Regional Ground-Water Flow and Geochemistry in the Midwestern Basins and Arches Aquifer System in Parts of Indiana, Ohio, Michigan, and Illinois

legional Aquifer-System Analysis

rofessional Paper 1423–C





## Availability of Publications of the U.S. Geological Survey

Order U.S. Geological Survey (USGS) publications from the offices listed below. Detailed ordering instructions, along with prices of the last offerings, are given in the current-year issues of the catalog "New Publications of the U.S. Geological Survey."

#### Books, Maps, and Other Publications

#### By Mail

Books, maps, and other publications are available by mail from—

USGS Information Services Box 25286, Federal Center Denver, CO 80225

Publications include Professional Papers, Bulletins, Water-Supply Papers, Techniques of Water-Resources Investigations, Circulars, Fact Sheets, publications of general interest, single copies of permanent USGS catalogs, and topographic and thematic maps.

#### Over the Counter

Books, maps, and other publications of the U.S. Geological Survey are available over the counter at the following USGS Earth Science Information Centers (ESIC's), all of which are authorized agents of the Superintendent of Documents:

- Anchorage, Alaska-Rm. 101, 4230 University Dr.
- Denver, Colorado-Bldg. 810, Federal Center
- Menlo Park, California—Rm. 3128, Bldg. 3, 345 Middlefield Rd.
- Reston, Virginia–Rm. 1C402, USGS National Center, 12201 Sunrise Valley Dr.
- Salt Lake City, Utah—2222 West, 2300 South (books and maps available for inspection only)
- Spokane, Washington–Rm. 135, U.S. Post Office Building, 904 West Riverside Ave.
- Washington, D.C.—Rm. 2650, Main Interior Bldg., 18th and C Sts., NW.

Maps only may be purchased over the counter at the following USGS office:

• Rolla, Missouri-1400 Independence Rd.

#### Electronically

Some USGS publications, including the catalog "New Publications of the U.S. Geological Survey" are also available electronically on the USGS's World Wide Web home page at <a href="http://www.usgs.gov">http://www.usgs.gov</a>

#### **Preliminary Determination of Epicenters**

Subscriptions to the periodical "Preliminary Determination of Epicenters" can be obtained only from the Superintendent of Documents. Check or money order must be payable to the Superintendent of Documents. Order by mail from—

Superintendent of Documents Government Printing Office Washington, DC 20402

#### **Information Periodicals**

Many Information Periodicals products are available through the systems or formats listed below:

#### **Printed Products**

Printed copies of the Minerals Yearbook and the Mineral Commodity Summaries can be ordered from the Superintendent of Documents, Government Printing Office (address above). Printed copies of Metal Industry Indicators and Mineral Industry Surveys can be ordered from the Center for Disease Control and Prevention, National Institute for Occupational Safety and Health, Pittsburgh Research Center, P.O. Box 18070, Pittsburgh, PA 15236–0070.

#### Mines FaxBack: Return fax service

- 1. Use the touch-tone handset attached to your fax machine's telephone jack. (ISDN [digital] telephones cannot be used with fax machines.)
- 2. Dial (703) 648-4999.
- 3. Listen to the menu options and punch in the number of your selection, using the touch-tone telephone.
- 4. After completing your selection, press the start button on your fax machine.

#### CD-ROM

A disc containing chapters of the Minerals Yearbook (1993–95), the Mineral Commodity Summaries (1995–97), a statistical compendium (1970–90), and other publications is updated three times a year and sold by the Superintendent of Documents, Government Printing Office (address above).

#### World Wide Web

Minerals information is available electronically at http://minerals.er.usgs.gov/minerals/

# Subscription to the catalog "New Publications of the U.S. Geological Survey"

Those wishing to be placed on a free subscription list for the catalog "New Publications of the U.S. Geological Survey" should write to—

U.S. Geological Survey 903 National Center Reston, VA 20192 Regional Ground-Water Flow and Geochemistry in the Midwestern Basins and Arches Aquifer System in Parts of Indiana, Ohio, Michigan, and Illinois

By SANDRA M. EBERTS and LORI L. GEORGE

REGIONAL AQUIFER-SYSTEM ANALYSIS—MIDWESTERN BASINS AND ARCHES

U.S. GEOLOGICAL SURVEY PROFESSIONAL PAPER 1423-C

# U.S. DEPARTMENT OF THE INTERIOR BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY

Charles G. Groat, Director

Any use of trade, product, or firm names in this publication is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Reston, Virginia 2000

#### Library of Congress Cataloging-in-Publication Data

Eberts, Sandra M.

Regional ground-water flow and geochemistry in the Midwestern basins and arches aquifer system in parts of Indiana, Ohio, Michigan, and Illinois / Sandra M. Eberts and Lori L. George.

p. cm. — (Regional aquifer-system analysis—midwestern basins and arches) (U.S. Geological Survey professional paper; 1423-C)

Includes bibliographical references.

ISBN 0-607-92669-4

1. Groundwater flow—Middle West. 2. Water chemistry—Middle West. I. George, Lori L. II. Title. III. Series. IV. Series: U.S. Geological Survey professional paper; 1423-C

GB1197.7.E23 2000 551.49'0977—dc21

#### **FOREWORD**

#### THE REGIONAL AQUIFER-SYSTEM ANALYSIS PROGRAM

The Regional Aquifer-System Analysis (RASA) Program represents a systematic effort to study a number of the Nation's most important aquifer systems, which, in aggregate, underlie much of the country and which represent an important component of the Nation's total water supply. In general, the boundaries of these studies are identified by the hydrologic extent of each system and, accordingly, transcend the political subdivisions to which investigations have often arbitrarily been limited in the past. The broad objective for each study is to assemble geologic, hydrologic, and geochemical information; to analyze and develop an understanding of the system; and to develop predictive capabilities that will contribute to the effective management of the system. The use of computer simulation is an important element of the RASA studies to develop an understanding of the natural, undisturbed hydrologic system and the changes brought about in it by human activities, and to provide a means of predicting the regional effects of future pumping or other stresses.

The final interpretive results of the RASA Program are presented in a series of U.S. Geological Survey Professional Papers that describe the geology, hydrology, and geochemistry of each regional aquifer system. Each study within the RASA Program is assigned a single Professional Paper number beginning with Professional Paper 1400.

Sproof

Charles G. Groat Director

## CONTENTS

Page

Forward	III	Model calibration	C37
Abstract	C1	Procedure	C37
Introduction	C1	Estimates of parameter values	C40
Purpose and scope	C2	Simulated hydraulic heads	
Approach	C2	Simulated flows	
Acknowledgments	C2	Model discrimination	C45
Geohydrology	С3	Reliability of parameter estimates	C46
Geologic setting		Simulated regional ground-water flow	
Hydrologic setting		Geochemistry	
Ground-water use		Spatial distribution of dissolved-solids concentrations and	
Aquifers and confining units		hydrochemical facies	C58
Ground water		Dissolved-solids concentrations	
Hydraulic characteristics		Hydrochemical facies	
Levels		Relation between dissolved-solids concentrations and	
Recharge		hydrochemical facies	C73
Discharge		Geochemical and hydrologic processes, by water type	
Regional ground-water flow		Calcium-magnesium-bicarbonate water	
Conceptual model		Calcium-magnesium-sulfate water	
Numerical model		Sodium-enriched water	
Model design		Sodium-chloride and sodium-calcium-chloride water	
Discrete geohydrologic framework		Insights into regional flow provided by geochemical data	
Boundaries, sources, and sinks		Major solutes	
No-flow boundaries		Isotopes	
Specified-head boundaries		Sulfur isotopes	
Specified-flux boundary		Oxygen and hydrogen isotopes	
Head-dependent flux boundaries		Tritium and carbon isotopes	
Approach to mapping regional recharge and	(33	Variation in ground-water chemistry with depth	
dischargedischarge and	Car		
Parameterization.		Summary and conclusions	
ILL	USTI	RATIONS	Page
ILI FIGURES 1, 2. Maps showing:	USTI	RATIONS	Page
FIGURES 1, 2. Maps showing:		RATIONS	
Figures 1, 2. Maps showing:  1. Location of study and modeled area	S		C4
Figures 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc	sation o	<del></del>	C4
FIGURES 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	s ation o	Geohydrologic sections $A$ – $A'$ and $B$ – $B'$	C4
FIGURES 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	seation or eologic a	geohydrologic sections A–A′ and B–B′and hydrologic units that compose the Midwestern Basins and	C4 C5 C7
FIGURES 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	seation or eologic a	geohydrologic sections A–A' and B–B'and hydrologic units that compose the Midwestern Basins and	C4 C5 C7
FIGURES 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	sation of eologic a	geohydrologic sections A–A′ and B–B′and hydrologic units that compose the Midwestern Basins and	C4 C5 C7
Figures 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	eation of eologic and an eation of eation of eation of eation of eather the eation of eather the ea	Geohydrologic sections $A$ – $A$ ′ and $B$ – $B$ ′	C4 C5 C7
Figures 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	eation of eologic and an eation of eation of eation of eation of eather the eation of eather the ea	Geohydrologic sections $A$ – $A$ ′ and $B$ – $B$ ′	C4 C5 C7
FIGURES 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	ation of cation	geohydrologic sections A-A' and B-B'	C4 C5 C7 C8 C9
FIGURES 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	s	geohydrologic sections A–A' and B–B'	C4 C5 C7 C8 C9
FIGURES 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	srian or ecologic a crian an ecation of aphy (grown osits in g typica	Geohydrologic sections $A$ – $A$ ′ and $B$ – $B$ ′	C4 C5 C7 C8 C9 C10 C11
FIGURES 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	srian or ecologic a crian an ecation of aphy (grown osits in g typica	Geohydrologic sections A–A' and B–B'	C4 C5 C7 C8 C9 C10 C11
FIGURES 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	s	Geohydrologic sections A–A' and B–B'	C4 C5 C7 C8 C9 C10 C11
FIGURES 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	s	Geohydrologic sections A-A' and B-B'	C4 C5 C7 C8 C9 C10 C11 C12
FIGURES 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	rian an cation of aphy (grows in graphy (grows in graphy	Geohydrologic sections A-A' and B-B'	C4 C5 C7 C8 C9 C10 C11 C12 C14 C16
FIGURES 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	s	Geohydrologic sections A-A' and B-B'	C4 C5 C7 C8 C9 C10 C11 C12 C14 C16
FIGURES 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	rian an cation of aphy (grows in a strong typics fer system and the carbon he carbon and the car	Geohydrologic sections A-A' and B-B'	C4 C5 C7 C8 C9 C10 C11 C12 C14 C16
FIGURES 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	s	Geohydrologic sections A-A' and B-B'	C4 C5 C7 C8 C9 C10 C11 C12 C14 C16
FIGURES 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	rian an cation of apply (growth apply (growt	Geohydrologic sections A-A' and B-B'	C4 C5 C7 C8 C9 C10 C11 C12 C14 C16 C18
FIGURES 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	rian an cation of aphy (growth	Geohydrologic sections A-A' and B-B'	C4 C5 C7 C8 C9 C10 C11 C12 C14 C16 C18
Figures 1, 2. Maps showing:  1. Location of study and modeled area 2. Generalized bedrock geology and loc 3. Generalized sections A-A' and B-B' showing g Arches aquifer system	rian an cation of apply (growth a specific results in a specific results in a specific results a specific re	Geohydrologic sections A-A' and B-B'	C4 C5 C7 C8 C9 C10 C11 C12 C14 C16 C18 C19

Page

IGURE 15.	Diagrams showing the effect of recharge from precipitation on the configuration of a water table and associated ground-water flow
16.	Graph showing base-flow duration curves for various ground-water recharge conditions for a streamflow-gaging station on the Kankakee River.
17.	Map showing relative amounts of mean ground-water discharge and mean sustained ground-water discharge to
10	streams in selected surface-water drainage basins
10.	with local, intermediate, and regional flow systems and flow systems simulated by the regional ground-water
19.	flow model
20 21	simulated with a numerical model
_0, _1.	20. Density of perennial streams that drain the modeled area at the scale of 1:100,000 and streams that are
	explicitly represented in the regional ground-water flow model by use of stream cells
	21. Model layers used to simulate the Midwestern Basins and Arches aquifer system, and the location of model
	sections D-D' and E-E': areal extent and boundaries
22.	Sectional diagrams showing the areal extent and boundaries of the model layers used to simulate the Midwestern  Basins and Arches aquifer system
23, 24.	Maps showing:
	23. Zones used for parameterization: model layer 1 and model layer 2
	24. Simulated and measured (observed) hydraulic heads in the carbonate-rock aquifer and the upper
~~	weathered zone water-bearing unit (model layer 2)
25.	Graph showing weighted residuals of hydraulic heads and flows plotted against weighted simulated values from the
oc	regional ground-water flow model for the Midwestern Basins and Arches aquifer system
20.	Map showing simulated ground-water discharge to selected stream reaches from regional flow systems and estimated
27.	mean sustained ground-water discharge (observed flow) to the reaches
21.	Basins and Arches Region are transmissive throughout their entire thickness
28-36	Maps showing:
20 00.	28. Simulated regional recharge and discharge areas
	29. Percentages of the surface area of selected surface-water drainage basins simulated as regional recharge and discharge areas
	30. Simulated patterns of advective regional flow in the Midwestern Basins and Arches aquifer system
	31. Simulated relative magnitudes of horizontal regional flow in the Midwestern Basins and Arches aquifer system: glacial deposits and bedrock
	32. Locations of wells sampled during this investigation, carbonate-rock and glacial cores sampled for isotopic
	analysis, and geochemical sections $A-A'$ , $B-B'$ , $C-C'$ , and $D-D'$
	33. Dissolved-solids distribution in ground-water from the glacial aquifers in the Midwestern Basins and
	Arches aquifer system
	34. Dissolved-solids distribution in ground-water from the carbonate-rock aquifer in the Midwestern Basins and Arches aquifer system
35, 36.	Trilinear diagrams showing:
	35. Water chemistry of the Midwestern Basins and Arches aquifer system, categorized by dissolved-solids concentration: glacial aquifers and carbonate-rock aquifer where it does not underlie the upper
	confining unit
	36. Water chemistry in the carbonate-rock aquifer of the Midwestern Basins and Arches aquifer system where
07.00	it underlies the upper confining unit, categorized by structural basin
37, 38:	Maps showing:
	37. Hydrochemical facies of ground water from the glacial aquifers in the Midwestern Basins and Arches aquifer system
	38. Hydrochemical facies of ground water from the carbonate-rock aquifer in the Midwestern Basins and
	Arches aquifer system
39–46:	Graphs showing:
	39. Concentration of calcium plus magnesium as a function of bicarbonate concentration in ground water from
	the glacial aquifers in the Midwestern Basins and Arches aquifer system
	40. Concentration of calcium plus magnesium as a function of bicarbonate concentration in ground water from
	the carbonate-rock aquifer in the Midwestern Basins and Arches aquifer system
	41. Saturation indices of calcite and dolomite as a function of dissolved-solids concentration for water from
	wells in the Midwestern Basins and Arches aquifer system
	42. Concentration of calcium plus magnesium as a function of concentration of sulfate plus one-half bicarbonate
	in ground water from the glacial aquifers in the Midwestern Basins and Arches aquifer system
	43. Concentration of calcium plus magnesium as a function of concentration of sulfate plus one-half bicarbonate in ground water from the carbonate-rock aquifer in the Midwestern Basins and Arches aquifer system
	in ground water from the carbonate-rock additier in the wildwestern dashis and Arches additier system

				Page
FIGURES 3	39–46.—Continued  44. Saturation indices of gyp	sum as a function of dissolved-sulfa	te concentration for water from wells in	
	the Midwestern Basi	ns and Arches aquifer system		. C79
	system along geocher	mical sections $A-A'$ , $B-B'$ , $C-C'$ , and	lwestern Basins and Arches aquifer	. C83
	46. Sulfate concentration in	water from wells in the Midwestern	Basins and Arches aquifer system along	
	47, 48. Maps showing:			
	47. $\delta^{34}$ S and $\Delta^{34}$ S values in w		Basins and Arches aquifer system	
			nd Arches aquifer systemes aquifer system	
	50. Tritium concentrations and carbon-	14 activities in water from wells in t	he Midwestern Basins and Arches aquifer	
		TANK DO		
		TABLES		
				Page
TABLE 1.	Relation between geologic and hydrologic u		Arches aquifer system and model layers	. C6
2.	Summary of hydraulic characteristics of aq	ruifers and confining units in the Mi		
3.	Parameter estimates and reliability of the Midwestern Basins and Arches aquifer		brated final model of regional flow in the	. C41
4.	Simulated ground-water budget of regional	l flow systems in the Midwestern Ba	sins and Arches aquifer system	
5.				. C48
6.	Well-construction information for wells san system, 1991–92		dwestern Basins and Arches aquifer	. C59
7.	Chemical analyses of selected constituents	in water from wells sampled during		
8.	Analyses of isotopes in water from wells sa		lidwestern Basins and Arches aquifer	C62
9.	Analyses of sulfur and carbon isotopes in ca	arbonate rocks and glacial deposits		
	Major water types, their specific cation and aquifers in the Midwestern Basins and	Arches aquifer system		. C70
11.	Summary of <sup>14</sup> C age estimates for ground v aquifer system, 1991–92		of the Midwestern Basins and Arches	. C93
CON	VERSION FACTORS, VERTICA	AL DATUM, AND ABBRE	VIATED WATER-QUALITY UN	ITS
	Multiply inch-pound unit	By	To obtain SI unit	
	inch (in)	25.4	millimeter	
	foot (ft)	0.3048	meter	
	mile (mi)	1.609	kilometer	
	square mile (mi <sup>2</sup> )	2.590	square kilometer	
	inch per year (in/yr)	25.4	millimeter per year	
	foot per day (ft/d)	0.3048	meter per day	
	foot squared per day (ft²/d)	0.09290	meter squared per day	
	cubic feet per second (ft <sup>3</sup> /s)	28.32	liter per second	

0.06309

0.04381

4.381 x 10<sup>-8</sup>

liter per second

cubic meter per second

cubic meter per second

gallon per minute (gal/min) gallon per day (gal/d) million gallons per day (Mgal/d) VIII CONTENTS

Sea Level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)— a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called "Sea Level Datum of 1929".

Water-quality units used in this report: Concentrations of dissolved consituents are given in milligrams per liter (mg/L) or micrograms per liter ( $\mu$ g/L), units expressing the concentration of chemical constituents as mass of solute per unit volume of water.

#### REGIONAL AQUIFER-SYSTEM ANALYSIS-MIDWESTERN BASINS AND ARCHES

# REGIONAL GROUND-WATER FLOW AND GEOCHEMISTRY IN THE MIDWESTERN BASINS AND ARCHES AQUIFER SYSTEM IN PARTS OF INDIANA, OHIO, MICHIGAN, AND ILLINOIS

By SANDRA M. EBERTS AND LORI L. GEORGE

#### ABSTRACT

This report synthesizes information on the regional ground-water flow and geochemistry in the Midwestern Basins and Arches aquifer system in parts of Indiana, Ohio, Michigan, and Illinois. Aquifers that compose this water-table aquifer system include glacial aquifers and an underlying, areally extensive carbonate-rock aquifer.

Water within the aquifers is most commonly a Ca-Mg-HCO<sub>3</sub> type or a Ca-Mg-SO<sub>4</sub> type. In general, the distribution of hydrochemical facies within the aquifer system is controlled by the mineralogy of the aquifer material, rather than by a chemical evolution of water along general directions of regional ground-water flow.

Some ground-water flow systems within the aquifer system provide base flow to streams in response to ground-water recharge events. Other (often deeper) ground-water flow systems respond minimally to variations in groundwater recharge from precipitation and provide a fairly constant supply of water to streams. Streamflow hydrographs and base-flow duration curves were used to estimate such components of base flow in selected streams for long-term steady-state conditions in the aquifer system. Mean sustained ground-water discharge (discharge from fairly stable ground-water flow systems) ranges from 3 to 50 percent of mean ground-water discharge (discharge from all ground-water flow systems) to the selected stream reaches. These percentages indicate that 50 to 97 percent of base flow in the streams within the study area can be attributed to transient ground-water flow systems, which typically have a major component of local-scale flow. Because ground-water flow across the external boundaries of the aquifer system is minimal, such percentages indicate that most ground-water flow in the aquifer system is associated with seasonally transient local flow systems.

Results of a ground-water flow model that was calibrated by use of regression methods and that simulates regional flow systems within the aquifer system (approximately 10 percent of total ground-water flow in the aquifer system) indicate that most water (99 percent) in simulated regional flow systems is from recharge at the water table. Most water (78 percent) discharges from simulated regional flow systems to the principal streams. Less than 3 percent of water in simulated regional flow systems discharges to the Ohio River, Lake Erie, or downdip areas in the Illinois (structural) Basin.

Simulations also indicate that most of the Midwestern Basins and Arches aquifer system is characterized by alternating regional recharge and discharge areas at intervals of less than every 10 miles along the dominant regional trends of the potentiometric surfaces in the aquifers. Such alternating regional recharge and discharge areas result in the absence of long flow paths from the very highest regional potentiometric levels to the very lowest regional potentiometric levels. The presence of tritiated ground water (less than 50 years old)

across most of the aquifer system also indicates that the aquifer system receives recharge across most of the study area.

The northeastern part of the aquifer system near Lake Erie differs from the rest of the system with respect to regional ground-water flow and chemistry. Specifically, part of the northeastern part of the aquifer system can be characterized as a broad area (tens of miles) of weak regional discharge (less than 0.5 inch per year). Results of the regional ground-water flow model indicate that regional flow systems have a limited ability to carry ground water away from this area; thus precipitation is prevented from recharging the regional flow systems in this part of the aquifer system. Some ground water recharged during Pleistocene glaciation was found in this area. Sulfide concentrations and sulfur isotope data, which indicate that extensive sulfate reduction has occurred in the aquifer system within this area, confirm that only minimal recharge of this part of the aquifer system has taken place over a long period of time.

The longest simulated ground-water flow paths within the aquifer system (nearly 50 miles) were also identified in the northeastern part of the aquifer system. These flow paths terminate at Lake Erie. On the basis of carbon-14 data, some of the oldest waters (approximately 13,000 years) were found at the downgradient end of these particularly long flow paths. The area near these flow paths is the only area within the aquifer system in which a systematic increase in ground-water ages was observed in the general direction of regional ground-water flow. Not all of the regional flow paths in the northeastern part of the aquifer system are particularly long. The very oldest waters that were found in the aquifer system (approximately 38,000-45,000 years) are associated with comparably short ground-water flow paths (approximately 10 miles). These waters are present beneath the Maumee River Basin and indicate that parts of the aquifer system beneath the Maumee River Basin are fairly stagnant.

#### **INTRODUCTION**

Quaternary glacial deposits and underlying Devonian and Silurian carbonate rock in parts of Indiana, Ohio, Michigan, and Illinois compose the Midwestern Basins and Arches aquifer system investigated as part of the Regional Aquifer-System Analysis (RASA) program of the U.S. Geological Survey (USGS) (Sun and Johnston, 1994). Objectives of the Midwestern Basins and Arches RASA project were to describe

the geohydrology, ground-water flow, and geochemistry in this aquifer system (Bugliosi, 1990). Large subregions of the Midwestern Basins and Arches aquifer system were previously investigated (Ohio Department of Natural Resources, Division of Water, 1970; Norris and Fidler, 1973; Bloyd, 1974; Weist, 1978; Indiana Department of Natural Resources, 1988, 1990); these investigations, however, were limited in areal extent by political boundaries (state lines) or surfacewater drainage divides. The RASA program provided an opportunity to synthesize earlier work and to study the full areal extent of the aquifer system.

Principal results of the Midwestern Basins and Arches RASA project are presented in Professional Paper 1423. Chapter A is a summary of the aquifer system. Chapter B describes the geohydrologic framework of the aquifer system. Chapter C (this chapter) describes regional ground-water flow and geochemistry in the aquifer system.

#### PURPOSE AND SCOPE

This report presents information on the geohydrology of and regional flow and geochemistry in the Midwestern Basins and Arches aquifer system in parts of Indiana, Ohio, Michigan, and Illinois. Specific report objectives are to describe (1) physical and hydraulic boundaries of the aquifer system; (2) regional relations between surface water and ground water; (3) a numerical model used to compute a regional groundwater budget, regional recharge and discharge areas, and patterns of regional ground-water flow; and (4) ground-water chemistry in relation to these patterns of regional flow. In the "Summary and Conclusions" section of the report, the hydrological and geochemical information are integrated to present a comprehensive analysis of the occurrence and flow of water in the aquifer system.

Regional flow, as defined for this report, is ground-water flow associated with flow systems that are minimally affected by seasonal variations in ground-water recharge from precipitation. Although local-scale flow systems that readily respond to variations in ground-water recharge are numerous and important throughout the aquifer system, it was outside the scope of the RASA project to investigate such flow systems. Specifically, local flow systems are not explicitly simulated by the numerical ground-water flow model.

#### **APPROACH**

A steady-state quasi-three-dimensional finite-difference ground-water flow model (numerical model) was constructed, calibrated, and used to describe regional flow in the Midwest-ern Basins and Arches aquifer system. Before this regional ground-water flow model was constructed, calibration targets were established. These calibration targets are based on measured ground-water levels and estimated ground-water dis-

charge from regional flow systems, as approximated from measured streamflows, and were used to judge how well the numerical model simulated field conditions in the aquifer system. The numerical model (a mathematical representation of regional flow in the aquifer system) was built from a conceptual model (a simplified description of the aquifer system). The conceptual model was developed by synthesizing information on the thickness and areal extent of the aquifers and confining units within the aquifer system, as well as information on hydraulic characteristics, boundary conditions, flow regimes, sources and sinks of water, and general directions of ground-water flow. A geographic information system (GIS) was used to prepare a geographically referenced data base of this information, which was then converted for input into the numerical model by use of an interface program (Van Metre, 1990). Available computer codes MODFLOW (McDonald and Harbaugh, 1988) and MODFLOWP (Hill, 1992) were used to construct and calibrate the numerical model on the basis of a nonlinear-regression method developed by Cooley and Naff (1990). Nonlinear regression was used to automatically adjust parameter values that represent hydraulic characteristics of the aquifers and confining units, as well as annual recharge, so that the calibration targets were matched as closely as possible. Aspects of the model other than the parameter values were calibrated by trial and error adjustment. A postprocessing routine (Harbaugh, 1990) was used to help quantify ground-water budgets. Output from the calibrated numerical model was also used in conjunction with the GIS to map regional recharge and discharge areas. The particle-tracking program MODPATH (Pollock, 1989) was used to determine and illustrate simulated advective regional groundwater flow patterns. An additional postprocessing routine was used to map discharge vectors (Scott, 1990).

Geochemistry data were used to describe the relations among ground-water chemistry, aquifer mineralogy, and present and past patterns of regional flow in the Midwestern Basins and Arches aquifer system. The spatial variability in the concentrations of major solutes in the ground water was evaluated and related to the source aquifers and general patterns of regional ground-water flow. Chemical and isotopic analyses of ground water and aquifer material along general directions of regional ground-water flow were used to evaluate the important hydrologic and geochemical processes controlling ground-water chemistry and to qualitatively estimate ground-water ages.

#### **ACKNOWLEDGMENTS**

The authors gratefully acknowledge numerous landowners for their cooperation in allowing water samples and other hydrologic information to be collected on their properties. In addition, the authors thank Frank Voss, Robert Hanover, and

Anthony Robinson, who helped with many aspects of the work presented herein.

#### GEOHYDROLOGY

The area of principal hydrologic interest of the Midwestern Basins and Arches RASA project encompasses approximately 44,000 mi<sup>2</sup>, most of which is in the Midwestern Basins and Arches Region as defined in Shaver (1985). Boundaries of this study area (fig. 1) are coincident with the contact between Devonian limestones and younger Devonian shales (fig. 2) or surface-water bodies.

#### **GEOLOGIC SETTING**

The Midwestern Basins and Arches aquifer system generally lies between the Appalachian, the Illinois, and the Michigan (structural) Basins and is located along the axes of the Cincinnati, the Findlay, and the Kankakee Arches in parts of Indiana, Ohio, Michigan, and Illinois (fig. 2). The sedimentary rocks within the area range in age from Precambrian through Mississippian; however, bedrock units of primary interest range in age from Ordovician (Cincinnatian) through Lower Mississippian (table 1). The oldest bedrock units exposed at the bedrock surface are generally found along the axis of the Cincinnati Arch in the south-central part of the study area, owing to several periods of erosion (figs. 2 and 3). In general, units exposed at the bedrock surface are progressively younger with distance from the axes of the arches. Four faults or fault zones partially dissect these sedimentary rocks within the region (fig. 2).

The bedrock units of Ordovician age (Cincinnatian) consist of interbedded shales and limestones. Shales predominate in these units; less than one-quarter of the sequence is made up of limestones (Gray, 1972). This sequence of interbedded shales and limestones thickens eastward from the western border of Indiana toward Ohio and is overlain by carbonate rocks (limestones and dolomites) of Silurian and Devonian age. These carbonate rocks locally contain some evaporite deposits in northwestern Ohio and northern Indiana (French and Rooney, 1969; Janssens, 1977); they contain sulfide minerals in an area associated with the Findlay Arch (Botoman and Stieglitz, 1978). The carbonate rocks of Silurian and Devonian age range in thickness from 0 ft at the contact with the rocks of Ordovician age to 2,500 ft in southeastern Michigan (Casey, 1994) (fig. 4). Erosion has resulted in the loss of hundreds of feet of carbonate rock from across the central part of the study area. The carbonate-rock sequence has been completely eroded in places by the ancient Teays-Mahomet River system, described in Melhorn and Kempton (1991). As a result of this erosion, the older shales and limestones of Ordovician age are present at bedrock surface in sinuous exposures north of their principal area of exposure (fig. 2).

The carbonate rocks are overlain by shales of Devonian and Mississippian age along the margins of the structural basins. Erosion has resulted in the loss of the shale sequence throughout the central part of the study area except for an area approximately 50 mi northwest of Columbus, Ohio (fig. 2). This shale outlier is referred to herein as the "Bellefontaine Outlier."

The bedrock is overlain by Quaternary glacial deposits throughout most of the study area (fig. 5 and table 1). These deposits directly overlie the carbonate rocks in the central part of the area (subcrop area of the carbonate rocks) and overlie the younger shales along the margins of the structural basins. Glacial deposits mask the ancient bedrock topography and bury numerous valleys in the bedrock surface.

The Quaternary glacial deposits—the result of multiple glacial advances—range in age from Kansan (oldest) to Wisconsinan (youngest) (Bennison, 1978). The deposits of Kansan and Illinoian age are not widespread within the study area and typically are present beyond the limit of the Wisconsinan ice sheet (fig. 5). The Kansan and Illinoian deposits are also thinner than the more widespread deposits of Wisconsinan age (Goldthwait and others, 1965; Geosciences Research Associates, 1982; Soller, 1986). The Wisconsinan ice sheet eroded much of these earlier glacial deposits; this resulted in landforms that contain material from multiple glacial advances. The resultant geomorphology is illustrated in figure 6; a photograph of a shaded relief generated from digital topographic data for every 30 seconds of latitude and longitude (U.S. Geological Survey, 1987).

The glacial deposits include ground- and end-moraine deposits, glaciolacustrine deposits, and outwash deposits (fig. 5); ice-contact stratified drift is present within the moraine deposits. The glacial deposits range in thickness from 0 to approximately 400 ft (fig. 7) (Mozola, 1969, 1970; Fleck, 1980; Gray, 1983; Soller, 1986). The areas dominated by ground- and end-moraine deposits are characterized by broad, low ridges with smooth, gentle slopes separated by flat, gently undulating plains (Mickelson and others, 1983). End moraines are close together where they abut highlands, such as the Bellefontaine Outlier (Young and others, 1985). The mineral composition of the moraines reflects local bedrock; about 4 percent of the material in Ohio was transported from the Canadian Shield north of the study area (Strobel and Faure, 1987).

Surficial glaciolacustrine deposits are present in the low-lands adjacent to Lake Michigan and Lake Erie and are the result of glacial lakes that formed along the margins of the retreating Wisconsinan ice (Young and others, 1985) (figs. 5 and 6). These glaciolacustrine deposits are dominated by lake bottom silts and clays. Minor sands and gravels mark the beaches of ancient shorelines (Goldthwait and others, 1965); some lakebed sands in Michigan just west of Lake Erie have been mapped (Western Michigan University, Department of Geology, 1981).

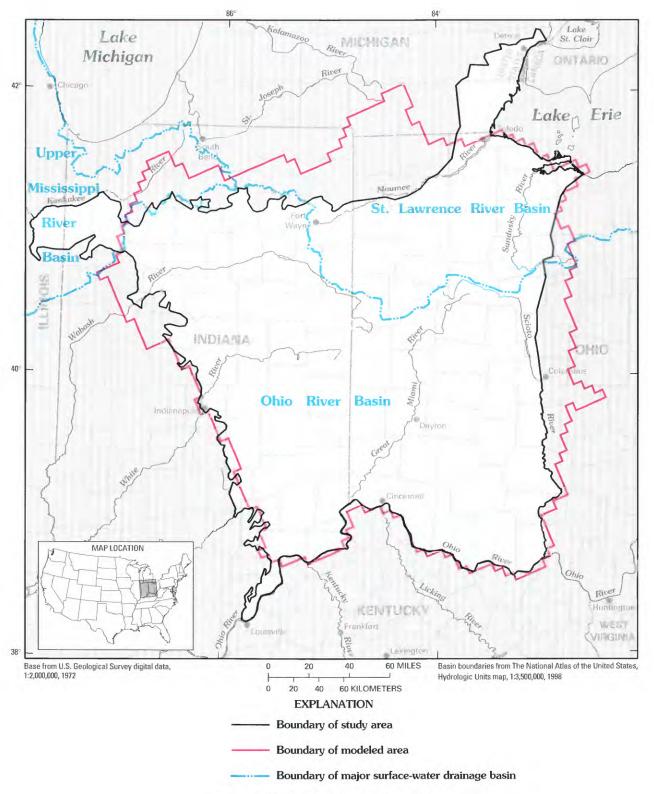


FIGURE 1.—Location of study and modeled areas.

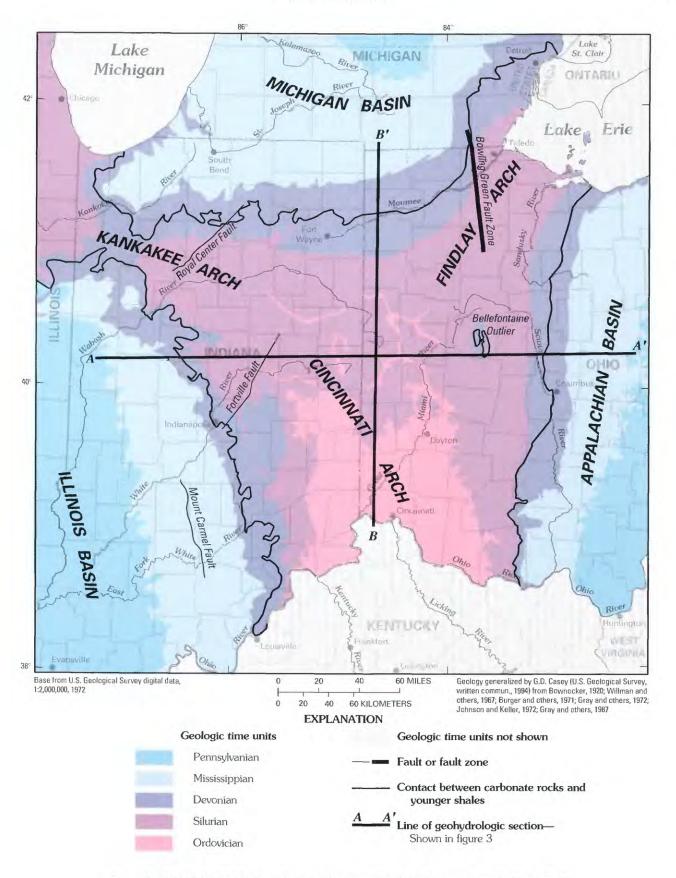
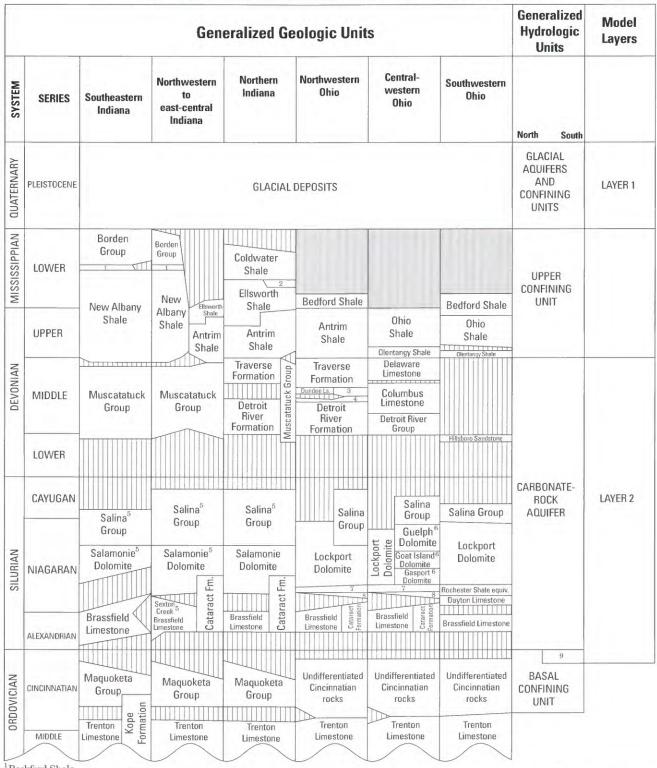


Figure 2.—Generalized bedrock geology and location of geohydrologic sections A-A' and B-B'.

Table 1.—Relation between geologic and hydrologic units of the Midwestern Basins and Arches aquifer system and model layers used to simulate regional flow within the aquifer system

[Fm, Formation; Ls, Limestone; equiv, equivalent; modified from Casey, 1992, fig. 3]



<sup>&</sup>lt;sup>1</sup>Rockford Shale

<sup>2</sup> Sunbury Shale Intervals not included in investigation

<sup>&</sup>lt;sup>3</sup>Delaware Limestone Interva

<sup>&</sup>lt;sup>4</sup>Columbus Limestone

<sup>&</sup>lt;sup>5</sup>Follows usage of the Indiana Geological Survey (Gray and others, 1985)

 $<sup>^6\</sup>mathrm{Follows}$  usage of the Ohio Geological Survey (Hull, 1990; Larsen, 1991)

<sup>&</sup>lt;sup>7</sup>Rochester Shale equivalent

<sup>&</sup>lt;sup>8</sup>Dayton Limestone

<sup>&</sup>lt;sup>9</sup>Upper weathered zone water-bearing unit (not an aquifer)

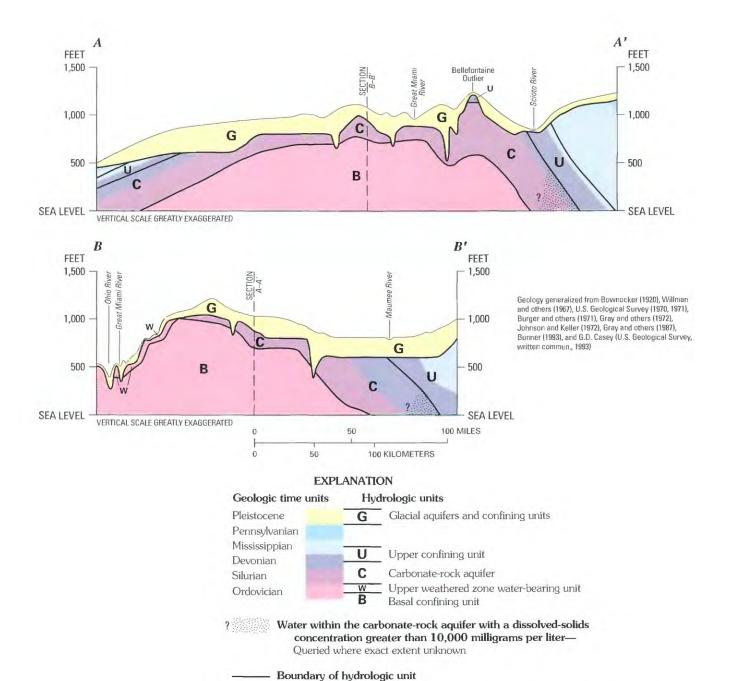


FIGURE 3.—Generalized sections A-A' and B-B' showing geologic and hydrologic units that compose the Midwestern Basins and Arches aquifer system (faults not shown; lines of section shown in fig. 2).

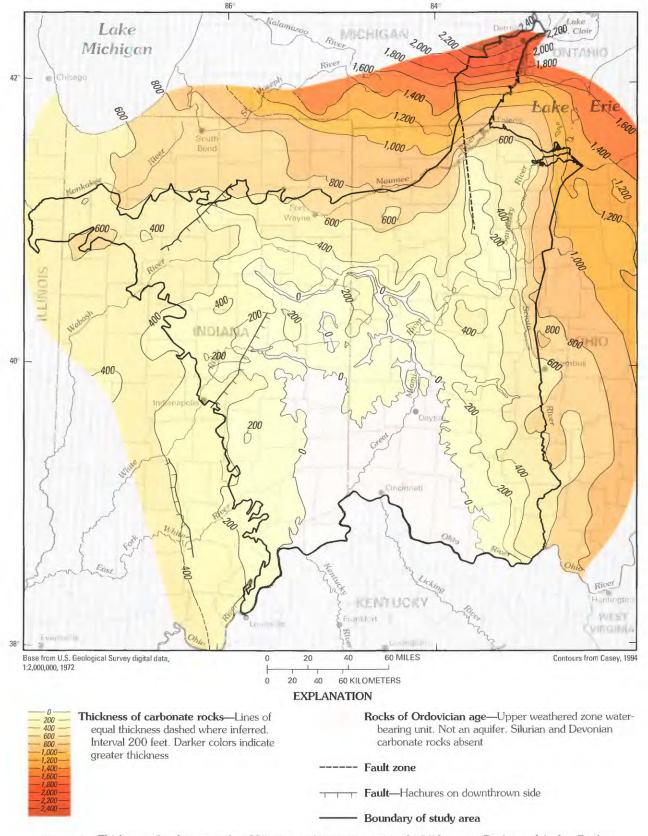


FIGURE 4.—Thickness of carbonate rocks of Silurian and Devonian age in the Midwestern Basins and Arches Region.

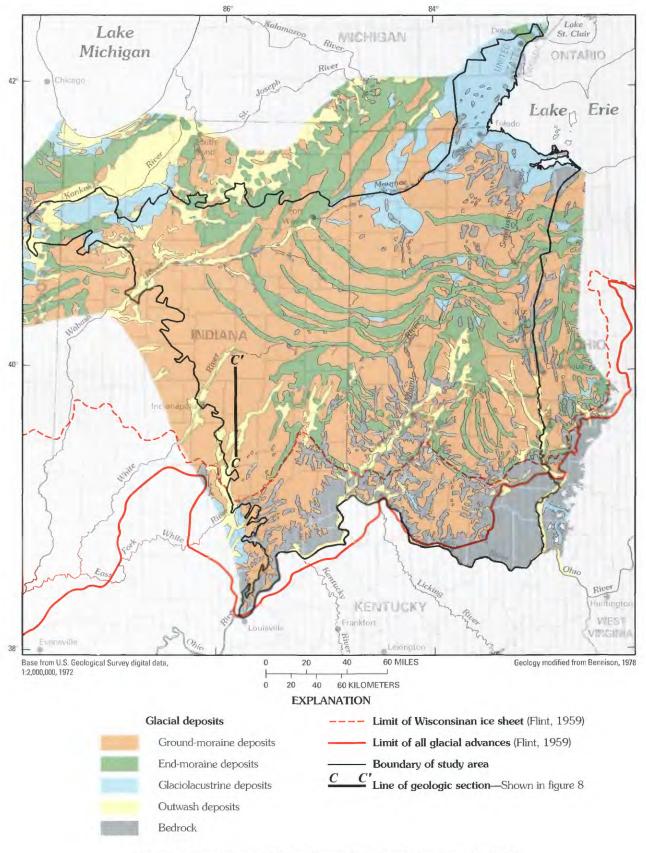


FIGURE 5.—Generalized surficial geology and location of geologic section C-C'.

