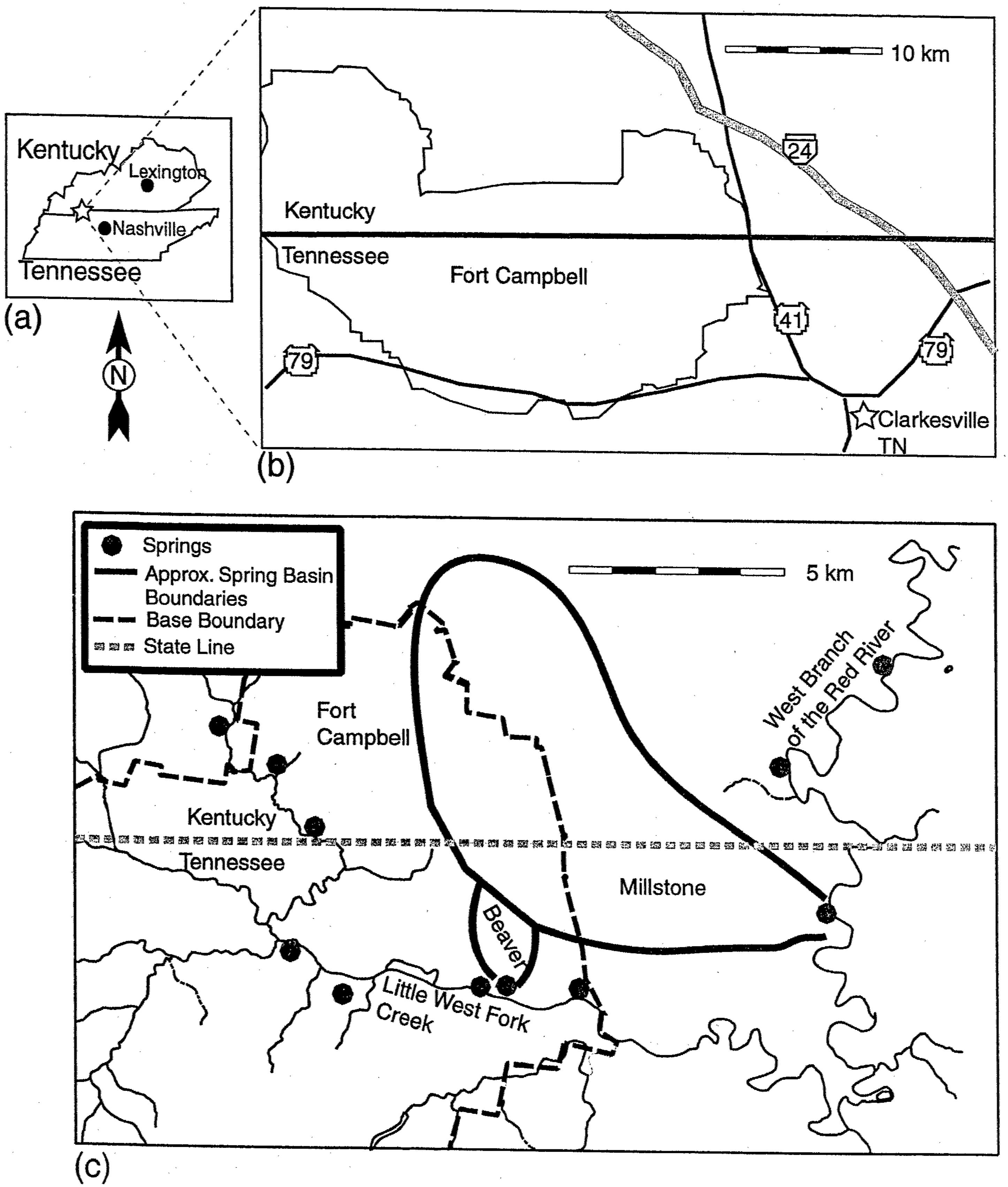
Figures 2a and 2b. Variability of digested sample concentrations for selected elements through the 1999 storm at (a) Beaver Spring, and (b) Millstone Spring. Stage (solid blank line) and specific conductance (solid gray line) are collected continuously; elemental concentrations indicated by symbols for each sample time. The lines between the individual samples are provided to aid the eye.

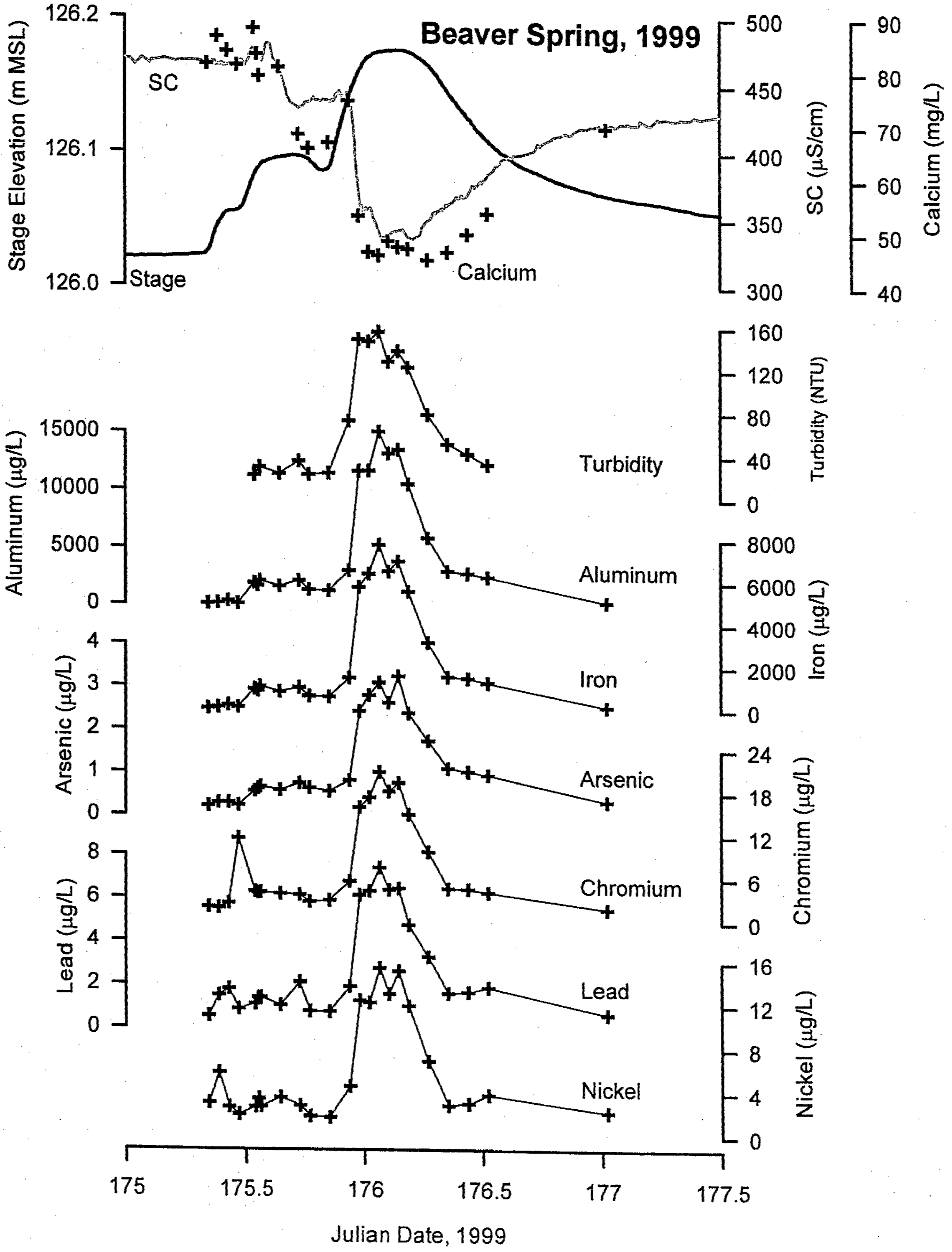
Figure 3. Chemographs for digested and filtered concentrations of selected sediment-associated elements at Millstone Spring, 2000. Symbols indicate individual water samples; the lines between the individual samples provided to aid the eye.

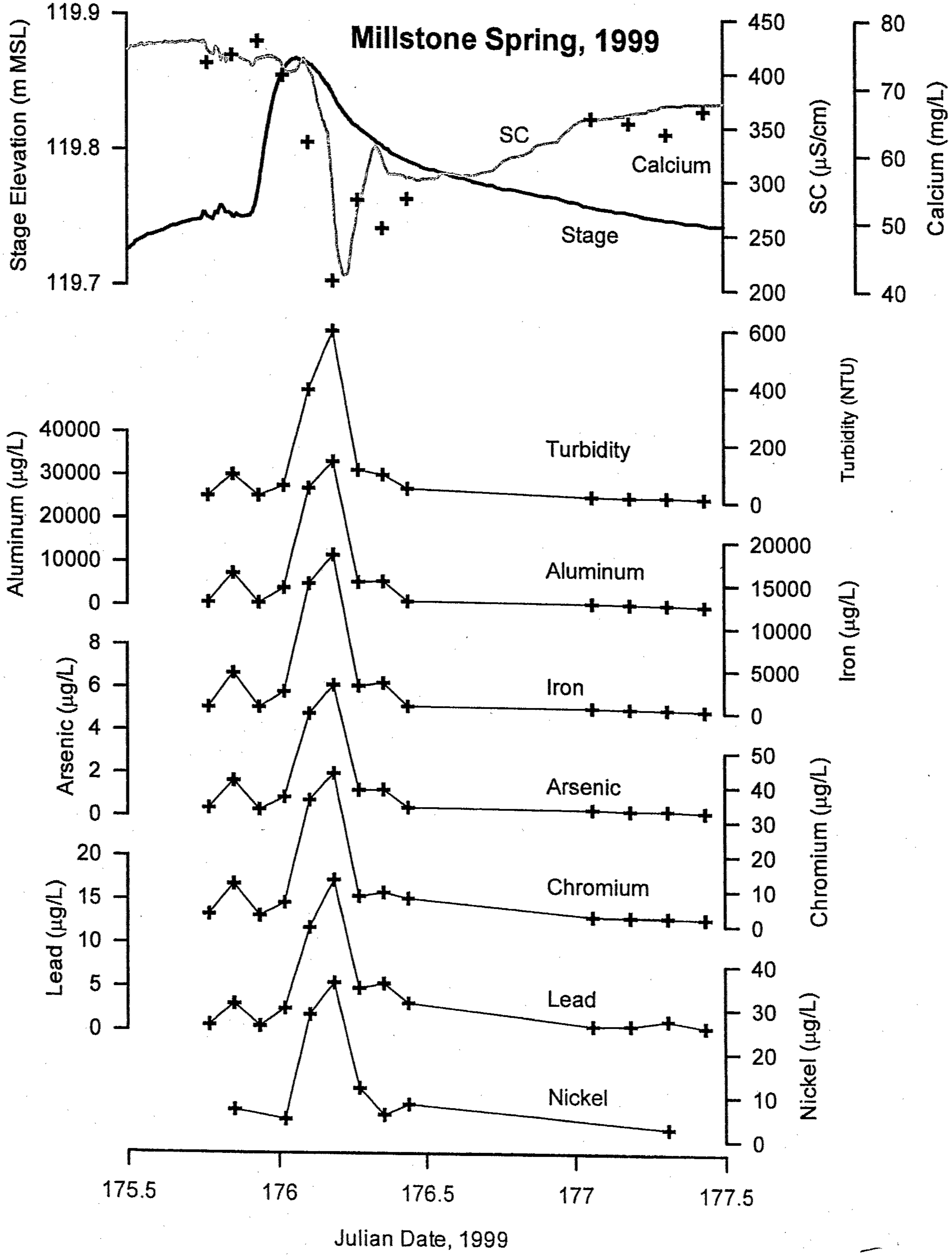
Figure 4a, 4b and 4c. Comparison of digested Al concentrations with (a) stage, (b) pH, and (c) through time. Data from Beaver Spring 1999.

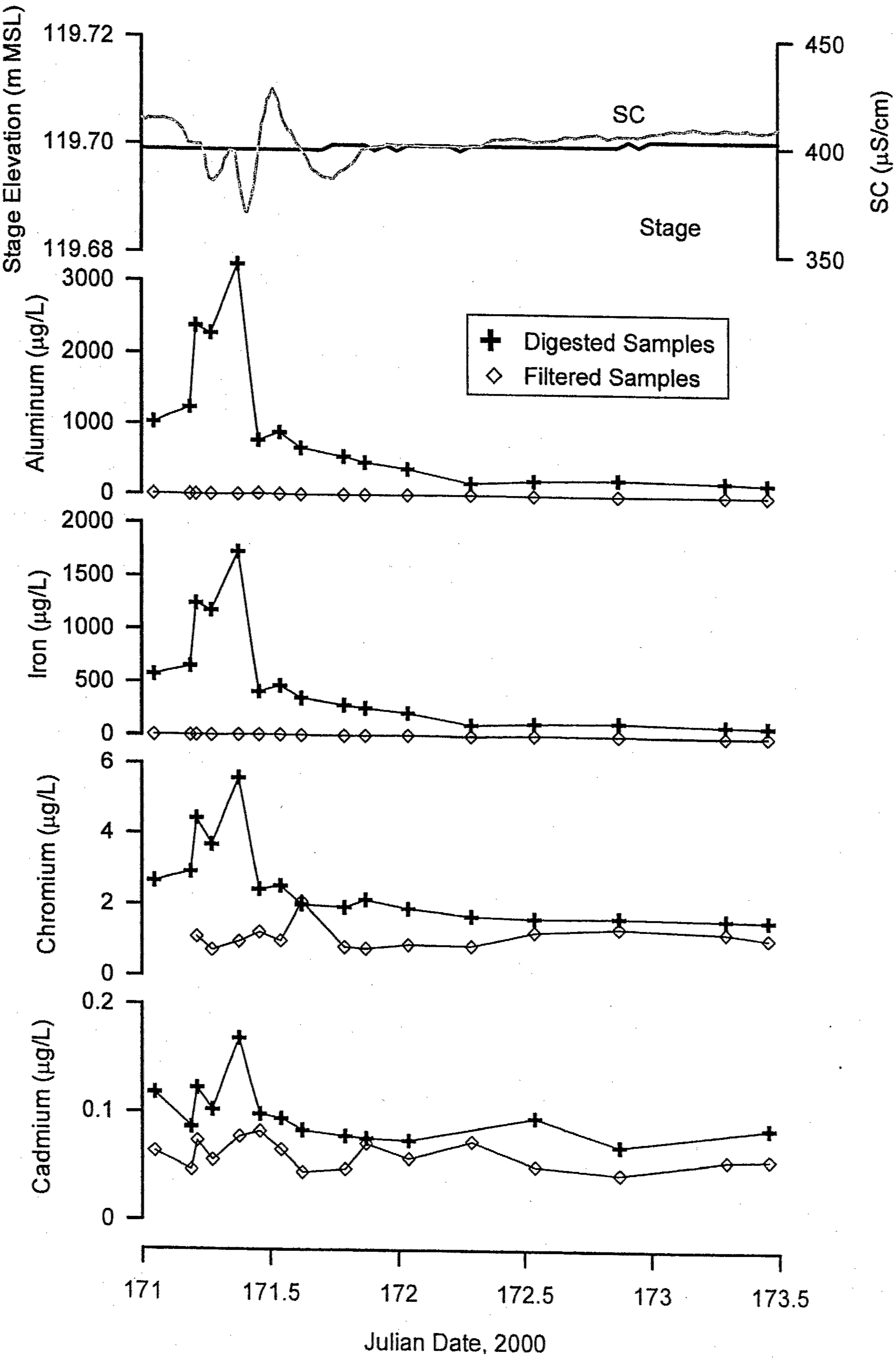
Figure 5a and 5b. SEM Micrographs of filter residues. During baseflow conditions (5a) the grains are predominately Ca (boxed) or Si (oval) on the fibrous filter. During the main storm response (5b) the filter is coated with fined grained Al-Si materials (solid background) or Si (large grain in center).

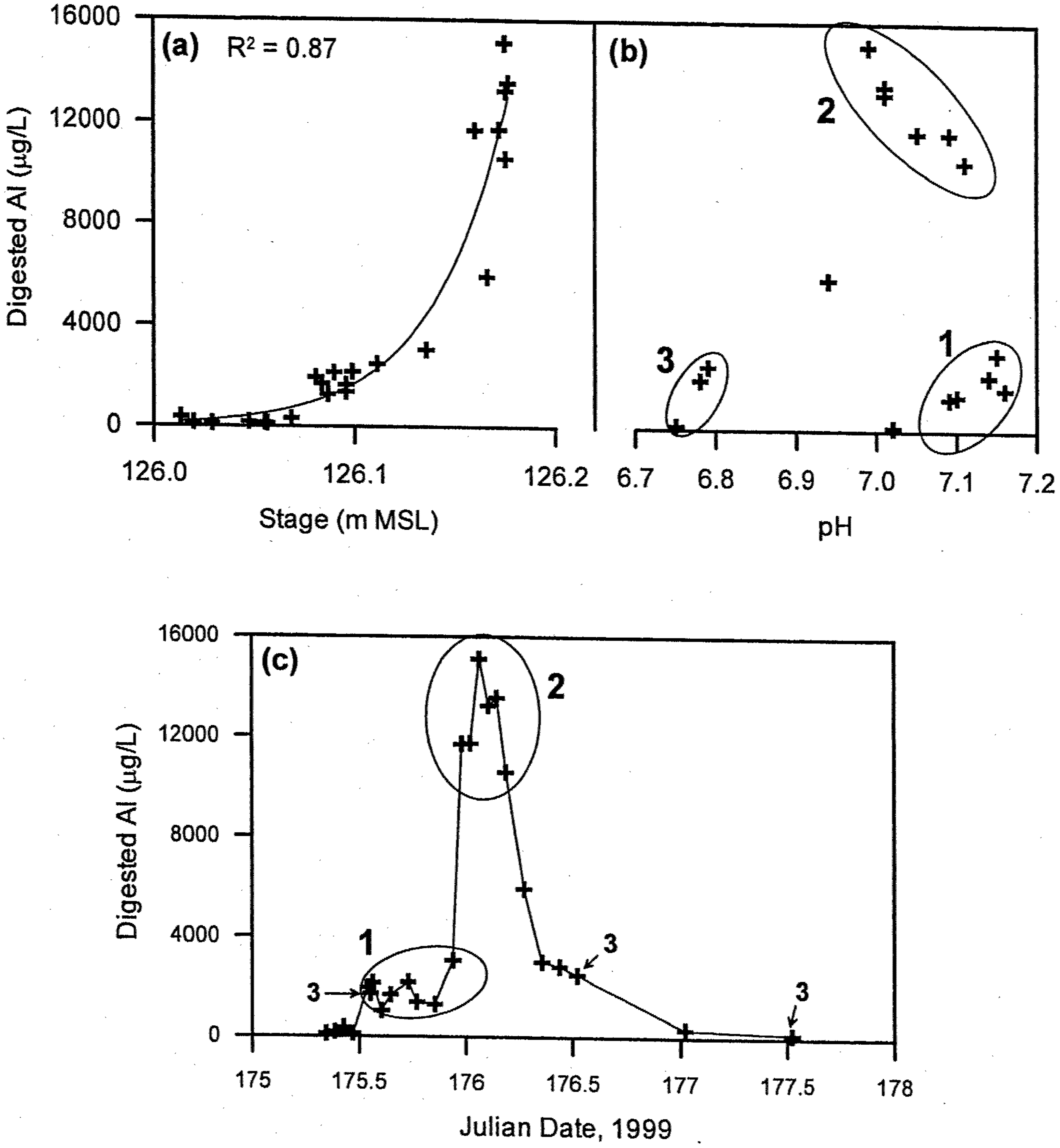
Figure 6. Complication of data types for Beaver Spring, 1999. (a) continuous field readings, (b) changes in water chemistry (from digested samples), (c) changes in the composition of filter residues.

