Assessment of the 3,000 ppm and 10,000 ppm Total Dissolved Solids Boundaries in Mississippian and Pennsylvanian Bedrock Aquifers of Southwestern Indiana

Chemical Analyses and QA/QC

By

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INTRODUCTION

Chemical data were gathered for ground-water samples taken from five survey drill holes located in southwestern Indiana (table 1) as part of a study to map the concentration of total dissolved solids (TDS) in the ground water from bedrock aquifers of Indiana. The TDS mapping project was undertaken by the Energy Resources Section of the Indiana Geological Survey (IGS) with partial funding from the Division of Oil and Gas of the Indiana Department of Natural Resources. Coordinated activities among the contracted driller (Hardesty Drilling and Testing Company, Linton, Indiana), the environmental consulting firm (ATEC Associates, Inc., Indianapolis, Indiana), and the IGS Energy Resources and Geochemistry Sections made possible the collection and analyses of water from specific aquifer units within each drill hole. Water samples were collected immediately after the holes were drilled to their total depth during the months of February, March, and April 1993. In addition to the chemical analyses of the major inorganic constituents performed by the IGS Geochemistry Section, analyses of dissolved methane were conducted at the Indiana University School of Public and Environmental Affairs (SPEA). Chemical analyses performed by IGS and SPEA are tabulated in this report (table 2) along with details of the methods of analysis and quality control.

FIELD DATA AND WATER SAMPLING

Each drill hole was cored using conventional wireline coring equipment and a suite of wireline geophysical logs was taken. Potential aquifers were identified for testing from the wireline log records. Ground-water sampling was accomplished by means of a down-hole tool; individual aquifers were isolated using inflatable packers (Aardvark Corp. Model 23B-30-0.510) and ground water was pumped to the surface by a Bennett model 1800-6 submersible pump. Details of the ground-water sampling procedures are given in the final report from ATEC (ATEC, 1993).

Field measurements, including temperature, pH, oxidation-reduction potential (Eh), specific conductivity (SpC), and dissolved oxygen (DO), were performed using calibrated electrodes and meters at the drill hole sites (table 2). A two-person crew used equipment supplied by the IGS Geochemistry Section to gather field data and they reported their measurements on field data

Table 1. Location of survey drill holes and depth of aquifers.

SDH[1] Number	Permit Number	County	Location[2]	Well Name	Depth Sampled (Feet)
377	1032	Daviess	23-2N-7W	IGS[3] No. 1 Troutman	90, 305-360, 540-596
378	1032	Daviess	11-4N-5W	IGS No. 1 Matthies	212-227, 348-399, 422-437
379	1036	Pike	17-2S-7W	IGS No. 1 Sugar Ridge	34-82
380	1034	Gibson	10 3S-9W	IGS No. 1 Gordon Wells	197-229, 229-261, 296-363, 436-468
382	1035	Posey	32-6S-13W	IGS No. 1 Walker	136-156, 333-373

[1]Survey drill hole
[2]Section - Township - Range
[3]Indiana Geological Survey

Table 2. Chemical data for water samples collected from five survey drill holes. Units are expressed in milligrams per liter (mg/L) except where noted in parentheses or footnotes.

