

COMPARISON OF BASE FLOW AND GROUNDWATER CHEMISTRY, OAK OPENINGS SAND, LUCAS COUNTY, OHIO^{1, 2}

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The Oak Openings Sand is a narrow belt of medium to fine-grained unconsolidated sand, underlain by glacial till, located just west of Toledo, Ohio and extending up into southern Michigan. Analysis of surface and groundwater samples from the poorly drained aquifer, in which the watertable is within five feet of the surface, indicates that the water quality generally is within Federal Drinking Water Limits. Equilibrium calculations of dissolved species suggest that both ground and surface waters are nearly saturated with respect to carbonate minerals, but undersaturated with respect to gypsum. Chemical and water quality data for three sampling periods are reported.

The Oak Openings Sand is a narrow, unconsolidated unit of medium-to-fine grained, moderately sorted sand extending about 80 miles southwest from Pontiac, Michigan into Lucas and Fulton Counties, Ohio. It is generally 1 to 2 miles wide and locally up to 40 feet thick. The physical and stratigraphic features have been described by Forsyth (1968) and Burke (1973).

An area of about 4,600 acres in the Oak Openings Sand located 14 miles west of Toledo and immediately northeast of Toledo Express Airport (fig. 1) has been selected by the Lucas County Renewal Department for future development. At the present time, the area is rural

with a population density of about 0.3 persons per acre and is heavily forested with slight agricultural use. Water supplies are generally obtained from shallow drive points, and sewage is disposed through septic tanks. It provides a good opportunity for determining changes in aquifer characteristics resulting from urbanization, by comparing its condition at the present time to that following development. Because the area is drained by a system of ditches, generally sustained by seepage from the aquifer, water chemistry changes between ditch water and groundwater can be compared in terms of dilution, external CO₂ pressure, and ion exchange.

The present investigation is part of a larger program to determine the hydrologic condition of the surficial sand aquifer. In addition to providing detailed base data on major and trace constituents for three sampling periods, surface and groundwater quality were compared, and solubility calculations were made to determine the degree of saturation of carbonate and sulfate minerals. When used as base data along with hydrologic parameters, this information will be useful for predicting effects of future urbanization.

GENERAL DESCRIPTION OF THE AQUIFER

The study area in the Oak Openings Sand is characterized by low reliefs which crests in a subtle ridge trending NE-SW with lateral slopes averaging about 5 feet per mile (fig. 1). It is about 30 feet thick near this ridge and thins to about 15 feet near the borders of the area (Burke, 1973). Immediately below the aquifer is a clay-rich till, about 30 feet thick, which is underlain by several hundred feet of Silurian-Devonian carbonates (Rowland and Kunkle, 1970). High infiltration capacity (120-260 gpd/sq. ft.)

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²This paper is based, in part, on the MS thesis of Nicholas Valkenberg (1973).

combined with relatively low permeability of clay-rich material below results in a shallow water table generally from 5 to 7 feet which may occasionally reach the surface after heavy precipitation. About 87% of precipitation reaches the water table while about 13% is returned through evapotranspiration (Hilty, 1971). Hilty studied such a small area that the possibility of surface runoff was not precluded. The area is drained by a system

of ditches because no natural streams occur, and most of the ditch water originates as groundwater.

The mineralogy of the aquifer was not studied in detail, but preliminary X-ray and optical examinations indicated that quartz composed about 85% or more of the mineral assemblage, with feldspar, carbonates, chlorite and illite making up the remainder. It is not known if the carbonates are secondary or were

