Strontium and Other Notable Chemical Constituents of Well-Water of Allen County, Indiana[1]

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Abstract

Fourteen waters from aquifers in glacial deposits and 31 samples from aquifers in bedrock were obtained for a water quality study of Allen County, Indiana.

Analysis of the waters from aquifers in glacial deposits revealed relatively high concentrations of iron, strontium and sulfate. The iron is probably derived from pyrite in particles of Antrim Shale in the glacial deposits. The calcium-magnesium ratio decreases generally from north to south and may reflect southward increasing dolomite content of the glacial deposits.

Bedrock waters contain considerably less iron than waters from aquifers in glacial deposits, but are generally higher in strontium and sulfate. Strontium, sulfate, total solids, bicarbonate alkalinity, hardness and the strontium atom/1000 calcium atoms ratio increase from northwest to southeast; areal distributions of these constituents reflect relationships with bedrock stratigraphy and groundwater flow.

Introduction

During the preparation of a report on the environmental geology of Allen County, located in northeastern Indiana, N. K. Bleuer and W. C. Herring sampled well waters for determination of water quality to provide data for use in county planning. The wells were chosen to yield as much information as possible with a limited number of samples. The logs of these and many other water wells are available in the files of the Division of Water, Indiana Department of Natural Resources. Chemical analysis of the samples revealed that the groundwaters of Allen County are sufficiently unusual to warrant attention. The areal distribution of some constituents, in particular sulfate and strontium, suggests that analyses of well waters can be useful in stratigraphic studies.

Geology

Most of the land surface in Allen County consists of the rolling uplands of the Fort Wayne and Wabash Moraines. In the east-central part of the county lies the ancient low flat lakebed of glacial Lake Maumee, with its apex centered on the city of Fort Wayne. The Maumee River flows down the axis of this lakebed. The glacial deposits range in thickness from 40 to over 300 feet. The surficial geology has been mapped by Johnson and Keller (6), and the subsurface glacial stratigraphy, composed of the clayey till of the Lagro Formation above

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and the sandy tills of the Trafalgar Formation below, has been described by Bleuer and Moore (2).

Most of the county (Fig. 1) is underlain by Devonian carbonate rocks of the Traverse and Detroit River Formations; the northeast corner of the county is underlain by the Antrim Shale, and the very southern part is underlain by the Wabash and Salina. Formations of Silurian age. The lithologies of the Devonian rocks include black shale, fossiliferous and micritic limestones, laminated dolomite, carbonate collapse-breccias, and possibly evaporites. The lithologies of the Silurian rocks include massive, dense, argillaceous to silty dolomite and pure, vuggy, skeletal dolomite of the Wabash Formation and dense laminated dolomite to pure vuggy dolomite of the Saline Formation. The stratigraphic relationships of these units are discussed by Pinsak and Shaver (9) and by E. J. Doheny, J. B. Droste and R. H. Shaver (unpublished data). Within about 100 miles, downdip to the north, the Salina Formation includes significant evaporite deposits.

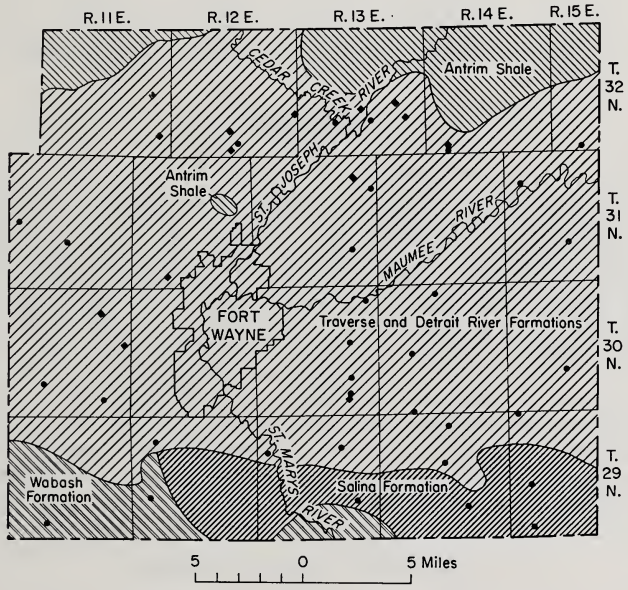

FIGURE 1. *Bedrock geology of Allen County, Indiana, with locations of water samples. (Dots represent bedrock aquifers and diamonds represent aquifers in glacial deposits.)*

Groundwater flow in the bedrock aquifer is toward the Maumee River from both the north and the south. The piezometric surface for wells completed in the confined (but leaky) bedrock aquifer (Fig. 2) reflects the surface topography. The static level of water in the aquifer is highest beneath the morainal uplands of the northwest and the southwest parts of the county, and lowest in the axis of the Maumee River within the glacial Lake Maumee plain.

