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AQUIFERS OF SOUTHWESTERN WISCONSIN

by

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SEASONAL GEOCHEMISTRY OF SPRINGS FROM DOLOMITE AQUIFERS OF SOUTHWESTERN WISCONSIN

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ABSTRACT

Twelve springs in Wisconsin's driftless area were sampled once a month for a year. The springs emerge from Middle to Lower Ordovician dolomites where local ground-water flow is often concentrated by thin shale layers. All springs contain very hard water of a calcium-magnesium-bicarbonate type which is supersaturated with carbon dioxide in comparison to the atmosphere. Springs emerging from the upper Prairie du Chien Group tend to be lower in total dissolved solids than springs located in dolomites higher in the stratigraphic column. Seasonal comparison of the water quality of the springs shows a January peak in pH, saturation index for calcite, and chloride; and an August peak in temperature and PCO₂. Total hardness and bicarbonate peaked in October. These effects (except for chloride) are due to carbonic-acid recharge to the springs during the growing season. The seasonal variation in geochemistry varied with each spring and was sometimes masked by discharge effects (dilution by spring runoff). The variation was large enough, however, to allow at least one spring to be considered as borderline between diffuse and conduit flow, according to the Shuster and White (1971) model. Two springs were supersaturated with calcite almost the whole year, although these were not depositing tufa. One spring seems to be receiving water contaminated with oxidized sulfide minerals (pyrite) on the basis of its unusual chemistry. The zinc concentration of all springs was less than 0.1 mg/l.

INTRODUCTION

Southwestern Wisconsin, part of the state's "driftless" area, is a gently dissected upland with mature dendritic drainage. The Paleozoic rocks in this region consist of approximately 200 m of mainly Ordovician dolomites which dip gently less than 1 degree to the south and southwest. Local relief is approximately 100 m, which increases to 150 m or more in the north, along the Wisconsin River, and in the southwest, along the Mississippi River. Ridges are broad or gently sloping, and are commonly capped by the Middle Ordovician

Sinnipee Group. Valley sides are steep with exposed outcrop; the broad, alluviated valley bottoms are generally in the Prairie du Chien group. A thin mantle of yellow-brown loess covers much of the area.

RELEVANT BACKGROUND MATERIAL

Compared to many geologic settings, the ground-water hydrology of carbonate rocks such as limestone and dolomite is poorly understood, because ground water can travel rapidly through conduits enlarged by solution of the bedrock. Much controversy continues to the present time concerning the nature of the karst water table and the origin of caverns. Well yields in karst areas can be highly unpredictable, depending on the number and nature of joints, fissures, and solution conduits that the well intersects.

Studies in limestone karst areas has shown the existence of two modes of ground-water flow (Shuster and White, 1971; White, 1969). In diffuse karst aquifers water travels relatively slowly and steadily through joints and fissures in the rocks. Because of the slow, steady travel of the ground water, it shows little variation in discharge and has a longer period to reach chemical equilibrium with the bedrock, allowing the ground water to become saturated with carbonate minerals (Shuster and White, 1972; Drake and Harmon, 1973). Conduit flow aquifers, on the other hand, exhibit highly variable behavior in both discharge and chemical characteristics. Conduit groundwater flow is localized by solutional modification of the bedrock, so that its travel time through the aquifer is much more rapid than that of diffuse flow.

Karst aquifers which exhibit conduit flow are unusually sensitive to pollution, because contaminants which enter the ground water have little opportunity to become filtered out as they travel through the aquifer. These contaminants can travel much more rapidly and easily through conduits, causing undesirable pollution of the drinking water supply.

STATEMENT OF THE PROBLEM

The dolomites of southwestern Wisconsin show some characteristics of karst aquifers: solution features such as sinkholes, caverns, and solution-widened joints and bedding planes can be found in scattered locations where the units crop out (Day, 1986, and Spong, 1980). Even some conduit flow has been found and dye-traced by Mohring and Alexander (1980) for the same aquifers in nearby southeastern Minnesota. Compared to other well-known

karst areas of the U.S.A., however, the surface karst features of southwestern Wisconsin are subdued, and the caves small. The purpose of this investigation was to determine how the geochemistry of the ground water varied seasonally, particularly with regard to whether ground-water flow through these dolomite aquifers occurs as diffuse and or conduit flow.