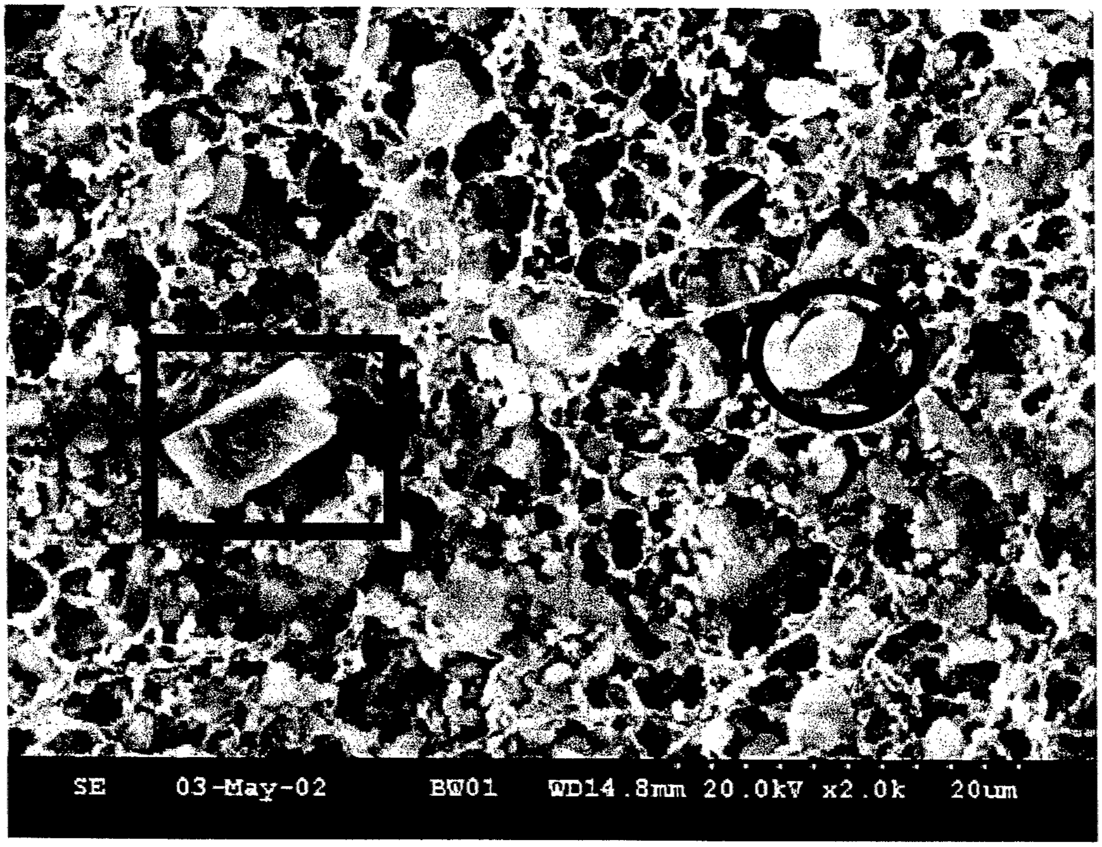

Kentucky
Lexington
Nashville
Tennessee
(a)
N
10 km
24
Kentucky
Tennessee
Fort Campbell
41
79
79
Clarkesville TN
(b)
Springs
Approx. Spring Basin Boundaries
Base Boundary
State Line
5 km
Fort Campbell
Kentucky
Tennessee
West Branch of the Red River
Millstone
Beaver
Little West Fork Creek
(c)

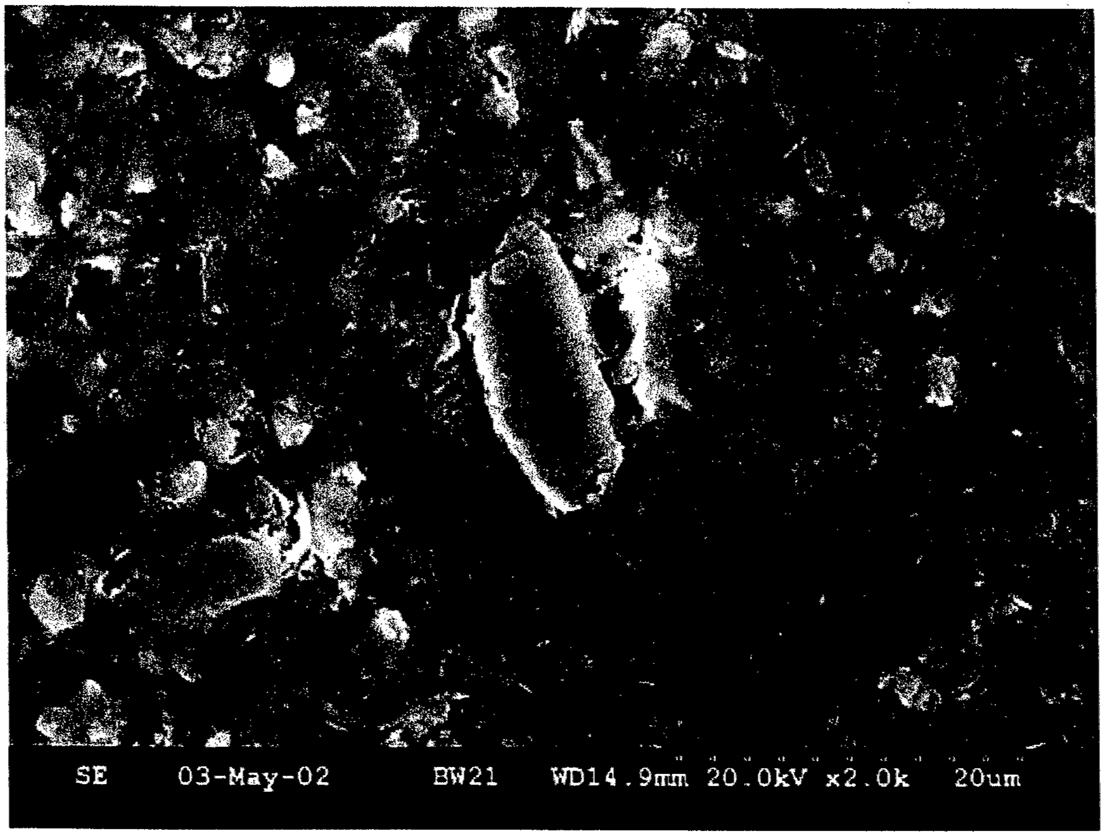

Beaver Spring, 1999
Stage Elevation (m MSL)
126.2
126.1
126.0
SC
Stage
Calcium
500
450
400
350
300
SC (µS/cm)
90
80
70
60
50
40
Calcium (mg/L)
160
120
80
40
0
Turbidity (NTU)
Turbidity
Aluminum (µg/L)
15000
10000
5000
0
Aluminum
8000
6000
4000
2000
0
Iron (µg/L)
Iron
Arsenic (µg/L)
4
3
2
1
0
Arsenic
24
18
12
6
0
Chromium (µg/L)
Chromium
Lead (µg/L)
8
6
4
2
0
Lead
16
12
8
4
0
Nickel (µg/L)
Nickel
175
175.5
176
176.5
177
177.5
Julian Date, 1999

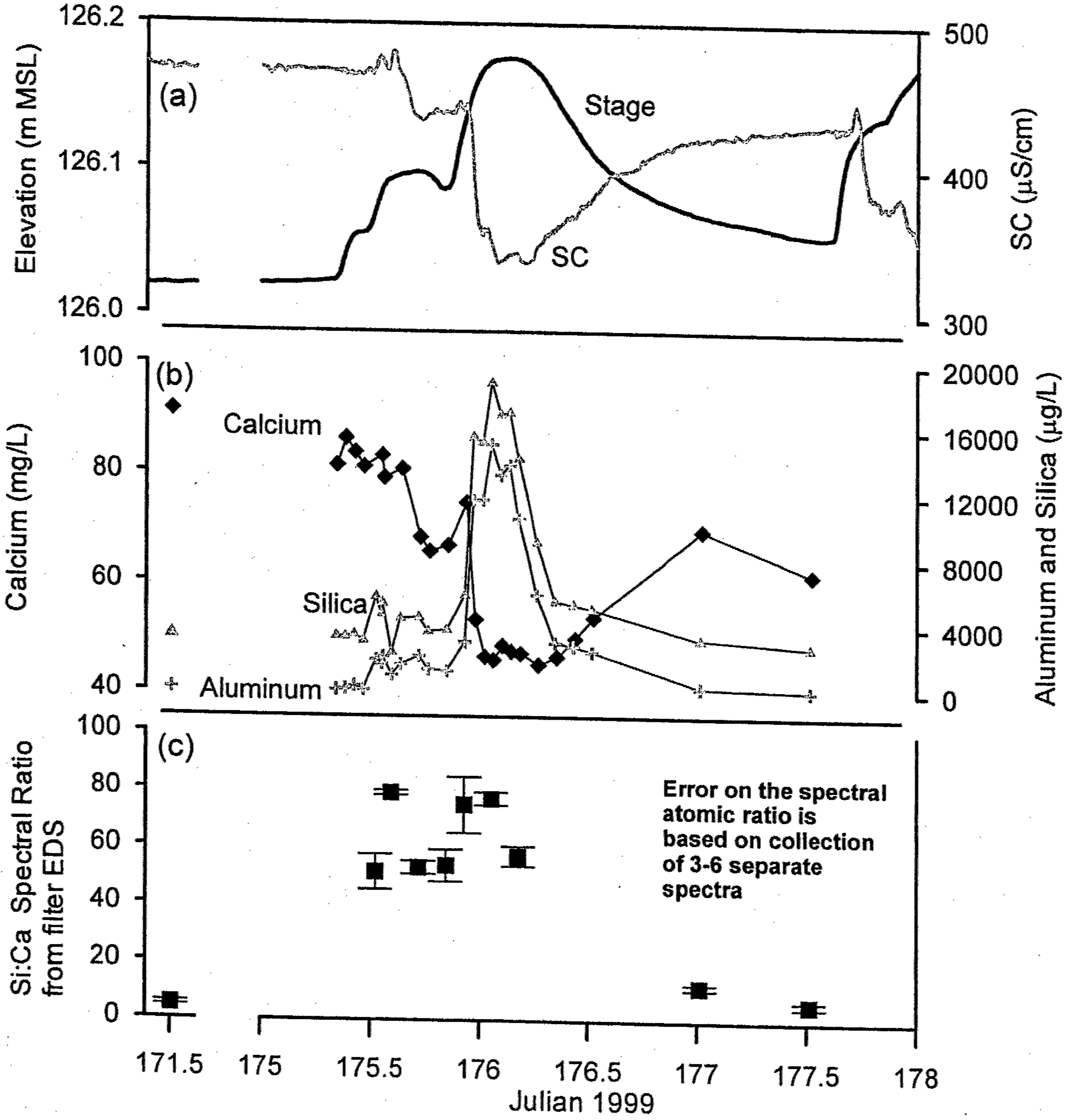

Millstone Spring, 1999
Stage Elevation (m MSL)
119.9
119.8
119.7
SC
Calcium
Stage
450
400
350
300
250
200
SC (µS/cm)
80
70
60
50
40
Calcium (mg/L)
600
400
200
0
Turbidity (NTU)
Turbidity
Aluminum (µg/L)
40000
30000
20000
10000
0
Aluminum
20000
15000
10000
5000
0
Iron (µg/L)
Iron
Arsenic (µg/L)
8
6
4
2
0
Arsenic
50
40
30
20
10
0
Chromium (µg/L)
Chromium
Lead (µg/L)
20
15
10
5
0
Lead
40
30
20
10
0
Nickel (µg/L)
Nickel
175.5
176
176.5
177
177.5
Julian Date, 1999


Stage Elevation (m MSL)
119.72
119.70
119.68
SC
Stage
450
400
350
SC (µS/cm)
Aluminum (µg/L)
3000
2000
1000
0
Digested Samples
Filtered Samples
Iron (µg/L)
2000
1500
1000
500
0
Chromium (µg/L)
6
4
2
0
Cadmium (µg/L)
0.2
0.1
0
171
171.5
172
172.5
173
173.5
Julian Date, 2000


(a)
R² = 0.87
Digested Al (µg/L)
16000
12000
8000
4000
0
126.0
126.1
126.2
Stage (m MSL)
(b)
2
3
1
6.7
6.8
6.9
7.0
7.1
7.2
pH
(c)
Digested Al (µg/L)
16000
12000
8000
4000
0
1
2
3
3
3
175
175.5
176
176.5
177
177.5
178
Julian Date, 1999


SE
03-May-02
BW01
WD14.8mm 20.0kV x2.0k
20um


SE
03-May-02
BW21
WD14.9mm 20.0kV x2.0k
20um



Error on the spectral atomic ratio is based on collection of 3-6 separate spectra

Appendix 5.3

Comparative Storm Response of Ground Water and Contaminant Chemistry in a Carbonate Aquifer, Fort Campbell, Kentucky-Tennessee, U.S.A.

Manuscript submitted to Environmental Science and Technology

Comparative Storm Response of Ground Water and Contaminant Chemistry in a Carbonate Aquifer, Fort Campbell, Kentucky-Tennessee, U.S.A.

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Abstract

Springs draining two ground water basins in the Mississippian limestone aquifer of western Kentucky-Tennessee were monitored through a storm event. The purpose of the monitoring to examine how storm periods affect water quality of a range of chemical types in a highly-heterogeneous aquifer. Parameters related to bulk carbonate chemistry and specific conductance (SC) decreased during a storm event, synchronous with the hydrograph for one spring and with a 12-hour lag at the second spring. Nitrate concentration also exhibited a minimum during storm flow. These responses were interpreted as dilution due to the rapid input of runoff into the aquifer. Heavy metal concentrations peak during storm flow and are closely correlated with turbidity and aluminum thus suggesting that they are transported on and within suspended particulates. Low concentrations of volatile organic compounds (VOCs) chloroform and trichloroethene (TCE) vary little during storm flow suggesting a constant reservoir of these contaminants within the aquifer. Overall, the data demonstrate that storm-induced changes in water quality vary considerably by analyte; and that this must be considered when designing monitoring programs for karst and other highly-heterogeneous aquifers.

Introduction

Scientists have long known that the transport of contaminants in ground water is closely linked to the contaminant's type, chemical form, mode of introduction, and interaction with the aquifer's chemical and physical properties. Contaminant migration can be further complicated by the presence of colloids which may facilitate movement [1]. In highly-heterogeneous aquifers, another layer of complexity may be introduced if precipitation events cause short-term variability in contaminant transport and water quality. While storm-related variability is well known in surface water quality, it has not been as closely studied in ground water systems.

Karst systems, with their highly localized permeability, are a useful example of a surface-influenced heterogeneous aquifer. Karst aquifers contain solution-enlarged fractures and pipe-like conduits. They are vulnerable to contamination due to the direct injection of contaminants (via sinkholes), the rapid transmission of ground water through fractures and conduits, and their ability to transport sediments. With these characteristics, flow regimes and water quality in a karst aquifer often resemble surface water more than they do ground water. Furthermore, these characteristics help to amplify the differences in the transport of various contaminants within the aquifer. Another advantage of using karst aquifers to monitor water quality changes is the presence of springs which can provide a means of integrating aquifer responses on a basin-wide scale.

The temporal variability of carbonate water chemistry in karst springs has been studied since the 1960s and has been used to probe the physical hydrogeology of aquifers. The degree of variability has been attributed, among other things, to ground water travel time [2], physical hydrogeology [3], and recharge style [4]. However, most of the spring water quality studies conducted to date have focused on analytes and parameters associated with the carbonate dissolution, such as calcium and hardness. These data have been used to construct conceptual models in which the most vulnerable, and most chemically variable, aquifers are characterized by rapid sinkhole injection, highly localized flow paths with high transmission capacity, and low storage capacities [5].

Until recently, little attention has been paid to the transport of sediment and contaminants in such aquifers. Recent work has shown that considerable sediment is transported in karst aquifers and that the transport is enhanced during storm events [6, 7]. Shevenell and McCarthy [8] observed that turbidity increased in well water in a karst aquifer following precipitation; bacteria [9] and pesticides [10] have also been shown to increase during storms. Nitrate response is more complicated because the concentration depends upon the type of recharge (quick-flow input via sinkholes vs. dispersed infiltration through the soil zone) [11]. Less data are available regarding volatile organic compounds (VOCs) and in particular for dense non-aqueous phase liquids (DNAPLs). Conceptual models for DNAPLs in karst suggest that they tend to be sequestered in the subsurface over relatively long time scales, [12, 13], resulting in water concentrations which are generally constant or decrease slightly during recharge events [12, 13]. However, there are limited data comparing the concurrent response of multiple types of contaminants and analytes in a single spring [14].

The purpose of this study was to obtain storm-period chemographs for a range of contaminant types in an aquifer that has highly variable permeability. The data illustrate the storm response for different types of contaminant storage and transport within a single aquifer. They also provide a useful guide for determining monitoring procedures within other temporally variable contaminated aquifers.