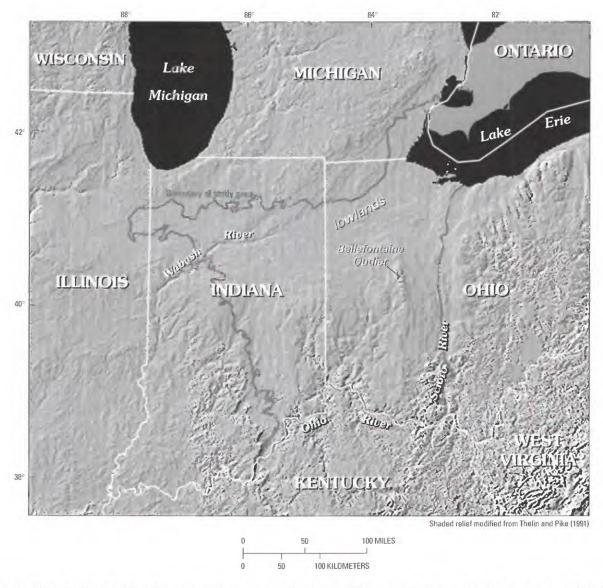


FIGURE 6.—Shaded relief of land-surface topography (geomorphology) in the Midwestern Basins and Arches Region, from digital data.

Outwash deposits commonly fill the ancient drainage systems, which served as channels for the deposition of such washed and sorted material. In many places, these outwash deposits underlie principal streams that currently drain the area.

#### HYDROLOGIC SETTING

The study area has a distinctly seasonal humid temperate climate. Precipitation in Indiana is greatest from March through July (Glatfelter and others, 1991). The wettest months in Ohio tend to be April through August, whereas February and October tend to be the driest (Sherwood and others, 1991). Mean annual precipitation computed from stations with at least 50 years of data ranges from 33 to 43 in.

across the study area (E.F. Bugliosi, U.S. Geological Survey, written commun., 1993). Approximately 26 in/yr are consumed by evapotranspiration in Indiana (Clark, 1980). Todd (1969) notes that potential evapotranspiration exceeded precipitation from mid-May through mid-September over a 30-year period in southwestern Ohio.

Parts of three major river systems—the Ohio, the St. Lawrence, and the Upper Mississippi—drain the study area (fig. 1).

#### GROUND-WATER USE

Ground water is plentiful throughout much of the study area and serves as an important resource. Approximately 433 Mgal/d of ground water was reported to have been withdrawn from the Midwestern Basins and Arches aguifer system in

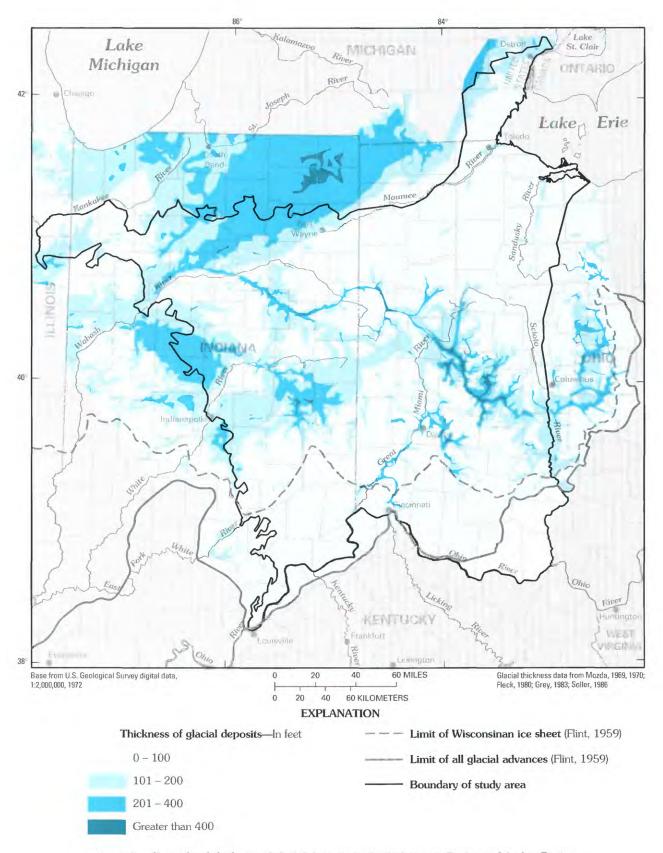


FIGURE 7.—Generalized thickness of glacial deposits in the Midwestern Basins and Arches Region.

Indiana and Ohio during the 1990 calendar year (Beary, 1993). Only 15 percent (67 Mgal/d) of this water was withdrawn from the carbonate rocks. Of the remaining 85 percent, much of the water was withdrawn from outwash deposits that underlie principal streams (E.A. Beary, U.S. Geological Survey, written commun., 1993). These pumpage figures reflect only ground-water withdrawals reported by users capable of pumping 100,000 gal/d or greater, and not all of this withdrawn water is consumed. Regardless of the actual amount of pumpage from the aquifer system, the system is not heavily stressed at the regional scale, as is apparent when the pumpage figures are compared to the amount of ground water that discharges to streams within the study area. Eberts (1999) estimates that, over a period of long-term steady-state conditions in the aquifer system, greater than 13,000 Mgal/d discharges from the aquifer system to streams within the study area.

No regional-scale cones of depression are present within the aquifer system. At the subregional scale, irrigation pumpage in northwestern Indiana results in seasonal water-level declines in the carbonate rocks. On an annual basis, however, the carbonate-rock aquifer appears to be able to support highcapacity irrigation pumpage without significant long-term depletion (Indiana Department of Natural Resources, 1990).

#### **AQUIFERS AND CONFINING UNITS**

The water table within the Midwestern Basins and Arches aquifer system generally is within Quaternary alluvium or glacial deposits. Glacial aquifers typically consist of sands and gravels that compose outwash deposits (fig. 5) or discontinuous lenses of ice-contact stratified drift within ground-and end-moraine deposits (fig. 8). These aquifers are most commonly unconfined where the outwash deposits are present along principal streams and are locally semiconfined or confined by clayey till elsewhere in the region. Because the glacial aquifers are not normally extensive, individual aquifers can supply large yields of ground water only locally (Ohio Department of Natural Resources, Division of Water, 1970).

The shale sequence of Mississippian and Devonian age functions as a confining unit. Specifically, the shale sequence restricts the flow of ground water between the glacial aquifers and the underlying carbonate-rock aquifer along the margins of the structural basins (fig. 3). In this report, these shales are referred to as the "upper confining unit."

The carbonate-rock aquifer directly underlies the upper confining unit along the margins of the structural basins and underlies the glacial deposits, which collectively function as a semiconfining unit, within the central part of the study area.

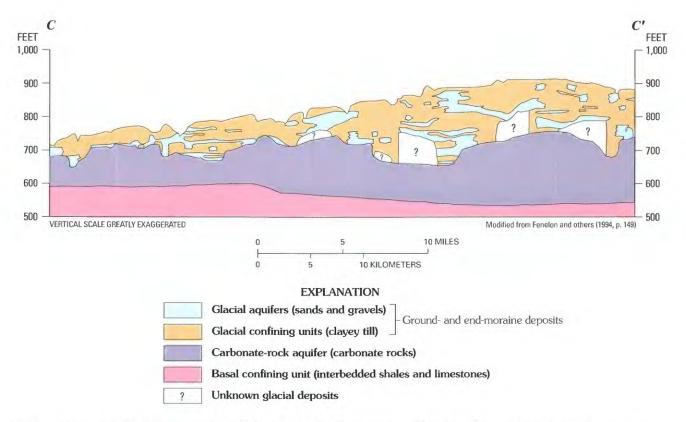


FIGURE 8.—Generalized hydrologic section *C*—*C'* showing typical relation between glacial aquifers and glacial confining units in the Midwestern Basins and Arches aquifer system (line of section shown in fig. 5).

The carbonate-rock aquifer is unconfined in areas where it is locally exposed at the land surface. Lateral boundaries of the carbonate-rock aquifer generally are coincident with the occurrence of waters that have a dissolved solids concentration of 10,000 mg/L or greater (see fig. 34, p. C65) or where the aquifer pinches out in the south-central part of the study area (fig. 4).

The carbonate-rock aquifer is confined below by a basal confining unit that is composed of interbedded shales and limestones of Ordovician age. Gupta (1993) demonstrates that these shales significantly limit the flow of ground water into or out of the bottom of the carbonate-rock aquifer but that some water moves across the basal confining unit of the Midwestern Basins and Arches aquifer system to become part of an even larger aquifer system. There is some evidence that the bottom of the carbonate-rock aquifer may actually be within the Silurian and Devonian carbonate rocks in some areas. Arihood (1994) notes that fractures in the carbonate rocks in a few fully penetrating wells in northwest Indiana are not productive in the bottom 60 to 400 ft of the wells.

Although the Ordovician rocks (basal confining unit) underlie the carbonate-rock aquifer throughout most of the study area, they are laterally contiguous with the aquifer along the axis of the Cincinnati Arch in the south-central part of the area. The contact between Silurian and Ordovician rocks, where it is exposed at the bedrock surface, has been described throughout the literature as a spring horizon. The role of the shales along this contact was summarized succinctly by Norris and others (1950, p. 23): "The chief importance of the impervious Ordovician shale with respect to ground water is that it deflects the water to the surface as springs." These interbedded shales and limestones, however, are used locally as a source of water in the south-central part of the study area where they are exposed at the bedrock surface and other aquifers are absent. Weathering has increased secondary porosity and permeability within this area and has allowed water circulation to increase at shallow depths. Yields from wells completed in the interbedded shales and limestones within this area are typically less than 10 gal/min, drawdowns commonly are extreme, and dry holes are common (Indiana Department of Natural Resources, 1988). In this report, the interbedded shales and limestones of Ordovician age that are exposed at the bedrock surface are referred to as the "upper weathered zone water-bearing unit." The upper weathered zone water-bearing unit is not considered to be an aquifer but may be hydraulically connected to the carbonate-rock aquifer.

#### **GROUND WATER**

The occurrence and flow of ground water in the Midwestem Basins and Arches aquifer system are controlled by the geohydrologic framework of the aquifer system and by the distribution and rate of recharge and discharge. Recharge and discharge also affect the long-term availability of ground water.

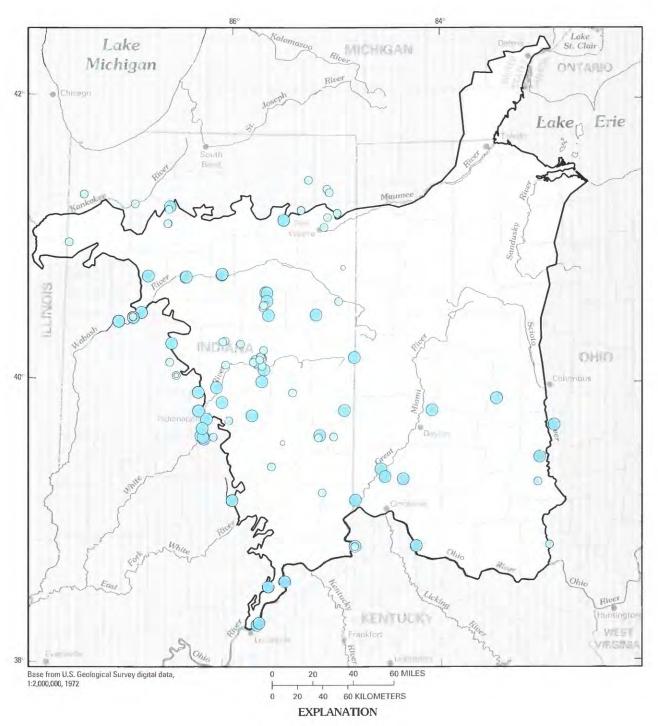
#### HYDRAULIC CHARACTERISITCS

The productivity of the glacial aquifers varies spatially within small distances because of variations in the composition, continuity, and structure of the deposits (Strobel, 1993). On the basis of data from 101 aquifer tests, transmissivities of the glacial aquifers within the study area range from 300 to 69,700 ft²/d (fig. 9 and table 2). Storage coefficients for the same material range from 0.00002 to 0.38 (Joseph and Eberts, 1994). Transmissivities at two wells within the study area that are completed in clayey till (not considered to be aquifer material) are 1.5 and 2.1 ft²/d (Strobel, 1993).

On the basis of available aquifer-test data, the vertical hydraulic conductivity at wells completed in glacial deposits within the study area ranges from 0.0001 to 0.77 ft/d (Norris, 1959, 1979, 1986; Fleming, 1989; Strobel, 1993). Strobel (1993) notes that clayey till within the study area may be fractured at shallow depths as a result of desiccation, biological action, oxidation of minerals, or isostatic rebound after the retreat of the last ice sheet. He observed fractures in till within the study area to depths of 15 ft, and he suggests that the intersection of such fractures with one another and with sand and gravel lenses within the clayey till can result in vertical hydraulic conductivities greater than those commonly considered restrictive to ground-water flow.

Vertical and horizontal hydraulic conductivities of the shales of Mississippian and Devonian age range from 10<sup>-7</sup> to 10<sup>-5</sup> ft/d, as determined from laboratory analysis of core samples (G.D. Casey, U.S. Geological Survey, written commun., 1993). Because these values do not account for fractures in the shales, effective hydraulic conductivities that represent field conditions may be orders of magnitude larger (Freeze and Cherry, 1979, p. 158).

Water in the carbonate-rock aquifer is primarily present in fractures, joints, bedding planes, and solution channels within the rock. These openings are due, in part, to the effects of weathering during the period of geologic history when the carbonate-rock aquifer was exposed at the land surface before glaciation (Ohio Department of Natural Resources, Division of Water, 1970). The productivity of the aquifer varies with the concentration of openings within the rock, which seldom approach conditions associated with karst terranes. These openings are interconnected on an areal basis. Previous researchers (Ohio Department of Natural Resources, Division of Water, 1970) noted that the hydraulic characteristics of the carbonate-rock aquifer approach those of a regionally homogeneous medium as the study area increases. Arihood (1994) also notes that aquifer tests that create drawdown cones over several miles depict the carbonate-rock aquifer as an equivalent porous medium. On the basis of data from 171 aquifer



Boundary of study area

Well location and transmissivity—Transmissivity range in feet squared per day

- o 100 to 1,000
- O Greater than 1,000 to 10,000
- Greater than 10,000 to 100,000

FIGURE 9.—Transmissivity of glacial aquifers.

Table 2.—Summary of hydraulic characteristics of aquifers and confining units in the Midwestern Basins and Arches aquifer system

|--, data not available; ft/d, feet per day; ft²/d, feet squared per day|

Aquifer or confining unit	Range of horizontal hydraulic conductivities (ft/d)	Range of vertical hydraulic conductivities (ft/d)	Range of transmissivities (ft²/d)	Range of storage coefficients
Glacial aquifers		<sup>b</sup> 0.0001 – 0.77	a300 - 69,700	a0.00002 - 0.38
Glacial confining units	22-1	0.0001 – 0.77	°1.5, 2.1	
Upper confining unit	$^{\rm d}10^{-7}-10^{-5}$			
Carbonate-rock aquifer			<sup>a,e</sup> 70 – 52,000	$^{\mathrm{a}}0.00001 - 0.05$
Upper weathered zone water-bearing unit	f0.0016 - 12		5-1	44
Basal confining unit	g10-7-10-5			

<sup>&</sup>lt;sup>a</sup>Joseph and Eberts (1994).

<sup>c</sup>Strobel (1993).

f Dumouchelle (1992).

tests, transmissivities of the carbonate-rock aquifer range from 70 to 52,000 ft²/d (fig. 10). These data were tested for normality by use of the Shapiro-Wilk test and were found to follow a lognormal distribution; they have a geometric mean of 1,912 ft²/d. Storage coefficients range from 0.00001 to 0.05 (Joseph and Eberts, 1994). No pumped-well test data are available for estimation of vertical-hydraulic conductivities of the carbonate-rock aquifer.

Very little information is available to describe the hydraulic characteristics of the interbedded shales and limestones that function as a basal confining unit to the Midwestern Basins and Arches aquifer system. Analyses of core collected from the upper part of the interbedded shale and limestone sequence in southwestern Ohio provide estimates of vertical and horizontal hydraulic conductivities that range from 10<sup>-7</sup> to 10<sup>-5</sup> ft/d (Lawrence Wickstrom, Ohio Geological Survey, written commun., 1991). These values do not account for secondary porosity within the rocks. Shales of Ordovician age, however, are considered favorable for underground storage of liquefied natural gas in southern Indiana, where they underlie the carbonate-rock aquifer, because of their low hydraulic conductivities (Droste and Vitaliano, 1976); thus, these shales can be assumed to be very restrictive to ground-water flow in this area. Hydraulic conductivities are likely to be higher in the upper weathered zone water-bearing unit where the shales have been exposed at the land surface. On the basis of slugtest data at four wells completed in the upper part of the interbedded shale and limestone sequence near the upper weathzone water-bearing unit, horizontal hydraulic conductivities range from 0.0016 to 12 ft/d (Dumouchelle, 1992).

#### **LEVELS**

Review of historical ground-water-level data indicates a long-term steady-state condition in the aguifer system. (Long-term steady-state conditions refer to a state of dynamic equilibrium in which no net change in storage in the aquifer system occurs over a long-term period. The long-term period referred to herein is a minimum of 10 years and includes wet and dry periods.) Extensive ditching to drain swampland in low-lying areas in northwestern Ohio (Kaatz, 1955) and northwestern Indiana in the late 1800's and early 1900's resulted in some dewatering of shallow glacial deposits (5 to 7 ft) in Indiana (Rosenshein, 1963; Indiana Department of Natural Resources, 1990) and possibly similar dewatering in Ohio; however, a new equilibrium has been established in these areas (Eberts, 1999). Annual ground-water-level fluctuations related to ground-water recharge range from 3 to 7 ft in the aquifer system (Clark, 1980; Shindel and others, 1991a, b). Annual high water levels are reached between March and June, and annual low water levels are reached near the end of the growing season.

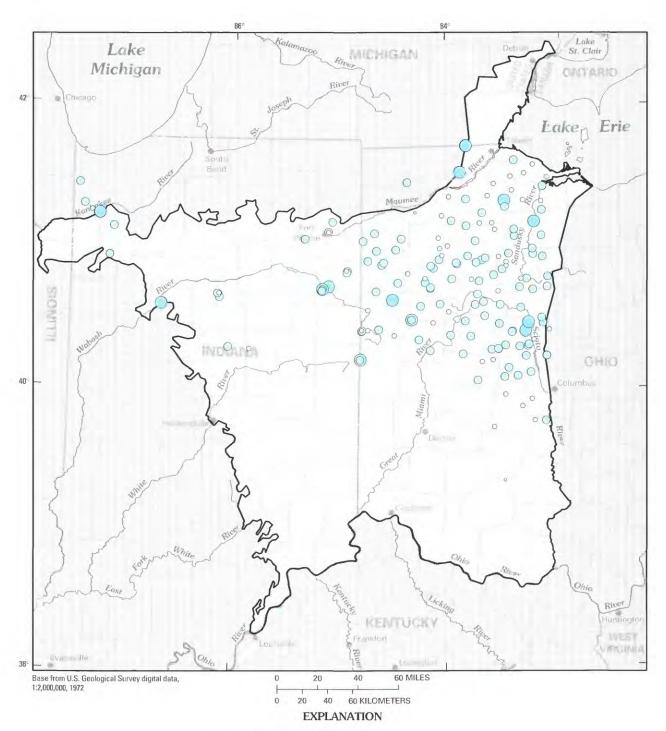
The altitude of the water table, which typically is in glacial deposits, is a controlling factor for regional flow in the Midwestern Basins and Arches aquifer system. Most regional variation in water-table altitude is a consequence of the variation in land-surface altitude, and depth to the water table varies predictably at the regional scale. The specific relation between land-surface altitude and water levels in glacial deposits was determined by use of a least-squares method of linear regression (Eberts, 1999). Depth to water is greatest in topographically high areas and decreases in areas such as stream valleys. A composite regional potentiometric-surface map of the glacial deposits was constructed from water levels

<sup>&</sup>lt;sup>b</sup>Norris (1959, 1979, 1986), Fleming (1989), Strobel (1993).

<sup>&</sup>lt;sup>d</sup>G.D. Casey (U.S. Geological Survey, written commun., 1993). From laboratory analyses of core samples.

<sup>&</sup>lt;sup>e</sup>Geometric mean, 1,912 ft<sup>2</sup>/d.

<sup>&</sup>lt;sup>g</sup>Lawrence Wickstrom (Ohio Geological Survey, written commun., 1991). From laboratory analyses of core samples.



#### Boundary of study area

Well location and transmissivity—Transmissivity range in feet squared per day

- 1 to 100
- O Greater than 100 to 1,000
- O Greater than 1,000 to 10,000
- Greater than 10.000 to 100.000

FIGURE 10.—Transmissivity of the carbonate-rock aquifer.

reported on drillers' logs and is shown in figure 11. Also shown in figure 11 is the lack of available drillers' logs for most areas south of the limit of the Wisconsinan ice sheet. Perhaps so few domestic wells have been completed in glacial deposits within these areas because the units are not productive.

The regional potentiometric surface in the carbonate-rock aquifer is a subdued reflection of the land surface and further illustrates the effect of variations in land-surface altitude on the aquifer system. A regional potentiometric-surface map of the carbonate-rock aquifer (fig. 12) was constructed from water levels synoptically measured during July 1990 (Eberts, 1999). Potentiometric highs are in west-central Ohio near the Bellefontaine Outlier and near the southern limit of the carbonate-rock aquifer along the border between Indiana and Ohio. Potentiometric lows less than or equal to 600 ft are along the Wabash and the Ohio Rivers and Lake Erie.

#### RECHARGE

Ground-water recharge at the water table of the Midwestern Basins and Arches aquifer system is primarily from infiltration of precipitation and the associated flow away from the water table within the saturated zone. Recharge from precipitation at the water table varies seasonally because evapotranspiration, which can intercept infiltrating precipitation, varies seasonally. Recharge to the carbonate-rock aquifer is primarily from percolation of ground water through overlying units. The rate at which the carbonate-rock aquifer is recharged by percolation depends on the permeability and thickness of the overlying deposits and the difference between the water table in the overlying deposits and the potentiometric surface in the carbonate-rock aquifer.

Very few estimates of recharge to the Midwestern Basins and Arches aquifer system have been made. Daniels and others (1991) estimated recharge rates through unsaturated glacial till to be 1.4 and 1.8 in/yr from a tritium profile obtained from a core collected in Indiana, but they stated that such rates are more applicable to a local scale than a regional scale. Walton and Scudder (1960) report recharge rates of 12 in/yr through outwash deposits and 8 in/yr through glacial till on uplands within parts of the Great Miami River Basin. All other available recharge estimates, excluding those determined by use of previously constructed numerical groundwater flow models, are for recharge to the carbonate-rock aquifer. These estimated recharge rates, based on analyses of flow nets and on cones of influence of pumped wells, range from 0.14 to 6.3 in/yr (Rosenshein, 1963; Watkins and Rosenshein, 1963; Rowland and Kunkle, 1970; Cravens and others, 1990; Roadcap and others, 1993).

#### DISCHARGE

Ground-water discharge from the aquifer system includes discharge to streams, ditches, lakes, and wetlands and the removal of water from the saturated zone by evapotranspiration and pumping. Ground water discharges to a stream if the water table or potentiometric surface is above the stage of the stream, whereas the stream loses water to the aquifers if the water table is below the stream stage. Ground-water discharge to streams (base flow) can be estimated from streamflow data by separating streamflow hydrographs into directrunoff and base-flow components.

Streamflow data were used to estimate ground-water discharge from the aquifer system to streams that drain the study area. Daily mean base flows for the period associated with unregulated or only minimally regulated low flow were computed for selected streamflow-gaging stations by means of the local-minimum method of hydrograph separation (Pettyjohn and Henning, 1979). A computer program (R.A. Sloto, U.S. Geological Survey, written commun., 1988) was used in this investigation to automate the local-minimum method of hydrograph separation; use of a computer program ensured that the separation technique was applied consistently.

Mean ground-water discharge to stream reaches above each selected streamflow-gaging station was estimated from the daily mean base flows. This was accomplished for each station by computing the average of all the daily mean base flows for the period selected for analysis (Eberts, 1999). Mean ground-water discharge to stream reaches between streamflow-gaging stations was estimated by computing the difference between mean ground-water discharge estimates for adjacent stations (fig. 13). These means describe the central tendency of ground-water discharge to the selected streams within the study area for long-term steady-state conditions in the aquifer system.

Mean ground-water discharge ranges from 17 to 80 percent of mean streamflow for the 43 selected stream reaches for which streamflow data were analyzed. (These values are the upper numbers in figure 14.) Mean ground-water discharge as a percentage of mean streamflow increases with distance downstream in about half of the principal surfacewater drainage basins. Stated another way, ground water generally makes up a greater proportion of streamflow at the bottom of these drainage basins than in areas higher up in the basins. Unusually large percentages of mean ground-water discharge occur along stream reaches that drain areas underlain by large amounts of outwash deposits (figs. 5 and 14). In contrast, a notable decrease in mean ground-water discharge as a percentage of mean streamflow with distance downstream occurs where the Maumee River drains an area underlain by glaciolacustrine deposits (figs. 5 and 14). A decrease in mean ground-water discharge as a percentage of mean streamflow also occurs in the south-central part of the study area where the streams flow over areas where the carbonaterock aquifer is absent (figs. 4 and 14). Cross (1949) also reported a relation between geology and base flow in Ohio.

Fluctuations of base flow in streams within the study area result from changes in hydraulic gradients in the Midwestern

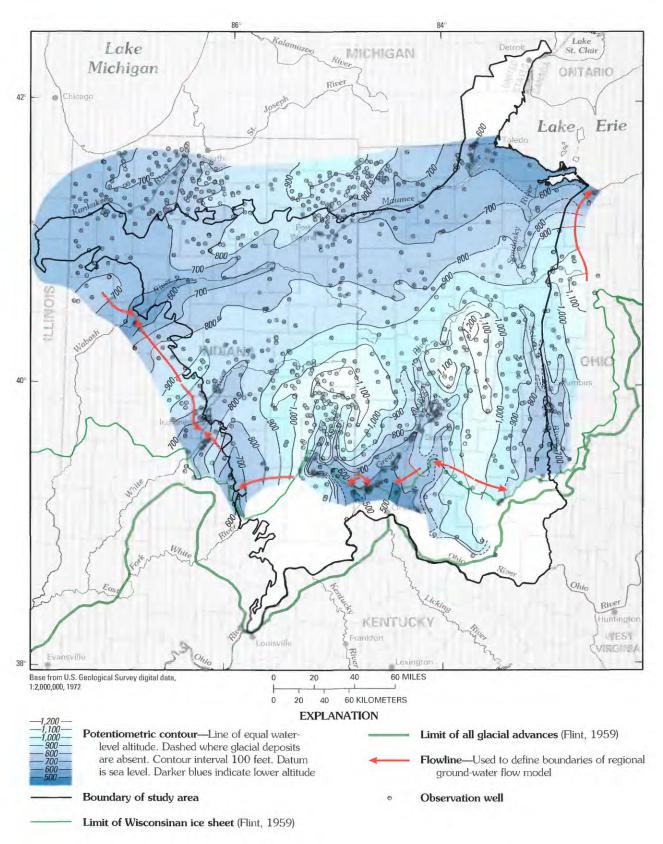


FIGURE 11.—Composite regional potentiometric surface in glacial deposits constructed from water levels on drillers' logs.

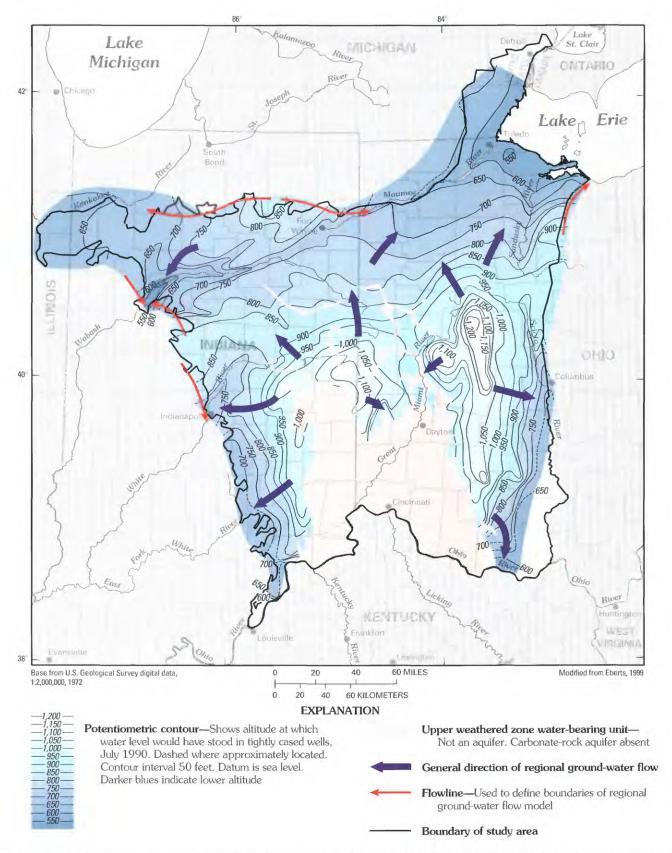


FIGURE 12.—Regional potentiometric surface in the carbonate-rock aquifer, July 1990, and general directions of regional ground-water flow.

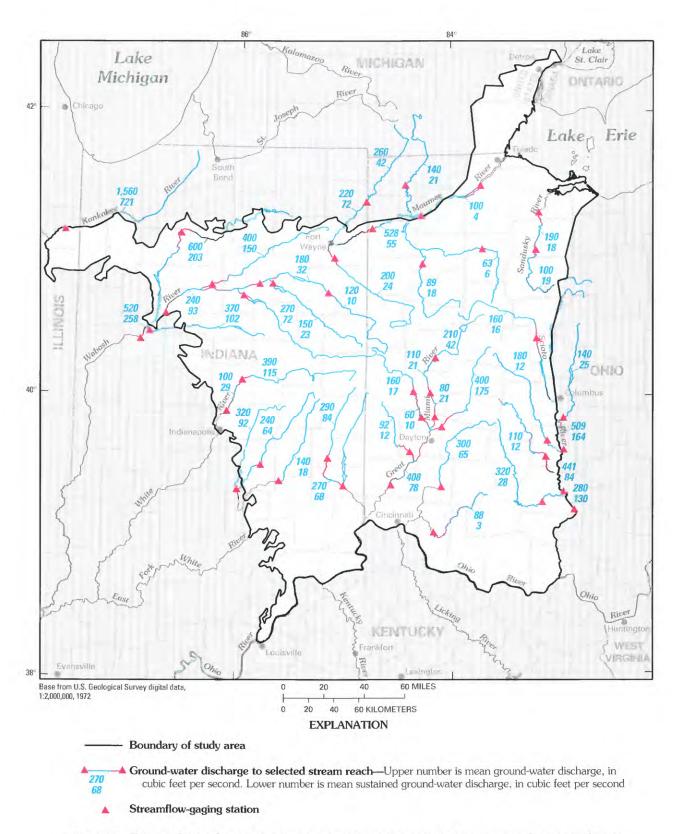
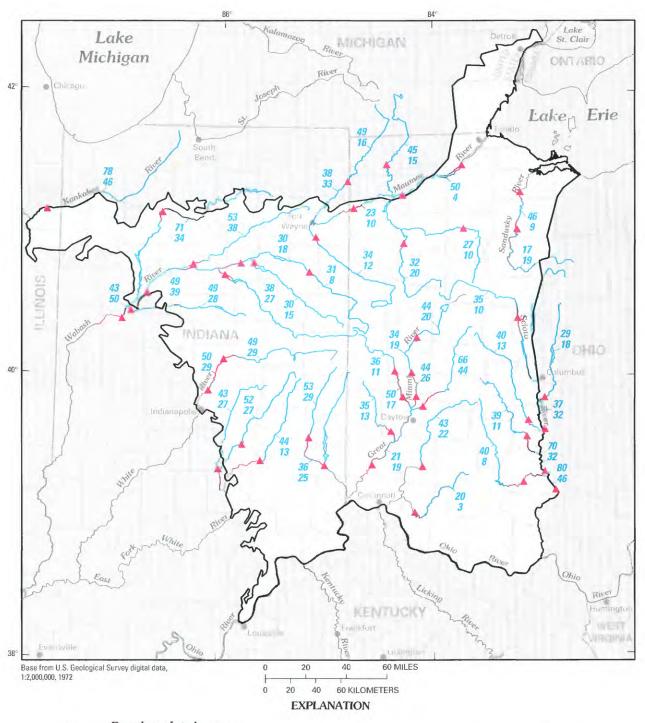


FIGURE 13.—Estimated ground-water discharge to selected stream reaches for long-term steady-state conditions in the Midwestern Basins and Arches aquifer system.



#### Boundary of study area

Discharge percentages for selected stream reach—Upper number is mean ground-water discharge as a percentage of mean streamflow. Lower number is mean sustained ground-water discharge as a percentage of mean ground-water discharge. Percentages represent long-term steady-state conditions in the Midwestern Basins and Arches aquifer system

#### Streamflow-gaging station

FIGURE 14.—Mean ground-water discharge as a percentage of mean streamflow, and mean sustained ground-water discharge as a percentage of mean ground-water discharge for selected stream reaches.

Basins and Arches aquifer system. Winter (1983) illustrates the effects of ground-water recharge from precipitation on hydraulic gradients in a water-table aquifer. He shows that hydraulic gradients in the areas of a water-table aquifer nearest a surface-water body are the first to respond to a recharge event because the water table is closest to land surface in these areas. Eventually, hydraulic gradients in the upland areas are affected by the recharge event (fig. 15). Seasonal fluctuations of base flow in streams are related to seasonal variations in ground-water recharge and the corresponding changes in hydraulic gradients at the water table. Some ground-water flow systems within an aquifer system are minimally affected by recharge events; these more stable groundwater flow systems provide a relatively constant source of ground-water discharge to streams over the course of a year and throughout long periods (fig. 15). The term "sustained ground-water discharge" is used herein to refer to this relatively constant source of base flow.

Base-flow duration curves constructed from daily mean base flows can be used to identify the component of base flow that is sustained during long periods, which include the driest periods (Eberts, 1999). (Base-flow duration curves are cumulative frequency curves that show the percentage of time during which specified base flows were equaled or exceeded in a given period; they are constructed by use of the method described by Searcy (1959), except that daily mean base flows are used instead of daily mean streamflows.)

Base-flow duration curves for streamflow-gaging stations along the principal streams within the study area are generally made up of two limbs when plotted on log-probability paper (fig. 16). The upper limb of each curve is commonly concave, whereas the lower limb of each curve is commonly a straight line, representing a flattening of the overall curve. This two-limb shape indicates the presence of at least two sources of ground-water discharge to these streams. Superimposed base-flow duration curves, constructed from periods of record that represent different ground-water recharge conditions, provide insight into the sources of ground-water discharge that result in the upper and lower limbs of the curves (fig. 16). Specifically, superimposed curves constructed from (1) the entire period of record, (2) from only summer months, when potential evapotranspiration exceeds precipitation (Todd, 1969), and (3) from a period of drought (U.S. Geological Survey, 1991) for single streamflow-gaging stations within the study area show that daily mean base flows that make up the upper limbs of the curves are from a groundwater source that readily responds to variations in groundwater recharge from precipitation. Conversely, the daily mean base flows that make up the lower limbs are from a groundwater source not greatly affected by variations in groundwater recharge (sustained ground-water discharge), as evident from the minimal differences in the lower limbs of the same curves. The base flows that make up the upper limb of each curve are likely to include a major component of transient,

local-scale ground-water flow, because ground-water levels in local ground-water flow systems commonly decline in the summer and during droughts in response to a decrease in ground-water recharge from precipitation. The base flows that make up the lower limb of each curve are from a more stable ground-water flow, and likely represent a more dominant influence of intermediate- and regional-scale ground-water flow systems.

Lower limbs are absent or indistinct on base-flow duration curves constructed for streams within the study area that cease or nearly cease to flow during periods of dry weather. Such streams include small tributaries and streams that drain areas underlain by poorly permeable rocks. The absence of a lower limb on a base-flow duration curve cannot be used in itself to infer that stable flow systems are absent in the underlying aquifer system. Rather, relatively stable ground-water flow systems may be present in the underlying aquifer system but may simply discharge at some other point.

Mean sustained ground-water discharge to the stream reaches above selected streamflow-gaging stations was estimated by constructing base-flow duration curves and computing the average, for each curve, of all the daily mean base flows that make up the lower limb (Eberts, 1999). These base-flow duration curves were constructed, with the aid of a computer program developed by Lumb and others (1990), for the same period of record used to estimate mean ground-water discharge to the streams. Mean sustained ground-water discharge to stream reaches between streamflow-gaging stations was estimated by computing the difference between mean sustained ground-water discharge estimates for adjacent stations (fig. 13). These means describe the central tendency of sustained ground-water discharge to the streams for long-term steady-state conditions in the aquifer system.

Mean sustained ground-water discharge ranges from 3 to 50 percent of mean ground-water discharge for the 43 selected stream reaches. (These values are the lower numbers in figure 14.) Mean sustained ground-water discharge as a percentage of mean ground-water discharge increases with distance downstream along many stream reaches. Notable exceptions are stream reaches in the south-central part of the study area, where the carbonate-rock aquifer is absent, and stream reaches along the Maumee and Sandusky Rivers, which drain into Lake Erie.

Relative amounts of mean ground-water discharge and mean sustained ground-water discharge to streams are illustrated by principal drainage basin in figure 17. These values are for the entire area above the most downstream streamflow-gaging station in each selected drainage basin. Circles are used to illustrate the relative volumes of ground-water discharge within the basins. The sizes of the circles were determined by use of an exponential-curve-scaling method because the range of volumes was too large to be represented effectively by linear scaling. Estimated mean ground-water discharges are noted in the figure for reference. Also repre-

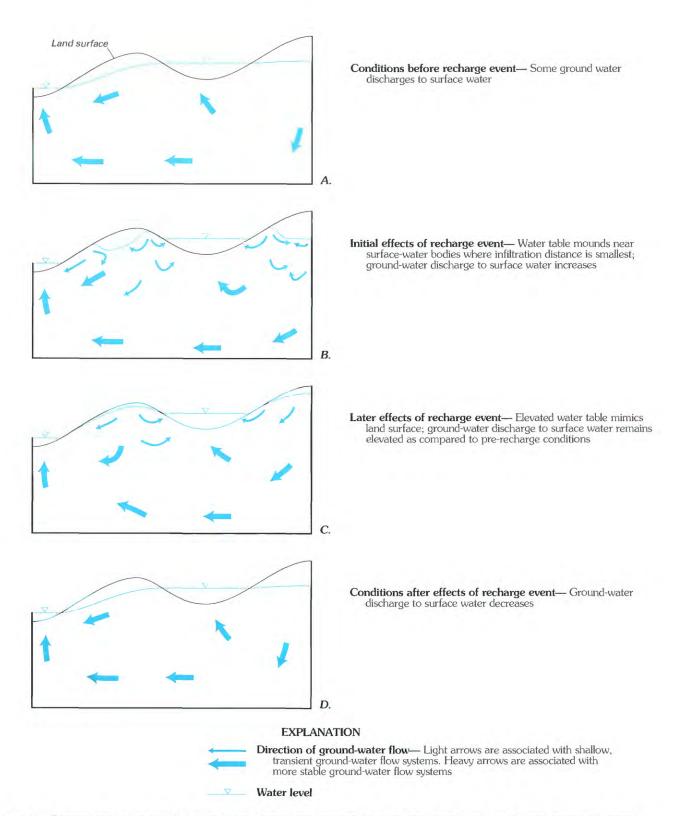


FIGURE 15.—Diagrams showing the effect of recharge from precipitation on the configuration of a water table and associated ground-water flow (modified from Winter, 1983).

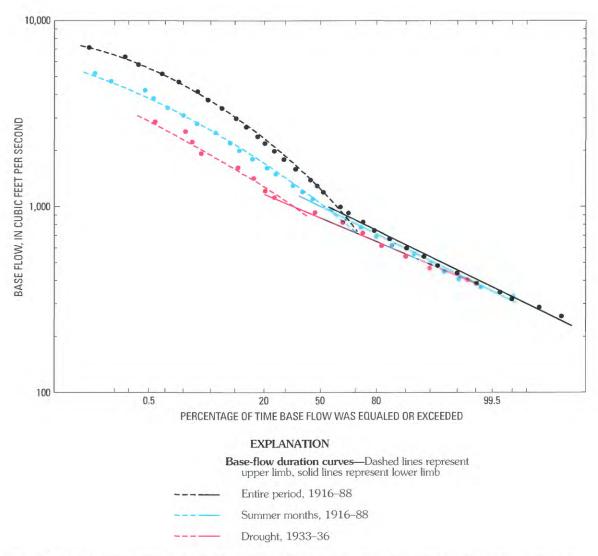


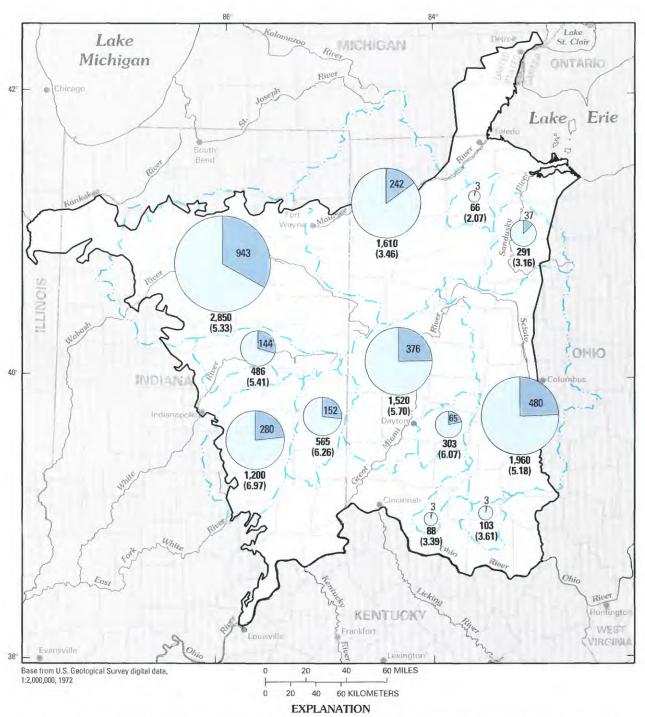
FIGURE 16.—Base-flow duration curves for various ground-water recharge conditions for a streamflow-gaging station on the Kankakee River.

sented in figure 17 are pie slices in each of the circles that shows the percentage of mean ground-water discharge to streams attributed to mean sustained ground-water discharge.

The greatest volume of ground-water discharge to streams is within the Wabash River Basin. This basin also has the highest mean sustained ground-water discharge as a percentage of mean ground-water discharge to the streams. Large amounts of outwash deposits are present within the basin. It is also the largest drainage basin within the study area. Bedrock crops out locally along the main stem of the Wabash River. In addition, the Wabash River is relatively deeply incised, and it has nearly the lowest base level within the study area. These factors likely contribute to the availability of ground-water recharge, resulting in a large volume of ground-water flow beneath the basin, and facilitate the interception of flow paths associated with the more stable ground-water flow systems.

The surface-water drainage basins with the smallest mean sustained ground-water discharge to streams as a percentage of mean ground-water discharge include the basins in the southeastern part of the study area. This may be due to the relatively small size of the basins, as well as their substantial local relief; transient, local ground-water flow systems generally dominate in such areas. These basins also differ from the Wabash River Basin in that glacial deposits are thin or absent within this area.

Flows of streams that drain into Lake Erie also consist of small percentages of mean sustained ground-water discharge. Hydraulic gradients within the aquifer system beneath the Maumee River Basin are fairly low. Because this basin is near Lake Erie and the base level of the aquifer system, the low hydraulic gradients may limit the capacity of the aquifer system to carry ground water away from recharge areas. As a result, much of the precipitation that potentially would



Mean sustained ground-water discharge to streams within selected surface-water drainage basins—Represented by pie slice. Number is discharge, in cubic feet per second, for long-term steady-state conditions in the aquifer system

Mean ground-water discharge to streams within selected surface-water drainage basins—Represented by entire circle. (3.16)Numbers are discharge, in cubic feet per second and inches per year (in parentheses). for long-term steady-state conditions in the aquifer system

#### Boundary of surface-water drainage basin

#### Boundary of study area

291

FIGURE 17.—Relative amounts of mean ground-water discharge and mean sustained ground-water discharge to streams in selected surface-water drainage basins.

recharge stable ground-water flow systems in these areas may be forced to discharge locally by means of drainage tile or shallow, transient ground-water flow systems. The Maumee River is also incised only a few feet, which may prevent it from intercepting flow from some stable ground-water flow systems. Poorly permeable glaciolacustrine sediments may also impede discharge from the carbonate-rock aquifer to the Maumee River. In general, glacial deposits in the Maumee River Basin are thin, absent, or poorly permeable. Toth (1963) notes that low ground-water discharge to streams within a drainage basin can be due to other areas of groundwater discharge within the basin. Before ditching in the early 1900's, much of the Maumee River Basin was swampland. Norris (1974) notes that the historic Black Swamp in this area resulted from a combination of poor drainage and groundwater discharge from regional ground-water flow into what was a relatively stagnant area of surface water and ground water.