METHOD

The project involved one year of data collection. Twelve springs, carefully chosen to represent various stratigraphic horizons in the dolomites, were sampled once monthly beginning October 1980 and ending October 1981. Spring locations are shown in Figure 1. Other pertinent information regarding the springs is listed in Table 1. At the time of collection temperature, electrical conductivity, and pH were measured in the field. Samples were then chilled and returned to the lab where the bicarbonate content was measured immediately. Finally, the samples were acidified for later analysis of calcium, magnesium, chloride, sulfate, iron, nitrate, and sodium content using colorimetric, titrametric, and atomic absorption techniques. Later computer analysis calculated the saturation indices with regard to calcite and dolomite (S_{1c} and S_{1d}), the theoretical aqueous carbon dioxide partial pressure (PCO₂), the calcium to magnesium equivalence ratio, and the percent charge-balance error for each sample.

CARBONIC ACID EFFECTS

The most pronounced seasonal effect on spring geochemistry in the study area was that caused by the recharge of carbonic-acid rich groundwater during the late summer and early fall growing season. This results in a growing season increase in temperature and PCO₂. The latter was calculated from the temperature, pH, and bicarbonate concentrations, and is expressed in atmospheres as a logarithm in Figure 2. Since atmospheric carbon dioxide partial pressure is 10^{-3.5} atmospheres, it is apparent that all of the spring waters are supersaturated with carbon dioxide in comparison to the atmosphere. During the summer growing season, the carbon dioxide partial pressure in the soil zone is greater because of the higher temperature, rate of decay, and plant root respiration. Percolation of water through this zone increases the carbon dioxide partial pressure of the shallow ground water during the summer. This results in a pH decrease because of the formation of

carbonic acid, which then partially dissociates to bicarbonate.

The growing season recharge of carbonic acid results in a corresponding increase in bicarbonate and also total hardness, because more carbonate rocks dissolve in the presence of the acid recharge. Both the bicarbonate and total hardness reach a maximum in October, then gradually decline until March and April. Some springs showed sudden temporary declines due to rapid recharge and dilution from spring snowmelt. The date of absolute maximum and minimum sampled values for bicarbonate and total hardness varied slightly with each spring, depending on its response time to the carbonic acid recharge. The response time, in turn, is most likely a function of the capture area size, the topographic relief, and the degree of conduit flow for each spring. Runde spring, for example, did not reach its minimum bicarbonate content until June, or its maximum until January, a two to three month delay. Of all the springs, Montfort spring showed the greatest seasonal variation in bicarbonate concentration and total hardness.

The summer recharge of carbonic acid rich ground waters causes a decrease in the degree of carbonate saturation because greater bicarbonate and hardness values are needed in the groundwater to achieve saturation at the lowered pH levels (Figure 3). Two springs stand out above the background of the remaining ten. Montfort and Potosi springs are both supersaturated with calcite most of the year, and with dolomite part of the year. Both are most supersaturated with these minerals in early spring; Montfort in January, Potosi in March. It is during these months that the water is least able to dissolve calcite and dolomite due to its relatively high pH, or lack of carbonic acid. On the other hand, during the late growing season (October), recharge of carbonic acid rich groundwaters causes a decrease in the degree of carbonate saturation.

As both Montfort and Potosi springs are supersaturated with calcite much of the year, both are capable of depositing tufa. Two other tufa depositing springs, not included in this study, showed very similar (even somewhat lower) SI_c values compared to these springs (Heller, 1986). Montfort and Potosi springs are not depositing tufa probably because the spring openings are situated quite close in both distance and elevation to a surface stream, which rapidly dilutes the spring water and reduces its saturation level. The tufa depositing springs, on the other hand, are located on cliffs high above surface streams. The vertical fall of the water promotes rapid degassing of carbon

dioxide and subsequent calcite deposition on a tufa mound along the cliff face directly below the spring outlet.

Figure 3 also shows that although the same seasonal trends are present, all springs are less saturated with dolomite than they are with calcite. This reflects the kinetically slower dissolution rate for dolomite compared to that of calcite. This effect is substantiated by Figure 4, which shows that the seasonal peak for magnesium occurs about one month after the late summer calcium peak. In this case the slower dissolution rate for dolomite delays the release of magnesium ions into the ground water.