	SDH-377[1]	SDH-377[2]	SDH-377[2]	SDH-378[2]	SDH-378[2]	SDH-378[1]	SDH-379[1]	SDH-380[1]	SDH-380[2]	SDH-380[2]	SDH-380[2]	SDH-382[2]	SDH-382[2]
Depth (ft)	90	305-360	540-596	212-227	384-399	422-437	34-82	197-229	229-261	296-363	436-468	136-156	333-373
Collect. Date	2/10	2/10	2/10	3/01	3/01	3/01	3/17	3/29	3/29	3/29	3/29	4/20	4/20
Field Temp °C	7.8	17.2	17.8	11.8	13.0	12.5	5.0	22.0	20.0	15.2	18.4	17.3	16.3
SpC (μmhos/cm)	425	2070	1820	766	591	1042	1231	1164	1117	845	1650	492	403
Field pH	7.5	7.4	7.0	7.8	9.0	7.7	6.2	7.9	7.2	7.0	6.8	7.9	8.0
D.O.	4.4	2.2	9.6	2.2	0.4	2.4	4.6	0.9	1.7	1.3	0.3	0.9	0.4
Eh vs SHE (mV)[3]	337	411	398	298	-91	338	292	255	186	185	151	323	351
Methane (ppmV)[4]	0	14714	3131	3766	2520	4203	0	0	0	53547	26360	247	1673
Alkalinity	320	340	310	280	220	370	130	380	380	350	440	220	150
Bicarbonate	400	420	380	350	260	450	160	470	460	430	530	270	190
Carbonate	0	0	0	0	0	0	0	0	0	0	0	0	0
Chloride	11	550	420	28	30	11	6	92	95	94	340	11	13
Bromide	nd[8]	1	1	nd	nd	nd	nd	nd	nd	nd	1	nd	nd
Nitrate	nd	1	1	3	nd	nd	nd	46	50	43	43	1	7
Sulfate	37	46	69	270	100	340	1000	100	110	95	89	79	98
Fluoride	0.2	0.7	0.5	0.5	0.9	0.8	0.8	0.3	0.3	0.6	0.5	0.6	0.7
Calcium	56	48	39	52	15	34	230	100	92	92	53	14	26
Magnesium	53	34	30	38	6	30	220	55	52	42	25	3	6
Potassium	nd	2	4	nd	3	3	2	nd	nd	1	11	5	10
Sodium	56	470	360	190	170	260	48	67	71	91	330	110	58
Total iron	nd	0.1	2.6	3.0	7.2	0.1	0.3	nd	nd	2.0	1.1	nd	0.1
Manganese	0.1	0.1	0.2	0.5	0.1	0.1	6.1	nd	nd	0.1	0.1	nd	0.1
Zinc	0.1	0.1	0.2	0.4	0.2	0.1	0.2	nd	nd	nd	0.1	nd	nd
Strontium	0.6	0.5	0.5	1.0	0.1	0.7	0.9	0.9	0.8	0.6	0.5	0.1	0.1
Barium	0.5	0.6	0.4	0.4	0.1	0.2	0.1	0.1	nd	0.3	0.8	nd	nd
Silicon	9.1	4.9	4.9	4.2	5.9	3.5	6.8	10.5	9.6	8.2	8.1	3.1	2.4
Anion Sum[5]	7.6	23.5	19.5	12.2	7.2	14.8	24.0	13.1	13.4	12.3	20.9	6.3	5.6
Cation Sum[5]	9.6	25.4	20.4	14.1	9.3	15.4	31.8	12.6	12.0	12.2	19.4	5.8	4.6
EPM Balance[6]	11.7	4.0	2.3	7.1	12.3	2.1	14.0	-2.1	-5.5	-0.4	-3.5	-4.9	-9.5
Total Dissolved Solids	620	1600	1300	940	600	1100	1700	940	950	900	1400	490	410
Total Hardness[7]	360	260	220	290	64	210	1480	480	440	400	230	49	91
Noncarb. Hard.[7]	40	0	0	8	0	0	1350	100	60	50	0	0	0

[1]field measurements taken from water collected in a bucket
[2]field measurements taken from water in flow-through cells
[3]millivolts
[4]parts per million by volume
[5]milliequivalents per liter (meq/L)
[6]percent
[7]alkalinity, total hardness and noncarbonate hardness expressed as mg/L of calcium carbonate
[8]nd - not detected (below detection limit)

forms which contained location information, property owner name and address, and a sample identification number derived from the IGS drill hole number and depth of the aquifer.

Field measurements were taken on water collected from the discharge tubing of the submersible pump either in flow-through cells or in a bucket. The flow-through cells were designed by IGS personnel and constructed by Charles Miller in the Indiana University Department of Geological Sciences machine shop. The flow-through cells were made of plexiglass and consisted of two cylindrical chambers fitted with rubber stoppers that were bored for the proper number and size of electrodes. A common garden hose connected the discharge tubing from the submersible pump to the flow-through cells and the water was allowed to run until water clarity was achieved and the temperature and pH readings stabilized. All field measurements were then recorded. Water was collected and tested in the bucket when discharge from the submersible pump was too low and the water too effervescent to fill the

flow-through cells.