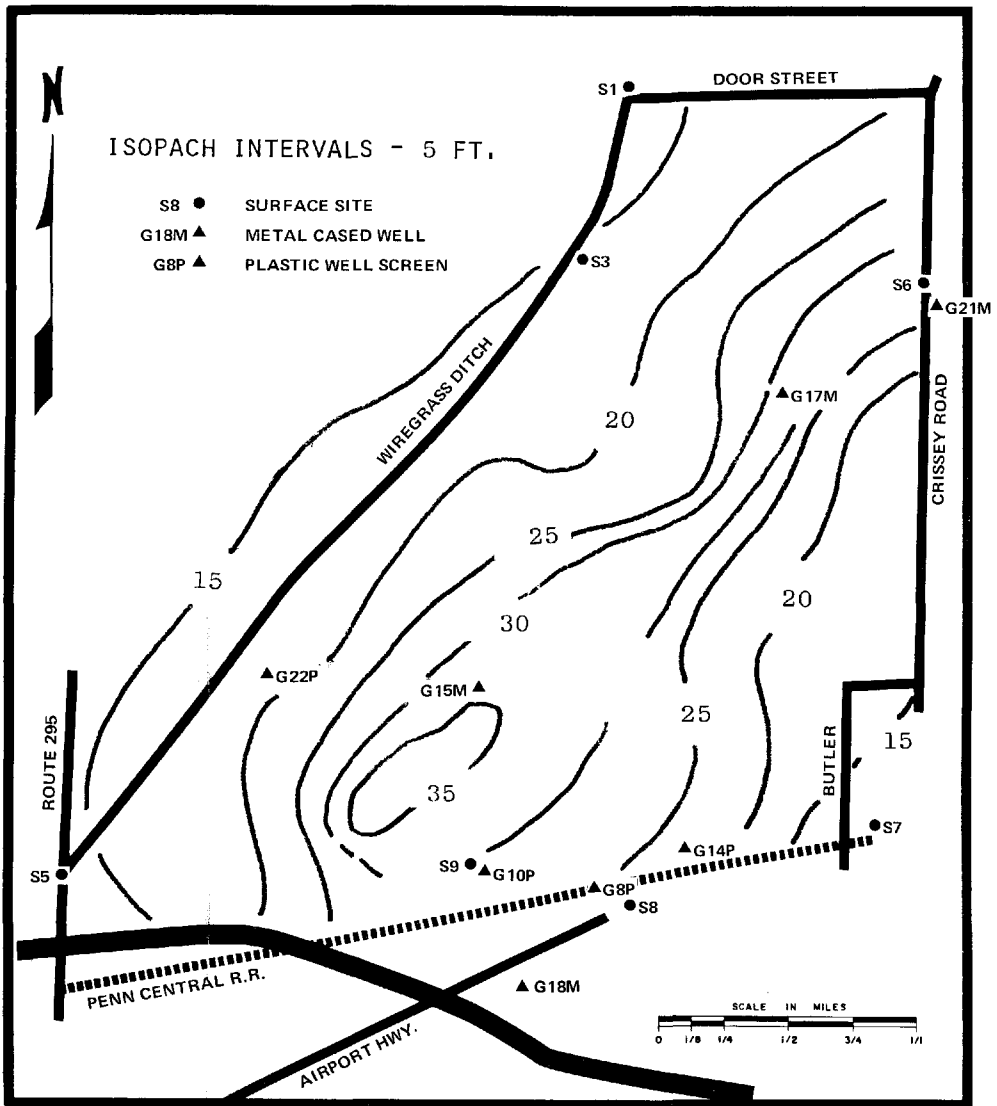


FIGURE 1. Isopach map of Oak Openings sand body with sample locations. Prefix S refers to surface samples sites and G to observation well sites. M refers to metal cased wells and P to plastic cased wells.

derived from the Paleozoic rocks, but locally they may compose up to 10% of the sand. The aquifer has been described as a composite beach ridge of glacial origin similar to others in the Michigan-Ohio-Indiana area (Forsyth 1968, Burke 1973).

SAMPLING AND ANALYTICAL PROCEDURES

Surface and groundwater samples were collected from ditches and shallow observation wells, on October 14, 1972, January 19, 1973, and March 9, 1973. The sampling locations and observation wells are shown in figure 1. In general, the ditches draining the area are not more than 5 or 10 feet wide and samples were collected near the center of flow at mid-depth. Groundwater samples were collected by the air lift method using a header described by Trescott and Pinder (1970) from either wells with metallic casing or wells with plastic (non-metallic) casings. In general, the deeper wells were metal-cased and extended to deeper portions of the aquifer (about 30 feet, but not into the till) while the plastic well screens were usually a few feet below the water table. Before collecting a well sample, each well was pumped until at least 10 well-volumes of water had been discharged in order to insure collection of fresh groundwater. Duplicate samples were collected at each site in pre-cleaned Nalgene bottles which were also rinsed with the water collected. One sample from each pair was acidified with HCl to about pH 3 and used for analyses of alkalies, alkaline earths, and sulfate. The untreated sample was used for conductance, TDS, nitrate, and chloride determinations. Temperature and pH were determined in the field. The portable pH meter was set at the sample temperature and calibrated with standard buffer solutions brought to within 1°C of the sample temperature.

