DEPARTMENT OF THE NAVY
CRANE DIVISION
NAVAL SURFACE WARFARE CENTER
300 HIGHWAY 361
CRANE, INDIANA 47522-5001

IN REPLY REFER TO
5090
Ser 095/U5289

28 SEP 1995

U.S. Environmental Protection Agency, Region V
Region V Waste Management Division
Attn: Ms. Carol Witt-Smith (HRP-8J)
77 West Jackson Blvd.
Chicago, IL 60604

Dear Ms. Witt-Smith:

Crane Division, Naval Surface Warfare Center (NAVSURFWARCENDIV Crane), in cooperation with the U.S. Army Corps of Engineers, Waterways Experiment Station (WES), reviewed the practicality and feasibility of conducting a pump-and-treat operation at the Ammunition Burning Grounds. Based upon the review of recent research, NAVSURFWARCENDIV Crane has decided not to proceed with pumping and treating at this time. Enclosure (1) is documentation from WES supporting this decision.

NAVSURFWARCENDIV Crane desires to pursue alternatives to the pump-and-treat system in order to minimize environmental impacts from the contaminated groundwater. Currently, NAVSURFWARCENDIV Crane and WES are working with Indiana University to design and conduct a quantitative dye trace of the contaminated groundwater aquifer. The dye trace study will better characterize the aquifer properties including flow direction, rates, and discharge points. The quantitative dye trace proposal is provided as enclosure (2) for U.S. EPA review and approval. Enclosure (3) is the requisite certification statement.

NAVSURFWARCENDIV Crane point of contact is Mr. Thomas J. Brent, Code 09510, telephone 812-854-6160.

Sincerely,

Deputy Director, Public Works Directorate
By direction of the Commander

Encl:
(1) Pump-and-Treat Technical Feasibility Review
(2) Indiana University Dye Trace Proposal
(3) Certification Statement

Copy to: (w/o encls)
SOUTHNAVFACENGCOM, (Code 1864)
COMNAVSEASYSCOM (SEA 07E)
USAE-WES (GG-YH)
IU (Noel Krothe)

CEWES-GG-Y
18 AUG 1995

REVIEW OF THE TECHNICAL FEASIBILITY OF A PUMP-AND-TREAT SYSTEM FOR FOUR WELLS IN THE AMMUNITION BURNING GROUND AT NAVY SURFACE WARFARE CENTER CRANE (NSWCC), INDIANA

Purpose

This letter report provides the results of a review of data to determine the feasibility of using a pump-and-treat system for four wells located in the Ammunition Burning Ground (ABG). A pump-and-treat system had been proposed based on data available before and during calendar year 1994. The proposal was funded and the US Army Engineer Waterways Experiment Station (WES) initiated the project during FY 95. The project responded to a need perceived at NSWCC to treat groundwater at the ABG that was contaminated with several organic explosives.

Although the project was progressing on schedule and according to its work plan, recent data from several sources and changing priorities at NSWCC suggested that the project status be reassessed. The WES team undertook a review of several applicable documents to determine whether or not the pump-and-treat project should be continued at this time.

Documents Reviewed

The reports reviewed were:

a. Geology and Hydrogeology of the Ammunition Burning Ground Crane Naval Weapons Support Center (Hunt, 1988).

b. Final Report, RCRA Facility Investigation, Phase III, Groundwater Release Characterization, SWMU 03/10, Ammunition Burning Ground (Murphy, 1994).

c. Dye Trace of Beech Creek Aquifer, Ammunition Burning Ground, Naval Weapons Support Center Crane, Indiana (Murphy and Ciocco, 1990).

d. Risk Assessment Methodology Analysis for NSWCC, (Henshel et al. 1994).

e. Geology and Hydropetrology of the Big Clifty Sandstone and Beech Creek Limestone Aquifer System at the Ammunition Burning Ground (Barnhill et al. 1994).

f. Report of Groundwater Flow and Contaminant Migration Modeling at the Ammunition Burning Ground, Crane NSWCC, Indiana (Haitjema et al. 1994).

Enclosure (1)

Encl

g. A Preliminary Hydrogeological Report on the Bedrock Aquifers at the Ammunition Burning Ground: Discharge Measurements, Water Chemistry and Hydrochemical Analysis (Krothe et al. 1994).

h. Impacts of Sorption on In-Situ Bioremediation of Explosives Contaminated Soils (Pennington, et al. 1994).

i. Bench Scale Treatability Studies on Soil From the Hastings Superfund Site: Desorption Enhancement Evaluation.

j. Geogeographic Information Systems at Crane Naval Surface Warfare Center (Frenkel et al. 1994).

k. Assessment of the Fate of Subsurface Organic Contaminants at Crane Naval Weapons Support Center (Stroh et al, 1995).

l. Bench Scale Treatability Studies on Soil from the Hastings Superfund Site: Desorption Enhancement Evaluation (Pennington et al 1992).

The data in these reports were evaluated in light of guidance provided by the United States Environmental Protection Agency (EPA) in two documents: Basics of Pump and Treat Ground-Water Remediation Technology (1990), and Guidance for Evaluating the Technical Impracticability of Ground-Water Restoration (1993).

Background

The NSWCC occupies 62,463 acres and is located in southwest Indiana about 75 miles southwest of Indianapolis (Figure 1). The ABG, consisting of approximately 50 acres, lies in the eastern part of the NSWCC as shown in Figure 2. Operations at the ABG date back to the 1940's. Materials burned in the area include various explosives, items contaminated with explosives, fuse materials, detonators, red phosphorus, flares, candles, and rocket motors. The area is currently used for burning out the residue from bombs and projectiles after the bulk of the explosives have been removed. Bulk propellent and high explosives are burned in clay-lined steel pans. Pyrotechnics, explosives and propellent contaminated solvents and liquids are burned in unlined steel pans. RDX and phosphorus sludge are also burned in the area. The primer pit and incendiary cage are used for burning various ammunition components (Murphy, 1994).

Hydrogeology

The topography is rugged in the area of the ABG with elevations ranging from about 480 ft to 845 ft (Hunt, 1988). A generalized stratigraphic section for the area is

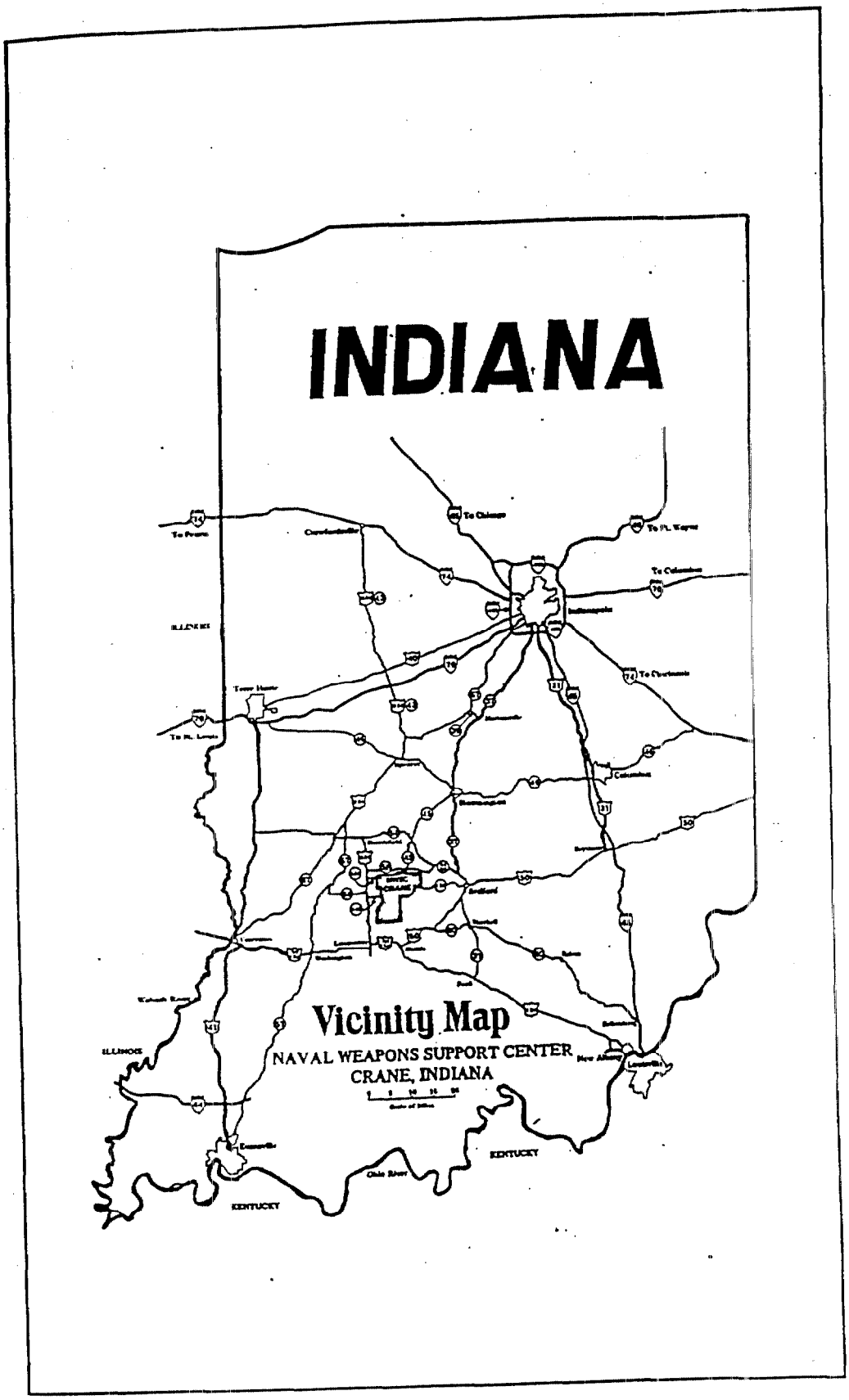


Figure 1. Location of Naval Surface Warfare Center, Crane, Indiana

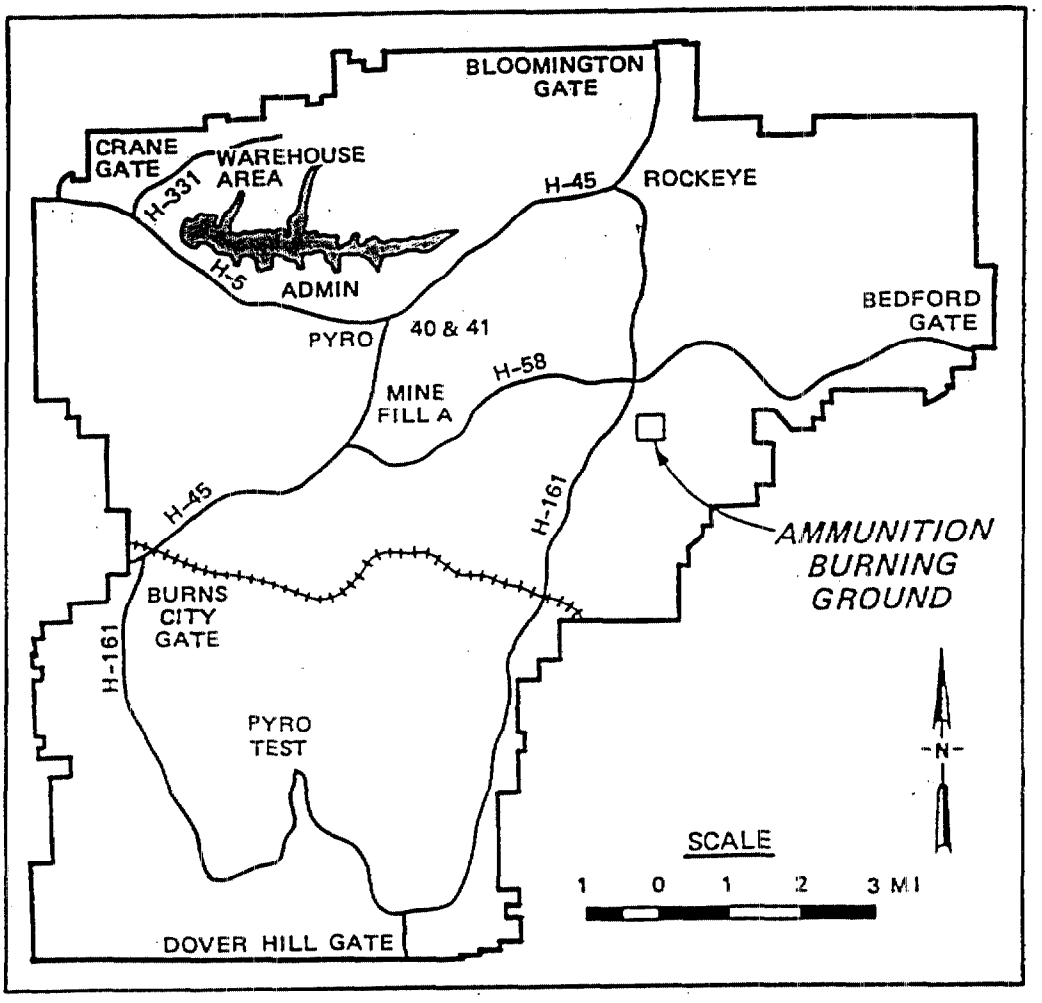


Figure 2. Crane Naval Surface Warfare Center and location of the Ammunition Burning Ground

shown in Figure 3. The formations of concern underlying the ABG in descending order are the Big Clifty, the Beech Creek, the Elwren, the Sample, and the Beaver Bend. The Big Clifty and the Beech Creek together combine to form the Beech Creek Aquifer. A generalized cross section shows the relationship of the various formations in the ABG is given in Figure 4. The location of the four wells of interest is shown in Figure 5.

Contaminants of Concern

Seventy-two wells in the ABG were monitored for RCRA 40 CFR Part 265 parameter Groups, I, II, and III; for selected volatile organics, and for the explosives RDX, TNT, and HMX. The contaminants of primary concern are RDX, TNT and TCE. Data available at the time of initiation of the project involving four wells indicated that they represented unusual and localized concentrations of contaminants.