The Sandusky River Basin is also associated with a fairly low percentage of sustained ground-water discharge to streams. Much of the ground water that flows through this drainage basin is likely to discharge to Lake Erie rather than to the streams within the basin.

#### REGIONAL GROUND-WATER FLOW

General concepts regarding flow within an aquifer system are reviewed herein to facilitate discussions of the conceptual and numerical models of the Midwestern Basins and Arches aquifer system. An aquifer system can comprise local, intermediate, and regional ground-water flow systems (fig. 18). In a local system of ground-water flow, recharge and discharge areas are adjacent to each other. In an intermediate ground-water flow system, recharge and discharge areas are separated by one or more topographic highs and lows. In a regional ground-water flow system, recharge areas are along ground-water divides, and discharge areas lie at the bottom of major drainage basins. Not all types of ground-water flow are present in every aquifer system (Toth, 1963).

The greatest amount of ground-water flow in an aquifer system is commonly in local flow systems. Ground-water levels and flow in local flow systems are the most affected by seasonal variations in recharge because recharge areas of these relatively shallow, transient ground-water flow systems make up the greatest part of the surface of a drainage basin (Toth, 1963). Regional flow systems are less transient than local and intermediate flow systems. For the remainder of this report, the term "regional flow systems" is used to describe flow systems that are minimally affected by seasonal variations in ground-water recharge and are capable of providing a fairly constant source of discharge to streams (sustained ground-water discharge). Although this use of the term "regional flow systems" refers, in large part, to intermediate

and regional flow systems as defined by Toth (1963), some local-scale flow also may be included.

#### **CONCEPTUAL MODEL**

A conceptual model of an aquifer system is a simplified, qualitative description of the physical system. A conceptual model may include a description of the aquifers and confining units that make up the aquifer system, boundary conditions, flow regimes, sources and sinks of water, and general directions of ground-water flow. The conceptual model of the Midwestern Basins and Arches aquifer system presented herein is based on information presented in the "Geohydrology" section of this report.

The Midwestern Basins and Arches aquifer system is in a state of dynamic equilibrium with respect to hydrologic variations over the long-term period. As a result, the aquifer system may be adequately described on the basis of long-term average water levels and ground-water discharges. In addition, annual ground-water-level fluctuations are quite small (less than 10 ft) compared to the thickness of the aquifer system (hundreds of feet).

The water table within the aquifer system generally is within alluvium or glacial deposits; glacial aquifers can supply large yields of ground water in only a limited number of places. The glacial deposits are underlain by an areally extensive carbonate-rock aquifer, which is semiconfined or locally confined by the glacial deposits across most of the study area. The carbonate-rock aquifer is confined by shale along the margins of the aquifer system. Very little water is produced from the carbonate-rock aquifer under the shales because shallower freshwater sources are generally available.

Spatial patterns in hydraulic characteristics of the glacial aquifers or the carbonate-rock aquifer are not readily apparent from the available transmissivity data (figs. 9 and 10); however, some of the highest transmissivities in the glacial aquifers are associated with outwash deposits along the principal streams (figs. 5 and 9). Despite the spatial variability of hydraulic characteristics within the carbonate-rock aquifer, the aquifer functions as a single hydrologic unit at a regional scale (Arihood, 1994).

The upper boundary of the aquifer system coincides with the water table. The lower boundary generally coincides with the contact between the carbonate-rock aquifer and interbedded shales and limestones of Ordovician age where they underlie the aquifer. Where the carbonate-rock aquifer is hundreds of feet thick, the lower boundary of the aquifer system may be within the carbonate rocks. Lateral boundaries of the carbonate-rock aquifer include the limit of potable water (waters that contain dissolved-solids concentrations less than 10,000 mg/L; U.S. Environmental Protection Agency, 1984)) to the north, east, and west (fig. 34), Lake Erie to the north-

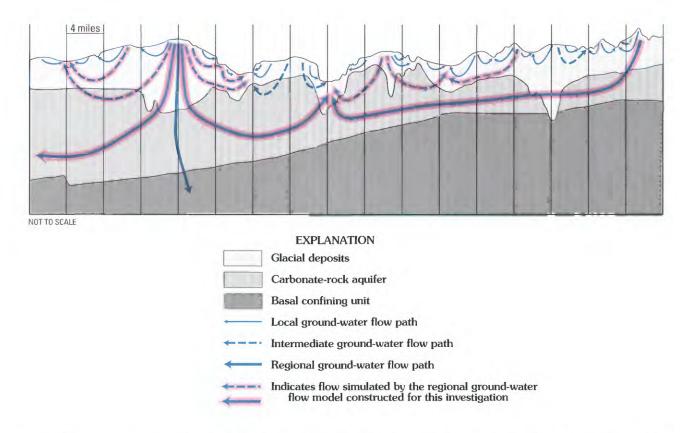


Figure 18.—Diagrammatic conceptual model of the Midwestern Basins and Arches aquifer system showing flow paths associated with local, intermediate, and regional flow systems (modified from Toth, 1963) and flow systems simulated by the regional ground-water flow model.

east, and the Ohio River and the upper weathered zone waterbearing unit to the south.

Several types of ground-water flow systems are present within the Midwestern Basins and Arches aquifer system, as evidenced by base-flow duration curves constructed for selected streamflow-gaging stations within the study area (discussed previously in the "Discharge" section). The amount of ground-water discharge to streams from fairly stable ground-water flow systems (regional, as defined in this report) relative to the amount of discharge from all scales of ground-water flow systems (local, intermediate, and regional) within the aquifer system (fig. 17) indicate that local flow systems dominate ground-water discharge to streams within the Midwestern Basins and Arches Region, Unless a large amount of ground water flows across lateral boundaries of the aquifer system or large volumes of ground water discharges to places other than streams, figures 14 and 17 can be used to infer that local flow systems dominate ground-water flow in the aquifer system.

The amount of recharge to regional flow systems (as defined in this report) within the Midwestern Basins and Arches aquifer system is approximately equal to mean sustained ground-water discharge to streams, ditches, lakes, and

wetlands and losses from the relatively stable parts of the aquifer system by means of evapotranspiration and pumping. Recharge to the deepest parts of the aquifer system occurs predominantly in the upland areas.

The amount of ground water available to sustain streams during the driest periods (discharge from regional flow systems) within the study area is related to a number of factors. These factors include the availability of recharge, the geology and hydraulic gradients within the aquifer system, the position of the streams within the drainage basins and relative to the aquifer system in general, the relative incisement of the streams, and the presence of other places of discharge within the drainage basins.

Ground water flows from recharge areas, which are associated with high ground-water levels, to discharge areas, which are associated with low ground-water levels. General directions of regional flow in the aquifer system are away from several potentiometric highs toward the principal streams and Lake Erie. Most active flow of freshwater (less than 10,000 mg/L dissolved solids) in the carbonate-rock aquifer within the aquifer system is confined to the subcrop area of the aquifer.

#### **NUMERICAL MODEL**

A numerical model was constructed to test and improve upon the conceptual model of regional ground-water flow within the Midwestern Basins and Arches aquifer system. Concepts that were tested include the assumption that the carbonate rocks are (are not) productive throughout their entire thickness and hypotheses about what contributes to the differences in the percentages of mean sustained ground-water discharge to streams across the study area. The numerical model was also used to investigate the absence of systematic increases in ground-water ages along general directions of regional flow throughout most of the study area and the presence of isotopically distinct ground water beneath the Maumee River Basin (see "Geochemistry" section). Various aspects of the qualitative conceptual model were also quantified by use of the numerical model. Specifically, a regional ground-water budget was computed; rates and patterns of recharge and discharge to and from regional flow systems were mapped; and natural regional ground-water flow patterns and relative magnitudes of regional ground-water flow were determined.

In a numerical model, aquifers and confining units within an aquifer system are represented by cells organized into layers. Hydraulic heads and flow in each layer and the exchange of water between adjacent layers and across boundaries are computed simultaneously. These calculations are most commonly accomplished by use of a computer code that solves finite-difference or finite-element approximations of the partial differential equations (three-dimensional ground-water flow equation, boundary conditions, and initial conditions) that form the numerical model (Anderson and Woessner, 1992, p. 20).

The specific computer code used in this investigation is a three-dimensional modular model that solves a finite-difference approximation of the partial differential equations that describe ground-water flow (MODFLOW) (McDonald and Harbaugh, 1988). In the governing ground-water flow equation represented by this model, the density of water is assumed to be constant. Although the density of the water in the aquifer system may change within the carbonate-rock aquifer along the margins of the Michigan and Appalachian (structural) Basins, the effects of the density variations on ground-water flow within the modeled part of the aquifer system were assumed to be small enough that a variable-density flow model was considered unnecessary. This is a reasonable assumption because most of the aguifer system that was modeled is miles from these margins, stresses on the aquifer system do not affect the lateral limits of freshwater, and any affect density variations may have on model estimates of hydraulic conductivity or simulated hydraulic heads are likely to be within the confidence limits of the estimated hydraulic conductivity or the error associated with the hydraulic-head observations.

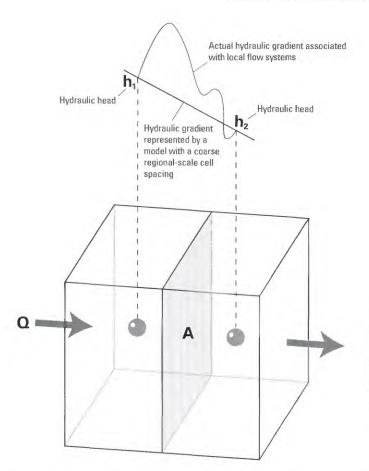
### MODEL DESIGN

The numerical model built as part of this investigation was designed to simulate steady-state regional flow systems within the aquifer system. These are flow systems that are minimally affected by seasonal variations in ground-water recharge from precipitation and are capable of sustaining discharge to the streams during the driest periods. On the basis of stream base-flow estimates, much less than 50 percent of ground-water flow in the aquifer system is associated with these regional flow systems (figs. 14 and 17).

The model was not designed to simulate the preponderant local flow systems that are juxtaposed on the regional flow systems (figs. 15 and 18). Such local flow systems are too small and numerous to be adequately represented with a regional-scale model. Specifically, the model cell spacing chosen for this investigation (4 mi on a side) is not fine enough to capture the curvature of the water table associated with such local flow systems. This effect of scale results in the simulation of less cross-sectional area and hydraulic gradient than actually exists in the aquifer system; thus, the model cannot simulate the corresponding flow (fig. 19). Because local flow systems cannot be explicitly simulated in a model with a coarse regional-scale cell spacing, a boundary condition (discussed later in this section) was used to simulate the influence of the local flow systems on the deeper regional flow systems. The simulated regional ground-water budget, therefore, represents the budget of just the regional flow systems and not all flow systems within the aquifer system. Because water in local flow systems moves from recharge areas to the nearest stream valley, a map of the density of perennial streams that drain the modeled area is included to help illustrate the relative number of local flow systems that may be present within the aquifer system but are not included in the model (fig. 20).

Some flow systems may cross the basal confining unit of the Midwestern Basins and Arches aquifer system and become part of an even larger aquifer system. These flow systems also are not simulated by the regional ground-water flow model (fig. 18).

Unlike some areally extensive aquifer systems elsewhere in the Nation, the Midwestern Basins and Arches aquifer system is not subject to regional-scale pumping stresses. It was therefore unnecessary to construct a transient model that is capable of simulating changes in ground-water levels, discharge, and storage with time to represent regional ground-water flow (see "Conceptual Model" section). As a result, once a steady-state calibration was achieved, the numerical model was not calibrated to transient conditions, nor was it used to make predictions about the effects of future pumpage on regional ground-water flow. Known volumes of pumpage were also not included in the model because reported pumpage from the aquifer system is approximately 3 percent of total flow in the aquifer system. Although it is not known how



DARCY'S LAW

 $Q = -KA \frac{dh}{dl}$ 

Q, Flow

K, Hydraulic conductivity

A, Area

 $\frac{dh}{dl}$ , Hydraulic gradient

A model with a coarse-regional-scale cell spacing often cannot capture the actual cross-sectional area and hydraulic gradients associated with local flow systems. On the basis of Darcy's Law, if K is constant, simulated flow (Q) in such a simulation will be less than actual flow in the aquifer system because simulated area (A) and hydraulic gradients ( $\frac{dh}{dl}$ ) will be less than actual area and hydraulic gradients.

FIGURE 19.—Effect of model-cell spacing (model scale) on the amount of flow in an aquifer system that can be simulated with a numerical model.

much of this reported pumpage is associated with the predominant local flow systems as opposed to the simulated regional flow systems, most pumpage is assumed to be from the local flow systems. Even if all reported pumpage from the carbonate-rock aquifer is associated with regional flow systems, pumpage from the carbonate-rock aquifer (67 Mgal/d) would be less than 5 percent of flow in the regional flow systems based on estimates of mean sustained ground-water discharge to streams (fig. 17). Although some pumpage from glacial aquifers is also likely to be from regional flow systems, many of the largest water users produce water from outwash deposits along principal streams that are commonly associated with local flow systems, which are not simulated in the model.

# DISCRETE GEOHYDROLOGIC FRAMEWORK

The numerical regional ground-water flow model is a quasi-three-dimensional two-layer model (table 1) structured within a 65-row by 61-column finite-difference grid (fig. 21). The upper model layer (layer 1) is used to simulate hydraulic heads and flow through glacial and other surficial deposits (fig. 22). Effective hydraulic conductivities were used to

account for the heterogeneities with the glacial deposits. (An effective hydraulic conductivity is a hydraulic conductivity of an equivalent homogeneous formation for which the mean flux is equal to that prevailing in the heterogeneous formation (Indelman and Dagan, 1993).) The lower model layer (layer 2) is used to simulate hydraulic heads and flow through the bedrock. A single layer was considered sufficient to simulate flow in the carbonate-rock aquifer because vertical hydraulic-head gradients within the aquifer are small and the carbonate-rock aquifer functions as a single hydrologic unit at a regional scale. Where the carbonate-rock aquifer is absent in the south-central part of the study area, parameter values in model layer 2 were chosen to simulate hydraulic heads and flow in the upper weathered zone water-bearing unit.

Because relatively little horizontal flow occurs within the shale that separates the glacial deposits and the carbonaterock aquifer along the margins of the modeled area, this upper confining unit is not represented as a separate layer in the model. Rather, a quasi-three-dimensional approach is used. With such an approach, only the resistance of the upper confining unit to vertical flow between the glacial deposits and the carbonate-rock aquifer is simulated (figs. 21A and 22).

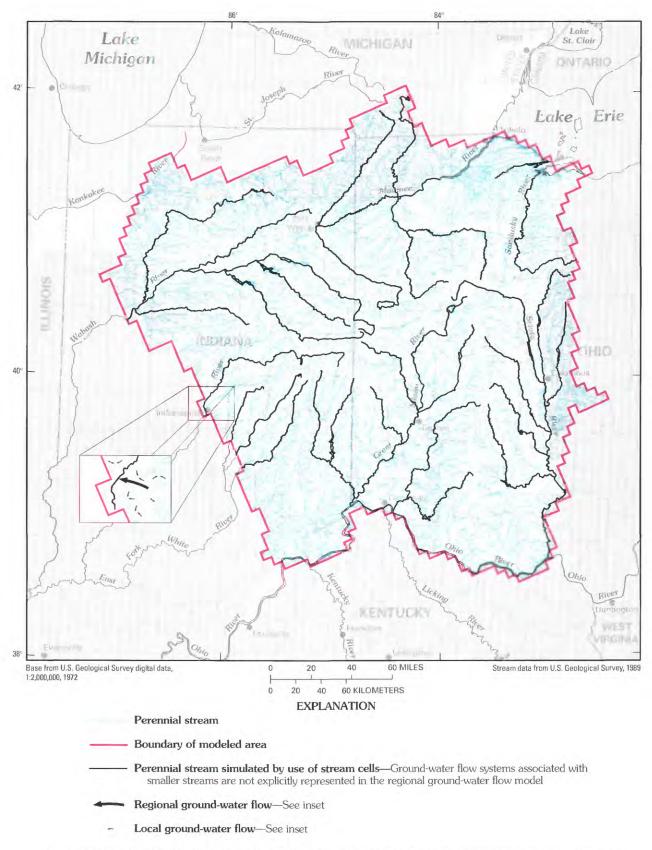


FIGURE 20.—Density of perennial streams that drain the modeled area at the scale of 1:100,000 and streams that are explicity represented in the regional ground-water flow model by use of stream cells.

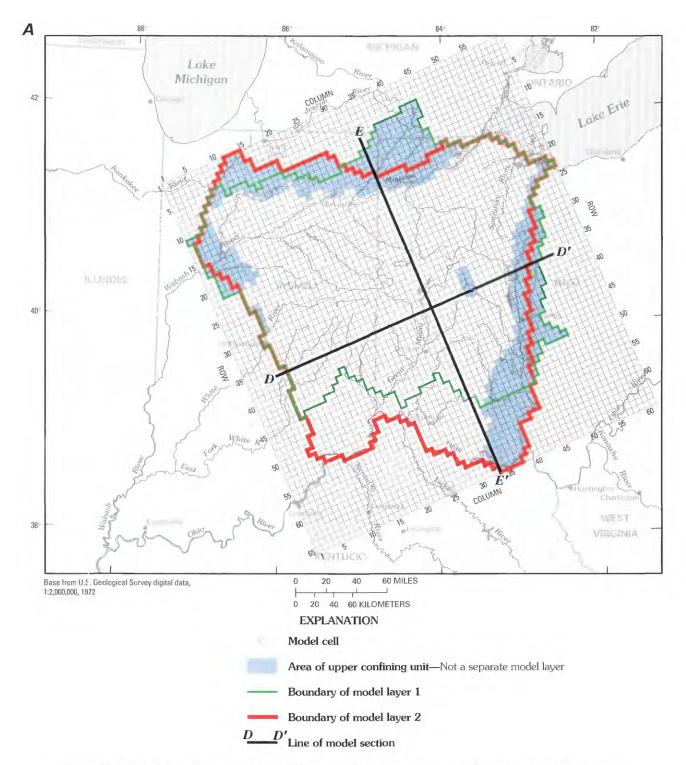


Figure 21.—Model layers used to simulate the Midwestern Basins and Arches aquifer system, and the location of model sections D–D' and E–E': (A) areal extent.

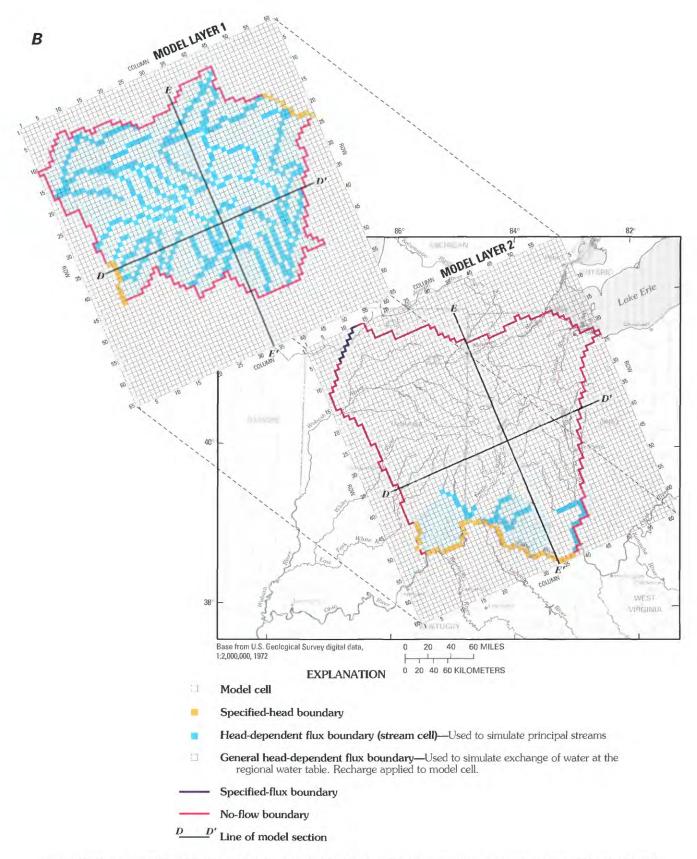


FIGURE 21. CONTINUED—Model layers used to simulate the Midwestern Basins and Arches aquifer system, and the location of model sections D–D′ and E–E′: (B) boundaries.

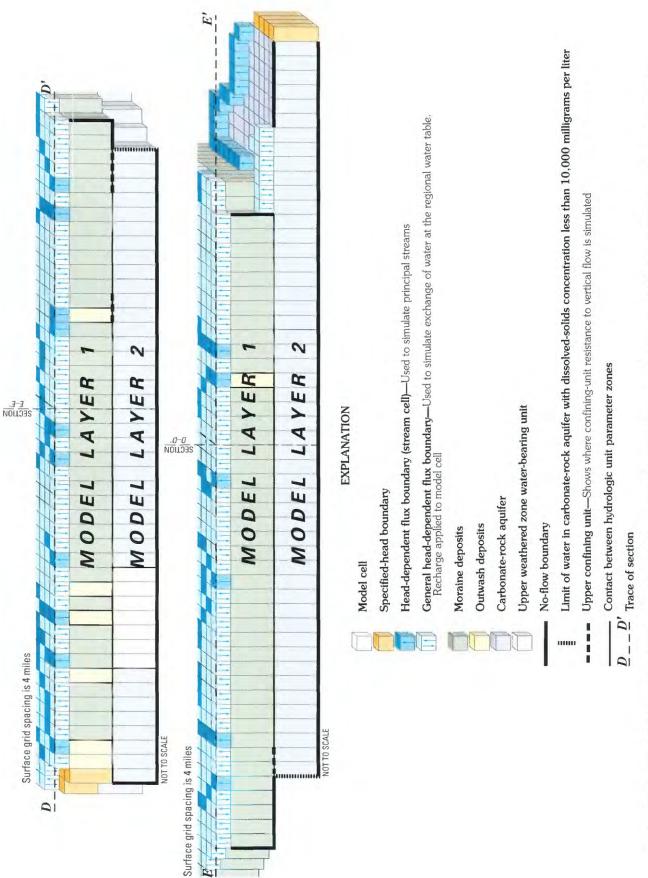


FIGURE 22.—Sectional diagrams showing the areal extent and boundaries of the model layers used to simulate the Midwestern Basins and Arches aquifer system (lines of section on figure 21).

Each model cell is 4 mi on a side. This cell spacing was chosen to allow the curvature in the regional potentiometric-surface map of the carbonate-rock aquifer in figure 12 to be represented by the model. It was assumed that flow in the fractured carbonate-rock aquifer behaves as flow in a porous medium at this simulation scale. It is noted in the "Hydraulic Characteristics" section of this report that this is assumption is probably valid.

The model grid is oriented so that it parallels the edge of the carbonate-rock subcrop along the margin of the Illinois (structural) Basin. This is because it was outside the scope of the investigation to study flow in the carbonate-rock aquifer within the Illinois Basin; a hydraulic boundary—which is easiest to simulate parallel to a finite-difference grid—rather than a physical boundary is simulated along this edge of the model. Anisotropy was not a consideration for model-grid orientation; it is assumed that no principal direction of horizontal anisotropy dominates regional flow within the aquifer system.

### BOUNDARIES, SOURCES, AND SINKS

The following types of boundaries are included in the numerical model and are represented on figures 21B and 22. Model boundaries were set for a given model construction and were not automatically adjusted by the nonlinear regression.

#### No-flow boundaries

Part of the eastern and all of the northern and northwestern boundaries of model layer 1, which represents glacial aquifers and confining units, coincide with principal surfacewater drainage divides that are assumed to coincide with ground-water divides in the glacial deposits. The northern part of the eastern boundary and most of the western boundary of model layer 1 coincide with regional flowlines in the glacial deposits (fig. 11); ground water flows parallel to and not across flowlines. The southern boundary of model layer 1 coincides with the limit of the Wisconsinan ice sheet (fig. 5). Glacial deposits are thin or absent, and few glacial aquifers are present south of this limit. Horizontal flow in glacial deposits beyond the limit of the Wisconsinan ice sheet is assumed to be negligible at the regional scale. In addition, the limit of the Wisconsinan ice sheet coincides with regional flowlines in the glacial deposits throughout much of the modeled area.

The eastern, northern, and part of the western boundaries of model layer 2, which represents the carbonate-rock aquifer or the upper weathered zone water-bearing unit, coincide with flowlines or the position of water in the carbonate-rock aquifer with a dissolved-solids concentration of 10,000 mg/L or greater (fig. 12; see also fig. 34). Water in the carbonate-rock aquifer is assumed to move slowly where it becomes saline (greater than 10,000 mg/L dissolved solids) and, for

the purposes of this investigation, no water is assumed to flow across these boundaries. In addition, the position of the saline waters is assumed to have remained constant over the short period of time (tens of years) represented by the model calibration targets. Part of the northwestern boundary of model layer 2 coincides with a ground-water divide in the carbonaterock aquifer.

Most of the water in the carbonate-rock aquifer along the northeastern model boundary is likely to flow upward into overlying glacial deposits and ultimately into Lake Erie. It is assumed that no water in the carbonate-rock aquifer flows laterally beyond the shore of the lake. Hanover (1994) notes that discharge from the carbonate-rock aquifer to Lake Erie is concentrated near the lakeshore. The assumption of no flow along this boundary was tested by constructing an alternative model with a specified-head boundary in model layer 2. The results of this alternative model are nearly identical to the results of the calibrated final model in which the no-flow boundary forces simulated ground water in the carbonaterock aquifer to discharge through the overlying glacial deposits. This finding indicates that the no-flow boundary does not limit the amount of simulated regional ground-water flow that can leave the aquifer system at this point.

Ground water flows toward part of the western boundary of model layer 2 (fig. 12); however, some of this western boundary is simulated as a no-flow boundary (fig. 21B). This decision was made because a specified-head boundary in model layer 1 (fig. 21B) was considered sufficient to simulate the outward flux from the glacial deposits and the carbonaterock aquifer; at the regional scale, the hydraulic heads in these hydrologic units are very similar along this boundary, owing to the absence of the upper confining unit. In addition, available ground-water-chemistry data (see "Tritium and Carbon Isotopes" section) indicate a notable increase in the age of water in the carbonate-rock aguifer just west of the model boundary where the aguifer dips beneath the upper confining unit. This combination of factors may indicate that much of the water in the carbonate-rock aquifer discharges through the overlying glacial deposits rather than moving downdip into the Illinois (structural) Basin.

The carbonate-rock aquifer is directly underlain by poorly permeable interbedded shales and limestones. As a result, a no-flow boundary condition is assigned to the lower model boundary where it coincides with the bottom of the carbonate-rock aquifer. Simulation of an alternative conceptual model, however (see "Model Discrimination" section), indicates that the lower limit of active freshwater flow may actually be within the carbonate rocks of Silurian and Devonian age where these rocks are hundreds of feet thick. The lower model boundary coincides with the top of the upper confining unit where water in the carbonate rock beneath the upper confining unit is saline.

It is assumed that flow in the upper weathered zone waterbearing unit is restricted to shallow depths (tens of feet) and that any exchange of water between this zone and deeper bedrock units is negligible. Therefore, the lower model boundary beneath the upper weathered zone water-bearing unit is simulated as a no-flow boundary.

#### Specified-head boundaries

The northeastern model boundary in model layer 1 coincides with the shore of Lake Erie. It is assumed that groundwater levels in the glacial deposits along this boundary are near lake level and that they can be represented by the average lake level for the long-term period. A specified-head boundary condition is also imposed on the southern part of the western boundary of model layer 1 where the boundary is coincident with the 700-ft equipotential line on the groundwater-level map of the glacial deposits (fig. 11).

Water-level data reported by Eberts (1999) indicate that ground-water flow in the bedrock on both sides of the Ohio River is toward the river. As a result, the southern boundary of model layer 2 coincides with the position of the Ohio River. Specified hydraulic heads used to simulate this boundary were derived from 1:250,000 topographic maps. A specified-head boundary condition also is imposed along a small section of the western boundary of model layer 2 where notable glacial aquifers, and thus model layer 1, are absent. This boundary coincides with the 700-ft equipotential line on the potentiometric-surface map of the carbonate-rock aguifer in figure 12.

## Specified-flux boundary

A specified-flux boundary condition is imposed on the most northwestern boundary of model layer 2. Ground-water flow across this boundary is approximated by use of Darcy's Law,

$$Q = -KA\frac{dh}{dl}, (1)$$

K is horizontal hydraulic conductivity,

A is the cross-sectional area through which flow

 $\frac{dh}{dl}$  is the hydraulic gradient approximated from the hydraulic-head contours in figure 12.

This boundary flow was manually recalculated and a new amount of flow was specified in the model after transmissivity estimates were updated by the model during calibration.

# Head-dependent flux boundaries (sources and sinks)

Principal streams that drain the modeled area are explicitly simulated by use of head-dependent-flux boundary conditions (figs. 21B and 22). Although these streams only partially penetrate the glacial deposits or carbonate-rock aquifer, analysis of streamflow data indicates that they are discharge points for regional flow within the aquifer system. Hydraulic heads along these stream cells are set equal to the stage of the streams.

The upper boundary of the aquifer system coincides with the water table, which is generally present in glacial deposits but is locally present in bedrock where glacial deposits are thin or absent. A discussion of the treatment of flow across the water-table boundary in the model can be found in the following section.

#### APPROACH TO MAPPING REGIONAL RECHARGE AND DISCHARGE

Anderson and Woessner (1992, p. 152) note that no universally applicable method has been developed for estimating ground-water recharge across a water table and that most proposed methods have been used with limited success. Although recent investigations have demonstrated that spatial variation in the rate of recharge across the water table of an aquifer system can be significant (Stoertz and Bradbury, 1989), modelers have traditionally assumed a spatially uniform recharge rate to simulate the water-table flux across areas of similar surficial geology. Such an approach prohibits adequate representation of flow across the water table because ground-water basins often include areas where the net flux is upward (Anderson and Woessner, 1992, p. 152).

A few recently published concepts, which have been used by other researchers to simulate a water-table flux, are summarized below. These ideas were considered during construction of the numerical model of regional flow in the Midwestern Basins and Arches aquifer system.

Jorgensen and others (1989a, b) and Stoertz (1989) demonstrate that the water-table flux, which is appropriate for simulation of an aquifer system, is scale dependent. If the size of a model cell is larger than the length of some flow paths within the aquifer system, some ground water recharges and discharges within the area represented by a single model cell. The result is a need to reduce the amount of net recharge applied at the water-table boundary of the model to simulate the aquifer system correctly at the desired scale. Buxton and Modica (1992) show that despite uniformity of surficial geology (and thereby recharge rates) in the physical aquifer system across a modeled area, net recharge may vary across the modeled area because the water-table boundary combines the effects of recharge from precipitation and ground-water discharge to streams. Stoertz (1989) also notes that a model-cell spacing that captures the general water-table curvature is necessary in order to equate simulated recharge with basin yield. An additional observation by Stoertz (1989) is that simulated patterns of recharge and discharge are not affected if the permeability of the entire basin is changed; however, simulated recharge and discharge rates are affected. To map recharge and discharge areas and to simultaneously estimate appropriate rates, the modeler must constrain the model solution with some measurements of flow such as streamflow or pumpage.

In the current investigation, the assumption was made that the amount of net recharge appropriate for simulation of regional ground-water flow equals the amount of water necessary to maintain the regional trend of the water table and to simultaneously supply the principal streams with a base flow equal to long-term average ground-water discharge from fairly stable flow systems within the aquifer system (mean sustained ground-water discharge). This net recharge excludes recharge across the water table that discharges near the point of recharge by means of evapotranspiration or by means of local-flow-system discharge to small tributary streams.

Because net regional recharge results from the combined effects of recharge from precipitation and local ground-water discharge, net regional recharge is simulated in the numerical model by applying a uniform rate of recharge to areas of similar surficial geology and allowing recharge in excess of the appropriate net regional recharge to discharge by application of a general head-dependent-flux boundary condition above the uppermost active model layer (figs. 21 and 22). This general head-dependent-flux boundary condition used to simulated the principal streams (stream cells); no recharge is applied to stream cells because the principal streams are areas of known regional discharge, and estimates of discharge from regional flow systems to these streams are used to constrain the model solution.

Hydraulic heads specified for the general head-dependent-flux boundary condition used to help simulate the exchange of water at the regional water table are equal to the altitude of the regional water table. These altitudes were estimated by a method in which digital topographic data and empirical equations relate water-table altitudes and land-surface topography (Williams and Williamson, 1989). The conductance term for the general head-dependent-flux boundary condition is defined to be proportional to the total length of small tributary streams in each model cell (fig. 20) because such streams are assumed to dominate the exchange of water at this boundary.

The inclusion of the general head-dependent-flux boundary condition in the numerical model allows for simulation of some discharge from regional flow systems to areas that are not coincident with the principal streams. Such upward net flux across the regional water table may include water that flows from the point of recharge by way of regional flow systems and subsequently leaves the aquifer system through evapotranspiration or discharge to springs, seeps, ditches, and streams smaller than those represented by the stream cells in the model. This approach to simulation of the water-table boundary also allows for simulation of horizontal flow in the water-table aquifer.

Regional recharge and discharge areas were mapped on a cell-by-cell basis by computing the difference between the amount of recharge applied to the uppermost active model layer and the amount of water lost by means of the head-dependent-flux boundary conditions. In localized areas near regional potentiometric highs, recharge to the deep regional flow systems may be higher than the amount of recharge applied to the model in areas with similar surficial geology. In these places, additional water may enter the simulated regional flow systems by means of the general-head-dependent-flux boundary condition. No net regional recharge or discharge was simulated or mapped where layer 2 is the uppermost active model layer and the carbonate-rock aquifer is isolated from the water table by the upper confining unit (fig. 21).

Head-dependent-flux boundary conditions have been used by other modelers to simulate the flux across a regional water-table boundary (Williamson and others, 1990; Leahy and Martin, 1993). Because the Midwestern Basins and Arches aquifer system is a relatively unstressed steady-state system at the regional scale, the application of a head-dependent-flux boundary condition in this investigation had to differ slightly from previous applications. Specifically, the approach taken in this investigation, as described above, allows net regional recharge to be computed by a steady-state model on a cell-by-cell basis while horizontal flow in the water-table aquifer is simulated. This is possible because, in addition to observations of hydraulic head, base-flow observations along the stream cells are included in the model. The combination of hydraulic-head and base-flow observations was necessary to prevent the general head-dependent-flux boundary condition from overly constraining the model solu-

# PARAMETERIZATION

To simulate steady-state regional ground-water flow in the aquifer system, the modeler specified the following system characteristics: (1) horizontal hydraulic conductivity or transmissivity, (2) vertical hydraulic conductivity, (3) streambed hydraulic conductivity, (4) recharge, and (5) a conductance term for the general head-dependent-flux boundary condition used to help simulate flux at the regional water table. These quantities were calculated by means of 16 parameters (a quantity that is estimated by use of trial and error or nonlinear regression) because it was found that regional ground-water flow in the aquifer system could be reasonably simulated with this few parameters. In addition, for reliable estimation of parameter values, the number of parameters must be a fraction of the number of observations of ground-water levels and flows used to estimate them (Hill, 1992, p.15).

Horizontal hydraulic conductivity in layer 1, used to simulate glacial deposits, is simulated with three parameters. The corresponding parameter zones (areas over which a parameter value is applied uniformly) are shown in figure 23A and represent areas of moraine deposits, outwash deposits, and glaciolacustrine deposits. The horizontal hydraulic conductivities

are effective values that represent the combined effects of sands and gravels (glacial aquifers) and clayey till (glacial confining units) on regional ground-water flow. (These horizontal hydraulic conductivities are multiplied within the computer program by specified saturated thicknesses to compute transmissivity.) Transmissivity in layer 2 is simulated with two parameter zones representing the carbonate-rock aquifer and the upper weathered zone water-bearing unit (fig. 23*B*). (In the "Model Discrimination" section of this report, results are presented for an alternative model in which the parameter value for the carbonate-rock aquifer zone is horizontal hydraulic conductivity rather than transmissivity. In this alternative model, the carbonate-rock aquifer's transmissivity varies systematically with aquifer thickness.)

The vertical hydraulic conductivity between the glacial deposits (layer 1) and the bedrock (layer 2) (fig. 23) is simulated with four parameters. One parameter is used to represent the vertical hydraulic conductivity of the upper confining unit. The other three represent the effective vertical hydraulic conductivities of the glacial deposits and the underlying bedrock where the shale is absent. The associated parameter zones coincide with areas of moraine deposits underlain by bedrock, outwash deposits underlain by bedrock, and glaciolacustrine deposits underlain by bedrock.

Streambed hydraulic conductivity is simulated by use of two parameters. One parameter is used to simulate most streams within the modeled area, and the other is used to simulate the effect of the upper confining unit where it separates the streams and the carbonate-rock aquifer in the southeastern part of the modeled area (fig. 21). Streambed thickness and area for each stream cell are specified.

Recharge from precipitation is simulated with four parameters. The principal recharge zone represents recharge to moraine deposits (ground- and end-moraine deposits) or locally to the carbonate-rock aquifer. The other smaller zones represent recharge to outwash deposits, glaciolacustrine deposits, or the upper weathered zone water-bearing unit directly (fig. 23).

Finally, the conductance term of the general head-dependent-flux boundary condition used to help simulate the exchange of water at the regional water table (fig. 21*B*) is simulated by use of one parameter. This conductance parameter is multiplied by the lengths of small streams present within each respective model cell to attain the conductance needed by the head-dependent boundary package of MOD-FLOWP.

## MODEL CALIBRATION

Calibration of a numerical ground-water flow model is the process of finding a set of boundary conditions, parameter values, and stresses that produce simulated ground-water levels and flows that match field-based measurements or estimates within a preestablished range of error (Anderson and Woessner, 1992, p. 223). The difference between the observed and simulated ground-water levels and flows are hydraulic-head and flow residuals, respectively. The observed values used for the regional ground-water flow model include 389 synoptic measurements of ground-water levels in the carbonate-rock aquifer and the upper weathered zone water-bearing unit, and 43 estimates of mean sustained ground-water discharge to principal streams that represent long-term steady-state conditions in the aquifer system. (These data are discussed in the "Levels and Discharge" sections of this report.) No observed ground-water levels in the glacial deposits were included in the model.

An estimate of the standard deviations for the errors in these observations was made in advance of model simulations to calculate weights for the regression, discussed below in the "Procedure" section. The estimated standard deviations for the errors in the ground-water-level data include the error associated with determination of the measuring-point elevations from topographic maps, deviation of measured values from long-term average ground-water levels (Eberts, 1999), and vertical hydraulic gradients in the aquifer system due to measurement of open-hole wells that may not represent water levels strictly associated with the regional flow systems. These sources of error were evaluated for each measurement; standard deviations of the errors ranged from 6 to 12 ft.

Estimates of mean sustained ground-water discharge to selected streams were assumed to be appropriate calibration values for simulation of steady-state regional flow in the aquifer system. These means range from 88 to 98 percent streamflow duration—streamflow that is equaled or exceeded 88 to 98 percent of the time—and all but four of the means fall between 88 and 94 percent streamflow duration. (Previous researchers (Cross, 1949; Schneider, 1957) have used streamflow that is exceeded 90 percent of the time as an approximate index of dry-weather flow in Ohio.)

For calculating the weights in the regression (see below), it is assumed that the error associated with the estimates of mean sustained ground-water discharge has a 90 percent chance of being 20 percent of the estimated discharge. Estimation of standard deviations associated with these values followed procedures described in Hill (1992, p. 49).

### PROCEDURE

An automated nonlinear-regression approach to calibration developed by Cooley and Naff (1990) and extended for complicated three-dimensional problems by Hill (1992) was used in this investigation. Specifically, parameter values were automatically adjusted to achieve the smallest possible value of the objective function. The objective function in this method is the weighted sum of squared differences between observed and simulated hydraulic heads and flows:

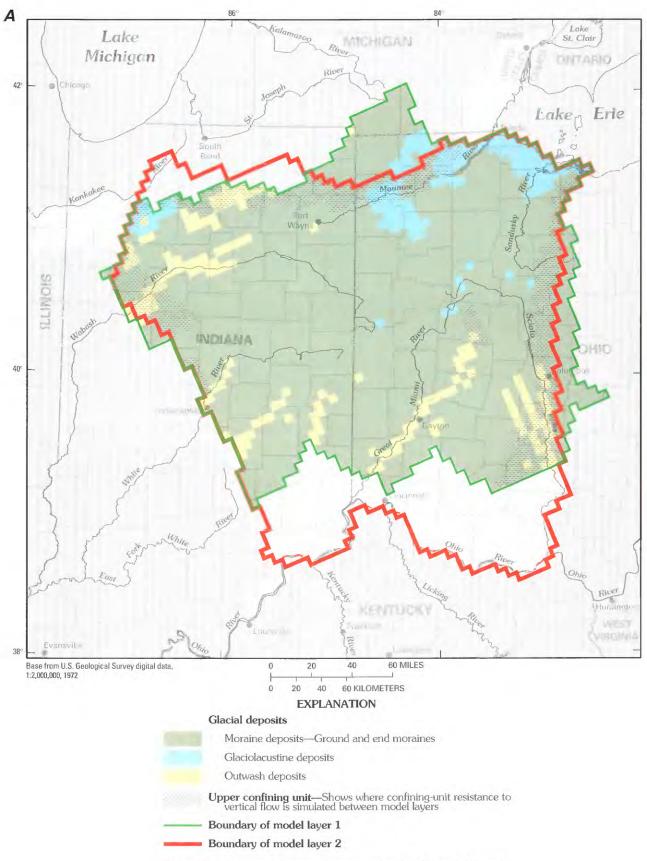


FIGURE 23.—Zones used for model parameterization: (A) model layer 1

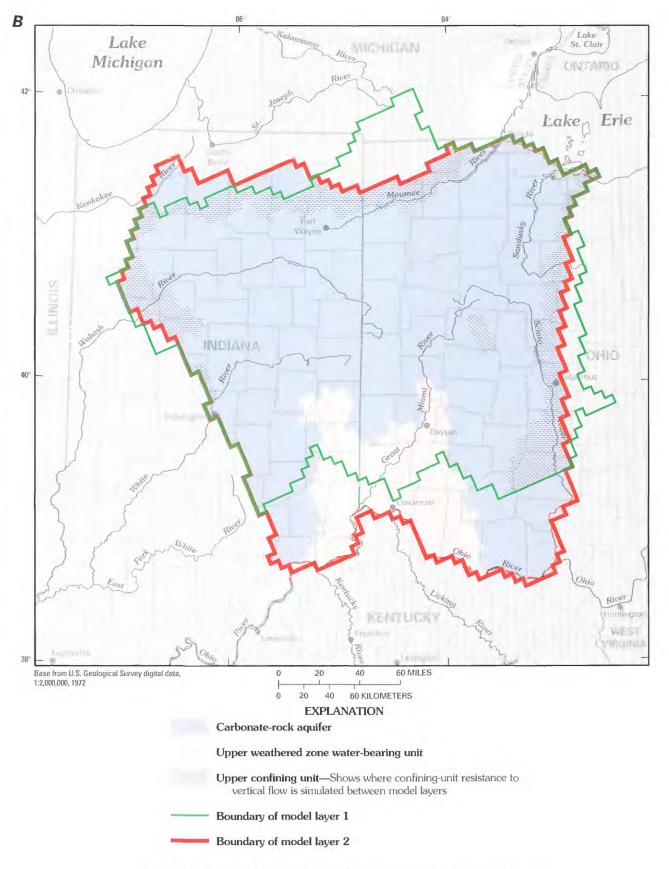


Figure 23. Continued—Zones used for model parameterization: (B) model Layer 2

$$SSE = \Sigma [w_i^{1/2} e_i]^2, i = 1, n,$$
 (2)

where  $e_i$  is the difference between the observed and calculated values of measurement i,

 $w_i^{1/2}$  is the square root of the weight assigned to the error in the observed value of measurement i;

 $w_i^{1/2}e_i$  is the weighted residual corresponding to measurement i; and

n is the number of observations.

The weights in this equation reflect the assumed reliability (standard deviations) of the hydraulic-head measurements or flow estimates (observations) and account for the different units of measure associated with hydraulic heads (L) and flows (L³/T). The weights equal 1 divided by the variance of the observation error. The parameter values that correspond to the smallest SSE possible for the parameterization and boundary conditions imposed on the model are called the optimal parameter values.