The total calcium and magnesium concentrations were determined on the acidified samples by atomic absorption spectroscopy by direct aspiration. Sodium and potassium were determined by flame emission. Concentrations of nitrate, chloride, sulfate and TDS were determined by methods recommended in Standard Methods for the Examination of Water and Waste Water (1965). Nitrate was determined by the brucine method, sulfate by the turbidimetric method, chloride by the argentometric method, and TDS by filterable residues.

Alkalinity levels were not determined directly, in part because of lack of facilities for analysis immediately after collection. Alkalinities used in equilibrium calculations were calculated from the cation-anion balance using the following relation:

$$(1) \quad \text{HCO}_3(\text{mg/l}) = [\sum \text{cations}(\text{meq/l}) - \sum \text{anions}(\text{meq/l})] \times \text{eq. wt. HCO}_3$$

Determinations of alkalinity by conventional potentiometric methods on spot samples col-

lected later were within 10% of the estimated values.

The error in precision determined by three replicate analyses on at least half the samples collected was generally less than 10% depending on the species and method used. About half this error was associated with calcium and magnesium. The largest uncertainty, of course, was in the alkalinity and a conservative estimate of pH values is ± 0.2 units. Solute concentration differences in Oak Openings sand water, both seasonally and with respect to sample locations, was several orders of magnitude greater than these errors. Chemical data for the surface and well samples are listed in table 1 for the three sampling periods. Analyses for trace amounts of lead, cadmium, zinc, and iron indicated that lead and cadmium were below atomic absorption detection limits, and zinc was generally less than 0.05 ppm, but locally present up to 1 ppm. Iron concentrations were about 0.5 ppm, varying locally up to 2 or 3 ppm. The high values of iron and zinc were from a well near an abandoned, small junk yard, but probably would have been higher, if junk yard leaching was a significant contributor.

EQUILIBRIUM CALCULATIONS

Activities of solute species, ionic strength, and P_{CO_2} values were calculated from the chemical data in table 1 using a program written by Wigley (1972). The program computes activities with respect to calcite, dolomite, and gypsum and derives saturation indices for these minerals along with $\text{Ca}^{++}/\text{Mg}^{++}$ and $\text{Ca}^{++}/\text{SO}_4^-$ molar ratios. Wigley's program was selected because most groundwaters in Northwestern Ohio are associated to some degree with carbonate aquifers, and even though the Oak Openings Sand is separated from carbonate by a till layer, the above noted minerals are most likely to precipitate from over saturated waters in this area as suggested by the presence of carbonate minerals in the sand. Moreover, Rowland and Kunkle (1970) have suggested that the Silurian-Devonian aquifer contributed carbonate bearing water to the sand in the past.

Activity coefficients were calculated from the Debye-Hückel equation using ionic strengths corrected for ion pairing. Solubility products for carbonates were taken from Langmuir (1971). The constants for calcite (c), dolomite (d), and gypsum (g) are expressed by Wigley as follows:

$$(2) \quad \text{pK}_C = -8.3389 - .001236T - .00005T^2$$

$$(3) \quad pK_D = -16.56143 - .012486T \\ - .00005T^2$$

$$(4) \quad pK_g = -4.6535 + .004545T \\ - .00010T^2$$

where $pK = -\log K$ and T is the temperature in degrees Celsius. Saturation indices are derived in terms of these constants and equal $\log(IAP/K)$, where IAP is the ion activity product of the mineral whose saturation level is desired. For example, the saturation index for gypsum (SATGYP) is $\log(aCa^{++} \times aSO_4^{-})/Kg$. When the saturation index is zero, the water is saturated with respect to the mineral in question, when less than zero the water is under-saturated, and when greater than zero, it is super-saturated. The saturation indices calculated with Wigley's (1972) program for each of the three minerals use ion activities corrected for common ions and ion pairing.