Ranking Factors

The reports were evaluated using ranking factors from the EPA document listed previously (1993). Example calculations and other pertinent data were taken from "Basics of Pump-and-Treat Ground-Water Remediation Technology" (EPA, 1990). The primary factors considered for this evaluation were site use, chemical properties, contaminant distribution, geology, and hydraulics/flow. Other factors also were considered and are summarized below (items a thru l).

a. Site Use. Large volumes of explosives were destroyed in the ABG. For example, 63,000 pounds per day of powder and high explosives were destroyed between 1956 and 1960 (Murphy, 1994). It is logical to assume that since the operations began in 1942, large volumes of RDX, TNT, and TCE entered the groundwater system in the ABG. The contamination continued for long periods with mostly slow continual releases and possibly occasional slug releases.

b. Chemical Properties (Abiotic). Photodegradation processes may be effective only for explosives present for the first few centimeters of surface soil where light is available. Due to a lack of ionizable chemical groups the munitions compounds will not be affected by acid/base reactions. Abiotic transformation of TCE is expected to be low (Stroh, 1995). The low water solubility of the explosive compounds implies that they will be released from the contaminated soils very slowly.

c. Chemical Properties (Biotic). Biological transformation of RDX, HMX, and TNT does occur in soils,

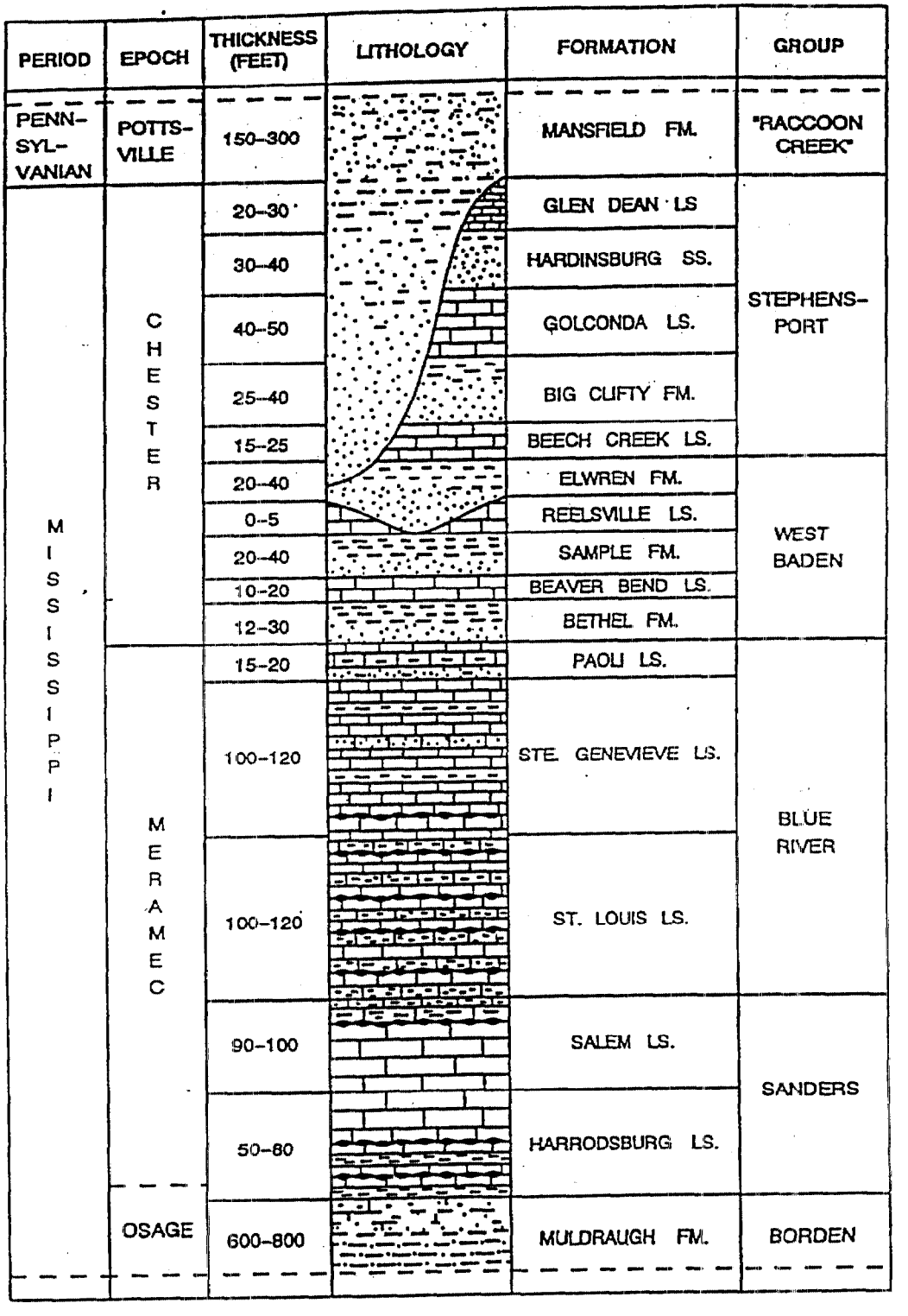


Figure 3. Stratigraphic column for rock units encountered at NSWCC (after Palmer, 1989)

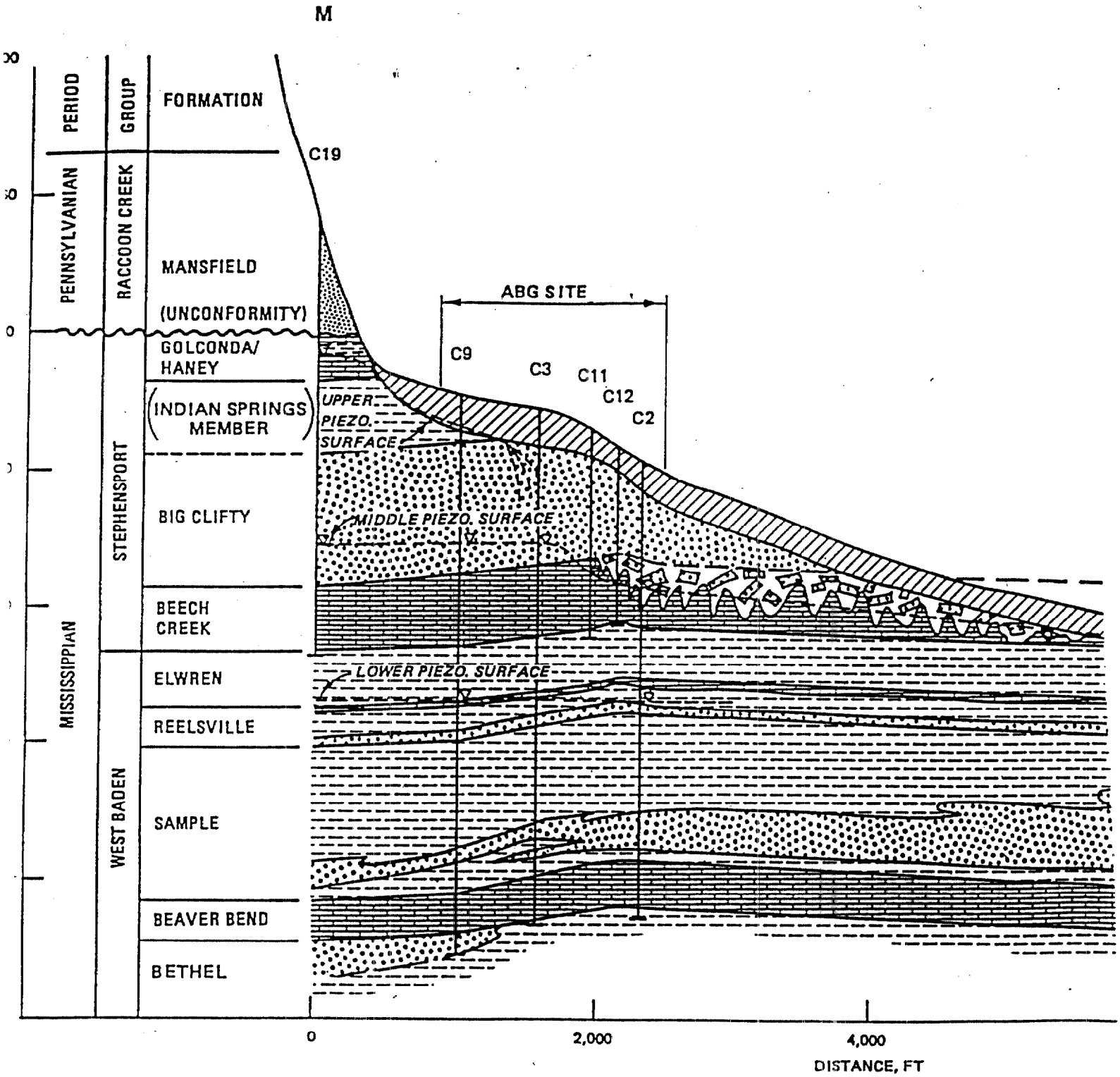


Figure 4. Stratigraphic section. (After Murphy,1994)

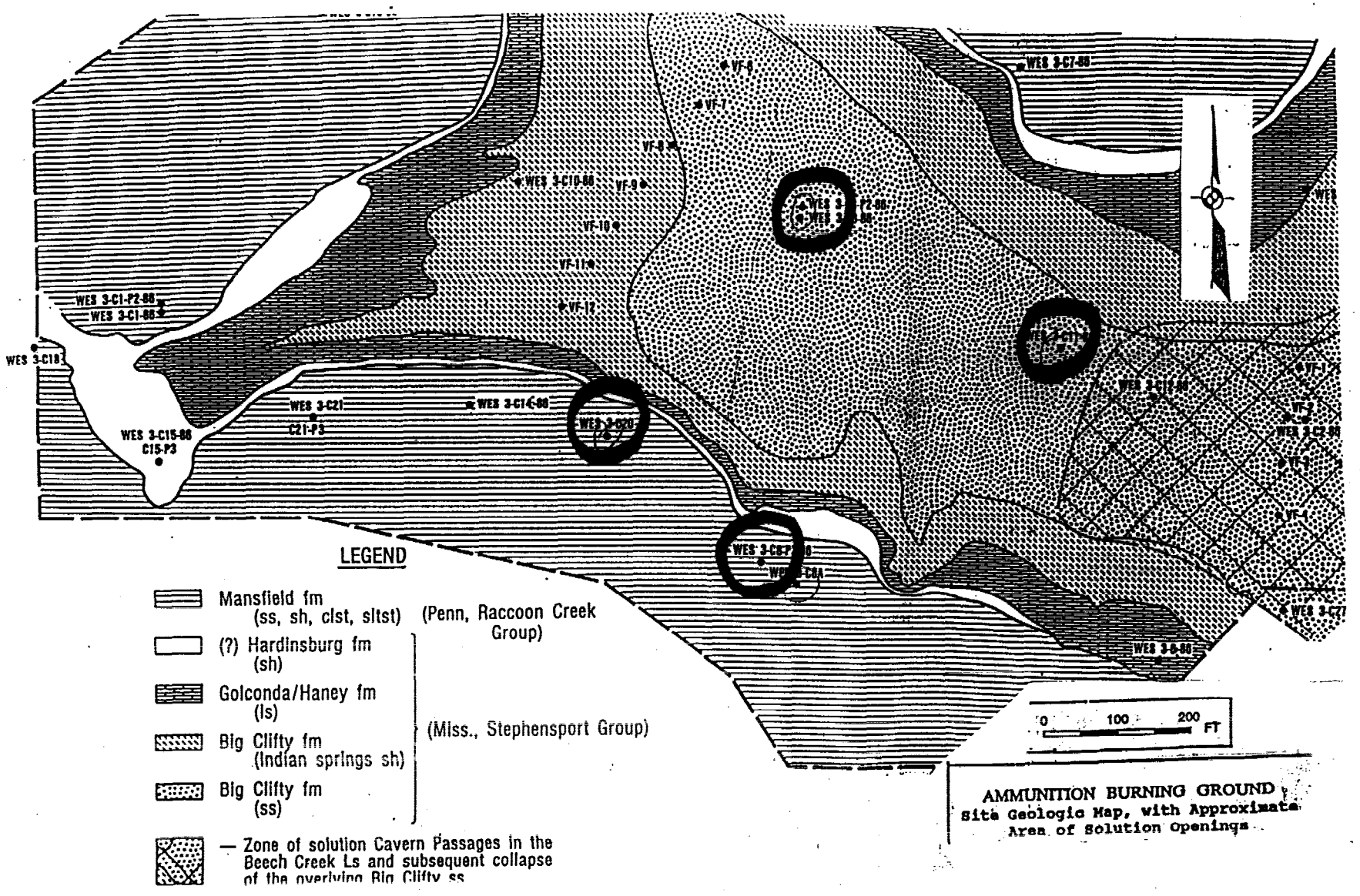


Figure 5. Location of proposed wells for pump and treat. (Map after Murphy, 1994)

but is believed by Stroh (1995) to be significant only under anaerobic conditions. Research at WES indicates some transformations will occur under aerobic conditions (Zappi, personal communication). Stroh stated that the rates of degradation will likely be lower than for photolysis in environmental compartments that receive light. Prediction of actual constants and half lives for biotransformation in the field is difficult and will be site specific (Stroh, 1995). TCE transformation by microbes can occur both aerobically and anaerobically. The actual rates of reaction will depend on the environmental conditions present.

d. Volatility. The Henry's Law constants and vapor pressures of the explosive compounds are low. This means that even during the heat of summer volatilization of explosive compounds from the unsaturated zone is expected to be minimal. Reentry of contaminants into the unsaturated zone by volatilization across the water table with subsequent loss from the unsaturated zone even for TCE is not likely (Stroh, 1995).

e. Retardation Potential (Sorption). Sorption of contaminants to immobile subsurface solids acts to slow down their movement through the unsaturated and saturated zones. The organic carbon content of the subsurface solids and hydrophobicity of the contaminant provides a good estimate of how much sorption will occur. For polar organic contaminants, like the explosives at ABG, sorption mechanisms in addition to partitioning into the soil organic matter may contribute to the overall sorption.

For TNT, the difference between the predicted and measured values suggest that additional sorption mechanisms may be contributing (Stroh, 1995). This observation seems to compliment the findings of Pennington (1992) on her work with the soil from the Hastings Superfund Site. She found that it was extremely difficult to remove TNT after sequential desorption of the soil using surfactants. Water alone removed only a small percentage of the TNT (Figure 6). In another study using explosive contaminated soils from NSWCC, Pennington et al. found that surfactants increased the solution phase concentrations 1.5 to 2 times greater than solution phase concentrations with water alone (1994). This indicates that removing all the explosives by pumping the groundwater would not be possible.