Site Description

The aquifer investigated is located on and near the Fort Campbell Army Base, along the Kentucky-Tennessee border (Figure 1a). Fort Campbell encompasses approximately 430 km^2 (Figure 1b) of which approximately 80 percent is used for military ranges and is largely undeveloped. Over 30 perennial springs have been identified within an area of approximately

250 km^2 around the base. The area surrounding Fort Campbell is largely agricultural with some commercial and industrial uses.

The region is located on the Western Highland Rim of the Nashville Basin and is underlain by the limestones of the Mississippian St. Louis and Ste. Genevieve formations [15, 16]. The Ste. Genevieve Formation is found in topographically high areas and largely consists of thickly-bedded limestone with thinner beds of dolomite. Discontinuous layers of chert and fossils are present. The St. Louis Formation outcrops primarily in the waterways and topographic lows to the south. It is dolomitic, argillaceous, silty, and fossiliferous. Between 0 and 30 m of unconsolidated regolith are present above the limestone. This consists of an upper layer of reddish brown clays and a lower layer of gravely clay. Chert nodules are commonly found at regolith – rock contact.

The bedrock surface has a strongly developed cutter and pinnacle topography with an internal relief of 3 to 10 meters (Figure 2). The cutters, solutionally-widened fractures, are filled with regolith and topped with soil. This portion of the recharge system, the epikarst, can act as temporary storage for infiltrating or perched ground water and also as storage for contaminants, particularly for strongly-sorbing organic compounds. The water in the epikarst is typically highly-conductive due to elevated carbon dioxide from the overlying soils and the high surface area of the fractured and broken rock [17]. Water may be flushed from the epikarst early during storms and can be identified at springs by its elevated conductivity.

Recharge to the aquifer is by dispersed infiltration through the regolith and by quickflow into sinkholes. Recharge by sinking streams (also called allogenic recharge) is a relatively minor contribution to the total recharge of the two ground water basins under investigation.

The primary focus of the study was on two springs, Beaver and Millstone (Figure 1c). Both springs are flashy end-member springs with variable water chemistry and discharge. Hydrographs from Beaver and Millstone springs crest soon after a rainstorm (approximately 12 to 24 hrs, respectively). The spring basins have similar geology, recharge types, topography, and potential contaminant sources. Estimated basin sizes are 1.5 km^2 for Beaver Spring and 65 km^2 for Millstone Spring.

Methods

Water samples were collected from the springs during short time intervals over storm events in June 1999 and June 2000. The samples were collected at intervals ranging from 0.5 hour to 12 hours; closely-spaced intervals were used initially when the springs were undergoing rapid changes while widely-spaced intervals were used as the springs neared baseflow conditions. The samples were collected using automated samplers programmed to begin sample collection with stage increase.

Field data collected concurrently with the water samples include precipitation, stage, specific conductance (SC), temperature, and turbidity. The precipitation data for 6-hour intervals were obtained from the Fort Campbell Army Airfield. Stage, SC and temperature data were collected by Ewers Water Consultants, Inc. of Richmond, Kentucky. The parameters were measured at 10-second intervals with 2-minute averaging and recorded on a digital datalogger.

Each water sample was split into aliquots and prepared as appropriate for the analyte and laboratory method (Table 1). Some of the metal samples were further split into two: one aliquot was digested and is interpreted as the total metal transport (dissolved plus particulate); a second aliquot was filtered to estimate the "dissolved" load [18, 19]. VOC samples were analyzed using an GC-MS as were part of the Fort Campbell environmental investigation [20]. The spacing of the VOC samples was less frequent than for the inorganic samples but they were collected during critical storm periods.

Results and Discussion

The precipitation events and the antecedent moisture conditions were considerably different for the two storms sampled. In 1999, the sampled storm produced 5.6 cm of rain between June 24th and 25th (Julian Date, JD 174-175). The 2000 sampled storm was preceded by a large rain event. The sampled storm was 2 cm on June 17th and 18th (JD 169-170). While these storms are not necessarily representative of much larger storms, they occur at regular frequency (six storms with greater than 5.6 cm of rain occurred 1999) and hence they represent commonly-encountered aquifer conditions.

The sampling frequency within the storms varied by spring; samples from Beaver Spring were more closely spaced and therefore provide a more detailed illustration of transport behavior. However, while the discussion is centered on the 1999 data from Beaver Spring, it should be noted that the conclusions are consistent at both springs and for both years of data.

Carbonate Data. Spring discharges and water chemistry changed in response to the rain events although clearly greater precipitation in 1999 elicited a larger spring response. Concentrations of carbonate-dissolution derived chemical species, such as Calcium, decreased during the storm (Figure 3). Calcium concentrations are high during baseflow conditions when the water has a longer contact time with the carbonate bedrock and are diluted by the influx of recharge water during storms. While the variability of carbonate species at springs during storms has been well studied, we provide the data here for comparison with the other components.

The timing of the arrival of the recharge water provides clues to the physical hydrogeology of the system [21, 22]. At Beaver Spring, the coincidence of the minimum Calcium concentration with the maximum discharge suggests that the ground water transmission system feeding the spring is open to the air (water table or vadose) and not fully submerged (phreatic). At Millstone Spring, the Calcium minimum lags the stage maximum by approximately 12 hours suggesting that the system may be, at least in part, phreatic (Figure 4). The lag is attributed to the time required for the recharge water to displace the antecedent water in the flow system [21]. This occurs because, in a phreatic system, the pressure pulse travels ahead of the recharge water. In contrast, the lack of a lag at Beaver Spring suggests it is fed by a vadose flow system in which the pressure pulse and fresh water travel simultaneously.

Particulate-Associated Metal Data. Increases in turbidity during storm events signify the transport of particulates (Figure 3). While granular or fractured aquifers may commonly transport colloid-sized materials, carbonate aquifers are capable of transporting large quantities and a much wider range of sediment sizes [6]. The digested water samples include both the dissolved and solid-phase transport, and therefore the metal concentrations measured in this study represent the total metal transport. Chemographs of both the major non-carbonate and trace metals demonstrate that the total metal transport is enhanced during storms (Figures 5 and 6). Comparison of the digested and filtered water samples confirms that nearly all of the non-carbonate metals (Fe, Mn, Al, As, Cu, Pb, Ni) are present in particulate form [19].

Karst aquifers are capable of transporting mobile sediments ranging from colloidal to boulder size, therefore we have not made a distinction between the sizes of particulates causing spring turbidity. Possible sources of turbidity include increased surface soil erosion and injection of solids into sinkholes, entrainment of solids already within the flow system, and the generation of colloids due to changes in water chemistry.

The greatest change in turbidity is coincident with the stage maximum at Beaver Spring and lags the stage maximum slightly at Millstone Spring (Figures 5 and 6). If the stage maximum, Calcium minimum, and turbidity maximum are concurrent, then the sources of the turbidity cannot be determined by the timing. However, at Millstone Spring the calcium and turbidity changes coincide and they both lag the stage maximum by approximately 12 hours. This suggests that the source of the turbidity is surface soils and that the storm is not re-entraining sediments already deposited in the flow system. If re-entrainment were a significant source of mobile sediments to the spring, then the turbidity maximum would be expected to coincide with the stage maximum.

Shevenell and McCarthy [8] found that turbidity increased in karst wells following precipitation although their total change (<5 NTUs) was considerably smaller than what was measured in springs during this study (~ 150 NTUs). Based on the lack of consistent relationships between turbidity and other chemical parameters, they concluded that chemistry alone could not account for the generation of turbidity. Using Al as a proxy for mobile sediment, we found that the total Al concentration is much more closely related to stage (discharge) than to pH (Figure 7). The "groupings" of the Al concentrations, relative to pH, can be attributed to the time of the storm. Because the high-velocity storm water introduces copious amount of recharge for dilution of the carbonate-buffered water, the pH is not independent of discharge.

Based on the strong relationship between stage and Al concentration, plus the timing of the maximum turbidity relative to discharge, we conclude that the primary source of particulate-associated metals to the spring is the erosion of surface soils and their injection into the aquifer.

Nitrate Data. Nitrate concentrations decreased during storms with a chemograph similar to that of calcium (Figure 8). Early spikes in nitrate concentrations suggest that the nitrate is being stored in the epikarstic zone. The coincidence of early-storm spikes in both nitrate and calcium suggests that the nitrate-rich epikarstic water is being flushed out of storage by the less-conductive rain water.

Studies of Floridian Springs [23] found that nitrate concentrations varied depending upon the availability of source nitrate. Nitrate concentrations in Mill Pond Spring, Florida, increased following storms. However, decreases in nitrate concentrations, similar to those observed at Fort Campbell, have been observed in Big Spring, Iowa [11]. Unlike Fort Campbell, the initial decrease in concentration at Big Spring was followed by a significant increase as the dominant recharge mechanism switched from quick-flow input to dispersed infiltration. The short spike followed by a longer decrease in nitrate concentration can be interpreted as (1) the flushing of the epikarstic zone, and (2) the influence of dilution from quick-flow recharge. Given the small size of the Fort Campbell springs relative to either Mill Pond Spring or Big Spring , it is likely that our spring basins are more simplistic and that recharge occurs over a shorter timeframe.

VOC Data. Samples collected concurrently with this study by the U.S. Army contained detectable concentrations of chloroform and trichloroethene (TCE) in spring water. Although only five samples were analyzed for VOCs at Beaver Spring in 1999, they were collected during critical times of the storm response (Figure 8). The VOC concentrations were constant within 1.6 ?g/L and the data suggest that a slight decrease may have occurred during the main storm. While the spacing of the VOC data make any conclusions speculative, low concentrations of chloroform and TCE in spring water have commonly been detected throughout Fort Campbell's spring sampling program during both storm and baseflow conditions [20].

The data are in agreement with the conceptual model by Loop and White [13] in which they proposed that DNAPLs are stored in the aquifer and are gradually released at fairly-constant low concentrations during low and moderate flow conditions. The concentration at the spring resulting from this gradual release will depend on the solubility of the compound, the amount of the DNAPL stored, and the location of storage. Above a threshold value, high velocities may entrain the DNAPL or the associated sediment and cause episodic transport. The threshold value will depend on the specific system, DNAPL, and mode of storage. At Fort Campbell, these compounds may be stored in the residuum or epikarst from which they are gradually released from either sorption or DNAPL form.

Variability by Chemical Type. Temporal variability in karst water quality has frequently been quantified by the coefficient of variation (CV) [3]. The data in this study illustrate that the carbonate-related CVs are not indicative of all groups of chemicals (Table 2). The CVs of the particulate-associated metals are consistently higher than those for the carbonate parameters. Dilution is the controlling process for carbonate variability while flow velocity is the controlling process for particulate chemistry variability; the different CVs suggest that these processes are at least partially decoupled. The 2000 storm was considerably smaller than the 1999 storm, but the relative relationships of the CVs were similar for both years, thereby suggesting that the size of storm may change the magnitude of the responses but not their relative sizes. These relationships were consistent in both of the springs included in the study.

Overall, the data demonstrate that storm-induced chemical changes can vary widely in an aquifer with highly-localized flow paths. During the studied storm, the particulate-associated metals increased in concentration, the carbonate metals and nitrates decreased in concentration, and the VOCs concentrations remained relatively constant. The processes controlling the storage and transport of each group of species likely also differ and contribute to the final form of the storm chemograph (Figure 9). Carbonate metals and nitrates are primarily controlled by dissolution and/or release during baseflow and dilution during storms. The particulate-associated metal concentrations are controlled by the injection of surface soils during storms and the aquifer's ability to transport solids. The VOCs relatively constant concentration suggests that they are continuously released from storage with little change due to storm events.

The degree and range of variability illustrate that contaminant transport in highly-heterogeneous aquifers may need to be assessed during storms. While this example is from a karst aquifer, similar changes may occur in fractured or other aquifers with localized flowpaths. Clearly, water quality monitoring in such aquifers will provide a range of results unless the data are collected and understood within the context of precipitation and recharge.

Acknowledgements

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Literature Cited

(1) McCarthy, J.F.; Zachara, J.M. *Environ. Sci. Technol.* **1989**, *23*, 496-502.
(2) Pitty, A.F. *Nature* **1968**, *217*, 939-940.
(3) Shuster, E.T.; White, W.B. *J. Hydrol.* **1971**, *14*, 93-128.
(4) Scanlon, B.R.; Thrailkill, J. *J. Hydrol.* **1987**, *89*, 259-279.

(5) White, W.B. Conceptual models for karstic aquifers. In *Karst Modeling*; Palmer, A. N., Palmer, M. V., Sasowsky, I. D., Eds.; Karst Waters Institute: Charlottesville, Virginia, 1999; Vol. Special Publication 5, pp 11-16.

(6) Atteia, O.; Kozel, R. *J. Hydrol.* **1997**, *201*, 102-119.

(7) Mahler, B.J.; Lynch, F.L. *J. Hydrol.* **1999**, *214*, 165-178.

(8) Shevenell, L.; McCarthy, J.F. *J. Hydrol.* **2002**, *255*, 50-68.

(9) Mahler, B.J.; Personné, J.C.; Lods, G.F.; Drogue, C. *J. Hydrol.* **2000**, *238*, 179-193.

(10) Currens, J.C. A sampling plan for conduit-flow karst springs: Minimizing sampling cost and maximizing statistical utility. In *The Engineering Geology and Hydrogeology of Karst Terranes*; Beck, B. F., Stephenson, B., Eds.; A.A. Balkema: Springfield Missouri, 1997, pp 193-198.

(11) Hallberg, G.R.; Libra, R.D.; Hoyer, B.E. Nonpoint source contamination of ground water in karst carbonate aquifers in Iowa. In *Perspectives on Nonpoint Source Pollution Proceedings*; EPA Office of Water Regulations and Standards, EPA/440/5-85-001, 1985, pp 109-114.

(12) Wolfe, W.J.; Haugh, C.J.; Webbers, A.; Diehl, T.H. *Preliminary conceptual models of the occurrence, fate, and transport of chlorinated solvents in karst regions of Tennessee*; Water-Resources Investigations Report 97-4097; U.S. Geological Survey: Nashville, 1997; 80.

(13) Loop, C.M.; White, W.B. *Ground Water* **2001**, *39*, 119-127.

(14) Vesper, D.J.; Loop, C.M.; White, W.B. *Theoretical and Applied Karstology* **2000**, *13*, 63-73.

(15) Klemic, H. *Geologic Map of the Oak Grove Quadrangle, Kentucky*; Map GQ-565; U.S. Geological Survey, 1966.

(16) Klemic, H. *Geologic Map of the New Providence Quadrangle, Kentucky*; Map GQ-301SW; U.S. Geological Survey, 1974.

(17) Williams, P.W. *J. Hydrol.* **1983**, *61*, 45-67.

(18) Vesper, D.J. Ph.D. Dissertation, Pennsylvania State University, University Park, PA, 2002.

(19) Vesper, D.J.; White, W.B. *J. Hydrol.* **In Press**.

(20) Arthur D. Little Inc. *Water and Sediment Quality of the Springs at Fort Campbell, Kentucky. 2000 Hydrogeologic Characterization Program*; Submitted to the Fort Campbell Public Works Business Center, Environmental Division, 2001; 530.

(21) Ashton, K. *Transactions Cave Research Group, Great Britain* **1966**, *7*, 161-203.

(22) Ryan, M.; Meiman, J. *Ground Water* **1996**, *34*, 23-30.

(23) Martin, J.; Gordon, S.L. Surface and ground water mixing, flow paths, and temporal variations in chemical compositions of karst springs. In *Groundwater Flow and Contaminant Transport in Carbonate Aquifers*; Sasowsky, I. D., Wicks, C. M., Eds.; A.A. Balkema: Rotterdam, Netherlands, 2000, pp 65-92.

Table 1. Analytical Methods Utilized

Analyte Group	Sample Handling	Analytical Method
Metals	- Preserved with HNO_3 - Samples digested using HNO_3 modified from USEPA (USEPA, 2000) - Limited number of aliquots filtered using a 0.45-?m pore flow-through filter prior to preservation	Finnegan high resolution Inductively-Coupled Plasma-Mass Spectrometer (ICP-MS)
Anions	- Samples filtered.	Dionex Ion Chromatograph (IC)
TOC	- Samples preserved with HCl	Shimadzu (TOC-5000) carbon analyzer
VOCs	- Collected with zero-air and preserved with HCl	Gas Chromatography – Mass Spectrometer (GS-MS)

Table 2. Chemical Concentrations and Variability for Various Analytes. Metal concentrations for digested samples.