The Ca^{++}/Mg^{++} ratios of natural waters have significant geochemical implications. Ratios close to unity suggest equilibrium with dolomite while higher values imply calcite equilibria, when sulfate is low. The Ca/SO_4 ratio, if close to unity, implies gypsum equilibrium and when higher, suggests input of carbonate calcium. These implications would, of course, inspire more confidence when applied to closed carbonate aquifer system. They appear, however, to be useful for interpreting water quality in shallow sand aquifers, if consideration is allowed for other possible processes such as soil influence on P_{CO_2} , incongruent solution of dolomite, and bacterial sulfate reduction.

The results of the computer calculations using the data of table 1 are shown in table 2. With ion activities, saturation indices, P_{CO_2} values, and cation ratios. P_{CO_2} values were calculated from

TABLE 1
Chemical data for waters in the Oak Openings Sand.¹

Sample No.	T°C	pH	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	ALK	SO ₄ ⁻	Cl ⁻	NO ₃ ⁻	Cond. μ	TDS
October 14, 1972												
S1	14	7.6	116	22	56	4	364	75	86	3	912	542
S3	12	7.6	93	16	11	3	290	57	19	3	579	333
S5	14	7.8	86	15	14	2	285	49	17	1	532	323
S6	12	8.1	89	15	19	3	284	46	29	3	567	336
S7	10	7.5	69	12	21	3	212	62	25	6	502	237
S8	13	7.8	96	15	24	37	244	123	51	4	689	383
S9	13	7.3	81	11	6	1	180	97	5	4	472	261
G8P	15	8.1	122	30	12	5	481	59	6	0	695	383
G10P	15	8.0	145	18	19	2	455	100	18	0	532	310
G14P	14	7.1	24	5	2	1	65	32	1	0	137	76
G15M	11	8.6	47	8	8	0.4	192	10	4	0	242	59
G17M	12	8.4	43	5	3	1	123	29	3	0	223	136
G18M	13	8.0	83	13	42	1	304	19	66	0	632	317
G21M	12	8.4	45	6	4	1	124	38	7	.6	282	137
January 19, 1973												
S1	4	7.5	84	16	26	3	274	61	33	1	745	347
S3	4	7.2	81	14	11	3	259	48	15	3	672	289
S5	3	7.6	63	11	15	3	220	35	18	1	445	223
S6	6	7.7	71	12	17	2	236	38	24	4	635	275
S7	2	7.7	57	11	18	2	171	56	20	1	445	213
S8	4	7.5	83	14	47	27	193	98	98	7	765	420
S9	9	7.0	67	11	4	1	149	87	6	1	422	243
G8P	5	8.4	128	29	22	2	458	64	33	0	772	467
G10P	5	8.5	98	14	14	2	248	105	18	0	512	306
G14P	4	7.0	38	10	2	1	135	30	1	0	111	77
G15M	4	8.3	61	9	36	2	311	4	11	0	212	98
G17M	8	8.3	41	6	3	.4	127	25	2	0	252	98

TABLE 1. *Continued.*

Sample No.	T°C	pH	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	ALK	SO ₄ ⁻	Cl ⁻	NO ₃ ⁻	Cond. μ	TDS
G18M	8	8.4	51	7	3	1	141	38	7	0	452	223
G21M	9	8.1	90	16	13	2	335	38	6	0	322	141
March 9, 1973												
S1	6	7.1	117	19	26	3	385	68	32	4	587	307
S3	7	7.5	76	15	12	2	241	58	15	4	493	233
S5	6	7.5	66	13	12	2	232	38	13	1	443	210
S6	7	8.3	79	14	15	2	252	55	17	4	593	219
S7	7	7.7	59	12	20	2	181	56	23	4	443	197
S8	7	7.9	83	16	61	29	233	102	99	8	793	423
S9	7	7.2	116	27	16	4	424	93	3	1	423	250
G8P	6	8.0	116	27	16	4	423	68	19	0	536	313
G10P	5	7.9	109	21	13	1	334	96	15	0	511	440
G14P	5	7.4	13	5	2	1	38	27	4	0	104	54
G15M	8	8.2	59	11	36	1	318	6	9	0	206	53
G17M	8	8.5	29	5	3	4	88	29	0	0	184	77
G18M	7	8.1	41	7	4	1	93	47	8	0	456	210
G21M	7	8.2	82	18	9	2	321	32	1	0	303	123

¹Ion Concentrations are total values in ppm. Specific conductance cond. μ is in micromhos, total dissolved solids (TDS) in ppm. S refers to surface samples and G to observation well samples.