Retardation coefficients for TNT and TCE are in the range of 13-160 indicating that they are expected to move at velocities less than 1/10 of the average groundwater velocity.

f. Contaminant Phase. Because of the long history of the ABG, it would be expected that TCE, which is a dense

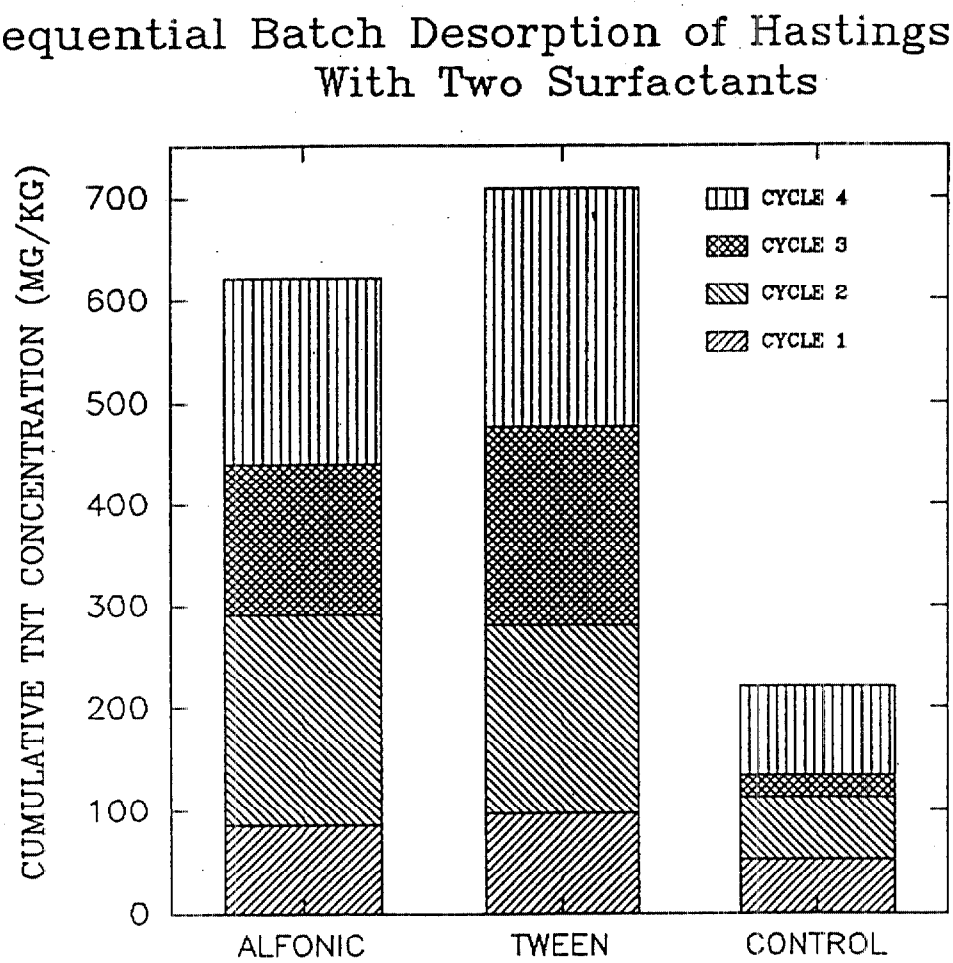


Figure 6. Cumulative concentrations of TNT after sequential desorption of Hastings soil with three percent Alfonic 1012-60, three percent Tween 80. and water (control). After Pennington 1992

non-aqueous phase liquid (DNAPL), would be at residual saturation in many areas. Residual DNAPL generally is not capable of migrating or being displaced by groundwater flow (EPA 1993). When NAPLs are trapped in pores by interfacial tension, diffusive liquid-liquid partitioning controls dissolution. Flow rates during remediation may be too rapid to allow aqueous saturation levels of partitioned contaminants to be reached locally. If insufficient contact time is allowed, the affected water may be advected away from the residual NAPLs before reaching chemical equilibrium. Ground water extraction is not generally efficient at cleaning up this type of contaminant (EPA, 1990).

An example of how long it would take TCE to dissolve in an aquifer with a hydraulic conductivity of 0.001 cm/sec was presented in "Basics of Pump and Treat Ground-Water Remediation Technology." The time was 122 years. Recent aquifer tests at the ABG indicate that the time required may be even longer.

g. Volume of Contaminated Media. The volume of the contaminated media is expected to be relatively large based on the many years of activity at the ABG.

h. Contaminant Depth. The depth of the reported contamination at the ABG is approximatey 160 ft or down to the Beaver Bend (Murphy, 1994).

i. Stratigraphy. Although the overall stratigraphy is not complex, local details and facies changes within the Big Clifty influence permeability and porosity. The lower portion of the Big Clifty is cemented with calcium carbonate. The Beech Creek has little permeability except in fractures or solution features (Barnhill, 1994).

j. Degree of Heterogeneity. The aquifer materials in the ABG are somewhat heterogeneous because of the inter-bedded silts, sands, and fractures in the Big Clifty and the fractures and solution features in the Beech Creek. The zones of calcium carbonate cement also add to the heterogeneity (Barnhill, 1994).

k. Temporal Variation and Vertical Flow. The flow in the aquifer is known to change rapidly with time. Both seasonal and rainfall events have been noted in past reports. A large vertical flow exists in the ABG with contamination down to the Beaver Bend formation.

l. Hydraulic Conductivity. Based on the available data the hydraulic conductivity in the areas proposed for pumping wells is generally very low. Some reported values for the hydraulic conductivities of the sandstone and

limestone range from 10^{-9} cm/sec to 0.010 cm/sec (Barnhill, 1994). In regard to pump-and-treat systems, this wide range of reported hydraulic conductivities may increase the probability of what is known as the "tailing effect." The "tailing effect" is a phenomenon that has been observed in pump-and-treat systems where contamination has penetrated material that has a low permeability. As pumping continues, the contaminants in the more permeable material and in the fractures are moved, but the contamination in the finer grained material is left behind. The well appears to be getting cleaner, but when pumping is stopped the residual contamination from the fine-grained material moves into the well and contaminant concentrations rise again. The wider the range of hydraulic conductivity, the more likely it is that this phenomenon will occur (EPA, 1990).

Recent pump tests conducted at the proposed pump-and-treat sites yielded hydraulic conductivities on the order of 0.00001 cm/sec, which are within the range reported by Barnhill (1994). Due to recharge limitations, it was not possible to run these tests for the prescribed 72 hours.

Conclusions

This review of data from several sources and application of guidance provided by the EPA indicates that a pump-and-treat system may not be able to remove significant amounts of contamination or control the groundwater flow. The EPA factor chart (Figure 7) indicates that most factors indicate pumping and treating in the proposed locations would have limited success. WES team members with specific expertise with fate and effects of explosives in groundwater concurred with this assessment.

Recommendations

It is recommended that pumping and treating of the proposed widely spaced wells to remove residual contaminants not be conducted at this time. The groundwater contour map of the ABG (Murphy 1994) indicates that a natural groundwater sink is located at the lower end of the ABG. In Figure 8, approximate groundwater flow lines have been added to the aforementioned contour map. This suggests that water and contaminants from the areas of the proposed pump-and-treat wells are moving toward the natural sink.

If significant contamination is reaching the area where a natural sink is indicated, a question which could be answered by field investigations, then this area could be more amenable to a pump-and-treat system and enhanced

Generalized Remediation Difficulty Scale

Increasing difficulty →

Contaminant Characteristics

Site Use	Nature of Release	Small Volume Short Duration Slug Release	→ Large Volume Long Duration Continual Release
Chemical Properties	Biotic/Abiotic Decay Potential	High	→ Low Abiotic Biotic
	Volatility	High	→ Low
	Contaminant Retardation (Sorption) Potential	Low	→ High
Contaminant Distribution	Contaminant Phase	Aqueous, Gaseous	→ Sorbed → LNAPLs → DNAPLs
	Volume of Contaminated Media	Small	→ Large
	Contaminant Depth	Shallow	→ Deep

Hydrogeologic Characteristics

Geology	Stratigraphy	Simple Geology, e.g., Planar Bedding	→ Complex Geology, e.g., ~~Interbedded~~ and Discontinuous Strata
	Texture of Unconsolidated Deposits	Sand	→ Clay N/A.
	Degree of Heterogeneity	Homogeneous (e.g., well-sorted sand)	→ Heterogeneous (e.g., interbedded sand and silts, clays, fractured media, karst)
Hydraulics/Flow	Hydraulic conductivity	High (>10^{-2} cm/sec)	→ Low (< 10^{-4} cm/sec)
	Temporal Variation	Little/None	→ High
	Vertical Flow	Little	→ Large Downward Flow Component

Figure 7. Ranking factors used to evaluate feasibility of proposed pump and treat system.

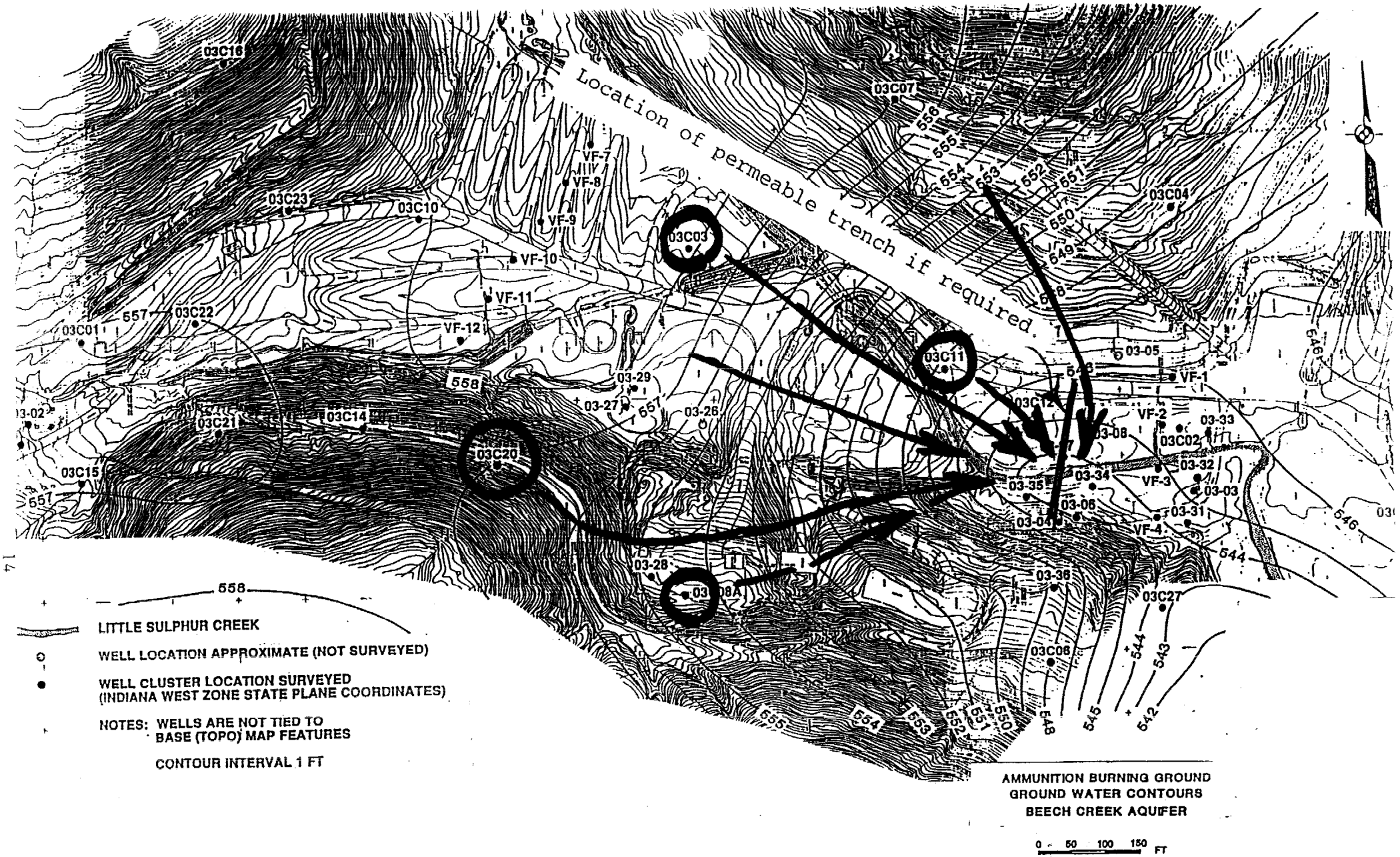


Figure 8. Flow lines showing general pathway of water from proposed well sites. (Map after Murphy, 1994)

groundwater control. Some other option, such as an aggregate-filled trench, could improve capture of groundwater. Some of the features of such a trench are shown in a very generalized schematic diagram in Figure 9.

A new technology using a trench filled with iron-rich permeable material and designed to remove contaminants without pumping is being tested by the EPA. The EPA research laboratory in Athens, GA, has expressed interest in using this area of the ABG as a demonstration site. This is not a well-established treatment technology, however, and calcium in the system could cause a problem in this area.

A short distance down gradient from the sink area, the Big Clifty\Beech Creek aquifer has been eroded and the groundwater becomes surface water. Additional studies of contaminants would be needed to determine the likely effectiveness of other options, such as treating the surface water and/or springs. The outlook for natural attenuation of explosives in this environment also should be addressed.

Questions about this report should be directed to Dr. James H. May.

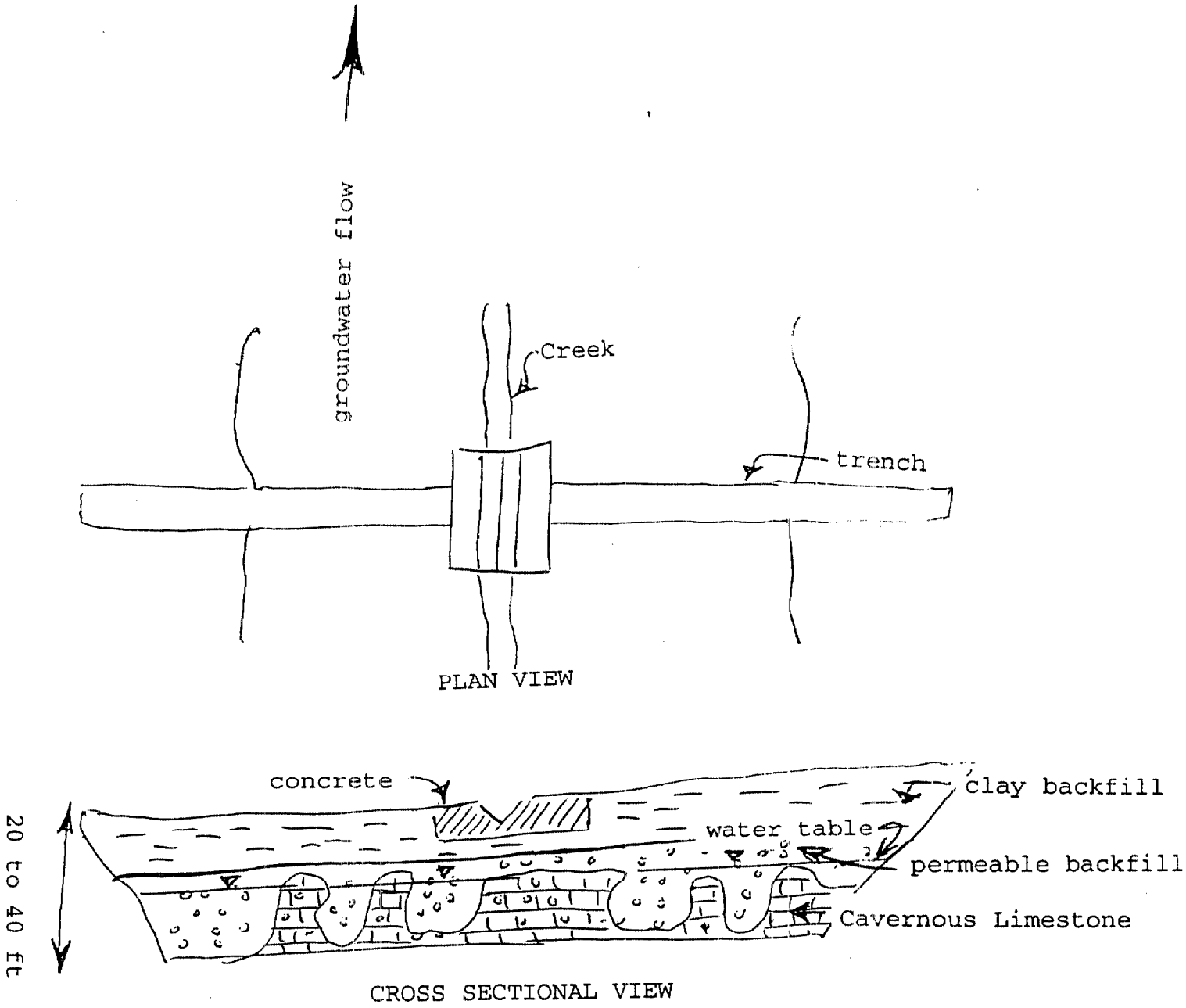


Figure 9. Schematic of permeable trench.