Parameter		1999 Beaver Spring					1999 Millstone Spring				
		n	Min	Max	Mean	CV (%)	n	Min	Max	Mean	CV (%)
Turbidity	(NTU)	19	2.7	156	68.0	79	15	4.4	589	105	165
Nitrate	(mg/L)	19	4.75	8.15	6.58	31	17	6.06	10.7	8.33	15
Calcium	(mg/L)	25	45.1	91.4	65.9	25	22	40.9	86.6	64.3	16
Aluminum	(? g/L)	25	123	15,100	4,160	120	22	54.0	33,495	5,000	173
Iron	(? g/L)	25	63.1	7,760	2,130	120	22	26.9	18,295	2,747	173
Lead	(? g/L)	25	0.57	7.45	2.65	82	22	0.52	17.4	3.02	136
TCE	(? g/L)	5	0.6	1.1	0.82	26	6	1.1	1.4	1.28	8.4
Chloroform	(? g/L)	6	0.8	2.4	1.4	42	6	0.5	0.6	0.54	10

CV: Coefficient of variation = standard deviation / mean

List of Figures

FIGURE 1

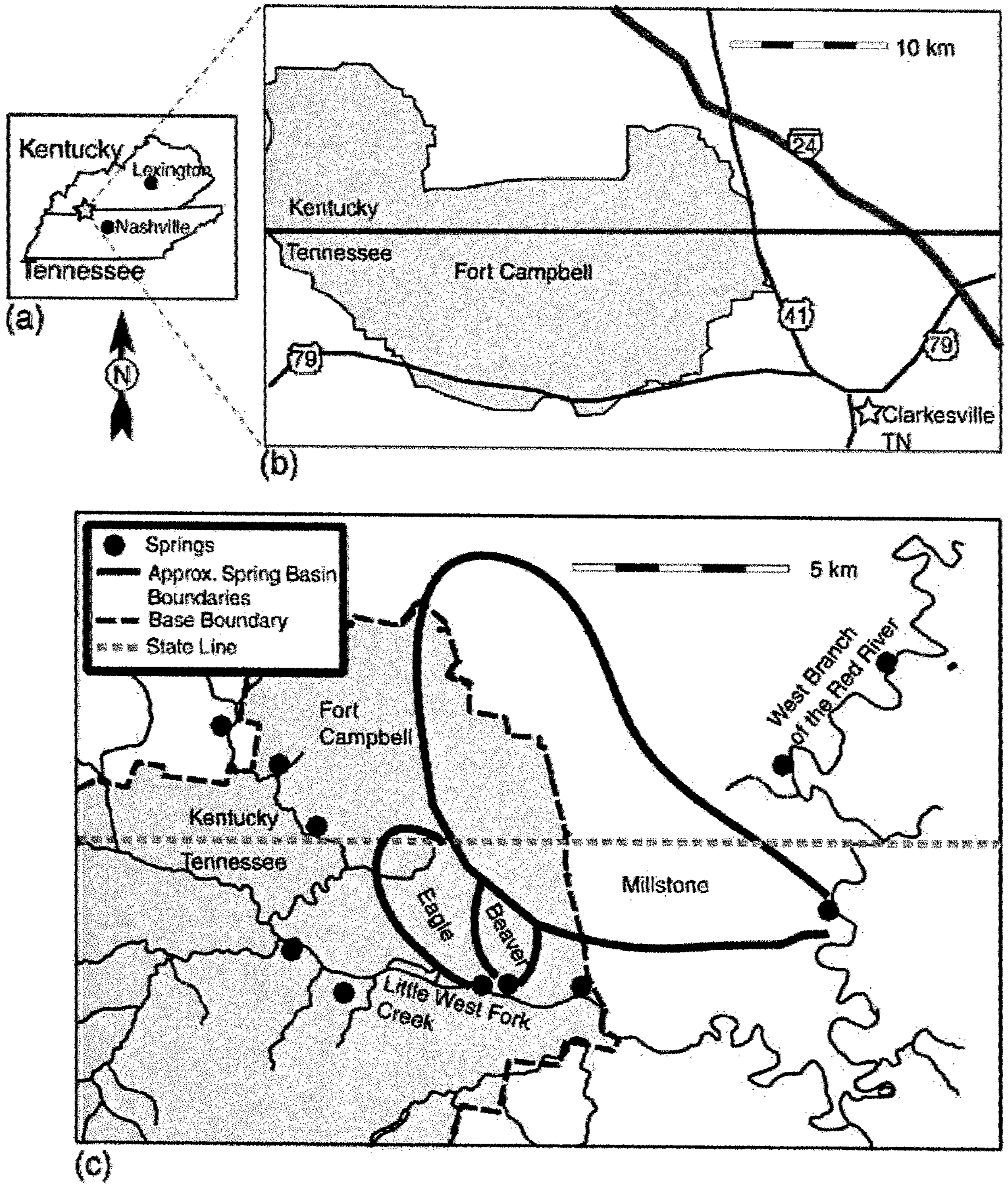

Kentucky
Lexington
Nashville
Tennessee
(a)
N
10 km
24
Kentucky
Tennessee
Fort Campbell
41
79
79
Clarkesville
TN
(b)
Springs
Approx. Spring Basin Boundaries
Base Boundary
State Line
5 km
Fort Campbell
Kentucky
Tennessee
West Branch of the Red River
Millstone
Eagle
Beaver
Little West Fork Creek
(c)

FIGURE 2

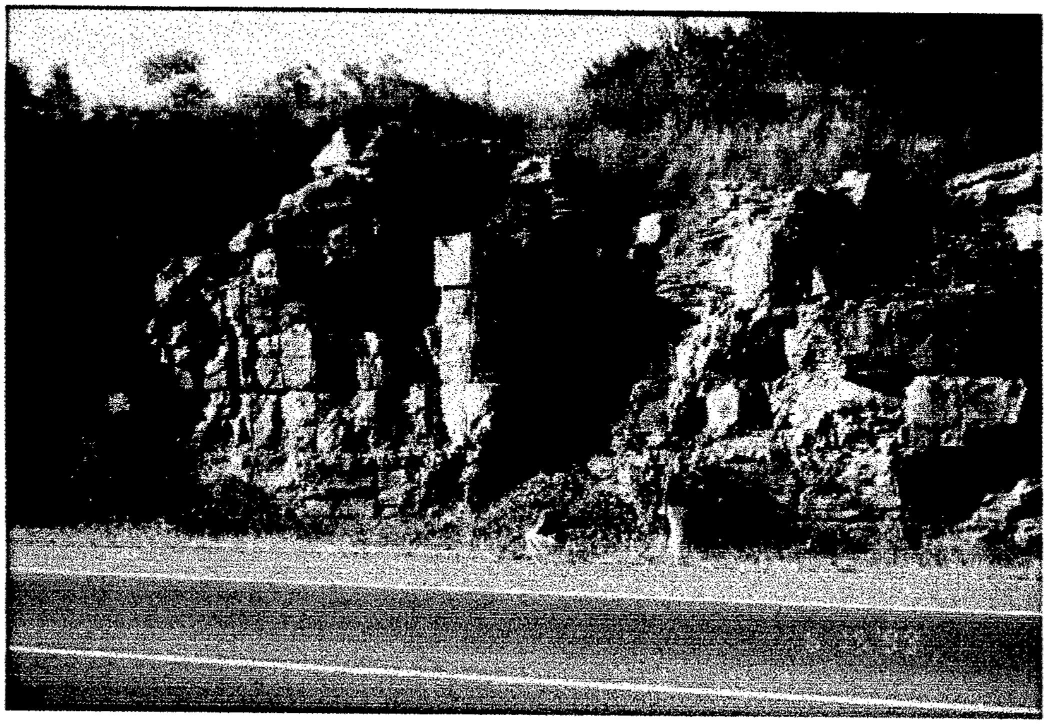


FIGURE 3

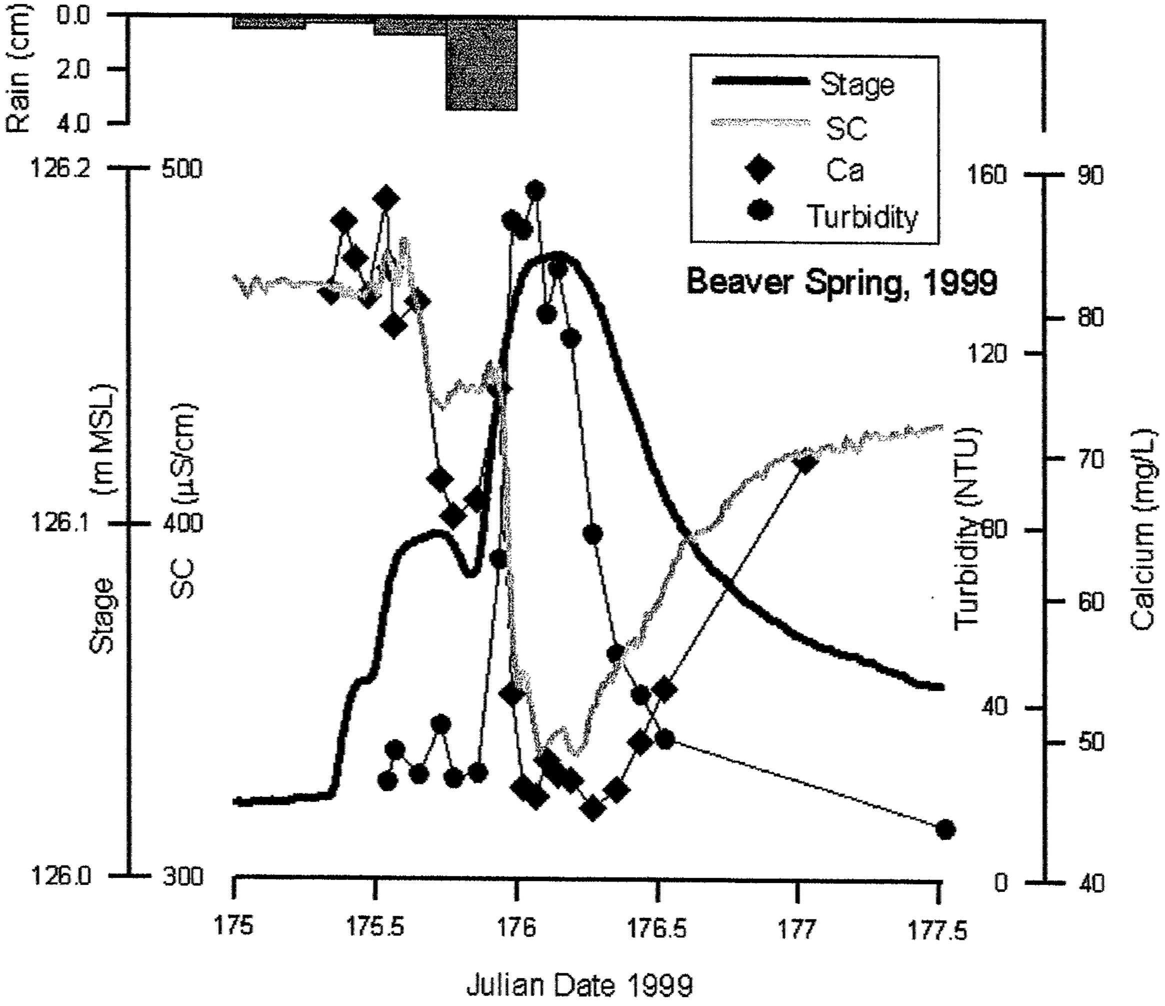

Rain (cm)
0.0
2.0
4.0
Stage
SC
Ca
Turbidity
Beaver Spring, 1999
126.2
126.1
126.0
500
400
300
Stage (m MSL)
SC (µS/cm)
160
120
80
40
0
Turbidity (NTU)
90
80
70
60
50
40
Calcium (mg/L)
175
175.5
176
176.5
177
177.5
Julian Date 1999

FIGURE 4

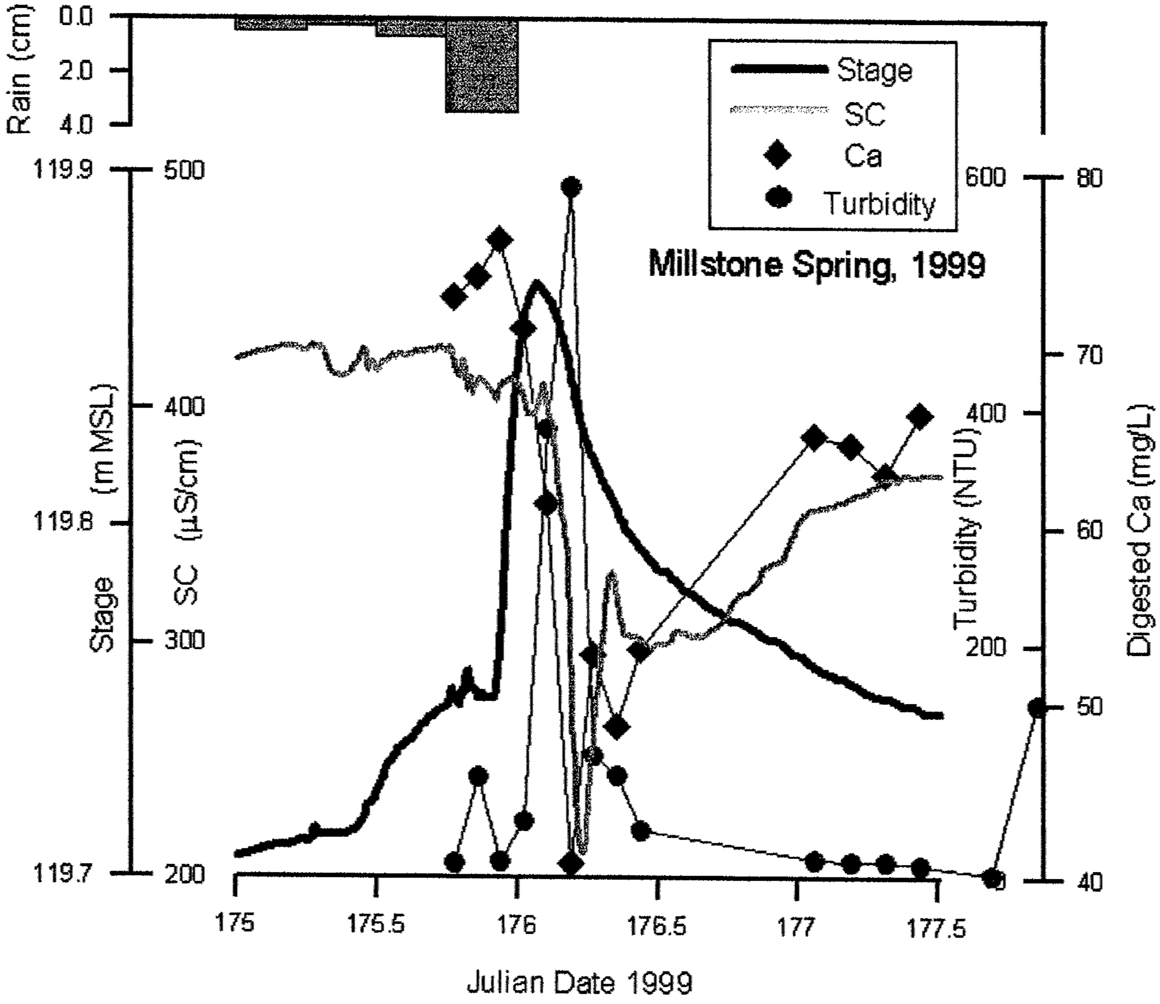

Rain (cm)
0.0
2.0
4.0
Stage
SC
Ca
Turbidity
Millstone Spring, 1999
119.9
119.8
119.7
Stage (m MSL)
500
400
300
200
SC (µS/cm)
600
400
200
0
Turbidity (NTU)
80
70
60
50
40
Digested Ca (mg/L)
175
175.5
176
176.5
177
177.5
Julian Date 1999

FIGURE 5

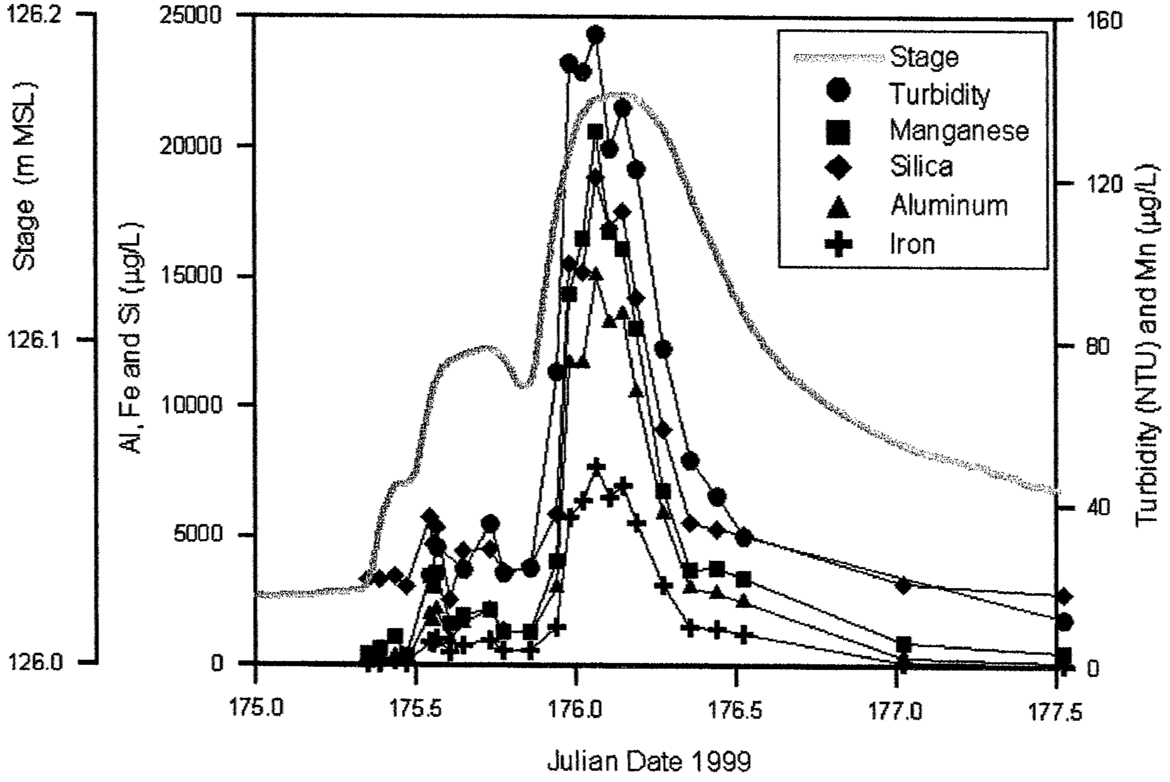

Stage (m MSL)
126.2
126.1
126.0
Al, Fe and Si (µg/L)
25000
20000
15000
10000
5000
0
Turbidity (NTU) and Mn (µg/L)
160
120
80
40
0
175.0
175.5
176.0
176.5
177.0
177.5
Julian Date 1999
Stage
Turbidity
Manganese
Silica
Aluminum
Iron