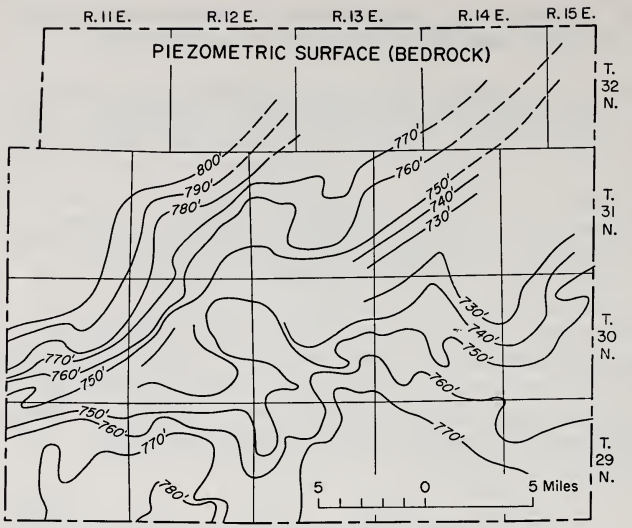

FIGURE 2. *Piezometric surface of water in bedrock aquifer, Allen County, Indiana.*

Methods

Water samples were obtained on June 6, 7, and 8, 1972. All samples were clear as sampled. After determination of alkalinity and pH, most of the samples were acidified and analyzed by R. K. Leininger and C. F. Foley; portions of four samples were analyzed by the Indiana State Board of Health, Indianapolis. Procedures from *Standard Methods for Examination of Water and Wastewater* (1) were used by the Indiana Geological Survey for determination of bicarbonate alkalinity (HCO_3^-), chloride, hardness (Ca, Mg, and Sr as $CaCO_3$), pH, sulfate, and total solids. No sample was found to contain carbonate or hydroxide. Atomic absorption spectrophotometry was used for determination of calcium, iron, magnesium, silicon, and zinc. Flame emission spectrophotometric methods were used for determination of aluminum, potassium, sodium, and strontium.

Discussion of Analytical Results

Thirty-three bedrock wells were sampled (Fig. 1), but two samples were eliminated from consideration because they are believed to have undergone home water softening treatment.

Iron values for the bedrock aquifer samples are difficult to assess in terms of areal differentiation, but are much lower than values for the glacial aquifer waters (Table 1). Bicarbonate alkalinity, hardness (Fig. 3) and chloride (not illustrated) show patterns of areal distribution. However, the strontium, sulfate and total solids values (Fig. 3) show the clearest evidence of the influence of bedrock and direction of groundwater flow. High concentrations of these constituents are derived

from the Silurian rocks in southern Allen County, and are modified by northward groundwater flow. These trends of increasing sulfate and total solids can be extended southeastward into Ohio (8) and southward into Adams County, Indiana (5).

TABLE 1. *Summary of range and median values for chemical constituents of waters of aquifers in glacial deposits and in bedrock. (Concentrations given in millgrams/liter.)*

	Glacial (14 Samples)			Bedrock (31 Samples)		
	range			range		
Constituents	low	high	mean	low	high	mean
Ca	58	207	108	31	132	81
Mg	27	86	50	26	70	44
Fe	1.1	25	5.4*	0.06	2.1	0.9
Sr	0.7	12.7	5.1	1.2	15.4	8.0
Na	8	43	25	16	50	38
K	5.2	11	7.1	5.4	10.3	8.2
HCO_3^-	330	569	467	152	438	303
Hardness	326	874	480	237	935	405
Tot. Solids	274	1150	620	238	1040	586
$SO_4^=$	4	510	151	6	630	214
Cl^-	0.9	23.3	4.1	1.1	37.9	6.8

*The median for 13 iron values, omitting the highest value, is 3.8 mg/l.

The determination of strontium concentrations (Fig. 3) are the most interesting geochemically because they are relatively high for groundwater. Skougstad and Horr (10) reported that of 175 groundwaters from water supplies in the United States, 60% were found to be less than 0.2 mg/1 in Sr. Rivers generally contain 0.5 to 1.5 mg/1, with the lower values in the midcontinent area. Hem (4) reports that the median Sr content of larger municipal water supplies is 0.11 mg/1.

Feulner and Hubble (3) reported on the occurrence of Sr in water in Champaign County, Ohio, where Sr concentrations of several tenths to 30 mg/1 were found in well waters from celestite-rich limestones of late Silurian age and glacial deposits that contain fragments of these limestones. Surface waters fed by springs or groundwater seepage from these celestite-rich limestones were reported to contain as much as 2.1 mg/1 Sr.

In a study of 100 Wisconsin municipal water supplies by Nichols and McNoll (7), all samples containing more than 1.0 mg/1 Sr were from the eastern part of the state from the Illinois border to the northeastern boundary with Michigan. The eastern part of the State (for which the high Sr values were encountered) is underlain by rock including evaporites of Devonian and Silurian age but rocks to the west are older and do not include evaporites.