Scaled sensitivities for each of the model parameters also can be computed by use of the nonlinear regression method. Scaled sensitivities equal

$$\frac{\partial y_i}{\partial b_i} w_i^{1/2} b_j, i = 1, n; j = 1 , \qquad (3)$$

where  $b_j$  is one of the model parameters and  $y_i$  is a calculated hydraulic head or flow.

A comparison of the scaled sensitivities for various parameters (hydraulic conductivity, transmissivity, recharge, conductance terms) in a specific model provides information on the relative effect of each parameter in the regression. Relatively small scaled sensitivities are associated with parameters that have little effect on simulated results and cannot be estimated by nonlinear regression.

Application of the nonlinear-regression procedure of model calibration in this investigation ensures that model error is due to model design rather than to suboptimal parameter values. This enables comparison of various model designs so that various aspects of the numerical and conceptual models can be tested. In general, the best models have (1) the smallest parameter coefficients of variation, (2) parameter correlations of less than 0.95, (3) the smallest calculated error variance (SSE divided by the difference between the number of observations and the number of estimated parameters (Draper and Smith, 1981)), and (4) weighted residuals that are normal, independent, and of equal variance. On the basis of these standards, the calibrated final model presented herein is the best representation of regional ground-water flow in the Midwestern Basins and Arches aquifer system among the

alternatives tested. (A brief discussion of what was learned from two alternative models is found in the section "Model Discrimination.")

#### ESTIMATES OF PARAMETER VALUES

For 8 of the 16 model parameters described in the "Parameterization" section of this report, scaled sensitivities are large enough for the parameter values to be estimated by nonlinear regression. The number and location of observations used for the model calibration affect these scaled sensitivities and are directly responsible for which parameters can be estimated. Estimated parameters in the calibrated final model, ordered from highest to lowest in terms of sensitivity, include (1) transmissivity of the carbonate-rock aquifer, (2) horizontal hydraulic conductivity of the moraine deposits, (3) recharge applied to the moraine deposits, (4) effective vertical hydraulic conductivity of the combined moraine/bedrock areas, (5) the conductance term for the general head-dependent-flux boundary condition used to simulate the regional water table, (6) hydraulic conductivity of streambeds throughout most of the modeled area, (7) horizontal hydraulic conductivity of the outwash deposits, and (8) vertical hydraulic conductivity of the upper confining unit.

The other model parameters were assigned values from available data in the literature and were held constant during the regression. Any adjustments to these values were made by trial and error. These values include an effective vertical hydraulic conductivity of 0.1 x 10<sup>-2</sup> ft/d for the combined glaciolacustrine/bedrock deposits and 0.1 ft/d for the combined outwash/bedrock deposits. The value for the hydraulic conductivity of the streambeds that are underlain by the upper confining unit is set at 0.1 x 10<sup>-2</sup> ft/d. Horizontal hydraulic conductivities of the glaciolacustrine deposits and the upper weathered zone water-bearing unit are set at 0.05 and 0.06 ft/d, respectively. Values for recharge applied to the glaciolacustrine deposits, the upper weathered zone water-bearing unit, and the outwash deposits range from 0.1 x 10<sup>-2</sup> to 11.8 in/yr.

Estimated values for the optimal parameter set from the calibrated final model are listed in table 3. Each of the parameter estimates falls within the range of published field values for the Midwestern Basins and Arches aquifer system where data are available (table 2). The estimated transmissivity for the carbonate-rock aquifer not only is within the range of field-determined estimates of transmissivity but also is within 16 percent of the geometric mean of these values. The estimated effective horizontal hydraulic conductivity for the moraine deposits falls within the range of textbook values for these materials (Freeze and Cherry, 1979). The estimated recharge value in table 3 does not represent net regional recharge to the regional flow systems nor does it represent all recharge to local, intermediate, and regional flow systems.

Table 3.—Parameter estimates and reliability of the optimal parameter set from the calibrated final model of regional flow in the Midwestern Basins and Arches aquifer system

[ft²/d, feet squared per day; ft/d, feet per day; in/yr, inches per year]

Parameter	Parameter estimate	Approximate 95-percent linear confidence interval	Relative parameter reliability
Transmissivity of the carbonate-rock aquifer	1,610 ft <sup>2</sup> /d	$1,030 - 2,500 \text{ ft}^2/\text{d}$	0.23
Horizontal hydraulic conductivity of the moraine deposits	21.3 ft/d	13.7 – 33.1 ft/d	.23
Recharge applied to the moraine deposits <sup>b</sup>	2.15 in/yr	1.41 – 2.88 in/yr	.18
Effective vertical hydraulic conductivity of the combined moraine/bedrock areas	$0.375 \times 10^{-2}  \text{ft/d}$	$0.139 \times 10^{-2} - 0.101 \times 10^{-1} \text{ ft/d}$	.59
Conductance term for the general head-dependent flux boundary condition used to simulate the regional water table <sup>b</sup>	$0.259 \text{ ft}^2/\text{d}$	$0.161 - 0.418 \text{ ft}^2/d$	.25
Hydraulic conductivity of streambeds throughout most of the modeled area <sup>c</sup>	0.0149 ft/d	0.0045 - 0.05 ft/d	.77
Horizontal hydraulic conductivity of the outwash deposits	168 ft/d	46.1 – 620 ft/d	.87
Vertical hydraulic conductivity of the upper confining unit	$0.466 \times 10^{-3}  \text{ft/d}$	0.645 x 10 <sup>-4</sup> - 0.338 x 10 <sup>-2</sup> ft/d	1.80

<sup>&</sup>lt;sup>a</sup>Coefficient of variation for the recharge parameter; comparable measure of reliability for the other parameters, which were log-transformed for the regression. Smallest values indicate greatest parameter reliability.

Rather, it represents the recharge rate applied to the moraine deposits that may be used in conjunction with the effects of the general head-dependent-flux boundary condition to estimate regional recharge rates. In a few areas near the regional potentiometric highs, the estimated recharge value was not great enough to balance observations of hydraulic heads and flow used to constrain the model solution, so water entered the model by means of the general head-dependent-flux boundary condition. This result was expected because the amount of recharge that reaches the deepest parts of an aquifer system is typically greatest near regional potentiometric highs. Net values of regional recharge or discharge are not apparent from table 3 but are presented in map form later in this report.

Model output indicates that no parameter correlations exceed 0.90. The greatest correlation (0.87) is between the recharge parameter and the conductance parameter associated with the general head-dependent-flux boundary condition.

## SIMULATED HYDRAULIC HEADS

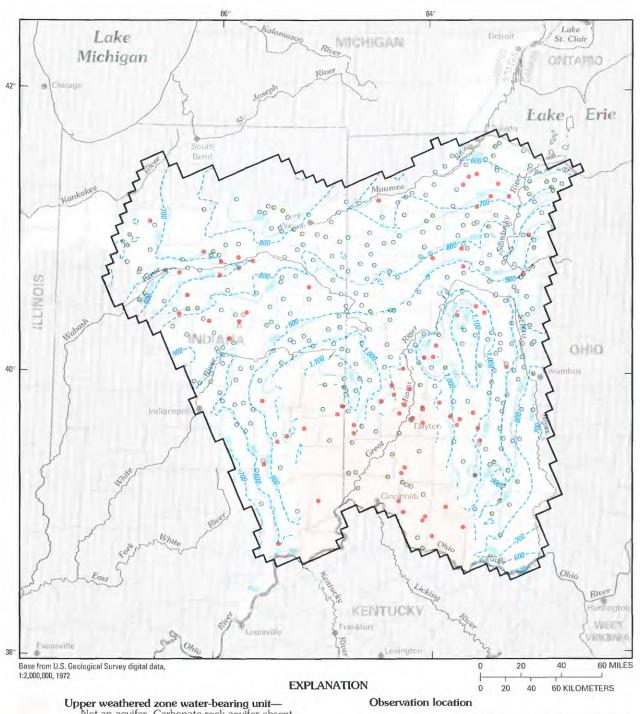
A total of 389 measured ground-water levels in the carbonate-rock aquifer and the upper weathered zone water-bearing unit (model layer 2) were used as observations in the regression. No water levels in the glacial deposits (model layer 1) were used because the available data, which are from

drillers' logs, are likely to reflect a local water table associated with local flow systems not explicitly simulated in the model. In addition, estimates of the regional water table, which is typically present in glacial deposits, were included as part of the general head-dependent-flux boundary condition.

A comparison of simulated and measured potentiometric surfaces in the carbonate-rock aquifer is illustrated in figure 24. Simulated equipotential lines closely follow equipotential lines contoured from measured ground-water-level data. Observation locations are coded on the map to indicate locations where the simulated and measured (observed) hydraulic heads differ by less than three times the standard deviation of the errors associated with the observation. Locations where simulated hydraulic heads are above or below this range also are noted. Figure 24 indicates that the simulated hydraulic head most commonly differs from the observed hydraulic head by more than three times the standard deviation of the errors associated with the observation in the areas along the Great Miami River and along the northeastern and southeastern edges of the model. Although these patterns indicate some lack of model fit in these areas, the overall model fit is good.

A graph of weighted residuals plotted against weighted simulated values (Draper and Smith, 1981; Hill, 1994) (fig. 25) shows that the hydraulic-head residuals are indeed ran-

<sup>&</sup>lt;sup>b</sup>The estimated recharge value is not net recharge to regional flow systems; net recharge to regional flow systems is computed by subtracting the flux associated with the head-dependent flux boundary conditions from this estimated value of the recharge parameter on a cell-by-cell basis (fig. 28). <sup>c</sup>Reported values range from 0.0007 – 18.7 ft/d (Meyer, 1978; Smith and others, 1985; Cunningham, 1992, Dumouchelle and others, 1993).



Upper weathered zone water-bearing unit— Not an aquifer. Carbonate-rock aquifer absent

Potentiometric contour—Carbonate-rock aquifer. Contour interval 100 feet. datum is sea level

Simulated Measured

Boundary of model layer 2

- Reasonably predicted. Simulated and observed hydraulic heads differ by less than three times the standard deviation of the errors associated with the observation
- Underpredicted. Simulated hydraulic head less than observed hydraulic head by more than three times the standard deviation of the errors associated with the observation
- Overpredicted. Simulated hydraulic head greater than observed hydraulic head by more than three times the standard devi-ation of the errors associated with the observation

FIGURE 24.—Simulated and measured (observed) hydraulic heads in the carbonate-rock aquifer and the upper weathered zone water-bearing unit (model layer 2).

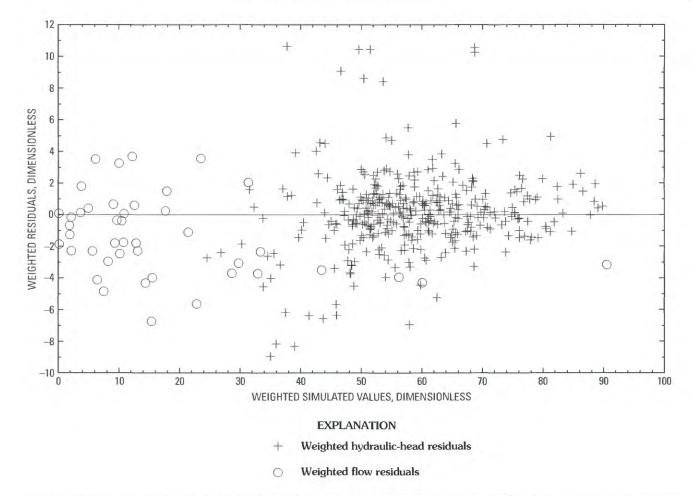


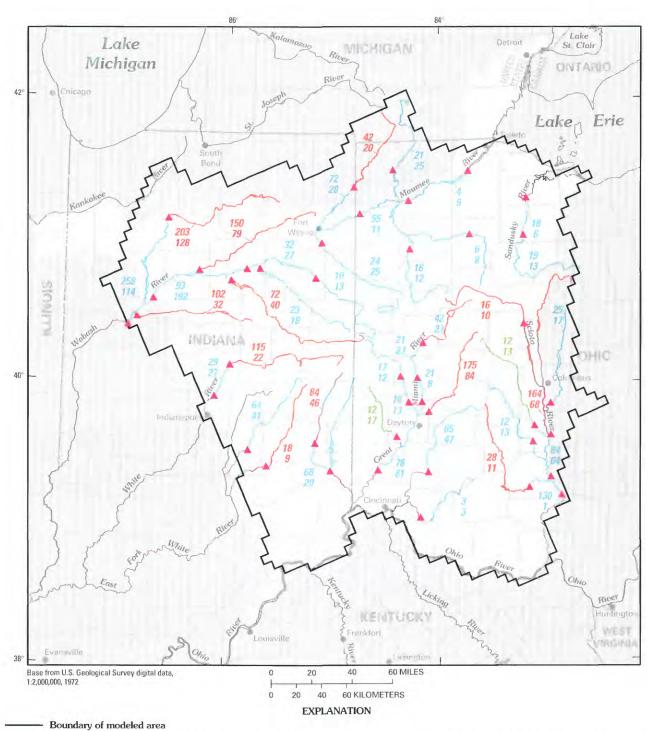
FIGURE 25.—Weighted residuals of hydraulic heads and flows plotted against weighted simulated values from the regional ground-water flow model for the Midwestern Basins and Arches aquifer system.

dom and have equal variance. Results of a runs test printed by MODFLOWP show that the hydraulic-head residuals are also independent. [The runs test takes into account the order of the residuals; too few runs commonly indicates positive serial correlation between residuals at individual locations (Hill, 1992).]

The root mean squared (RMS) error associated with hydraulic heads, which is the average of the squared differences in measured and simulated hydraulic heads, is another measure of model fit. Anderson and Woessner (1992, p. 241) note that if the ratio of the RMS error to the total head loss in the system is small, then the errors are only a small part of the overall model response. The RMS error computed from measured and simulated hydraulic heads in the regional groundwater flow model is 40 ft. The total head loss from the highest recharge area to the lowest discharge area in the model is 710 ft. The ratio of the RMS error to the total head loss in the system is 0.06. In summary, the model errors are only a small part of the overall model response; thus the model satisfactorily approximates ground-water-level observations.

# SIMULATED FLOWS

Simulated and observed flows (estimates of mean sustained ground-water discharge) along 43 stream reaches were compared to help evaluate overall model response. Estimates of mean sustained ground-water discharges and simulated flows are listed by stream reach in figure 26. These values are difficult to compare without knowledge of the error associated with the observation for each stream reach. This is because each streamflow-gaging station that bounds a selected stream reach is assumed to contribute the same amount of error to the observation; some stream reaches are bounded by one streamflow-gaging station, whereas others are bounded by as many as five. Mean sustained groundwater discharges to stream reaches bounded by five streamflow-gaging stations are less well known than observations for other reaches bounded by fewer gaging stations. Stream reaches in figure 26 are coded to indicate locations where the simulated and observed flows differ by less than three times the standard deviation of the errors associated with the observation. Most simulated flows fall within this range. Reaches



▲ Ground-water discharge to selected stream reach—Color corresponds to deviation of simulated from observed flow. Upper number is estimated mean sustained ground-water discharge (observed flow), in cubic feet per second. Lower number is simulated ground-water discharge, in cubic feet per second

Reasonably predicted—Simulated and observed flows differ by less than three times the standard deviation of the errors associated with the observation

Underpredicted—Simulated flow less than observed flow by more than three times the standard deviation of the errors associated with the observation Overpredicted—Simulated flow greater than observed flow by more than three times the standard deviation of the errors associated with the observation

Streamflow-gaging station

FIGURE 26.—Simulated ground-water discharge to selected stream reaches from regional flow systems and estimated mean sustained ground-water discharge (observed flow) to the reaches.

where simulated flows are above or below this range are also noted.

The graph of weighted residuals plotted against weighted simulated values in figure 25 indicates that the flow residuals are approximately random and have nearly equal variance except for weighted simulated values greater than about 40. These values are consistently less than observed values. (Negative weighted flow residuals calculated by MOD-FLOWP indicate underprediction of flow because the convention within the model is to represent ground-water losses to streams as negative values.) Simulated flows underpredict the flow observations slightly more often than they predict and overpredict them. All of the underpredicted stream reaches are in the upbasin areas; all of the streams at the bottom of the basins are well predicted considering the error on the observations. An alternative model that was constructed to test a hypothesis about why some upstream reaches are underpredicted in the regional ground-water flow model is discussed below. Results of a runs test for combined hydraulic-head and flow residuals, however, indicate randomness among weighted residuals.

#### MODEL DISCRIMINATION

Model discrimination is the process of comparing different hypotheses about an aquifer system by comparing results of models constructed using the different hypotheses (Hill, 1992). Two alternative models were developed to test two hypotheses used in the construction of the regional groundwater flow model. For the first alternative model, it was hypothesized that flow to streams in the upbasin areas may be underpredicted because a notable amount of ground water that sustains flow in the principal streams during the driest periods may be recharged at the water table within the area of the stream cells. No recharge is applied to the stream cells in the calibrated final model, therefore, this intracell flow is not represented in the model. Such a model design would have a greater affect on model calibration along upstream reaches as compared to downstream reaches because the area represented by the stream cells makes up a greater proportion of the drainage basins associated with upstream reaches.

To test whether some upstream reaches were underpredicted simply because no recharge is applied to the stream cells, an additional recharge parameter that represents recharge to stream cells was added to the model. The optimal recharge rate for this new recharge parameter is virtually zero, and the same stream reaches are underpredicted by this new model. In other words, the results of the new model are similar to the results of the model without the additional recharge parameter. It was concluded that lack of recharge to stream cells in the calibrated final model is not a factor that affects the overall model response. Locally, however, the underprediction of upstream reaches that flow along highly permeable outwash valleys, such as the Mad River (a tribu-

tary to the Great Miami River), may be related to this lack of simulated recharge.

Because simulation of an increased amount of curvature at the water table equates with simulation of an increased amount of flow within an aquifer system (fig. 19), the underprediction of some upstream reaches in the calibrated final model is possibly related to the cell spacing and the inability of the selected spacing to capture the curvature of the water table necessary to balance mean sustained ground-water discharge to the underpredicted stream reaches. Such a scale effect would be smallest in relation to the most downstream reaches because a greater proportion of sustained groundwater discharge to these streams is associated with the most regional trends of the water table, which are well represented by the coarse cell spacing of the calibrated final model. In other words, the mean sustained ground-water discharges used as observations in the regional ground-water flow model may be slightly high for some of the upstream reaches because of the cell spacing chosen for this investigation.

The calibrated final model presented in this report, however, is a reasonable representation of regional ground-water flow in the Midwestern Basins and Arches aguifer system. This is demonstrated, in part, by the estimated transmissivity for the areally extensive carbonate-rock aquifer, which is within 16 percent of the geometric mean of reported transmissivities. On the basis of Darcy's Law, calculated flows vary in direct proportion to aquifer transmissivity and hydraulic gradient. If the mean sustained ground-water discharges to streams used to help calibrate the numerical model were not generally appropriate as calibration targets, transmissivities and hydraulic conductivities could not have been so reasonably estimated while hydraulic gradients were so well predicted. Stated another way, if flow observations and thereby simulated flows were not generally appropriate for the scale of the model, transmissivities or hydraulic gradients would have to have been inappropriately adjusted to accommodate the associated excess or missing flow.

A second alternative model was used to test whether the transmissivity of the carbonate-rock aquifer varies systematically with the thickness of the carbonate rocks. In this model, horizontal hydraulic conductivity rather than transmissivity of the carbonate-rock aquifer is estimated and multiplied by the thickness of the carbonate rocks to determine optimal transmissivities. This alternative model construction is graphically depicted in figure 27. It differs from the calibrated final model in that the lower part of the carbonate rocks is represented in this second alternative model, whereas the use of a single transmissivity in the calibrated final model would be similar to a model with a third layer of near-zero transmissivity used to represent the deepest part of the carbonate rocks.

The optimal parameter set for this second alternative model includes an estimated vertical hydraulic conductivity for the upper confining unit that is orders of magnitude higher than is considered reasonable. In addition, vertical hydraulic

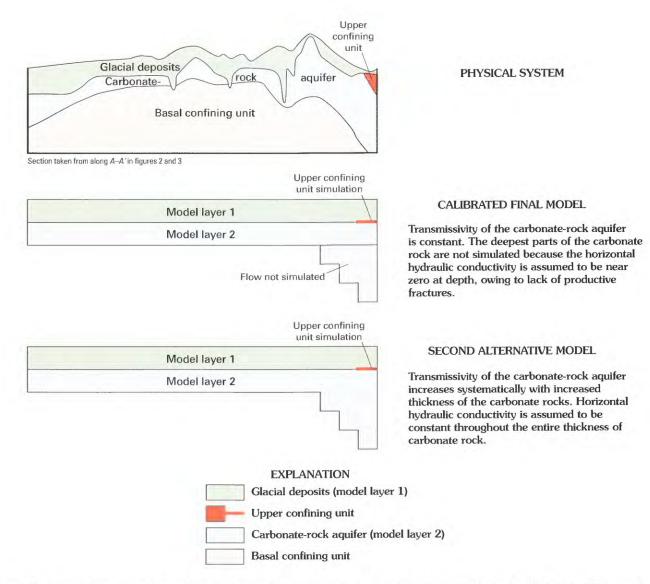


FIGURE 27.—Diagrams of two regional ground-water flow models used to test whether the carbonate rocks in the Midwestern Basins and Arches Region are transmissive throughout their entire thickness.

gradients between the carbonate-rock aquifer and the glacial deposits are tens of feet greater than gradients considered reasonable. Results of the runs test indicate that the residuals for this alternative model are not independent. In general, the largest head residuals are associated with the areas where the carbonate rock is very thick and computed transmissivities are thereby quite large.

To summarize, the second alternative model cannot match field conditions and simultaneously accommodate the ground-water flows associated with the large simulated transmissivities in areas where the carbonate rocks are very thick. It is concluded that the entire thickness of the carbonate rocks may not contribute substantially to the transmissivity of the carbonate-rock aquifer. This is consistent with findings that fractures at depth in the carbonate rocks may not be transmis-

sive (Arihood, 1994). In addition, local anhydrite deposits are present at depths greater than 150 ft in the Sandusky Bay area, an area where the carbonate rock is very thick (Carlson, 1991). The presence of anhydrite is indicative of little active freshwater flow in the carbonate rock at these depths in at least one part of the aquifer system.

## RELIABILITY OF PARAMETER ESTIMATES

Confidence intervals on estimated parameter values can help indicate the reliability of the estimates. Linear confidence intervals on the parameters can be computed if the model is correct and linear in the vicinity of the optimal set of values and if the parameters are normally distributed (Hill, 1994). Beale's measure and its critical values can be used to test model linearity (Cooley and Naff, 1990). The Beale's

measure for the calibrated final model is 0.38. This value falls between the critical value of 0.046 (a value below which Beale's measure would indicate model linearity) and 0.52 (the value above which would indicate model nonlinearity).

If weighted residuals are independently distributed, the model is likely to be correct; if weighted residuals are normally distributed and the model is linear, the estimated parameter values are generally normally distributed (Hill, 1994; Seber and Wild, 1989). To test whether the weighted residuals are independent and normally distributed, they were compared with expected independent values from a standard normal distribution. The  $R_N^2$  statistic (Hill, 1992) for the calibrated final model is 0.948, which is less than the critical value of 0.987 at the 95-percent confidence level. This statistic indicates that the weighted residuals may not be independent and normally distributed. However, this test is more restrictive than the less powerful Kolmogorov test (Hill, 1992, p 63). On the basis of the Kolmogorov test, Yager (1993) demonstrated that a  $R_N^2$  statistic of 0.946 indicates that weighted residuals are independent and normally distributed at the 99-percent confidence interval for a model with a similar number of parameters and observations as for the calibrated final model. These results indicate that the weighted residuals from the calibrated final model are at least nearly independent and normally distributed. The distribution of the residuals was not investigated further.

Beale's measure indicates that the calibrated final model is at least slightly nonlinear; moreover, figure 24 indicates some spatial patterns in the weighted residuals for hydraulic head, and figure 25 indicates some nonrandomness of the weighted residuals for flow. As a result, the confidence intervals given in table 3 should be considered approximate.

The relative reliability of estimated parameter values were compared by use of coefficients of variation. Smaller coefficients of variation indicate greater reliability than do larger coefficients of variation. For parameters that are log-transformed during the regression, a substitute for the coefficient of variation (pseudo coefficient of variation) can be calculated by determining the difference between the upper and lower confidence limits divided by the exponential of the estimated parameter value and dividing this result by two times the critical value from the Students-t probability distribution used to compute the confidence limits. This measure is exactly the coefficient of variation for the parameters that were not log-transformed and is a comparable measure of reliability for those parameters that were log-transformed. All of the parameter values except the recharge parameter in the calibrated final model of this investigation were log-transformed during calibration. (Hydraulic-conductivity measurements in various geohydrologic situations are commonly lognormally distributed (Hill, 1992, p. 18)). Coefficients of variation and pseudo coefficients of variation for the optimal parameter set of the calibrated final model are listed in table 3. The parameter values for recharge applied to the moraine deposits, transmissivity of the carbonate-rock aquifer, and horizontal hydraulic conductivity of the moraine deposits are the most precisely known parameter values, whereas the vertical hydraulic conductivity of the upper confining unit is the least precisely known parameter value.

It should be noted once more that the recharge parameter estimate listed in table 3 does not represent net recharge to regional flow systems. Because net regional recharge (or net regional discharge) was computed by subtracting the simulated flux associated with the head-dependent-flux boundary conditions from the flux associated with this estimated value of recharge applied to the moraine deposits (see fig. 28), the reliability of net recharges or net discharges is not known.

### SIMULATED REGIONAL GROUND-WATER FLOW

The calibrated final model can be used to quantify various aspects of the conceptual model and to draw conclusions about regional ground-water flow in the Midwestern Basins and Arches aquifer system. A ground-water budget that quantifies flow associated with the regional flow systems represented by the model is given in table 4; simulated net recharges or net discharges across the regional water table were used in the computations.

The calibrated final model represents the movement of 1,292 Mgal/d of water through the parts of the aquifer system not greatly affected by seasonal variations in ground-water recharge from precipitation; this is approximately 10 percent of the total flow in the aquifer system. Ninety-nine percent of this water is from recharge at the water table. Seventy-eight percent of the water (1,006 Mgal/d) leaves the system by means of the principal streams that were explicitly represented in the model by use of the stream cells. Nineteen percent of simulated regional ground-water flow discharges by means of seeps, springs, ditches, small streams, or evapotranspiration—discharge that was simulated by use of the general head-dependent-flux boundary condition. Two percent of the water (24 Mgal/d) leaves the system along the margin of the Illinois (structural) Basin. Much of this water probably discharges to streams just beyond the model boundary, but some of it may move downdip into the Illinois Basin. (Previous work (Cartwright, 1970) demonstrates, by means of temperature data, that some water enters the Illinois Basin and that water in the deep parts of the Illinois Basin ultimately discharges near the center of the basin through fracture zones associated with faults and anticlines in the basin.) Approximately 1 percent (18 Mgal/d) of the water associated with regional ground-water flow represented in the model discharges to the Ohio Valley aguifer that follows the Ohio River (local-scale alluvial aquifer not represented in the calibrated final model) and ultimately discharges to the Ohio River. Most of this discharge is from the carbonate-rock aquifer; less than 1 Mgal/d is from the upper weathered zone waterbearing unit (not an aquifer). Discharge attributed to regional ground-water flow in these bedrock units is a very small percentage of total ground-water discharge to the Ohio River; discharge directly to the Ohio River from the Ohio Valley aquifer along the boundary of the modeled area has been computed at approximately 1,400 Mgal/d (C.G. Norman, Ohio River Valley Water Sanitation Commission, written commun., 1989). These relative amounts of discharge to the Ohio River are consistent with a conceptual model in which local flow systems dominate flow in the Midwestern Basins and Arches aquifer system. Less than 1 percent of the regional ground-water flow represented in the model discharges to Lake Erie.

A ground-water budget that quantifies regional flow within the carbonate-rock aquifer, as represented by the

TABLE 4.—Simulated ground-water budget of regional flow systems in the Midwestern Basins and Arches aquifer system
[Mgal/d, million gallons per day]

	Flow (Mgal/d)	Percent recharge or discharge
Recharge		
Across the regional trend of the water table	1,277	99
From losing stream reaches	15	1
Total	1,292	100
Discharge		
To principal streams	1,006	78
Across the regional trend of the water table to seeps, springs, ditches, small streams, or by means of evapotranspiration	242	19
Along the margin of the Illinois (structural) Basin	24	2
From the carbonate-rock aquifer to the Ohio River	18	1
To Lake Erie	1	<1
Across the northwestern boundary of the modeled area	1	<1
From the upper weathered zone water-bearing unit to the Ohio River	<1	<1
Total	1,292	100

model, was also computed (table 5). Of the 386 Mgal/d of water that moves along simulated regional flow paths in the carbonate-rock aquifer, 85 percent enters the aquifer by means of percolation through the overlying glacial deposits. Fifteen percent is associated with recharge by precipitation directly onto the carbonate-rock aquifer. Most of the water that enters the carbonate-rock aquifer flows back into the overlying glacial deposits. Eight percent of simulated regional flow in the carbonate-rock aquifer discharges to seeps, springs, ditches, and streams smaller than those represented in the model by use of the stream cells. Less than 1

Table 5.—Simulated ground-water budget of regional flow systems in the carbonate-rock aquifer in the Midwestern Basins and Arches aquifer system [Mgal/d, million gallons per day]

	Flow (Mgal/d)	Percent recharge or discharge
Recharge		
From percolation of water through glacial deposits	327	85
Across the regional trend of the water table from precipitation directly onto the aquifer	59	15
From the upper weathered zone water-bearing unit	<1	<1
Total	386	100
Discharge		
By means of flow into overlying glacial deposits	322	84
Across the regional trend of the water table to seeps, springs, and small streams	32	8
To the Ohio River	18	5
To principal streams	9	2
Along the margin of the Illinois (structural) Basin	5	1
Into the upper weathered zone water-bearing unit	<1	<1
Across the northwestern boundary of the modeled area	<1	<1
Total	386	100

percent of the simulated ground-water flow in the carbonaterock aquifer is into the upper weathered zone water-bearing unit.

The simulated amount of water that reaches the carbonate-rock aquifer by means of regional flow paths is only 30 percent of simulated regional ground-water flow in the aquifer system. The rest of the water remains within the glacial deposits. Because glacial deposits contribute so much to regional ground-water flow as defined in this report, it is not surprising that drainage basins where glacial deposits are thin, absent, or poorly permeable are associated with small amounts of sustained ground-water discharge to streams (see "Discharge" section). Such basins include those that drain to Lake Erie and those in the southeastern part of the study area (fig. 17).

One of the principal objectives of this investigation, which was met by use of the calibrated final model, was to map regional recharge and discharge areas. This was an important objective because water and contaminants that enter the aquifer system in regional recharge areas are likely to traverse a greater length of aquifer than water that enters the system at local recharge areas (Stoertz, 1989). Computed net amounts of recharge to and discharge from regional flow systems, as represented by the model, were used to construct the regional recharge and discharge map shown in figure 28. This map is regional in scale; therefore, the map is not meant to imply that recharge to flow systems too small to be represented in the model is not possible in areas designated as regional discharge areas and that discharge from local flow systems is not possible in areas designated as regional recharge areas. The map simply implies that more water recharges the fairly stable flow systems than discharges from such systems within areas mapped as regional recharge areas. The opposite holds true for regional discharge areas.

The Midwestern Basins and Arches aquifer system is characterized by alternating regional recharge and discharge areas, typically on a scale of less than 10 mi, except in the northeastern part of the modeled area (fig. 28). Ground water generally does not move from recharge areas associated with the very highest potentiometric levels (figs. 11 and 12) along long, continuous flow paths to areas associated with the very lowest potentiometric levels, such as the Wabash and Ohio Rivers and Lake Erie, while remaining isolated from additions of recharge. Rather, regional recharge and discharge areas are present all along the regional potentiometric gradient depicted by the potentiometric-surface maps in figures 11 and 12, except in the northeastern part of the study area. These patterns of regional recharge and discharge may explain the differences in ground-water ages between the northeastern part of the study area and the rest of the aquifer system (see "Geochemistry" section).

The regional potentiometric high near the Bellefontaine Outlier (fig. 6) is associated with some of the highest recharge rates. Another area associated with high recharge rates is the area of extensive outwash deposits north of the Wabash River in Indiana (fig. 5). The lowest regional recharge rates are associated with the area where the upper weathered zone water-bearing unit is exposed at the land surface or is overlain by thin glacial deposits.

High discharge rates are commonly associated with the principal streams within the modeled area. Mapped discharge areas, however, are not limited to the width of the stream cells. Specifically, a broad area (tens of miles) of regional discharge was simulated in the northeastern part of the modeled area. This area likely represents an area in which water that follows regional ground-water flow paths leaves the system by means of ditches, small streams, or evapotranspiration because ground-water levels are near land surface. The finegrained glaciolacustrine deposits in the area may be associated with a thick capillary fringe that could help facilitate evapotranspiration. In addition, the hydraulic gradient towards the Maumee River is minimal. Toth (1963) notes that ground-water discharge in basins characterized by low relief, such as the Maumee River Basin in the lowlands near Lake Erie (fig. 6), takes place between the midline and the bottom of the drainage basin. In addition, he notes that only a small proportion of the ground water discharges as base flow in the principal streams in such basins. This pattern is similar to what is observed and simulated for the drainage basins in the northeastern part of the modeled area near Lake Erie. Because some regional ground-water flow discharges before it reaches the streams, estimates of base flow in the streams cannot be equated with recharge to the aquifer system in this area.

Rates of simulated discharge associated with this broad regional discharge area are extremely low. Typically, discharge rates are less than 0.5 in/yr in these areas. It is noteworthy that this broad area of weak discharge is largely coincident with an area characterized by the highest concentrations of dissolved sulfide within the modeled area, which also indicates that oxygenated recharge is not readily available to this part of the aquifer system (Ohio Department of Natural Resources, 1970). In addition, low recharge rates may also explain the presence of isotopically distinct ground water at depth beneath the Maumee River Basin (see "Geochemistry" section).

Areas that are not designated as regional recharge or discharge areas are evident on the regional recharge and discharge map (fig. 28). These are areas in which model layer 2 was the uppermost active layer of the model and the carbonate-rock aquifer is isolated from the water table by means of the upper confining unit. Neither recharge nor the general head-dependent-flux boundary condition was applied to these model cells.

On an areal map, discharge areas commonly constitute a smaller part of the surface area of a watershed than recharge areas do (Freeze and Cherry, 1979, p.197). Percentages of the surface area simulated as regional recharge and discharge

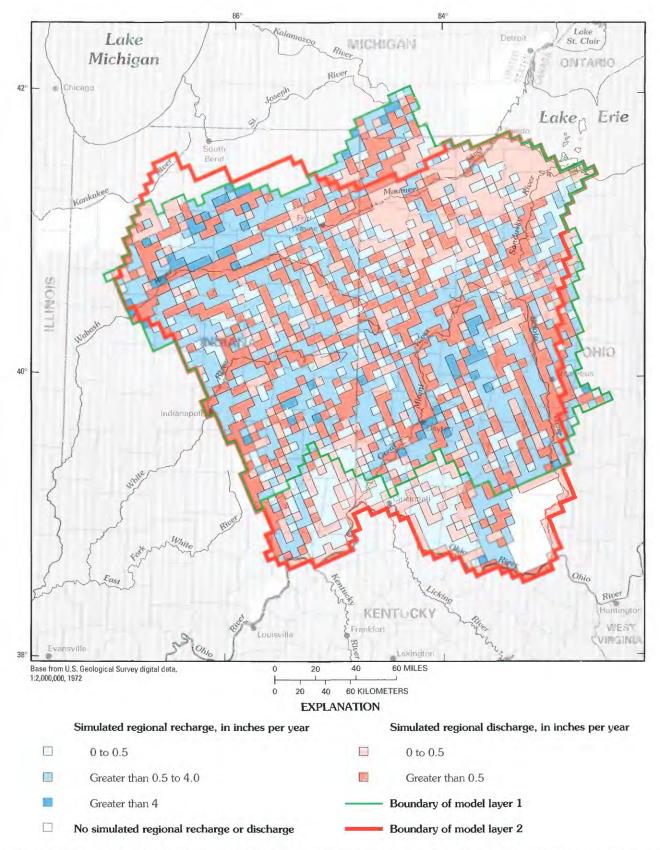


FIGURE 28.—Simulated regional recharge and discharge areas. (These areas do not necessarily coincide with recharge and discharge areas of local flow systems.)

areas were computed for eight selected surface-water drainage basins that drain the modeled area (fig. 29). Regional recharge areas are larger than regional discharge areas across most of the modeled area; however, regional discharge areas predominate in the northeastern part of the study area.

Regional discharge areas that are associated with the largest simulated upward hydraulic gradients are near the downstream end of the Wabash and Scioto Rivers, where model layers 1 and 2 are present, and just east of the mouth of the Sandusky River. Simulated hydraulic heads in the carbonaterock aquifer in a few of these model cells were above land surface. The area east of the mouth of the Sandusky River was previously mapped as an area of flowing wells and large springs (Breen, 1989).

Patterns of advective regional ground-water flow that were computed from the model output are shown in figure 30. The flow paths represent flow in glacial deposits and bedrock units rather than flow associated with individual aquifers, although some individual flow paths may represent flow solely in either the glacial deposits or the bedrock units. Regional ground-water flow is generally from regional recharge areas to adjacent regional discharge areas. Some simulated regional flow paths on this figure bypass an adjacent regional discharge area and indicate discharge in an area further down the potentiometric gradient. Such areas worth noting include the downstream end of the Wabash River (A), the areas west of the Scioto River (B) and near Lake Erie (C), the area north of the Maumee River (D), and the areas near the highest regional potentiometric levels (E) (fig. 30). These regional flow paths that bypass adjacent regional discharge areas cannot be determined from two-dimensional potentiometric-surface maps of the aquifer system. Such flow paths develop because regional recharge is available across most of the aquifer system; the result is a three-dimensional flow field.

The flow paths can also be used to identify areas where regional ground-water flow does not discharge to principal streams. One example is in the northeastern part of the modeled area (F, fig. 30). Many of the flow paths that discharge in this area are relatively short and may be associated with discharge to ditches and streams that are too small to be represented in the model by use of the stream cells or by means of evapotranspiration. A second example is the south-central part of the modeled area (G, fig. 30). These simulated flow paths likely indicate discharge to springs and seeps, which are common in the interbedded shales and limestones of the upper weathered zone water-bearing unit. They could also indicate discharge to small streams.

A ground-water divide is noted in the southeastern part of the modeled area (H, fig. 30). Water south of a certain point is diverted away from the Scioto River and discharges to the Ohio River.

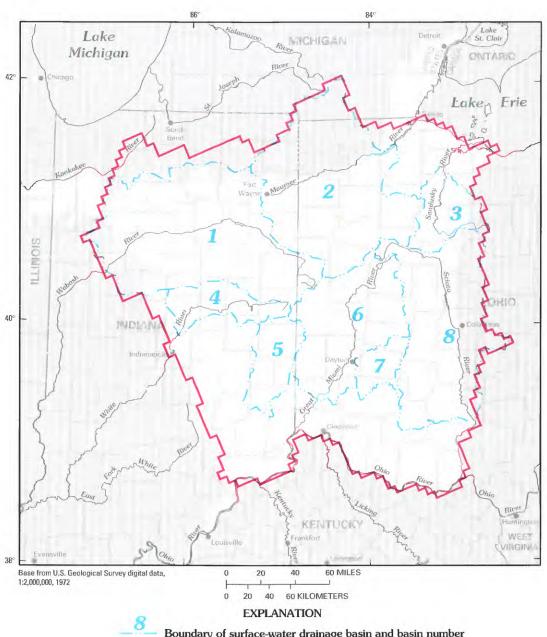
Simulated flow paths near Lake Erie indicate that the Lake diverts water away from some of the principal streams within the area (I, fig. 30). Flow paths near Lake Erie also indicate that recharge at the potentiometric high along the eastern boundary of the modeled area is likely to be the source of water that discharges in the area characterized by flowing wells and large springs east of the mouth of the Sandusky River (J, fig. 30; see also figs. 12 and 28).

Some of the simulated ground-water flow paths that terminate at Lake Erie are the longest within the modeled area (at nearly 50 mi). Simulated flow paths that begin just west of the Sandusky River and continue to Lake Erie are associated with a recharge area characterized by thin or absent glacial deposits. This recharge area has been previously referred to as the "limestone ridge area" and is the site of an exposed fossil coral reef (K, fig. 30). Other researchers have noted that this area of the carbonate-rock aquifer is vulnerable to contamination; nitrate contamination of ground water in the vicinity of this regional recharge area has been recognized since 1965 (Richards, 1990).

A comparison of regional ground-water flow paths and the position of the continental divide within the modeled area (the surface-water drainage divide that separates streams that flow toward the Atlantic Ocean from those that flow toward the Gulf of Mexico) illustrates the relation between surface-water and ground-water drainage basins (fig. 30). Ground-water divides associated with regional flow in the aquifer system are generally coincident with surface-water divides. Locally, however, deep regional ground-water flow paths can cross even major surface-water drainage divides (L, fig. 30). The amount of ground water that flows across the major surface-water drainage divides is likely to be a very small percentage of water that moves through the aquifer system because very few flow paths cross these divides.

Relative magnitudes (or volumes) of regional groundwater flow are not apparent from the map of regional groundwater flow patterns. Discharge vectors that illustrate the relative magnitude and resultant direction of horizontal regional flow within each cell of each model layer are shown in figure 31. The lengths of these discharge vectors are scaled linearly; units are feet cubed per day.

The greatest magnitudes of horizontal regional ground-water flow in the glacial deposits are associated with the most extensive outwash deposits. These outwash deposits tend to be concentrated along the principal streams within the modeled area. Notably large magnitudes of horizontal regional flow can be found in areas of outwash deposits within the Wabash River Basin. This drainage basin has the highest mean sustained ground-water discharge as percentage of mean ground-water discharge to the streams within the modeled area. In the northeastern part of the study area, magnitudes of horizontal regional flow in the glacial deposits are so small the vectors do not show up in figure 31A. Glacial deposits in this region are thin, locally absent, or poorly permeable. In addition, horizontal hydraulic gradients are fairly low. Such low magnitudes of horizontal regional flow are



Boundary of surface-water drainage basin and basin number

Boundary of modeled area

Basin Number	Basin Name	Percent Regional Recharge Area	Percent Regional Discharge Area
1	Wabash River Basin	58	42
2	Maumee River Basin	44	56
3	Sandusky River Basin	48	52
4	White River Basin	59	41
5	Whitewater River Basin	63	37
6	Great Miami River Basin	62	38
7	Little Miami River Basin	67	33
8	Scioto River Basin	52	48

FIGURE 29.—Percentages of the surface area of selected surface-water drainage basins simulated as regional recharge and discharge areas.

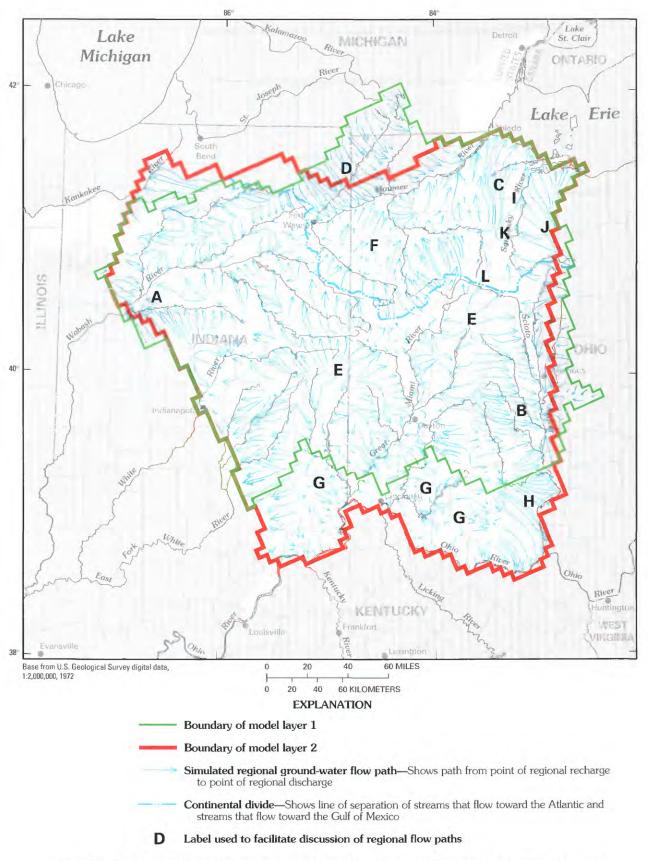


FIGURE 30.—Simulated patterns of advective regional flow in the Midwestern Basins and Arches aquifer system.

