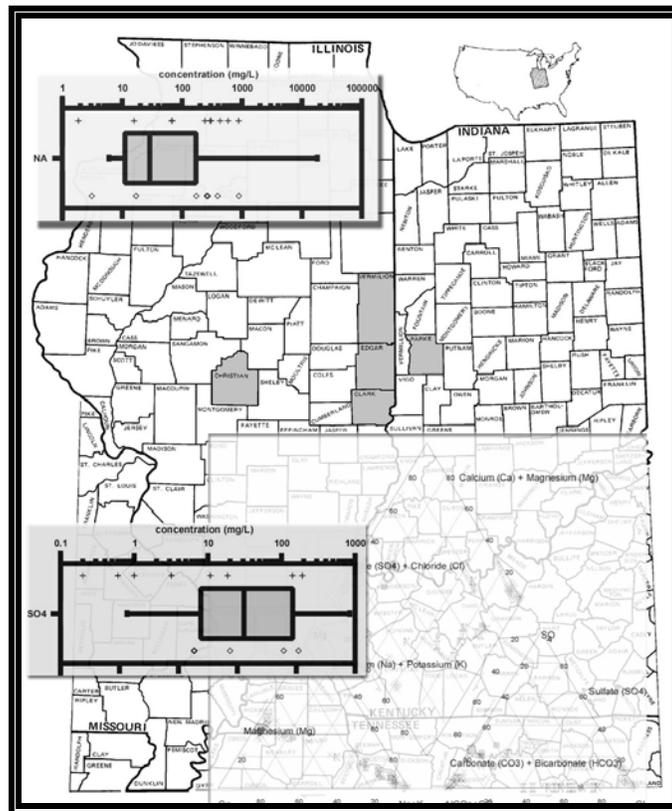


# *The Geochemistry of Groundwater from the Shallow Bedrock in Central Vermilion County, Illinois*

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## **ABSTRACT**

The background groundwater conditions in the shallow bedrock of central Vermilion County, Illinois, were assessed by reviewing available geochemical data and by analyzing a limited number of water and rock samples. Water samples were collected from monitoring wells and water-supply wells and were analyzed for anions, cations, and carbon and hydrogen isotopes. Rock samples were obtained from cores collected by KELRON and were analyzed using a portable infrared mineral analyzer and x-ray diffraction.

Great variability was observed in the geochemical data for the Pennsylvanian bedrock, Pennsylvanian groundwater, and other data collected for this project. Some of this variability is due to the different lithologies which included sandstone, shale, coal, limestone, and sand and gravel. Some of this variability is also due to the depth of the sample. For example, groundwater samples from KELRON 26 and 28 are significantly different from other samples because they were from shallow wells and are completely connected to the local groundwater system, whereas water samples from deeper wells were largely isolated from the local groundwater flow system. Overall, the geochemical data collected for this project are similar to the available data from Vermilion and surrounding counties.

## **1. INTRODUCTION**

Using available data and limited sampling, we sought to define the background groundwater conditions in the shallow bedrock of central Vermilion County. Most of the wells sampled for this study were concentrated around the Middle Fork of the Vermilion River, as shown in figures 1 and 2. We had access to and sampled monitoring wells on land owned by Dynegy, Inc. as well as private and public water supply wells (figure 2). Because of the limited number of Vermilion County wells completed in the bedrock, we sought and used available data from surrounding counties in Illinois and Indiana.

## **2. GEOLOGY**

The surficial bedrock geology in Vermilion County is variable. The youngest formation, the Pennsylvanian-aged Bond Formation, is found beneath southwestern Vermilion County (figure 3). Pennsylvanian-aged bedrock underlies most of Vermilion County, except in the northern portion of the county where Mississippian and Devonian rocks are present. Older units can be found at the bedrock surface to the west and north, which reflects the erosional surface of the Mahomet Bedrock Valley and the structure of the Illinois Basin. In Vermilion County, the thickness of the Pennsylvanian bedrock varies from 0 feet in the

Figure 1. Map showing sampling locations in Illinois and Indiana



Figure 2. Map showing sampling locations in Vermilion County, Illinois

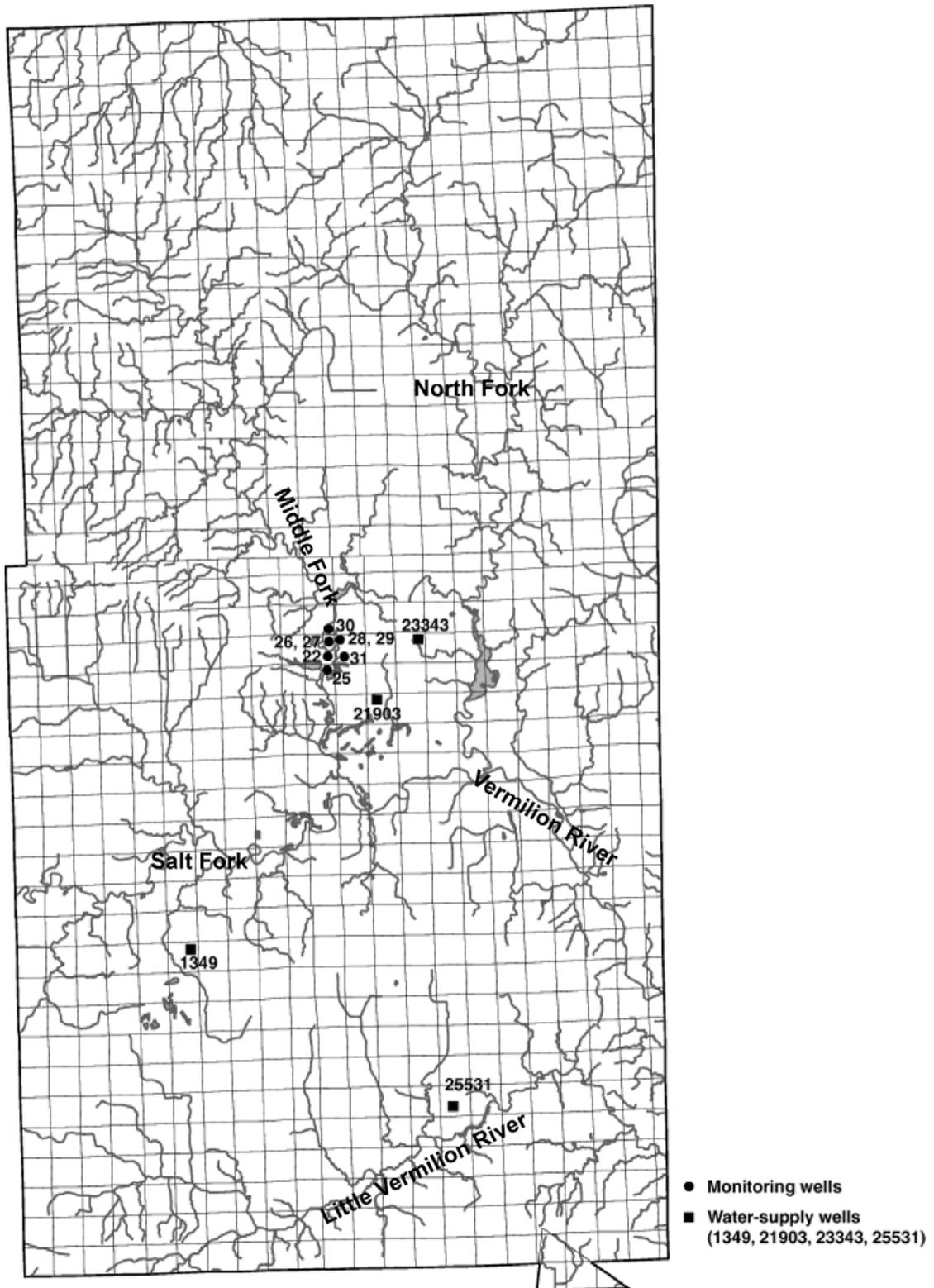
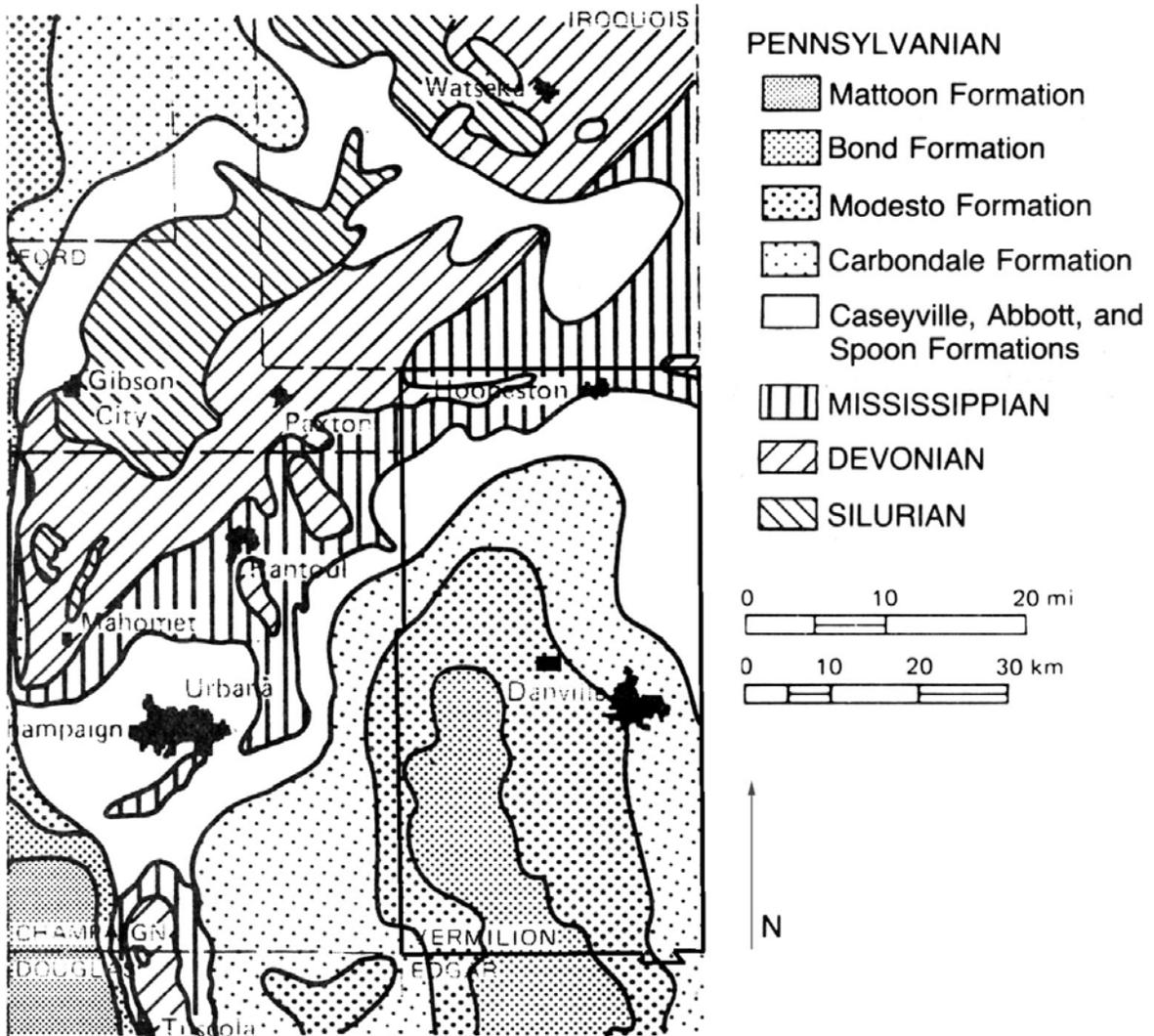


Figure 3. Surficial Bedrock Geology in Vermilion County (adapted from Kempton et al., 1982)



north to greater than 400 feet in the southeast (Willman et al., 1975).

The location of the Mahomet Bedrock Valley can be seen in the drift thickness map (figure 4). The thalweg of the valley, defined by the 400-foot thickness contour, runs east-west through the northern tier of townships in Vermilion County. In addition, a northwest-southeast trending tributary underlies parts of T23N R13W, T22N R13W, T22N R12W, and T21N R12W. The drift thickness also exceeds 200 feet in the southwest portion of the county. However, in the central portion of the county, the drift is generally less than 100 feet thick and bedrock outcrops are common in the river valleys (Piskin and Bergstrom, 1975).

KELRON collected core at 3 locations in T20N R12W (KELRON 25, KELRON 30, and KELRON 31). Descriptions of these cores appear in Appendices A and B. At this location, the uppermost bedrock was mapped as the Pennsylvanian-aged, Modesto Formation by Willman et al. (1975). The core from KELRON 30 penetrated 3 feet into the Danville (No. 7) Coal Member, which was considered the uppermost member of the Carbondale Formation. The stratigraphic nomenclature of the Pennsylvanian system was recently revised by the Tri-State Committee (2001). Using this new nomenclature, the bedrock from the three cores collected by KELRON (KELRON 25, KELRON 30, and KELRON 31) was assigned to the Shelburn Formation (Appendix A). Natural gamma logs for these wells, collected by the ISGS, appear in Appendix B.