SNOWMELT RECHARGE EFFECTS

A winter thaw event in late February 1981 caused rapid recharge of snowmelt into the aquifers, resulting in a dramatic drop due to dilution of bicarbonate, total hardness, temperature, sulfate, and magnesium of some springs (Figures 2, 4, and 5). The event caused a sudden rise in the calcium ion concentration with a corresponding drop in magnesium, followed by a rise in magnesium a month later. The February thaw released almost enough calcium into the water to bring some springs up to their peak late summer values, although this effect was temporary. Two possible explanations are postulated for this calcium peak: 1) The snowpack itself contained a calcium source from dust or air pollution, so that the meltwater recharge was rich in calcium ions but diluted the ambient magnesium concentration of the ground waters. 2) The snowpack contained enough acid of a non-carbonic type to quickly dissolve the limestone portions of the aquifer (enriching the recharge in calcium ions), then more slowly dissolving the dolomitic portions of the aquifer (causing the magnesium peak a month later). Since the ground-water sulfate concentration is also diluted by the thaw (Figure 5), the only possible source of acid in the snowpack is nitric. The nitrate plot shows some indication of a snowmelt peak for February, although this peak was well within the error range for this parameter.

Acid rain is a well-documented problem in the Midwest. Southwestern Wisconsin precipitation averaged pH 4.6 in 1979 (Ember, 1981). Acid precipitation storage in the winter snowpack, and a subsequent flush of acid recharge in the spring, is also a well-known phenomenon. Given the lack of a calcium source in the snowpack (no nearby dust-producing quarries), the delayed magnesium peak in the ground water, and the abundance of acid

precipitation in the study area, the second explanation is more likely.

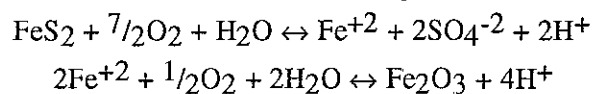
OTHER EFFECTS

Most springs contained less than 20 mg/l chloride, but Union, Tracey, and University springs showed higher concentrations (Table 2). Quite a few springs showed a seasonal chloride peak in December due to contamination from road salts. (Interestingly, not all of these springs were located adjacent to country roads; some may be receiving chlorides from cattle salt licks). A few (Union and Potosi) showed later seasonal peaks, probably due to a delayed flushing of road salts through the system.

Four springs consistently showed fewer dissolved components, particularly magnesium, than the other eight (Table 2). Castle Rock, Big Spring, Green River, and Sixmile Spring, all of which issue from the Prairie du Chien group, also generally showed larger estimated discharges (see Table 1). These phenomena are the probable result of 1) the enhanced permeability of the Prairie du Chien Group due to the exhumation of a lower Ordovician karst surface represented stratigraphically as an unconformity between the Prairie du Chien Group and the overlying St. Peter sandstone, and 2) the sulfide mineralization of the Sinnipee Group, which causes the eight springs in this aquifer to be higher in total dissolved solids from sulfide weathering (discussed below).

Castle Rock and Green River springs showed an interesting seasonal trend in their calcium to magnesium equivalence ratios: the springs showed a higher proportion of calcium to magnesium during the spring months, compared to most springs whose ratio did not change significantly during the year. It is quite likely that these two springs received more limestone derived recharge during the spring months when water levels were higher.

Some springs deriving water from the Sinnipee Group were affected by the weathering of sulfide minerals in this aquifer, particularly pyrite and sphalerite. Oxidation of pyrite by contact with aerated ground water contributes iron, sulfate, and acid to the water by the following reactions:



The extra hydrogen ions reduce the pH of the water, thus allowing more calcite and dolomite to dissolve. University spring was most strongly affected by pyrite oxidation (Table 2). It also showed elevated levels of both nitrate and

chloride, indicating possible contamination by sewage or animal wastes. The zinc concentration of this spring, as well as all the others, was less than 0.1 mg/l.

IMPLICATIONS FOR CONDUIT VS. DIFFUSE FLOW

Montfort spring showed the greatest seasonal variability in chemical parameters, behaving more like a conduit spring than any of the others except for its carbonate saturation characteristics. Unlike conduit springs in other karst areas, the Montfort spring discharge fluctuated very little, and the water never became turbid from suspended sediments. Shuster and White (1971) used a coefficient of variation for total hardness to distinguish conduit springs:

$$CV = 100 \sigma/x$$

σ = standard deviation of total hardness values

x = arithmetic mean of total hardness values

CV = coefficient of variation

These authors found that most conduit springs had a coefficient of variation of 10-25%; most diffuse springs had a coefficient of variation of less than 5%. The coefficient of variation for Montfort spring's total hardness was 6.7%. Unfortunately the coefficient of variation also depends upon sampling frequency; if Montfort spring had been sampled daily (for a year) rather than monthly, its coefficient of variation may have been larger. From the evidence in this study, however, it seems likely that "classical" conduit flow does not occur in Montfort spring or any of the others sampled. What does seem likely, based on well drillers reports, observation of the many small local dolomite quarries, and the fact that small caverns do exist in the area, is that ground-water movement does occur as turbulent flow through somewhat widened bedding planes and joints (known as "crevices" to well drillers). It can be characterized neither as true conduit nor true diffuse flow, but lies somewhere in between, probably closer to the latter.