TABLE 2
Calculated activities of species in solution in ppm.¹

Sample No.	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	HCO ₃ ⁻	SO ₄ ⁻	STCAL	STDOL	STGYP	pPCO ₂	Ca/SO ₄	Ca/Mg	I
October 14, 1972												
S1	111	20	55	357	59	.49	.52	-1.56	2.14	4.54	3.32	.014
S3	89	15	10	286	46	.31	.07	-1.70	2.24	4.66	3.72	.010
S5	83	14	13	279	39	.50	.49	-.79	2.44	5.03	3.62	.009
S6	84	13	19	273	38	.77	.98	-1.80	2.76	5.33	3.83	.009
S7	65	11	21	210	52	-.08	-.73	-1.75	2.29	3.03	3.67	.003
S8	88	14	24	239	100	.42	.29	-1.39	2.51	2.12	3.91	.011
S9	75	10	6	179	81	-.24	-1.13	-1.50	2.13	2.23	4.82	.008
G8P	115	26	12	456	44	1.13	1.91	-1.65	2.53	6.25	2.65	.013
G10P	134	15	19	438	76	1.08	1.49	-1.36	2.45	4.21	5.37	.014
G14P	23	5	2	65	30	-1.31	-3.03	-2.34	2.35	1.87	2.80	.003
G15M	44	7	8	178	8	.94	-1.14	-2.66	3.44	13.28	3.57	.005
G17M	41	4	3	118	26	.45	.17	-2.18	3.41	3.77	5.52	.004
G18M	81	12	42	295	16	.69	.82	-2.20	2.62	12.23	4.02	.010
G21M	43	6	4	118	34	.46	.30	-2.05	3.41	3.07	4.47	.004
January 19, 1973												
S1	80.2	15	25	271	50	.02	-.54	-1.67	2.19	3.81	3.27	.010
S3	78	13	11	257	40	-.30	-1.24	-1.77	1.91	4.86	3.65	.008
S5	62	11	15	218	30	-.08	-.77	-1.97	2.38	5.02	3.42	.007
S6	69	12	17	232	32	.14	-.32	-1.91	2.45	5.17	3.58	.008
S7	54	10	18	169	48	-.15	-.92	-1.80	2.59	2.70	3.37	.007
S8	78	13	46	191	82	-.15	-.93	-1.49	2.35	2.30	3.65	.011
S9	63	10	4	148	74	-.94	-2.50	-1.58	1.73	2.03	3.99	.007

TABLE 2. *Continued.*

Sample No.	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	HCO ₃ ⁻	SO ₄ ⁼⁼	STCAL	STDOL	STGYP	pPco ₂	Ca/SO ₄	Ca/Mg	I
G8P	119	25	22	425	50	1.27	2.03	-1.56	2.90	5.71	2.91	.014
G10P	89	12	14	231	87	1.01	1.32	-1.40	3.26	2.49	4.50	.010
G14P	37	10	2	134	26	-1.26	-2.07	-2.20	1.78	3.39	2.37	.004
G15P	59	8	36	296	4	.33	-.04	-2.66	3.22	11.31	4.30	.004
G17M	39	6	3	123	25	.29	-.07	-2.20	3.31	3.73	4.19	.004
G18M	49	6	3	138	34	.91	1.16	-2.02	3.03	37.99	4.28	.007
G21M	87	15	13	330	32	.24	-.22	-2.00	3.06	3.54	4.88	.005
March 9, 1973												
S1	112	18	26	381	54	-.08	-.79	-1.55	1.64	5.00	3.89	.012
S3	73	14	12	239	48	-.02	-.57	-1.73	2.32	3.65	3.16	.008
S5	64	12	12	229	32	-.10	-.73	-1.94	2.25	4.78	3.13	.007
S6	74	13	15	240	46	.79	1.01	-1.74	3.03	3.88	3.48	.008
S7	57	11	20	179	49	-.04	-.61	-1.80	2.56	2.75	3.11	.007
S8	78	14	60	229	85	.36	.17	-1.50	2.66	2.20	3.31	.011
S9	109	24	16	140	80	-.82	-1.83	-1.57	2.16	1.78	3.49	.007
G8P	110	24	16	409	54	.84	1.20	-1.56	2.51	4.91	2.77	.013
G10P	101	19	13	325	77	.60	.63	-1.41	2.51	3.15	3.31	.011
G14P	13	5	2	38	25	-2.61	-5.50	-2.60	1.92	1.21	1.64	.002
G15M	58	10	36	309	5	.06	-.42	-2.79	3.21	8.02	3.25	.003
G17M	27	5	3	84	26	.18	-.20	-2.32	3.67	2.51	3.50	.003
G18M	38	7	4	90	47	.60	.62	-2.32	2.72	29.34	3.60	.007
G21M	79	17	9	314	32	.03	-.52	-1.94	3.34	1.93	3.44	.004