In west-central Indiana, the surficial bedrock is Pennsylvanian-age along the IL-IN state line and Mississippian-age to the east (figure 5).

### **3. GEOCHEMISTRY**

We reviewed the available geochemical data for both groundwater and bedrock from Vermilion County and surrounding counties in Illinois and Indiana. In addition, during June 2002, we collected groundwater samples from several monitoring wells and water wells. We also analyzed samples from core collected from three KELRON monitoring wells. To determine the geochemistry of the groundwater in chemical equilibrium with the host rock, equilibrium geochemical modeling was conducted.

#### **3.1 Review of Available Data**

To obtain data on the geochemistry of groundwater from Pennsylvanian bedrock and the Pennsylvanian bedrock itself, we searched the scientific literature and databases at the Illinois State Geological Survey, Illinois State Water Survey, Illinois Environmental Protection Agency, and the Indiana Geological Survey. These data are summarized in tables 1 through 5. The locations for available groundwater samples are summarized by county in table 1. The geochemical data for these 31 samples are presented in table 2. The lithologies of the Pennsylvanian bedrock samples are summarized in table 3. We obtained data for 56 bedrock samples— 35 coal and 21 non-coal samples. The geochemistry of the non-coal samples (table 4) and the coal samples (table 5) has been summarized. Table 5 includes 1 sample from the Springfield (No.

Figure 4. Drift Thickness in Vermilion County (adapted from Piskin and Bergstrom, 1975)

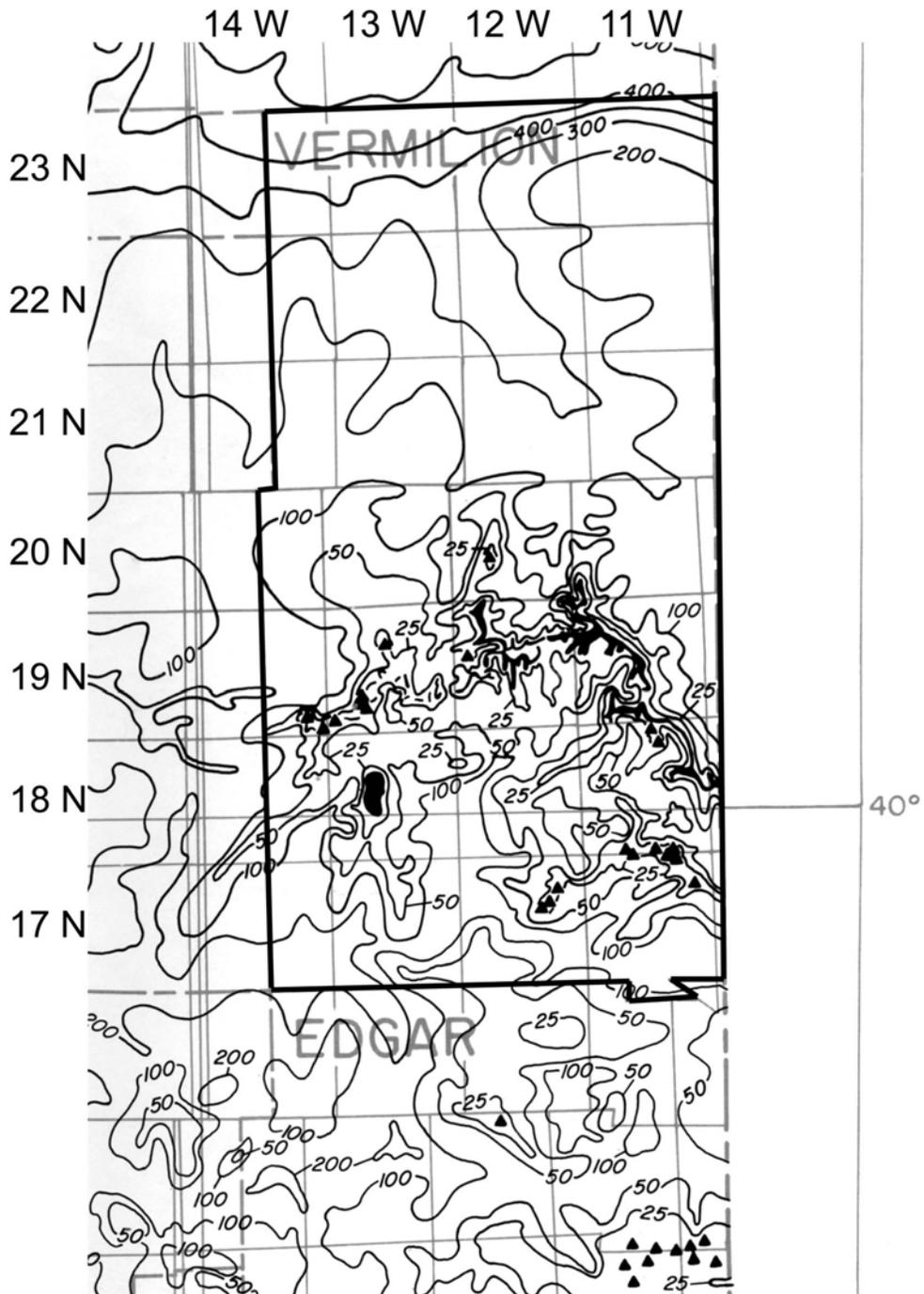


Figure 5. Surficial Bedrock Geology of west-central Indiana including Parke County (from Indiana Geological Survey, 1970) The dashed line shows the limit of the Wisconsin Episode glacial sediments.

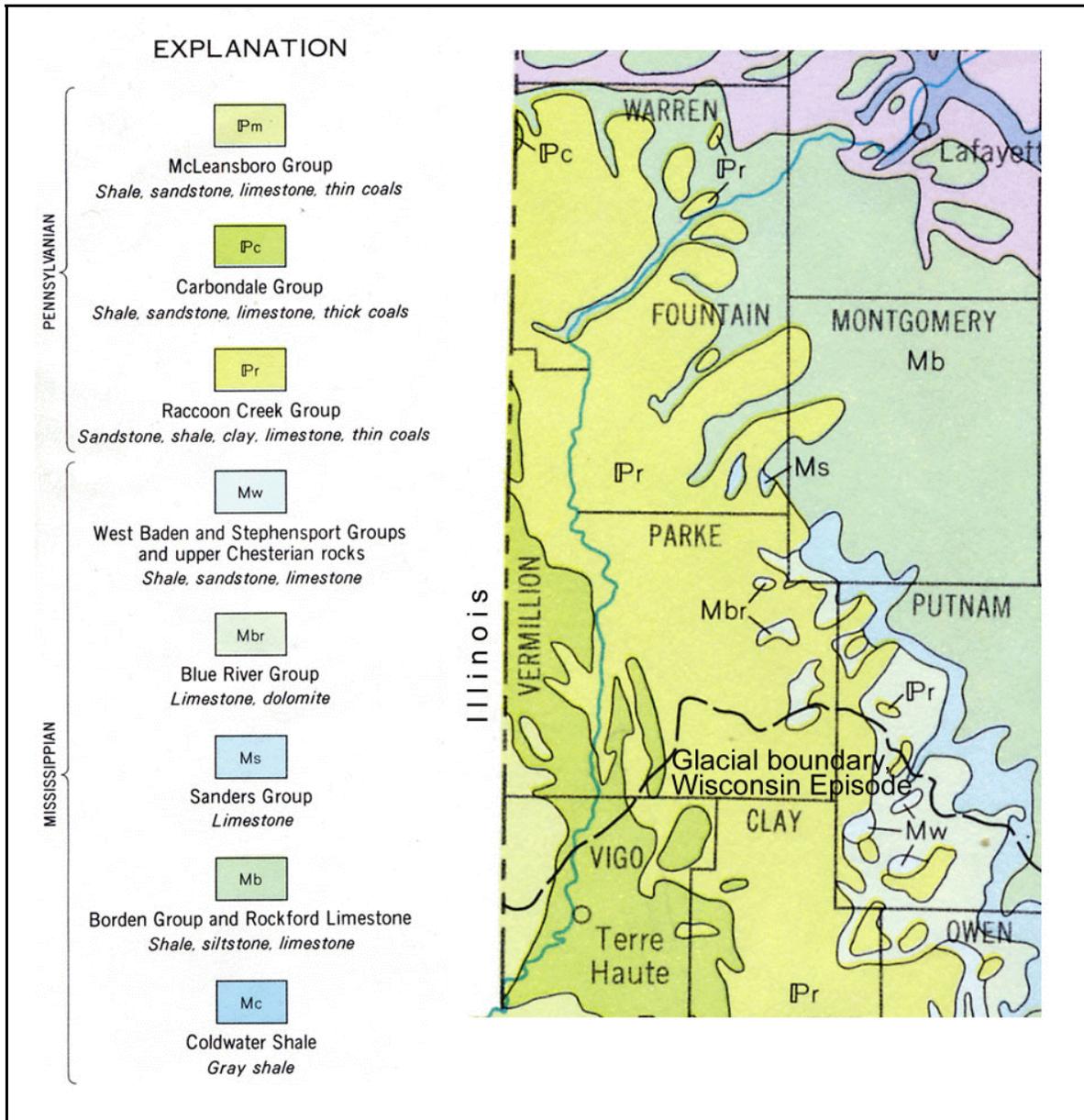


Table 1: Summary of available well data

County	# of Wells	Sampling Dates	Well Depths (ft)
Vermilion	6	10/9/74 - 11/9/93	72 - 220
Clark	1	6/3/99	155
Edgar	1	8/7/48	422
Christian	4	1/22/97 - 2/20/97	276 - 344
Parke (IN)	19	7/10/95 - 7/20/95	100 - 307
TOTAL	31	10/9/74 - 2/20/97	72 - 422

Table 2: Geochemical summary for available water samples  
(Sources: Chugh et al., 1997; ISGS Geochemical Database, Meents et al., 1952)

	Units	# of Records	Minimum*	Maximum	Mean	Median
TDS	ppm	28	280	52100	3540	426
Alkalinity	mg/L as CaCO <sub>3</sub>	30	56	485	321	335
pH	--	27	6.5	10.0	7.5	7.3
Temperature	°C	23	11.0	22.8	15.5	14.8
Bicarbonate	mg/L	31	63	591	389	407
Chloride	mg/L	31	2.1	30269	1689	13
Fluoride	mg/L	26	0.09	1.06	0.49	0.47
Nitrate	mg/L	31	<0.01	29.0	***	2.95
Sulfate	mg/L	31	<1	847	***	31
Aluminum	mg/L	27	<0.02	8.47	***	0.20
Arsenic	mg/L	30	<0.001	0.023	***	0.0050
Barium	mg/L	30	0.02	2.44	***	0.28
Boron	mg/L	30	ND**	2.08	***	0.0047
Cadmium	mg/L	30	<0.0002	0.0044	***	0.00020
Calcium	mg/L	31	<1	951	***	83
Chromium	mg/L	30	<0.001	0.005	***	0.0015
Iron	mg/L	31	<0.006	26.8	***	0.69
Lead	mg/L	29	<0.001	0.018	***	0.003
Magnesium	mg/L	31	<0.5	454	***	31.1
Manganese	mg/L	31	0.015	1.47	***	0.10
Mercury	mg/L	30	<0.00005	1.0	***	0.000025
Potassium	mg/L	30	0.67	63	7.4	2.1
Selenium	mg/L	30	<0.001	0.002	***	0.001
Silicon	mg/L	31	0.69	10.0	6.51	7.12
Sodium	mg/L	31	6	18078	1083	28.7
Zinc	mg/L	30	<0.01	1.43	***	0.21

\* Some parameters had multiple detection levels. The lowest detection level is reported.

\*\* Not detected, detection limit was not reported.

\*\*\* Sample data contain censored values, did not compute mean.