A Hydrochemical Study to Determine the Groundwater Flow and Chemical Transport in the Big Clifty/Beech Creek Aquifer Beneath the Ammunition Burning Grounds, Naval Weapons Support Center, Crane, Indiana.

Submitted to: Commander
Crane Division Naval Surface Warfare Center
300 Highway 361
Code 095 Building 3260
Crane, IN 47522-5009

Principal Investigator: Dr. Noel C. Krothe
RM 425 Geology Bldg.
Department of Geological Sciences
1005 E. 10th St.
Indiana University
Bloomington, IN 47405

ANY AWARD resulting from this proposal should indicate the RECIPIENT to be
INDIANA UNIVERSITY
P.O. Box 1847
Bloomington, Indiana 47402

George Walker, Vice President for Research and Dean of the Graduate School
Telephone: 812-855-0516

Background Geology and Hydrogeology

The northeast corner of the Naval Weapons Support Center, Crane (NWSCC) has Mississippian age rocks cropping out at the surface. The rest of the depot is capped by Pennsylvanian age strata (Figure 1). The Mississippian rocks dip gently to the southwest beneath the Pennsylvanian age strata but are exposed along deeply entrenched valleys, such as Little Sulphur Creek, Sulphur Creek and Turkey Creek. The carbonate units at the NWSCC are prone to solution and formation of karst features such as the solutional enlargement of fractures, joints and the development of conduits.

The stratigraphy beneath the Ammunition Burning Grounds (ABG) is shown in Figure 2. The Beech Creek limestone is the main karst forming unit in the Little Sulphur Creek watershed. It is a dense, thinly bedded and highly jointed limestone. Hunt (1988) describes three aquifers beneath the ABG (Figure 2). An upper relatively low yielding aquifer in the Golconda limestone perched on the Indian Springs shale. A second deeper aquifer in the lower Big Clifty sandstone and Beech Creek limestone is perched on the Elwren shale. The third deepest aquifer in the Beaver Bend limestone is isolated from the ABG by the Elwren shale. The Big Clifty/Beech Creek aquifer is the major aquifer therefore is important to groundwater flow beneath the ABG. A line of groundwater seeps issue from the west wall of the ABG along the Golconda limestone and flows down the ABG to Little Sulphur Creek at high flow. At low flow all of the upper part of Little Sulphur Creek is dry. The reason is that the Indian Spring shale is not present across most of the ABG, exposing the Big Clifty sandstone. This unit is highly fractured and permeable, allowing surface water to infiltrate rapidly to the underlying Beech Creek limestone which is highly fractured and modified by solution to form a major conduit under the Little Sulphur Creek Valley. A hypothetical flow diagram is presented in Figure 3. During storm conditions the Big Clifty can not accommodate all of the surface water, therefore Little Sulphur Creek flows on the surface along its entire length. When the storm flow subsides the Big Clifty can accommodate the flow and the upper section becomes dry again. The groundwater flows along the underlying Beech Creek limestone beneath Little Sulphur Creek Valley until it reaches a lower elevation where the Elwren shale is exposed in the stream bed. It is at this point that Springs A, A', B and C issue from the Beech Creek limestone to form a perennial section of the stream. The low flow is sustained by Springs A and C. Springs A' and B are upper level conduits that flow during wetter periods.

The focus of this research will be Springs A, A', B and C in the Little Sulphur Creek Drainage Basin since it is believed that these springs account for most of the groundwater leaving the ABG. In addition, springs off-site to the north, east and south and wells in Johnson Hollow will also be studied.

Technical Description of Research

Research Completed

A V-shaped weir or flume has been constructed on springs A, A', B and C which provide the sustained flow of Little Sulphur Creek for most of the year. In addition, to the weir or flume, a data logger, pressure transducer, temperature probe and specific conductance sensor have been installed at each spring to provide instantaneous reading of discharge, temperature and specific conductance for any designated time interval. The data loggers are presently logging at one hour intervals and programmed to log every 15 minutes when the stage of the stream rises to a designated height. Storm events will be accurately monitored with this design.

In addition, each spring is instrumented with an automatic water sampling device that can also be programmed for any time interval and collect up to 24 samples. Two rain gauges have been installed to record yearly precipitation.

The following hydrochemical data has been collected to date:

1) Two hundred water samples from springs A, A', B and C have been analyzed for major ion chemistry and selected trace elements.
2) Ninety-six background fluorescence samples for the springs have been collected and analyzed to provide information for future dye tracing tests.
3) Equivalents per million (EPM), epm balances and saturation states for major minerals have been computed from major ion chemistry with the computer program WATEQF.

4) The WATEQF output was used to create trilinear plots of major ions and will serve as input into mass transfer chemical models (Figures 4-9).
5) A data base of all pre-existing water data for the ABG has been prepared.
6) A nitrate data base has been prepared for wells in the ABG area.
7) Isotope separations of a storm hydrograph was completed to show the amount of storm and prestorm groundwater issuing at Spring A (Figures 10-11).
8) Plots of major ions versus time were prepared for the same storm event. (Figures 12-13)

Purpose

The identification and correct interpretation of groundwater flow beneath the ABG is central to future remediation plans. The development of Karst in the Beech Creek limestone creates a hydrologic flow regime that differs from that of porous media. Since the conduits developed in the Beech Creek limestone are capture zones for the ABG, springs not wells, need to be studied in detail. Wells are only useful if they are drilled on a major fracture or conduit. Statistically, the chances of drilling such wells are low.

Figure 3 shows the flow pattern in karst aquifers. This research will concentrate on Springs A, A', B and C in the Little Sulphur Valley, wells in Johnson Hollow and springs across the groundwater divide of Little Sulphur Creek. A quantitative dye tracing test and a water chemistry study prior to, during and after a storm will be the main focus of this research project.

During high flow conditions water can travel through abandoned karst features in the vadose zone across groundwater divides (McCann and Krothe, 1991). It is essential to conduct field studies to understand the complicated flow if meaningful models are to be developed for the area. Groundwater flow in karst terrains are best determined by dye tracing studies. A small scale qualitative dye trace was attempted for a portion of the NWSCC in the Beech Creek limestone at the ABG. The site is at the headwaters of the Little Sulphur Creek drainage (Murphy and Ciocco, 1990). The results of the test showed :

1) Spring AIA' is the primary discharge point for dye injected in well WES 3C2P2.

2) Spring C may be an outlet at higher flows.

3) Spring B shows a different hydrograph response and may receive water from areas other than the ABG.

4) The test showed the flow velocities were typical of conduit (non-Darcian flow)

Murphy and Ciocco (1990) point out that a large scale quantitative test is necessary since problems with the 1990 test were:

1) The amount of dye injected was not adequate to allow for accurate assessment of dye discharging from a spring or well outside of the ABG,

2) The use of ultraviolet light to detect dyes is very subjective. A spectrofluorophotometer is the state of the art detection instrumentation capable of detection in the parts per trillion range.

3) The method of sampling wells for background and monitoring samples was inadequate to detect an organic dye.

4) The duration of the test was too short (9 days) to detect dyes in springs located outside of the NWSCC or wells located in the Little Sulphur Creek drainage (See Appendix 1).

5) The test was qualitative in nature which only provides connection between two points. It does not determine the percentage of the tracer moving between two points, which is necessary to plan future remediation projects.

It is the intent of this proposal to design a large scale tracer test based on the results of the 1990 test to

provide accurate flow data for proposed hydrologic models.

RESEARCH APPROACH

I. Preparation for dye tracing of carbonate rocks (Karst)

1) Aerial photograph's will be studied with special emphasis on the northeast corner where the Blue River Group limestones crop-out.
2) Springs outside of the N.W.S.C.C. on Sulphur Creek and beyond the boundary of Crane down Little Sulfur Creek will be located with assistance from William Murphy.
3) Well logs of all existing wells on the ABG will be studied to determine which wells will serve as injection points for future dye tracing tests.
4) Protocol for future dye tracing tests will be established (Appendix 1).

II. Water Sampling

1) Springs along Little Sulphur Creek, Sulphur Creek and off of Crane will be analyzed for major and minor ion chemistry and background fluorescent dyes.*
2) Ion chemistry and isotope studies will allow for separation of flow units into storm and prestorm water at Springs A, A', B and C. This information is essential for development and verification of models for the site.
3) Four of the springs along Little Sulphur Creek (Spring A, A', B and C) have been instrumented to obtain continuous measurements of discharge, ion chemistry, background fluorescence and stable isotope analyses. These springs will be used as discharge points for later dye trace testing (Appendix 1). They will also supply valuable information concerning the groundwater flow characteristics in the karst bedrock and possible connection with overlying and deeper aquifers. Chemistry studies for several major storm events will be studied with special emphasis on major ions, stable isotopes, metals and ammunition burning by-products such as Ba^{+}, PO_4^{2-}, TNT, RDX and HMX.
4) Wells in the ABG watershed will be sampled and analyzed for major ions and selected trace elements and organics.
5) Wells containing elevated nitrate will be sampled for nitrate and nitrogen isotopes to determine the sources of the nitrogen.**

*Sampling Technique: Grab water samples will be taken when springs are located. The water samples will be analyzed for background fluorescence dyes. Passive detectors of charcoal and cotton will be placed in each spring and collected biweekly. If dyes can not be detected from the grab water sample then the charcoal will be elutriated to release the dye accumulated. Bromide background will be determined from grab samples. This method will provide accurate background fluorescence and bromide in groundwaters in the ABG area. (See appendix 1)

**Nitrate is a by-product of ammunition burning. Twelve wells in the vicinity of the ABG have nitrate concentrations in excess of 15mg/l and seven of those wells exceed the drinking water standard of 45mg/l. The sources of the nitrate is either munition detonation or human waste (septic or sludge). Nitrogen isotopes ($\delta^{15}N$) should be ≈0.0 for munition by-products and +10 to +15% for animal waste. This significant difference is $\delta^{15}N$ values may allow for discerning the source of the nitrate. Water samples will be taken from the twelve wells and analyzed for nitrate and the ratio of N^{15}/N^{14} in the water (Appendix 2).

III. Water level monitoring

1) Selected wells will be instrumented with transducers for continuous water level monitoring.*

*Selected wells screened in the Golconda/Haney, Big Clifty-Beach Creek and Beaver Bend Formations will be instrumented with transducers to obtain a continuous water level record through time in each aquifer. This data will provide insight into vertical gradients, direction of flow, and changes in hydraulic gradient during major storm events. Since the ABG is located on or near a groundwater divide the response of the water levels in each formation is important to determine if water can flow across the

groundwater divide to the north, east (into Sulfur Creek) or to the west (into Johnson Hollow).

IV. Laboratory Equipment

1) Major and minor anion analysis- Dionex Conductivity Detector (Series 4500i)
2) Major and minor cation analysis- Inductively Coupled Plasma Injection, Atomic Adsorption
3) Fluorescent Dyes [Rhodamine WT, Fluorescein (Acid Yellow 73), Optical Brightener, Direct Yellow 96 and Eosine]- Shimadzu (RF5000) Spectrofluorophotometer
4) Stable isotope (oxygen and deuterium) separation lines and mass spectrometer

V. Chemical Modeling

1) Geochemical speciation models will be produced from the chemical data collected from the springs and selected wells to determine whether the natural waters in the study area are in thermodynamic equilibrium with the surrounding rock types or influenced by activities at the ABG (Baedke, 1990).
2) Preliminary reaction modeling runs using the United States Geological Survey's computer program PHRQPITZ will be performed to evaluate possible controls on the chemical variations in the groundwater system by predicting the results of various water/rock interaction scenarios (Plummer et al., 1988).

VI. Final Report

1) Maps of all springs in the Little Sulphur Creek area and beyond the Crane boundaries down Little Sulfur Creek will be provided.
2) Data for major and minor ion chemistry, stable isotopes, background fluorescence, and discharge of selected springs and wells will be reported.
3) Seasonal and storm fluctuations in spring discharge will be provided.
4) Data, trilinear diagrams and speciation results for the four main springs and all wells in the ABG watershed and Johnson Hollow will be provided (Preliminary results are shown in Figures 4-9).
5) Results of water chemistry and isotope studies on important springs in the Little Sulphur Creek storm hydrograph studies will be presented (Preliminary results are shown in Figures 10-13).
6) Results of the quantitative tracer test will be prepared.
7) Flucuations in water levels in wells beneath the ABG will be reported with emphasis on changes in the potentiormetric level during major storm events.
8) Recommendations for groundwater remediation will be provided based on the tracer test and hydrochemical studies.

REFERENCE LIST

Baedke, S.J., 1990, A model for the chemical evolution of spring waters in south-central Indiana. Masters Thesis. Indiana University.

McCann, M.R., and Krothe, N.C., 1991. Development of a monitoring program at a Superfund Site in a karst terrain near Bloomington, Indiana. Proceedings of the 3rd Conference on Hydrogeology, Ecology, Monitoring and Management of Ground Water in Karst Terrains, Nashville, Tennessee, pp. 349-371.

Murphy, W.L., and Ciocco, J., 1990. Dye trace of Beech Creek Aquifer Ammunition Burning Ground, Naval Weapons Support Center Crane, Indiana. US Army Corps of Engineers, Technical Report GL-90-21.

Plummer, L.N., Parkhurst, D.L., Fleming, G.W., and Dunkle, S.A., 1988, A computer program incorporating Pitzer's equations for calculation of geochemical reactions in brines. U.S. Geological Survey Water-resources Investigations Report 88-4153, 309 pp.

Quinlan, J.F., 1987. Qualitative water-tracing with dyes in karst terranes; In: Quinlan, J.F. (editor), Practical karst hydrogeology with emphasis on groundwater monitoring (Course Manual). National Water Well Association, Dublin, Ohio, vol. 6, p. E1-E24.

Wells, E.R., and Krothe, N.C., 1989. Seasonal fluctuations in $\delta^{15}N$ of groundwater nitrate in a mantled karst aquifer due to macropore transport of fertilizer-derived nitrate. Journal of Hydrology, v. 112, pp. 121-201.

WORK PLAN
1995 to 1996

This proposal has three main components:

1) Collect background fluorescence and bromide from springs and wells to be monitored during the proposed tracer test.

2) Conduct a quantitative tracer test at the Ammunition Burning Grounds (ABG) to establish the groundwater hydraulic connection with springs and wells in the Little Sulphur Creek drainage area, wells in Johnson Hollow and springs across the groundwater divide.

3) Conduct water chemistry tests for explosive byproducts (RDX, TNT, barium, nitrate, etc.) before, during and after a storm event to study chemical transport from the ABG during different discharges at Springs A, A', B and C.

The purpose of this research is to understand the role of karst development in the Beach Creek limestone on the groundwater flow and chemical transport beneath the ABG at the Naval Weapons Support Center Crane (NWSCC). The research is essential to establish capture zones necessary for meaningful groundwater remediation.