For pH measurements, an Orion model 91-56 electrode and an automatic temperature compensation (ATC) probe were used with a battery-powered pH/mV/temp digital Orion model 231 meter. The meter and probe were calibrated with a pH 7.00 buffer and the slope adjusted with a pH 10.00 buffer solution. The calibration was checked with the pH 7.00 buffer before aquifers were sampled. If the value was off by more than 0.02 pH units, then the system was recalibrated.

Eh was determined using a Corning combination electrode consisting of a platinum electrode and either a calomel reference electrode or a silver/silver chloride (Ag/AgCl) reference electrode. The same meter used to measure pH was set to read millivolts (mV) for the Eh measurements. A check standard solution, the Zobell solution (Zobell, 1946), was used to monitor electrode performance and analytical accuracy. Because two different types of reference electrodes were used, the measured Eh was mathematically converted to an Eh value equivalent to that of the standard hydrogen electrode (SHE) using the procedure described in the National Handbook of Recommended Methods for Water-Data Acquisition (U.S. Geological Survey, 1980).

Conductivity measurements (SpC) were made using a Yellow Springs Instruments (YSI) 3417 (3400 series) plastic electrode with a YSI model 32 conductance meter. Performance and accuracy were checked with a 0.01 Normal (N) potassium chloride (KCl) solution prepared with reagent grade KCl from Mallinckrodt. Units are expressed in micromhos per centimeter (μmhos/cm) and are converted to the standardized reporting temperature of 25 degrees celsius (°C) using a published formula (American Public Health Association; American Water Works Association; Water Pollution Control Federation, 1985a).

Dissolved oxygen (DO) was measured with a YSI 5739 (5700 series) probe connected to a YSI model 54ARC meter. Calibrations were made from the ambient atmospheric oxygen concentration corrected for temperature and elevation. Information in the chart included with the YSI meter was used to set the calibration. The meter measures DO in milligrams per liter (mg/L).

Water samples for the analysis of inorganic aqueous solutes in the laboratory were collected in 125 milliliter (ml) high-density polyethylene (HDPE) bottles. Three types of water samples were collected and appropriately labelled: 1) a raw aliquot for alkalinity titrations (RAW), 2) a filtered aliquot for anion analysis (F), and 3) a filtered plus acidified aliquot for major cation analysis (FA). The acidified aliquot was adjusted to a pH value less than 2 with analytically pure concentrated nitric acid (HNO_3). RAW samples were collected from the discharge tubing after the field measurements were completed and the flow-through cell disconnected. F and FA aliquots were filtered through 0.2 micrometer (μm) filters placed in a stainless steel pressure filtration holder that was connected by adapters to the discharge tubing from the pump. All aliquots were placed in an ice chest and delivered to the IGS Geochemistry Section laboratory within 6 hours of collection where they were stored at 4°C until analyzed.

ALKALINITY

Total alkalinity (table 2) was performed by manually titrating each sample to a pH endpoint of 4.5 using standardized 0.02N sulfuric acid (H_2SO_4). The normality of the H_2SO_4 standard was checked prior to visiting each well site by titrating with 0.02N sodium hydroxide (NaOH). The normality of the NaOH solution had been determined by titrating with a solution of 0.02N potassium hydrogen phthalate (KHP) that was made from primary standard KHP obtained from the National Institute of Standards and Technology (NIST). Alkalinity determinations were completed in the laboratory within 24 hours of collection using the RAW aliquots. After water samples were allowed to equilibrate to room temperature, a 20 ml aliquot was pipeted into a titration flask and H_2SO_4 added

dropwise from a 50 ml buret calibrated in 0.1 ml increments until the endpoint was reached. The pH changes were monitored with an Orion Ross combination electrode attached to an Orion 940 meter.