Table 3: Lithology of the available Pennsylvanian bedrock samples

Lithology	Number of Samples
Sandstone	2
Limestone	2
Shale	4
Carbonaceous Shale	13
Coal	35
TOTAL	56

Table 4: Geochemical summary for available non-coal solid samples  
(Sources: Bradbury et al., 1962; Chugh et al., 1997; Schultz and Coveney, 1992)

Analyte	Units	# of Records	Minimum	Maximum	Mean	Median
Al <sub>2</sub> O <sub>3</sub>	wt. %	21	0.42	20.8	11.7	11.1
CaO	wt. %	21	0.15	54.1	7.57	1.27
Fe <sub>2</sub> O <sub>3</sub>	wt. %	21	0.63	21.4	8.65	7.02
K <sub>2</sub> O	wt. %	21	0.09	4.20	2.51	2.61
MgO	wt. %	21	0.36	2.17	1.44	1.63
MnO	wt. %	18	0.017	1.83	0.20	0.045
Na <sub>2</sub> O	wt. %	21	0.030	1.68	0.59	0.58
P <sub>2</sub> O <sub>5</sub>	wt. %	17	0.030	18.4	2.31	0.53
SiO <sub>2</sub>	wt. %	21	2.09	85.7	37.0	33.8
TiO <sub>2</sub>	wt. %	21	<0.1	0.92	***	0.51
As	mg/kg	18	19.8	119	57.7	53.8
B	mg/kg	18	31	385	123	112
Ba	mg/kg	18	122	543	***	333
Be	mg/kg	16	<1	4.8	***	2.0
Ce	mg/kg	18	52	233	134	125
Co	mg/kg	18	15.9	68.5	28.3	24.6
Cr	mg/kg	18	68.5	643	289	281
Cs	mg/kg	18	<2	13.4	***	7.0
Cu	mg/kg	16	9.0	192.3	94.3	84.3

Analyte	Units	# of Records	Minimum	Maximum	Mean	Median
Ga	mg/kg	18	6.5	29.3	18.7	17.9
Hg	mg/kg	6	<0.5	5.4	***	2.8
La	mg/kg	18	16.4	99.2	50.8	44
Li	mg/kg	16	11	130.	51.2	37.0
Ni	mg/kg	18	50.	530.	288	280
Pb	mg/kg	16	32	812	167	79
Rb	mg/kg	18	<3.	201	***	127
Sb	mg/kg	18	1.9	56.0	27.2	29.7
Sc	mg/kg	18	9.3	23.6	15.5	14.9
Se	mg/kg	18	4.0	260	104	97
Sr	mg/kg	18	<80	699	210	147
V	mg/kg	18	80.	5600	1770	790
Zn	mg/kg	18	30.3	3350	1000	522
Zr	mg/kg	16	20.8	103	***	49.3
Cl	mg/kg	7	240	698	532	563
Total Carbon	wt. %	17	0.91	>33	***	6.0
Inorganic Carbon	wt. %	17	0.02	11.7	1.7	0.49
Organic Carbon	wt. %	16	0.48	>33	***	3.7

\*\*\* Sample data contain censored values, did not compute mean.

Table 5: Geochemical summary for available coal samples  
(Sources: Bradbury et al., 1962; Chugh et al., 1997; Schultz and Coveney, 1992; Yates, 1984)

	Sample Data						Illinois Basin Coals*		
	Units	# of Records	Min.	Max.	Mean	Median	Min.	Max.	Mean
Al	mg/kg	34	2300	16800	10400	10400	4300	30000	12000
As	mg/kg	35	0.4	52	***	5.1	1	120	14
B	mg/kg	32	37	149	97.3	99.0	12	230	110
Ba	mg/kg	33	8.9	231	64.6	38.8	5	750	100
Be	mg/kg	35	<0.12	2.5	***	1.5	0.5	4	1.7
Ca	mg/kg	34	1500	21300	8740	8100	100	27000	6700
Ce	mg/kg	33	2.0	30	10.0	8.0	4.4	46	14
Co	mg/kg	35	0.9	23.9	5.1	4.0	2	34	7.3
Cr	mg/kg	35	4.0	32	14.7	13.0	4	60	18
Cs	mg/kg	33	<0.3	3.2	***	0.9	0.5	3.6	1.4
Cu	mg/kg	35	2.0	39	10.6	9.0	5	44	14
Fe	mg/kg	35	4300	57900	19500	18600	4500	41000	20000
Ga	mg/kg	35	1.7	5.55	3.4	3.3	0.8	10	3.2
Hg	mg/kg	34	0.07	0.52	0.14	0.11	0.03	1.6	0.2
K	mg/kg	35	300	3800	1610	1500	400	5600	1700
La	mg/kg	33	1.2	12.7	***	4.2	2.7	20	6.8
Li	mg/kg	30	2.0	39.7	13.7	12.5	Not determined		
Mg	mg/kg	34	<100	2200	***	600	100	1700	500
Na	mg/kg	35	400	2300	989	1000	40	2000	500
Ni	mg/kg	35	2.0	93	15.7	9.0	7.6	68	21
Pb	mg/kg	35	2.0	191	***	8.0	0.8	220	32
Rb	mg/kg	33	1.6	44	13.1	11.5	2	46	19
Sb	mg/kg	35	0.06	3.3	1.0	0.8	0.1	8.9	1.3
Sc	mg/kg	33	0.8	5.2	2.7	2.6	1.2	7.7	2.7
Se	mg/kg	35	0.7	12.3	2.2	1.8	0.4	7.7	2.2
Si	mg/kg	34	3300	37800	21200	20700	5800	47000	24000
Sr	mg/kg	33	9	127	***	20.6	10	130	35
Ti	mg/kg	34	100	1000	550	500	200	1500	600
V	mg/kg	35	3.3	59	14.2	11	11	90	32
Zn	mg/kg	35	7.0	318	***	51.5	10	5300	250

	Sample Data						Illinois Basin Coals*		
	Units	# of Records	Min.	Max.	Mean	Median	Min.	Max.	Mean
Zr	mg/kg	33	3.1	42	20.3	18.0	12	130	47
Cl	mg/kg	22	400	4600	1700	1600	100	5400	1400
Org. S	wt. %	33	0.6	2.04	1.6	1.7	0.37	3.2	1.6
Pyr. S	wt. %	33	0.36	4.18	1.8	1.8	0.29	4.6	2
Su. S	wt. %	33	0.01	0.42	0.1	0.1	0.01	1.1	0.1
Tot. S	wt. %	33	1.68	6.01	3.5	3.5	0.56	6.4	3.6
Ash	wt. %	34	3.71	19.7	12.1	11.5	4.6	20	11

\* Gluskoter et al.,1977

\*\*\* Sample data contain censored values, did not compute mean.

5) coal, 23 samples from the Herrin (No. 6) coal, 10 samples from the Danville (No. 7) coal, and one other sample whose stratigraphic source is unknown.

For the liquid samples, the available data have been plotted on box plots and a Piper diagram. A box plot shows the distribution of concentrations. The left side of the box shows the 25<sup>th</sup> percentile. The center of the box shows the 50<sup>th</sup> percentile or the median. The right side of the box shows the 75<sup>th</sup> percentile. The difference between the 75<sup>th</sup> percentile and 25<sup>th</sup> percentile is the Hspread, which is used to define outliers. The whiskers on the box show approximately the 5<sup>th</sup> percentile (left) and the 95<sup>th</sup> percentile (right). Additional data outside these ranges are shown with asterisks (points between 1.5\*Hspread and 3\*Hspread) and circles (points >3\*Hspread). Box plots were constructed for major cations (figure 6) and anions (figure 7) using SYSTAT version 9. A Piper diagram (figure 8) was constructed for the water samples using RockWorks (Rockware Inc.).

Of the major cation concentrations, sodium (Na) had the greatest variability and calcium (Ca) and magnesium (Mg) had the least variability. Of the major anion concentrations, chloride (Cl) had the greatest variability and bicarbonate (HCO<sub>3</sub>) had the least variability. The Piper diagram will be discussed later in this report.

### 3.2 Summary of New Chemical and Mineralogical Data

New chemical and mineralogical data were obtained from samples of cores previously collected by KELRON (KELRON 25, KELRON 30, and KELRON 31). In addition, we collected groundwater samples from 6 KELRON wells and 4 water-supply wells in central Vermilion County. KELRON provided geochemical data for 7 wells.

Figure 6. Box plot of major cations for the available groundwater samples

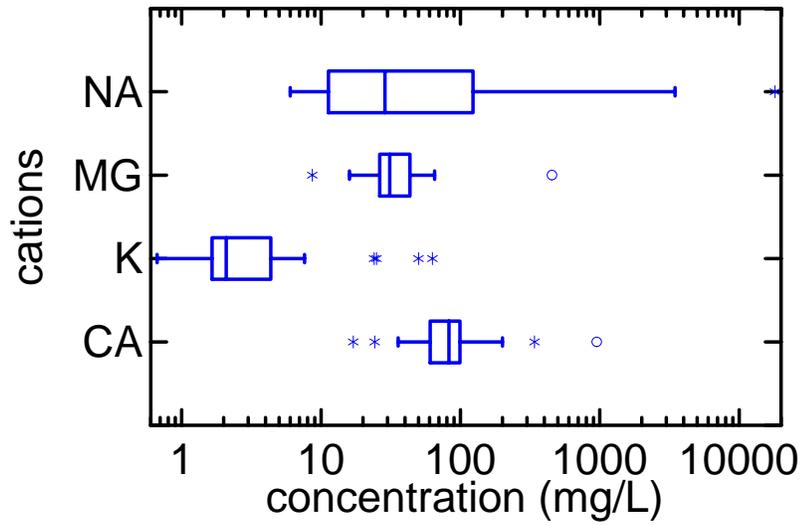


Figure 7. Box plot of major anions for the available groundwater samples

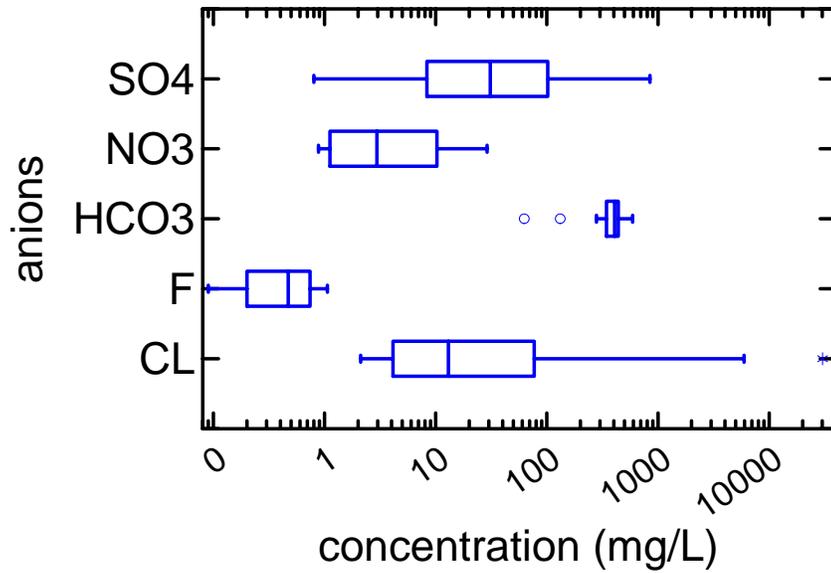
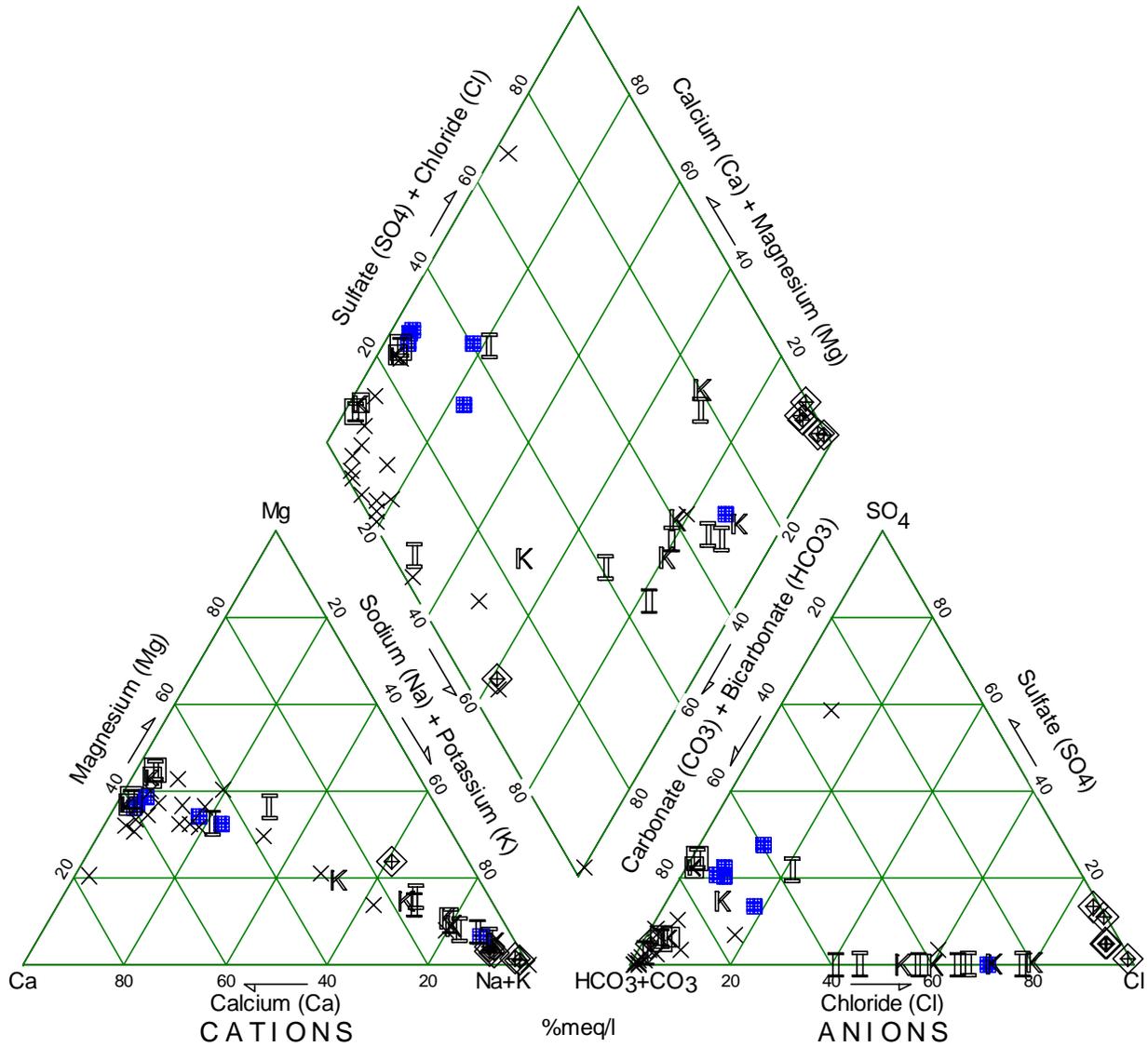