¹Ion ratios are in molar units. STCAL=saturation index calcite; STDOL=saturation index for dolomite; STGYP=saturation index for gypsum; pPco₂=-log Pco₂ in atmospheres; I=ionic strength.

carbonate equilibria which included the alkalinity estimate. Interpretations based on these values are limited to the assumption that estimated alkalinity approximates analytical alkalinity.

DISCUSSION

The chemical data can be interpreted, with regard to ground and surface water flow (fig. 2), to suggest some of the geochemical processes that are dominant in the study area. Firm conclusions of chemical equilibria in the Oak Openings Sand would require a thorough study of aquifer mineralogy in addition to water analysis. In general, groundwater quality in the area exceeds U.S. Public Health Service minimum standards, and is usually the calcium-bicarbonate type. Surface waters from the ditches were chemically similar and tended to be more uniform than groundwater, as expected from a shallow aquifer in a region of poor surface drainage. This occurs because of a greater degree of mixing in the ditches cessation of contact with aquifer minerals, and exposure to relatively stable Pco₂.

conditions in the atmosphere. The low nitrate levels suggest little contamination from sewage disposal facilities (most residents in the area have septic tank systems). The small number of sampling stations in the 4600-acre area does not permit a definite conclusion regarding sewage contamination, but the correspondingly low sodium and chloride levels seem to support the suggestion of low contamination. Although all waters appear to be near saturation with respect to carbonate minerals, there is a slight decrease in dissolved constituents during the winter months. Both lower temperatures and a reduction of organic influences on factors such as Pco₂ are probably contributory, but the subtle decrease in dissolved material suggest the organic influence is small.

Saturation levels shown by calculated saturation indices in table 2 suggest near saturation with respect to carbonate minerals, and the high Ca/Mg ratios imply that dissolved calcite is more abundant than dolomite. The high levels of saturation in wells G8P, G10P, and