PROTOCOL
(1995-1996)

The following will be undertaken:

A. Preparation of field equipment (automatic samplers, charcoal detectors, etc.), necessary to collect background water fluorescence and bromide concentration.

B. Activated charcoal packages will be emplaced in each designated spring and well. They will be collected bi-weekly and analyzed. At the time of each collection a grab water sample will also be taken for bromide and fluorescence analysis. It would be ideal to have both high and low flow conditions during the background study.

C. Collect background fluorescence and bromide from all springs and wells to be used in the proposed tracer test. This includes wells at the Dye Burial Grounds that may influence background fluorescence in groundwaters in the ABG basin.

D. Recalibrate transducers and specific conductance probes on Springs A, A', B and C in Little Sulphur Creek Valley to assure accurate readings for dye tracer tests.

E. Visit research personnel at the U.S. Army Corps. of Engineers, Waterway Experimental Station to decide which wells should be monitored for water levels and dye injection.

F. Instrument selected wells in all three of the aquifers with transducers to obtaining water level measurements in groundwater beneath the ABG.

G. In the Spring (1996), if flow conditions are determined to be moderate in nature, a quantitative tracer test* will be conducted. Well 3C2P2 will be used as the injection point since it showed hydraulic connection with Springs A and A' (Murphy and Ciocco, 1990). A second well may be chosen for injection if the hydraulic properties are suitable for dye injection.

* The quantitative tracer test will be conducted as follows: Eosine (a fluorescent dye) and bromide will be injected simultaneously in well WES3-C2-P2 at the ABG. Eosine has high visibility and should be detected when discharging from springs in the Little Sulphur Creek valley. Eosine is not conservative in nature and may be attenuated by geologic material along the flow path. Bromide which will be injected simultaneously will not be attenuated. Therefore a mass balance of tracer emerging at any designated spring can be calculated. Considering that Springs A, A', B and C have weirs or flumes, then discharge is available for the other unknown in the mass balance equation.

H. After completion and evaluation of the dye tracing test a chemical study will be conducted prior to, during and after a storm event to establish the concentration of each chemical related to burning activities (RDX, TNT, etc.). In addition, the relationship of concentration to flow will be studied .

I. The detection of naturally occurring inorganic ions sucn as Mg^{2+}, NO_3^- and Ba^{2+}, that appear to be elevated by activities at the ABG will be studied. The chemistry of water from springs and wells will also be considered.

J. Nitrogen isotope studies will be conducted on wells showing elevated nitrate to determine if the origin of the nitrate is munitions burning.

PROPOSED BUDGET
Fiscal Year 1995-1996
Dr. Noel C. Krothe
Department of Geological Sciences

Salaries	Effort	
N.C. Krothe	Summer	$13,750
Graduate Students	2 @ 50% (12 Months)	$26,400
Hourly	25 hrs/week @ $8/hr x 52 wks	$10,400
		$50,550
Fringe		
N.C. Krothe	16.41% x $13,750	$2,256
Student Health Ins.	2 @ $430	$860
Social Security (Hourly)	7.36% of $10,400	$765
		$3,881
Travel		
Mileage and Vehicle Rental		$2,500
		$2,500
Equipment		
ISCO Continuous Water Samplers	3 @ $2500/each	$7,500
1 Kech-Redi, Flo 2 Sampling pump		$4,900
8 Geoguard Model #54000 transducers with cable		$12,460
1 water level probe (Solinst)		$ 700
		$25,560
Materials and Supplies		
Laboratory		$800
Field Supplies (sampling bottles,screen, charcoal, dyes,etc.)		$2,000
		$2,800
Other Direct Cost		
Dye Analysis (Spectrofluorophotometer) background & tracer test		$6,750
450 samples @ $15/sample		
Bromide (Dionex Anion Analyzer) background & tracer test		$6,750
450 samples @ $15/sample		
Hazwoper Training and Refresher Course		$1,600
Graduate Fee Remissions		$3,390
2 students, 30 credits @ $113/credit		
Copying, Fax, Communications, etc.		$ 500
Nitrogen istope analysis		$3,000
20 samples @ $150/sample, Univ. of Nebraska		
		$21,990
Total Direct Cost		$107,281
Indirect Cost* 26% of 78,331		$20,366
Total Proposal Cost		$127,647

* Indirect Cost = 26% of (Total Direct Costs minus Permanent Equipment and Fee Remissions).

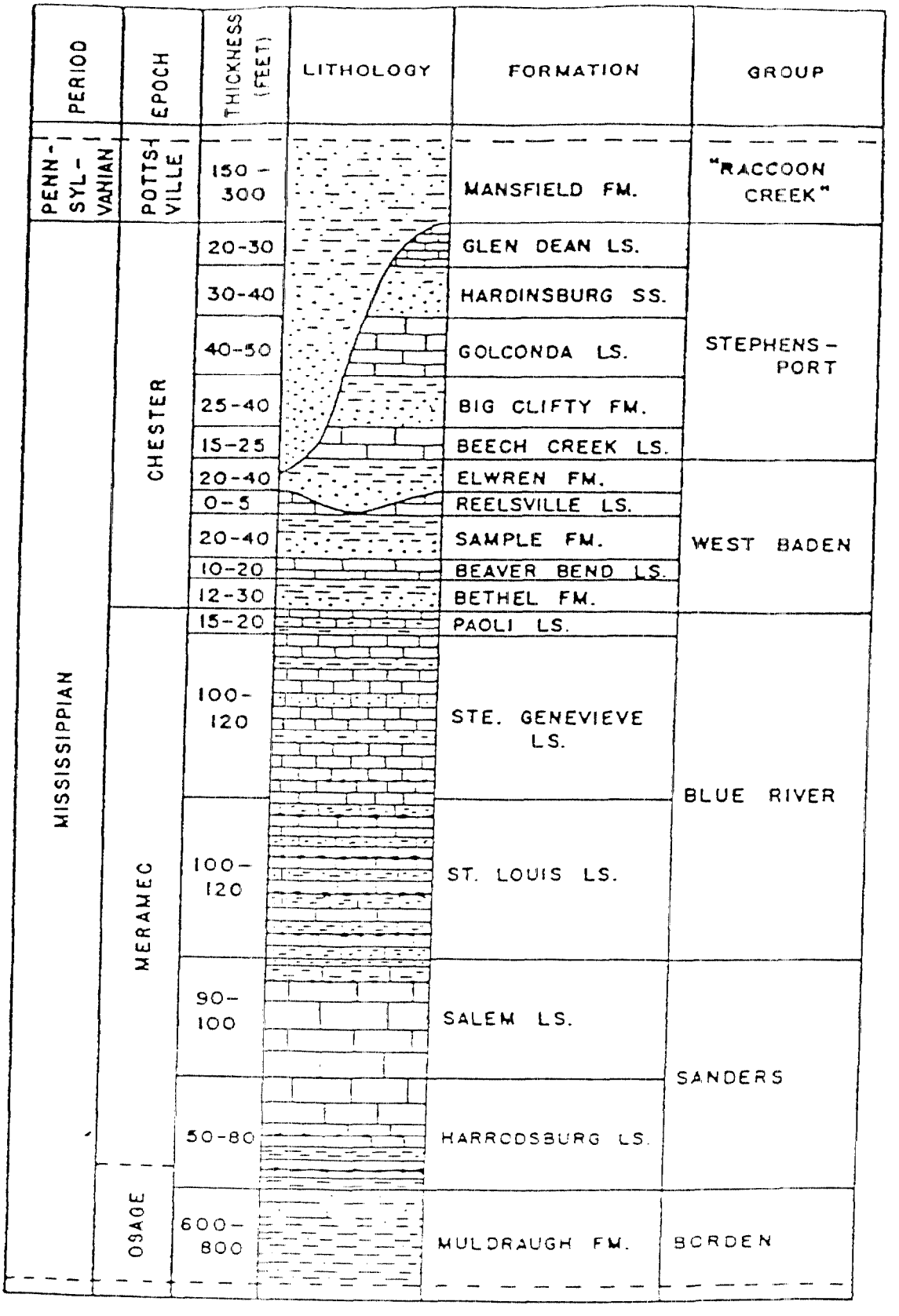


Figure 1. Stratigraphic column for rock units encountered at NWSCC (Murphy and Ciocco, 1990).

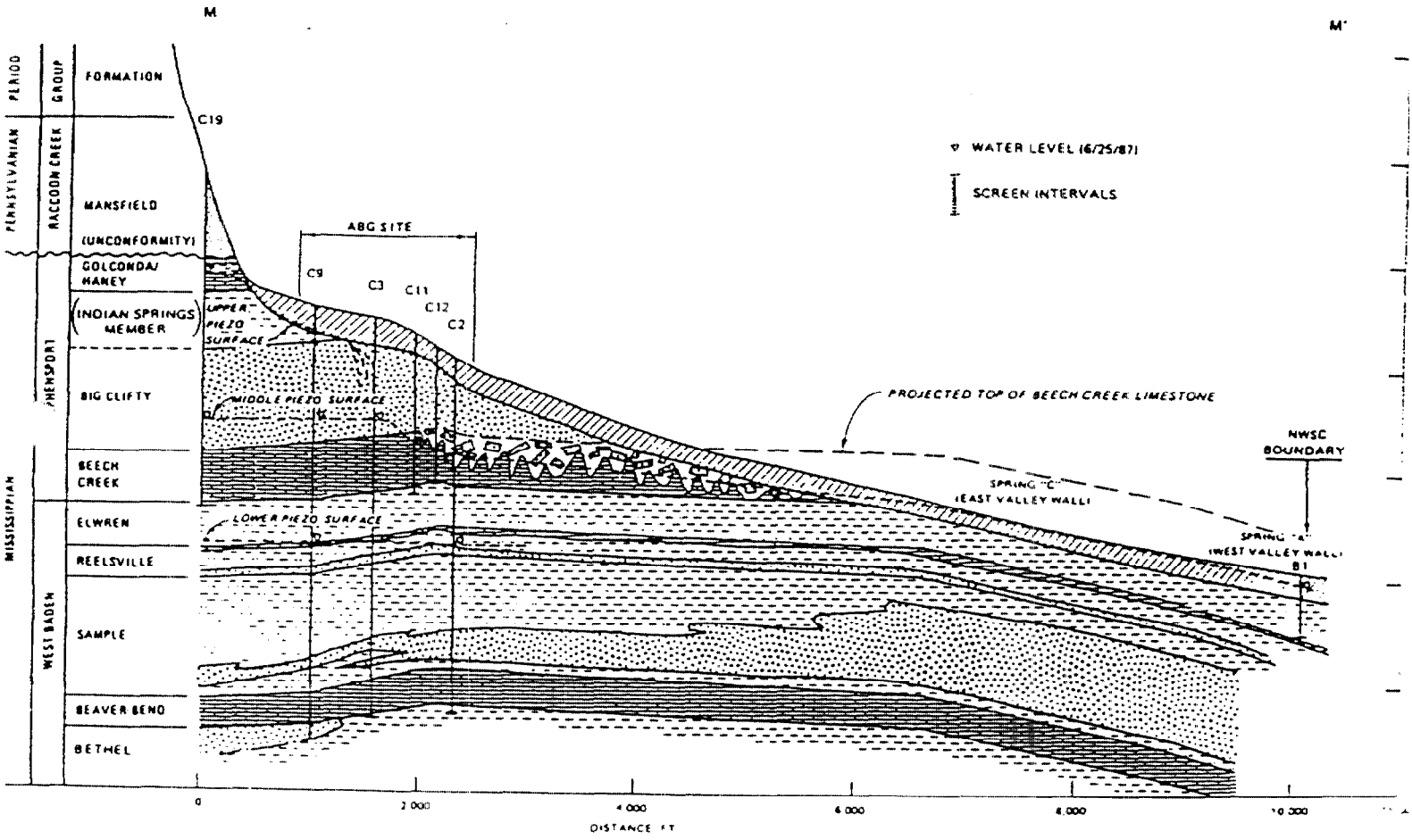


Figure 2. Geologic profile of the valley of Little Sulfur Creek at the ABG to the NWSCC boundary (Murphy and Ciocco, 1990).

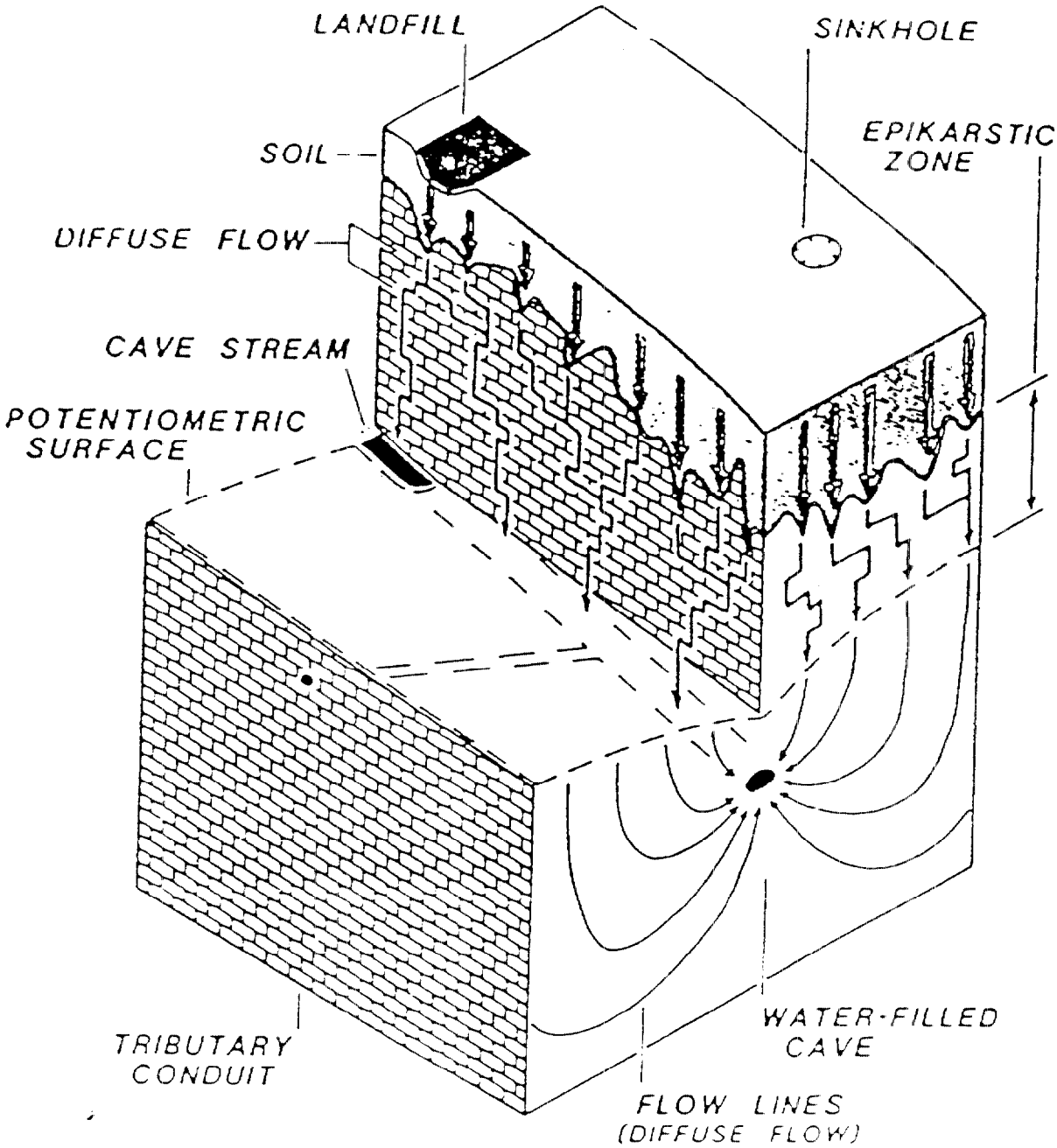


Figure 3. Mixed flow aquifers in karst systems (Quinlan, 1987)