FIGURE 6

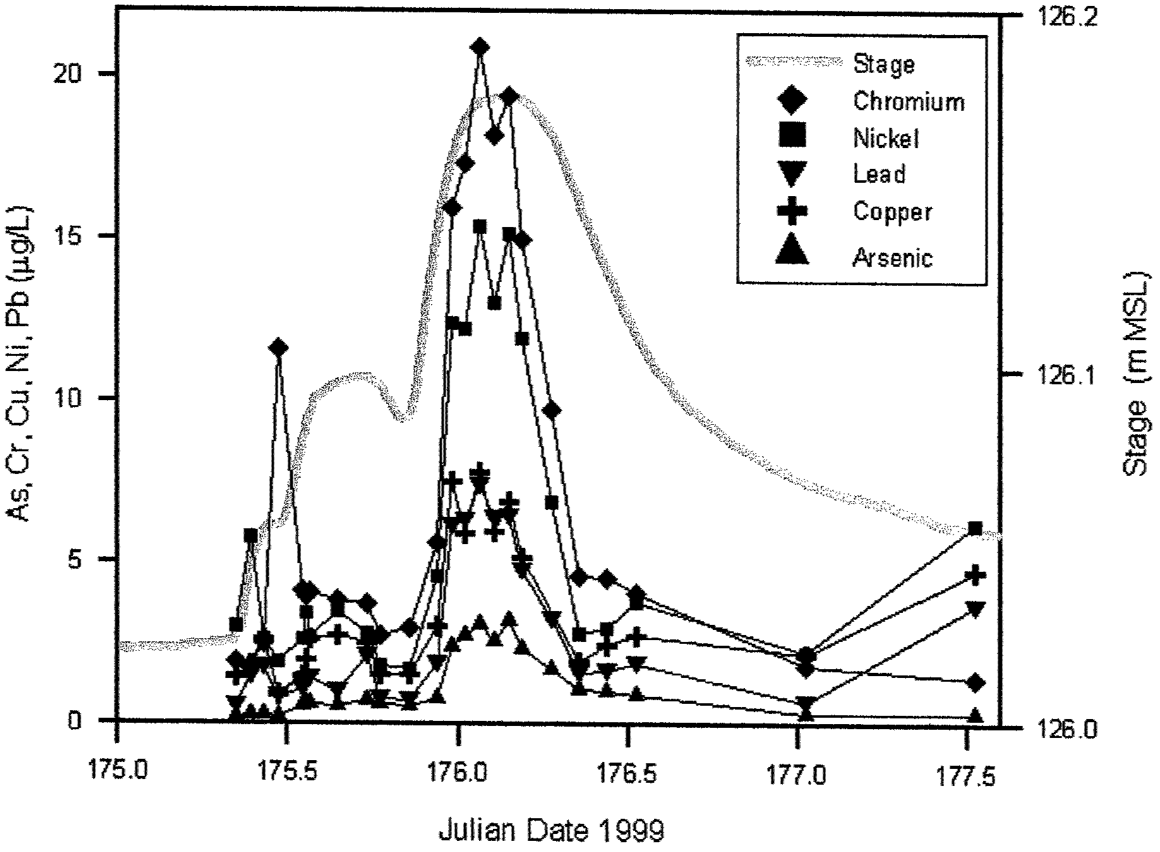

Stage
Chromium
Nickel
Lead
Copper
Arsenic
As, Cr, Cu, Ni, Pb (µg/L)
0
5
10
15
20
Stage (m MSL)
126.0
126.1
126.2
175.0
175.5
176.0
176.5
177.0
177.5
Julian Date 1999

FIGURE 7

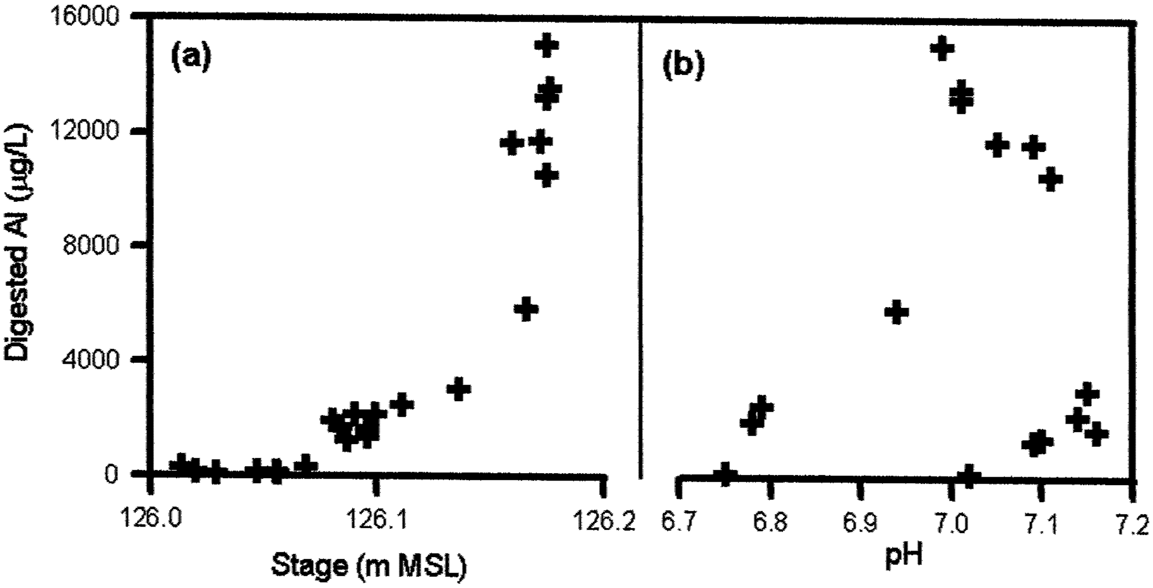


FIGURE 8

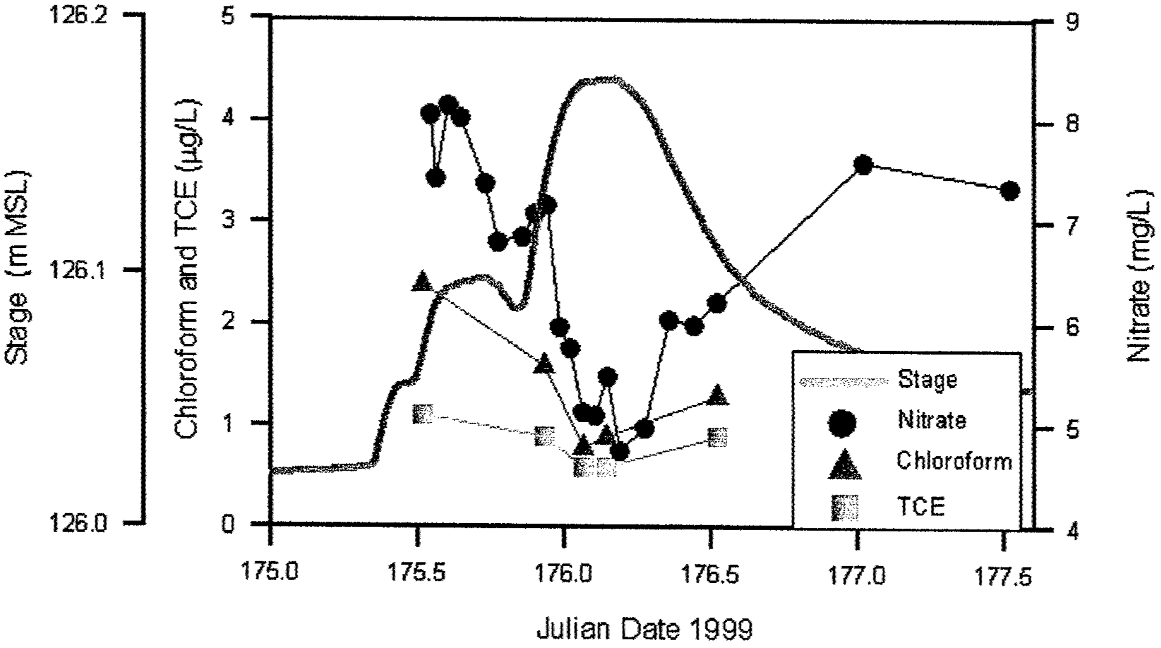
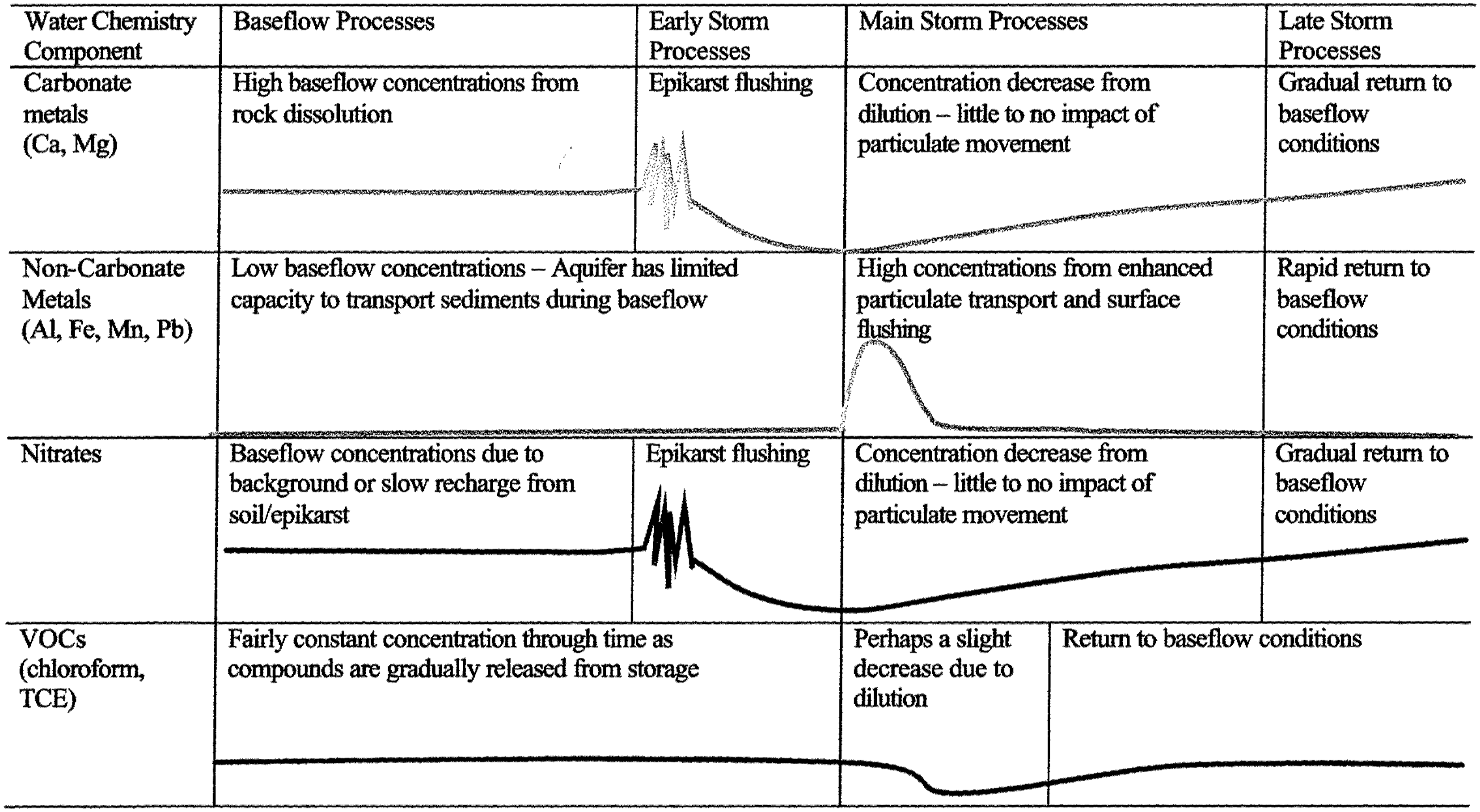


FIGURE 9



Water Chemistry Component	Baseflow Processes	Early Storm Processes	Main Storm Processes		Late Storm Processes
Carbonate metals (Ca, Mg)	High baseflow concentrations from rock dissolution	Epikarst flushing	Concentration decrease from dilution – little to no impact of particulate movement		Gradual return to baseflow conditions
Non-Carbonate Metals (Al, Fe, Mn, Pb)	Low baseflow concentrations – Aquifer has limited capacity to transport sediments during baseflow		High concentrations from enhanced particulate transport and surface flushing		Rapid return to baseflow conditions
Nitrates	Baseflow concentrations due to background or slow recharge from soil/epikarst	Epikarst flushing	Concentration decrease from dilution – little to no impact of particulate movement		Gradual return to baseflow conditions
VOCs (chloroform, TCE)	Fairly constant concentration through time as compounds are gradually released from storage		Perhaps a slight decrease due to dilution	Return to baseflow conditions	

Appendix 5.4

Spring and Conduit Sediments as a Storage Reservoir for Metals in Karst Aquifers

Manuscript prepared for submission to Environmental Geology

Spring and Conduit Sediments as Storage Reservoirs for Heavy Metals in Karst Aquifers

Dorothy J. Vesper* and William B. White**

Abstract Sediment samples were collected from six springs draining the karst aquifer at Fort Campbell, Kentucky/Tennessee. The samples were analyzed using a selection extraction procedure that separates the metals into 5 operationally-defined fractions: exchangeable, carbonate, oxides, organics and residual. These and the total metal concentrations were analyzed by inductively-coupled plasma mass spectroscopy. The data show that metal distribution between fractions varies significantly between metals and by location. Aluminum and iron are primarily present in the residual fraction, while calcium is split between exchangeable, carbonate and residual fractions. Manganese may be dominantly in either the oxide or carbonate fraction. The redox-sensitive metals (Fe and Mn) have the greatest fractional distribution in the spring with the thickest sediments. Trace metals detected include Cr, Cd, Ni, and Pb in the range of a few to 200 mg/kg. Trace metal distribution between fractions is dependent on the location. In Beaver Spring nickel is distributed between the exchangeable, carbonate and organic fractions while in Gordon Spring nickel is largely residual. Chromium is almost entirely associated with the organic fraction in Beaver Spring while it is largely residual in Gordon Spring. The differences in the trace metals are likely to depend on both the source of the metal (particularly the differences between background and contaminant sources) and the sediments physical and chemical characteristics.

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Introduction

A characteristic of karst aquifers is that much of the water that moves through them is localized in a system of conduits which drain to karst springs. Flow velocities in the conduits often become sufficiently high that clastic sediments are also flushed though the conduit system either as bed load or as suspended load. Transport of sediment is episodic with most transport taking place during storm flow in the conduit system. As storm flows recede, clastic sediments are left behind in the conduit system and at the spring mouths. The clastic material consists of either weathering residues from nearby clastic rocks flushed into the system by sinking streams or surface soils and regolith injected through sinkholes and open fractures at the base of the epikarst. Sand, silt, clays and occasionally larger rock fragments make up the bulk of most clastic cave sediments.

Numerous recent studies have reported the transport of suspended particulates in karst aquifers during storm events. Ryan and Meiman (1996) measured the turbidity of a spring in Mammoth Cave National Park over two storm events and were able to show that the suspended particulate concentration increased during storms and that it originated from an agricultural recharge area. Atteia and Kozel (1997) showed that the size of particulates discharged from a karst spring changed over the course of a storm. They found that the concentration of small particles increased slowly during a storm and remained high when the water level decreased. The concentration of large particles increased and then decreased quickly after a storm flow receded. Mahler and Lynch (1999), in an investigation of Barton Spring, Texas, found that the maximum particle diameters were discharged coincident with the maximum total suspended solids concentration. Prout (2001), investigating springs in Pennsylvania, found similar changes in particle sizes and mineralogy over the course of a storm. Shevenell and McCarthy (2002) used turbidity in karst monitoring wells to argue that turbidity in large storm was controlled by flow dynamics whereas water chemistry played a more important role in small storms.

The flux of sediment serves to transport metals through karst aquifers attached to fine-grained suspended sediments (Vesper and White, 2003). It might be expected, then, that the clastic sediment held in storage within the conduit system is also a storage site for metal contaminants. Spring mouth sediments are convenient sampling points for the investigation of heavy metal storage and can be assumed to also be representative of sediments stored upstream in the conduits. The present paper is concerned with clastic sediments as a storage medium for both the naturally occurring metals iron and manganese and a suite of trace contaminant heavy metals.

Field Site and Experimental Techniques

The Western Kentucky Karst Aquifer

The spring sediments and soils investigated in this paper were collected on and near the Fort Campbell Army Base, along the Kentucky – Tennessee border approximately 80 km northwest of Nashville, Tennessee. The Base is permitted under the Resource Conservation and Recovery Act (RCRA). It is a useful site for the present study because of the large number of other investigations concerning source area contaminant identification, ground water tracer tests, spring ground water basin delineation, and surface water and spring chemistry studies. The developed areas of the Base make up less than 20 percent of the 430 km^2 reservation. The remainder is undeveloped and used for ranges and military training exercises. The area surrounding Fort Campbell is largely agricultural with some residential, commercial and industrial uses.

Fort Campbell is located on the western Highland Rim of the Nashville Basin (Fig. 1). The region is bordered by the central basin to the east and south, and the western valley of the Tennessee River to the west. To the north the region transitions into the Kentucky Pennyroyal Plain, a well-known karst terrain. The Highland Rim is a broad flat area that tilts slightly to the west. The surface elevation is approximately 120 m above the Nashville Basin and only 90 m above the western valley (Luther, 1977). In the region of Fort Campbell, the Highland Rim surface has been highly dissected by the Cumberland River and its tributaries.

Fort Campbell and the surrounding areas are underlain by limestones of the Mississippian Ste. Genevieve and St. Louis formations. The strata are nearly horizontal with a regional dip of 4 – 11 m/km to the west-northwest (Kemmerly, 1980). However, locally, there may be a slight dip to the south (Klemic, 1966, 1974). The St. Louis Formation is typically a calcarenite with discontinuous layers of siliceous and dolomitic calcarentite and cherty layers in the lower part of the formation. It outcrops primarily along river valleys and in topographic lows. The Ste. Genevieve Formation consists of thick bedded limestone with thinner beds of dolomite. A zone of chert nodules (the Lost River Chert) is often found in the lower 3 – 6 meters of the formation. The Ste. Genevieve Formation is found at the surface only at higher elevations, particularly in the northern part of the army base.

The limestone surface, where exposed in road cuts, is seen to be deeply etched by solution into a cutter and pinnacle topography with a relief of 5 – 10 m. This weathered zone (the epikarst) is draped with a thick regolith that completely covers the bedrock surface. The regolith consists of an upper layer of reddish brown clays and a lower layer of gravely clay. Discontinuous bands and partings of silty materials are present. Chert nodules are commonly found at the regolith – bedrock contact. The cherty rubble provides a zone of high permeability at the base of the epikarst. Overlying the regolith is a well drained loamy soil of the Pembroke-Crider association, a typical soil derived from the weathering of cavernous limestone.

Recharge to the carbonate aquifer is mainly by dispersed infiltration through the epikarst along with storm runoff into sinkholes. In spite of the generally thick regolith, storm recharge is very rapid and produces well-defined storm peaks on the spring hydrographs. Sinking streams are a minor part of the recharge.

More than 30 perennial springs have been identified within a 250 km^2 area around the Base. Locations of those selected for detailed investigation are shown in Fig. 2. The ground water basins that drain to these springs were determined by extensive dye tracer studies carried out by Ewers Water Consultants as part of the Fort Campbell environmental assessment activities. The location and characteristics of the chosen spring are given in Table 1.

Sediment Sampling

The samples collected include both spring sediments and soils (Fig. 3). These were selected to provide an initial assessment of site conditions. Three of the Fort Campbell springs – Beaver, Eagle and Millstone – were also used in water chemistry studies (Vesper and White, 2003; Vesper and White, in press). The other two Fort Campbell springs – Gordon and Quarles – have very different morphologies and were included to determine the importance of morphology on sediment accumulations and chemistry. Nine surface soil samples and four subsurface samples were collected at Fort Campbell to provide data for suspected source areas (Table 2). Three of the subsurface samples were from a single location with a matching surface sample.