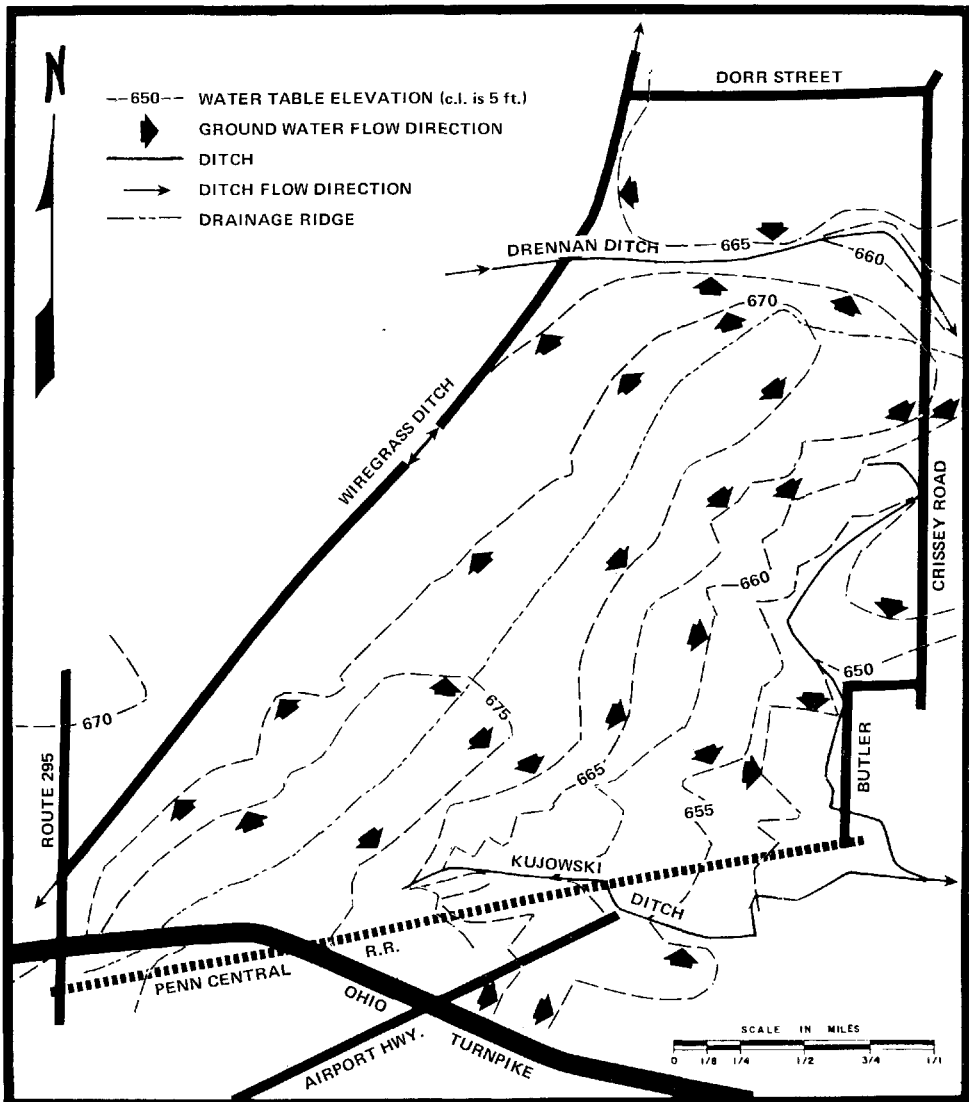


FIGURE 2. Generalized water table elevation and flow patterns. After Mortensen *et al.*, 1972.

G18M (fig. 1) may be influenced by other factors. These wells are adjacent to major transportation arteries including the Penn Central Railroad, Ohio Turnpike and Airport Highway, and residence time for groundwater flow from the ridge area to these wells could be high. This may result in increased amounts of dissolved constituents (Jacobson and Langmuir, 1970). The apparently high Cl^- and SO_4^- levels may be related to

the railroad and highway, or housing density in this local area which may tend to increase ionic strength in waters from this part of the study area. The relatively high levels of Cl^- and SO_4^- in G8P and G10P (fig. 1) may be because they are relatively shallow wells.

All waters are undersaturated with respect to gypsum; groundwater more so than surface waters. Sulfate also appears to have little influence on carbonate