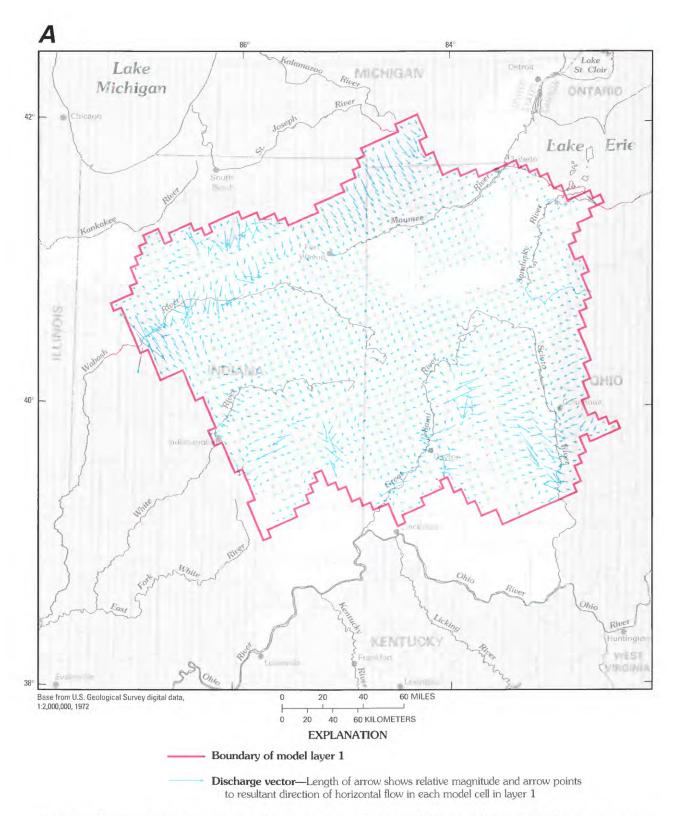


Figure 31.—Simulated relative magnitudes of horizontal regional flow in the Midwestern Basins and Arches aquifer system: (A) glacial deposits.

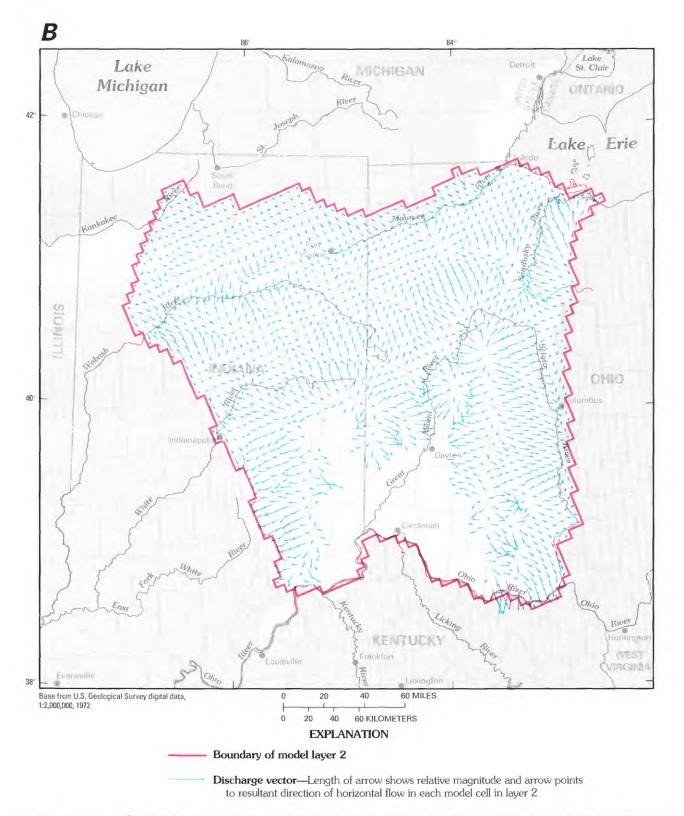


FIGURE 31. Continued—Simulated relative magnitudes of horizontal regional flow in the Midwestern Basins and Arches aquifer system: (B) bedrock.

consistent with the hypothesis that regional recharge to this part of the aquifer system could be limited by the inability of the aquifer system to carry ground water away from the area. This area is largely coincident with the area of weak regional discharge (fig. 28).

Simulated discharge vectors indicate high magnitudes of horizontal regional flow in the carbonate-rock aquifer in the areas around the regional potentiometric highs (fig. 31B). High magnitudes of horizontal regional flow are also associated with the downstream end of the Wabash and White Rivers, the margin of the Illinois (structural) Basin, the Ohio River, an area west of the Scioto River, and the area east of the Sandusky River. Discharge vectors along part of the Lake Erie shore indicate that the magnitude of horizontal regional flow in the carbonate-rock aquifer in this area is fairly small. Ground-water flow may be predominantly vertical in this area because it is an area of regional ground-water discharge. Simulated discharge vectors were computed for the upper weathered zone water-bearing unit, but the relative magnitudes of flow in this poorly permeable unit are so small that the vectors do not show up at the scale of figure 31B.

It should be noted that the discharge vectors show only relative magnitudes of horizontal regional ground-water flow and do not indicate flow velocities. Additional information on the effective porosity of the aquifers would be necessary to compute flow velocities. Appropriate effective-porosity data for fractured carbonate rock are difficult to obtain and were not available for this investigation. Ground-water ages presented in the following section, however, provide insight into ground-water residence times.

The calibrated final model was not used to simulate potential effects of future pumpage on regional ground-water flow in the aquifer system. Data on future pumpage needs at the regional scale are not available, and any simulations of future pumpage at this time would be contrived. It is noteworthy, however, that only a small percentage of current pumpage is associated with the regional flow systems explicitly simulated with this model. Therefore, more water associated with such regional flow systems almost certainly could be used. The quality of the ground water associated with some parts of the aquifer system, however, may limit its use.

# **GEOCHEMISTRY**

Geochemical data were collected from the Midwestern Basins and Arches aquifer system to investigate the relations among ground-water chemistry, aquifer mineralogy, and present and past patterns of regional flow. The data include a synthesis of basic data from more than 1,300 ground-water analyses of water samples from the aquifer system, as well as detailed chemical and isotopic analyses of ground water and aquifer material along general directions of regional flow. The analyses represent two hydrologic units (table 1) within the

Midwestern Basins and Arches aquifer system — aquifers within glacial deposits and the carbonate-rock aquifer - and were obtained from records in the U.S. Geological Survey's National Water Information System (NWIS) data base; files of the Indiana Department of Natural Resources, the Ohio Department of Natural Resources, and the Ohio Environmental Protection Agency; various published reports; and samples collected as part of this investigation. The data were compiled and analyzed to investigate the ground-water chemistry of the aquifer system on a regional scale. Ground-water chemistry of subregional areas of the Midwestern Basins and Arches aquifer system is described in the following reports: in Ohio, by Ohio Department of Natural Resources, Division of Water (1970), Norris and Fidler (1973), Norris (1974), Deering and others (1983), Breen and Dumouchelle (1991); and in Indiana, by Geosciences Research Associates, Inc. and Purdue University, Water Resources Research Center (1980) and Indiana Department of Natural Resources (1988, 1990). Analyses of brines from rocks of Silurian and Devonian age are found in Stout and others (1932), Lamborn (1952), Walker (1959), Stith (1979), Keller (1983) and Wilson and Long (1993a, b).

Data compiled from the literature and the available data bases were selected on the basis of the following criteria: (1) major-ion concentrations (Ca, Mg, Na, Cl, SO<sub>4</sub>, and HCO<sub>3</sub>) were determined, (2) the analyses balanced electrochemically within 10 percent and, (3) lithologies of the water-producing units were determined. In cases where multiple analyses were available for a well, the most recent analysis that met the above criteria was selected. The dissolved-solids data for most of the analyses that were used in this report were calculated by summing the concentrations of all major constituents according to the method described in Fishman and Friedman (1989). Dissolved-solids concentrations for waters in the Illinois and Michigan Basins were estimated from borehole geophysical data where available laboratory determinations were sparse (D.J. Schnoebelen, U.S. Geological Survey, written commun., 1993).

New data that were collected during this investigation include detailed chemical and isotopic analyses of ground water from the aquifer system along general directions of regional ground-water flow, as determined from the map of the potentiometric surface of the carbonate-rock aquifer (fig. 12), and isotopic analyses of aquifer material collected from cores of glacial deposits and carbonate rock. The locations of the ground-water and aquifer-material samples are shown in figure 32. At each sampling location along four transects across the aquifer system, ground-water samples were collected from the carbonate-rock aquifer, and, where possible, from a glacial aquifer. Sampling was restricted to existing domestic wells or test wells; wells with short open intervals in the deep parts of the aquifer were generally not available. At each sampling location, an attempt was made to sample the deepest available well in the carbonate-rock aguifer in

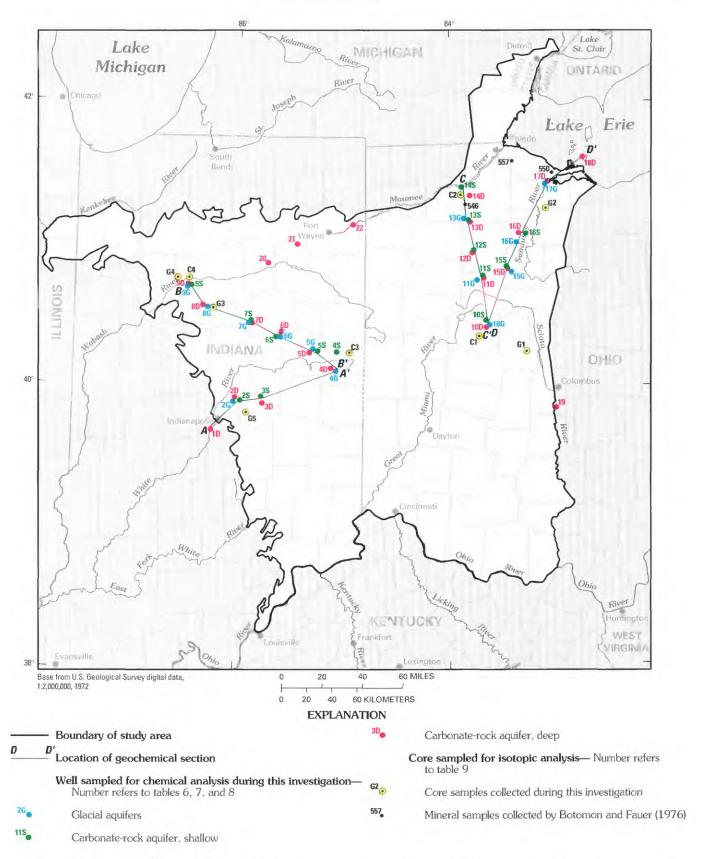


FIGURE 32.—Locations of wells sampled during this investigation, carbonate-rock and glacial cores sampled for isotopic analysis, and geochemical sections A–A', B–B', C–C', and D–D'.

order to intersect the dominant regional ground-water flow paths in the aquifer system. The deep bedrock wells are completed from 100 to nearly 450 ft into the carbonate-rock aquifer. To evaluate the effects of sampling the deep wells with long open intervals, RASA investigators also sampled a nearby well with a short open interval. These wells were shallow and completed in the top 5 to 50 ft of the carbonate-rock aquifer. Well depth and length of open interval for each well sampled are listed in table 6. Deep bedrock wells that are cased through the top part of the carbonate-rock aquifer are also noted in table 6. Where possible, a glacial well, a shallow bedrock well, and a deep bedrock well within several miles of each other were identified and grouped as a sample site.

Ground-water samples were collected during 1991-92 and analyzed for major and minor constituents according to the methods described in Fishman and Friedman (1989). Field determinations were made for pH, temperature, and alkalinity according to methods described in Wood (1976). Dissolved sulfide was determined in the field with a Hach DR-2000 spectrophotometer according to the procedure described in the instrument manual (Hach Chemical Company, 1989).

Samples were collected and analyzed for dissolved gas concentrations; stable isotope ratios of oxygen, hydrogen, carbon and sulfur; and the radioactive isotopes tritium (<sup>3</sup>H) and carbon-14 (14C) by use of standard methods. Samples of aquifer material were collected from cores in the core repositories of the Indiana Geological Survey and the Ohio Geological Survey. The samples were analyzed for carbon and sulfur isotopes by use of standard methods. By convention, stable isotope ratios are expressed in delta units ( $\delta$ ) as per mil (parts per thousand, or per mil) differences relative to the appropriate standard: Standard Mean Ocean Water (SMOW) for oxygen ( $\delta^{18}$ O) and hydrogen ( $\delta$ D), Pee Dee Formation belemnite for carbon ( $\delta^{13}$ C), and Canyon Diablo troilite for sulfur  $(\delta^{34}S)$ . Tritium concentrations are expressed in tritium units (TU), and <sup>14</sup>C values are presented in percent modern carbon (pmc). The chemical and isotopic data are listed in tables 7-9.

# SPATIAL DISTRIBUTION OF DISSOLVED-SOLIDS CONCENTRATIONS AND HYDROCHEMICAL FACIES

Knowledge of the spatial distribution of dissolved-solids concentrations and hydrochemical facies can help in distinguishing recharge and discharge areas, identifying areas of ground-water mixing, and estimating relative rates of ground-water flow. Water chemistry in the glacial and carbonate-rock aquifers was classified by calculating the dissolved-solids concentrations and the percentages of major cations and anions composing the total dissolved cations and anions, respectively. Maps were prepared showing the areal distribution of dissolved solids and hydrochemical facies indicated by the predominant cations and anions. These maps were

used to delimit zones of potable water in the carbonate-rock aquifer, to examine the relation between the glacial aquifers and the carbonate-rock aquifer, and to evaluate possible geochemical and hydrological processes that control the distribution of major dissolved solutes.

Generally, dissolved-solids concentrations in ground water increase along flow paths — from the surface to the saturated zone and through the aquifer — because of dissolution of minerals (Freeze and Cherry, 1979). Additional processes such as evaporation or evapotranspiration can increase concentrations of dissolved solutes. Some ground waters, notably brines, contain extremely high concentrations of dissolved solids because of combined effects of mineral dissolution and evaporation. Thus, dissolved-solids concentrations generally can be used as an indicator of the degree of chemical evolution of ground water in an aquifer system.

The predominant major ions in ground water can also be used as indicators of the important chemical and hydrologic processes in an aquifer system. Chebotarev (1955) characterized regional changes in the dominant anion species in ground water. The general evolutionary sequence that he observed for the dominant anions was HCO3 to SO4 to Cl, which correlated with increasing distance along the flow path and an increasing age of water. This anion sequence also corresponded to an increase in dissolved-solids concentration. Water containing predominantly bicarbonate is generally present in areas of active ground-water flushing, water containing predominantly sulfate is present where ground-water circulation is less active, and water containing predominantly chloride is generally present where ground-water flow is very sluggish and flushing of the aquifer is minimal. Back (1960) introduced the concept of hydrochemical facies based on the dominance of cations and anions. Using hydrochemical facies and dissolved-solids concentrations, he inferred the general sequence of reactions and hence the general directions of regional ground-water flow.

### DISSOLVED-SOLIDS CONCENTRATIONS

Dissolved-solids concentrations of ground water from the Midwestern Basins and Arches aquifer system are shown in figures 33 and 34. Dissolved-solids concentrations in water from the glacial aquifers (fig. 33) range from less than 100 to greater than 2,600 mg/L; the median is 378 mg/L. In more than 80 percent of available water analyses for the glacial aquifers, dissolved-solids concentrations are less than 500 mg/L. Ground water with dissolved-solids concentrations less than 500 mg/L is found in the glacial aquifers across most of the study area, as is ground water with concentrations ranging from 500 to 1,000 mg/L. Concentrations greater than 1,000 mg/L, however, are restricted primarily to the northeastern part of the study area. Few analyses of water from the glacial aquifers are available for this area because many of the wells are completed in the underlying carbonate-rock aquifer rather

**GEOCHEMISTRY** C59

 ${\tt Table 6.} \textbf{--Well construction information for wells sampled during investigation of the \textit{Midwestern Basins and Arches}$ aquifer system, 1991–92

 $[Map\ number\ is\ location\ in\ figure\ 32;\ ft,\ feet; --,\ not\ applicable;\ N.A.,\ data\ not\ available;\ G,\ glacial\ aquifer;\ C-R,\ carbonate-rock\ aquifer;\ data\ not\ available;\ G,\ glacial\ aquifer;\ C-R,\ carbonate-rock\ aquifer;\ data\ not\ available;\ G,\ glacial\ aquifer;\ data\ not\ available;\ data\ no$ all depth data are in feet below land surface]

Well name	Map number	Well depth (ft)	Depth to bedrock (ft)	Depth to top of open interval (ft)	Depth to bottom of open interval (ft)	Length of open interval (ft)	Aquifer
Ross	10 G	102		N.A.	N.A.	N.A.	G
Birt	10 S	86	76	80	86	6	C-R
Ben Logan H.S.	10 D	340	97	160	340	<sup>a</sup> 180	C-R
Searfoss	15 G	60		N.A.	N.A.	N.A.	G
Rife	15 S	39	34	34	39	5	C-R
Schoenberger	15 D	240	33	36	240	205	C-R
Beasley	16 G	81		61	81	20	G
Hill	16 S	80	52	63	80	17	C-R
Gillig	16 D	310	45	55	310	255	C-R
Lamalie	17 G	75		71	75	4	G
S-18	17 D	340	70	180	340	<sup>b</sup> 160	C-R
Finnegan	18 D	185	2	26	185	159	C-R
Wilson	11 G	50		N.A.	N.A.	N.A.	G
Spencer	11 S	43	16	22	43	21	C-R
Stair	11 D	250	18	21	250	229	C-R
Francis	12 S	62	40	43	62	20	C-R
Augustine	12 D	320	6	9	320	311	C-R
Richard	12 D 13 G	81			N.A.	N.A.	G
Kern	13 G	102	72	N.A. 75	102	N.A. 27	C-R
			73			°291	C-R C-R
Auckerman	13 D	400	78 22	109	400		
Rice	14 S	35	32	32	35	3 d90	C-R
City of Weston	14 D	500	65	410	500		C-R
Hartman	19	144	114	114	144	30	C-R
Lacy	4 G	67		64	67	3	G
Hummel	4 S	121	88	90	121	31	C-R
Jones	4 D	201	119	122	201	79	C-R
Harrison	3 S	117	108	108	117	9	C-R
Martin	3 D	200	135	138	200	62	C-R
Lockhart	2 G	140		136	140	4	G
Mattingly	2 S	150	140	140	150	10	C-R
Merchant	2 D	310	170	170	310	140	C-R
Gates	1 D	320	88	88	320	°232	C-R
Bickford	5 G	45		41	45	4	G
Bartlett	5 S	106	74	74	106	32	C-R
Desoto Substation	5 D	265	88	91	265	174	C-R
Staggs	6 G	116		113	116 .	3	G
Ice	6 S	110	92	92	110	18	C-R
Underwood	6 D	302	161	162	302	140	, C-R
Cohee	7 G	99		84	89	5	G
Ellis	7 S	102	49	55	102	47	C-R
Harmon	7 D	293	51	53	293	240	C-R
Fox	8 G	89		84	89	5	G
Skiles	8 D	202	63	64	202	138	C-R
Justice	9 G	62		59	62	3	G
Lee	9 S	113	65	67	113	46	C-R
Starbuck	9 D	182	76	79	182	103	C-R
Geradot	22	260	70 72	70	260	190	G, C-R
Stenzel	21	260	170	170	260	90	C-R
Rees	20	230	160	160	230	70	C-R

 $<sup>^{\</sup>rm a}$  Well is cased through the top 83 ft of bedrock.  $^{\rm b}$  Well is cased through the top 110 ft of bedrock.

<sup>&</sup>lt;sup>c</sup>Well is cased through the top 31 ft of bedrock.

<sup>&</sup>lt;sup>d</sup>Well is cased through the top 345 ft of bedrock.

<sup>&</sup>lt;sup>e</sup>Well is open to the New Albany Shale (upper confining unit) from 88 to 204 ft below land surface.

Table 7.—Chemical analyses of selected constituents in water from wells sampled during investigation of the Midwestern Basins and Arches aquifer system, 1991–92

[Map number is location in figure 32;  $\mu$ S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter;  $\mu$ g/L, micrograms per liter; --, data not collected]

			mic	rograms p	er liter;, d	ata not colle	cted]				
Well name	Map number	Date of collection	Specific conductance (µS/cm)	pH (standard units)	Eh (millivolts)	Temperature (degrees Celsius)	Dissolved oxygen (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)
Ross	10 G	08-06-91	2,360	6.83	121	12.1	0.1	290	200	38	4.5
Birt	10 S	08-07-91	1,010	7.10	512	11.5	4.5	120	55	16	2.4
Ben Logan H.S.	10 D	07-28-92	707	7.35	397	13.8	.9	87	34	13	1.6
Searfoss	15 G	08-15-91	2,400	7.08	145	11.5	<.1	490	75	62	3.9
Rife	15 S	08-12-91	2,400	6.93	58	11.1	.1	490	69	46	4.6
Schoenberger	15 D	08-14-91	2,720	6.95	52	11.2	<.1	540	79	53	5.0
Beasley	16 G	08-19-91	772	7.32	70	10.5	.1	88	34	15	1.4
Hill	16 S	08-20-91	1,760	7.37	126	11,5	.1	200	75	71	4.0
Gillig	16 D	08-21-91	1,660	7.40	102	11.6	<.1	220	66	65	4.0
Lamalie	17 G	08-22-91	2,450	7.18	72	12.1	<.1	400	140	40	4.2
S-18	17 D	08-27-91	2,690	6.99	3	12.6	<.1	490	160	27	4.6
Finnegan	18 D	06-13-92	765	7.15	82	11.8		100	47	1.4	1.4
Wilson	11 G	08-03-92	1,470	7.38	35	11.3	<.1	190	72	47	3.5
Spencer	11 S	07-29-92	1,010	7.02	176	12.8	.1	140	50	16	2.4
Stair	11 D	08-04-92	1,070	7.21	153	11.4	.1	140	56	21	3.0
Francis	12 S	08-05-92	991	7.30	-36	12.1		120	48	19	3.6
Augustine	12 D	08-06-92	1,260	7.34	<del>-</del> 79	11.3	<.1	140	62	41	3.8
Richard	13 G	07-30-92	2,080	7.85	67	11.5	.1	250	88	120	4.1
Kern	13 S	08-07-92	1,610	7.75	127	12.3	.1	170	57	120	3.2
Auckerman	13 D	08-13-92	1,690	7.20	-132	12.4	<.1	190	73	69	7.0
Rice	14 S	08-12-92	1,180	7.41	-88	12.8	.1	130	62	45	2.8
City of Weston	14 D	08-11-92	3,250	7.25	-96	12.9	<.1	540	180	74	3.7
Hartman	19	09-10-92	1,330	7.00		13.5		100	67	53	9.1
Lacy	4 G	09-06-91	670	7.42	72	7.4	<.1	86	36	11	1.2
Hummel	4 S	09-05-91	953	7.22	95	11.3	.l	110	58	22	2.0
Jones	4 D	09-03-91	695	7.19	126	11.3	<.1	98	35	8.8	1.8
Harrison	3 S	10-07-91	595	7.49	77	12.2	.2	76	26	14	1.3
Martin	3 D	09-04-91	570	7.40	56	13.5	<.1	77	26	16	1.0
Lockhart	2 G	09-09-91	1,140	7.23	104	12.4	<.1	110	35	87	3.4
Mattingly	2 S	09-11-91	1,060	7.32	70	12.1	.1	110	46	43	2.5
Merchant	2 D	09-11-91	908	7.30		13.2		100	43	31	2.3
Gates	1 D	10-08-91	1,210	7.30 7.41	-84	13.7	<.1	44	27	170	8.2
Bickford	5 G	09-03-92	958	7.41	-64 97	13.7	<.1 <.1	110	44	32	1.9
Bartlett	5 S	09-03-92	765	7.17	143	12.0	.1	100	42	8.5	1.5
Desoto Substation	5 D	08-19-92	738	7.26		13.0	.2	96	37	10	1.5
		08-19-92			149						1.3
Staggs Ice	6 G	2 2 2	723	7.37	128	11.4	:1	100	32	10 12	3.2
Underwood	6 S 6 D	09-02-92	713	7.31	132	12.6	<.1	88 79	35 32	19	2.1
		08-21-92	653	7.44	124	11.7	.1				
Cohee	7 G	09-04-92	673	7.35	76	12.5	<.1	95 06	32	10	2.1
Ellis	7 S	08-24-92	746	7.34	123	12.0	<.1	96	34	13	2.2
Harmon	7 D	08-25-92	711	7.31	87	12.3	<.1	98 75	31	7.1	1.5
Fox	8 G	08-29-92	683	7.15	124	11.9	.1	75 02	29 34	18	1.4
Skiles	8 D	08-26-92	782	7.44	-1	13.3	<.1	92	34	17	0.90
Justice	9 G	08-27-92	736	7.20	113	12.4	.1	100	32	6.2	1.0
Lee	9 S	08-28-92	834	7.31	125	11.6	.1	100	39	13	2.9
Starbuck	9 D	05-29-92		7.22	-28	11.3	.1	75	35	11	3.4
Geradot	22	08-28-92		7.24	76	13.3	<.1	110	47	26	3.0
Stenzel	21	08-30-91		7.40	30	11.8	<.1	62	29	22	2.0
Rees	20	08-29-91	603	7.48	-68	12.1	<.1	59	22	45	5.1

GEOCHEMISTRY C61

Table 7.—Chemical analyses of selected constituents in water from wells sampled during investigation of the Midwestern Basins and Arches aquifer system, 1991–92.—Continued

[Map number is location in figure 32;  $\mu$ S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter;  $\mu$ g/L, micrograms per liter; --, data not collected]

Well name	Map number	Bicarbonate, as HCO <sub>3</sub> (mg/L)	Sulfate, as SO <sub>4</sub> (mg/L)	Sulfide (mg/L)	Chloride (mg/L)	Bromide (mg/L)	Silica (mg/L)	Dissolved solids, sum of constituents (mg/L)	1ron (μg/L)	Strontium (µg/L)	Dissolved organic carbon (mg/L)
Ross	10 G	533	1,200	< 0.01	7.0	0.12	22	1,930	9,000	16,000	2.0
Birt	10 S	397	240	<.01	7.2	.04	11	665	4	13,000	1.0
Ben Logan H.S.	10 D	383	60	<.01	20	.04	10	427	3	8,900	.60
Searfoss	15 G	224	1,600	.02	23	.08	17	2,400	5,200	12,000	1.3
Rife	15 S	266	1,600	<.01	6.3	.08	17	2,430	3,100	12,000	1.2
Schoenberger	15 D		1,500	.01	17	.15	16	2,340	2,100	11,000	1.3
Beasley	16 G	346	120	.01	6.4	.05	13	454	520	4,400	1.1
Hill	16 S	168	850	<.01	16	.19	12	1,330	1,500	14,000	1.6
Gillig	16 D	179	860	<.01	15	.25	12	1,350	2,200	12,000	1.6
Lamalie	17 G		1,500	.02	37	.45	17	2,270	2,600	13,000	1.3
S-18	17 D		1,600	0.35	44	.36	12	2,490	780	12,000	1.6
Finnegan	18 D	528	19	1.1	2.2	.02	7.2	439	12	200	2.4
Wilson	11 G	285	610	.04	10	.02	15	1,110	2,700	17,000	1.0
Spencer	11 S	463	180	.02	28	.08	15	668	720	5,000	1.5
Stair Stair	11 D	490	190	<.01	13	.07	20	702	3,100	13,000	1.1
Francis	12 S	454	170	.28	27	.12	16	656	770	27,000	1.3
Augustine	12 D	478	180	3.3	100	.16	16	784	14	4,700	1.3
Richard	12 D 13 G			.02	34	.32	11	1,670	1,700	14,000	1.1
Kicharu Kern	13 G 13 S	89 144	1,100 750	<.01	3 <del>4</del> 35	.32	8.4		990	22,000	.80
								1,240			.90
Auckerman Rice	13 D	283	530	23.3	110	.51	6.5	1,150	13	18,000	1.5
	14 S	227	440	2.3	12	.09	13	836	52	17,000 10,000	1.0
City of Weston	14 D		1,900	7.4	45	.38	9.0	2,860	350		
Hartman	19	472	65		100		9.5	826	180	7,100	3.8
Lacy	4 G	432	33	.03	9.5	.06	19	416	2,800	3,200	1.1
Hummel	4 S	536	130	<.01	9.2	.09	20	630	2,200	11,000	1.7
Jones	4 D	466	6.5	<.01	4.4	.04	15	402	1,200	1,300	1.3
Harrison	3 S	390	0.10	.01	5.5	.10	16	334	1,400	620	1.7
Martin	3 D	397	<.10	.01	5.6	.04	20	344	1,000	530	1.6
Lockhart	2 G	427	49	<.01	150	.09	12	658	1,600	220	1.0
Mattingly	2 S	410	40	.02	140	.20	14	603	2,700	1,100	1.0
Merchant	2 D	395	28	<.01	85	.06	14	501	64	1,100	1.1
Gates	1 D	407	19	4.1	210	1.20	7.0	694	7	1,800	1.4
Bickford	5 G	439	83	.02	61	.04	15	566	2,200	430	.90
Bartlett	5 S	476	43	.02	6.0	.02	18	459	2,300	3,000	1.4
Desoto Substation	5 D	420	74	<.01	4.9	.02	15	453	1,600	5,200	1.2
Staggs	6 G	412	48	<.01	21	.03	20	439	1,900	1,500	1.2
Ice	6 S	439	42	.03	5.4	.03	17	426	1,100	4,800	1.2
Underwood	6 D	441	5.0	.03	8.6	.04	16	383	890	1,500	1.5
Cohee	7 G	401	40	.02	5.1	.02	17	403	2,000	1,600	1.1
Ellis	7 S	421	65	.01	12	.01	16	452	2,000	3,000	1.2
Harmon	7 D	376	65	<.01	14	.03	16	421	1,800	860	1.2
Fox	8 G	472	.40	<.01	5.3	.03	19	393	4,000	930	3.6
Skiles	8 D	371	43	.11	54	.06	17	445	2,100	510	1.7
Justice	9 G	377	71	<.01	26	.04	18	442	2,300	190	1.2
Lee	9 S	388	85	<.01	39	.07	15	489	1,700	1,500	.90
Starbuck	9 D	440	6.9	1.8	7.6	.05	10	368	8	1,100	1.0
Geradot	22	395	190	.01	35	.05	15	628	1,500	5,300	1.8
Stenzel	21	371	30	.03	1.9	.02	16	357	370	9,700	1.3
Rees	20	384	16	.13	2.9	.04	11	355	250	2,400	1.6

Table 8.—Analyses of isotopes in water from wells sampled during investigation of the Midwestern Basins and Arches aquifer system, 1991–92

[Map number is location in figure 32; delta notation ( $\delta$ ) explained on p. C92; TU, tritium units; --, data not available]

Well name	Map number	$\delta^{18}O$ (per mil)	δD (per mil)	δ <sup>13</sup> C (per mil)	δ <sup>34</sup> S, sulfate (per mil)	δ <sup>34</sup> S, sulfide (per mil)	Tritium (TU)	Carbon-14 (percent modern)
Ross	10 G	-8.35	-51.5	-14.9	-10.40		1.7	49.1
Birt	10 S	-8.60	-54.0	-14.2	-5.80		9.1	58.9
Ben Logan H.S.	10 D	-8.55	-54.5	-14.1	4.80		11.2	69.5
Searfoss	15 G	-8.10	-51.0	-16.6	4.00		3.4	37.9
Rife	15 S	-8.00	-50.0	-15.4	3.20		<.1	30.3
Schoenberger	15 D	-8.10	-50.0	-15.7	3.20		<.1	24.5
Beasley	16 G	-8.55	-56.5	-13.2	-9.60		<.1	54.6
Hill	16 S	-7.90	<del>-48.5</del>	-14.7	-7.60		<.1	6.2
Gillig	16 D	-7.85	<b>-4</b> 9.0	-13.7	-9.60		<.1	8.6
amalie	17 G	-8.40	-54.5	-10.8	23.30		<.1	3.9
5-18	17 D	-8.45	-54.5	-8.5	26.70	-42.40	<.1	4.7
Finnegan	18 D	-9.05	-59.0	-10.0	-3.20	-22.90	.5	47.7
Vilson	11 G	-7.95	-50.0	-10.0 -15.4	-9.20	-22.70	<.1	18.5
pencer	11 S	-7.93 -8.15	-50.0 -51.0	-13.4 $-13.8$	-9.20 -9.80		10.9	58.1
tair	11 D	-8.15 -8.15	-51.0 -50.5	-15.0 -15.0	-9.80 -7.70		6.2	55.7
rancis	12 S	-8.13 -8.20	-50.5 -51.5	-13.0 -14.1	1.50	-53.20	11.6	45.0
Augustine	12 D	-8.20 -8.05	-51.0	-14.1 -15.3	-1.80	-51.50	10.6	62.0
Richard	12 D	-8.05 -9.65	-65.5	-13.3 -17.2	.30		.5	
Kern	13 G	-9.63 -9.90					 <.1	1.3
uckerman	13 D		-67.5	-13.3	6.60			
lice		-14.35	-99.5	-10.7	29.00	-27.80	<.1	0.2
	14 S	-8.40	-55.0	-14.1	4.40	-33.00	<.1	8.8
City of Weston	14 D	-10.05	-67.5	-7.1	25.90	-42.50	<.1	1.4
lartman	19	-8.45	-55.5	-1.2	20.50		.6	5.5
acy	4 G	-7.85	-47.5	-14.6	3.10		3.0	60.6
lummel	4 S	-7.70	<b>-46.5</b>	-14.9	-7.90		<.1	56.1
ones	4 D	-7.90	-49.0	-14.3	.40		<.1	56.9
Iarrison	3 S	-7.15	-44.5	-12.7			<.1	43.4
/lartin	3 D	-7.40	-46.0	-14.4			<.1	45.6
ockhart	2 G	-7.50	-45.5	-14.1	2.40		16.9	100.0
<b>Mattingly</b>	2 S	-7.40	-46.0	-13.8	2.50		19.1	78.1
/lerchant	2 D	-7.40	-45.0	-13.8	2.00		14.1	67.5
ates	1 D	-6.95	-43.5	-11.0		2.2	<.1	1.2
Sickford	5 G	-7.70	-47.0	-14.9	80		20.6	78.3
Bartlett	5 S	-7.60	<del>-4</del> 7.5	-14.4	-7.90		.3	61.8
esoto Substation		-7.75	-47.5	-13.8	-10.00		.2	42.3
taggs	6 G	-7.75	-46.5	-14.5	-2.10		7.8	66.8
ee	6 S	-7.45	-46.5	-15.0	-2.20		.7	61.8
Inderwood	6 D	-7.40	-44.5	-15.6		-43.40	<.1	35.7
Cohee	7 G	-7.65	-47.5	-14.7	-5.90		.4	58.0
llis	7 S	-7.65	-46.5	-15.1	-5.50		1.6	56.9
larmo <b>n</b>	7 D	-7.65	-46.5	-14.2	-3.90		10.9	68.0
ox	8 G	-7.25	-45.0	-8.8			<.1	44.2
kiles	8 D	-7.75	-47.0	-13.7	1.90	-37.80	20.0	51.3
ustice	9 G	-7.65	-48.5	-13.8	20		18.1	72.3
ee	9 S	-7.75	-47.5	-14.2	3.00		15.0	65.3
tarbuck	9 D	-7.40	-45.5	-3.1		-12.20	<.1	28.1
Geradot	22	-7.75	<b>-49.0</b>	-16.2	-8.10		12.2	74.3
tenzel	21	-7.60	-47.5	-14.9	9.40		<.1	35.1
Rees	20	-7.50	-46.5	-17.9	5.50	-27.60	<.1	20.8

Table 9.—Analyses of sulfur and carbon isotopes in carbonate rocks and glacial deposits from the Midwestern Basins and Arches Region

[Core locations shown in figure 32; delta notation ( $\delta$ ) explained on p. C92; --, data not available]

Core number	Geologic unit	Interval sampled (feet below land surface)	δ <sup>34</sup> S, sulfate (per mil)	δ <sup>34</sup> S, sulfide (per mil)	δ <sup>13</sup> C (per mil)
<sup>a</sup> 546	Detroit River Group-pyrite			-21.9	(22)
a550	Salina Group-anhydrite	1	24.9		<del>,==</del>
<sup>a</sup> 557	Lockport dolomite-pyrite		=	7.0	
Gl	Glacial deposits	3 – 25	-14.8	-13.1	
G2	Glacial deposits	5 - 60	-9.8	-14.6	45
G3	Glacial deposits	18 - 70	-9.8	-12.8	05
G4	Glacial deposits	10 - 180	-9.9	-8.0	55
G5	Glacial deposits	12 - 130	-8.2	-14.0	.00
C1	Columbus Limestone	235	9.6	-24.9	1.45
	Salina Group	273 - 375	-1.0	-7.8	
	Salina Group	425 - 575	8.2	-1.9	
C2	Detroit River Group	35	26.4	-14.0	
	Salina Group	100	6.5	-8.8	.10
	Salina Group	150	7	-7.1	-3.20
	Salina Group	301	28.3	-9.9	
	Salina Group	350	9.2	-10.0	25
	Salina Group-bedded gypsum	320 - 465	28.7		
	Lockport Dolomite	650	14.6	2.4	1.30
C3	Salamonie Dolomite	105	18.3	3.6	1.35
C4	Salina Group	20 – 173	-2.3	-6.8	
	Salina Group-pyrite	173		-19.4	

<sup>&</sup>lt;sup>a</sup>Data from Botoman and Faure (1976).

than the less productive glacial deposits, which were derived from clay-rich lacustrine sediments.

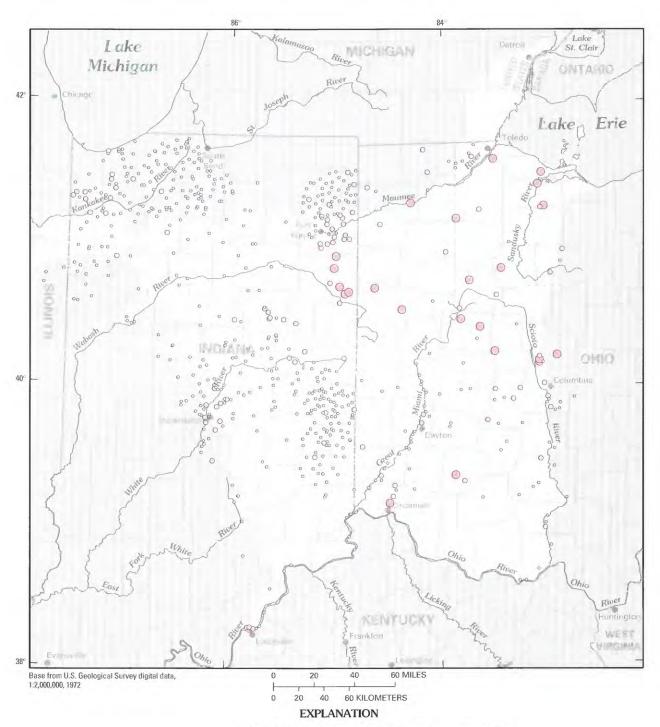
Water from the carbonate-rock aquifer (fig. 34) ranges in dissolved-solids concentration from 170 to more than 350,000 mg/L. Where the carbonate-rock aquifer does not underlie the upper confining unit, dissolved-solids concentrations range from 170 to 3,830 mg/L; the median is 560 mg/L. Ground water with dissolved-solids concentrations less than 500 mg/L is present in many areas of the carbonate-rock aquifer where it is does not underlie the upper confining unit; however, it is found only locally in the northeastern part of the study area. Ground water with dissolved-solids concentrations between 500 and 1,000 mg/L is present primarily in the northeastern part of the area. Water with dissolved-solids concentrations greater than 1,000 mg/L in the carbonate-rock aquifer where the upper confining unit is not present is restricted to the northeastern part of the study area.

Dissolved-solids concentrations for the carbonate-rock aquifer where it underlies the upper confining unit also are shown in figure 34. Lines of equal dissolved-solids concentration are drawn for those areas in the basins where dis-

solved-solids concentrations are greater than 10,000 mg/L. The dissolved-solids concentration data for water in the structural basins are from wells completed in oil- and gas-producing zones within the carbonate rocks of Silurian and Devonian age. Dissolved-solids concentrations were computed either from chemical data of brines that were reported in the literature or calculated from borehole geophysical data (D.J. Schnoebelen, U.S. Geological Survey, written commun., 1993).

The distribution of dissolved-solids concentrations in the carbonate rocks differs greatly among the three structural basins (Appalachian, Michigan, and Illinois) in the Midwestern Basins and Arches Region:

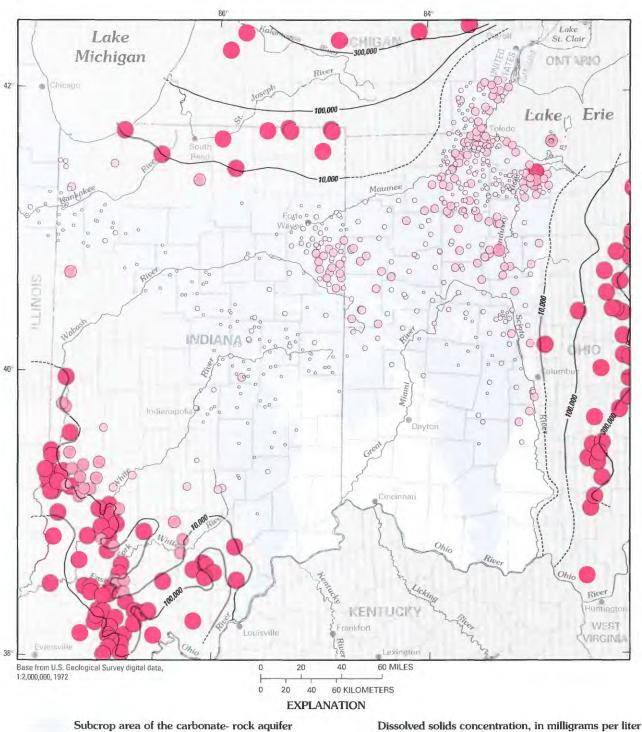
Appalachian Basin—Dissolved-solids concentrations within the Appalachian Basin range from less than 10,000 to greater than 350,000 mg/L; all but two reported brine analyses list dissolved-solids concentrations greater than 200,000 mg/L. The few analyses that are available from the Appalachian Basin where the dissolved-solids concentrations are less than 100,000 mg/L indicate that the zone of transition from freshwater to saltwater is narrow. Chloride concentra-



Dissolved solids concentration, in milligrams per liter

- Less than or equal to 500
- $\circ$  Greater than 500 and less than or equal to 1.000
- Greater than 1,000

 $\textit{Figure 33.--Dissolved-solids distribution in ground water from the glacial aquifers in the \textit{Midwestern Basins and Arches aquifer system.} \\$ 



Dashed where approximately located. Interval, in milligrams per liter, is variable

Line of equal dissolved-solids concentration—

Dashed where approximately located. Interval, in milligrams per liter, is variable

Less than or equal to 500

Greater than 500 and less than or equal to 1,000

Greater than 3,000 and less than or equal to 10,000

Greater than 10.000

FIGURE 34.—Dissolved-solids distribution in ground water from the carbonate-rock aquifer in the Midwestern Basins and Arches aquifer system.

tions increase from less than 50 to greater than 9,300 mg/L within approximately 7 mi downbasin from where the carbonate-rock aquifer becomes confined above by the upper confining unit (Schmidt, 1979).

Michigan Basin—In the Michigan Basin, dissolved-solids concentrations of water from carbonate rocks of Devonian and Silurian age range from less than 10,000 to greater than 350,000 mg/L. The transition zone from freshwater to highly concentrated brine is comparatively wider than in the Appalachian Basin. Brines with dissolved-solids concentrations greater than 350,000 mg/L in the Michigan Basin are first noted more than 75 mi downbasin from the contact between the carbonate-rock aquifer and the upper confining unit, where it is exposed at the bedrock surface, whereas similarly concentrated brines in the Appalachian Basin are found less than 50 mi downbasin from where the carbonate rocks are confined.

Illinois Basin—Dissolved-solids concentrations of water from carbonate rocks of Devonian and Silurian age in the Illinois Basin range from less than 3,000 to greater than 100,000 mg/L. The contrast in the distribution of dissolved-solids concentrations between the Illinois Basin and the Appalachian and Michigan Basins is striking. The largest dissolved-solids concentrations in the Illinois Basin are approximately 150,000 mg/L, much lower than in the other two basins. Water with dissolved-solids concentrations less than 10,000 mg/L is found more than 70 mi downbasin from where the carbonate-rock aquifer dips beneath the upper confining unit.