Extractions and Analysis

The spring sediments and soil samples were analyzed for their physical characteristics, mineralogy, bulk chemistry and extractable metals. Mineralogy was determined by x-ray powder diffraction (XRD) with grain-by-grain chemical analysis by energy dispersive x-ray spectroscopy (EDX). Also analyzed were cation exchange capacity (CEC) and total organic carbon (TOC). The extractions included a sequential analysis that separates metals into five operational fractions.

Total metal concentrations were determined by digesting dried sieved samples in hydrochloric and hydrofluoric acids using a microwave digester. The resulting solutions were analyzed for major elements by atomic emission spectroscopy and for trace metals with a Finnegan inductively coupled plasma mass spectrometer (ICP-MS). An indium spike was used as an internal standard. Nine pairs of duplicate samples were analyzed. Agreement between pairs was generally within 10 percent.

The extraction procedures were modified from the European Community Bureau of Reference (BCR) protocol (Quevauviller et al., 1993, 1994). For sample preparation, samples were weighed out into centrifuge tubes. Each sample was analyzed in duplicate or triplicate and one tube from each set of 12 was reserved as a process blank. The mass added to each tube was the equivalent of 0.8 g dry weight. The fractions are outlined below:

Fraction #1 : $MgCl_2$ – exchangeable ions.

Fraction # 2 : Acetic acid – carbonate extraction.

Fraction # 3 : Hydroxylamine – reducible cations.

Fraction # 4 : Hydrogen peroxide – oxidizable cations.

Fraction # 5 : Residue.

Sediment Mineralogy and Bulk Chemistry

Characteristics of Spring Sediments and Upland Soils

The distribution of spring sediment and soil particle sizes is shown in Fig. 4. According to particle size alone, the spring sediments contain between 10 and 30 percent clay. The Gordon Spring sediment has the highest sand content of any of the springs. The subsurface soil samples have the highest percent clay.

X-ray diffraction data indicate quartz as the dominant mineral in all samples. Minor minerals identified include feldspar, muscovite, and kaolinite. Calcite and dolomite occur very sparsely in only a few samples showing that both soils and spring sediments are well leached. In an effort to identify clay minerals, random mounts, packed slides, preferred orientation slides, and slides of separated fine-grained materials were examined. The diffraction patterns did not depend on slide preparation and except for minor kaolinite, the quantity of clay identified in the x-ray diffraction pattern did not account for the clay sized particles found in the particle size analysis.

The EDX chemical analyses (Fig. 5) generally complimented the XRD data. The two samples with calcite peaks in their XRD patterns also had high Ca by EDX. As expected from the dominant quartz in the XRD data, 70 – 80 elemental percent is silicon in most samples. Aluminum is in the range of 10 percent. Aluminum should be a proxy for clay, along with the minor feldspar. On a mole basis, a matching amount of silicon is required for the clay structures, for example, kaolinite, $Al_4Si_4O_{10}(OH)_8$. Thus, a substantial amount of clay appears to be present in all samples in spite of its sparse occurrence in the x-ray diffraction patterns. Another element with a ubiquitous presence in the EDX spectra, which does not appear in the x-ray diffraction patterns, is iron, also typically present in the range of 10 – 15 percent. Iron in the form of hydroxides and oxyhydroxides often occurs as coatings on other mineral grains. The electron beam in the scanning electron microscope has a relatively low penetrating power so that chemical analyses are obtained mainly from the surfaces of the mineral grains. A significant concentration of iron determined by EDX in the absence of iron-containing minerals by x-ray is entirely consistent with iron hydroxide coatings on mineral grains.

Comparisons of the composition of shallow surface soils, deep soils, and spring sediments (Fig. 5) did not reveal any dramatic differences. The subsurface soils tend to have higher aluminum concentrations as would be expected from their higher content of clay-sized particles.

Bulk Metallic Elements

Chemical analyses obtained from complete digestion of the sediment samples revealed silicon, aluminum, iron, and some calcium as major constituents, potassium, sodium, magnesium, and manganese as minor constituents, and zinc, chromium, nickel lead, and cadmium as trace metals. Complete numerical data for all samples may be found in the thesis from which this paper is extracted (Vesper, 2002).

Linear correlations exist between the concentrations of certain of the constituents. Matrix correlations for the spring sediment samples (Table 3) indicate that statistically consistent correlations exist for the parameters CEC-Al-K-Fe. The silicon concentration which is closely correlated with Al and Fe in suspended sediment samples (Vesper and White, 2003) was negatively correlated in the spring sediment samples. Similar patterns exist in the surface soil data (Table 4).

Because the analytical data suggest that the spring sediments and the soils do not represent distinct chemical populations, they can be combined into a larger data set in which more correlations are statistically significant at $\alpha = 0.01$ (Table 5). While the combined data set has more statistically significant correlations, many of the correlation coefficients are low, especially for the trace metals. As was found for the individual data sets, silicon does not correlate with aluminum and iron although it does correlate with manganese.

The lack of correlation between Si and Al reflects the high concentration of quartz in both sets of sediments and the variability of clay content. While manganese correlations between Si and Fe are not strong (R^2 values of 0.49 and –0.60 respectively), they suggest that Mn occurs predominantly as coatings on quartz particles. Manganese coatings are known to deposit preferentially on sandstone pebbles or on chert nodules in cave streams.

Extractions

Distribution of Major Components and Trace Metals

In general, the major metal distributions identified by selective extraction fell into two groups: those that fell primarily into the residual fraction and those that were more widely distributed between multiple fractions. The trace metals varied more by location and metal. The sum of the extracted fractions was compared to the total concentration for each metal. The correlation was stronger for the major metals than for trace metals. The correlation for Al, Ca, Cr, and Mn had R^2 values greater than 0.8. Fe had an R^2 value of 0.73. Cd, Ni, Pb, and Si had R^2 values below 0.5. Higher analytical error for the trace metals as well as sample heterogeneity both contribute to the lack of perfect correlation between the two analytical procedures.

Iron was primarily present only in the residual fraction (Fig. 6) suggesting that iron coatings on mineral grains are not extracted by the hydroxylamine hydrochloride.

Only samples from Quarles Spring (QD200 and QD201) contained substantial concentrations of iron in the carbonate and oxide fractions. Quarles Spring is a rise pool with up to 0.3 meters of loose, fine-grained sediment with a substantial organic content. Thus the sedimentary environment of the spring is important is determining the partitioning of iron between immobile coating and more mobile forms.

This distribution of manganese between fractions was the most variable of the major metals (Fig. 7) and the distribution is somewhat surprising. Observations of many cave stream sediments suggest that manganese is common and occurs as black coatings on mainly silica surfaces. These coatings are usually the highly disordered mineral birnessite (δ-MnO_2) which is known as an effective scavenger for transition and rare earth metals. MnO_2 is easily reduced to Mn^{2+} and this may account for the dominance of Mn in the F3 (reducible) fraction. However, a significant percentage of the manganese remains in the F5 (residual fraction) and apparently represents a form of manganese that was not reduced during the extraction procedure. As was the case with iron, the fractionation of manganese in the organic-rich, rise pool environment of Quarles Spring is different from the fractionation in the other free-flowing, organic-poor springs. Much of the Mn in Quarles Spring appeared in the F2 (carbonate) fraction. The more reducing environment of Quarles Spring brings the manganese into the Mn^{2+} state but the high bicarbonate activity in the water is apparently sufficient to precipitate Mn^{2+} as a carbonate phase. Quarles Spring also has a significant percentage of the Mn in the F1 (exchange) fraction, consistent with more Mn^{2+} in the water.

Extraction data for four of the five trace metals are shown in Figs. 8-11. Chromium is present in the range of 5 – 140 mg/kg with most of it concentrated in the residual (F5) fraction. The valence state of chromium is not known. If present as Cr^{3+}, it will be highly insoluble. Under these circumstances it is not surprising to find chromium in the residual fraction. Cadmium is a very minor constituent in most of the sediments, present at less than 10 mg/kg (Fig. 9). In spite of the low concentration, cadmium was mainly concentrated in the residual fraction with some distribution into the other fractions. Only in the case of surface soil BD101 was cadmium concentration higher in the carbonate fraction than in the residual fraction. Nickel occurred in the concentration range of 20 to almost 200 mg/kg. Nickel was primarily in the residual fraction although some samples contained observable organic or oxide-bound concentrations (Fig. 10). The distribution of these three trace metals between fractions in the spring sediments was not significantly different from the distribution in surface soils.

Lead is present in all sediment samples in the range of 20 – 90 mg/kg. Lead was the only trace metal for which there may be a difference between the soil samples and the spring sediment samples (Fig. 11). Lead is much more widely distributed over the extraction fractions. Although a portion of the lead remains in the residual fractions, substantial fractions of the lead occur in both oxidizable (F4) and reducible (F3) fraction. Although lead carbonates might be expected in these karst waters, lead in the carbonate fraction was negligible.

Comparison of Sediment Composition with Water Composition

In the parallel investigation to this study (Vesper and White, 2003), it was shown that metals in the spring water itself primarily moved during storm discharges. It was shown that the primary transport mechanism for metals was by adsorption onto small suspended particulates in the storm water. Comparison of the total concentration of each metal in the spring mouth bed sediments (from the sum of the fractions) and the mean maximum concentration in unfiltered storm water (Fig. 12) gives a power law fit of

$$C_{sed} = AC_{water}^{0.93}$$

This is probably a direct proportion to within the fit of the data, $R^2 = 0.89$. A similar relation is obtained if the metal concentrations in surface soils are plotted against the concentrations in the spring water. Whether the bed or suspended sediment concentration is the dependent variable depends on whether the suspended sediments contribute to the bed sediments (a depositional process within the conduit system) or the other way around (an erosional process within the conduit system). It is likely that both processes occur depending on storm intensity. This would provide for considerable sediment mixing and homogenization of the metal concentrations.

It is also possible to compare metal concentrations in the spring mouth sediments with the concentrations of metals actually dissolved in the spring waters (Fig. 13). The metal concentrations in the water were obtained by analyzing water samples that had passed through a 0.45 μm filter. These data can be also fitted with a power law

$$C_{sed} = AC_{water}^{1.82}$$

For this fit, $R^2 = 0.93$. There is a relation between metal concentrations in bed sediments and concentrations of dissolved metals in the water but it is not linear.

An attempt was made to compare the metal concentrations from the individual fractions with the concentrations in the water. Reasonable plots similar to Figure 12 were obtained for the residual fraction (F5) and the organic fraction (F4). Data for the other fractions had too much scatter to be useful. In part, this may have been due to the very low concentrations in these fractions.

Discussion and Conclusions

The results of this investigation can be summarized in a conceptual model (Fig. 14). It appears that surface soils are the primary source of spring and conduit sediments in the hydrogeologic setting investigated. They are injected into the aquifer during storm events and are stored within the aquifer and discharged through the springs. Storm flow provides a means of winnowing the metal concentrations by flushing out the fine-grained materials. The strong major-trace metal correlations in the suspended sediments are not present in the stored bed sediments.

In addition to transport of sediments from the surface and through the aquifer, spring sediment is introduced via slumpage at the spring mouth. Back flood deposits from adjacent surface waters may also introduce considerable sediments in some locations. Sediments stored in both the conduits and the springs interact with the water chemically; the interaction may be limited by the degree to which the water flows through the sediments. Springs in which the water discharges in a wide area through the sediments have considerable sediment/water interaction while other springs have limited interaction because of low diffusion capacities in the sediments and a localized water source.

Geomorphology at the spring may be the most important control on the bed sediment chemistry. Springs that decant water from rise pools and have a low gradient spring run are more likely to accumulate fine-grained sediment than are spring with highly variable discharges and a high-gradient spring run. Accordingly, spring sediments that are characterized by erosional processes are less likely to accumulate and alter sediments than are springs characterized by depositional processes. The presence of organic compounds, regardless of whether their source is contamination or detrital organic matter, can catalyze microbial induced reducing conditions and thereby alter the spring sediment significantly.

Ultimately, physical processes control both sediment type and chemistry. While chemical processes may be important in local condition (e.g., redox conditions), they are governed in turn by the physical process (such as the potential for a spring to accumulate sediments). Although the trace metals investigated in this study could be expected to exhibit a range of speciation and behavior, that was not observed. For example, the speciation of three of the six metals should be controlled by oxidation state (Fe, Mn and Cr) but they do not behave in a consistent manner. While Cr may be expected to differ from the first two because Cr is more mobile in its oxidized form whereas Fe and Mn are more mobile in their reduced forms, no obvious trends were observed. Four of the six metals are commonly associated with carbonates (Fe, Mn, Pb, and Cd) yet Mn was the only metal with a considerable mass extracted in the carbonate (F2) fraction. The discrepancy between the expected and observed fractionation may also be explained by the dominance of physical over chemical processes. The bulk chemical relationship between suspended and bed sediments implies that the two are closely linked by physical processes. Hence the different in surface chemistry between individual metals may not be important to the overall system.

Acknowledgements

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References

ATTEIA O and KOZEL R (1997) Particle size distributions in water from a karstic aquifer: from particles to colloids. J Hydrol 201:102-119

BRADY NC and WEIL RR (1996) The Nature and Properties of Soils. 11th Edition, Upper Saddle River, NJ: Prentice Hall, 740 p

KEMMERLY PR (1980) Sinkhole Collapse in Montgomery County, Tennessee. Tennessee Div Geol, Environ Geol Ser No 6, 37 p

KLEMIC H (1966) Geologic map of the Oak Grove Quadrangle, Kentucky. US Geol Survey Map GQ-565

KLEMIC H (1974) Geologic map of New Providence Quadrangle, Kentucky. US Geol Survey Map GQ-301SW

LUTHER ET (1977) Our Restless Earth. The Geologic Regions of Tennessee. University of Tennessee Press, Knoxville, TN, 94 p

MAHLER BJ and LYNCH FL (1999) Muddy waters: temporal variation in sediment discharging from a karst spring. J Hydrol 214:165-178

PROUT EE (2001) Temporal variation of sediment distribution in a karst aquifer, Easton, Pennsylvania. MA Thesis, Temple University, 102 pp

QUEVAUVILLER P, URE A, MUNTAU H and GRIEPINK B (1993) Improvement of analytical measurements within the BCR-Programme: single and sequential extraction procedures applied to soil and sediment analysis. Internatl. J. Environ. Anal. Chem. 51:129-134.

QUEVAUVILLER P et al (1994) Evaluation of a sequential extraction procedure for the determination of extractable trace meal contents of sediments. Fresenius J. Anal. Chem. 349: 808-814.

RYAN M and MEIMAN J (1996) An examination of short-term variations in water quality in a karst spring in Kentucky. Ground Water 34:23-30

SHEVENELL L and McCARTHY JF (2002) Effects of precipitation events on colloids in a karst aquifer. J Hydrol 255:50-68

VESPER DJ (2002) Transport and storage of trace metals in a karst aquifer: An example from Fort Campbell, Kentucky. Ph.D. thesis, The Pennsylvania State University

VESPER DJ and WHITE WB (2003) Metal transport to karst springs during stormflow: An example from Fort Campbell, Kentucky/Tennessee, U.S.A. J Hydrol (in press)

VESPER DJ and WHITE WB (In press) Storm pulse chemographs of saturation index and carbon dioxide pressure: Implication for shifting recharge sources during storm events in karst aquifers. Hydrogeol. J. (submitted).

Table 1. Summary of springs and spring characteristics.

Location	Spring Name, Latitude-Longitude	Media Sampled	Measured Base-flow Discharge[2]	Estimated Basin Size (km^2)	Spring Description	Spring sediment description
Fort Campbell and Surrounding Area, Kentucky	Gordon 87 30 47.23 W 36 39 16.10 N	Sediment	0-110 L/s (0-4 cfs)	2	Intermittent spring. Flows upward through sand in a circular depression.	Coarse chert sand (fossiliferous)
	Quarles 87 31 27.74 W 36 39 50.07 N	Sediment	30-700 L/s (1-24 cfs)	20	Single rise-pit in topographic low.	Fine-grained sediment in spring and spring run.
Fort Campbell and Surrounding Area, Tennessee	Beaver 87 27 15.39 W 36 36 37.73 N	Water Sediment	0.5 – 130 L/s (0.02 –5 cfs)	2.5	Free flowing from base of stepped limestone outcrop.	Generally coarse sand, gravel and cobbles
	Eagle 87 27 38.95 W 36 36 48.55 N	Water Sediment	0.9 – 140 L/s (0.03 – 5 cfs)	3	Steephead spring on bank of Little West Fork Creek. Flows upward through clay and rock openings.	Hard clay at orifices, loose material increases closer to creek.
	Millstone 87 21 59.58 W 36 37 39.64 N	Water Sediment	30 – 600 L/s (1-20 cfs)	65	Free flowing from base of rock outcrop located in head of an erosional valley.	Mixture from very fine to very coarse gravels.
Central Pennsylvania	Sand 77 57 36 W 40 43 07 N	Sediment	Not Measured	Unknown	Flows from the Silurian Tuscarora (sandstone) formation at the contact with the Juniata (shale) formation.	Uniform quartz sand with little to no fines.
East-Central Tennessee	Cold House 85 10 44.76 W 36 18 49.68 N	Sediment	20-140 L/s (0.7-5 cfs)	Unknown	On the bank of Cub Creek downgradient from an abandoned coal mine.	Sands and gravels coated with a white precipitate.
	John's Cave 85 10 45.48 W 36 18 34.56 N	Sediment	0-15 L/s (0-0.5 cfs)	Unknown	A flowing stream from a small cave; downgradient from an abandoned coal mine.	Sand and fine materials, coated orange. Organic matter common.

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[2] Values approximate, based on base-flow conditions.

Table 2. Description of sediment and soil samples.

Location	Sample ID	Location Description
Fort Campbell Spring Sediments	BD200	Beaver Spring - from underneath rock ledge
	ED200	Eagle Spring - from orifice furthest from creek
	GD200	Gordon Spring - central location, spring nearly dry
	MD200	Millstone Spring - from underneath rock ledge
	QD200	Quarles Spring - at edge of central depression
	QD201	Quarles Spring - in spring run near central depression
Fort Campbell Soils and Subsurface Soils	BS-E	Wooded area above Beaver Spring
	BD101	Soil peninsula at Beaver Spring
	BS-D	Wooded area above Eagle Spring
	ED101	Soil bank at Eagle Spring. Sample collected approximately 1 m below grade from side of bank.
	BS-A	Lawn near filled sinkhole in Main Cantonment Area
	BS-B	Fill material used for railroad construction (above Beaver and Eagle). No vegetated covering yet.
	BS-C	Edge of wooded and grassy area, above Eagle Spring. May be near former gravel road.
	ES-0-2	From drilling of boring "EDIP", 0-0.6 meters (0-2 feet) below grade
	ES-9-11	From drilling of boring "EDIP", 2.7-3.4 meters (9-11 feet) below grade
	ES-19-21	From drilling of boring "EDIP", 5.8-6.4 meters (19-21 feet) below grade
	ES-39-41	From drilling of boring "EDIP", 11.9-12.5 meters (39-41 feet) below grade
	PX01	Sediment collected from void in well at PX Service station, approximately 27 meters below grade (approximately 16 meters into rock).
Spring Sediments for Comparison	CL04H	Roadside Spring, orange from acid mine drainage, Overton County, Tennessee
	CL10H	Coldhouse Spring, white from acid mine drainage, Overton County, Tennessee
	Sand	Sand Spring, discharges from the Tuscarora formation (quartz sandstone), Centre County, Pennsylvania

Table 3. Matrix correlation with R^2 values for total metal concentrations in spring sediment samples.