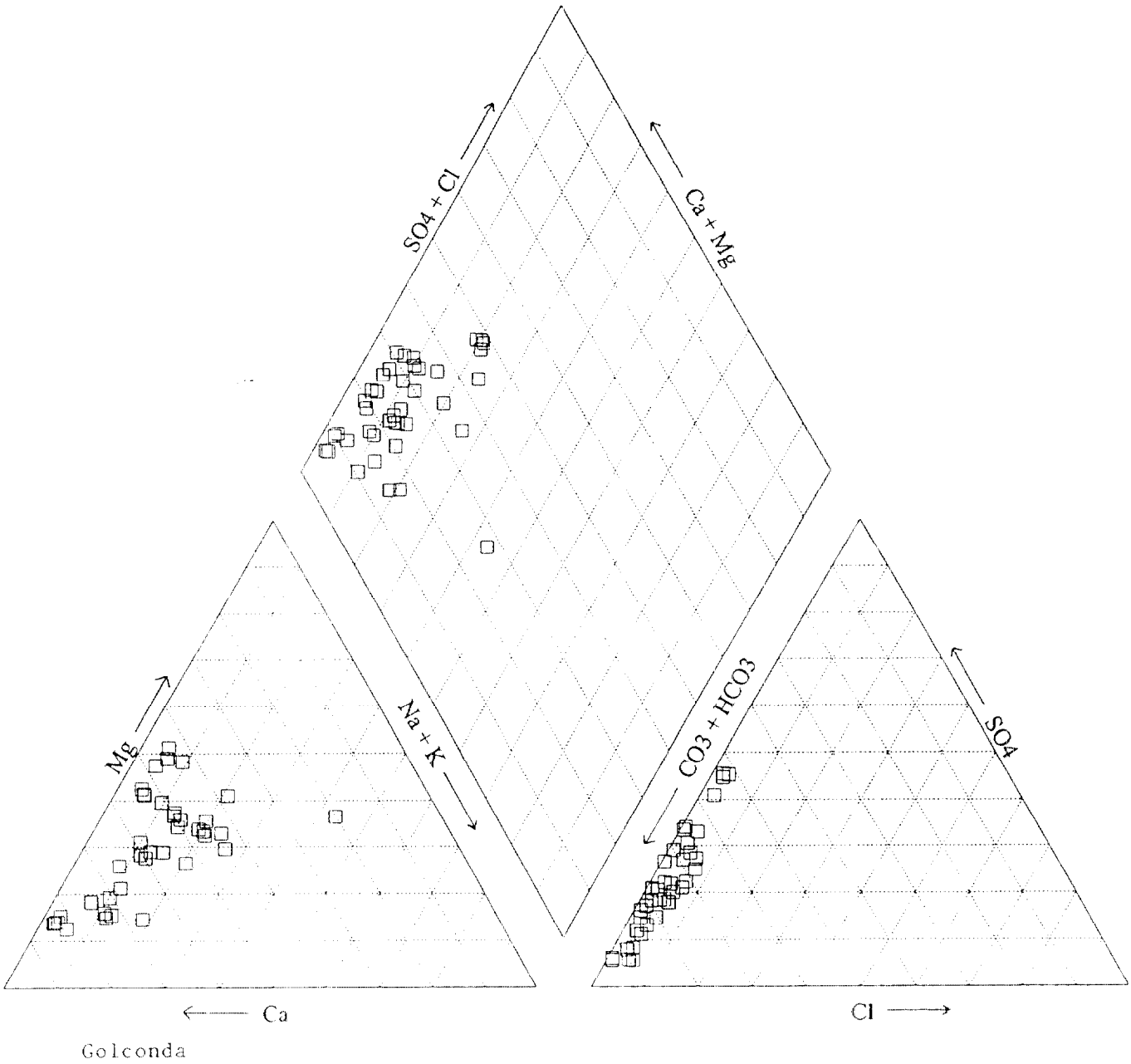
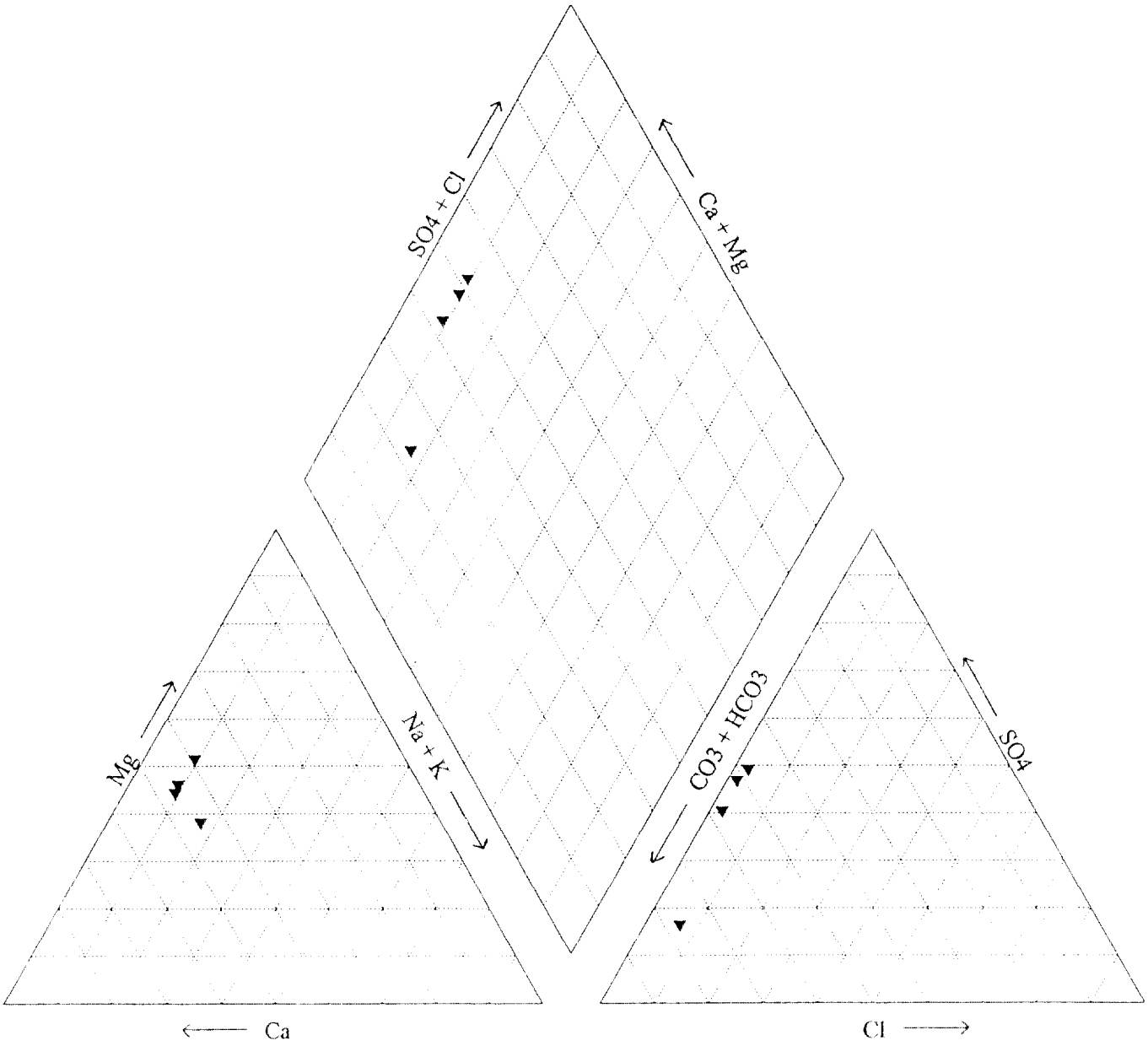
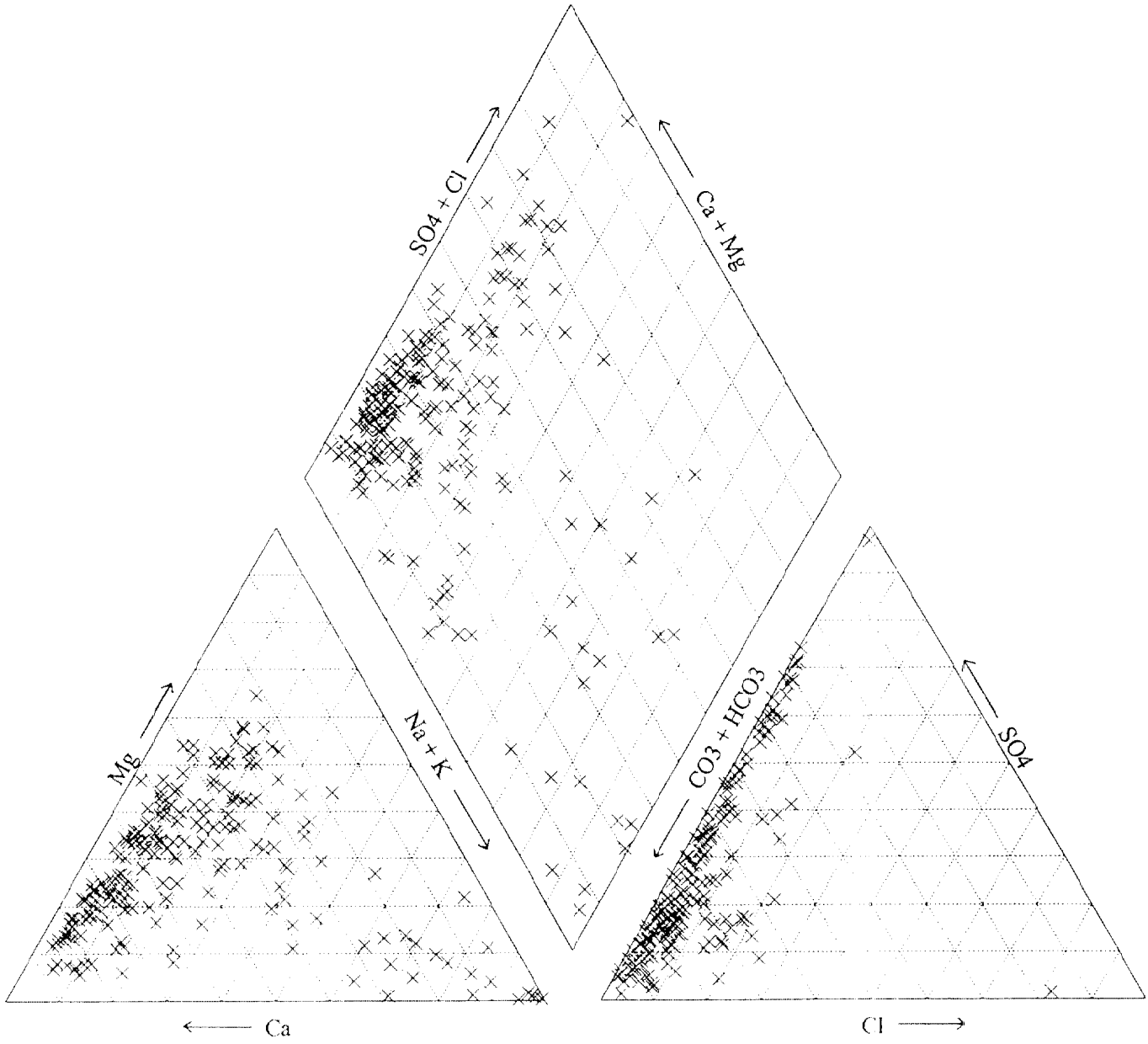


Figure 4. Trilinear diagram of water chemistry for Golconda wells in the ABG area



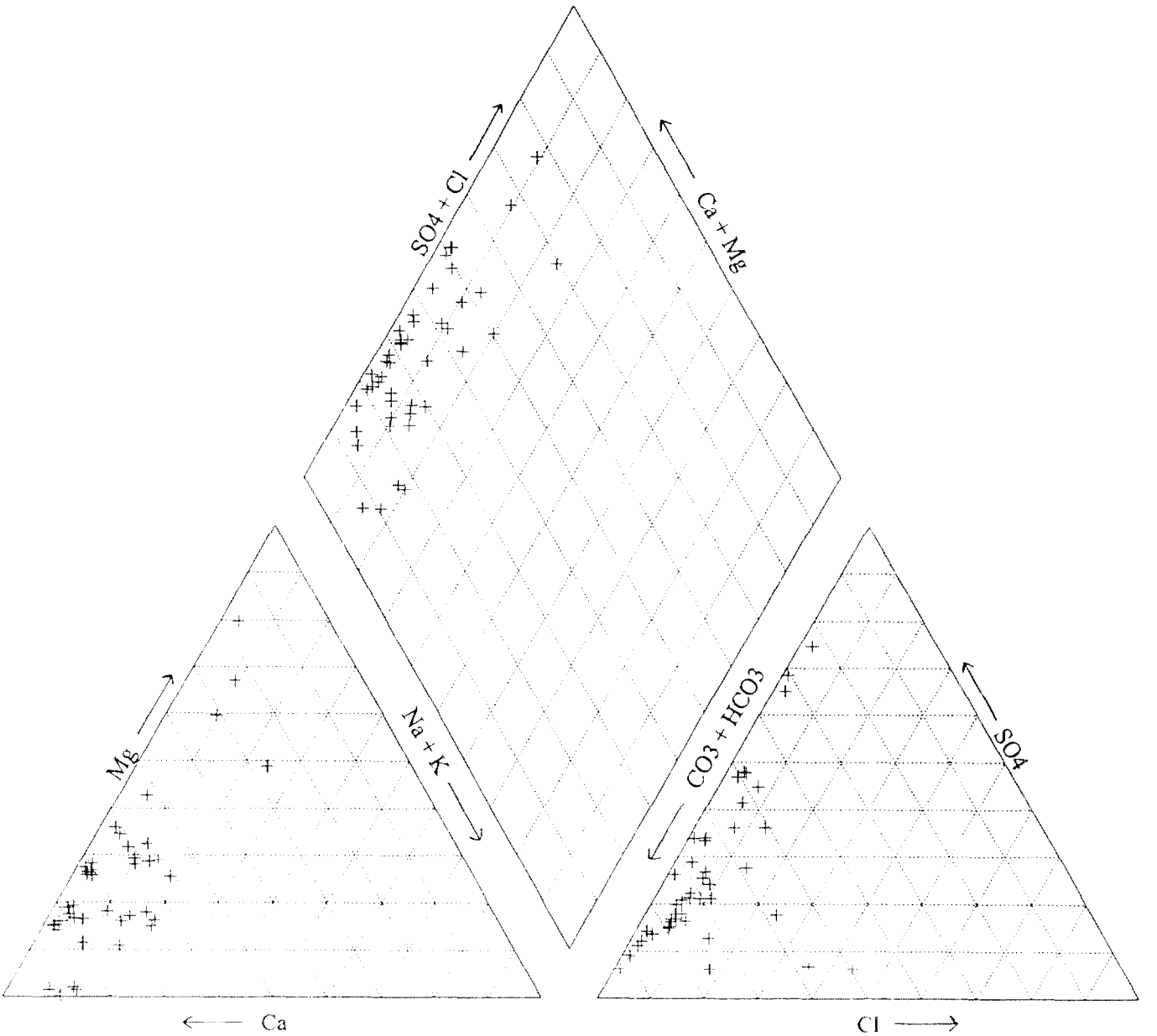
Big Clifty

Figure 5. Trilinear diagram of water chemistry for Big Clifty wells in the ABG area.