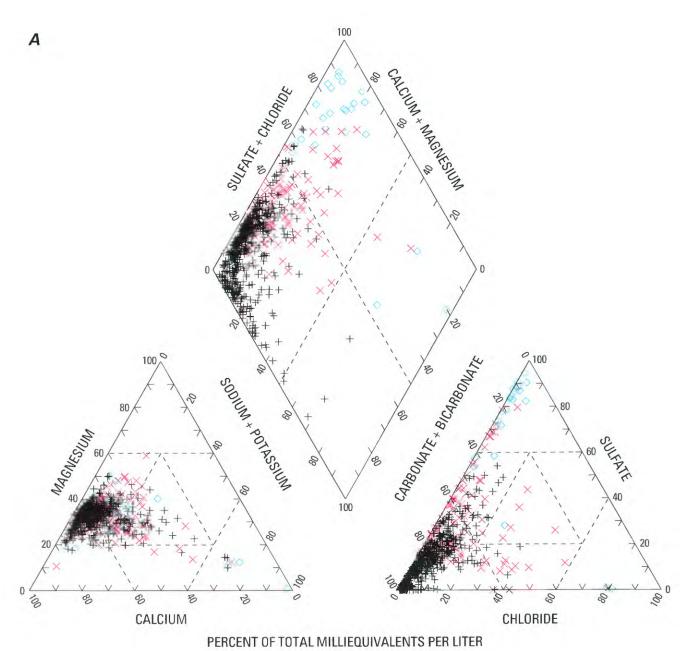
Generally, the dissolved-solids concentration of water in structural basins increases with depth. In the Midwestern Basins and Arches aquifer system, dissolved-solids concentrations increase as the carbonate rocks dip toward the center of each structural basin (fig. 34). However, the relation between dissolved-solids concentration and depth is not consistent among the three basins. In the Appalachian and Michigan Basins, water with dissolved-solids concentrations of approximately 10,000 mg/L is first noted where the carbonate rocks are about 300 to 800 ft below land surface; in the Illinois Basin, water with dissolved-solids concentrations of approximately 10,000 mg/L is first noted where the carbonate rocks are more than 2,000 ft below land surface. The presence of dilute water at such depths in the Illinois Basin is unusual and has been investigated by various researchers (Clayton and others, 1966; Rupp and Pennington, 1987; Stueber and others, 1987; and Stueber and Walter, 1991). Several hypotheses have been advanced to explain the presence of the dilute formation water at the margins of the Illinois Basin and include (1) dilution of formation water by meteoric water of Pleistocene age, (2) precipitation of solid phases during mixing of formation water with meteoric water, and (3) increased infiltration through fracture systems within the carbonate rocks. The origin of dilute formation water in the carbonate rocks of Devonian and Silurian age is unclear, and further research is necessary to explain more fully the chemical and hydrological processes that have occurred in the Illinois Basin. Although water with dissolved-solids concentrations less than 10,000 mg/L is potentially potable (U.S. Environmental Protection Agency, 1984), the dilute formation water is produced as a by-product of oil and gas production and is not used as a source of drinking water.

The only regionally extensive areas of water with dissolved-solids concentrations greater than 10,000 mg/L in the Midwestern Basins and Arches aquifer system are beneath the upper confining unit in the structural basins. However, in a small area along Lake Erie near the mouth of the Sandusky River, ground water from the carbonate-rock aquifer contains dissolved-solids concentrations ranging from 10,000 to greater than 70,000 mg/L (Breen and Dumouchelle, 1991). Breen and Dumouchelle (1991) evaluated bromide and chloride data and concluded that the source of salinity in this area is halite dissolution. Although Janssens (1977) states that the extensive halite beds found in the Salina Group in eastern Ohio disappear more than 50 mi east of where the saline water is present, the data indicate that perhaps an isolated remnant of bedded halite may be present in the carbonate rocks in this area. All other available data indicate that water with dissolved-solids concentrations less than 10,000 mg/L is found throughout the total thickness of the carbonate-rock aquifer where it does not underlie the upper confining unit. Data are not available, however, in the northern part of the study area where the thickness of the carbonate-rock aquifer increases to more than 2,500 ft. Dilute ground water may not be present at depth in this area.

#### HYDROCHEMICAL FACIES

Identification of hydrochemical facies in the Midwestern Basins and Arches aquifer system was based on the distribution of water types in the glacial and carbonate-rock aquifers. Water types were defined by use of the trilinear plotting technique (Piper, 1944); the trilinear diagrams are shown in figures 35 and 36.

The seven water types that were identified in the Midwestern Basins and Arches aguifer system and their abundance are listed in table 10. The two most abundant water types in the glacial aquifers and in the carbonate-rock aquifer where it does not underlie the upper confining unit are Ca-Mg-HCO<sub>3</sub> and Ca-Mg-SO<sub>4</sub> types. Nearly 80 percent of all available ground-water analyses from the glacial and carbonate-rock aquifers would be classified as either of these two water types. The next most common ground-water types are Ca-Mg-Na-HCO3 and Ca-Mg-Na-SO4 and are distinguished from the more common Ca-Mg-HCO3 and Ca-Mg-SO4 waters by an increased percentage of dissolved sodium. The Cl-influenced ground-water type, present in small but notable quantities, is distinguished by chloride percentages that range from at least 20 percent to no more than 60 percent of the total anion milliequivalents. Na-Cl or Ca-Na-Cl type water



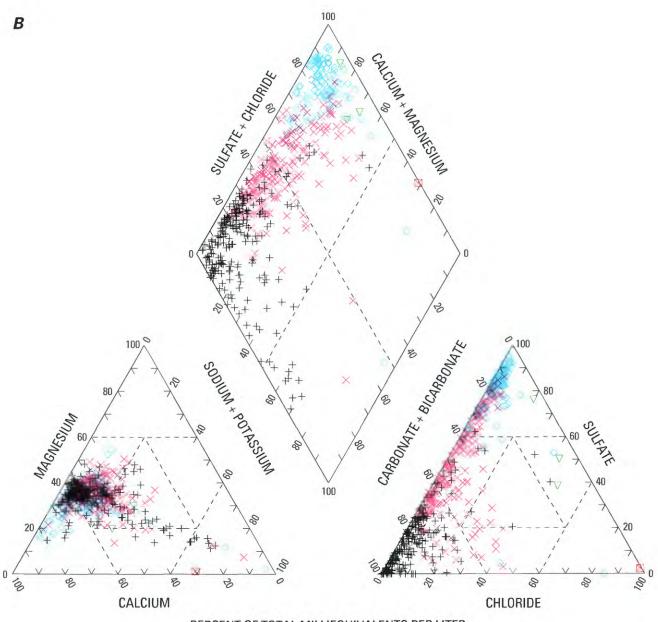
# Dissolved-solids concentration, in milligrams per liter

Less than or equal to 500

**EXPLANATION** 

- $\times$  Greater than 500 and less than or equal to 1,000
- Greater than 1,000

 $\label{thm:concentration: All properties} Figure~35. — Trilinear~diagram~of~water~chemistry~of~the~Midwestern~Basins~and~Arches~aquifer~system,~categorized~by~dissolved-solids~concentration:~(A)~glacial~aquifers. \\$ 



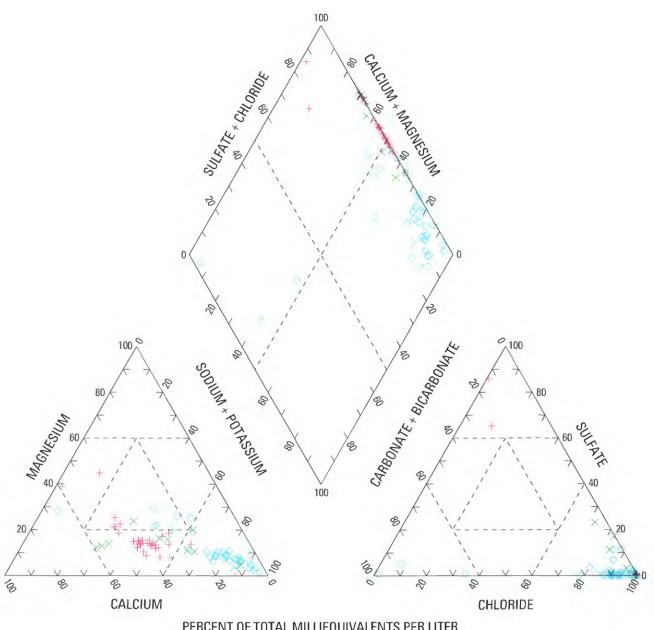
PERCENT OF TOTAL MILLIEQUIVALENTS PER LITER

# **EXPLANATION**

# Dissolved-solids concentration, in milligrams per liter

- + Less than or equal to 500
- X Greater than 500 and less than or equal to 1,000
- Greater than 1,000 and less than or equal to 3,000
- $\nabla$  Greater than 3,000 and less than or equal to 10,000

FIGURE 35.—CONTINUED. Trilinear diagram of water chemistry of the Midwestern Basins and Arches aquifer system, categorized by dissolved-solids concentration: (B) carbonate-rock aquifer where it does not underlie the upper confining unit.



PERCENT OF TOTAL MILLIEQUIVALENTS PER LITER

# **EXPLANATION**

- Appalachian basin
- Michigan basin
  - Illinois basin

FIGURE~36. — Trilinear~diagram~of~water~chemistry~in~the~carbonate-rock~aquifer~of~the~Midwestern~Basins~and~Arches~aquifer~system~approximately~approximawhere it underlies the upper confining unit, categorized by structural basin.

Table 10.—Major water types, their specific cation and anion compositions, and their abundance in the glacial and carbonate-rock aquifers in the Midwestern Basins and Arches aquifer system

[%, percent; -, data not available]

	Cation types	Anion types	Number (percentage) of samples, by aquifer				
Water type			Glacial	Carbonate-rock aquifer			
y de la constant de l	ound, types		aquifers1	Does not underlie the upper confining unit <sup>2</sup>	Underlies the upper confining unit <sup>3</sup>		
Ca-Mg-HCO <sub>3</sub>	Ca,Ca-Mg	HCO <sub>3</sub>	479	215	1		
			(75%)	(40%)	(1%)		
Ca-Mg-SO <sub>4</sub>	Ca, Ca-Mg	HCO <sub>3</sub> -SO <sub>4</sub>	69	207	2		
		$SO_4$	(11%)	(38%)	(2%)		
Ca-Mg-Na-HCO <sub>3</sub>	Ca-Mg-Na,	$HCO_3$	55	44	2		
	Ca-Na		(9%)	(8%)	(2%)		
Ca-Mg-Na-SO <sub>4</sub>	Ca-Mg-Na,	HCO <sub>3</sub> -SO <sub>4</sub> , SO <sub>4</sub>	11	41			
	Ca-Na		(2%)	(8%)			
Na-HCO <sub>3</sub>	Na	HCO <sub>3</sub>	3	9			
			(<1%)	(2%)			
Na-Cl	Na, Ca-Na,	Cl	2	3	79		
or Ca-Na-Cl	Ca-Mg-Na		(<1%)	(<1%)	(93%)		
Cl-influenced	All cation types	HCO, -SO <sub>4</sub> -Cl,	18	20	Ī		
		HCO <sub>3</sub> -Cl, SO <sub>4</sub> -Cl	(3%)	(4%)	(1%)		

Total number of samples from the glacial aquifers is 637.

<sup>3</sup>Total number of samples from the carbonate-rock aquifer where it underlies the upper confining unit is 85.

predominates in the carbonate-rock aquifer where it underlies the upper confining unit; however, this water type is rare in other parts of the carbonate-rock aquifer and in the glacial aquifers. Na-HCO<sub>3</sub> water is uncommon in the aquifer system.

Hydrochemical facies (figs. 37 and 38) were identified for the glacial and carbonate-rock aquifers on the basis of the spatial distribution of water types in table 10. Large areas of the Midwestern Basins and Arches aguifer system are characterized by the presence of either the Ca-Mg-HCO<sub>3</sub> or the Ca-Mg-SO<sub>4</sub> type; these areas are called Ca-Mg-HCO<sub>3</sub> facies and Ca-Mg-SO<sub>4</sub> facies, respectively. The remaining areas of the aquifer system are not characterized by a single water type; rather, they are distinguished by the presence of either Ca-Mg-HCO<sub>3</sub> water or Ca-Mg-SO<sub>4</sub> water or both types, along with water types with increased percentages of sodium (Ca-Mg-Na-HCO<sub>3</sub>, Ca-Mg-Na-SO<sub>4</sub>, and Na-HCO<sub>3</sub> waters) and, in some places, sodium and chloride (Na-Cl and Cl-influenced waters). These areas where several different water types are present together are called multiple-water-type facies.

Hydrochemical facies of water from glacial aquifers are shown in figure 37. A Ca-Mg-HCO<sub>3</sub> facies in the glacial aqui-

fers extends throughout much of the Midwestern Basins and Arches Region. A facies of Ca-Mg-SO<sub>4</sub> water is present in the northeastern part of the aquifer system. Multiple-water-type facies are present in the glacial aquifers along the north and northwest boundaries between the underlying carbonate-rock aquifer and the upper confining unit. Another multiple-water-type facies is present in the south-central part of the study area where the glacial deposits are directly underlain by Ordovician-age shales and limestones (the upper weathered zone water-bearing unit).

Hydrochemical facies of water from the carbonate-rock aquifer are shown on figure 38. Ca-Mg-HCO<sub>3</sub> water is present in the carbonate-rock aquifer throughout much of the Midwestern Basins and Arches aquifer system except in the northeastern part, where it is highly localized. The predominant water type in the northeastern part of the study area is Ca-Mg-SO<sub>4</sub>. Multiple-water-type facies are present in the carbonate-rock aquifer along the north boundary between the carbonate-rock aquifer and the upper confining unit. Another multiple water-type facies is present along a part of the west contact between the carbonate-rock aquifer and the upper confining unit.

<sup>&</sup>lt;sup>2</sup>Total number of samples from the carbonate-rock aquifer where it does not underlie the upper confining unit is 539.

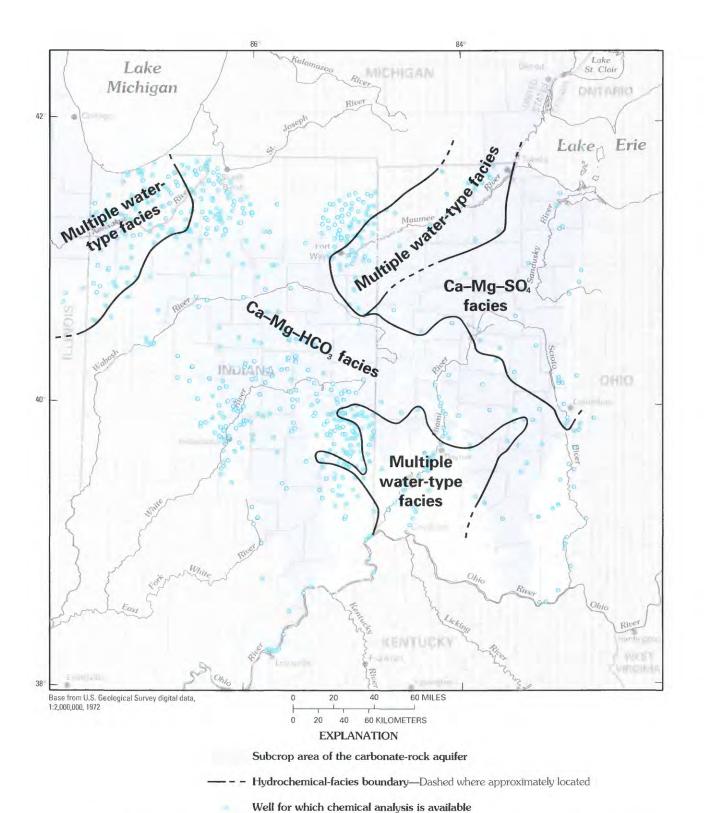


FIGURE 37.—Hydrochemical facies of ground water from the glacial aquifers in the Midwestern Basins and Arches aquifer system.

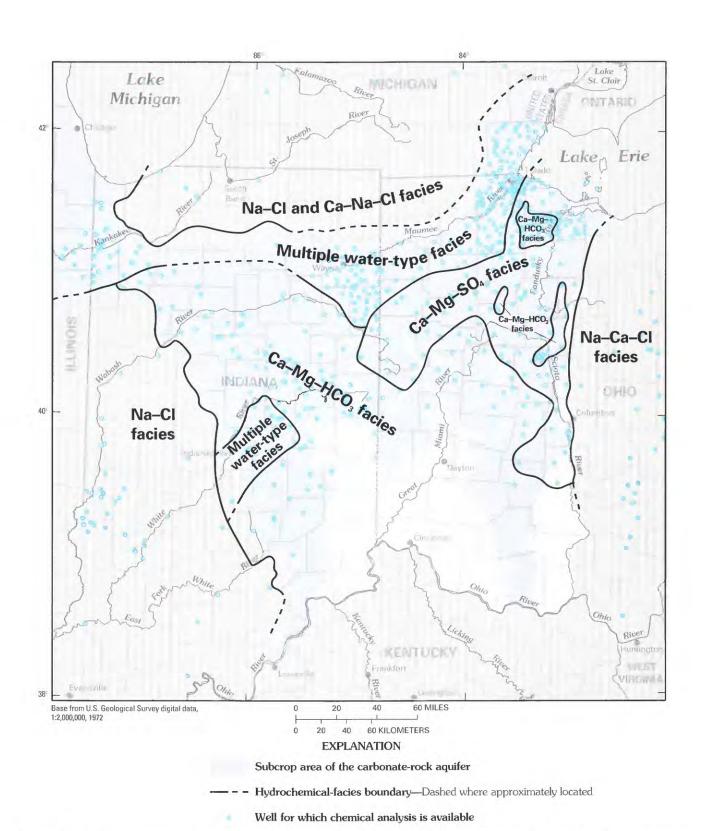


FIGURE 38.—Hydrochemical facies of ground water from the carbonate-rock aquifer in the Midwestern Basins and Arches aquifer system.

Water in the carbonate-rock aquifer in the Appalachian Basin is predominantly the Na-Ca-Cl type with nearly equal milliequivalent percentages of Na and Ca. In the Michigan Basin, water is either a Na-Cl or Ca-Na-Cl type, depending on the specific bedrock unit within the carbonate rocks from which the water is produced. The predominant water type in the Illinois Basin is Na-Cl; however, an area of Ca-Mg-Na-HCO<sub>3</sub> water is present in the basin as far as 15 miles downdip from where the carbonate-rock aquifer becomes confined.

# RELATION BETWEEN DISSOLVED-SOLIDS CONCENTRATIONS AND HYDROCHEMICAL FACIES

Examination of figures 33, 34, 37, and 38 indicates a strong relation between the distribution of dissolved-solids concentrations and the distribution of hydrochemical facies in the glacial and carbonate-rock aquifers. The trilinear diagrams (figs. 35 and 36) of water from the glacial aquifers and the carbonate-rock aquifer, where it is does not underlie the upper confining unit, also show that water type changes as dissolved-solids concentrations change. The Ca-Mg-HCO<sub>3</sub> water found throughout the aquifer system is characterized by dissolved-solids concentrations that are generally less than 500 mg/L. Ca-Mg-SO<sub>4</sub> water has dissolved-solids concentrations that range from about 500 to more than 3,000 mg/L. As figure 35 shows, dissolved-solids concentrations increase as the percentage of sulfate in water increases. The dissolvedsolids concentrations of ground water in the multiple-watertype facies are varied, as one would expect given the variability in water types in such facies.

Water type and dissolved-solids concentrations are also related in the carbonate-rock aquifer where it underlies the upper confining unit. Ground water from the carbonate-rock aquifer in each of the surrounding structural basins is categorized by basin on the trilinear diagram in figure 36. Based on the available analyses, waters from the Appalachian Basin have dissolved-solids concentrations that are generally greater than 200,000 mg/L and are Na-Ca-Cl type waters. Waters from the Michigan Basin range in dissolved-solids concentration from around 10,000 mg/L to more than 300,000 mg/L; water type changes from a Na-Cl to a Ca-Na-Cl as dissolved-solids concentrations increase. The dissolved-solids concentration in waters from the Illinois Basin is generally less than 100,000 mg/L, and the waters are primarily of the Na-Cl type.

Examination of figures 33, 34, 37, and 38 indicates that the spatial distribution of dissolved-solids concentrations and hydrochemical facies in the glacial and carbonate-rock aquifers is similar. The similarity likely reflects the hydraulic connection between the units. Ground water can flow through the glacial deposits and into the bedrock, then can discharge to streams and lakes back through the glacial deposits. Moreover, the source rock of the glacial deposits in the region is primarily the underlying bedrock (Strobel and Faure, 1987). Thus, the similarity in chemistry is also likely due to the pres-

ence of the same reacting mineral phases in the glacial and carbonate-rock aquifers.

# GEOCHEMICAL AND HYDROLOGICAL PROCESSES, BY WATER TYPE

The trends in major-ion chemistry in the Midwestern Basins and Arches aquifer system are controlled, in a large part, by interactions between ground water and minerals that compose the aquifers. Important geochemical reactions that can affect solute concentrations in ground-water systems include mineral dissolution and precipitation, oxidation and reduction, and ion exchange. Additional processes such as evaporation and mixing of water from various sources can also be important controls of solute concentrations. The extent to which these processes control ground-water chemistry is affected by the paths and rates of ground-water flow and the sequence of reactions in an aquifer system. The geochemical and hydrologic processes responsible for the various water types in the Midwestern Basins and Arches aquifer system are discussed in the following sections.

#### CALCIUM-MAGNESIUM-BICARBONATE WATER

Ca-Mg-HCO<sub>3</sub> water, the predominant type in the glacial and carbonate-rock aquifers, is generally produced by dissolution of the carbonate minerals calcite and dolomite. The reaction of calcite and dolomite with water and carbon dioxide can be written as follows:

$$CaCO_3 + H_2O + CO_2 < --> Ca^{2+} + 2HCO_3$$
 (4) (calcite)

$$CaMg(CO_3)_2 + 2H_2O + 2CO_2 < --> Ca^{2+} + Mg^{2+} + 4HCO_3^-$$
 (5) (dolomite)

Typically, CO<sub>2</sub> is derived from the oxidation of organic matter and root respiration in the soil zone and is dissolved by recharge water. Dolomite is more abundant than calcite in the aquifer system (Harrison, 1960; Steiger and Holowaychuk, 1971; Wilding and others, 1971; Casey, 1994); if dolomite dissolves according to equation 5, the molar proportions of [Ca+Mg] to [HCO<sub>3</sub>] should be linear, with a slope of 0.5. A fairly strong relation exists between [Ca+Mg] and [HCO<sub>3</sub>] for Ca-Mg-HCO<sub>3</sub> type water from the glacial and carbonaterock aquifers (figs. 39 and 40); however, the Ca-Mg-SO<sub>4</sub> and Ca-Mg-Na-SO<sub>4</sub> water types do not follow the trend predicted by the dolomite dissolution model and are highly enriched in calcium and magnesium relative to bicarbonate ([Ca+Mg]/  $[HCO_3] > 0.5$ ). The Ca-Mg-Na-HCO<sub>3</sub> waters plot slightly below the line and are depleted in calcium and magnesium relative to bicarbonate ( $[Ca+Mg]/[HCO_3] < 0.5$ ). (The mechanism by which calcium and magnesium are depleted is ion

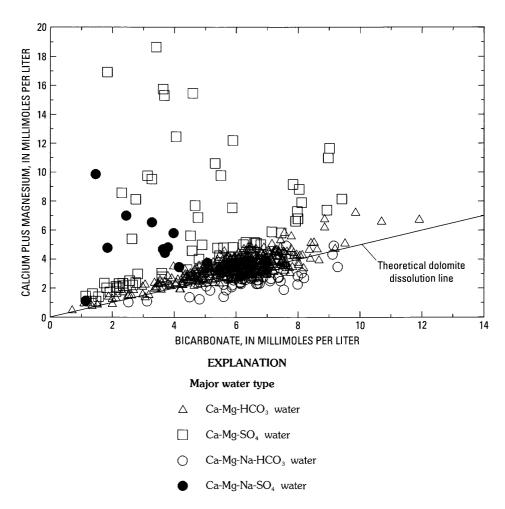


FIGURE 39.—Concentration of calcium plus magnesium as a function of bicarbonate concentration in ground water from the glacial aquifers in the Midwestern Basins and Arches aquifer system.

exchange of calcium and magnesium for sodium and is discussed in the section on "Sodium-Enriched Water.")

The state of equilibrium between ground water and calcite, dolomite, and other minerals in the aquifer system can be evaluated by the computation of saturation indices (SI), expressed as

$$SI_{mineral} = log(IAP/K_T),$$
 (6)

where IAP is the ion-activity product of the mineral calculated from analytical data, and  $K_{\rm T}$  is the thermodynamic equilibrium constant at the measured temperature of the water sample (Plummer and others, 1976). If the saturation index is negative, the water is undersaturated with respect to the particular mineral, and dissolution of the mineral is possible. If the saturation index is positive, the water is oversaturated with respect to the mineral, and precipitation of the mineral in the aquifer is possible. A saturation index of zero indicates that the mineral is in equilibrium with the water and that the tendency or rates of dissolution and precipitation should be equal. Thermodynamics can only indicate the potential for

such phase transfers. In reality, various kinetic factors may cause systems to behave differently than predicted (Nordstrom and Ball, 1989; Busby and others, 1991).

Saturation indices were calculated for calcite and dolomite (and other mineral phases discussed later in this report) by use of the computer model WATEQF (Plummer and others, 1976) and chemical data for the water collected as part of this investigation. The accuracy of the saturation index for predicting equilibrium of carbonate minerals depends largely on the accuracy of the field measurements of pH and alkalinity. Uncertainty in these and other analytical data produces an uncertainty estimate in the saturation index of  $\pm$  0.1 for calcite and  $\pm$  0.2 for dolomite (Nordstrom and Ball, 1989; Busby and others, 1991). Because the accuracy of the pH measurements could not be verified for much of the historical groundwater-chemistry data, saturation indices were not calculated for historical samples.

The saturation indices for calcite and dolomite generally do not correlate with dissolved-solids concentrations (fig. 41). Nearly all the Ca-Mg-HCO<sub>3</sub> water is in equilibrium or oversaturated with respect to calcite and dolomite, an indica-

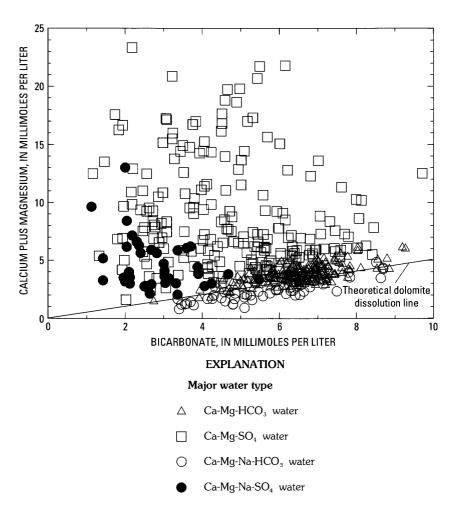


FIGURE 40.—Concentration of calcium plus magnesium as a function of bicarbonate concentration in ground water from the carbonate-rock aquifer in the Midwestern Basins and Arches aquifer system.

tion that carbonate mineral equilibria could be controlling concentrations of calcium, magnesium, and bicarbonate in Ca-Mg-HCO<sub>3</sub> water in the aquifer system. The tendency toward oversaturation with respect to calcite has been noted in other aquifers by Nordstrom and Ball (1989), who conclude that kinetic effects may inhibit calcite precipitation. Reactions that add calcium, magnesium, and bicarbonate or that consume carbon dioxide can promote oversaturation with calcite and dolomite. For example, dissolution of gypsum may add calcium at a rate that exceeds calcium removal by calcite precipitation, causing oversaturation with calcite. Several Ca-Mg-SO<sub>4</sub>-type waters are saturated with calcite but are significantly undersaturated with respect to dolomite. Undersaturation with respect to dolomite is an important factor in dedolomitization, a process that can promote the formation of Ca-Mg-SO<sub>4</sub>-type water. (Dedolomitization is discussed further in the next section.)

Ca-Mg-HCO<sub>3</sub> water is the predominant water type in the glacial and carbonate-rock aquifers because calcite and dolomite are abundant in these aquifers (Harrison, 1960; Steiger

and Holowaychuk, 1971; Wilding and others, 1971; Casey, 1994) and recharge takes place across most of the study area. A steady supply of  $\mathrm{CO}_2$  is available for carbonate dissolution in the glacial aquifers because ground-water recharge generally takes place through the organic-rich soils overlying these deposits. Dissolved  $\mathrm{CO}_2$  and other solutes are also recharged to the underlying bedrock because the glacial aquifers provide most of the recharge to the carbonate-rock aquifer at the regional scale.

### CALCIUM-MAGNESIUM-SULFATE WATER

The predominant water type in the northeastern part of the Midwestern Basins and Arches aquifer system is Ca-Mg-SO<sub>4</sub>. This water is characterized by high concentrations of dissolved solids, calcium, magnesium, and sulfate. The predominance of sulfate over bicarbonate and the lack of agreement of the Ca-Mg-SO<sub>4</sub> water with the simple dolomite dissolution model (figs. 39 and 40) indicates that other processes are controlling the chemistry of this water type. Two reactions can produce this type of water: (1) dedolomitization, which

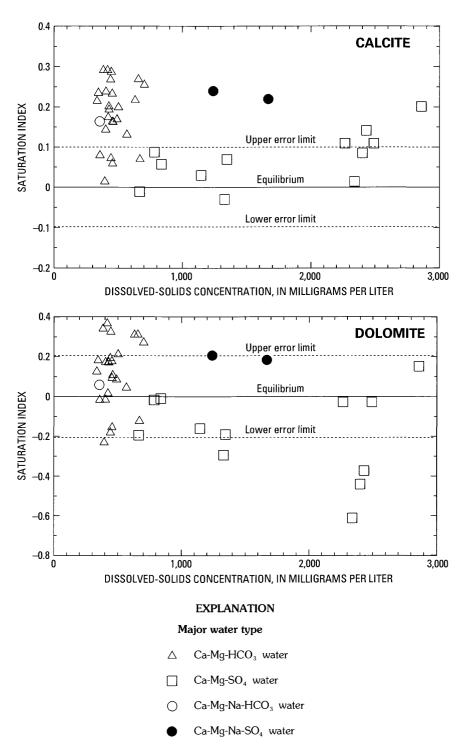


FIGURE 41.—Saturation indices of calcite and dolomite as a function of dissolved-solids concentration for water from wells in the Midwestern Basins and Arches aquifer system. (Error limits are due to analytical and thermodynamic data uncertainties.

Points plotting within these lines are considered to be in equilibrium with the given mineral.)

involves dissolution reactions with carbonate minerals and gypsum, and (2) sulfuric acid neutralization, which involves dissolution of carbonate minerals with sulfuric acid generated by the oxidation of pyrite.

The results of investigations of other regional carbonate-rock aquifers show that dedolomitization may be a control-ling process (Pearson and Rightmire, 1980; Back and others, 1983; Busby and others, 1991). Ground water that moves through the aquifer initially dissolves calcite, dolomite and gypsum (or anhydrite). Once calcite and dolomite reach saturation, gypsum is still undersaturated and continues to dissolve, adding calcium and sulfate to the water. Consequently, calcite becomes oversaturated and, as it precipitates, the bicarbonate concentration decreases. The decrease in bicarbonate concentration causes the water to be undersaturated with respect to dolomite and promotes dissolution of dolomite. Dissolution of dolomite causes increases in the concen-

tration of magnesium in the water. The overall reaction can be written as:

$$\begin{aligned} & CaMg(CO_3)_2(s) + CaSO_4 \cdot 2H_2O(s) + H^+ &\longleftrightarrow \\ & (dolomite) \qquad (gypsum) \end{aligned}$$

$$CaCO_3(s) + Ca^{2+} + Mg^{2+} + SO_4^{2-} + HCO_3^{-} + 2H_2O.$$
 (7) (calcite)

As the reaction proceeds, Ca:Mg ratios in the water decrease to 1.0, and sulfate concentrations increase. The ratio of [Ca+Mg]/[HCO<sub>3</sub>] is 1:1, in contrast to reaction 5, in which the ratio of [Ca+Mg]/[HCO<sub>3</sub>] is 1:2 or 0.5. On a plot of [Ca+Mg] as a function of [SO<sub>4</sub> + 0.5HCO<sub>3</sub>], the dedolomitization reaction yields a straight line with a slope of 1. Plots of the water-chemistry data for the glacial aquifers (fig. 42) and the carbonate-rock aquifer (fig. 43) show very close agree-

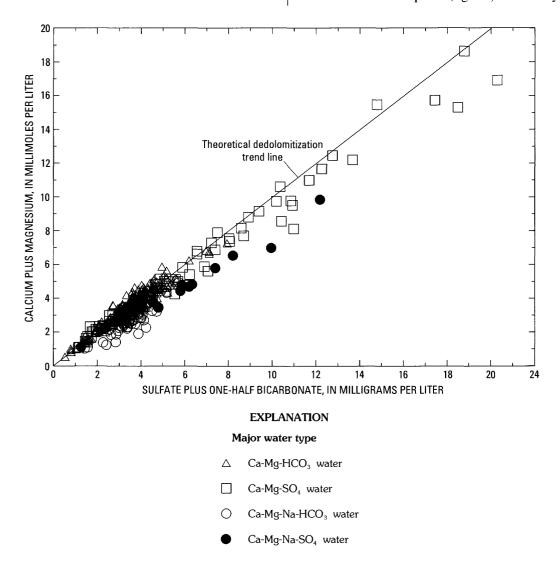


FIGURE 42.—Concentration of calcium plus magnesium as a function of concentration of sulfate plus one-half bicarbonate in ground water from the glacial aquifers in the Midwestern Basins and Arches aquifer system.

ment between the theoretical trend for the dedolomitization model and the trends for the Ca-Mg-HCO $_3$ - and the Ca-Mg-SO $_4$ -type waters. The Ca-Mg-Na-HCO $_3$ - and Ca-Mg-Na-SO $_4$ -type waters tend to plot below the 1:1 line.

Gypsum saturation indices for ground water collected as part of this investigation (fig. 44) increase with increasing sulfate concentrations. A value of  $\pm\,0.2$  is used as the estimate of uncertainty in the saturation index of gypsum. Saturation with respect to gypsum generally is indicated for a few samples in which sulfate concentrations are greater than about 1,500 mg/L. Gypsum would tend to dissolve in water that is undersaturated with respect to gypsum.

Dedolomitization is not the only process, however, that yields the relation between Ca, Mg, SO<sub>4</sub>, and HCO<sub>3</sub> shown in figures 42 and 43. An alternative model involves dissolution

of dolomite by sulfuric acid  $(H_2SO_4)$  produced by the oxidation of pyrite  $(FeS_2)$ :

$$FeS_2 + 15/4O_2 + 7/2H_2O \leftrightarrow Fe(OH)_{3(s)} 2H_2SO_4$$
 (8)

(Nordstrom and others, 1979). The sulfuric acid reacts with dolomite:

$$CaMg(CO_3)_{2(s)} + H_2SO_4 \leftrightarrow Ca^{2+} + Mg^{2+} + SO_4^{2-} + 2HCO_3^{-}.$$
 (9)

The overall stoichiometry of the dissolved products in reaction 9 is identical to that of the dedolomitization reaction (7). Thus, either model could produce the trends shown in figures 42 and 43, and gypsum and (or) pyrite could be the sources of sulfate in the Ca-Mg-SO<sub>4</sub> water in the northeastern part of the aquifer system.

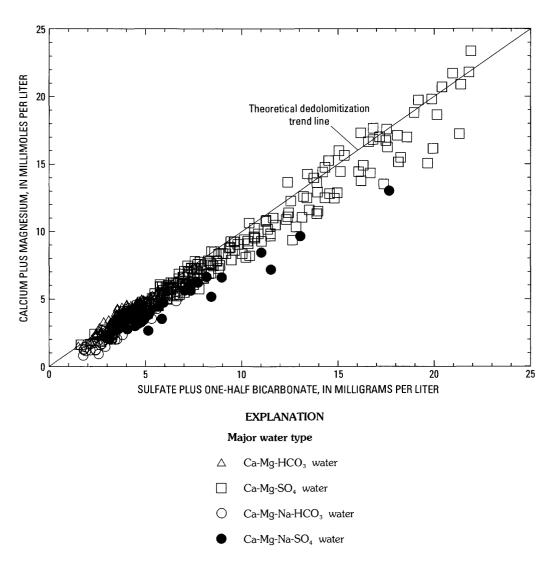


FIGURE 43.—Concentration of calcium plus magnesium as a function of concentration of sulfate plus one-half bicarbonate in ground water from the carbonate-rock aquifer in the Midwestern Basins and Arches aquifer system.

The mineralogy of the carbonate rocks indicates that gypsum and pyrite both are present in the northeastern part of the aquifer system. Gypsum beds as thick as 5.5 ft are present at or just below land surface in the rocks of the Salina Group in the Sandusky Bay area of northwestern Ohio (Carlson, 1991). Lesser quantities of gypsum are also found in carbonate rocks of Silurian and Devonian age throughout the northeastern part of the aquifer system. Pyrite is present in the Findlay Arch mineral district as defined by Carlson (1991) and is associated with a suite of ore minerals that includes celestite, fluorite, sphalerite, and galena. The Findlay Arch mineral district forms a northeasterly trending belt that extends from the Ohio and Indiana State line south of the Maumee River to the islands in Lake Erie. Structural controls on the mineralization in the Findlay Arch mineral district appear to be the Findlay Arch and the Bowling Green Fault zone (Carlson, 1991). Sulfide minerals are present throughout the carbonate rocks in the Findlay Arch mineral district, but they are generally concentrated at or just below surfaces of past erosion and in collapsed solution cavities (Botoman and Stieglitz, 1978). Abundant pyrite and marcasite are found in the Columbus Limestone in south-central Ohio and in the Devonian shales along the entire east boundary between the carbonate rocks and the younger shales (Carlson, 1991). Gypsum and sulfide minerals also may be present in the glacial deposits because the mineral composition of tills in the study area consists of fragments of the local bedrock (Strobel and Faure, 1987).

The isotopic composition of sulfur in mineral and dissolved phases can be useful in distinguishing sources of sulfate to ground water and determining whether dedolomitization, driven by gypsum dissolution, or sulfide-mineral oxidation is the predominant geochemical reaction in the

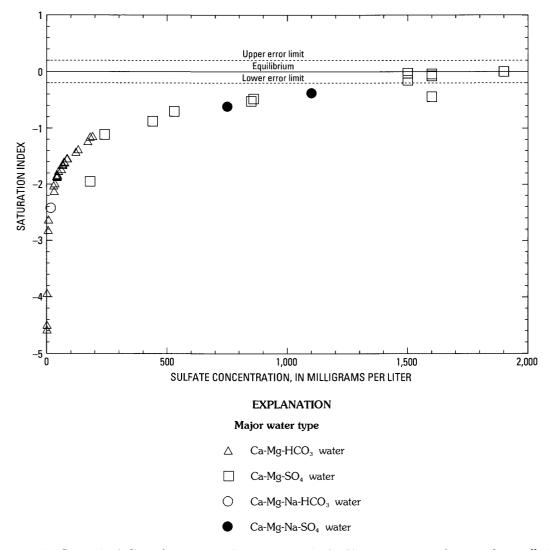


FIGURE 44.—Saturation indices of gypsum as a function of dissolved-sulfate concentration for water from wells in the Midwestern Basins and Arches aquifer system. (Error limits are due to analytical and thermodynamic data uncertainties. Points plotting within these lines are considered to be in equilibrium with gypsum.)

aquifer system (Pearson and Rightmire, 1980). The sulfur isotope data presented in tables 8 and 9 and discussed more fully in the section "Sulfur Isotopes" indicate that pyrite is the primary sulfate source for the glacial and carbonate-rock aquifers in most of the aquifer system; however, both pyrite and gypsum contribute sulfate to the Ca-Mg-SO<sub>4</sub>-type ground water in the northeastern part of the aquifer system.

Deering and others (1988) noted that the chemistry of ground water in the carbonate-rock aquifer in northwestern Ohio is established chiefly by the mineralogy of the carbonate rocks. Other researchers (Norris and Fidler, 1973; Norris, 1974) have discussed the distribution of water types in western Ohio in the context of chemical evolution of bicarbonatedominated water to sulfate-dominated water as ground water flows down the potentiometric gradient from the potentiometric high near the Bellefontaine Outlier to Lake Erie and to the Ohio River. The results of the ground-water flow model presented in the "Numerical Model" section, however, indicate that water in the aquifer system does not follow long, continuous paths from the highest potentiometric levels to Lake Erie or the Ohio River. Rather, ground-water recharge and discharge areas alternate across western Ohio. Thus, it is likely that the distribution of Ca-Mg-SO<sub>4</sub> water in the northeastern part of the aquifer system is primarily controlled by the mineralogy of the aquifer material.

The relatively large area of Ca-Mg-HCO<sub>3</sub> water within the Ca-Mg-SO<sub>4</sub> facies in the carbonate-rock aquifer in north-western Ohio corresponds to an area of thin or absent glacial deposits where the Lockport dolomite, a relatively pure dolomite (Janssens, 1977), crops out at the surface (fig. 5). The Ca-Mg-HCO<sub>3</sub> water also generally corresponds to areas of active ground-water recharge (fig. 28). Breen and Dumouchelle (1991) showed that, in northwestern Ohio, water in the carbonate-rock aquifer where the glacial deposits are thin or absent has tritium concentrations indicative of recharge since the 1950's. Thus, active ground-water flushing favors the formation of Ca-Mg-HCO<sub>3</sub> water in the carbonate-rock aquifer in the northeastern part of the study area where it is at or near the surface and recharge to the aquifer system occurs.

# SODIUM-ENRICHED WATER

Multiple-water-type facies described in the preceding section (figs. 37 and 38), are characterized by the presence of one or more of the following ground-water types: Ca-Mg-Na-HCO<sub>3</sub>, Ca-Mg-Na-SO<sub>4</sub>, and Na-HCO<sub>3</sub>. Many researchers have shown that an increase in sodium concentration in ground water without an associated increase in chloride can be caused by cation exchange of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions for Na<sup>+</sup> ions on clay minerals (Foster, 1950; Back, 1966; Freeze and Cherry, 1979; Thorstenson and others, 1979; Chapelle and Knobel, 1983). In an aquifer system with abundant carbonate

minerals, cation exchange may be accompanied by the dissolution of calcite and dolomite.

Na-HCO<sub>3</sub> water can be produced from Ca-Mg-HCO<sub>3</sub> waters by cation exchange on clay minerals according to the reaction:

$$(1-x) Ca^{2+} + x Mg^{2+} + Na_2 \cdot Ex ---> 2Na^+ + (Ca_{1-x}Mg_x) \cdot Ex,(10)$$

where  $0 \le x \le 1$ . By combining reactions 4, 5, and 10, the overall stoichiometry of dissolution of calcite and dolomite and cation exchange may be represented as:

$$(Ca_{1-x}Mg_x)CO_3 + H_2O + CO_2 + Na_2 \cdot Ex ---> 2Na^+ + 2HCO_3^- + (Ca_{1-x}Mg_x) \cdot Ex.$$
 (11)

As Ca<sup>2+</sup> and Mg<sup>2+</sup> are removed from solution and are replaced with Na<sup>+</sup> by cation exchange, the solution becomes undersaturated with respect to calcite and dolomite. The carbonate minerals dissolve, providing more Ca2+ and Mg2+ in solution to exchange with Na<sup>+</sup> and causing HCO<sub>3</sub><sup>-</sup> concentrations to increase. The Ca-Mg-Na-HCO3 water in figures 39 and 40 plots below the line predicted by the dolomite-dissolution model; this pattern, which indicates that the water is enriched in bicarbonate and depleted in calcium and magnesium relative to the dolomite dissolution model, is consistent with cation-exchange reactions. Ca-Mg-Na-SO<sub>4</sub> water is associated with Ca-Mg-SO<sub>4</sub> water in the glacial and carbonate-rock aquifers and is likely formed by the mixing of Na-HCO<sub>3</sub> and Ca-Mg-SO<sub>4</sub> waters or incomplete cation exchange of the Ca-Mg-SO<sub>4</sub> waters. The Ca-Mg-Na-SO<sub>4</sub> water does not plot with the Ca-Mg-Na-HCO<sub>3</sub> water in figures 39 and 40 because of the additional calcium and magnesium from dedolomitization (7) or sulfuric acid neutralization (9).