	CEC	TOC	Al	Ca	Fe	K	Mg	Mn	Na	Si	Zn	Cr	Ni	Cd
TOC	---													
Al	*0.78	---												
Ca	---	---	---											
Fe	0.84	---	0.81	---										
K	---	---	0.89	---	---									
Mg	---	---	---	*0.78	---	---								
Mn	---	*0.77	---	---	---	---	---							
Na	---	---	---	---	---	0.89	---	---						
Si	-0.89	---	-0.97	---	-0.84	-0.80	---	---	---					
Zn	---	---	---	---	---	---	---	---	---	---				
Cr	---	---	---	---	---	---	---	---	---	---	*0.77			
Ni	---	---	---	0.93	---	---	---	---	---	---	---	---		
Cd	---	---	---	---	---	---	---	---	---	---	---	---	---	
Pb	---	---	---	---	---	---	*0.77	---	---	---	---	---	---	0.80

Only the correlations with probability less than an α of 0.01 are included; correlations with probability between 0.05 and 0.01 are marked with an asterisk.

Table 4. Matrix correlation with R^2 values for total metal concentrations in surface soil samples.

	% Clay	CEC	TOC	Al	Ca	Fe	K	Mg	Mn	Na	Si	Zn	Cr	Ni	Cd
CEC	---														
TOC	---	---													
Al	0.90	0.80	---												
Ca	---	---	---	---											
Fe	---	---	---	---	---										
K	---	---	---	---	---	---									
Mg	---	0.74	---	0.73	*0.68	---	---								
Mn	---	---	---	---	---	---	---	---							
Na	---	---	---	---	---	*-0.83	---		---						
Si	-0.80	---	---	-0.73	---	---	*-0.63	---	---	---					
Zn	---	---	---	---	---	*0.70	---	---	---	*-0.67	---				
Cr	---	---	---	---	---	0.94	---	---	---	-0.90	---	0.85			
Ni	---	---	---	---	---	---	---	---	---	-0.79	---	0.84	0.76		
Cd	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
Pb	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---

Only the correlations with probability less than an α of 0.01 are included; correlations with probability between 0.05 and 0.01 are marked with an asterisk.

Table 5. Matrix correlation with R^2 values for combined spring sediment and surface soil analyses.

	% Clay	CEC	TOC	Al	Ca	Fe	K	Mg	Mn	Na	Si	Zn	Cr	Ni	Cd
CEC	0.55														
TOC	---	---													
Al	0.96	0.62	---												
Ca	---	*0.47	---	---											
Fe	0.80	0.60	---	0.75	---										
K	0.51	0.65	---	0.55	---	---									
Mg	---	0.76	---	---	0.80	---	0.58								
Mn	---	---	---	-0.46	---	-0.60	---	---							
Na	---	---	0.54	---	---	---	0.81	---	---						
Si	-0.94	-0.66	---	-0.88	---	-0.70	-0.63	*-0.41	0.49	---					
Zn	0.62	---	-0.49	0.57	0.51	0.68	---	0.32	---	-0.66	-0.48				
Cr	0.67	*0.42	---	0.55	---	0.84	---	---	-0.47	---	-0.51	0.72			
Ni	---	---	---	*0.38	---	0.49	---	---	---	-0.44	---	0.68	0.45		
Cd	---	---	---	---	---	---	---	0.41	---	----	---	---	---	0.57	
Pb	---	*0.55	---	---	---	---	0.48	*0.43	---	---	---	---	---	---	---

Only the correlations with probability less than an α of 0.01 are included; correlations with probability between 0.05 and 0.01 are marked with an asterisk.

Legends for Figures

Fig. 1 Location and general regional layout at Fort Campbell.

Fig. 2 Approximate delineation of ground water basins for Beaver, Blue, Eagle, Gordon, Millstone and Quarles Springs. Other labeled springs are: BO – Boiling Spring (Base water supply); BM – Barker's Mill Spring; DN – Dennis Spring; HU – Hunter's Spring (Oak Grove water supply).

Fig. 3 Approximate locations for Fort Campbell soil samples. Spring samples are identified as: GO – Gordon Spring; BL – Blue Spring; BO – Boiling Spring; DN – Dennis Spring; EA – Eagle Spring; BE – Beaver Spring; G1 – Gate One Spring. Additional shallow soil samples were collected near the spring mouth of Eagle Spring (soil ED101) and Beaver Spring (soil BD101).

Fig. 4 Grain size distribution for spring sediments and surface soils. Sizes are based on U.S. Department of Agriculture classification (Brady and Weil, 1996). Clay = <0.002 mm; silt = 0.002 to 0.05 mm; and sand = 0.05 to 2 mm.

Fig. 5 Comparison of elemental surface chemistry based on EDX data. Spectra were collected under 400X magnification and averaged over three frames per sample.

Fig. 6 Extraction of iron into fractions. The BS-A samples are duplicates.

Fig. 7 Extraction of manganese into fractions. The BS-A samples are duplicates.

Fig. 8 Distribution of chromium among extraction fractions.

Fig. 9 Distribution of cadmium among extraction fractions.

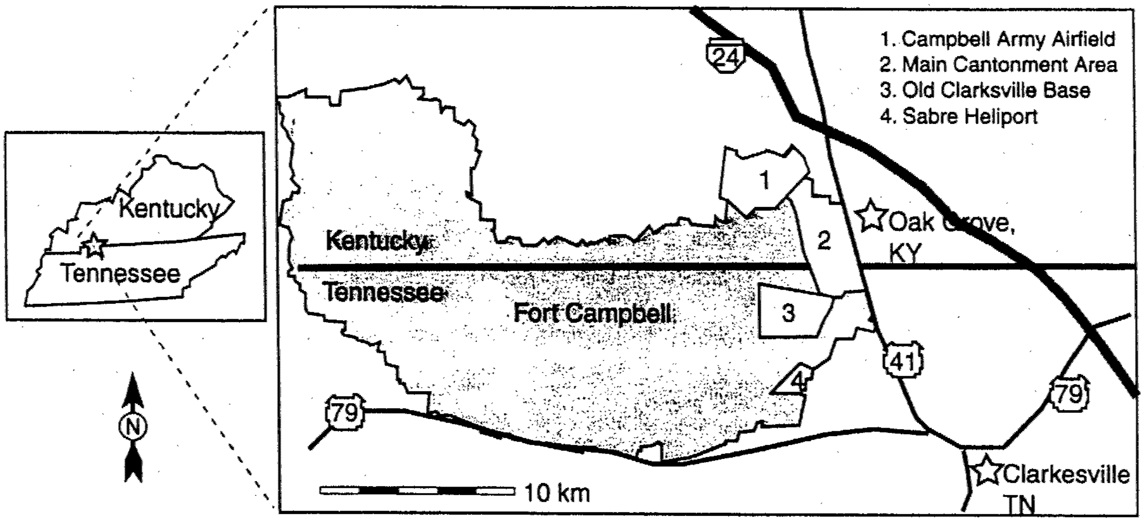
Fig. 10 Distribution of nickel among extraction fractions.

Fig. 11 Distribution of lead among extraction fractions.

Fig. 12 Comparison of metal concentrations in unfiltered water samples with total concentrations in the spring bed sediments. Water concentration was calculated as the mean of the three highest values from the digested samples.

Fig. 13 Comparison of metal concentrations in filtered water samples with the total concentrations in the spring bed sediments. Water concentrations calculated as the mean of the three highest values from the filtered samples.

Fig. 14 Schematic model of sources and physical processes controlling the chemistry of spring bed sediments.



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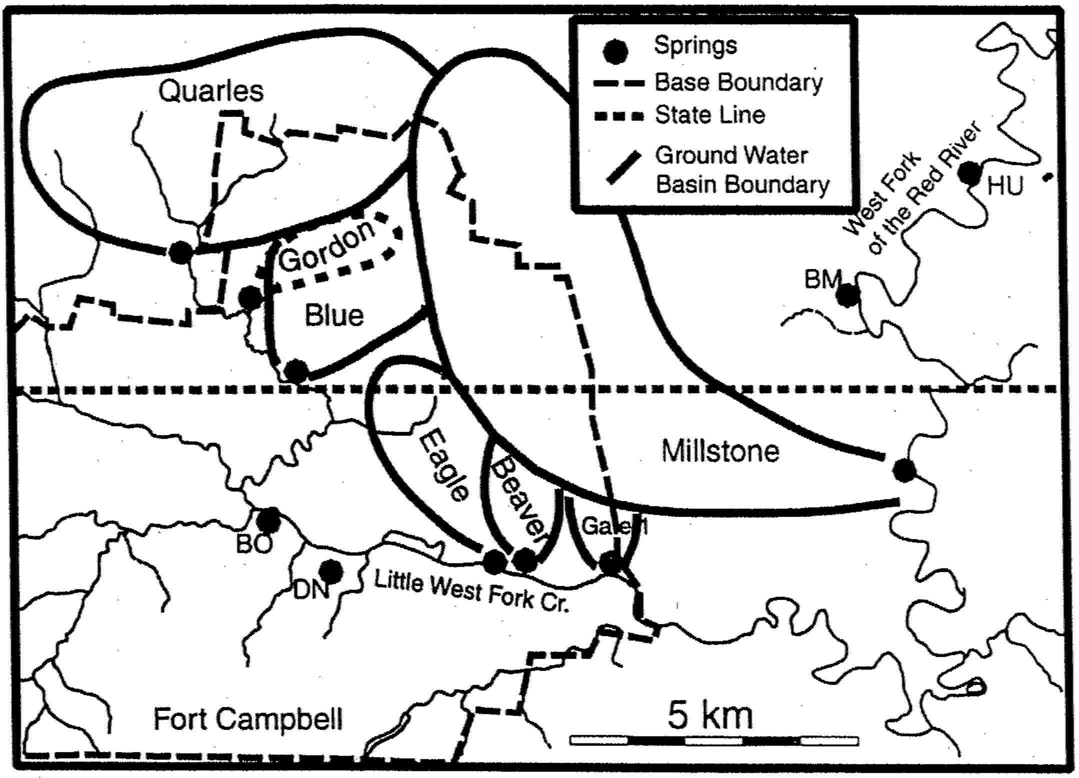

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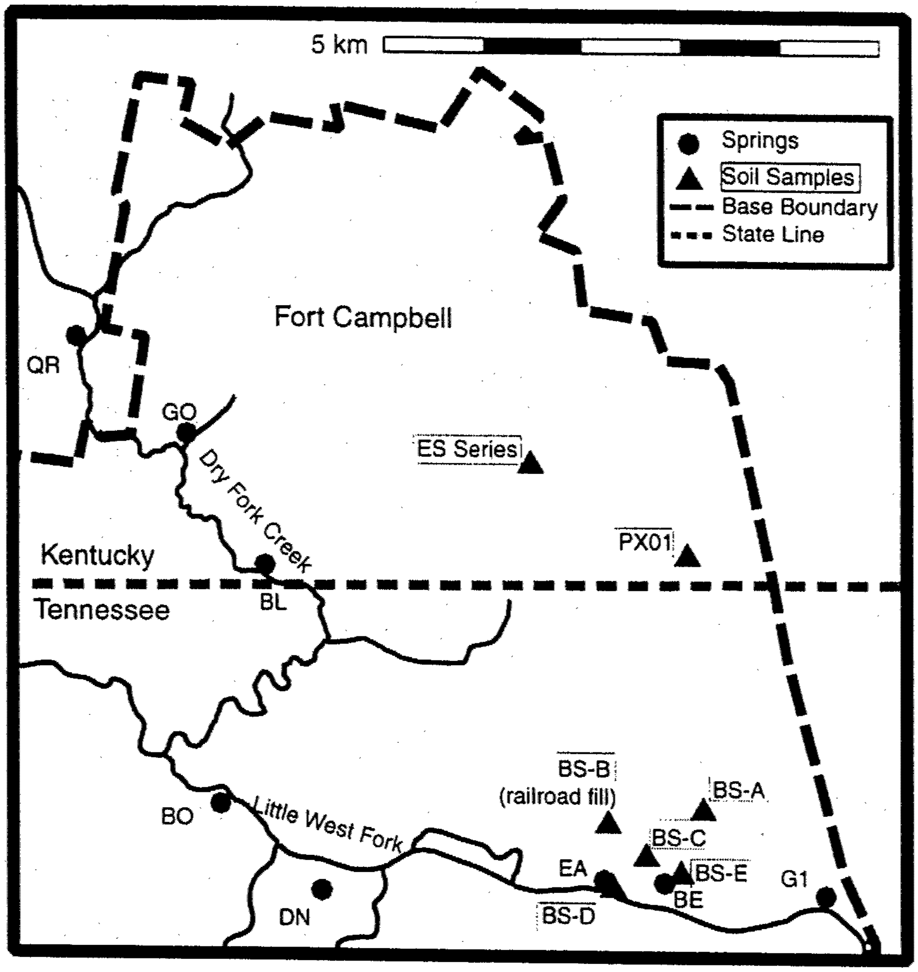
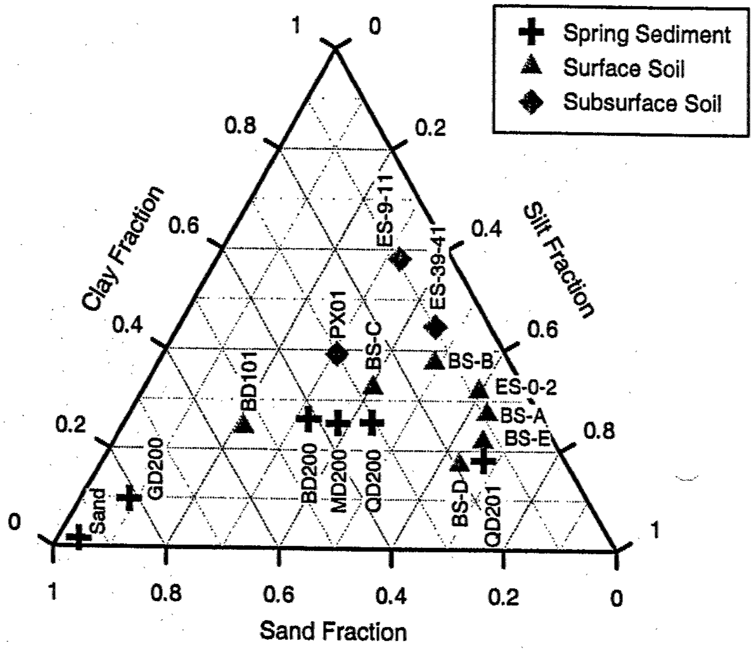

5 km
● Springs
▲ Soil Samples
Base Boundary
State Line
Fort Campbell
QR
GO
Dry Fork Creek
ES Series
PX01
Kentucky
Tennessee
BL
BS-B
(railroad fill)
BS-A
BS-C
BO
Little West Fork
EA
BS-E
G1
BE
BS-D
DN

Figure 3.



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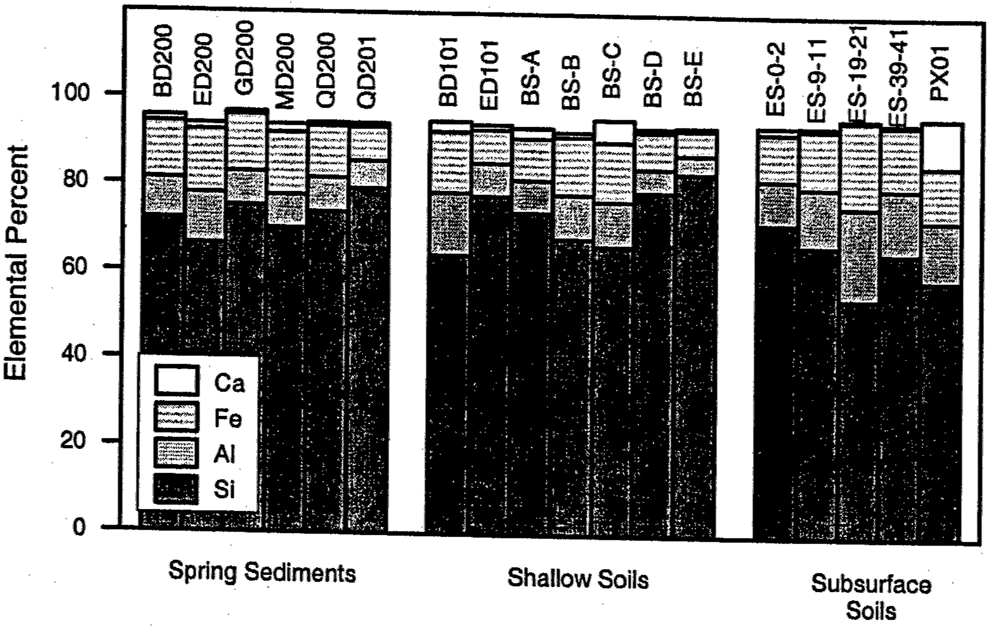