Beech Creek

Figure 6. Trilinear diagram of water chemistry for Beech Creek wells in the ABG area.



Beech Creek / Big Clifty

Figure 7. Trilinear diagram of water chemistry for Beech Creek/Big Clifty wells in the ABG area.

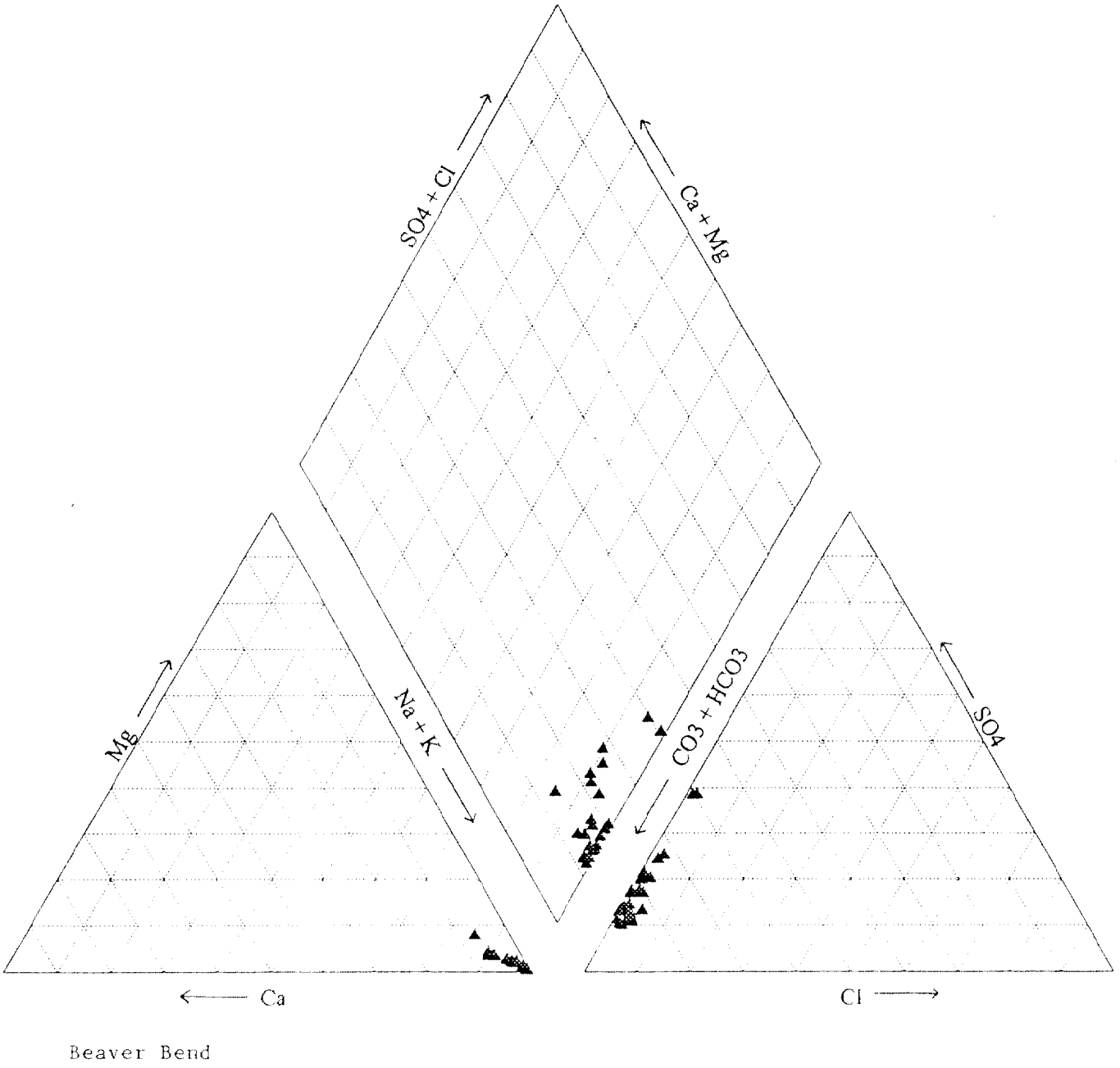


Figure 8. Trilinear diagram of water chemistry for Beaver Bend wells in the ABG area.

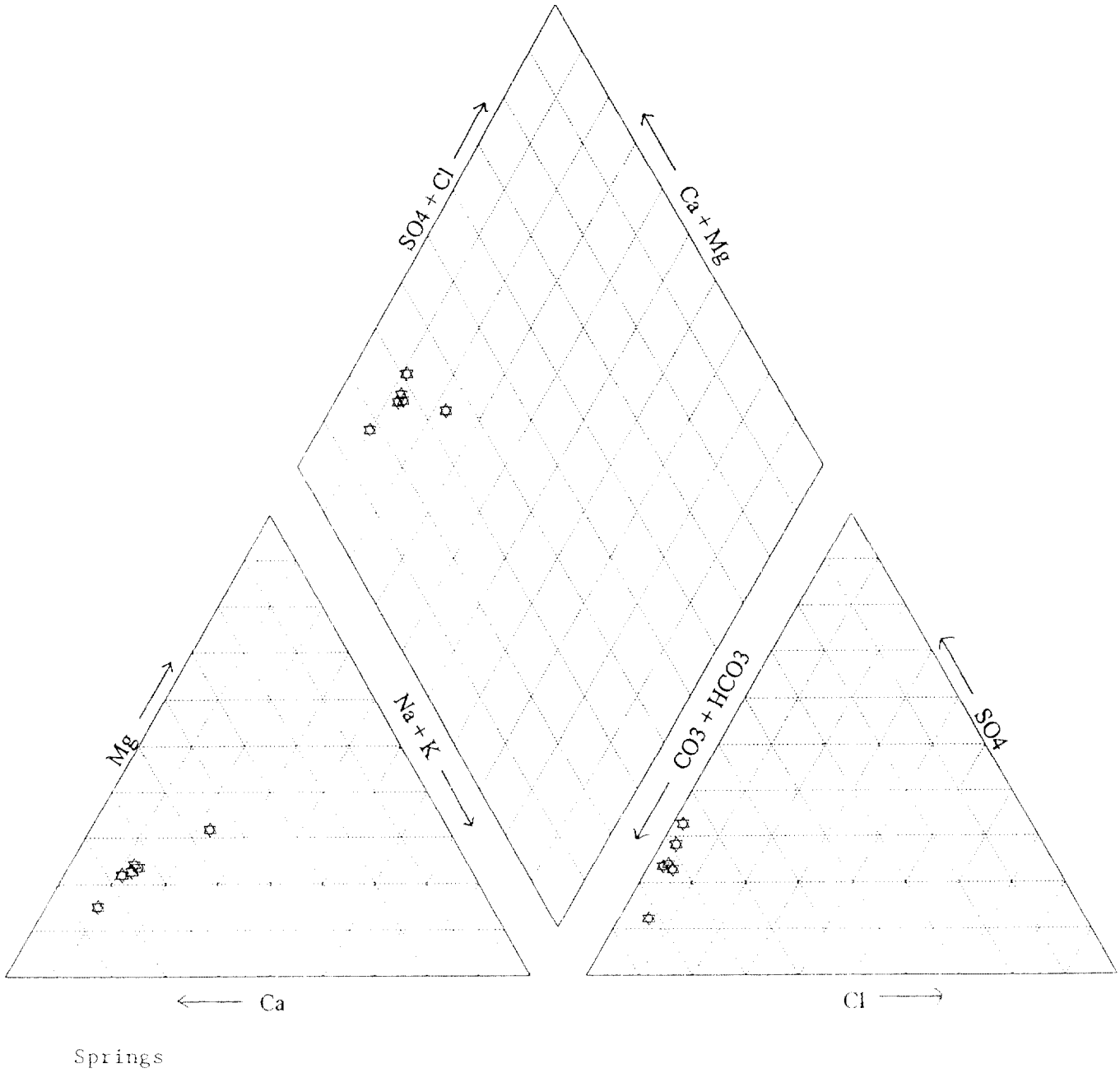


Figure 9. Trilinear diagram of water chemistry for all springs in the ABG area.

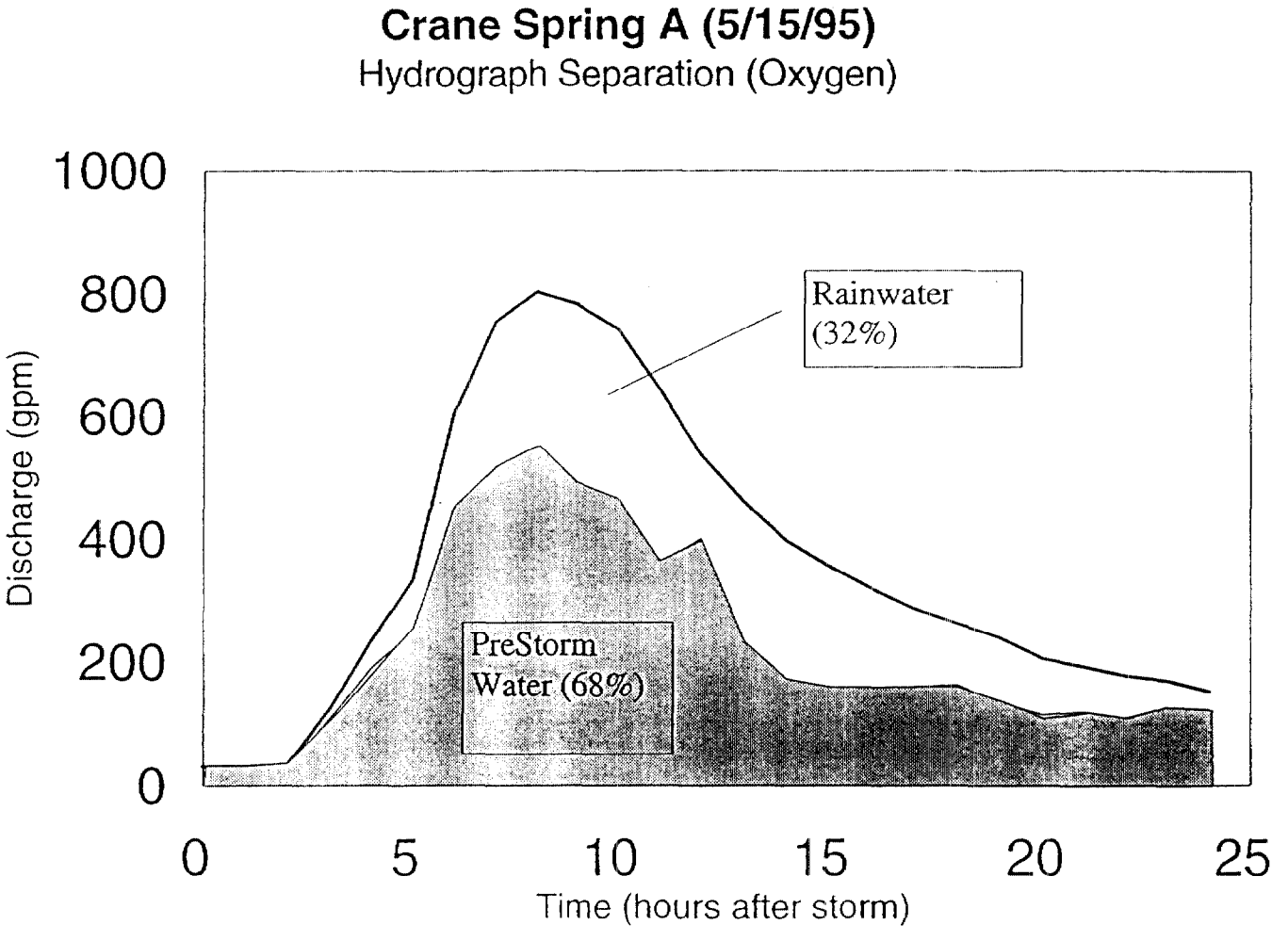


Figure 10. Oxygen isotope separation for a storm hydrograph at Spring A.