Figure 8. A Piper diagram of the groundwater samples (Vermilion Co., IL= squares, other IL counties= diamond, Parke Co., IN= x, ISGS samples= I and KELRON samples= K, non-bedrock samples from ISGS & KELRON are boxed.)



### ***Analytical Methods***

*PIMA and X-ray diffraction (XRD) analyses.* Core samples were analyzed using a portable infrared mineral analyzer (PIMA), manufactured by Integrated Spectronics Pty. Ltd. (Baulkham Hills, New South Wales, Australia). The PIMA-SPT<sup>TM</sup> reflectance spectrometer (figure 9) provided analyses as quickly as one per minute, portability, and good data from irregular, round or flat core- or hand-specimen samples. The instrument's 1.25 cm-diameter window allowed close-interval core logging and determinations on small features in samples. In the analysis mode, the PIMA's 1300 to 2500 nm spectra were matched with reference spectra to determine percentages for up to six minerals. Quartz and feldspar produce no PIMA spectra, thus PIMA sees through these grains to give better-than-expected spectra for minerals that are usually of primary concern, e.g., clay minerals, iron hydroxides, and carbonates. Custom reference spectra can be created for the specific minerals of concern, and the spectral processing programs provide several methods for analyzing spectra, including instantaneous display of calculated features in each spectrum in a "special stack" from outcrop or borehole samples (figure 10).

For six geochemical-PIMA-XRD samples, the core was sawed and about a 15-cm-thick composite of half of the core was crushed and split. The other 13 samples of the three cores were removed, either by drilling perpendicular to bedding with a ¼ inch carbide drill bit, or, for core segments that broke into thin bedding layers, by breaking a 5 to 10 g fragment of the layer. For PIMA and XRD analyses, all 19 samples were hand ground with a mortar and pestle, and packed into end-loading XRD sample holders. The samples were x-rayed using standard operating procedures (SOPs) on file at the ISGS. The same sample surface was later inverted into a calibrated petri dish for PIMA analyses. Hughes and Warren (1989) Hughes et al. (1994) and Hughes et al. (2002) summarize the methods used. Demir et al. (2001), Hughes et al. (1987), Hughes et al. (1989), Hughes et al. (1992), Hughes (1993), Hughes et al. (1994), and Hughes et al. (2002) summarize the range of composition normally found for these types of sediments.

*Smear samples.* Smears of the particles with diameters <8µm were prepared by placing 1 to 3 g of sample in a 150 mL beaker, adding 100 mL of deionized H<sub>2</sub>O, dispersing the slurry with an ultrasonic probe for 60 seconds, and allowing the samples to soak overnight. For samples that flocculated and had clear supernates, the clear water was decanted and the beakers refilled with deionized water. Five drops of dispersant solution were added to each of the beakers, each beaker was stirred for 30 seconds, and the samples were allowed to settle 3 minutes per cm of slurry depth. After settling, the fine fractions were poured into 400 mL glass beakers and flocculated with CaCl<sub>2</sub>•nH<sub>2</sub>O. The glass beakers were refilled, two drops of dispersant were added, the mixtures were stirred, allowed to settle, and the fine fractions were added to the glass beakers containing the first settlings. A third settling was completed, and the >8 µm fractions were allowed to dry, after which, the sample and beaker were weighed, to estimate the weights of the coarse and fine fractions. The <8 µm fractions were flocculated and allowed to settle overnight, the clear supernate was decanted, the fines were transferred to 40 mL centrifuge tubes, and after centrifuging 20 minutes @ 2000 RPM, the clear supernates were decanted, the sediment plugs were thoroughly mixed with a microspatula, and the paste was smeared on a round, glass XRD slide. After the smear dried in air, the slides were x-rayed using ISGS SOPs.

Figure 9. A typical laboratory setup for PIMA showing the power supply at left, a limestone sample on the PIMA's analysis window on the tabletop, and a laptop computer with a spectrum for pure calcite from a limestone sample.

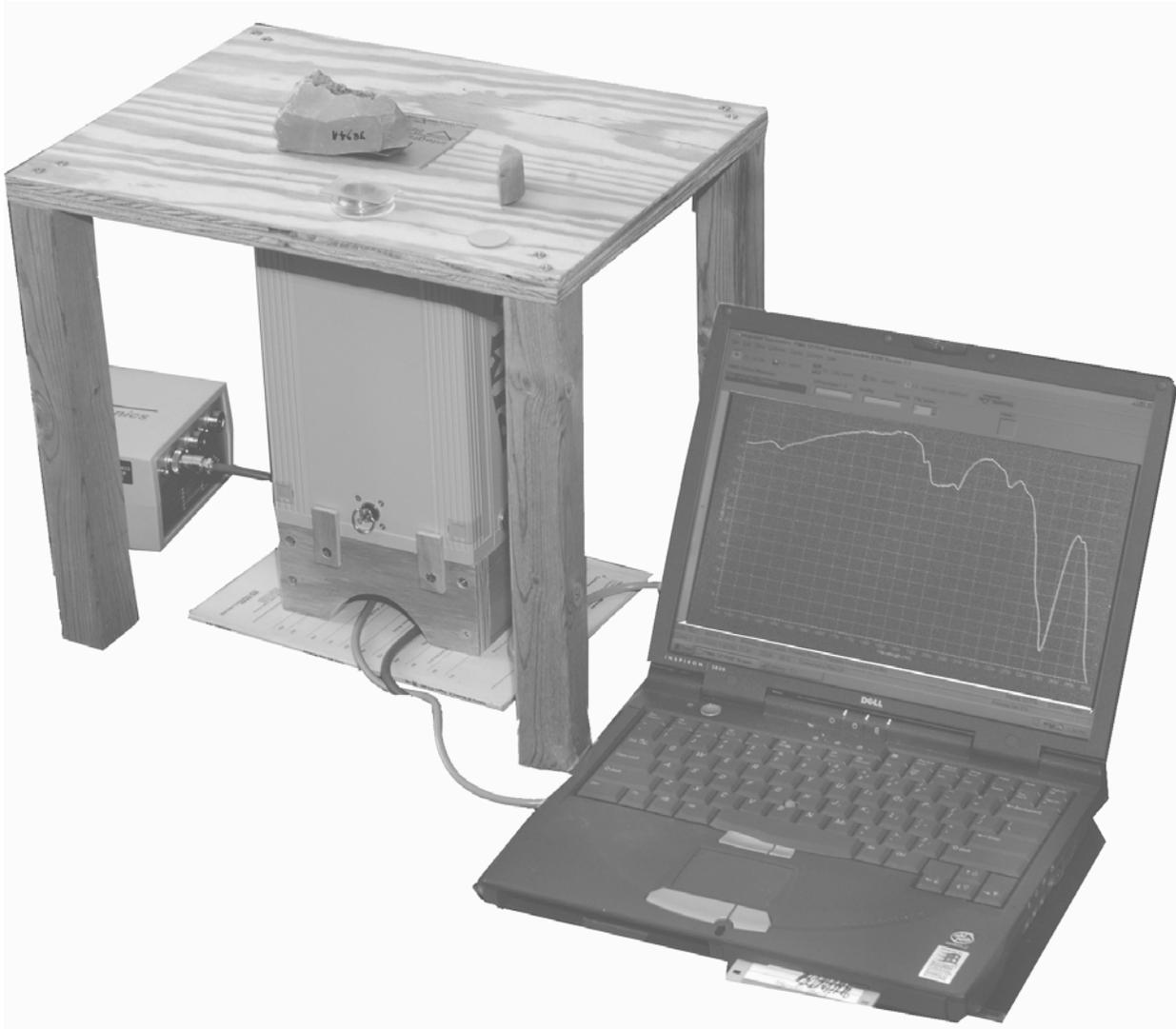
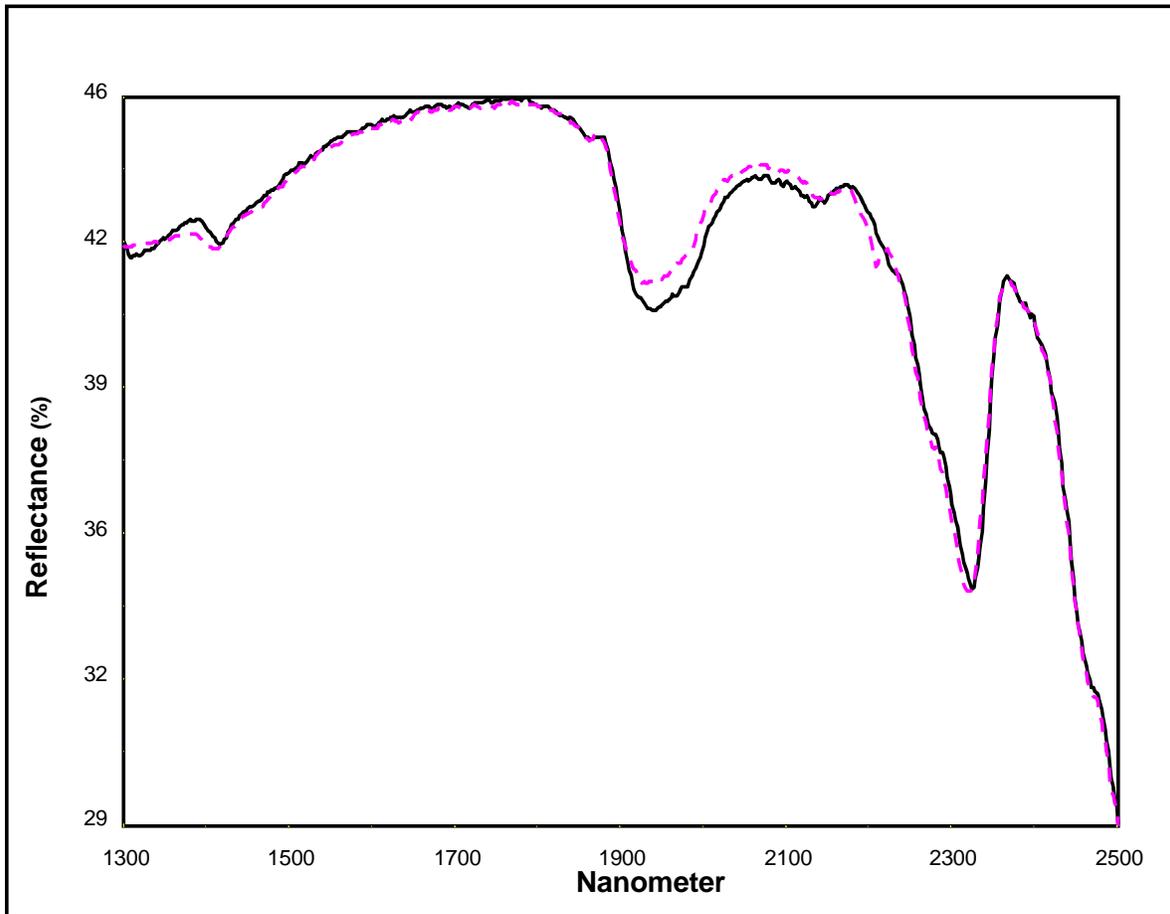


Figure 10. Overlay of the spectrum for western Illinois dolomite (dark trace) and a calculated spectrum (light, dashed trace) for 100% dolomite (PIMA's MinIDB reference standards library).