SUMMARY

Carbonic acid recharge during the growing season produced early fall peaks in temperature, total hardness, aqueous carbon dioxide partial pressure and bicarbonate, and early spring peaks in pH and the saturation indices for calcite and dolomite. A winter thaw event caused a dilution effect in

bicarbonate, total hardness, sulfate, and magnesium of some springs, although the same thaw produced a calcium ion surge in these same springs, possibly due to acid precipitation recharge. A few springs showed contamination from sulfide mineral oxidation and road salts. The four springs emerging from the Prairie du Chien Group were lower in total dissolved solids from those emerging higher in the stratigraphic column, probably due to the greater overall permeability of this aquifer and its lack of sulfide mineralization. Ground-water flow in the dolomites was neither completely diffuse nor conduit in its geochemical behavior, but somewhere in between.

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Table 2. Mean chemical parameters for each of the twelve springs, based on twelve monthly samples.

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Figure 2. Mean values for all springs showing seasonal variations in the theoretical aqueous partial pressure of carbon dioxide, or PCO_2 , and bicarbonate concentration. PCO_2 is expressed in atmospheres as a negative logarithm of 10, so carbon dioxide partial pressure increases toward the bottom. Small arrow shows snowmelt recharge event

Figure 3. Mean values for all springs showing seasonal variations in the saturation index for calcite and dolomite, both expressed as a logarithm of 10. Water above the zero line is supersaturated; water below the zero line is undersaturated. Montfort and Potosi springs are indicated separately.

Figure 4. Mean values for all springs showing seasonal variations in the calcium and magnesium ion concentrations. Small arrow marks a snowmelt recharge event.

Figure 5. Mean values for all springs showing seasonal variations in the nitrate and sulfate concentrations. Small arrow marks a snowmelt recharge event.

Table 1

NAME ABBREV.	GROUP FORMATION MEMBER	ELEV	7 1/2 QUAD	LOCATION	ESTIM GAL/MIN
Arthur AR	Sinnipee Decorah Guttenberg	950	Rewey	Trout pond, E bank of Little Platte Riv. T4N R1W SEC 1 SE1/4 SW 1/4 UTM 092466	1000
Big Spring BS	Prairie du Chien	890	Highland W	Located on topographic map T7N R1E SEC 18 SE 1/4 SE 1/4 UTM 107726	2000
Castle Rock CR	Prairie du Chien	820	Castle Rock	Located on topographic map T7N R2W SEC 36 SW 1/4 NE 1/4 UTM 992678	3000
Green River GR	Prairie du Chien	840	Long Hollow	Pnd on W. S. Collins property T6N R3W SEC 4 SE 1/4 SE 1/4 UTM 851654	2000
Montfort MT	Sinnipee Platteville Pecatonica	1010	Montfort	Pipe on D. Thomas farm, Badger Hollow T6N R1E SEC 19 NW 1/4 SE 1/4 UTM 106615	40
Pecatonica PC	Sinnipee Decorah Guttenberg	1055	Linden	Culvert under County X, Caygill property T5N R1E SEC 13 NW 1/4 NW 1/4 UTM 182547	300
Potosi PT	Sinnipee Galena Prosser	765	Potosi	Pool next to old brewery T3N R3W SEC 34 NE 1/4 SW 1/4 UTM 873285	50
Runde RD	Sinnipee Galena Prosser	1005	Rewey	Pond on Runde property T4N R1W SEC 36 NE 1/4 SE 1/4 UTM 102390	?
Sixmile SX	Prairie du Chien	740	Highland W	Located on topographic map T7N R1W SEC 2 NW 1/4 SE 1/4 UTM 068759	500
Tracey TR	Sinnipee Platteville Pecatonica	960	Rewey	South bank of trib. to Litt. Platte Riv. T4N R1W SEC 24 SW 1/4 NW 1/4 UTM 091422	100
Union UN	Sinnipee Platteville Pecatonica	980	Ellenboro	Located on topographic map, springhouse T4N R1W SEC 7 SE 1/4 NE 1/4 UTM 018453	50
University UV	Sinnipee Decorah Guttenberg	835	Dickeyville	South bank of Rountree Branch T3N R1W SEC 16 SW 1/4 SW 1/4 UTM 046336	60