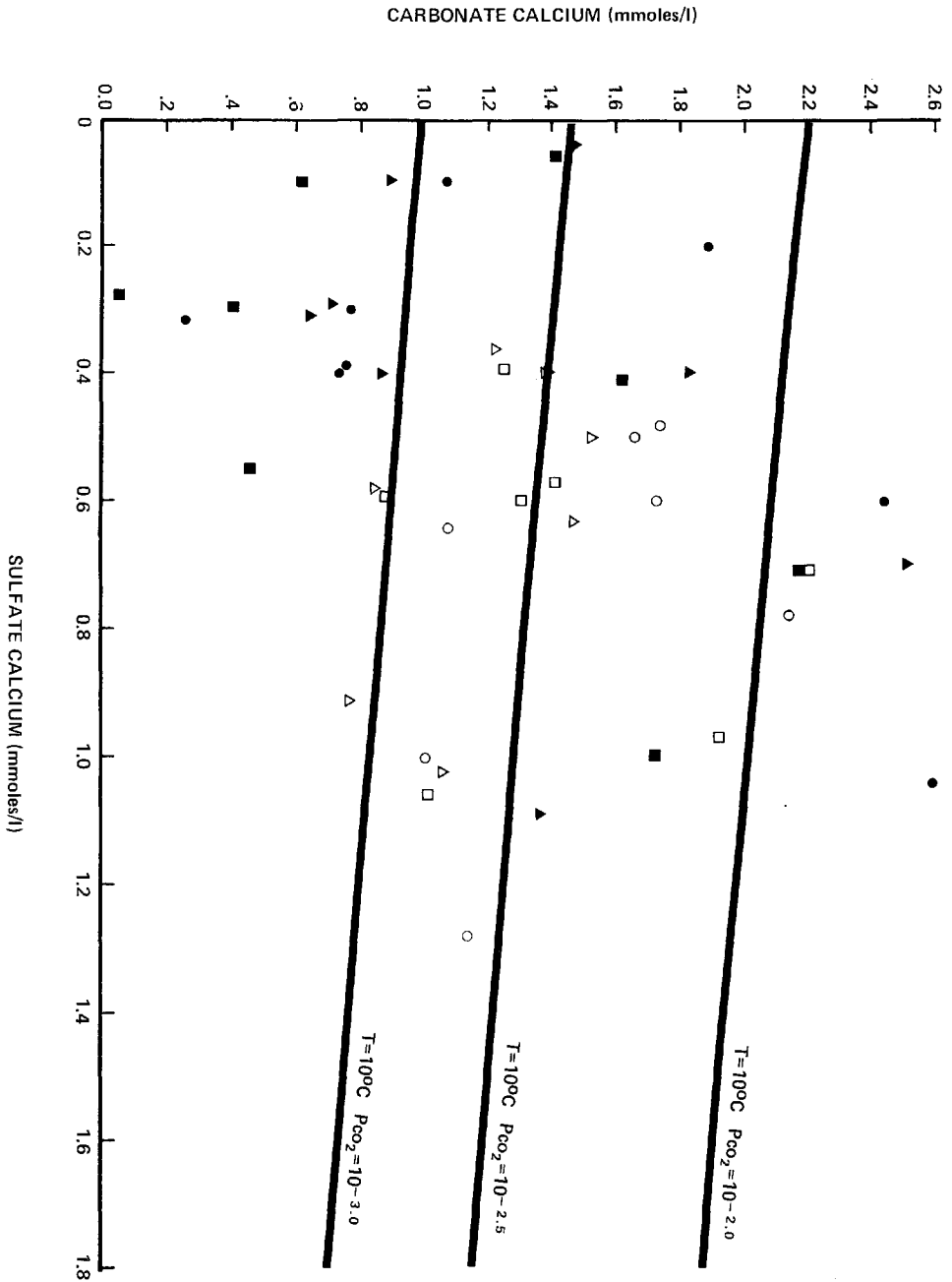


FIGURE 3. Calcium input in terms of calcite and gypsum. Open symbols refer to surface water samples, solid symbols to groundwater samples. Sampling periods were Oct. 14, 1972—●, Jan. 19, 1973—▲, and Mar. 9, 1973—■. Constructed similar to diagrams calculated by Wigley (1973).

solubility as shown in figure 3, which shows calcium input from carbonate minerals as a function of sulfate calcium. Carbonate calcium was calculated by subtracting a molar equivalent of sulfate from total calcium. Superimposed on figure 3 are calcite saturation levels for 10°C and various P_{CO_2} values which were taken from Wigley (1973). This diagram illustrates the approximate magnitude of carbonate precipitation from saturated waters as CO_2 pressure decreases. For the sulfate levels in the Oak Openings Area, it implies that P_{CO_2} fluctuation rather than sulfate concentration changes would be more influential in controlling carbonate precipitation. Figure 3 also shows the uniformity of ditch waters at an average P_{CO_2} of $10^{-2.5}$ illustrating the normalizing influence of atmospheric CO_2 pressure. Groundwaters, on the other hand, show a somewhat wider range in carbonate calcium which is perhaps caused by biological and mineralogical factors influencing subsurface CO_2 pressure.

In general, the metal-cased wells extend nearly to the base of the aquifer and the plastic-cased wells extend to just below the water table. Although the number of wells studied was too small to draw firm conclusions, Table 2 suggests that the deeper wells exhibit a more uniform seasonal chemistry than the shallower wells. As expected, the shallower wells also seem to have chemical properties roughly similar to the ditch samples. The concentration of dissolved species is slightly higher in the southern part of the area near concentrations of transport facilities, but the levels of chloride are still considerably less than the USPHS maximum of 250 ppm. This could imply that dilution may be effective in moderating the pollution potential at least from deicing of highways. The apparent near saturation of carbonate minerals in the Oak Openings waters should be considered in future

development plans. Actions resulting in a decrease of CO_2 pressures may produce carbonate precipitation resulting in reduced permeability, although this effect would probably be minor.

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