*Water samples.* Water samples were collected from monitoring and water-supply wells. Groundwater samples from the KELRON monitoring wells were collected using Dynegey-owned equipment including dedicated, low-flow sampling pumps. The June 18, 2002 samples were collected as split samples during Dynegey's regular sampling. Groundwater samples from water-supply wells were collected using the installed pumps, from taps prior to any water treatment such as water softeners. Prior to sample collection, field parameters (temperature, dissolved oxygen, pH, Eh, and specific conductance) were monitored and were allowed to stabilize, unless the well appeared to be running out of water. Water samples were transported on ice and stored at 4 °C until analyzed.

Water samples collected by the ISGS were analyzed for anions and cations by the ISGS Geochemistry Laboratory. Anions were determined using a Dionex DX-120 Ion Chromatograph with Ionpac AG14 Guard Column, Ionpac AS14 Analytical Column, and ASRS-ULTRA (4mm) suppressor module. Analytes were measured with a CDM-3 conductivity detector cell with a DS4 detection stabilizer. The eluent was 3.5mM sodium carbonate and 1.0 mM sodium bicarbonate. The following were approximate retention times in minutes: fluoride, 2.9; chloride, 4.0; bromide, 5.6; nitrate, 6.4; phosphate, 8.0; and sulfate, 9.5. Instrument operation and data collection were controlled using PeakNet 5.01 software. A calibration check standard and blank were run with each analysis set.

Cations were determined with a Thermo Jarrell-Ash Model ICAP 61e inductively coupled plasma spectrometer. The list of elements and their wavelengths in nanometers are: Al(308.2), As(193.6), B(249.6), Ba(493.4), Be(313.0), Ca(393.3, 317.9), Cd(228.8), Co(228.6), Cr(267.7), Cu(324.7), Fe(259.9, 271.4), K(766.4), Li(670.7), Mg(279.5, 383.2), Mn(257.6), Mo(202.0), Na(588.9, 330.2), Ni(231.6), P(214.9), Pb(220.3), S(182.0), Sb(206.8), Sc(361.3), Se(196.0), Si(288.1), Sr(421.5), Te(214.2), Ti(334.9), Tl(190.8), V(292.4), and Zn(213.8). Instrument operation, inter-element interference correction, background correction, and data collection were controlled using ThermoSPEC/AE 6.20 software. Blanks, calibration check standards, and reference standards were run with each analysis set.

For tritium analyses, water samples were collected in 1L HDPE bottles. Tritium was determined with 200 mL of water using the enrichment technique (Ostlund and Dorsey, 1977). The tritium enriched samples were purified by vacuum distillation, mixed with a scintillation cocktail, and counted in a low-level scintillation counter (Packard 2000 CA/LL). The tritium results are reported in tritium units (TU), which is defined as one tritium atom per  $10^{18}$  hydrogen atoms.

The dissolved inorganic carbon (DIC) in water was analyzed at the ISGS for carbon-14 activity using conventional techniques (Hackley, 2002). The DIC is extracted from water samples by the addition of acid. The carbon dioxide released from water samples is quantitatively collected and cryogenically purified on a vacuum line. The purified carbon dioxide is converted to high-purity benzene following the technique described in Coleman (1976). The carbon-14 activity is measured using the liquid scintillation spectrometry method developed by Noakes et al. (1965, 1967).

Groundwater samples from the KELRON wells also were collected and analyzed by Dynegey. Prior

to sample collection, Dynegy monitored several field parameters (temperature, dissolved oxygen, pH, Eh, and specific conductance) using a calibrated Hydrolab Minisonde. Cations were determined by inductively coupled plasma emission spectroscopy (ICP) (USEPA method 200.7). Alkalinity was determined by a titrimetric method (USEPA method 310.1). Total dissolved solids were determined by a gravimetric method (USEPA method 160.1). Sulfate was determined using a turbidimetric method (USEPA method 375.4). Total phosphorus was determined using an ascorbic acid/colorimetric method (USEPA 365.2). Finally, chloride was determined using a potentiometric method (Standard method 4500-Cl).

### ***Solid Samples***

Detailed descriptive logs (see DeMaris logs, Appendix A) were compiled for three new holes drilled by KELRON and used to select 19 samples for PIMA-SP<sup>TM</sup> and XRD analyses. Table 6 gives the lab number, core number, depth, and material type for the 19 samples. The coal in core KELRON 30 had been sealed, and a sample of the white oxidation product on top of the coal was analyzed by PIMA and XRD. Separately, one or two siderite nodules were analyzed, and 19 PIMA and XRD samples were chosen to contrast the mineralogical composition of silt- and clay-rich zones. Over 90 PIMA analyses were run for this project, 54 on the cores, and 39 on bulk and <8µm smear samples. The results from the PIMA analyses of the cores were quite uniform, suggesting that little mineralogical variation was present. Table 6 gives the XRD analysis results for bulk sample preparations that show: a) 10 to 60% clay minerals, b) 35 to 75% quartz, 0 to 3% K-feldspar, 2 to 13% plagioclase feldspar, and 0 to 10% siderite. Samples 3955S and T also contained 2.3 and 10% pyrite/marcasite, respectively. The iron sulfide in both samples is mostly marcasite, a form of the compound that oxidizes very quickly. The needle-like white precipitate above the coal in core KELRON 30 is undoubtedly the result of this rapid oxidation. In general, silt-rich samples had lower clay mineral contents and higher quartz and feldspar contents than shaly zones.

The XRD analyses of the <8µm smear samples (table 7) showed that the clay mineral suites were composed mostly of illite, kaolinite, chlorite, and small amounts of mixed-layered illite/smectite (I/S). Coarser, more permeable zones normally have higher fluid flow rates and this results in higher kaolinite contents, and so as expected, the silt-rich samples in this set contained relatively more kaolinite, a higher kaolinite:chlorite ratio, and less illite, I/S, and chlorite. Table 8 gives the ranges of the clay mineral contents from the smear slides- 50 to 65% illite, 12 to 32% kaolinite, 9 to 22% chlorite, and 3 to 7% I/S (atypical sample 3955T had 19% I/S).

PIMA analyses of core, hand specimen, bulk powder, and smear samples confirmed the generally uniform composition of these strata, but showed significant differences in the compositions of the silty and shaly samples. These results also are qualitatively consistent with the XRD results. Finally, the PIMA analyses of the core required only a few minutes each, and these results confirmed the value of the PIMA to identify compositional changes and refine the sample selection process.

Table 6. PIMA-XRD sample description and mineral percentages from XRD analysis

Well	Sample No.	Depth (ft)	Material	% Clay minerals	% Quartz	% K-Feldspar	% Plagioclase feldspar	% Siderite
KELRON 25	3955A1	18.17	siltstone	14	72	2.3	10	1.2
	3955A2	18.13	siltstone	14	69	0.9	12	3.6
	3955A3	18.10	shale	25	61	0.8	8.8	4.5
	3955B	28.17	shale	11	74	0.0	12	2.6
	3955C	36.0	shale	26	59	1.1	8.1	5.8
	3955E	12.55-12.75	silty-shale	21	63	1.8	11	3.6
	3955G	32.0-32.25	shale	23	61	0.0	9.0	6.5
KELRON 31	3955I	156.6-156.8	shale	24	60	1.5	10	3.8
	3955J1	154.22	shale	27	56	1.2	11	4.5
	3955J2	162.0	shale	22	55	0.0	13	10
	3955K	165.7-165.95	shale	26	60	1.5	8.4	4.0
	3955L	178.18	shale	36	53	0.0	7.8	2.8
	3955M	174.4-174.62	shale	34	53	0.0	7.4	5.0
KELRON 30	3955N	120.3	shale	24	67	0.0	9.1	0.0
	3955O	127.2-127.45	shale	34	52	1.4	8.8	4.2
	3955P	132.5	shale	36	55	0.0	7.2	2.6
	3955Q	136.25-136.43	shale	40	51	0.0	5.1	3.2
	3955S	141.15-141.4	shale	39	49	0.0	6.2	3.1
	3955T	144.0	C-Py-shale	56	30	2.5	2.0	0.0

Key: C = carbonaceous; Py = pyritic (pyrite or marcasite)

Samples 3955S and T had pyrite/marcasite, which was mostly marcasite; percentages = 2.3 and 6.7%, respectively.

Table 7. Percentages of mixed-layered illite/smectite, illite, kaolinite, and chlorite from X-ray diffraction data based on 8µm smear samples. The ratio of kaolinite:chlorite (K:C), the clay index (CI), and %<8µm also are given.

Sample	%I/S	%I	%K	%C	K:C	CI	%<8µm
3955A1	3.6	48	32	16	0.67	0.73	35
3955A2	3.9	48	30	18	0.63	0.78	49
3955A3	4.0	62	15	19	0.44	0.87	54
3955B	3.3	51	29	16	0.64	0.81	38
3955C	4.5	62	16	17	0.48	0.84	59
3955E	5.0	59	17	18	0.49	0.91	31
3955G	4.5	60	17	19	0.47	0.89	39
3955I	5.8	58	15	21	0.42	0.88	40
3955J1	5.8	60	16	18	0.47	0.90	44
3955J2	4.9	60	17	18	0.49	0.83	57
3955K	4.3	64	13	19	0.40	0.89	47
3955L	5.0	60	13	22	0.36	0.86	79
3955M	5.1	60	14	21	0.39	0.85	72
3955N	4.8	57	18	20	0.48	0.88	47
3955O	5.4	62	13	20	0.41	0.88	75
3955P	6.0	59	14	21	0.39	0.85	75
3955Q	6.4	58	13	22	0.38	0.85	91
3955S	6.6	61	12	20	0.39	0.86	88
3955T	19	60	13	8.6	0.60	0.81	62

Key: I/S = mixed-layered illite/smectite; I = illite; K = kaolinite; C = chlorite; K:C = the ratio of the kaolinite 002 peak to the chlorite 004 peak; CI = the clay index, which equals the corrected sum of the peaks for the clay minerals divided by the sum of the corrected intensities of the clay and nonclay minerals; the higher the ratio, the higher the clay mineral content; the %<8µm was estimated from the initial weight of the sample minus the final weight of the >8µm.

### ***Water Samples***

The ISGS sampled the wells described in table 8 in mid- to late June 2002. These wells included 6 monitoring wells and 4 water-supply wells located in Vermilion County. All but two wells were completed in shallow bedrock. Two monitoring wells (KELRON 26 & 28), completed in shallow Quaternary materials, were sampled to provide data on shallow groundwater. The chemical data for the ISGS samples are summarized in table 9. Dynegy sampled numerous monitoring wells from February through August 2002 (table 10). Some of these data are reported here. On June 18<sup>th</sup>, split samples were collected from 6 KELRON wells and sent to ISGS and Dynegy laboratories. The results for these split samples were within 20%, except for a few samples for chloride, iron, and potassium.

Table 8. Description of wells sampled by the ISGS and/or Dynegy

Well #	Location	Total Depth (ft)	Lithology @ screen
1349	T18N, R13W, Sec 9	72	sandstone & shale
21903	T20N, R12W, Sec 34	147	sandstone & shale
23343	T20N, R12W, Sec 23	175	sandstone & shale
25531	T17N, R12W, Sec 1	140	rock & shale
KELRON 25	T20N, R12W, Sec 29	39	shale
KELRON 26	T20N, R12W, Sec 20	16	sand & shale
KELRON 27	T20N, R12W, Sec 20	44	shale
KELRON 28	T20N, R12W, Sec 21	15	sand & silt
KELRON 29	T20N, R12W, Sec 21	45	shale
KELRON 30	T20N, R12W, Sec 20	148	shale & coal
KELRON 31	T20N, R12W, Sec 21	184	shale

The range of concentrations of major anions (figure 11) and major cations (figure 12) for the samples collected for this study (by the ISGS and Dynegy) are shown by the dots, while the box plots display the available data. These box plots were generated using GRAPHER version 3. The whiskers cover the entire range of data, which differs from the whiskers for the SYSTAT box plots (e.g., figure 6).

The dot and box plots are similar; thus, the data collected from the sampled wells are similar to the available data, which cover a broader geographic area. Only 2 sampled wells (well 23343 and KELRON 26) had TDS values below 250 mg/L. Well 23343 is a 175-foot, domestic well completed in bedrock. KELRON 26 is a 16-foot monitoring well completed in Quaternary geologic materials. Another shallow monitoring well, KELRON 28, had a TDS similar to the bedrock wells.