Table 2

CHEMICAL PARAMETER	UNITS	CR	BS	GR	PC	MT	SX	PT	TR	AR	UV	UN	RD
pH	—	7.10	7.10	7.10	7.05	7.25	7.25	7.25	6.95	7.00	6.75	6.95	6.90
Temp	deg C	10.1	9.8	10.3	9.5	9.1	10.1	10.1	9.5	9.6	10.0	9.2	9.7
SPC	uhos/cm	405	669	427	514	507	323	573	605	541	1070	605	504
HCO3	mg/l	328	315	340	371	409	279	456	386	373	476	440	401
Tot. Hard.	mg/l CaCO3	281	269	296	349	369	227	395	369	368	715	420	346
Ca	mg/l	72.1	63.9	78.3	77.6	85.2	51.9	91.4	85.7	83.2	157	100	78.2
Mg	mg/l	24.5	26.5	24.3	37.6	37.9	23.6	40.5	37.6	38.8	78.2	41.2	36.5
Cl	mg/l	8.7	10	10	16	12	6.0	13	36	16	56	35	7.4
NO3	mg/l	7	6	8	19	15	5	10	10	31	39	27	10
SO4	mg/l	14	14	20	28	25	9	37	42	40	378	31	24
Fe	mg/l	0.01	0.01	0.02	0.01	0.02	0.02	0.01	0.01	0.05	0.07	0.02	0.02
Na	mg/l	4	3	3	5	3	2	8	14	5	57	14	3
Ca/Mg	—	1.8	1.46	1.97	1.26	1.37	1.35	1.39	1.39	1.32	1.26	1.5	1.32
Slc	—	-0.2	-0.26	-0.12	-0.19	0.08	-0.22	0.16	-0.22	-0.21	-0.16	-0.12	-0.31
Sld	—	-0.38	-0.40	-0.32	-0.30	-0.05	-0.34	-0.04	-0.34	-0.32	-0.25	-0.27	-0.43
PCO2	—	-1.66	-1.69	-1.68	-1.57	-1.73	-1.91	-1.68	-1.48	-1.53	-1.20	-1.41	-1.37
ERROR	%	2.03	2.91	2.89	1.64	1.96	4.05	3.12	2.44	2.13	3.29	1.69	2.83