Each sample was analyzed twice to monitor method precision. If the values differed by more than 5 percent, then a third titration was performed. Alkalinity values are reported as equivalent calcium carbonate ($CaCO_3$) in milligrams per liter (mg/L). In addition to total alkalinity, bicarbonate (HCO_3^-) and carbonate (CO_3^{-2}) ion concentrations were calculated from the alkalinity data (American Public Health Association; American Water Works Association; Water Pollution Control Federation, 1985b) and reported in mg/L.

ANIONS

Filtered, unacidified (F) samples were analyzed within 48 hours of collection for the anions chloride (Cl^-), bromide (Br^-), nitrate (NO_3^-), and sulfate (SO_4^{-2}) (table 2). A 100 microliter (μl) volume of each sample was injected into a Wescan Model 261, single column, unsuppressed Ion Analyzer with a conductivity detector. The Wescan analyzer was connected to a Shimadzu CR3-A integrator for peak processing. A resin-based Anion/R column from Alltech which was 250 millimeters (mm) long by 4.1 mm inside diameter with a guard column was utilized for peak separation. The aqueous carrier phase was 7 millimolar (mM) para-hydroxybenzoic acid (PHBA) with the pH adjusted to 8.4. A two-point calibration method was used to analyze for each of the anions. One EPA (Environmental Protection Agency) water-supply quality check standard (WS 378 Sample 17) and one water-pollution quality control standard (WP 1290) were run each day after calibration to check accuracy and day-to-day precision. In addition, a mixed standard from Alltech, containing fluoride (F^-), chloride (Cl^-), nitrite (NO_2^-), bromide (Br^-), nitrate (NO_3^-), phosphate (PO_4^{-3}), and sulfate (SO_4^{-2}), was run to verify peak separations and identification.

The lowest calibration standard for each anion was determined to be the lowest quantifiable concentration at which the relative standard deviation and relative error were less than 10 percent. Sample component values less than the lowest standard are reported as less than the lowest standard value. Duplicate samples were run for every tenth sample to determine analytical precision. Accuracy was determined from the relative error for the EPA check standards. Samples with component concentrations greater than the calibrated range were diluted and rerun.

Fluoride (table 2) was analyzed using an ion-specific electrode (ISE) (Orion, 1983; American Public Health Association; American Water works Association; Water Pollution control Federation, 1985c). An Orion fluoride ISE, model 94-09, and an Orion double junction reference electrode, model 90-02, were used with an Orion 940 meter. A three-point calibration from 0.1 parts per million (ppm) to 2 ppm was performed using standards prepared from a 1000 ppm stock solution. The stock solution was prepared from reagent grade sodium fluoride. Calibration was verified with three EPA check standards (WS 378 Samples 2, 5, and 17) that span the calibrated range. Interferences were minimized by adding 10 ml of an ionic strength adjuster, TISAB II (Orion, 1983), to 10 ml aliquots of each sample and standard. The relative standard deviation was determined based on the check standards and duplicate samples, and the relative error was calculated from check standards and spiked samples.

CATIONS

The 125 ml FA aliquot of each sample was analyzed for calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), total iron (Fe), total manganese (Mn), zinc (Zn), strontium (Sr), barium (Ba), and silicon (Si) by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) utilizing a Jarrell Ash model 975

The plasma gas flow was set at 30 liters (L) per minute and the auxiliary flow at 0.5 L per minute. The radio frequency (RF) forward power was set at incident of 1.0 kilowatt (kW) with the reflected power at less than 5 watts (W). The integration time was 0.5 seconds and each sample was exposed six times with the observation height 15 mm above the coil. A Rainin peristaltic pump and a Leeman cross flow nebulizer were used to introduce the aqueous samples into the torch.