Some of the concentration data can be explained by the lithology of the aquifer materials (table 8). KELRON 30 was completed in shale and coal, wells 1349, 21903 and 23343 in sandstone and shale, well

25531 in rock and shale, KELRON 26 and 28 in sand, while the remaining wells were completed in shale. For example, a groundwater sample from KELRON 30 (the only well completed in coal) had the highest concentration of Ba, Li, Na, and Cl. Data from tables 4 and 5 show that coal generally has higher concentrations of Cl than other geologic materials.

Table 9. Geochemical data for ISGS sampled wells

	Well Number									
	1349	21903	23343	25531	KELRON 25	KELRON 26	KELRON 27	KELRON 28	KELRON 29	KELRON 30
n*	1	1	1	1	2	2	2	2	2	2
Al	<0.1**	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
As	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
B	0.29	0.50	1.4	1.2	1.14	.055	.086	0.09	1.2	0.93
Ba	0.14	0.98	0.26	0.47	2.0	0.031	0.77	0.034	0.55	5.3
Be	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Ca	131	44.2	67.4	36.8	84.4	87.3	34.8	186	30.4	42.0
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Co	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fe	2.4	<0.01	1.6	3.8	0.06	<0.01	0.20	0.04	0.22	1.9
K	3.0	4.0	5.0	5.0	6.5	3.5	4.5	<1	4.0	7.0
Li	0.01	0.02	0.01	0.06	0.07	<0.01	0.04	0.03	0.04	0.10
Mg	56	29	45	27	45	34	21	98	15	29
Mn	0.11	0.041	0.035	0.041	0.057	<0.001	0.020	0.081	0.015	0.047
Mo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Na	67	240	68	590	430	1.9	300	16	290	870
Ni	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.005	0.005	<0.01
Pb	<0.02	<0.02	<0.02	<0.02	<0.02	0.015	0.015	<0.02	<0.02	<0.02
S	49	0.03	5.4	0.38	0.46	7.9	0.19	72	0.3	1.5
Sb	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Sc	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Se	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Si	8.0	3.4	7.5	3.3	5.4	4.4	6.1	6.2	5.8	4.7
Sr	0.23	0.52	1.5	0.57	0.7	0.1	0.4	0.3	0.4	0.8
Ti	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Tl	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
V	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Zn	0.055	<0.001	0.018	0.074	<0.001	<0.001	<0.001	0.004	<0.001	0.003

	1349	21903	23343	25531	KELRON 25	KELRON 26	KELRON 27	KELRON 28	KELRON 29	KELRON 30
F	0.2	0.2	0.5	0.5	0.5	0.1	0.7	0.1	0.8	0.7
Cl	100	230	5.0	640	690	7.0	320	7.0	240	970
Br	<0.05	<0.05	<0.05	0.72	1.3	<0.05	0.61	<0.05	0.51	2.5
NO <sub>3</sub> - N	<0.02	<0.02	<0.02	<0.02	<0.02	6.7	<0.02	<0.02	<0.02	0.15
PO <sub>4</sub>	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
SO <sub>4</sub>	140	<0.1	11	0.6	1.0	19	0.2	190	0.6	3.2
Total Alk	380	460	390	480	280	280	340	600	400	670
pH	7.7	7.8	8.2	8.0	7.8	7.9	8.0	7.9	8.1	8.2
TDS	470	550	210	1300	1300	150	700	450	590	1900

\* n= number of samples. For n>1, average values are reported.

\*\* : All values are reported in units of mg/L except pH.

Table 10. Geochemical data from KELRON well samples

Parameter	Units	Well Number						
		KELRON 25	KELRON 26	KELRON 27	KELRON 28	KELRON 29	KELRON 30	KELRON 31
n*	–	7	1	7	1	7	7	7
pH	--	7.3	7.2	7.6	7.0	7.5	7.4	7.2
Temperature	°C	12.5	11.6	12.0	13.6	13.0	14.5	12.4
TDS	mg/L	1500	350	900	900	830	2400	860
Alkalinity	mg/L	280	290	330	600	390	670	560
B	mg/L	1.2	<0.05	0.83	0.11	1.1	0.9	0.7
Ba	mg/L	1.6	0.03	0.7	0.03	0.47	4.6	0.58
Ca	mg/L	85	92	32	190	29	34	82
Fe	mg/L	0.15	<0.025	0.18	0.05	0.26	1.8	0.40
K	mg/L	5.8	2.2	3.7	0.88	3.7	7.7	9.5
Li	mg/L	0.11	<0.005	0.04	0.03	0.05	0.12	0.10
Mg	mg/L	45	34	20	94	15	25	35
Mn	mg/L	0.05	<0.005	0.02	0.07	0.01	0.04	0.08
Na	mg/L	390	3.1	270	17	260	890	170
Sr	mg/L	0.57	0.07	0.4	0.3	0.3	0.7	0.7
Cl	mg/L	820	12	360	11	320	1200	59
PO <sub>4</sub>	mg/L	0.03	0.10	0.02	0.01	0.03	0.04	0.06
SO <sub>4</sub>	mg/L	6.6	20	<5	170	<5	6.5	110

\* n= number of samples. For n>1, average values are reported.

Figure 11. Major anions: box plot for the available wells along with dot plots of the ISGS (+) and Dynegy (◇) samples

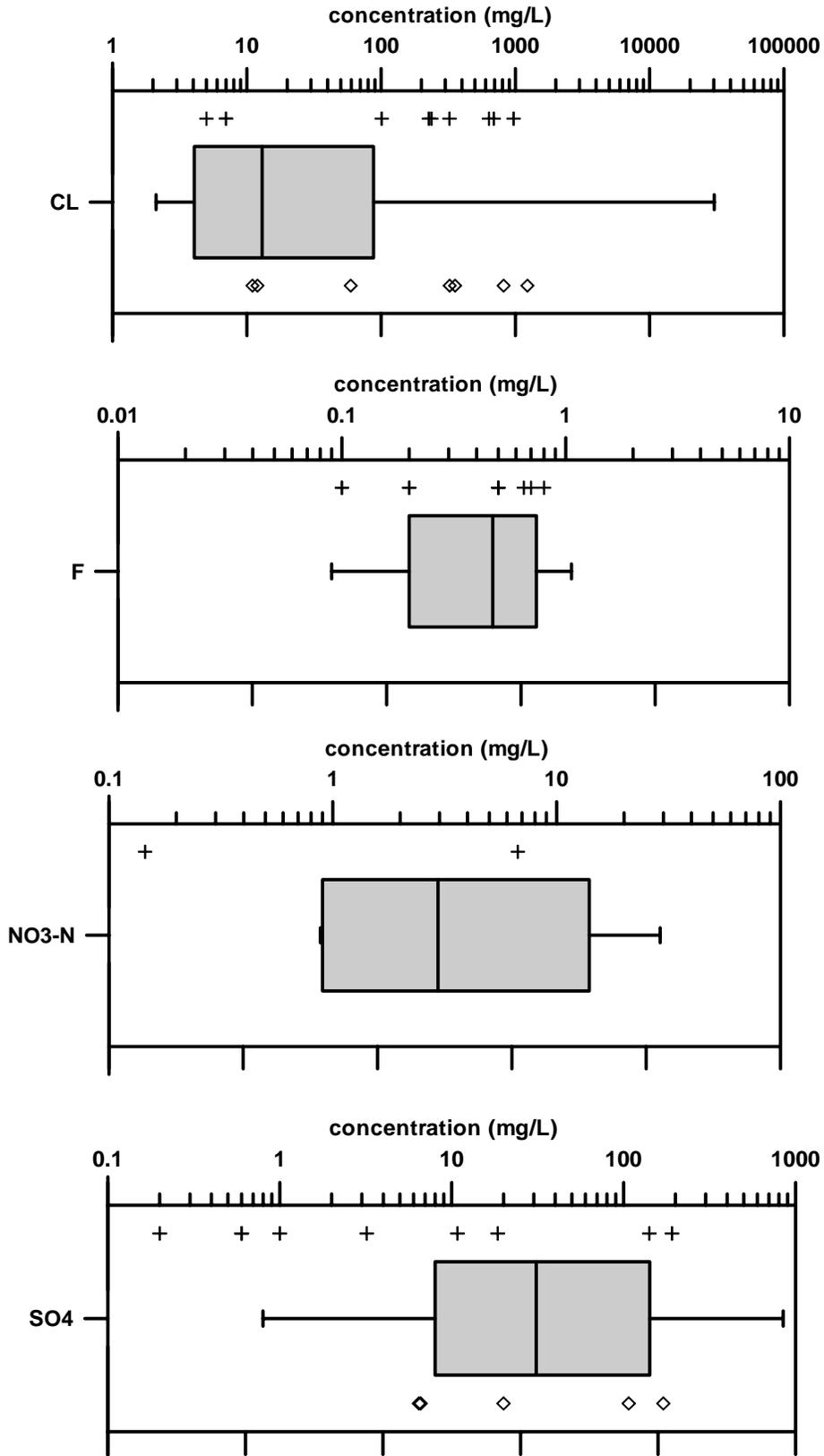
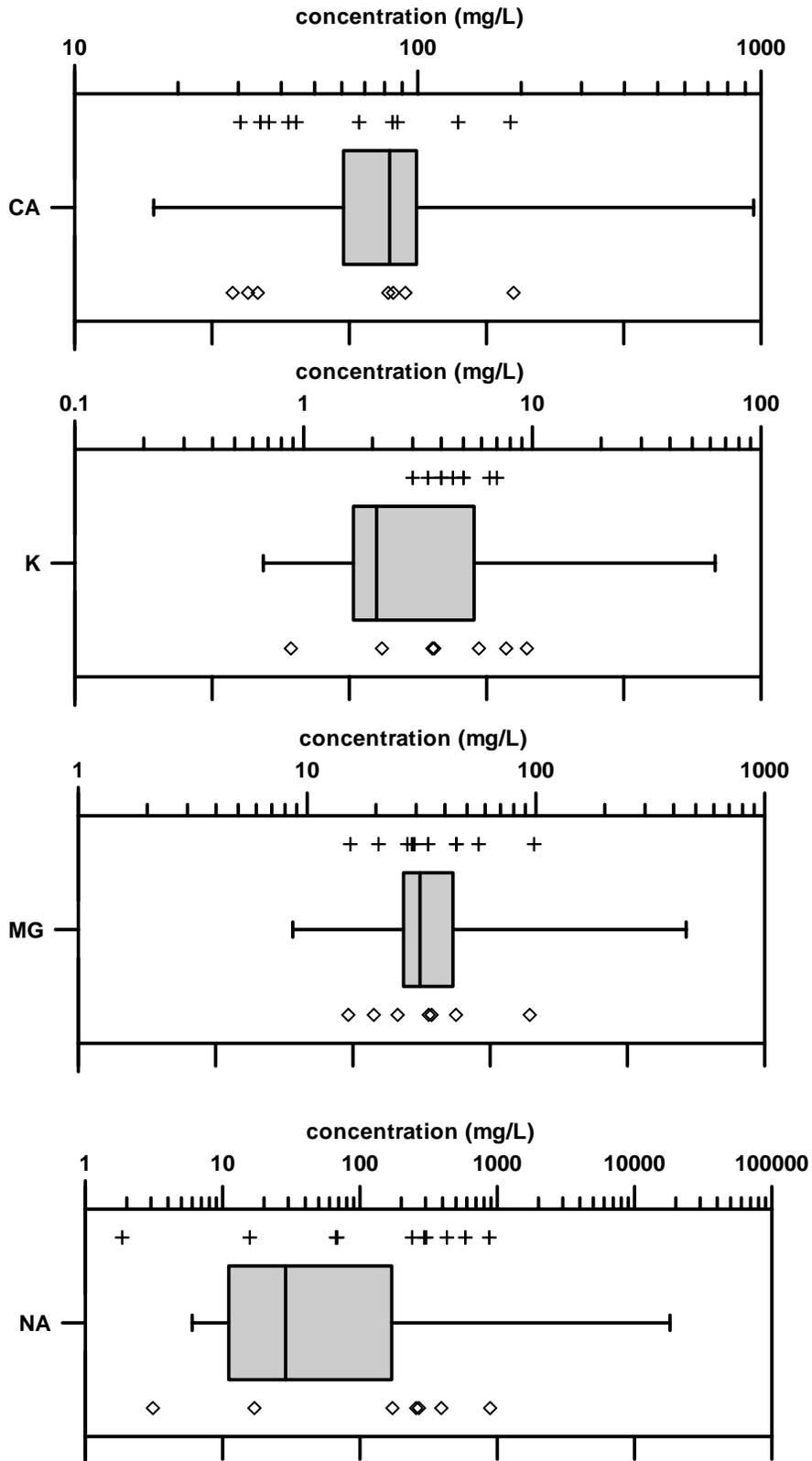


Figure 12. Major cations: box plot for the available wells along with dot plots of the ISGS (+) and Dynegy (◇) samples



The concentration data for the ISGS and Dynegey groundwater samples were also plotted on a Piper diagram (figure 8). The major cation concentrations for these groundwater samples appear in the left-hand ternary plot of the Piper diagram (figures 8 & 13). The linear nature of the data points leads to the hypothesis that groundwater with the greater concentrations of sodium plus potassium (Na+K, e.g., KELRON 27 or KELRON 29) migrated over a longer distance from the recharge area to the respective well than samples with lower concentrations of Na+K (e.g., well 23343). During migration, the groundwater dissolved increasingly greater amounts of sodium from the aquifer rocks and increasing amounts of calcium and magnesium were removed from the water, probably by adsorption by clay minerals in the aquifer rocks. In general, the chemistry of the water samples tends to cluster based on the lithology of the geologic materials in which they are screened. For example, the two wells completed in Quaternary materials plot to the far left in figure 13, and wells 1349 and 23343 (sandstone and shale) in the center of the plot. Well 25531 is the only well that does not fit this pattern.