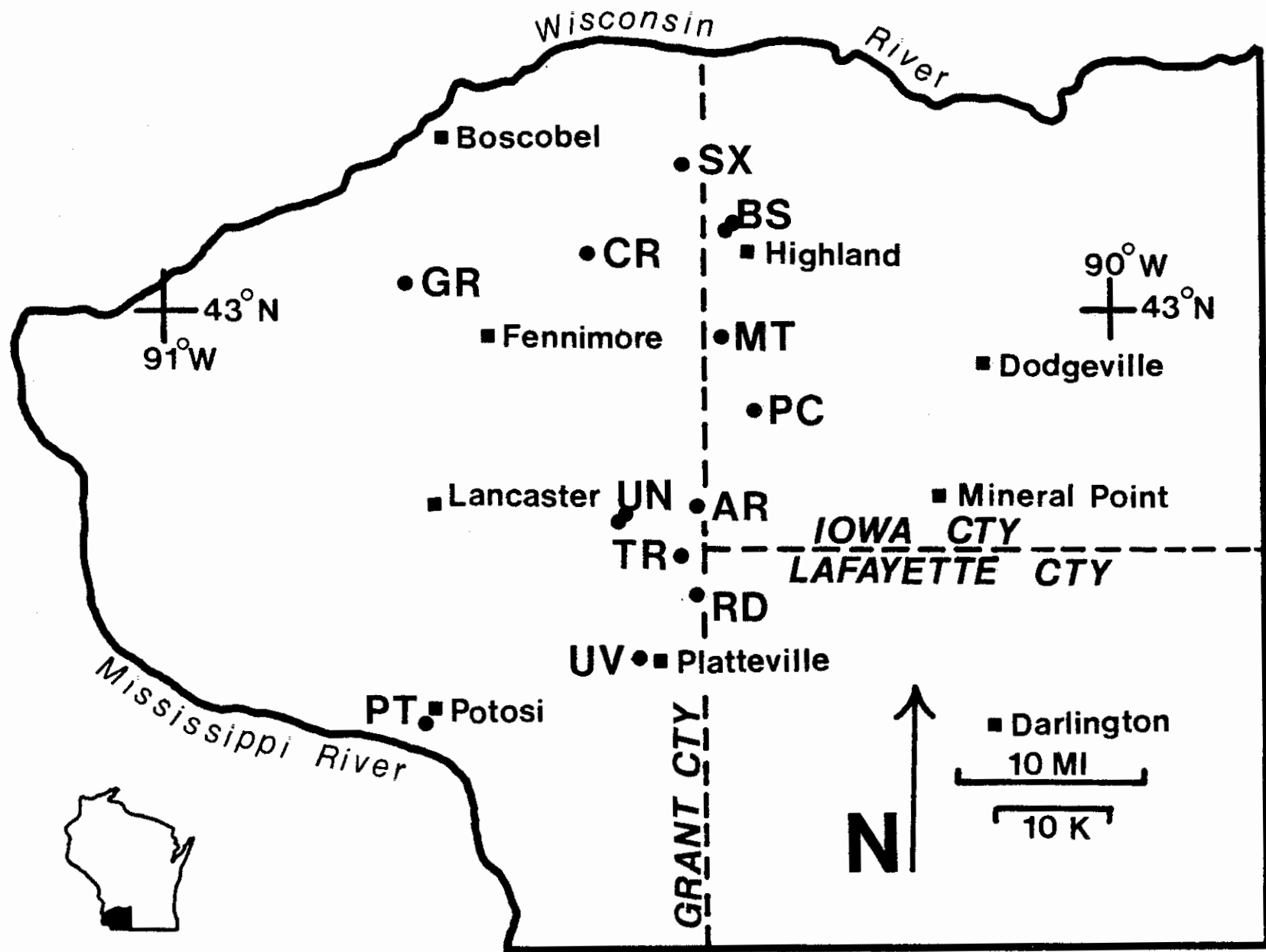


FIG 1

FIG 2