Two calibration standards were prepared from Baker standard solutions with the first containing elemental concentrations at least ten times the detection limits of the instrument. The second standard contained one hundred times the amount in the first for all elements except potassium (K). Because of the weak energy band used for potassium, the lowest standard had to be spiked with the result that the high standard contained only 25 times the amount in the low standard. The instrument was recalibrated after each set of five samples was analyzed and the high standard was then run as a check standard. Commercial check standards or blanks were run within each group of five. The six burns per sample were averaged; if the relative standard deviation was greater than 1 percent, the sample was rerun. Based on relative standard deviations, two significant figures were reported for an element when the concentration was at least a factor of ten higher than the lowest standard, and one significant figure was reported when the concentration was less than a factor of ten higher than the lowest standard. Concentrations below the lowest calibration standard are reported as less than the lowest standard value.

METHANE

Ground-water samples for dissolved methane (CH_4) analysis (table 2) were collected at the well site by filling 10 ml glass syringes fitted with butyl rubber stoppers to which a plastic stopcock was attached. Samples were stored at 4°C and were analyzed within 72 hours of collection.

Methane analyses were performed by R. D. Shannon at the SPEA laboratories in Bloomington, Indiana. Dissolved methane concentrations in pore waters were determined by a phase equilibrium technique (McAuliffe, 1971). The volume of ground water was reduced to exactly 5 ml in the syringe, 5 ml of helium was added, the sample was shaken vigorously for 2 minutes, and the headspace gas was injected directly into a Shimadzu model GC-14A gas chromatograph with flame ionization detector. Samples were flushed directly from the syringes into a 2 ml injection loop, and carried by helium (50 ml/min) into a Poropak R column (80/100 mesh, 1 m by 3 mm). The oven temperature was kept at 70°C. Methane peaks were integrated using a Shimadzu CR501 integrator.

The detection limit for methane was 0.1 parts per million by volume (ppmV) (0.004 micromolar (μM) in ground water). The gas chromatograph was calibrated using certified ($\pm$2 percent) standards of methane in helium (Scott Specialty Gases, Plumsteadville, PA) and a two-point standard curve (1002 and 10,000 ppmV). For each standard, the mean peak area from triplicate injections was used for the calibration. Periodically, check standards (102.2 ppmV or 9.4 volume percent CH_4) were injected to confirm the linearity of the calibration.

CALCULATED DATA

Calculated data included the anion sum, cation sum, EPM (equivalents per million) balance, total dissolved solids (TDS), total hardness, and noncarbonate hardness (table 2). The anion and cation sums are the algebraic sum of the negatively and positively charged ions, respectively, in terms of milliequivalents per liter (Hem, 1985). The EPM balance measures the net charge of an aqueous sample and is computed as the percent difference between the cation and anion sums.

(Cation Sum - Anion Sum)/(Cation Sum +

Anion Sum) X 100 = EPM Balance (percent)

The theoretical value for the EPM balance is 0 percent. Analytical error or the presence of ions that were not analyzed may result in values other than 0 percent. Values of ± 5 percent are considered acceptable. Analytical values for samples with EPM balances outside of this range should be used only with caution when attempting to interpret the chemical data. Samples having EPM balances greater than ± 5 percent were not rerun because the recommended holding time for some ions had been exceeded (U.S. Environmental Protection Agency, 1979).

The TDS value (table 2) was calculated by adding the mass in milligrams per liter for each chemical component. This value was calculated to check the TDS values measured by ATEC using an evaporation technique (American Public Health Association; American Water Works Association; Water Pollution Control Federation, 1985d; ATEC, 1993). The measured TDS values are not included in this report because their analysis and quality assurance was the responsibility of ATEC.

The total hardness is related to calcium and magnesium content. Total hardness was calculated by converting the concentrations of calcium and magnesium ions to the equivalent concentration of $CaCO_3$ in terms of mg/L, then adding (American Public Health Association; American Water Works Association; Water Pollution Control Federation, 1985e). The calculation of noncarbonate hardness is determined by subtracting the value for alkalinity from that of total hardness. Noncarbonate hardness is defined as that portion of total hardness not derived from carbonate sources such as limestone ($CaCO_3$) or dolomite ($MgCa(CO_3)_2$). Examples of mineral sources of noncarbonate hardness are gypsum ($CaSO_4 \cdot 2H_2O$) and plagioclase feldspar ($CaAl_2Si_2O_8$).

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