Eberts and others (1990) and Lesney (1992) describe the presence of water ranging in composition from Ca-Mg-Na-HCO3 to Na-HCO3 in bedrock units underlying shales and siltstones of Mississippian age in northeastern Ohio. Their research attributes this chemistry to mixing of Na-HCO<sub>3</sub> water, produced by cation exchange in the shales and siltstones, with water in the underlying aquifers. A similar water composition of Ca-Mg-Na-HCO<sub>3</sub> to Na-HCO<sub>3</sub> is present in the carbonate-rock aquifer in the Midwestern Basins and Arches aguifer system where the carbonate-rock aguifer is overlain by Devonian shales (upper confining unit) along the margins of the Michigan Basin. This similarity indicates that Na- and HCO<sub>3</sub>-enriched water produced by cation exchange in the shales is mixing with water in the underlying carbonate-rock aquifer. However, significant areas of Ca-Mg-Na-HCO<sub>3</sub> water, associated with some Na-HCO<sub>3</sub> water, are present in the carbonate-rock aguifer and the glacial aguifers where shales do not overlie the carbonate-rock aguifer south of the boundary between the aquifer and the upper confining unit. If Na-HCO<sub>3</sub> water from the upper confining unit is the source of Na-enriched water south of this boundary, then it

must have flowed in an updip direction out of the shales and into the adjacent carbonate-rock aquifer and associated glacial deposits.

Research on regional aquifers in the northern Midwest (Siegel and Mandle, 1984; Siegel, 1989, 1991) suggests a mechanism by which Na-HCO3 water produced by cation exchange in the shales at the margin of the Michigan Basin may have moved into the carbonate-rock aquifer. On the basis of distributions of solutes and isotopes in water from the Cambrian-Ordovician aquifer in eastern Wisconsin, Siegel (1989, 1991) proposed that loading of glacial ice during Pleistocene glaciation may have reversed ground-water flow gradients and caused ground water from within the Michigan Basin to discharge at the west margin of the Michigan Basin in eastern Wisconsin. A numerical model that simulated ground-water flow during Late Wisconsinan glaciation in northern Illinois (Filley, 1985) showed that increased pore pressures may have caused water from within the Michigan Basin to discharge at the basin margins. Panno and Bourcier (1990) proposed that the formation of karst features in carbonate rocks adjacent to the Appalachian, Michigan, and Illinois Basins was caused by mixing of ground water and deepbasin saline water that was flushed from the basins during Pleistocene glaciation. A similar flow of ground water out of the Michigan Basin during the Pleistocene may have occurred at its southern margin, pushing through the Devonian shales and emplacing Na-HCO3 water in the carbonate-rock aquifer and overlying glacial aquifers.

An alternative hypothesis for the presence of multiplewater-type facies along the northern boundary of the carbonate-rock aquifer and upper confining unit is cation exchange within the glacial and carbonate-rock aquifers. Some bedrock units within the Salina Group and carbonate rocks of Devonian age in northern Indiana and northwestern Ohio contain numerous thin shales (Janssens, 1977; Turner, 1977; Doheny and others, 1975). Cation exchange within these shale-rich carbonate rocks may result in the formation of Na-enriched water. Mazor and others (1993) suggest that significant differences in water composition in an area indicate that water may be stored in distinct pockets within an aquifer and that such pockets are caused by changes in lithology. Thus, the presence of multiple-water-type facies may be the result of a transitional bedrock lithology in the aquifer along the subcrop boundaries.

The Ca-Mg-Na-HCO<sub>3</sub> water found along the west subcrop boundary of the carbonate-rock aquifer is not associated with Na-HCO<sub>3</sub> water, nor is it as enriched in sodium as the Ca-Mg-Na-HCO<sub>3</sub> water along the north subcrop boundary of the carbonate-rock aquifer. The Ca-Mg-Na-HCO<sub>3</sub> water found in the carbonate-rock aquifer beyond the west boundary of the carbonate-rock aquifer and upper confining unit increases in chloride concentration in a downdip direction and most likely results from mixing of Ca-Mg-HCO<sub>3</sub> water with Na-Cl water from the Illinois Basin.

The multiple-water-type facies in the glacial aquifers in the south-central part of the study area is associated with the area where Ordovician shales and limestones (the upper weathered zone water-bearing unit) directly underlie the glacial deposits. Most of the water in this facies is the Ca-Mg-HCO<sub>3</sub> type; however, some ground water that is enriched in sodium or chloride or both is present in this area. Research on glacial buried-valley aquifers in the Great Miami River Valley (Dumouchelle and others, 1993) indicates two potential sources of sodium and chloride to the glacial aquifers. In the Great Miami River Valley, shallow ground water in highly permeable outwash valleys contains elevated concentrations of sodium and chloride that are related to human activities. Moreover, small amounts of moderately saline Na-Cl water discharges from the shale bedrock to the glacial aquifers in the Great Miami River Valley. Thus, sodium and chloride from both sources may be affecting the chemistry of water in the glacial aquifers in the south-central part of the aquifer system.

Water with elevated percentages of sodium and chloride is also present in the carbonate-rock aquifer where it is not overlain by the upper confining unit. Na-Cl or Cl-influenced ground water is uncommon in the carbonate-rock aquifer; most of the few areas of such water are within the multiplewater-type facies that borders the Michigan Basin. Possible sources of sodium and chloride to these ground waters include the dissolution of halite from the carbonate rocks, mixing with small amounts of formation brine from deeper bedrock units, or surface contamination by water affected by road-deicing salts or formation brine associated with petroleum exploration and production activities (Breen and Dumouchelle, 1991). The presence of Na-Cl water in the carbonate-rock aquifer along the margin of the Michigan Basin may also be related to the hydrodynamic displacement of brine by Pleistocene glaciation.

In summary, the exact geochemical and hydrologic processes responsible for the multiple-water-type facies are unknown, especially along the north boundary of the Midwestern Basins and Arches aquifer system. The distribution of water types in the multiple-water-type facies however, is clearly related to the change in lithology, from carbonate rocks to shales, at the boundaries of the carbonate-rock aquifer. The multiple-water-type facies along the margin of the Michigan Basin may also be related to changes in the groundwater flow regime during Pleistocene glaciation.

### SODIUM-CHLORIDE AND CALCIUM-SODIUM-CHLORIDE WATER

Na-Cl type water with dissolved-solids concentrations less than 10,000 mg/L is present in the carbonate-rock aquifer beneath the upper confining unit at the margins of the structural basins. Its presence likely results from mixing of freshwater with brines from within the basins. Processes responsible for the chemistry of brines in the Illinois, Michi-

gan, and Appalachian Basins are complex (Stueber and others, 1987; Lowry and others, 1988; Walter and others, 1990; Stueber and Walter, 1991; Stueber and others, 1993; Wilson and Long, 1993a, b) and are beyond the scope of this report. Na-Cl, Na-Ca-Cl and Ca-Na-Cl type waters with dissolvedsolids concentrations greater than 10,000 mg/L are present just beyond the boundary between the carbonate-rock aquifer and the upper confining unit in the Michigan and Appalachian Basins, an indication that the upper confining unit prevents water from recharging the carbonate-rock aquifer in these areas. The presence of water with dissolved-solids concentrations less than 10,000 mg/L in the Illinois Basin more than 70 mi downdip from the boundary of the carbonate-rock aquifer and the upper confining unit may be related to present or past patterns of flow in the carbonate-rock aquifer. Results of the regional ground-water flow model show that a small percentage of water may flow from the subcrop area down into the Illinois Basin. Such water could contribute to the current distribution of solutes. Other research on Illinois Basin brines (Clayton and others, 1966; Rupp and Pennington, 1987; Stueber and Walter, 1991) suggests that dilution of the brines may have occurred as a result of increased infiltration through fracture systems in the carbonate rocks or from meltwater that recharged the carbonate-rock aquifer during the Pleistocene. The origin of low dissolved-solids water deep in the Illinois Basin is uncertain, and more research would be needed for a full understanding of this part of the aquifer system.

# INSIGHTS INTO REGIONAL FLOW PROVIDED BY GEOCHEMICAL DATA

Ground-water samples were collected from the glacial and carbonate-rock aquifers along four general directions of regional ground-water flow, as determined from the potentiometric surface map of the carbonate-rock aquifer (fig. 12). The locations of the sampling points are shown in figure 32. The data are listed in tables 7 and 8. Although the regional ground-water flow model indicates that ground water in the Midwestern Basins and Arches aquifer system does not follow long paths from the highest regional potentiometric levels to the lowest regional potentiometric levels, it is useful to evaluate the differences in ground-water chemistry along the general directions of regional ground-water flow.

# MAJOR SOLUTES

Dissolved-solids and sulfate concentrations have been used as indicators of chemical evolution of ground water in various regional-scale carbonate-rock aquifers, such as the Floridan aquifer in Florida, the Edwards aquifer in Texas, and the Madison aquifer in parts of Montana, South Dakota and Wyoming (Plummer, 1977; Rye and others, 1981; and Busby and others, 1991). In these aquifers, concentrations of dis-

solved solids and sulfate generally increase along the principal directions of regional ground-water flow. Figures 45 and 46 show dissolved-solids and sulfate concentrations along geochemical sections A-A', B-B', C-C' and D-D' in the Midwestern Basins and Arches aquifer system. In general, no consistent systematic change in dissolved-solids and sulfate concentrations is evident along the geochemical sections. The deep bedrock wells along section C-C' are the only subset of the data indicating consistent increases in dissolved-solids and sulfate concentrations in the direction of regional flow. This general absence of systematic trends in chemistry along the general directions of regional ground-water flow indicates that the aquifer system is not characterized by long flow paths that are isolated from additions of recharge, as have been postulated for regional carbonate-rock aquifers in other parts of the United States.

Figures 45 and 46 also can be used to compare the chemistry of ground water from the glacial aquifers and the carbonate-rock aquifer. In general, dissolved-solids and sulfate concentrations in the glacial and carbonate-rock aquifers are similar. The only notable exception to this is sample 10G (fig. 32) from a glacial aquifer, which has considerably higher dissolved-solids and sulfate concentrations than samples 10S and 10D from the carbonate-rock aquifer.

In addition, figures 45 and 46 show the relation of chemistry between ground water from the shallow bedrock wells and ground water from the deep bedrock wells. In general, the dissolved-solids and sulfate concentrations in ground water from shallow bedrock wells were similar to those in ground water from deep bedrock wells. The exceptions are wells 4S and 4D and wells 14S and 14D. Of all the wells shown in figure 32, the wells that show the largest variations in ground-water chemistry with aquifer type or depth at a single sampling location (well groups 4, 10, and 14) are in the groups that have the greatest distance between the wells. Apparent variations with depth may be more related to spatial variability than to specific differences with depth.

#### ISOTOPES

Interpretation of isotopic data can often provide more insight into chemical and hydrologic processes than can be provided by interpretation of chemical data alone. The isotopic composition of ground water can be used to distinguish between competing reactions that contribute dissolved sulfur and carbon to water, to examine the possibility of different water masses mixing in an aquifer, and to estimate the relative or absolute ages of ground water in different parts of an aquifer system. Consequently, isotopic data can provide an independent confirmation of the interpretations made from the hydrologic and chemical data.

In this investigation, the stable isotopes  $\delta^{34}S$  (for the sulfate and sulfide phases),  $\delta^{18}O$ ,  $\delta D$ ,  $\delta^{13}C$  and the radioactive isotopes  $^{14}C$  and tritium were measured in ground water

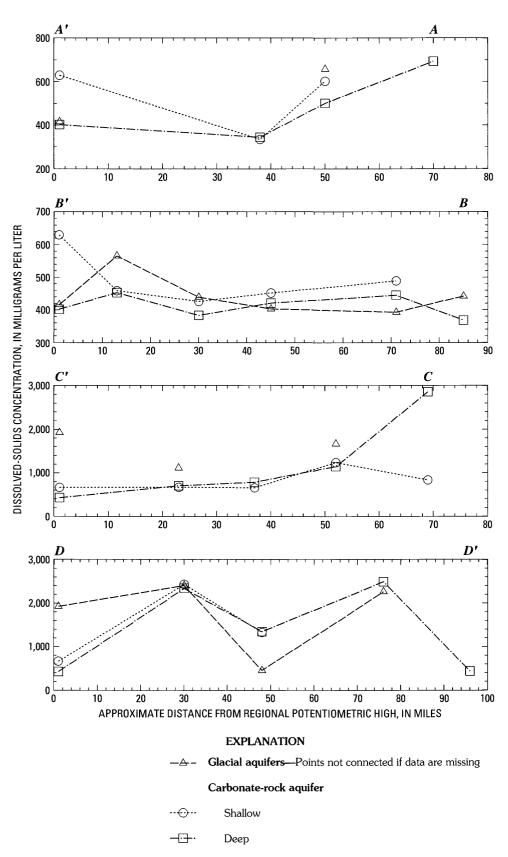


FIGURE 45.—Dissolved-solids concentration in water from wells in the Midwestern Basins and Arches aquifer system along geochemical sections A–A', B–B', C–C', and D–D' (locations of wells shown in fig. 32).

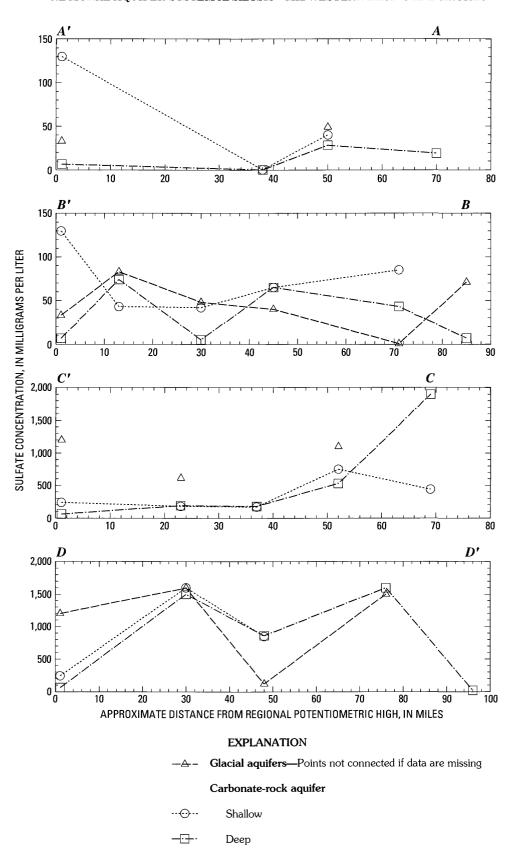


FIGURE 46.—Sulfate concentration in water from wells in the Midwestern Basins and Arches aquifer system along geochemical sections A–A', B–B', C–C', and D–D' (locations of wells shown in fig. 32).

along the four selected directions of regional ground-water flow. In addition,  $\delta^{34}S$  (for the sulfate and sulfide phases) and  $\delta^{13}C$  values for aquifer material, including glacial deposits and carbonate rocks, were determined at several locations within the study area. The isotopic data are summarized in tables 8 and 9 and are discussed in the sections that follow.

#### SULFUR ISOTOPES

Aquifer-material and ground-water samples were analyzed for sulfur isotopes to determine the origin of dissolved sulfate and sulfide and to assist in the identification of the geochemical processes that affect ground-water chemistry in the Midwestern Basins and Arches aquifer system. Because various geochemical processes such as sulfate reduction or dedolomitization can affect the ground-water ages calculated from the carbon isotope data, as well as the associated interpretations made about regional ground-water flow, it is important to be able to distinguish the sources of sulfur in the ground water.

The most abundant sulfur-containing minerals in the study area include pyrite and, in the northeastern part of the area, gypsum. Sedimentary sulfide minerals such as pyrite can exhibit a wide range in  $\delta^{34}$ S values, from -70 to +70 per mil; however,  $\delta^{34}$ S normally ranges from -30 to 10 per mil (Ohmoto and Rye, 1979). In gypsum derived from marine evaporites,  $\delta^{34}$ S values reflect the isotopic composition of dissolved sulfate in the ocean at the time that the gypsum was deposited. Gypsum of Silurian and Devonian age has  $\delta^{34}$ S values that range from about +16 to +30 per mil (Holser and Kaplan, 1966; Krouse, 1980).

Because such a wide range of  $\delta^{34}S$  values is possible for sources of sulfur, samples of aquifer material, including glacial deposits and carbonate rocks, and samples of pyrite and gypsum from the carbonate rocks were analyzed for  $\delta^{34}S$  of the sulfate and sulfide fractions to constrain the variability in sulfur isotope values of the aquifer material. The data are shown in table 9, along with sulfur isotope data on pyrite and anhydrite samples from Ohio first given in Botoman and Faure (1976).

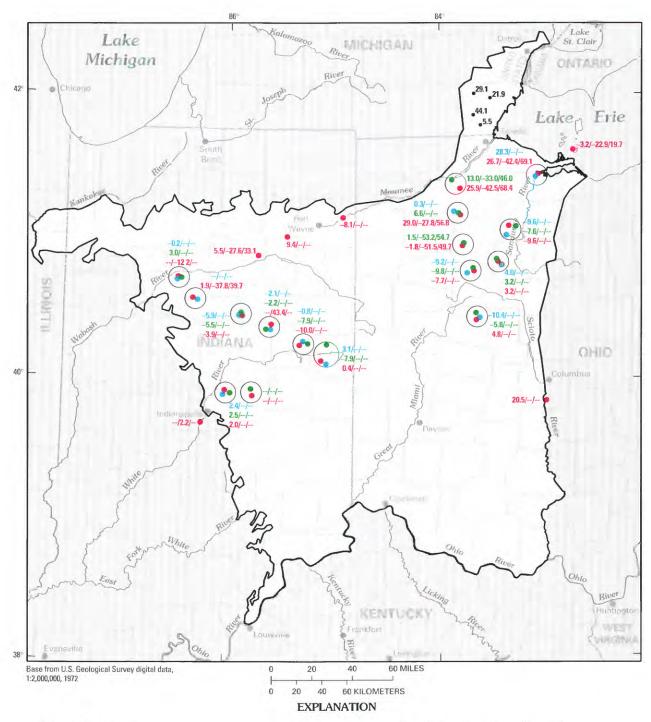
The  $\delta^{34}S_{(sulfate)}$  values for gypsum and anhydrite samples, 28.7 per mil and 24.9 per mil, are in close agreement with those expected for marine sulfates of Silurian and Devonian age. The  $\delta^{34}S_{(sulfide)}$  values of the pyrite samples, -21.9 per mil, -19.4 per mil, and 7.0 per mil, fall within the expected range for sedimentary sulfides. Organic sulfur, which has  $\delta^{34}S_{(sulfide)}$  values similar to those of pyrite, was not specifically analyzed for, but it may be an additional source of reduced sulfur in the aquifer system.

The  $\delta^{34}S_{(sulfate)}$  values for the glacial deposits fall within a fairly narrow range, from -14.8 to -8.2 per mil, which is nearly identical to the range in  $\delta^{34}S_{(sulfide)}$  values for the same material, -14.0 to -8.0 per mil. These  $\delta^{34}S_{(sulfide)}$  values are within the same range as the  $\delta^{34}S_{(sulfide)}$  values deter-

mined for the pyrite samples collected in the area and indicate that pyrite is a likely source of solid-phase sulfide in the glacial deposits. A likely explanation for the similarity in the  $\delta^{34}S_{(sulfate)}$  and  $\delta^{34}S_{(sulfide)}$  values for the glacial deposits is that sulfide (pyrite) in the glacial deposits oxidized to sulfate and, in the presence of dissolved calcium from the dissolution of carbonate minerals, precipitated as gypsum. This process has been shown to occur in the tills of the Interior Plains Region in Canada (Hendry and others, 1986; Keller and Van Der Kamp, 1988). These researchers based their conclusions on the similarity in sulfur isotope values between reduced organic sulfur in unoxidized tills and the sulfate from gypsum crystals found in the oxidized tills. They suggest that a largescale lowering of the water table during an extended dry climatic episode in western North America from 11,000 to 3,000 years before present produced geochemical changes in the till that resulted in the formation of the gypsum and the subsequent development of fractures in the oxidized till. Similar secondary gypsum has also been found in glacial deposits near the Great Lakes. Desaulniers and others (1981) note that secondary gypsum usually is found in fractures of clayey tills and glaciolacustrine clays in southwestern Ontario near Lake Erie. Authigenic gypsum crystals have been found in lacustrine clays within Wisconsinan glacial deposits in northeastern Ohio (Carlson, 1991). Possible gypsum crystallization has been noted by Strobel (1990) along fractures in clayey till in northwestern Ohio. Therefore, given the similarity in  $\delta^{34}S_{(sulfide)}$  and  $\delta^{34}S_{(sulfide)}$  values in the glacial deposits in the Midwestern Basins and Arches aquifer system, processes similar to those in the Interior Plains Region of Canada may have resulted in the formation of gypsum in the glacial deposits with an isotopically light sulfur signature.

The  $\delta^{34}S_{(sulfate)}$  values of the carbonate rocks are highly variable. The  $\delta^{34}S_{(sulfate)}$  values of core C3 and various intervals of core C2 range from 18.3 to 28.7 per mil and clearly reflect sulfate from marine evaporates of Silurian and Devonian age. However,  $\delta^{34}S_{(sulfate)}$  values of all other samples of the carbonate rocks range from -2.3 to 14.6 per mil and do not indicate a clearly defined sulfur source. The wide range in  $\delta^{34}S_{(sulfate)}$  values of the carbonate rocks may reflect post-depositional processes, such as cementation, recrystallization, dolomitization, and weathering, that affected the carbonate rocks in the study area (Casey, 1994). The range in  $\delta^{34}S_{(sulfide)}$  values of the carbonate rocks, from -24.9 to 3.6 per mil, is consistent with the  $\delta^{34}S_{(sulfide)}$  values of the pyrite samples from the study area.

Sulfur isotope ratios in ground water in the Midwestern Basins and Arches aquifer system (fig. 47) are highly varied;  $\delta^{34}S_{(sulfate)}$  values range from -10.4 to +44.1 per mil, and  $\delta^{34}S_{(sulfide)}$  values range from -53.2 to -12.2 per mil. Variability in sulfur isotope values of the aquifer material is a major control on the distribution of sulfur isotope values in ground water from the aquifer system. For example, in the western part of the study area where little or no gypsum is contained



# Boundary of study area

 $\delta^{34}S_{sulfate}$   $\delta^{34}S_{sulfide}$   $\Delta^{34}S$ 

# Sample locations from other studies

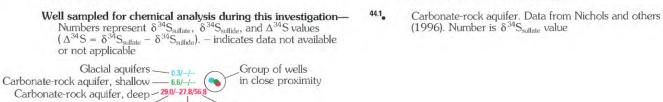


FIGURE 47.— $\delta^{34}S$  and  $\Delta^{34}S$  values in water from wells in the Midwestern Basins and Arches aquifer system.

in the carbonate-rock aquifer, the highest  $\delta^{34}S_{(sulfate)}$  value in ground water is 9.4 per mil, an indication that the primary source of sulfate to ground water is from the oxidation of sulfide minerals or from the dissolution of gypsum formed by the oxidation of sulfide minerals. Ground water with  $\delta^{34}S_{(sulfate)}$  values consistent with the dissolution of marine gypsum or anhydrite of Silurian and Devonian age are found only in the northeastern part of the study area, coincident with the location of the only significant deposits of gypsum and anhydrite.

Sulfur isotope values in ground water reflect the  $\delta^{34}$ S values of the sulfur source but are also dependent on chemical reactions that can cause isotopic fractionation. For example, sulfate reduction can affect the isotopic composition of dissolved sulfate in ground water. Sulfate reduction is mediated by bacteria, which reduce sulfate to sulfide and oxidize organic carbon to  $CO_2$  under anaerobic conditions. The sulfate-reduction reaction can be written as

$$SO_4^{2-} + C_{organic} + 2H_2O < --> H_2S + 2HCO_3^{-}.$$
 (12)

If the pH is greater than 7, HS will predominate over  $H_2S$  as the sulfide product (Garrels and Christ, 1990). Bacterial sulfate reduction preferentially incorporates  $^{32}S$  into the sulfide product, causing the residual sulfate to be enriched in the heavier isotope,  $^{34}S$ . Thus, as sulfate reduction progresses,  $\delta^{34}S$  of sulfide will be less than that of sulfate, and  $\delta^{34}S_{(sulfate)}$  will increase relative to the original composition.

Bacterial sulfate reduction is the likely source of the dissolved sulfide in the Midwestern Basins and Arches aquifer system as indicated by the values of  $\delta^{34}S_{(sulfide)}$  in ground water from the aquifers, which range from -53.2 to -12.2 per mil (fig. 47). Sulfate reduction has probably produced the extensive areas of the carbonate-rock aquifer in northwestern Ohio that are characterized by dissolved sulfide concentrations exceeding 3.0 mg/L (Ohio Department of Natural Resources, 1970); sulfide concentrations as high as 70 mg/L were noted in this area. Dissolved sulfide is less abundant in other parts of the aquifer system.

The differences between the  $\delta^{34}S_{(sulfate)}$  values and the  $\delta^{34}S_{(sulfide)}$  values,  $\Delta^{34}$ , are also shown in figure 47. The  $\Delta^{34}$  values range from 19.7 to 69.1 per mil. The largest  $\Delta^{34}$  values in the aquifer system, 69.1 and 68.4 per mil, were found for water from the deep bedrock wells near the Maumee River and Sandusky Bay. Equilibrium fractionation between sulfate and sulfide is estimated to be between 65 and 74 per mil (Pearson and Rightmire, 1980). Thus, the large  $\Delta^{34}$  values in the northeastern part of the study area may indicate isotopic equilibrium between dissolved sulfate and sulfide. In addition, the large  $\Delta^{34}$  values in ground water near the Maumee River and Sandusky Bay may indicate a long residence time in the aquifer; in the Floridan aquifer of central and southern Florida, for example,  $\Delta^{34}$  values were reported to be directly related to ground-water residence time in the aquifer. In addi-

tion, the largest  $\Delta^{34}$  values were found in the areas of the Floridan aquifer farthest from the recharge area (Rye and others, 1981).

The sulfur isotope data were also used to evaluate the processes responsible for the elevated concentrations of dissolved sulfate in much of the northeastern part of the study area. Ground waters with sulfate concentrations greater than 1,000 mg/L were found along geochemical sections C-C' and D-D'. These ground waters are saturated or nearly saturated with respect to gypsum, but their  $\delta^{34}S_{(sulfate)}$  values indicate several different sources of sulfate. The  $\delta^{34}S_{(sulfate)}$  values of 25.9, 26.7, and 28.3 per mil in ground water from wells 14D, 17D, and 17G (sulfate concentrations of 1,900, 1,600, and 1,500 mg/L, respectively) are consistent with the dissolution of Silurian-Devonian-age gypsum (or anhydrite). However, ground water with similar sulfate concentrations but  $\delta^{34}S_{(sul$ fate) values that range from -10.4 to 4.0 per mil (wells 10G, 13G, 15G, 15S, and 15D) cannot be explained by the dissolution of Silurian-Devonian age gypsum (or anhydrite) but are consistent with pyrite as the sulfur source. The limit on the amount of sulfate that can be produced in ground water by pyrite oxidation (reaction 8) in a closed system is less than 25 mg/L owing to solubility constraints on dissolved-oxygen concentrations. Thus, closed-system pyrite oxidation could not generate the high sulfate concentrations that are found in the northeastern part of the aquifer system. Closed-system conditions are unlikely in much of the aquifer system, however, because the glacial aquifers are generally water-table aquifers, and the carbonate-rock aquifer is generally only semiconfined by the overlying glacial deposits. Thus, where pyrite is abundant in the glacial deposits, sulfate produced by the oxidation of pyrite (or other sources of reduced sulfur) in the glacial deposits may be continually added to the ground water as the water table rises and falls. Alternatively, high sulfate concentrations and isotopically light  $\delta^{34}S_{(sulfate)}$  values in ground water in the northeastern part of the aquifer system can be explained by the dissolution of gypsum composed of isotopically light sulfate, such has been noted in tills in Canada (Hendry and others, 1986; Keller and Van Der Kamp, 1988).

The sulfur isotope data include a wide range in sulfur isotope signatures of sulfur sources in the Midwestern Basins and Arches aquifer system. In addition, sulfur isotope values for ground water in the aquifer system are highly varied, and the geochemical and hydrological processes affecting sulfur isotope values are not completely understood. As a consequence, use of the sulfur isotope data to help constrain the possible mass balance reactions may not be particularly effective, and large uncertainties in the <sup>14</sup>C ages estimated for ground water in the aquifer system may result.

# OXYGEN AND HYDROGEN ISOTOPES

Variation in the isotope ratios of <sup>18</sup>O/<sup>16</sup>O and <sup>2</sup>H/<sup>1</sup>H (deuterium/hydrogen) in meteoric water (water that originates in the Earth's atmosphere) results from a combination of physical and chemical processes that change the isotopic composition from that of seawater. By definition, the isotopic composition of seawater, Standard Mean Ocean Water (SMOW), is 0 per mil for both  $\delta^{18}$ O and  $\delta$ D (Fritz and Fontes, 1980). Meteoric water is depleted in  $\delta^{18}$ O and  $\delta$ D relative to seawater because of isotopic fractionation; the lighter isotopes, <sup>16</sup>O and <sup>1</sup>H, evaporate preferentially, whereas the heavier isotopes, <sup>18</sup>O and <sup>2</sup>H, are concentrated in seawater. The distribution of  $\delta^{18}$ O and  $\delta$ D in modern precipitation is related to mean annual temperature and latitude (Dansgaard, 1964). Generally, a greater amount of fractionation takes place at colder temperatures than at warmer temperatures; hence,  $\delta^{18}O$  and  $\delta D$  values decrease with a decrease in temperature, which corresponds to an increase in latitude or altitude. This covariance of  $\delta^{18}$ O and  $\delta$ D is reflected by the composition of meteoric water throughout the world and defines an average meteoric water line (Craig, 1961) defined

$$\delta D = 8 \, \delta^{18} O + 10. \tag{13}$$

Ground water recharged under present-day climatic conditions should have an isotopic composition similar to that of present-day meteoric water. However, if ground water was recharged during a colder climate, its isotopic composition should be lighter than that of present-day precipitation but should still plot on the meteoric water line.

Values for the stable isotopes of oxygen and hydrogen in ground water samples that were collected as part of this investigation are listed in table 8;  $\delta^{18}$ O values are shown spatially in figure 48. All the data plot on or slightly above the meteoric water line (fig. 49), an indication that the ground water in the Midwestern Basins and Arches aquifer system originated as atmospheric precipitation. Surface-water samples collected at U.S. Geological Survey Benchmark Stations in Indiana, Michigan and Ohio (Tyler Coplen, U.S. Geological Survey, written commun., 1992) were used to determine the isotopic composition of present-day recharge in the area. Most of the ground water in the aquifer system has an isotopic composition similar to surface water in the study area and therefore was most likely recharged under similar climatic conditions as the present. A few ground-water samples collected from the northeastern part of the study area are isotopically light relative to the rest of the ground-water samples and present-day recharge. These relatively light waters probably recharged the aquifer system during a climate colder than the present.

Ground water with isotopically light  $\delta^{18}O$  values may represent either water that recharged aquifers beneath Wisconsinan-age ice sheets or meltwater from those ice sheets.

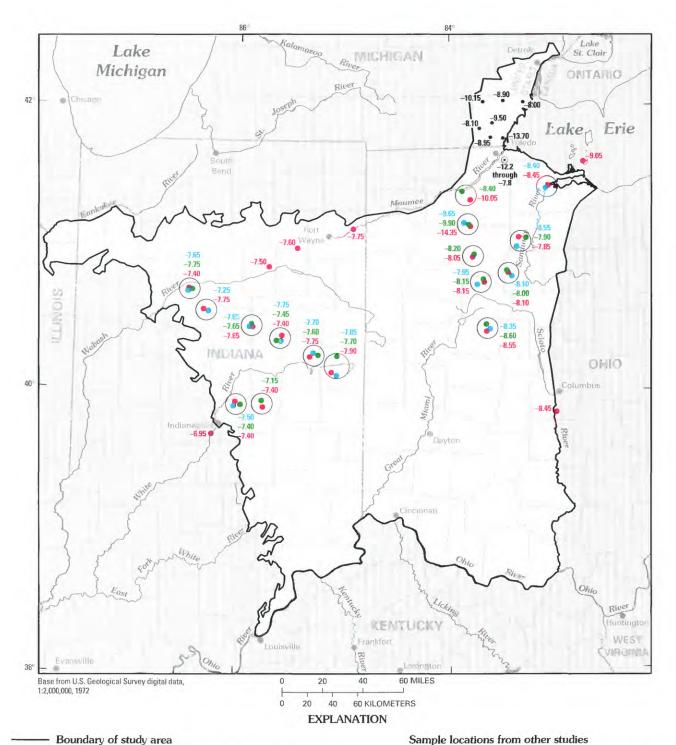
Estimates of the  $\delta^{18}O$  value of Wisconsinan-age ice sheets range from -20 to -12 per mil (Yapp and Epstein, 1977; Desaulniers and others, 1981). Isotopically light ground water in areas around the Great Lakes has been previously found in east-central Michigan near Lake Michigan (Long and others, 1988) and southwestern Ontario near Lake Erie (Desaulniers and others, 1981; Clayton and others, 1966). The  $\delta^{18}O$  values from these studies range from -18.5 to -7 per mil in Michigan and -17 to -9 per mil in southwestern Ontario.

The areas of isotopically light ground water in the Midwestern Basins and Arches aquifer system and in the areas discussed above are all associated with lowlands that were once occupied by late Wisconsinan glacial lakes (Wayne and Zumberge, 1965). The glacial deposits in these areas are typically lacustrine clays or clay-rich tills derived from the lacustrine sediments. The presence of clay-rich deposits in the areas once occupied by glacial lakes may inhibit groundwater recharge. In addition, glaciolacustrine clays in areas close to the Great Lakes are typically found near the base level of the various aquifer systems and are generally coincident with regional ground-water discharge areas. Vertical ground-water flow velocities through glaciolacustrine clays and clayey tills in southwestern Ontario (Desaulniers and others, 1981) were determined to be on the order of 40 to 80 ft in 10,000 years. Pore waters in these deposits exhibit a distinct regular shift in  $\delta^{18}$ O values with depth from  $\delta^{18}$ O values characteristic of present-day recharge at the water table to values between -14 to -17 per mil at depths of 60 to 100 ft. A similar decrease in  $\delta^{18}$ O values with depth is seen in the Midwestern Basins and Arches aquifer system in well groups 13 and 14 and in the data presented by de Roche and Breen (1989). This decrease indicates that a lack of substantial recharge has likely preserved Pleistocene-age water in deeper parts of the aquifer system beneath the Maumee River Basin.

#### TRITIUM AND CARBON ISOTOPES

Tritium (<sup>3</sup>H) and carbon-14 (<sup>14</sup>C) are radioactive isotopes whose concentrations in ground water can be used as a guide to ground-water age. Estimated ground-water ages can help validate or refute interpretations made about ground-water flow based on other chemical and isotopic data or results of ground-water-flow modeling.

Because large quantities of tritium were introduced into the atmosphere during atmospheric testing of nuclear bombs from 1953 to the mid-1960's, tritium is a useful indicator of post-1953 recharge to ground water. Tritium concentrations in precipitation peaked at several thousand tritium units (TU; 1 TU is equal to 1 tritium atom in 10<sup>18</sup> hydrogen atoms or 3.24 picocuries per liter, pCi/L) during 1963-64 (Michel, 1989). Since the signing of the nuclear test ban treaty in the late 1960's, tritium concentrations in present-day precipitation have been decreasing to the pre-bomb levels of 2 to 8 tri-



# Well sampled for chemical analysis during this investigation— Numbers is $\delta^{18}$ O value, in per mil Glacial aquifers — 9.85 Group of wells in close proximity Carbonate-rock aquifer, shallow — 9.90 in close proximity Carbonate-rock aquifer, deep — 14.35 in close proximity All the sampled for chemical analysis during this investigation— 8.10 Nicholas and others (1996). Number is $\delta^{18}$ O value, in per mil de Roche and Breen (1989). Numbers represent the range in $\delta^{18}$ O values from 14 wells

FIGURE 48.— $\delta^{18}$ O values in water from wells in the Midwestern Basins and Arches aquifer system.

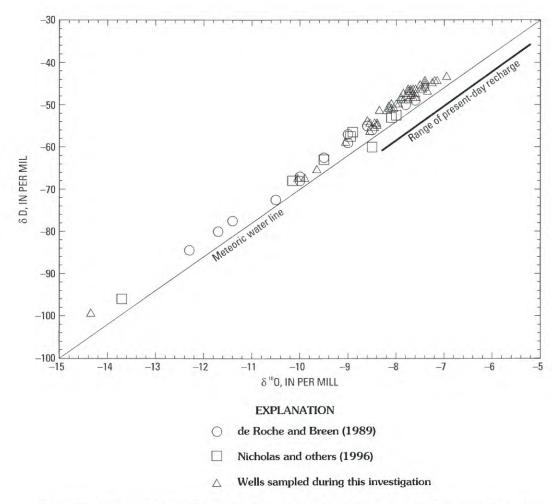
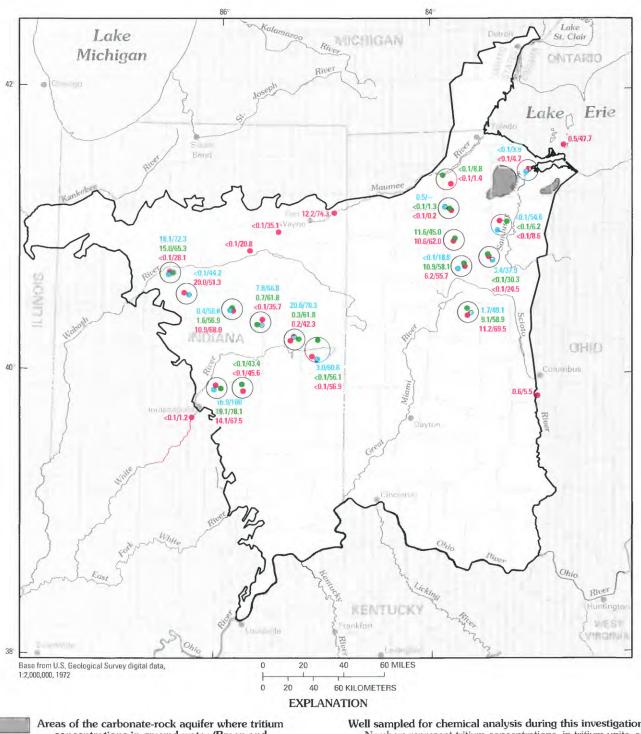


FIGURE 49.— $\delta$  <sup>18</sup>O -  $\delta$  D relation for ground water in the Midwestern Basins and Arches aquifer system. (Other sources of data include de Roche and Breen [1989], and Nicholas and others [1996]).

tium units estimated by Thatcher (1962). Ground water derived exclusively from pre-bomb precipitation would have a maximum tritium concentration of 0.8 TU by the early 1990's if the maximum pre-bomb estimate of 8 TU in atmospheric precipitation is used (Plummer and others, 1993). For ground water with tritium concentrations greater than 0.8, some fraction of that water must have recharged the aquifer system since 1953.

Tritium concentrations for waters sampled as part of this investigation are listed in table 8 and shown spatially in figure 50. Ground water with tritium concentrations greater than 0.8 TU are found across most of the study area and indicate that post-1953 recharge has entered the aquifers in many parts of the Midwestern Basins and Arches aquifer system. Tritium concentrations vary somewhat predictably with depth; water from about half of the glacial and shallow bedrock wells has tritium concentrations greater than 0.8 TU, whereas only one-third of the deep bedrock wells produce tritiated water. Tritium concentrations are also spatially varied in the aquifer system. Ground water with tritium concentrations greater

than 0.8 TU is found in at least one well at nearly all sample locations; however, no ground-water samples from well groups 13, 14, 16, and 17 in the Maumee and Sandusky River Basins, including the wells completed in glacial aquifers, contain tritium. Breen and Dumouchelle (1991) determined that areas of the carbonate-rock aquifer in northwestern Ohio with tritium concentrations indicative of post-1953 recharge (fig. 50) are more likely to be found where the glacial deposits are absent or are less than 20 ft thick. A similar relation between tritium concentrations in ground water from the carbonate-rock aguifer and the thickness of the overlying glacial deposits is apparent in southeastern Michigan (Nicholas and others, 1996). This relation between tritium concentrations and thickness of glacial deposits is not apparent over the entire study area; the thickness of the overlying glacial deposits for wells producing water with tritium concentrations greater than 0.8 TU ranges from 6 to 160 ft. The thickness of the overlying glacial deposits for wells producing water with the highest tritium concentrations (greater than 15 TU) ranges from about 40 to 160 ft.



Areas of the carbonate-rock aquifer where tritium concentrations in ground water (Breen and Dumouchelle, 1991) indicate post-1953 recharge

Boundary of study area

Well sampled for chemical analysis during this investigation— Numbers represent tritium concentrations, in tritium units, and carbon-14 activities, in percent modern carbon. — indicates data not available



Tritium data can help in making qualitative estimates of ground-water ages on the order of tens of years. Alternatively,  $^{14}\mathrm{C}$  data can help date ground water that is thousands of years old. The maximum age that can be dated using  $^{14}\mathrm{C}$  is about 50,000 years given the isotope's half-life of 5,730 years (Freeze and Cherry, 1979). Ground-water samples were collected in the study area for  $^{14}\mathrm{C}$  analysis to help constrain ground-water ages and to help describe regional ground-water flow in the Midwestern Basins and Arches aquifer system. Values for  $\delta^{13}\mathrm{C}$  were also determined to provide information regarding the sources of dissolved inorganic carbon in the ground water and to help correct the measured  $^{14}\mathrm{C}$  values for the dilutional effects caused by various geochemical processes. The data are listed in table 8, plotted in figure 50 and discussed below.

The radioactive decay expression for <sup>14</sup>C can be expressed as

$$t = -8270 \ln(R),$$
 (14)

where t equals the decay age of the carbon, in years, and R equals the measured <sup>14</sup>C activity of the sample expressed as a percentage of the <sup>14</sup>C activity of modern carbon (Mook, 1980). This equation indicates the time, in years, since the water was in contact with CO<sub>2</sub> in the soil zone; use of the equation requires the assumption that there have been no other inputs of dissolved inorganic carbon. However, dissolution of carbonate minerals or oxidation of organic matter can contribute nonradioactive carbon to ground water, diluting the amount of <sup>14</sup>C originally in the water and yielding an unadjusted age that is too old. To correct for nonradioactive carbon, an adjustment factor is added to the decay equation:

$$t = -8,270 \ln(R) + 8,270 \ln(Q)$$
. (15)

For waters in which all the inorganic carbon is produced by the dissolution of carbonate minerals in the soil zone, the Q value is 1.0. The Q value will become some fraction of 1.0 if dissolution continues below the water table where exchange with soil-gas CO<sub>2</sub> cannot occur. Wigley (1975) has shown that in aquifers where CO2 is not produced below the water table, the minimum Q value will not be less than 0.5. Where gypsum dissolution or the exchange of Ca<sup>2+</sup> and Mg<sup>2+</sup> for Na<sup>+</sup> drives the incongruent dissolution of dolomite under closed-system conditions (dedolomitization), or where CO<sub>2</sub> is produced by the oxidation of old organic matter during bacterially mediated sulfate reduction, Q values may be quite small because of the introduction of significant amounts of <sup>14</sup>C with zero activity. The Q values for ground water in the Madison Limestone in parts of Montana, South Dakota, and Wyoming, range from about 0.5, where minor dedolomitization has occurred, to less than 0.1, where ground waters have been affected by dedolomitization, cation exchange, and substantial sulfate reduction (Busby and others, 1991).

To produce accurate estimates of Q, one must use geochemical models that incorporate the effects of dedolomitization, sulfate-reduction, cation exchange, and isotopic exchange. This type of analysis, however, was beyond the scope of this investigation. As a first approximation, <sup>14</sup>C ages were estimated from O values that were selected somewhat arbitrarily. The raw-age estimates (Q=1.0) were corrected by use of O values of 0.5, 0.3, and in some cases, 0.2 (table 11). A O value of 0.5 is expected for closed-system dissolution of carbonate minerals where no additional source of CO2 is added and where no secondary mineral precipitates (Wigley, 1975). Thus, a Q value of 0.5 can overestimate the age of ground water that has undergone dedolomitization or sulfate reduction. A Q value of 0.3 was used in this investigation to account for geochemical reactions that produce additional sources of nonradioactive carbon to the ground water system. A Q value of 0.2 was used for ground waters with small <sup>14</sup>C activities and δ<sup>13</sup>C values that are isotopically heavy. Much of the ground water in the aquifer system has  $\delta^{13}$ C values of around -14 or -15 per mil; however, ground water from wells 1D, 13D, 14D, 17G, and 17D has  $\delta^{13}$ C values that range from -11.0 to -7.1 per mil, an indication that a greater proportion of the dissolved inorganic carbon in these waters was derived from the dissolution of carbonate rocks with  $\delta^{13}C$  values of about 0 per mil than in the waters with  $\delta^{13}$ C values of around -14 or -15 per mil. Samples 8G, 9D, and 19 also have heavier  $\delta^{13}$ C values (-8.8, -3.1, and -1.3 per mil) than do most other samples. These waters, however, have likely been affected by methanogenesis, a reaction in which organic matter is metabolized by methanogenic bacteria to produce CO2, methane (CH<sub>4</sub>), and dissolved organic compounds. The concentration of dissolved methane in well 8G was 18.65 mg/L (Eurybiades Busenberg, U.S. Geological Survey, written commun., 1992). Ground water from wells 9D and 19 were not analyzed for dissolved methane, but these samples had elevated concentrations of dissolved organic carbon and (or) little or no dissolved sulfate, a composition consistent with methanogenesis. The age of these waters cannot be accurately determined without measuring the  $\delta^{13}$ C value of the dissolved methane.