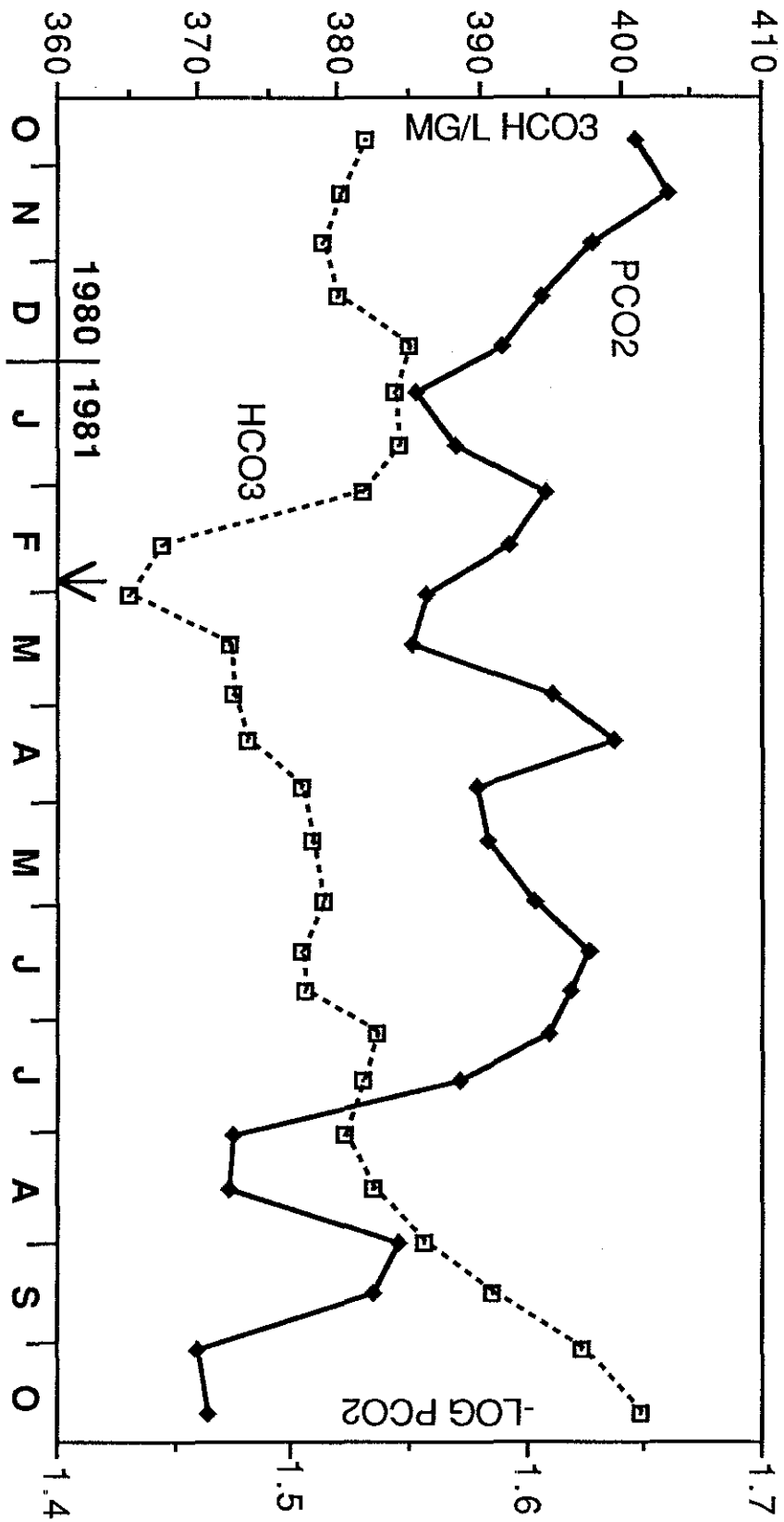


FIG 5

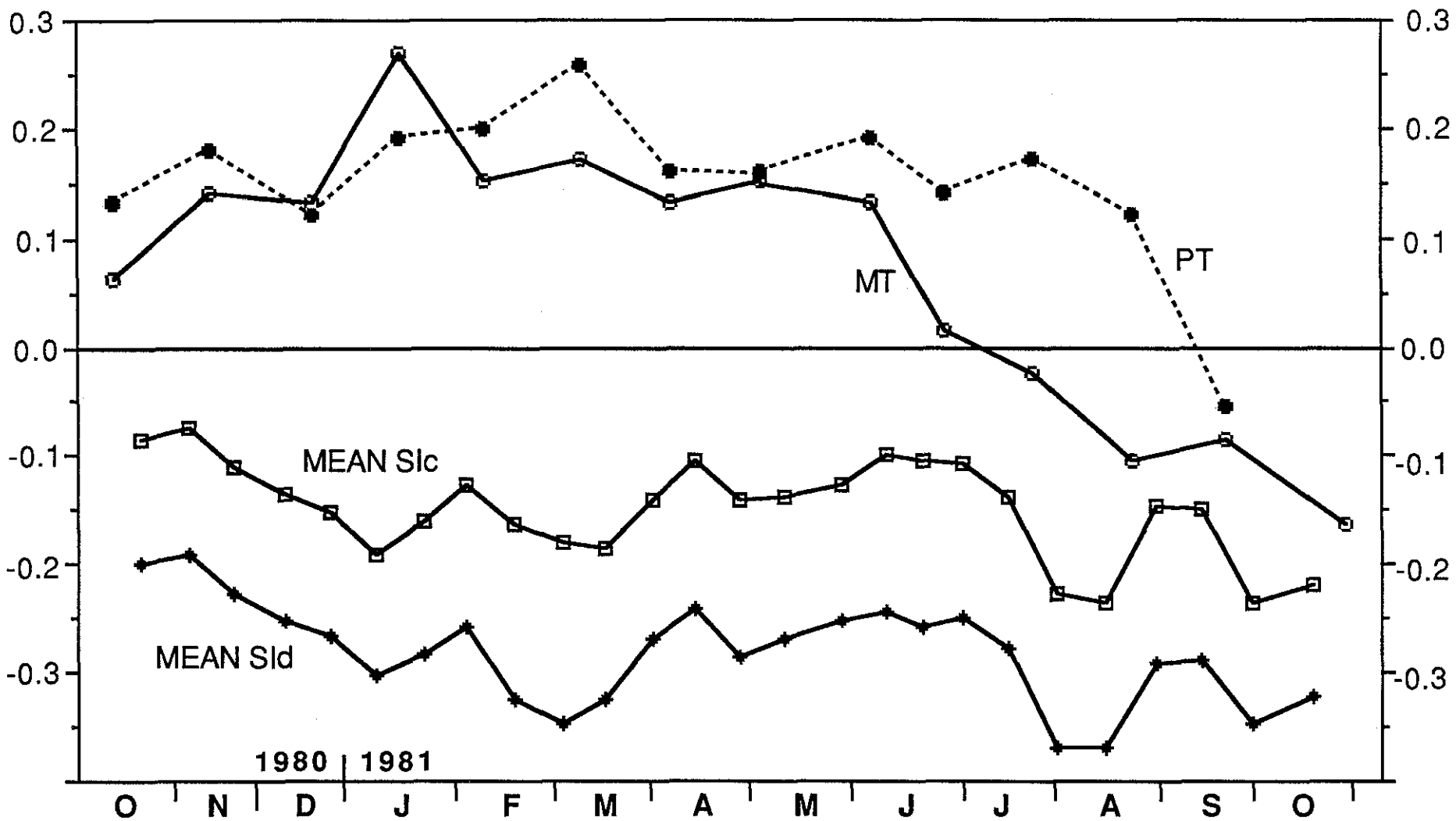