The diamond-shaped plot in the Piper diagram (figure 8) indicates that for the water samples collected in June 2002, 35% displayed temporary hardness (moderate amounts of Mg, Ca, and  $\text{HCO}_3^-$ ); 41% of these samples are classified as saline (contained relatively large amounts of Na and Cl); the remaining samples were of intermediate classification between temporary hardness and saline.

The position of water quality results plotted on a Piper diagram can be misleading, however, because the Piper diagram is based on the mole percent of four major cations and four major anions. For a given water sample, the number of moles of each of the eight major ions is calculated, then the mole percent is calculated on the basis of the total moles of either cations or anions, respectively. The mole percent of sodium, for example, in a water sample that contains low concentrations of the major cations and anions can be the same as in a water sample that contains high concentrations of major anions and cations. A water that is classified as temporarily hard might not be hard at all, according to the accepted definition of hard water. The hardness of water is defined by the concentration of calcium carbonate in the water. Water containing 0 to 60 mg  $\text{CaCO}_3/\text{L}$  is defined as “soft,” whereas water that contains 121 to 180 mg  $\text{CaCO}_3/\text{L}$  is defined as “hard” (Hem, 1970).

The carbon and hydrogen (tritium) isotopic data (table 11) reveal that some wells produce recent water, while others yield much older water. Tritium values in Illinois precipitation typically range from 3 to 10 tritium units (TU) (Hackley et al., 1996; Hackley, personal communication, 2002). Tritium is generated in the atmosphere. In the subsurface, tritium decays exponentially with a half-life of 12.3 years (Freeze and Cherry, 1979). Thus, water with tritium concentrations greater than 5 TU is considered recent water (wells 1349, KELRON 26, and KELRON 28), while water with nondetectable tritium concentrations is considered to be >50 years old.  $^{14}\text{C}$  has a longer half-life than tritium and is expressed as radiocarbon years before present (RYBP) and as % modern carbon. Both units provide relative ages. Due to the complexities of carbon chemistry, a great deal of additional analysis is needed to obtain definitive dates. The  $^{14}\text{C}$  data are consistent with the tritium data,

Figure 13. Cation plot of the Piper diagram for ISGS and Dynegy samples

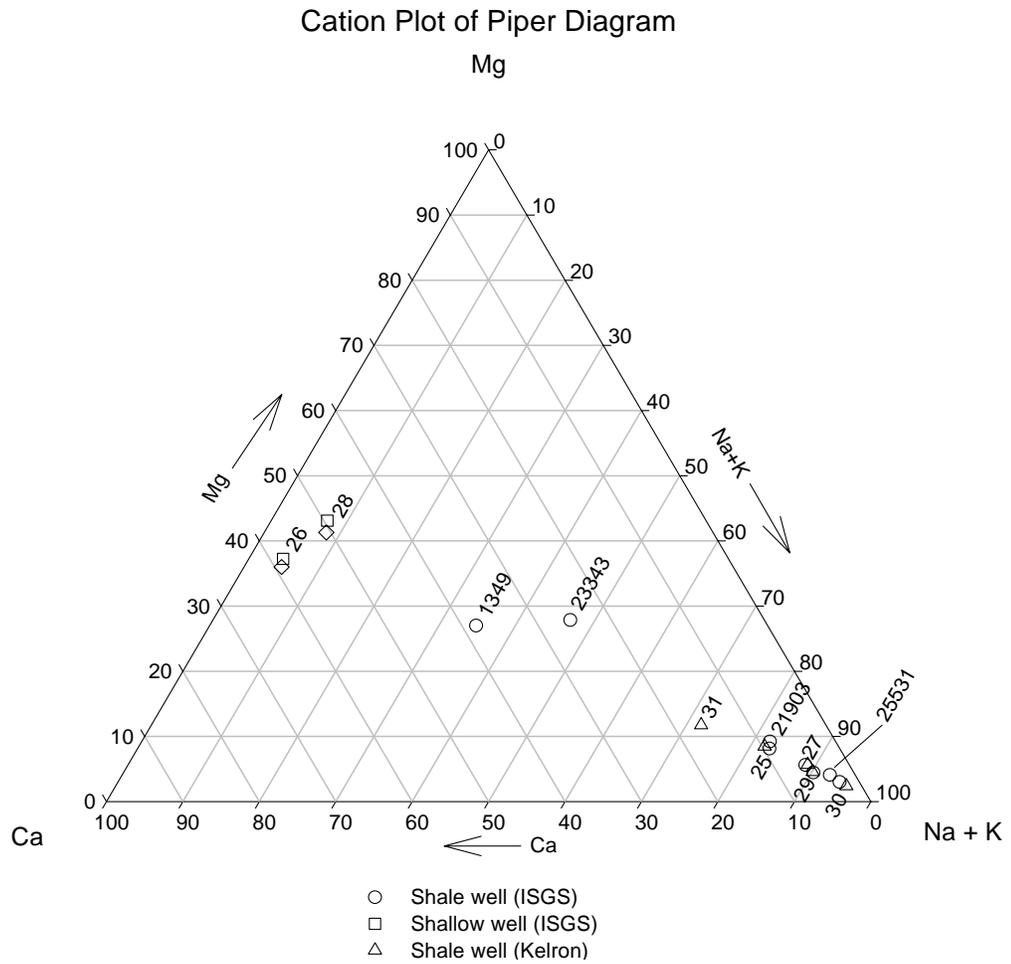


Table 11. Isotopic data for ISGS sampled wells

Parameter	Units	Well Number							
		1349	25531	KELRON 25	KELRON 26	KELRON 27	KELRON 28	KELRON 29	KELRON 30
<sup>14</sup> C	RYBP	2,180	21,160	13,920	210	19,400	modern	34,610	20,850
	% modern carbon	76	7.2	18	97	8.9	102	1.4	7.5
Tritium	TU	7.8	<0.43	<0.43	5.3	<0.43	5.8	<0.52	<0.43

showing that three wells (wells 1349, KELRON 26 and KELRON 28) yield recent water and the others yield much older water. Two wells (KELRON 26 and KELRON 28) were completed in Quaternary geologic materials and appear to draw water from the local groundwater flow system. The third well (well 1349) is completed in the shallow bedrock, but apparently draws some recent water from the overlying Quaternary geologic materials. The remaining wells (KELRON 25, KELRON 27, KELRON 29, KELRON 30, and KELRON 31) apparently draw water from the bedrock and are either only slightly connected to or completely isolated from the local groundwater flow system.

When expressing <sup>14</sup>C as % modern carbon, <sup>14</sup>C has an inverse linear relationship with TDS, sodium, and chloride and a positive linear relationship with calcium. These relationships were determined using linear regression and had coefficients of determination or R<sup>2</sup> ranging from 0.46 (for TDS) to 0.73 (for Ca).

### 3.3 Equilibrium Geochemical Modeling

The geochemical model, MINTEQA2 (Allison et al., 1990), is an equilibrium geochemical model used to calculate the theoretical composition of an aqueous solution at equilibrium, with or without contacting solids (minerals). Because they are in dynamic relationships with their environment, most groundwater systems are not at equilibrium. The use of a geochemical equilibrium model, however, provides an approximation of the geochemical reactions that might occur in a groundwater system.

Input data for MINTEQA2 from the two KELRON wells screened in Pennsylvanian shale (KELRON 25 and KELRON 30) included major element water chemistry and selected mineral components of the shale in the screened interval of the wells. The aqueous components input to the model were carbonate (from alkalinity determinations), calcium, iron (as Fe<sup>2+</sup>), magnesium, potassium, sodium, silicon (as H<sub>4</sub>SiO<sub>4</sub>), chloride, sulfate, Eh, and pH. Trace elements were not used because of their negligible influence on the water chemistry. The only minerals included in the model were kaolinite, quartz, and siderite. Thermodynamic data for other minerals present in the shale, such as illite, K-feldspar, plagioclase feldspar, and chlorite, were not available in the model's

database. Kaolinite, quartz, and siderite were set as infinitely available, i.e., they were assumed to never completely dissolve from the rock.

In operation, MINTEQA2 initially calculates the charge balance of the input solution. The errors for the charge balances between anions and cations were 2% and 6% for KELRON 25 and KELRON 30, respectively, using data derived by the ISGS for the aqueous composition. After the initial calculation of the charge balance, the model determines which minerals in its database could potentially precipitate, due to the components in the aqueous phase. For example, if manganese were not present as an aqueous component, then rhodochrosite ( $\text{MnCO}_3$ ) would not be among the potential precipitates. The model then calculates which of the potential solid phases is most supersaturated according to a comparison of the mineral's solubility product ( $K_{sp}$ ) with the activity product of the relevant components of the aqueous phase. For example, if calcite ( $\text{CaCO}_3$ ) is the most supersaturated mineral, MINTEQA2 calculates the activity product of  $(\text{Ca}^{2+})(\text{CO}_3^{2-})$  and compares this product with the  $K_{sp}$  for calcite. Sufficient  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  are subtracted from the aqueous phase and added to the solid phase so that the resulting aqueous activity product equals the  $K_{sp}$ . At this point, the solid and aqueous phases are in equilibrium with respect to calcite. MINTEQA2 then calculates the next most supersaturated solid phase and repeats the above procedure. Dissolution of minerals is also accomplished in an iterative manner, by addition of solutes from the solid phase to the aqueous phase.

The modeling results for KELRON 25 and KELRON 30 were that calcite ( $\text{CaCO}_3$ ) and wustite ( $\text{FeO}$ ) are allowed to precipitate from the water in both wells. In addition, magnesite ( $\text{MgCO}_3$ ) is allowed to precipitate from the water in KELRON 30. The mass of minerals that were calculated to precipitate per liter of water were small: 0.1 to 0.2 g calcite, 0.08 to 0.4 g wustite, and approximately 0.09 g magnesite. The calculated equilibrium pH values for the water in KELRON 25 and KELRON 30 were 8.55 and 9.20 while the mean observed pH values at the time of collection were 7.78 and 8.24, respectively.

When the mean observed pH values were imposed as the equilibrium values, then only about 0.09 g of calcite was calculated to precipitate per liter of water in both wells, with neither wustite nor magnesite precipitating. This is the most likely scenario. Given sufficient time, calcite will probably precipitate in the wells screened in the Pennsylvanian shale. If water were removed from the wells and stored (e.g., in a tank), then calcite and siderite ( $\text{FeCO}_3$ ) were calculated to precipitate when the observed pH was imposed as the equilibrium pH.

#### **4. SUMMARY & CONCLUSIONS**

Great variability was observed in the geochemical data for the Pennsylvanian bedrock, Pennsylvanian groundwater, and other data collected for this project. Some of this variability is due to the different lithologies which includes sandstone, shale, coal, limestone, and sand and gravel. Some of this variability is also due to the depth of the sample. For example, groundwater samples from KELRON 26 and 28 are significantly different from other samples because they were from shallow wells and are completely connected to the local groundwater system, whereas water samples from deeper wells were largely isolated from the local groundwater flow system. Although little data are available regarding the hydraulic connection between the Vermilion River and the shallow bedrock which crops out locally, we suspect that a well's position relative to recharge and discharge areas affects the concentrations of major cations and anions in the groundwater samples.

Some general observations can be made regarding the groundwater compositions, although exceptions can be found for most of these observations.

The samples collected for this study have a similar range in the concentrations of major anions and cations as those from available groundwater samples collected over a broader geographic area.

The average concentrations of calcium, magnesium, sulfate, and alkalinity were higher in water from two shallow wells (KELRON 26 and 28) than in the wells developed in shale (KELRON 25, 27, 29, 30, and 31). This indicates a possibility that the aquifer rocks of the shallow wells contained greater contents of calcite/dolomite and gypsum or magnesite than the wells completed in shale. Water from the wells completed in shale contained higher concentrations of aluminum, barium, bromide, boron, chloride, fluoride, iron, lithium, potassium, sodium, and strontium. The greater aluminum concentration in the water suggests greater clay contents in the shale aquifer rocks than in the shallow wells.