Skougstad and Horr (10) reported atomic Sr/Ca ratios (number of atoms Sr/1000 Ca atoms) of 396, 285, and 208 calculated from data on three Waukesha, Wisconsin, wells. Two additional samples from

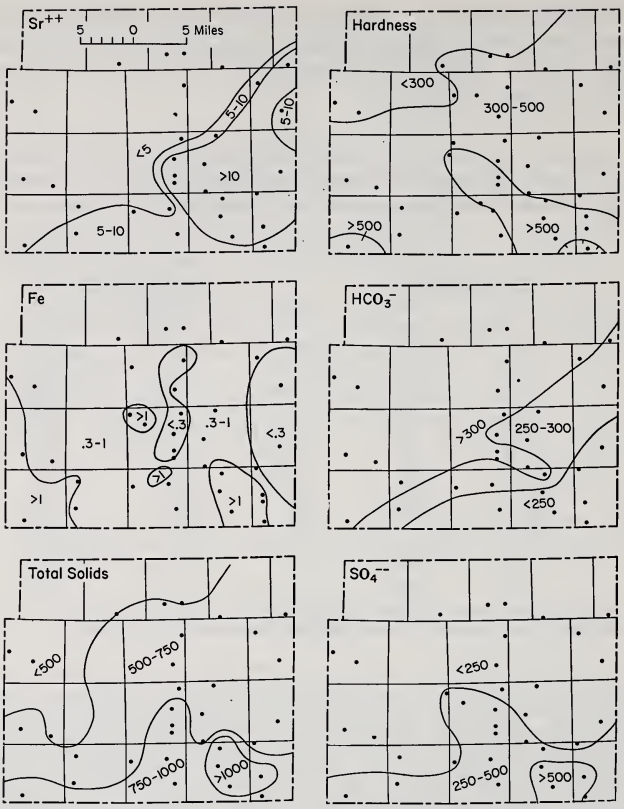

FIGURE 3. *Contour plots of concentrations of some constituents of waters from bedrock aquifer, Allen County, Indiana.*

this same area collected for Skougstad and Horr's study gave atomic Sr/Ca ratios of 162 and 65.5.

The waters from Allen County (bedrock wells) gave atomic Sr/Ca ratios as high as 134; ratios of 12 of the samples were above 41. These ratios, significantly, show an areal distribution when plotted as contours from low in the northwest part of the county to high in the east-central and southeast parts. The glacial aquifers also reflected higher than ordinary Sr/Ca ratios for groundwater, though lower ratios than for the bedrock aquifers.

Waters from glacial materials (Fig. 1) were sampled from one near-surface gravel aquifer, seven intersequence aquifers, from within the unit separating tills of the Lagro and Trafalgar Formations, five aquifers which are probably within the Trafalgar Formation and one basal sand aquifer.

Waters sampled from glacial deposits (Table 1) were generally unremarkable, with the exception of iron concentrations. The relatively

high iron values may be the result of pyrite in particles of Antrim Shale in the glacial materials. Strontium values are also higher than the reported median for larger municipal water supplies, but considerably lower than for the waters from bedrock aquifers. The zinc content of the glacial aquifer waters was generally significant, although the highest values are for samples high in iron.

Although the number of samples is not large, a decreasing trend of Ca/Mg ratios (from 2.5 in the northernmost tier of townships to 1.5 in the north-central and south-central tiers) is apparent, and may reflect increasing dolomite content of the drift. However, there is no obvious specific correlation between the results of any analyses and the stratigraphic position of the glacial aquifer.

Conclusion

What seems stratigraphically significant and enigmatic is that the Silurian rocks (not just Salina rocks) of several lithologies in Allen County appear to be the source of unusually high strontium and sulfate in bedrock water flowing toward the axis of the Maumee River from the south and southwest. Evaporites or their residues from which these ions would be most expected, of course, are present in the Silurian Salina Formation, but they are not known closer than about 100 miles to Allen County. The circulation of groundwater may dissolve the more soluble evaporites preferentially over carbonates, shales, or sandstones in the local strata, to the extent of forming caverns and subsequent collapse breccia, with residues of celestite or strontianite left behind. Such dissolved matter may reprecipitate farther along the direction of groundwater flow, possibly some distance from the original locality of supply or in permeable underlying strata. Bedrock waters flowing toward the Maumee River axis from the northwest through the Devonian dolomites have much lower concentrations of these ions. This is so despite the fact that evaporites occur in the Devonian strata just a few miles north of Allen County and that solutional collapse breccias are known in the Devonian rocks of Allen County itself. The authors believe that the high values of strontium and Sr/Ca ratios are similar to those anomalies reported in Wisconsin and in Ohio.

The areal pattern of strontium, sulfate, and other ionic constituents in well waters does seem to parallel regional stratigraphic boundaries, as modified by groundwater flow, and might well serve as a guide to future geochemical-stratigraphic correlation.

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