FIG 4

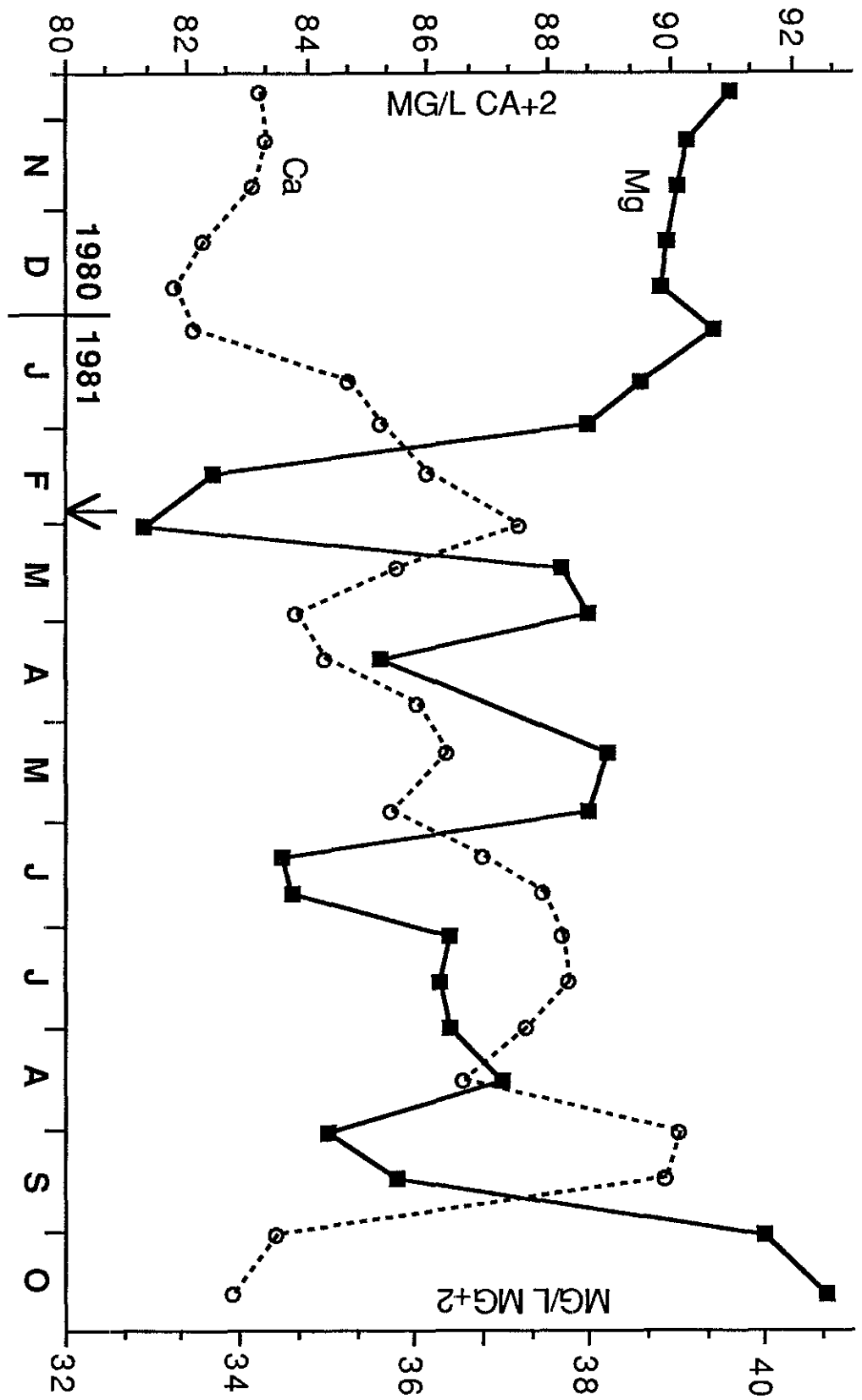


FIG 5