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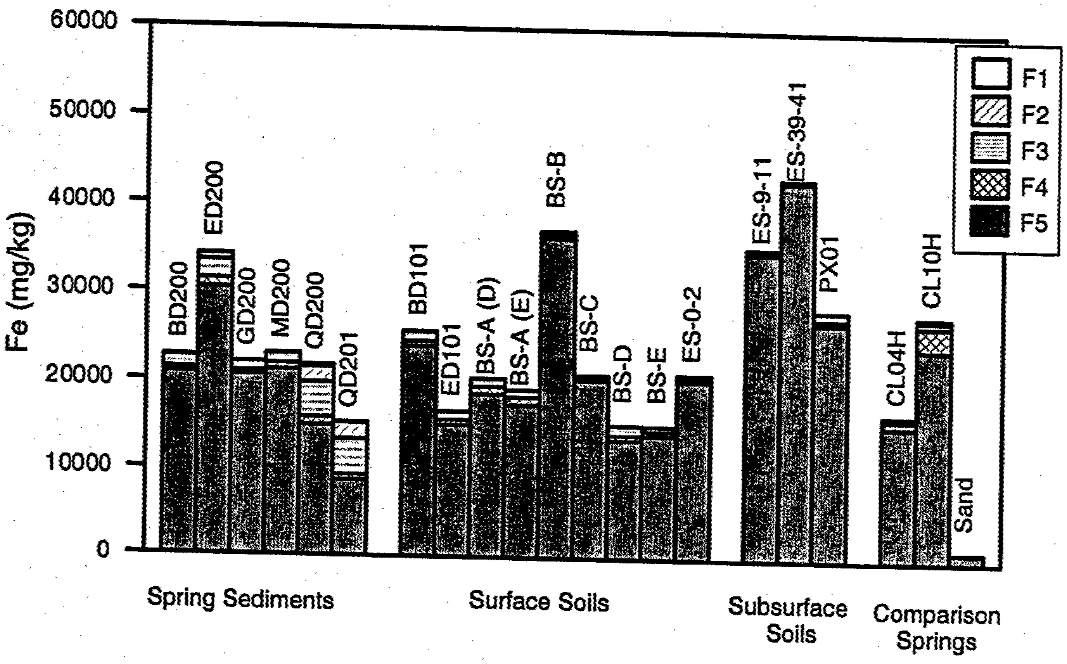

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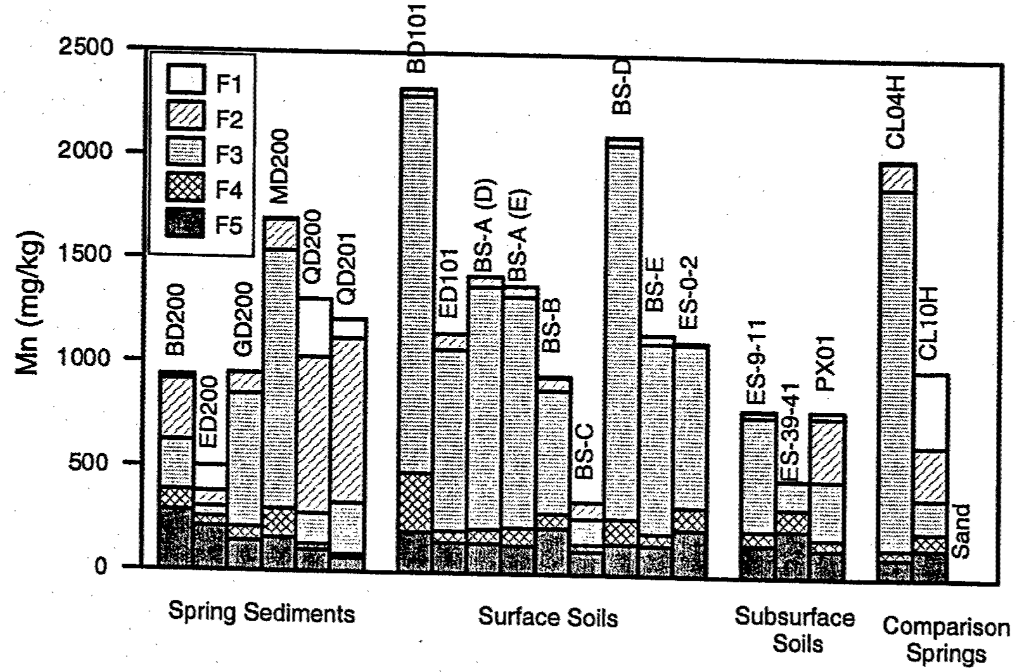

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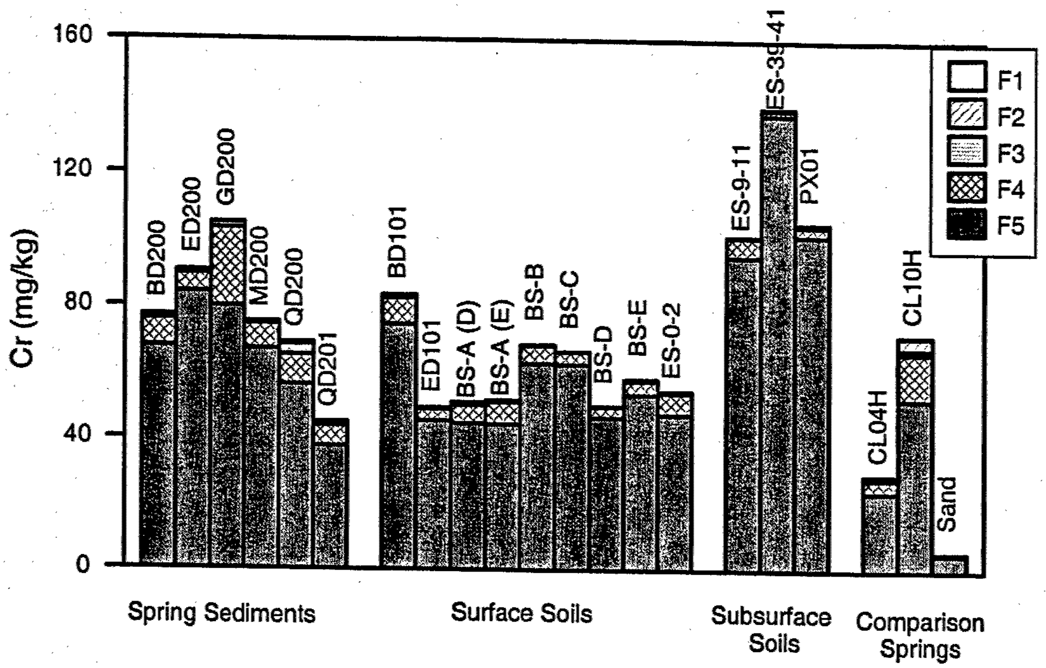

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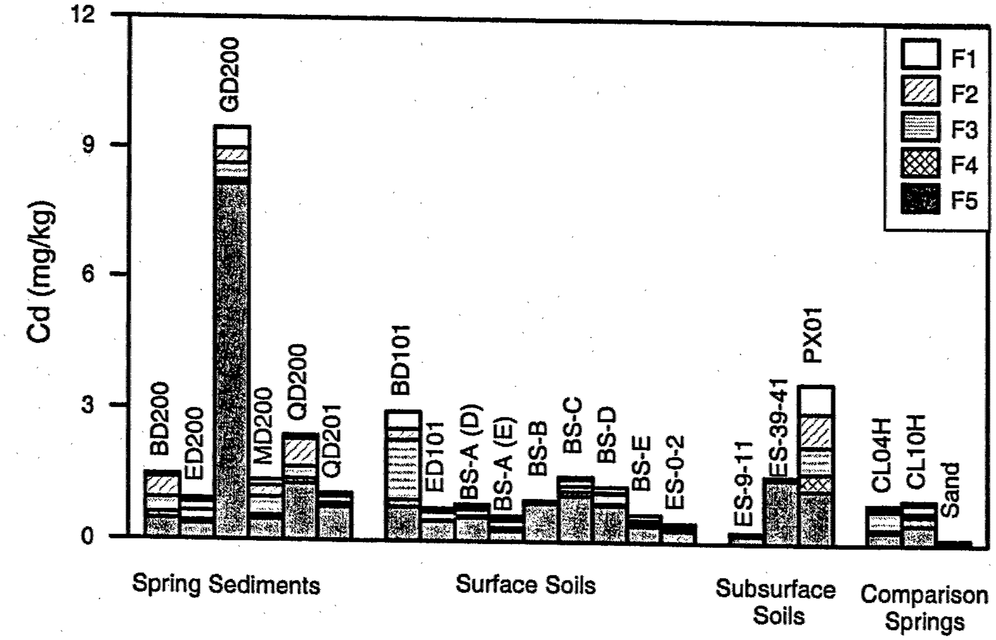

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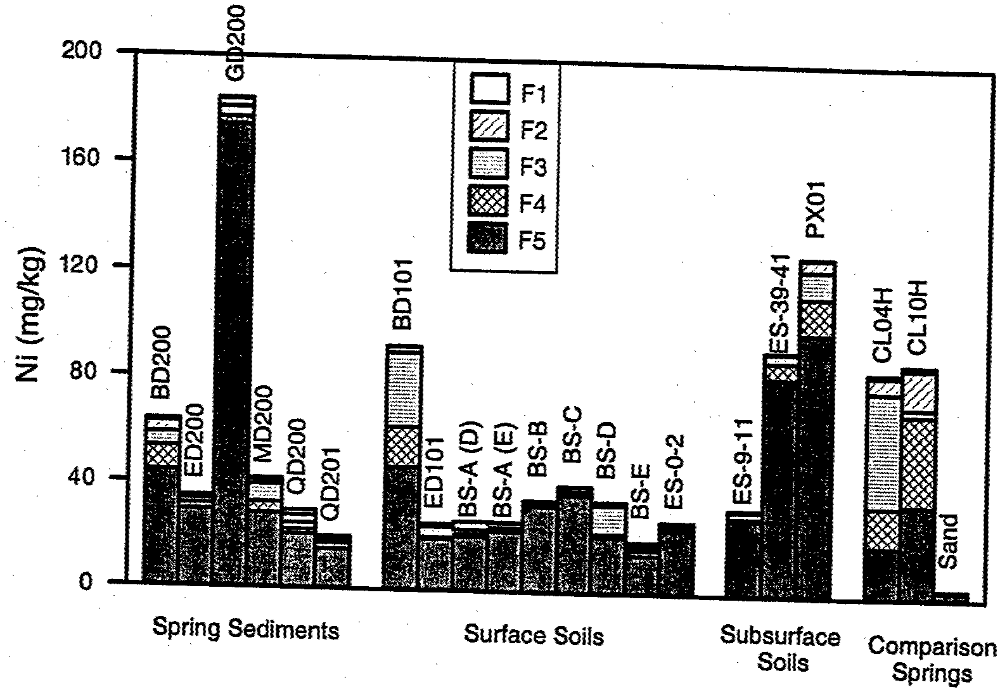

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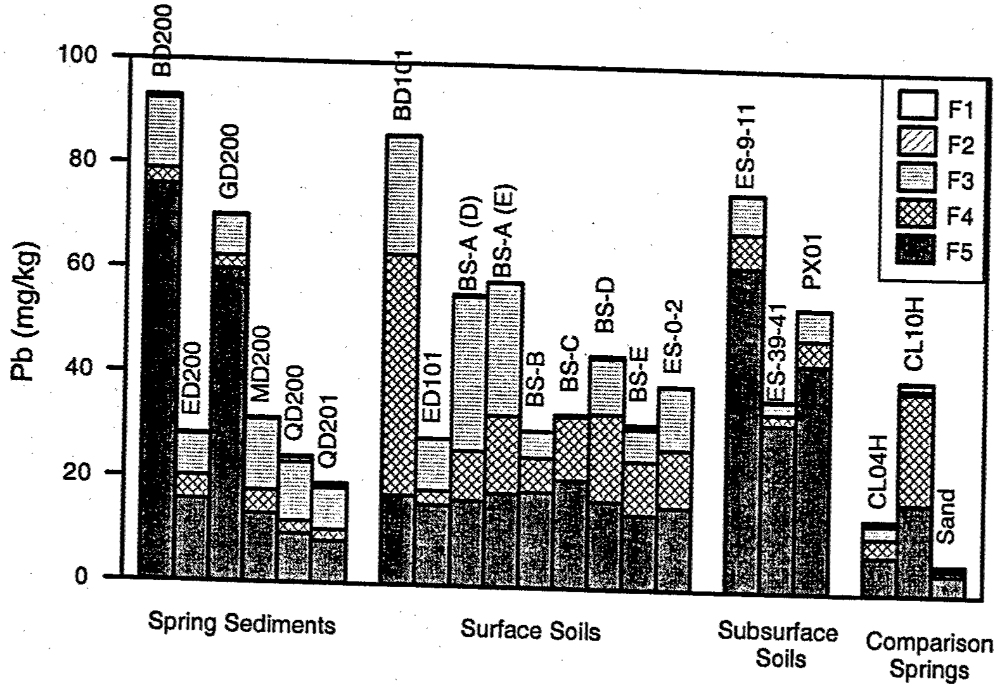

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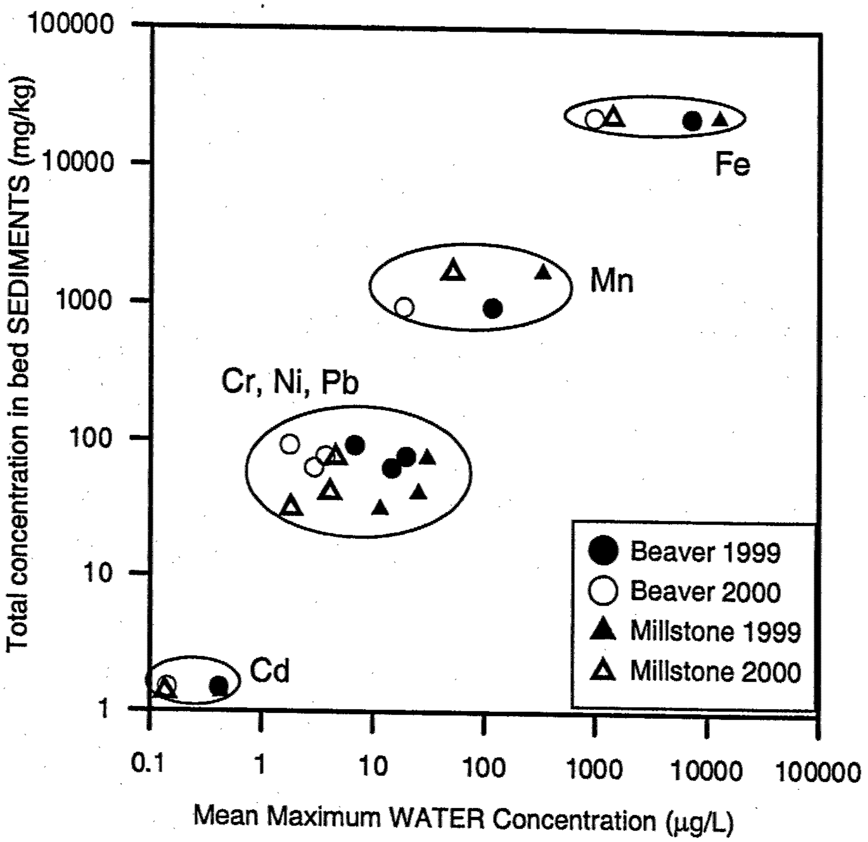

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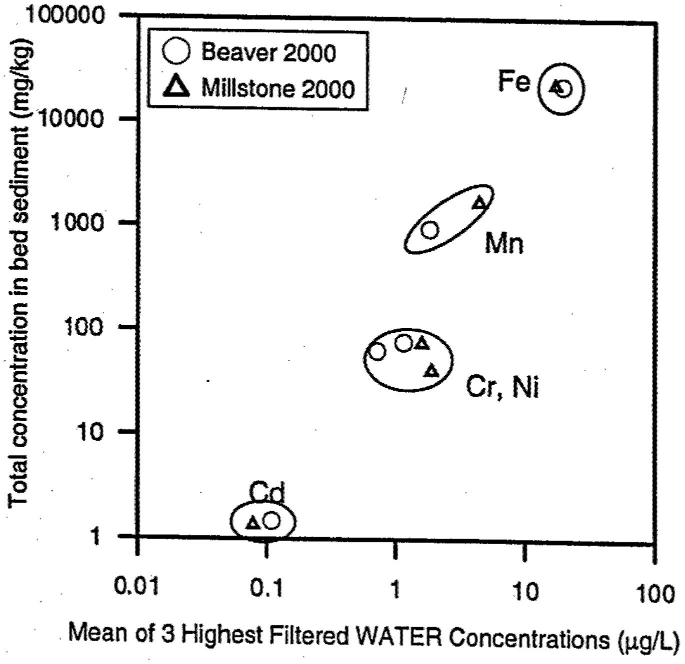

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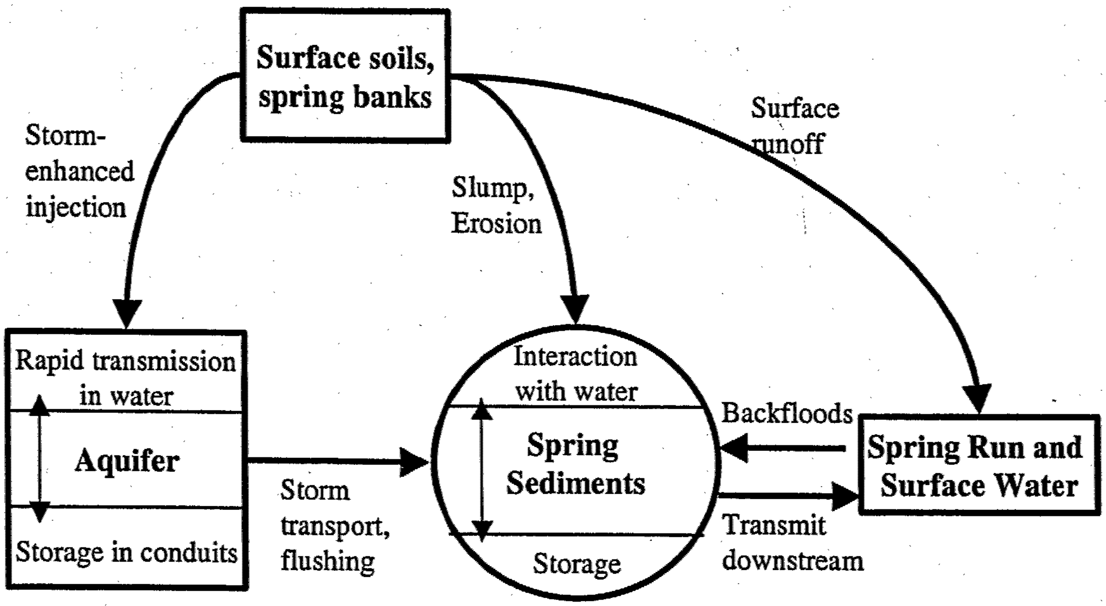
Surface soils, spring banks
Storm-enhanced injection
Slump, Erosion
Surface runoff
Rapid transmission in water
Aquifer
Storage in conduits
Storm transport, flushing
Interaction with water
Spring Sediments
Storage
Backfloods
Transmit downstream
Spring Run and Surface Water

Figure 14.