For samples from bedrock wells, sodium and chloride concentrations apparently increase at the expense of calcium, magnesium, and other higher valence cations due to adsorption as groundwater moves away from recharge areas.

Compared to samples from the deeper bedrock wells, samples from shallow wells generally have higher tritium and % modern carbon, suggesting the addition of recent water.

Equilibrium modeling showed that calcite is expected to precipitate from water derived from the shale wells, given enough time for equilibrium to become established. The calcite might eventually plug well screens. If water is pumped from the shale aquifer and stored in a tank, calcite is expected to precipitate in the tank and accumulate slowly on the tank walls and bottom.

The mineralogy of an aquifer governs the chemical composition of the associated groundwater. Mineralogical analyses were conducted to aid in understanding the chemical composition of the groundwater, and to provide information for geochemical modeling. The mineralogical analyses showed that three cores collected during this project (KELRON 29, KELRON 30, and KELRON 31) consisted principally of shale, composed of clay minerals and quartz with minor amounts of K-feldspar, plagioclase feldspar, siderite, and marcasite or pyrite. Coal was penetrated while drilling KELRON 30, and a small amount was recovered at the bottom of that core. The most abundant clay minerals in the cores were illite, kaolinite, and chlorite, with minor amounts of illite/smectite mixed-layer clay.

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Chris Stohr, ISGS, collected the natural gamma logs from 3 wells.

Randy Hughes, Phil DeMaris, Makiko Otao, and Mary Hynes of the ISGS conducted the PIMA and XRD analyses.

The ISGS Isotope Geochemistry Lab ran the tritium and  $^{14}\text{C}$  analyses. Keith Hackley, ISGS, assisted with the interpretation of the isotopic data.

Alec M. Davis, ISGS, compiled much of the geochemical data and prepared some of the figures for this report.

Mike Knapp, ISGS, drafted figures 1 & 2 for this report.

Tracy D. Branam, Indiana Geological Survey, provided data for the Indiana wells included in this report.

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## **Appendix A. Geologic Logs of Selected Bedrock Core**

The core descriptions by Kolata and Jacobson include a stratigraphic interpretation of the core and appear first. The core descriptions by DeMaris emphasize lithologic and structural features of the core.

### **Kelron Environmental MW 25**

Vermilion Power Station

Danville, Vermilion County, IL

(NW, NW, NW, Sec. 29, T. 20 N., R. 12 W.)

Description by Dennis R. Kolata and Russell J. Jacobson, March 14, 2002

Pennsylvanian System

Shelburn Formation

Unnamed Shale above the Danville Coal

9' to at 39' (TD)

Shale, light to medium gray, massive beds, blocky fracture, silty, micaceous, abundant carbonized plant material, bioturbated; interbeds of very light gray shale between 1 mm and 30 mm thick.

### **Kelron Environmental MW 30**

Vermilion Power Station

Danville, Vermilion County, IL

(SW, NE, NE, Sec. 20, T. 20 N., R. 12 W.)

Description by Dennis R. Kolata and Russell J. Jacobson, March 14, 2002

Pennsylvanian System

Shelburn Formation

Farmington Shale

116' to 135'

Shale, medium gray, massive beds, blocky fractures, silty, micaceous; 1-2 " thick brownish-gray siderite nodules beginning a 128', non-marine.

135' to 144'

Shale, medium to dark gray, somewhat less silty than above, brownish-gray siderite nodules mostly 1 cm thick; first appearance of marine fossils 135.5' (strophomenid brachiopods, gastropods, and bivalves increase in abundance downward).

144' to 145'

Shale, dark gray to black, organic-rich, contains white needle-like crystals.

Danville Coal

145' to 148'

Coal, abundant pyrite along cleats

**Kelron Environmental MW 31**

Vermilion Power Station

Danville, Vermilion County, IL

(SW, NE, NE, Sec. 20, T. 20 N., R. 12 W.)

Description by Dennis R. Kolata and Russell J. Jacobson, March 14, 2002

Pennsylvanian System

Shelburn Formation?

Unnamed Shale above the Danville Coal

154' to 173'

Shale, medium gray, massive beds, blocky fractures, bioturbated, silty, micaceous, not fossiliferous.

173' to 183' (TD)

Shale, medium to dark gray, siderite nodules up to 3 cm thick, bioturbated, silty, micaceous; small bivalves suggest that this is a marine shale.

Boring: **KELRON 25** (HQ or 2.5 inch core)

Location: NW/4 of NW/4 of NW/4, Sec 29, T20N, R12W, Vermilion County, IL

Total Depth= 39 feet, Surface Elevation= 578.8 feet

Description by Philip J. DeMaris, June 2002

Interval (ft)			Description
Top	Bottom	Thickness	
9.00	11.25	2.25	Shale– light to medium gray, slightly silty, especially as silt lenses from 10.35 to 11.25', slightly micaceous, horizontal bedding, slightly weathered at top
11.25	30.60	19.35	Shale– medium gray, silty, slightly micaceous and finely carbonaceous, multiple siltstone bands in interval from 18.10 to 30.60', planar bedding
30.60	36.87	6.27	Shale– medium gray, slightly silty, some pyrite, predominantly planar bedding
36.87	38.82	1.95	Shale– medium gray, very slightly silty, some clay lenses, silt lenses and carbonaceous debris rare, faint planar bedding with some bioturbation
			total core= 29.82'

Boring: **KELRON 30** (HQ or 2.5 inch core)

Location: SW/4 of NE/4 of NE/4, Sec 20, T20N, R12W, Vermilion County, IL

Total Depth= 148 feet, Surface Elevation= 645.7 feet

Description by Philip J. DeMaris, June 2002

Interval (ft)			Description
Top	Bottom	Thickness	
119.00	126.92	7.92	Shale– light to medium gray, slightly silty, sparsely micaceous above 123', slightly weathered at top, fractured on multiple low-angle planes in top 1.5', generally planar bedding throughout, two medium-angle faults from 121.1 to 121.7'
126.92	131.20	4.28	Shale– medium gray, nonmicaceous, multiple siderite bands/nodules

Interval (ft)			Description
Top	Bottom	Thickness	
131.20	138.68	7.48	Shale– medium gray, finely carbonaceous, many siderite bands/nodules throughout, scattered marine fossils in interval 136-138'
138.68	144.38	5.70	Shale– dark gray, becoming more carbonaceous and pyritic downward, siderite nodules present in top 1.3', sulfide-rich carb. claystone at base, strongly weathered
144.38	148.00	3.62	Coal (Danville Coal)– normally bright banded, well cleated, pyritic, calcite and kaolinite on cleat, some fusain present throughout
			total core= 29.0'

Boring: **KELRON 31** (HQ or 2.5 inch core)

Location: NE/4 of SW/4 of SW/4, Sec 21, T20N, R12W, Vermilion County, IL

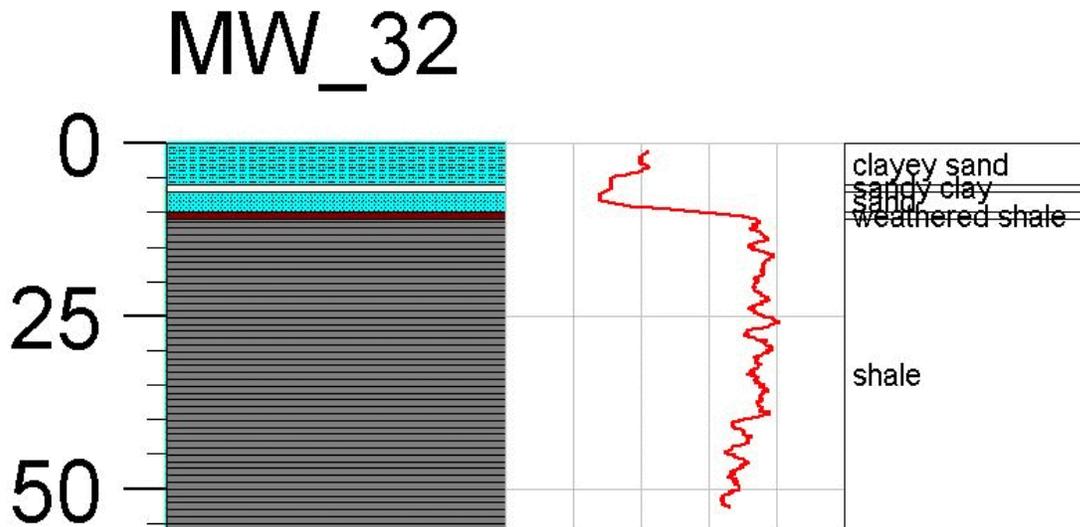
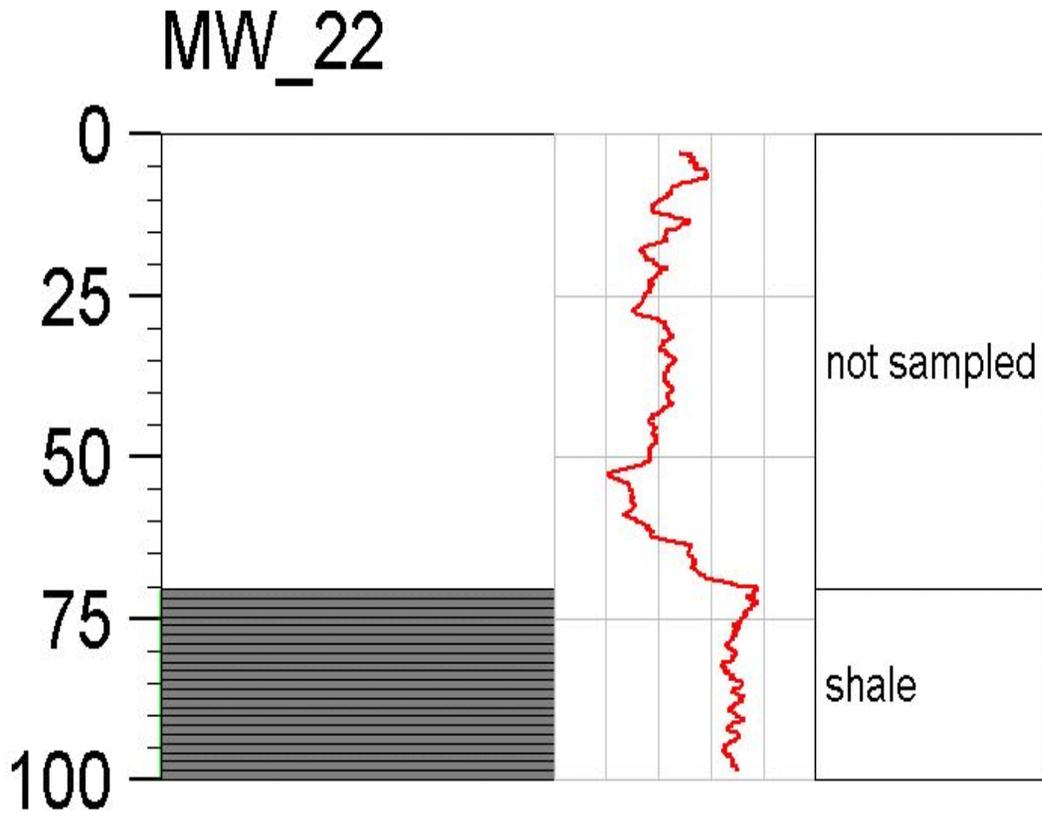
Total Depth= 184 feet, Surface Elevation= 698.2 feet

Description by Philip J. DeMaris, June 2002

Interval (ft)			Description
Top	Bottom	Thickness	
153.00	157.55	4.55	Shale– light to medium gray, slightly silty, well weathered in top 1.2', carbonaceous debris rare, several low angle faults
157.55	170.30	12.75	Shale– light to medium gray, silty, slightly micaceous, unweathered, competent, uniformly faintly laminated, less silty below 164', very faintly horizontally bedded, planar fault (59° dip) centered at 168.8'
170.30	180.80	10.50	Shale– medium gray, slightly silty at top, minor sideritized banding near top of interval, many siderite bands and nodules from 173.7' to base
180.80	182.82	2.02	Shale– dark gray, with multiple siderite bands, very finely carbonaceous
			total core= 29.82'

### Appendix B. Natural Gamma Logs of Selected KELRON Wells

Natural gamma logs for three KELRON wells (KELRON 22, KELRON 30, and KELRON 32) were collected by Chris Stohr of the ISGS in May 2002. The natural gamma logs shown in this appendix are scaled from 0 to 100 cps. In general, higher gamma counts reflect geologic materials with higher clay content such as shales and clayey diamictons.



# MW\_30