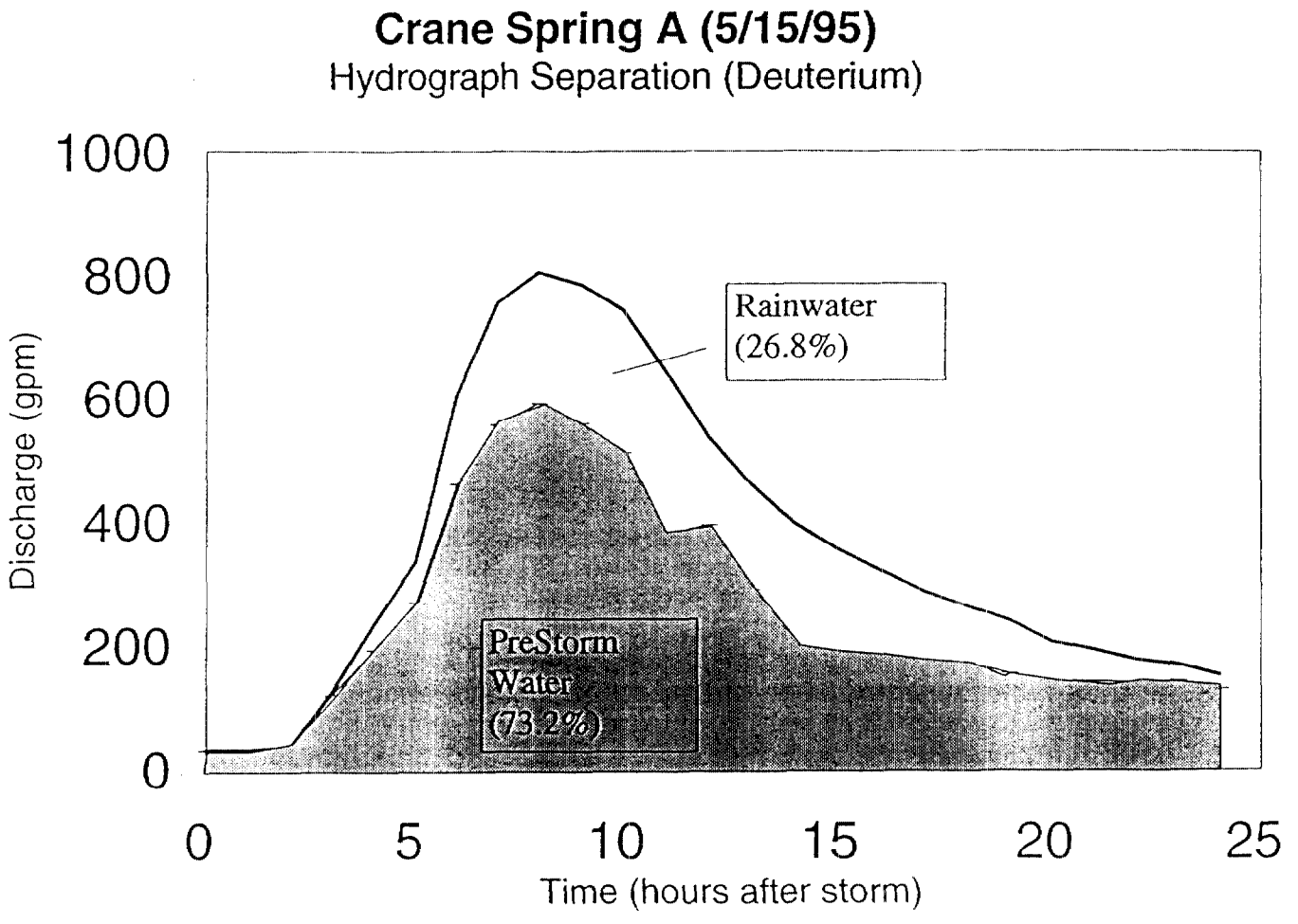


Figure 11. Deuterium isotope separation for a storm hydrograph at Spring A

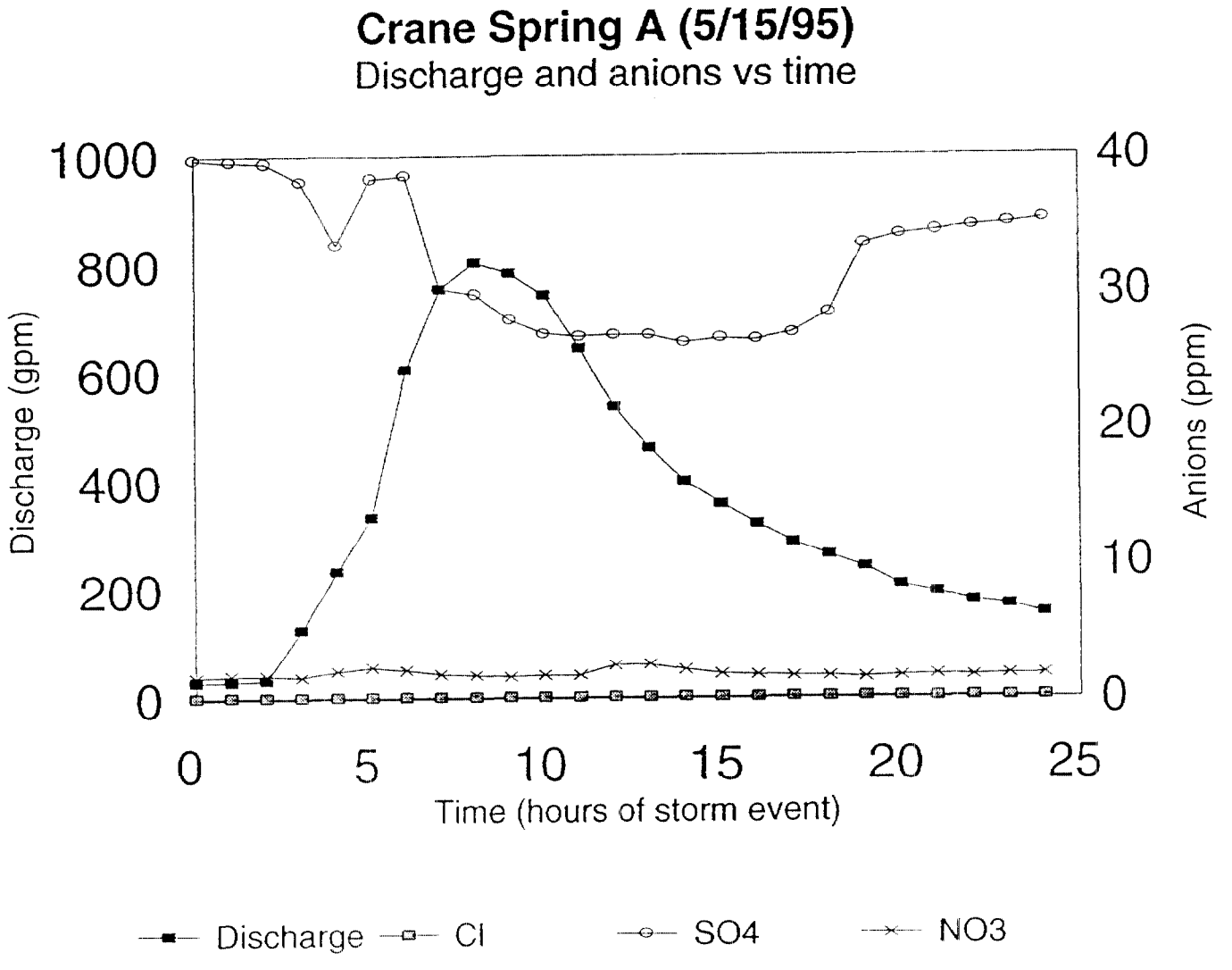


Figure 12. Major anions versus time across a storm hydrograph.

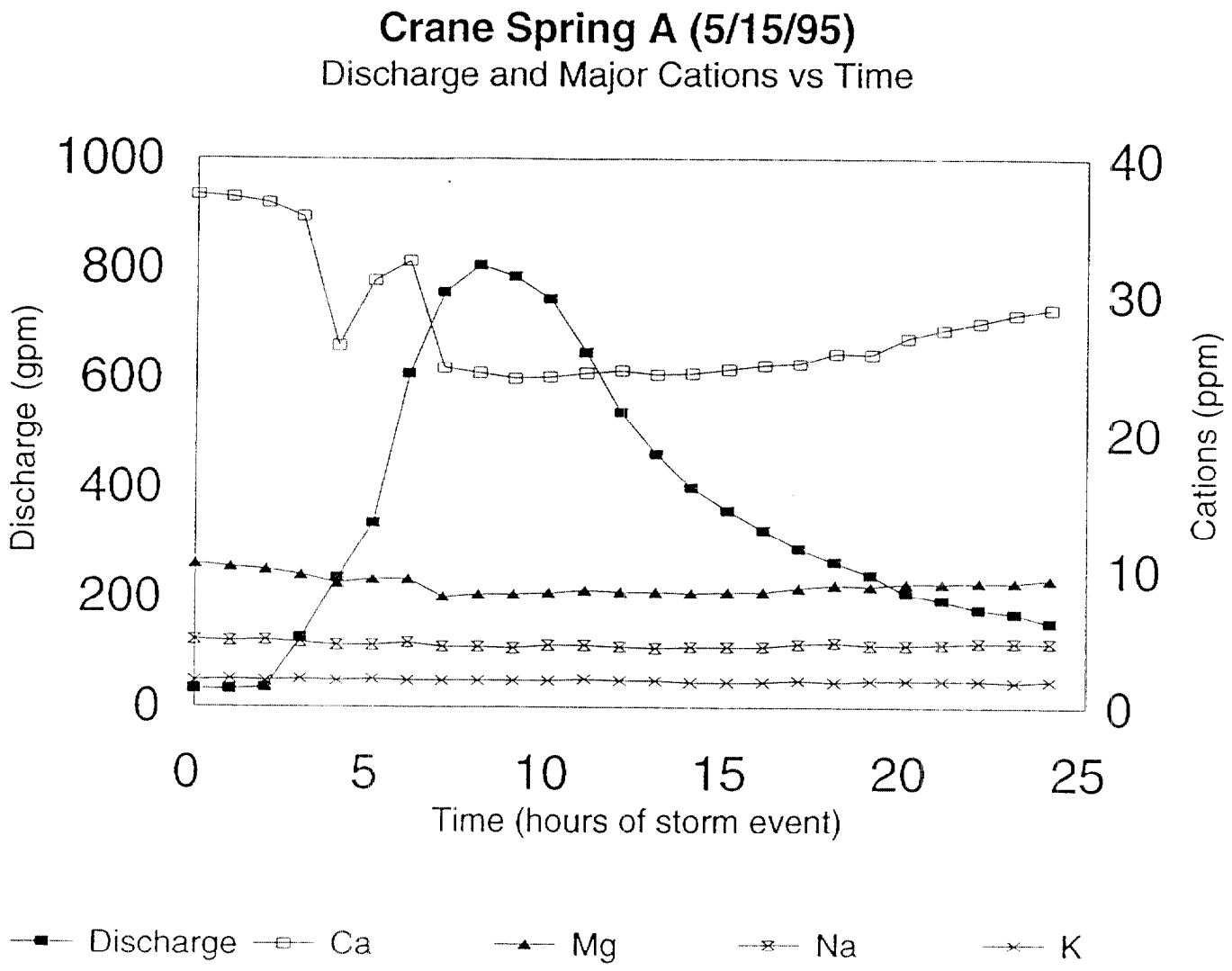


Figure 13. Major cations versus time across a storm hydrograph

Appendix 1

The proposed dye tracing tests will be conducted using the following general protocols. Detailed discussion of such procedures can be found in Quinlan (1987).

I. Dye Tracing Philosophy

The proposed dye tracing test will be a quantitative trace with dye and bromides being injected simultaneously in a well. In order to conduct a quantitative trace the following is necessary:

1) Accurate discharge measurements at the major springs in the ABG watershed;
2) A fluorescing dye that will be visible at emergence (organic dyes will adhere to soil and rock surfaces);
3) A conservative second tracer such as Br^- or F^- injected at the same time as the organic dye.
4) A sampling protocol to insure frequent measurements when the dye pulse discharges at the spring.

Organic dyes such as rhodamine and fluorescein and eosine adhere to soil and rock particles limiting a quantitative trace since the total mass injected will not emerge at the discharge point. If you inject a conservative tracer such as Br^- or F^- in the wells with the dye you can then get an accurate quantitative trace since the halogens will not adhere to soil and rock (100% of the Br^- or F^- should come through the system). The use of the organic dye gives you the approximate time of arrival of the bromide or fluoride so that the sampling interval can be increased. In a quantitative test both grab water samples and passive detectors (charcoal packages) are necessary. The passive detectors will be used on springs located on the periphery of the site and wells that show connection with high conductivity zones. Both grab and passive detectors will be used on springs A, A', B and C. This type of test will provide valuable information for future monitoring or remediation procedures since it will indicate what percentage of the water from the ABG is discharging at springs A, A', B and C and what percentage may be flowing from the ABG in other subterranean routes.

II. Injection and Monitoring Wells

Monitoring wells for the most part are ineffective as injection or dye tracing monitoring points unless they have been drilled on major subsurface fractures (McCann and Krothe, 1991), but as mentioned above will have to serve as injection points since the Karst is covered by the Big Clifty sandstone. The dye tracer test conducted by Murphy and Ciocco (1990) showed that well WES3-C2-P2 is a good well for injection. Dye injected into wells that are not drilled into subsurface fractures will move slowly, depending upon the hydraulic conductivity of the rock, in the vicinity of the well. The flow is generally toward larger conduits that act as groundwater sinks (Figure 3). The dye may therefore take weeks, months, or even years to resurge at a spring. Likewise, wells used as monitoring stations not located on a fracture will receive little dye since the flow is largely toward the conduit. Dye will be detected in the well only if the major conduits are flooded to the point that the hydraulic gradient is changed and water is forced into the rock matrix. Therefore, wells between the injection point and possible discharge points are of little value as dye tracing monitoring stations, unless accurate drilling logs and water level data can establish that the well is located on a fracture. Large scale water level fluctuations and murky water in sample bottles during rain events can also be used as evidence of possible fracture connection. Wells at the ABG that test positive for a given dye should also be used as dye tracing monitoring sites in future studies. Water from the springs located along Little Sulphur Creek, Sulphur Creek and wells in Johnson Hollow will be analyzed for ion chemistry and fluorescence.

III. Springs and Wells to be Monitored

Springs A, A', B and C are the primary discharge points to be considered in these tests since past dye tracing show hydrologic connection with the ABG. They are also instrumented for continuous discharge which is necessary for the calculation of the total tracer transported through that spring. Well logs will be studied to determine if other wells can be used as sampling points. Selection of off-site springs will be determined after field reconnaissance.

IV. Sampling Frequency

The major on-site springs will be sampled every half hour after time zero (injection time) until a visible show of dye appears at springs A and A'. At that point the interval will be shortened to 15 minutes until the

breakthrough curve flattens on the receding limb. Then the sampling interval will return to ½ hour until the storm discharge recedes and dye concentration returns to background levels. Springs B and C will be sampled at the same frequency, even though a dye visual may not occur. All springs , including those to the north and off-site, will have charcoal detectors to concentrate dye. The frequency of changing these detectors will be decided at a later date. A more detailed tracer test procedure will be presented and discussed with Crane personnel prior to the actual test.

Appendix 2

Elevated nitrate has been detected in the groundwater at the ABG, several water samples from springs and wells containing measurable nitrate will be analyzed for nitrogen isotopes. If the $\delta^{15}N$ value is significantly different from the other three major sources of nitrate, which are organic waste (human and animal), inorganic fertilizers, and natural soil nitrogen (Wells and Krothe, 1989), then the nitrogen isotope value can be used to identify contamination plumes moving from disposal areas on the NWSCC. In addition, wells and springs will be tested for by-products of munitions explosions and burning.

The chemistry for all wells with major ions has been plotted on trilinear diagrams. Figures 4-9 show a plot of the well water chemistry for 1991. Additional water samples will be taken and analyzed for major ions, selected trace elements and organics of concern at the ABG. By-products of munitions burning, such as barium and phosphorus, in addition, TNT, RDX and HMX will also be considered. Examination of the trilinear diagrams show definite groundwater chemistry patterns (Figures 4-9). The deeper Beaver Bend waters are NA-HCO_3 in nature and may be the result of long term isolation and ion exchange/membrane processes. The shallower and more open Big Clifty and Beech Creek wells show wide variations in the ions CA^{2+}, Mg^{2+}, Na^{+}, HCO_3^{-} and SO_4^{2-}. These fluctuations may be due to natural seasonal changes in chemistry or they are impacted by the ABG. The ions of interest are Mg^{2+}, SO_4^{2-}, NO_3^{-} and Ba^{+} since they are by-products of munitions burning. We propose to study these fluctuations and sources of ions across a storm hydrograph as part of this research.

Based upon the above chemical analysis, a thermodynamically based dissolution-precipitation reaction path model will be developed to account for the variations in naturally occurring spring water and groundwater chemistries. The USGS program PHRQPITZ (Plummer et al., 1988) will be used to calculate results of possible water-rock interactions. This procedure has been successfully used to identify a unique set of mineral phases (i.e. rock types) that are responsible for the chemical evolution of groundwater/spring waters that originate approximately 5 miles south of the NWSCC (Baedke, 1990).

I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

SIGNATURE

G. K. HILL
Assistant Public Works Officer

TITLE

28 SEP 1995

DATE

Enclosure (3)