Also listed in table 11 are ages calculated by use of the method proposed by Pearson and White (1967), in which  $\delta^{13}C$  values are used to correct for isotopic dilution due to congruent carbonate dissolution according to the equation

$$^{14}C(adjusted) =$$
 (16)

$$^{14}C(measured) \times \left[\frac{\delta^{13}C_{soil} - \delta^{13}C_{carbonate}}{\delta^{13}C_{water} - \delta^{13}C_{carbonate}}\right],$$

Table 11.—Summary of  $^{14}$ C age estimates for ground water sampled during investigation of the Midwestern Basins and Arches aquifer system, 1991-92

[Map number is location in figure 32. Q values are adjustment factors used to account for addition of nonradioactive carbon to the ground-water system. Negative ages indicate that local geochemistry does not reflect the assumed conditions used in assigning the Q value. Question mark indicates that age cannot be determined from available data. —, value not determined]

Well name	Map number	Age, Q = 1.0 (years)	Age, Q = 0.5 (years)	Age, Q = 0.3 (years)	Age, Pearson-White (years)	Pearson- White Q value	Q value(s) used for age estimate	Ground- water age (years)
Ross	10 G	5,900	200	-4,100	2,500	0.66	0.66	<50 - 2,500
Birt	10 S	<50	< 50	<50	< 50			<50
Ben Logan H.S.	10 D	<50	<50	< 50	<50			<50
Searfoss	15 G	8,000	2,300	-1,900	5,500	.74	.74	<50 - 5,500
Rife	15 S	9,900	4,100	-100	6,700	.68	.68	6,700
Schoenberger	15 D	11,600	5,900	1,700	8,700	.70	.70	8,700
Beasley	16 G	5,000	-700	-5,000	600	.59	.59	600
Hill	16 S	23,000	17,300	13,000	19,500	.65	.3 – .65	13,000 - 19,500
Gillig	16 D	20,300	14,600	10,300	16,200	.61	.3 – .61	10,300 – 16,200
Lamalie	17 G	26,800	21,100	16,900	20,800	.48	.2 – .48	13,500 - 20,800
S-18	17 D	25,300	19,600	15,300	17,200	.38	.2 – .38	12,000 – 17,200
Finnegan	18 D	6,100	400	-3,900	-600	.44	.44	<50
Wilson	11 G	14,000	8,300	4,000	10,800	.68	.3 – .68	4,000 – 10,800
	11 S	<50	<50	<50	<50	.00	.5 – .08	<50
Spencer Stair	11 D	<50	<50	<50	<50	.00		<50
Francis	12 S	<50	<50	<50	<50	.00		<50
Augustine	12 S 12 D	<50 <50		<50	<50 <50	77	= = =	<50 <50
Richard			<50	<30		-		<30
	13 G	 25 000	20.200	26,000	31 (00		 2 50	26,000 21,600
Kern	13 S	35,900	30,200	26,000	31,600	.59	.3 – .59	26,000 – 31,600
Auckerman	13 D	51,400	45,700	41,400	45,200	.48	.248	38,100 – 45,200
Rice	14 S	20,100	14,400	10,100	16,200	.63	.363	10,100 – 16,200
City of Weston	14 D	35,300	29,600	25,300	25,800	.32	.232	22,000 – 25,800
Hartman	19	24,000	18,300	14,000	-300	.05		?
Lacy	4 G	4,100	-1,600	-5,800	600	.65	.65	<50 - 600
Hummel	4 S	4,800	-1,000	-5,200	1,400	.66	.66	1,400
Jones	4 D	4,700	-1,100	-5,300	900	.64	.64	900
Harrison	3 S	6,900	1,200	-3,100	2,200	.56	.56	2,200
Martin	3 D	6,500	800	-3,500	2,800	.64	.64	2,800
Lockhart	2 G	<50	<50	< 50	<50			<50
Mattingly	2 S	< 50	<50	<50	<50			<50
Merchant	2 D	< 50	<50	< 50	<50			<50
Gates	1 D	36,600	30,800	26,600	30,700	.49	.249	23,300 - 30,700
Bickford	5 G	< 50	<50	< 50	<50	0	77.	<50
Bartlett	5 S	4,000	-1,800	-6,000	300	.64	.64	300
Desoto Substation	5 D	7,100	1,400	-2,800	3,100	.61	.61	3,100
Staggs	6 G	< 50	<50	< 50	<50			<50
Ice	6 S	4,000	-1,800	-6,000	600	.67	.67	600
Underwood	6 D	8,500	2,800	-1,400	5,500	.69	.3 – .69	<50 - 5,500
Cohee	7 G	4,500	-1,200	-5,500	1,000	.65	.65	1,000
Ellis	7 S	4,700	-1,100	-5,300	1,400	.67	.67	<50 – 1,400
Harmon	7 D	<50	< 50	< 50	< 50			<50
Fox	8 G	6,800	1,000	-3,200	-1,000	.39		?
Skiles	8 D	< 50	< 50	< 50	< 50			<50
Justice	9 G	<50	< 50	< 50	<50			<50
Lee	9 S	< 50	< 50	< 50	<50			<50
Starbuck	9 D	10,500	4,800	500	-5,900	.14		?
Geradot	22	< 50	< 50	< 50	<50			< 50
Stenzel	21	8,700	2,900	-1,300	5,300	.66	.66	5,300
Rees	20	13,000	7,200	3,000	11,100	.80	.380	3,000 - 11,100

where  $^{14}C$  (adjusted) is the  $^{14}C$  activity adjusted for dissolution of carbonate rocks with known  $\delta^{13}C$  values,  $^{14}C$  (measured) is the measured activity in the water sample,  $\delta^{13}C_{soil}$  is the isotopic composition of soil-gas  $CO_2,\ \delta^{13}C_{carbonate}$  is the isotopic composition of the carbonate minerals in the study area, and  $\delta^{13}C_{water}$  is the isotopic composition of the dissolved inorganic carbon in the water sample. Values of  $\delta^{13}C_{soil}$  in temperate climates vary from -25 to -18 per mil (Mook, 1980; Back and others, 1983); a value of -22.5 per mil was used in equation 16 for this investigation. Values of  $\delta^{13}C_{carbonate}$  from samples of the carbonate-rock aquifer and the glacial aquifers are listed in table 9. The average  $\delta^{13}C_{carbonate}$  value of the 10 samples, 0.0 per mil, was used in equation 16.

A summary of ages calculated from equations 15 and 16 is given in table 11. Ages were not calculated for the samples with tritium concentrations greater than 6 TU because such waters may contain a significant component of recent recharge with unknown amounts of bomb-derived <sup>14</sup>C. On the basis of the range of calculated ages and the chemical and isotopic data, each ground water sample was assigned an approximate age. In some ground water samples, tritium concentrations are between 0.8 and 3 TU and may represent a mixture of old water and recent recharge. Such waters were assigned an age ranging from less than 50 years to the age calculated by use of equation 16. Waters that are saturated with respect to calcite and dolomite and apparently unaffected by dedolomitization or sulfate reduction were assigned the age estimated from equation 16. The range of adjustment factors (Pearson-White Q value) for these waters is 0.56 to 0.67, which is in close agreement with the Q values calculated by Wigley (1975) for ground water that is undergoing congruent dissolution of calcite and dolomite in the soil zone and below the water table. Waters that have undergone dedolomitization or sulfate reduction were assigned a range of ages that bracket those calculated with a Q value of 0.3, or for waters with heavy  $\delta^{13}$ C values, 0.2, and ages that were calculated by use of equation 16 (Pearson-White method).

The ground-water ages in the aquifer system are consistent with a conceptual model of regional ground-water flow in which the aquifer system alternately receives recharge and discharges across most of the study area except in the northeastern part, where the aquifer system does not receive a notable amount of recharge. Ground-water ages across most of the study area range from less than 50 years to several thousand years and generally do not follow any spatial trends. This pattern is consistent with a ground-water flow regime that is largely dominated by local flow systems that have short flow paths relative to the areal extent of the aquifer system. The oldest ground waters in the aquifer system range in age from at least 3,000 to possibly more than 40,000 years and are in the discharge areas in the northeastern part of the study area near the Maumee and Sandusky Rivers and Lake Erie. Relatively old waters were also found near the Wabash River in northern Indiana and at the margin of the Illinois Basin where the upper confining unit overlies the carbonaterock aquifer.

Ground water from wells 13S, 13D, and 14D ranges in age from about 22,000 to more than 45,000 years and has δ<sup>18</sup>O and δD values expected for water recharged during the Pleistocene. The age ranges of ground water from wells 14S, 16S, 16D, 17G, and 17D are also Pleistocene; however, the  $\delta^{18}$ O values are similar to those for present-day recharge. The retreat of Late-Wisconsinan glaciers in the Great Lakes area began about 13,300 years ago and was nearly complete by 10,000 years ago (Barry, 1983). Isotopic data presented by Yapp and Epstein (1977) indicate that the  $\delta^{18}$ O and  $\delta$ D values of precipitation during the interval between 10,000 and 9,500 years before present were similar to those of present-day precipitation. Data on  $\delta^{18}$ O values in mollusk shells from sediment cores in Lake Erie (Fritz and others, 1975) indicate a rapid increase in δ<sup>18</sup>O values in water in Lake Erie after 13,000 years before present because of a rapid rise in average land temperatures. The lower ages presented in table 11 for ground water from wells 14S, 16S, 16D, 17G, and 17D range from 10,300 to 13,500 years. Because the isotopic composition of precipitation during this time period may have been similar to that of today, the  $\delta^{18}O$  and  $\delta D$  data for these ground waters indicates that the lower age limits listed in table 11 for these waters may be the more reasonable. Thus, ground water from wells 13S, 13D, and 14D may represent water that recharged the aquifer system from beneath the glacial ice, whereas ground water from wells 14S, 16S, 16D, 17G, and 17D may represent precipitation that entered the aguifer system at the end of glaciation. Alternatively, Siegel (1991) observed a similar disparity between  $\delta^{18}$ O values and estimated <sup>14</sup>C ages for Pleistocene-age ground water in the northern Midwest. He suggested that the calculated groundwater ages may be too great if  $\delta^{13}$ C values of soil gas increased because of a reduction of the amount of organic matter that was present in the soil during the colder climate. As a result, the actual ages of ground water recharged during the Pleistocene may be less than those listed in table 11. Although considerable uncertainty is inherent in the absolute ages of ground water because of assumptions used in the calculations, the ages given in table 11 are helpful for evaluating the relative age of ground waters in the Midwestern Basins and Arches aquifer system.

## VARIATION IN GROUND-WATER CHEMISTRY WITH DEPTH

The sampling methodology for this investigation, discussed earlier in this report, was designed to use existing wells to obtain as much information as possible on the variation in ground-water chemistry with depth in the Midwestern Basins and Arches aquifer system. Two types of deep bedrock wells were sampled: those that were open hole through the entire length of the well and those that were cased through

various lengths of the top section of the carbonate-rock aquifer (table 6). Data from these deep bedrock wells were compared to data from nearby shallow bedrock wells to assist in understanding the ground-water chemistry at depths as great as 450 ft below the top of the carbonate-rock aquifer.

A comparison of the chemical and isotopic data and the estimated ground water ages (tables 7, 8, and 11) between the shallow bedrock wells and the deep bedrock wells that are open hole through the entire length of the well shows that the chemistry and the ground-water ages between these wells are generally similar. The differences in ground-water ages in all these wells ranges from several hundred to less than 3,000 years. Of the pairs of shallow and deep bedrock wells that have ages greater than 50 years, ground water in the deep bedrock well is older than in the shallow bedrock well in well groups 3, 5, and 15; whereas ground water in the shallow bedrock well is older than in the deep bedrock well in well groups 4 and 16. The similarity between ground water from wells that are open only to the shallow part of the carbonaterock aquifer and ground water from wells that are open to a much greater part of the carbonate-rock aquifer indicates that either (1) the chemistry and age of the ground water is similar throughout the sampled thickness of the carbonate-rock aquifer or (2) if ground water at depth has a distinctly different chemistry or older age, then the carbonate rocks are not transmissive enough at the greater depths to contribute significantly to the overall chemistry of the sampled water, and most ground water is produced from the upper part of the carbonate-rock aquifer.

Data from a shallow interval (less than 50 ft below the top of the aquifer) and an isolated deeper interval (as great as 450 ft below the top of the aquifer) within the carbonate-rock aquifer are available for well groups 10, 13, 14, and 17. A comparison of ground-water chemistry and ages between the shallow and deep bedrock wells at well groups 13 and 14 shows a systematic change in chemistry with depth and a distinctly different ground water in the deeper part of the carbonate-rock aquifer than in the shallow part. The chemical and isotopic data from these two well groups indicate that, in this area of the aquifer system, some recharge water enters the glacial aquifers and the shallow zones of the carbonaterock aguifer but does not penetrate deeply into the aguifer system. In contrast, a comparison of ground-water chemistry and ages at well groups 10 and 17 shows little difference between the shallow and deeper parts of the aquifer system. At well group 10, tritium concentrations indicative of post-1953 recharge are found throughout the entire sampled thickness of the carbonate-rock aquifer. These wells are located at the highest potentiometric level in the aquifer system, where recharge rates to the deepest parts of the aquifer system should be relatively high. The chemical and isotopic data for ground water from wells 17G and 17D, located near the Sandusky River and Lake Erie, is quite similar. The age of the water in the overlying glacial aquifer is slightly older than water from deeper within the carbonate-rock aquifer (13,500 years compared to 12,000 years, using the lower age limit as discussed in the previous section). This slight decrease in age with depth may reflect an upward flow of ground water as it discharges the aquifer system.

Chemical and isotopic data are also available for ground water that was sampled from specific intervals in three deep wells that penetrate the entire thickness of the carbonate-rock aquifer in northwestern Indiana (D.J. Schnoebelen, U.S. Geological Survey, written commun., 1993). Ground water was sampled from various 10-ft intervals of the carbonate-rock aquifer by use of an inflatable packer system. Hydrogeologic data for these three wells and a description of the packer technology are given in Arihood (1994). The chemical and isotopic data from all the sampled intervals in each well are very similar, an indication that there is no stratification of groundwater chemistry with depth in this part of the aquifer system; however, the samples do not represent water from the deepest part of the carbonate-rock aquifer because the rocks in the bottom 60 to 400 ft of the wells are not necessarily transmissive (Arihood, 1994).

#### SUMMARY AND CONCLUSIONS

Aquifers in Quaternary glacial deposits and underlying Silurian and Devonian carbonate rock in parts of Indiana, Ohio, Michigan, and Illinois compose an integrated regional-scale water-table aquifer system. This aquifer system generally lies between the Appalachian, the Illinois, and the Michigan (structural) Basins and is located along the axes of the Cincinnati, the Findlay, and the Kankakee Arches.

Glacial deposits within the study area are the result of multiple glacial advances and directly overlie the carbonate rocks along the axes of the structural arches in the central part of the study area. These glacial deposits mask the ancient bedrock topography and bury numerous valleys in the bedrock surface. The glacial deposits and the carbonate rocks are separated by a shale sequence along the margins of and within the surrounding structural basins.

The water table within the Midwestern Basins and Arches aquifer system generally is within the glacial deposits. Glacial aquifers typically consist of sands and gravels in outwash deposits or as discontinuous lenses within ground or end moraines. Because such lenses are not necessarily areally extensive, the glacial aquifers can supply large yields of ground water only locally.

An areally extensive aquifer is present in the carbonate rocks that underlie the glacial deposits. At the regional scale, the carbonate-rock aquifer is semiconfined by the finer grained glacial deposits where the aquifer directly underlies these deposits (subcrop area of the carbonate-rock aquifer) but is confined where the aquifer underlies the intervening shale sequence, called the upper confining unit, along the

margins of the aquifer system. Most active freshwater flow in the carbonate-rock aquifer is limited to the subcrop area of the aquifer because the upper confining unit inhibits recharge to the carbonate-rock aquifer. This lack of freshwater flow beneath the upper confining unit results in a transition from freshwater to saltwater in the carbonate-rock aguifer within the surrounding structural basins. Saline water is present within 5 mi of the subcrop boundary along the Michigan and Appalachian Basins. Freshwater extends as far as 70 mi downdip from the western subcrop boundary along the Illinois Basin; however, <sup>14</sup>C data for one freshwater sample (1D) (fig. 32) collected from the aquifer just west of the subcrop boundary indicates that this water may be 23,000 to 31,000 years old. The fact that this water is older than most waters throughout the subcrop area may indicate that freshwater in the carbonate-rock aquifer in the Illinois Basin is not associated with active freshwater flow.

The hydraulic characteristics of the aquifers within the Midwestern Basins and Arches aquifer system are varied. On the basis of available aquifer-test data, transmissivities of the glacial deposits span four orders of magnitude, ranging from 1.5 to  $69,700 \text{ ft}^2/\text{d}$ , whereas transmissivities in the carbonaterock aquifer span three orders of magnitude, ranging from 70 to 52,000 ft<sup>2</sup>/d. Such variability in the carbonate-rock aguifer is attributed to the nonuniform distribution of fractures, joints, bedding planes, and solution channels in the rocks. The results of a numerical ground-water flow model, which simulates regional flow systems within the aquifer system, indicate that where the carbonate rocks are hundreds of feet thick, the entire thickness of the rocks may not contribute substantially to the transmissivity of the aquifer. Some of the available aquifer-test data support these model results. In addition, the local presence of anhydrite within the carbonate rocks at depths of only a few hundred feet near Sandusky Bay in the northeastern part of the aquifer system indicates that active freshwater flow may be restricted to the upper few hundred feet of the carbonate rocks in this area.

The types and distribution of hydrochemical facies of water within the glacial aquifers and the subcrop area of the carbonate-rock aquifer are similar. Water of a Ca-Mg-HCO3 type is present throughout much of the area but is found only locally in the northeastern part of the study area, where Ca-Mg-SO<sub>4</sub> type water predominates. The dissolution of calcite and dolomite is responsible for the presence of the Ca-Mg-HCO3 water, whereas dedolomitization driven by gypsum dissolution and the oxidation of pyrite are responsible for the Ca-Mg-SO<sub>4</sub> water. Multiple-water-type facies in the aquifer system, which are found near the margins of the Michigan and Illinois Basins, are characterized by the presence of Ca-Mg-Na-HCO<sub>3</sub> water or Ca-Mg-Na-SO<sub>4</sub> water, or both; cation exchange in shales within the aquifer system is responsible for the presence of these Na-enriched waters. The distribution of these multiple-water-type facies may be related to past patterns of ground-water flow associated with Pleistocene glaciation. Water in the carbonate-rock aquifer under the upper confining unit in the Appalachian and Michigan Basins is a Na-Ca-Cl type, whereas the water under the upper confining unit in the Illinois Basin is a Na-Cl type. In general, the distribution of hydrochemical facies observed within the aquifer system is controlled by the mineralogy of the aquifer material rather than the evolution of water chemistry along paths of regional ground-water flow, as is commonly observed in closed aquifer systems.

Some ground-water flow systems within the Midwestern Basins and Arches aquifer system provide base flow to streams in response to ground-water recharge events, whereas other (often deeper) ground-water flow systems respond minimally to variations in ground-water recharge from precipitation. These latter, more stable flow systems have a more dominant influence of intermediate- and regional-scale flow than do the flow systems that readily respond to ground-water recharge, and they provide a fairly constant supply of water to streams over the course of a year and throughout long periods. Discharge to streams from such stable flow systems within the aquifer system is termed "sustained ground-water discharge" in this report.

Mean sustained ground-water discharge (discharge from fairly stable ground-water flow systems) to selected stream reaches within the study area ranges from 3 to 50 percent of mean ground-water discharge (discharge from all ground-water flow systems) to the stream reaches. These percentages indicate that the greatest amount of ground-water discharge to the streams (50 to 97 percent) is generally associated with transient flow systems, which typically have a major component of local-scale flow. Because results of the regional ground-water flow model indicate that most water in regional flow systems within the aquifer system discharges to streams within the study area, these percentages imply that seasonally transient local flow systems dominate flow in the Midwestern Basins and Arches aquifer system.

Values of mean sustained ground-water discharge as a percentage of mean ground-water discharge increase with distance downstream in nearly half of the principal surface-water drainage basins; this pattern indicates that streams at the bottoms of these drainage basins receive more base flow from stable flow systems within the aquifer system than streams in the upbasin areas. Percentages decrease with distance downstream along stream reaches in the south-central part of the study area, where the carbonate-rock aquifer is absent and the underlying bedrock is not an aquifer, and along stream reaches in the Maumee and Sandusky River Basins.

Differences in the relative amounts of base flow in the principal surface-water drainage basins that can be attributed to discharge from fairly stable ground-water flow systems are notable for long-term steady-state conditions in the aquifer system. On the basis of historic streamflow data, the Wabash River Basin has the greatest percentage (33 percent) of base

flow that can be attributed to discharge from fairly stable flow systems. In contrast, less than 15 percent of the base flow in the principal surface-water drainage basins that drain into Lake Erie can be attributed to such stable flow systems.

The numerical model of regional flow systems within the aquifer system, which simulates approximately 10 percent of total ground-water flow in the system, indicates that most water (99 percent) in simulated regional flow systems is from recharge at the water table. Most water (78 percent) discharges from simulated regional flow systems to the principal streams within the area. Some water (19 percent) leaves simulated regional flow systems by means of evapotranspiration or discharge to seeps, springs, ditches, or small streams. Less than 3 percent of the water in simulated regional flow systems discharges to the Ohio River or Lake Erie or flows downdip into the Illinois Basin.

The Midwestern Basins and Arches aquifer system is generally characterized by alternating regional recharge and discharge areas, typically on a scale of less than 10 mi. Ground water does not follow long, continuous flow paths from recharge areas associated with the very highest potentiometric levels to discharge areas associated with the very lowest potentiometric levels while remaining isolated from additions of recharge. Rather, regional recharge areas exist all along the regional potentiometric gradient, except in the northeastern part of the aquifer system. Some of the highest regional recharge rates are associated with the Bellefontaine Outlier in Ohio.

The presence of tritiated water across most of the aquifer system can also be used to conclude that the aquifer system receives recharge across most of the study area. On the basis of tritium concentrations and modeled <sup>14</sup>C activities, groundwater ages throughout most of the aquifer system range from less than 50 years to several thousand years. Significant amounts of post-1953 water is found more than 100 ft beneath the surface of the bedrock in the area of the Bellefontaine Outlier.

High rates of simulated discharge from regional flow systems are typically associated with the principal streams that drain the area underlain by the aquifer system. Simulated regional discharge areas, however, are not limited to the vicinity of these streams. Specifically, a broad area (tens of miles) of weak regional discharge (less than 0.5 in/yr) exists within the northeastern part of the study area. This broad regional discharge area likely represents an area in which water that moves through regional flow systems leaves the aquifer system by means of ditches, small streams, or evapotranspiration. The Maumee and Sandusky River Basins in the northeastern part of the study area are the only principal river basins where simulated regional discharge areas are larger than simulated regional recharge areas.

A number of factors help explain the existence of the broad, weak regional discharge area. The streams in this area are incised only a few feet, which limits their ability to intercept regional ground-water flow. In addition, the area has a very low hydraulic gradient, which results in the presence of regional discharge areas that are broader than the streams themselves. Results of the regional ground-water flow model indicate that the magnitude of regional-scale horizontal ground-water flow in the poorly permeable glaciolacustrine deposits within the area is lower than elsewhere in the aquifer system. In general, model results indicate that the regional flow systems have a limited ability to carry ground water away from the area, which prevents precipitation from recharging the regional flow systems. Previous researchers have noted that much of this area was swampland before being ditched in the early 1900's and that the historic Black Swamp resulted from poor surface drainage in addition to ground-water discharge from regional flow into what was a relatively stagnant area. Conclusions based on results of simulations are consistent with the low percentages of mean sustained ground-water discharge to streams relative to mean ground-water discharge to the streams in the area; much of the precipitation that is prevented from recharging the regional flow systems in the area is likely to be forced to discharge locally by means of drainage tile or shallow, transient local flow systems.

Chemical data also indicate that the aquifer system receives limited recharge in the northeastern part of the study area. Water with isotopically light  $\delta^{18}{\rm O}$  values (-10.05, -14.35) is found in the aquifer system near the Maumee River; these values indicate that the water may have entered the aquifer system beneath Wisconsinan ice sheets. On the basis of  $^{14}{\rm C}$  ages, these are the oldest waters in the aquifer system. These data indicate minimal flushing of ground water since the last glaciation at depths greater than 100 ft below land surface in this part of the aquifer system. The occurrence of extensive sulfate reduction in this area, as indicated by sulfide concentrations and sulfur isotope data, confirms that only minimal recharge has taken place in this area over a long period of time.

A three-dimensional flow field exists within the aquifer system at the regional scale because regional recharge is available to the regional flow systems across most of the study area, as previously discussed. As a result, individual regional ground-water flow paths cannot be determined from two-dimensional potentiometric-surface maps of the aquifer system. They can be determined, however, by use of the three-dimensional regional ground-water flow model. Results of the model indicate that the longest regional ground-water flow paths within the aquifer system (at nearly 50 mi) terminate at Lake Erie.

Chemical data also indicate that water in the regional flow systems generally does not follow long flow paths (tens of miles). On the basis of dissolved-solids and sulfate concentrations in the ground water, there is a general absence of chemical evolution of ground water from the highest regional potentiometric levels to the lowest regional potentiometric levels. There also is no systematic increase in ground-water ages along the dominant regional trends of the potentiometric surfaces. An exception to this apparent absence of systematic increase in ground-water ages was identified along a geochemical section that terminates near Lake Erie.

Ground water at the downgradient end of the flow paths that terminate at Lake Erie is some of the oldest in the aquifer system (approximately 13,000 years). The very oldest ground water (approximately 38,000-45,000 years) was identified further west, beneath the Maumee River Basin. The  $\Delta^{34}$ S values (69.1 per mil, 68.4 per mil) for ground water sampled near Lake Erie and the Maumee River also indicate relatively long residence times in these parts of the aquifer system. Because the very oldest ground water, which is present beneath the Maumee River Basin, is associated with short (typically less than 10 mi) regional ground-water flow paths as compared to the flow paths that terminate at Lake Erie, it is likely that this part of the aquifer system is fairly stagnant. The old ground water near Lake Erie, however, is more likely to be associated with position along regional flow paths rather than with a stagnation point in the aquifer system. Results of the regional ground-water flow model indicate that flow in the aquifer system near Lake Erie at the end of relatively long flow paths may be predominantly vertical and may be associated with discharge from the deep parts of the aquifer system. Ground-water ages from <sup>14</sup>C data for selected wells near Lake Erie increase slightly with decreasing depth, a pattern that is consistent with the modeled upward flow of ground water in this area.

No effects of future pumping on the aquifer system were investigated as part of the Midwestern Basins and Arches Regional Aquifer-System Analysis project. Nearly 433 Mgal/d of ground water was reported to have been withdrawn from the aquifer system by users capable of pumping 100,000 gal/d or greater during the 1990 calendar year. Only 15 percent of this water was reported to have been withdrawn from the carbonate-rock aquifer. Of the remaining 85 percent, most of the water was reported to have been withdrawn from outwash deposits that underlie principal streams. Estimates of mean ground-water discharge to streams for long-term steady-state conditions in the aquifer system indicate that more than 13,000 Mgal/d of water discharges from the aquifer system to streams within the study area. Current pumpage, therefore, is only a small percentage of the total amount of water that moves through the aquifer system. No regionalscale cones of depression are present within the aquifer system; the aquifer system is not heavily stressed at the regional scale, and much more of the water in the Midwestern Basins and Arches aquifer system could be used.

# **REFERENCES CITED**

- Anderson, M.P., and Woessner, W.W., 1992, Applied groundwater modeling—Simulation of flow and advective transport: London, Academic Press, p. 20, 152.
- Arihood, L.D., 1994, Hydrogeology and paths of flow in the carbonate bedrock aquifer, northeastern Indiana: Water Resources Bulletin, v. 30, no. 2, p. 205-218.
- Back, William, 1960, Origin of hydrochemical facies of ground water in the Atlantic Coastal Plain, *in* Back, William, and Freeze, R.A. eds., Chemical hydrogeology: Stroudsville, Pa., Hutchinson Ross Publishing Co., Benchmark Papers in Geology, v. 73, p. 79-87.
- \_\_\_\_\_1966, Hydrochemical facies and ground water flow patterns in northern part of Atlantic Coastal Plain: U.S. Geological Survey Professional Paper 498-A, 42 p.
- Back, William, Hanshaw, B.B., Plummer, L.N., Rahn, P.H., Rightmire, C.T., and Rubin, Meyer, 1983, Process and rate of dedolomitization-mass transfer and <sup>14</sup>C dating in a regional carbonate aquifer: Geological Society of America Bulletin, v. 94, p. 1415-1429.
- Barry, R.G., 1983, Late-Pleistocene climatology, *in* Wright, H.E., Jr., ed., Late-Quaternary environments of the United States, v. 1, The Late Pleistocene: Minneapolis, University of Minnesota Press, p. 390-407.
- Beary, E.A., 1993, Ground-water withdrawal in 1990—Midwestern Basins and Arches regional aquifer systems study area: U.S. Geological Survey Open-File Report 93-119 [Water Fact Sheet].
- Bennison, A.P., comp., 1978, Geological highway map of the Great Lakes Region: American Association of Petroleum Geologists, United States Geological Highway Map Series, Map 11.
- Bloyd, R.M., Jr., 1974, Summary appraisals of the Nation's ground-water resources—Ohio region: U.S. Geological Survey Professional Paper 813-A, 41 p.
- Botoman, George, and Faure, Gunter, 1976, Sulfur isotope composition of some sulfide and sulfate minerals in Ohio: Ohio Journal of Science, v. 76, no. 2, p. 66-71.
- Botoman, George, and Stieglitz, R.D., 1978, The occurrence of sulfide and associated minerals in Ohio: Ohio Department of Natural Resources, Division of Geological Survey Report of Investigations 104, 11 p.
- Bownocker, J.A., comp., 1920, Geologic map of Ohio: Ohio Department of Natural Resources, Division of Geological Survey, reprint 1981, scale 1:500,000.
- Breen, K.J., 1989, Potentiometric-surface map of the carbonate aquifer in Silurian and Devonian rocks, Lucas, Sandusky, and Wood counties, northwestern Ohio, July 1986: U.S. Geological Survey Water-Resources Investigations Report 88-4144, scale 1:126,720.
- Breen, K.J., and Dumouchelle, D.H., 1991, Geohydrology and quality of water in aquifers in Lucas, Sandusky, and Wood Counties, Northwestern Ohio: U. S. Geological Survey Water-Resources Investigations Report 91-4024, 234 p.
- Bugliosi, E.F., 1990, Plan of study for the Ohio-Indiana carbonate-bedrock and glacial-aquifer system: U.S. Geological Survey Open-File Report 90-151, 26 p.
- Bunner, D.W., 1993, Bedrock-surface altitude in the Midwestern Basins and Arches Region of Indiana, Ohio, Michigan, and Illinois: U. S. Geological Survey Water-Resources Investigations Report 93-4050, scale 1:750,000,
- Burger, A.M., Forsyth, J.L., Nicoll, R.S., and Wayne, W.J., 1971, Geologic map of the 1° x 2° Muncie quadrangle, Indiana and Ohio, showing bedrock and unconsolidated deposits: Indiana Geological Survey Regional Geologic Map 5, Muncie Sheet, Part A, scale 1:250,000.
- Busby, J.F., Plummer, L.N., Lee, R.W., and Hanshaw, B.B., 1991, Geochemical evolution of water in the Madison aquifer in parts of Montana,
   South Dakota, and Wyoming: U.S. Geological Survey Professional Paper 1273-F, 89 p.

- Buxton, H.T., and Modica, Edward, 1992, Patterns and rates of ground-water flow on Long Island, New York: Ground Water, v. 30, no. 6, p. 857-866
- Carlson, E.H., 1991, Minerals of Ohio: Ohio Department of Natural Resources, Division of Geological Survey Bulletin 69, 155 p.
- Cartwright, Keros, 1970, Groundwater discharge in the Illinois Basin as suggested by temperature anomalies: Water Resources Research, v. 6, no. 3, p. 912-918.
- Casey, G.D., 1992, Hydrogeology of the basal confining unit of the carbonate-rock aquifer system in the Midwestern Basins and Arches Region of Indiana, Ohio, Michigan, and Illinois: U.S. Geological Survey Open-File Report 92-489, 2 sheets, scale 1:1,000,000.
- \_\_\_\_\_1994, Hydrogeology of the Silurian and Devonian carbonate-rock aquifer system in the Midwestern Basins and Arches Region of Indiana, Ohio, Michigan, and Illinois: U.S. Geological Survey Open-File Report 93-663, 14 p., 2 sheets, scale 1:1,000,000.
- Chapelle, F.H., and Knobel, L.L., 1983, Aqueous geochemistry and the exchangeable cation composition of glauconite in the Aquia aquifer, Maryland: Ground Water, v. 21, no. 3, p. 343-352.
- Chebotarev, I.I., 1955, Metamorphism of natural waters in the crust of weathering: Geochimica et Cosmochimica Acta, v. 8, p. 22-48.
- Clark, G.D., ed., 1980, The Indiana water resource—Availability, uses, and needs: Indianapolis, Governor's Water Resources Study Commission, Indiana Department of Natural Resources, 508 p.
- Clayton, R.N., Friedman, I., Graf, D.L., Meyeda, T.K., Meents, W.F., and Shimp, N.F., 1966, The origin of saline formation waters: Journal of Geophysical Research, v. 71, no. 16, p. 3869-3882.
- Cooley, R.L., and Naff, R.L., 1990, Regression modeling of ground-water flow: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. B4, 232 p.
- Craig, Harmon, 1961, Isotopic variations in meteoric waters: Science, v. 133, p. 1702-1703.
- Cravens, S.J., Wilson, S.D., and Barry, R.C., 1990, Regional assessment of the ground-water resources in eastern Kankakee and northern Iroquois Counties: Illinois State Water Survey Report of Investigation 111, p. 22, 23.
- Cross, W.P., 1949, The relation of geology to dry-weather stream flow in Ohio: Transactions of the American Geophysical Union, v. 30, no. 4, p. 563-566.
- Cunningham, W.L., 1992, Hydrogeology and simulation of transient groundwater flow at the South Well Field, Columbus, Ohio: Columbus, Ohio, Ohio State University, unpublished Master's thesis, 154 p.
- Daniels, D.P., Fritz, S.J., and Leap, D.I., 1991, Estimating recharge rates through unsaturated glacial till by tritium tracing: Ground Water, v. 29, no. 1, p. 26-34.
- Dansgaard, W., 1964, Stable isotopes in precipitation: Tellus, v. 16, p. 436-468
- Deering, M.F., Mohr, E.T., Sypniewski, B.F., and Carlson, E.H., 1983, Regional hydrogeochemical patterns in ground water of northwestern Ohio and their relation to Mississippi Valley-type mineral occurrences: Journal of Geochemical Exploration, v. 19, p. 225-241.
- deRoche, J.T., and Breen, K.J., 1989, Hydrogeology and water quality near a solid- and hazardous-waste landfill, Northwood, Ohio: U.S. Geological Survey Water-Resources Investigation Report 88-4093, 76 p.
- Desaulniers, D.E., Cherry, J.A., and Fritz, Peter, 1981, Origin, age and movement of pore water in argillaceous quaternary deposits at four sites in southwestern Ontario: Journal of Hydrology, v. 50, p. 231-257.
- Doheny, E.J., Droste, J.B., and Shaver, R.H., 1975, Stratigraphy of the Detroit River Formation (Middle Devonian) of Northern Indiana: Indiana Department of Natural Resources, Division of Geological Survey Bulletin 53, 86 p.
- Draper, N.R., and Smith, Harry, 1981, Applied regression analysis: New York, John Wiley & Sons, 709 p.
- Droste, J.B., and Vitaliano, C.J., 1976, Geologic report of the Maquoketa Shale, New Albany Shale, and Borden Group rocks in the Illinois

- Basin as potential solid waste repository sites: U.S. Energy Research and Development Administration, Y/OWI/SUB-7062/1, 25 p.
- Dumouchelle, D.H., 1992, Report of slug-test analyses of wells at Wright Patterson Air Force Base: Unpublished data on file in Columbus office of the U.S. Geological Survey.
- Dumouchelle, D.H., Schalk, C.W., Rowe, G.L., and de Roche, J.T., 1993, Hydrogeology, simulated ground-water flow, and ground-water quality, Wright-Patterson Air Force Base, Ohio: U.S. Geological Survey Water-Resources Investigations Report 93-4047, 152 p.
- Eberts, S.M., 1999, Water levels and ground-water discharge, regional aquifer system of the Midwestern Basins and Arches Region, in parts of Indiana, Ohio, Illinois, and Michigan: U.S. Geological Survey Hydrologic Investigations Atlas 725, scale 1:2,000,000, 3 sheets.
- Eberts, S.M., Bair, E.S., and de Roche, J.T., 1990, Geohydrology, ground-water quality, and simulated ground-water flow, Geauga County, Ohio:
   U. S. Geological Survey Water-Resources Investigations Report 90-4026, 117 p.
- Fenelon, J.M., Bobay, K.E., and others, 1994, Hydrogeologic atlas of aquifers in Indiana: U.S. Geological Survey Water-Resources Investigations Report 92-4142, 197 p.
- Filley, T.H., 1985. The hydrogeological response to continental glaciation: University Park, Pennsylvania, Pennsylvania State University, unpublished M.S. thesis, 210 p.
- Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 709 p.
- Fleck, W.B., 1980, Geology and hydrology for environmental planning, Washtenaw County, Michigan: U. S. Geological Survey Open-File Report (unnumbered), 23 p.
- Fleming, A.H., 1989, Description and results of the pumping test at the Julietta Landfill, Marion County, Indiana: Unpublished memorandum report on file in Bloomington office of the Indiana Geological Survey, 11 p.
- Flint, R.F., committee chairman, 1959, Glacial map of the United States east of the Rocky Mountains: Boulder, Colo., Geological Society of America, scale 1:1,750,000.
- Foster, M.D., 1950, The origin of high sodium bicarbonate waters in the Atlantic and Gulf Coastal Plains: Geochimica et Cosmochimica Acta, v. 1, p. 33-48.
- Freeze, R.A., and Cherry, J.A., 1979, Groundwater: Englewood Cliffs, N.J., Prentice-Hall, 604 p.
- French, R.R., and Rooney, L.F., 1969, Gypsum resources of Indiana: Indiana Geological Survey Bulletin 42-A, 34 p.
- Fritz, P., Anderson, T.W., and Lewis, C.F.M., 1975, Late-Quaternary climatic trends and history of Lake Erie from stable isotope studies: Science, v. 190, 267-269.
- Fritz, P., and Fontes, J. Ch., 1980, Handbook of environmental isotope geochemistry, volume 1, The terrestrial environment, A: New York, Elsevier Scientific Publishing Company, 545 p.
- Garrels, R.M., and Christ, C.L., 1990, Solutions, minerals, and equilibria: Boston, Jones and Bartlett Publishers, 450 p.
- Geosciences Research Associates, Inc. and Purdue University, Water Resources Research Center, 1980, An inventory of groundwater data and aquifer assessment for Indiana: Bloomington, Indiana, Part III, Appendixes [no pagination].
  - \_\_\_1982, Hydrogeologic atlas of Indiana: Bloomington, Ind., 31 pl.
- Glatfelter, D.R.; Newman, J.E.; Mann, Martin; and Beik, Siavash, 1991,
   Indiana, floods and droughts, in Paulson, R.W., and others, comps.,
   National water summary 1988-89—Hydrologic events and floods and droughts: U.S. Geological Survey Water-Supply Paper 2375, p. 271-278
- Goldthwait, R.P., Dreimanis, Aleksis, Forsyth, J.L., Karrow, P.F., and White, G.W., 1965, Pleistocene deposits of the Erie lobe, *in* Wright, H.E., Jr.,

- and Frey, D.G., eds., The Quaternary of the United States: Princeton, N.J., Princeton University Press, p. 85-97.
- Gray, H.H., 1972, Lithostratigraphy of the Maquoketa Group (Ordovician) in Indiana: Indiana Geological Survey Special Report 7, 31.
- \_\_\_\_\_1983, Map of Indiana showing thickness of unconsolidated deposits:
  Indiana Geological Survey Miscellaneous Map 37, scale 1:500,000.
- Gray, H.H., Forsyth, J.L., Schneider, A.F., and Gooding, A.M., 1972, Geologic map of the Cincinnati quadrangle, Indiana and Ohio, showing bedrock and unconsolidated deposits: Indiana Geological Survey Regional Geologic Map 7, Cincinnati Sheet, Part A, scale 1:250,000.
- Gray, H.H., Droste, J.B., Patton, J.B., Rexroad, C.B., and Shaver, R.H., 1985, Correlation chart showing Paleozoic stratigraphic units of Indiana: Indiana Department of Natural Resources, Geological Survey Supplement to Miscellaneous Map 48, 1 sheet.
- Gray, H.H., Ault, C.H., and Keller, S.J., 1987, Bedrock geologic map of Indiana: Indiana Geological Survey Miscellaneous Map 48, scale 1:500,000.
- Gupta, Neeraj, 1993, Geologic and fluid-density controls on the hydrodynamics of the Mt. Simon Sandstone and overlying geologic units in Ohio and surrounding states: Columbus, Ohio, Ohio State University, Ph.D. dissertation, 266 p.
- Hach Chemical Company, 1989, Water analysis handbook: Ames, 10wa, 690 p.
- Hanover, R.H., 1994, Analysis of ground-water flow along a regional flow path of the Midwestern Basins and Arches Aquifer System in Ohio:
   U.S. Geological Survey Water-Resources Investigations Report 94-4105, 29 p.
- Harbaugh, A.W., 1990, A computer program for calculating subregional water budgets using results from the U.S. Geological Survey modular three-dimensional finite-difference ground-water flow model: U.S. Geological Survey Open-File Report 90-392, 23 p.
- Harrison, P.W., 1960, Original bedrock composition of Wisconsin till in central Indiana: Journal of Sedimentary Petrology, v. 30, p. 432-446.
- Hendry, M.J., Cherry, J.A., and Wallick, E.I., 1986, Origin and distribution of sulfate in a fractured till in southern Alberta, Canada: Water Resources Research, v. 22, no. 1, p. 45-61.
- Hill, M.C., 1992, A computer program (MODFLOWP) for estimating parameters of a transient, three-dimensional, ground-water flow model using nonlinear regression: U.S. Geological Survey Open-File Report 91-484, 358 p.
- \_\_\_\_\_1994, Five computer programs for testing weighted residuals and calculating confidence and prediction intervals on results from the ground-water parameter-estimation computer program MODFLOWP: U.S. Geological Survey Open-File Report 93-481, 81 p.
- Holser, W.T., and Kaplan, 1.R., 1966, Isotope geochemistry of sedimentary sulfates: Chemical Geology, v. 1, p. 93-135.
- Hull, D.N., 1990, Generalized column of bedrock units in Ohio: Ohio Department of Natural Resources, Division of Geological Survey, 1 p.
- Indelman, P., and Dagan, F., 1993, Upscaling of permeability of anisotropic heterogeneous formations—1. The general framework: Water Resources Research, v. 29, no. 4, p. 917-923.
- Indiana Department of Natural Resources, 1988, Water resource availability in the Whitewater River basin, Indiana: Water Resource Assessment 88-2, 126 p., 3 pls. in pocket.
- \_\_\_\_\_1990, Water resource availability in the Kankakee River basin, Indiana: Water Resource Assessment 90-3, 247 p.
- Janssens, Adriaan, 1977, Silurian rocks in the subsurface of northwestern Ohio: Ohio Department of Natural Resources, Division of Geological Survey Report of Investigations 100, 96 p.
- Johnson, G.H., and Keller, S.J., 1972, Geologic map of the 1° x 2° Fort Wayne quadrangle, Indiana, Michigan, and Ohio, showing bedrock and unconsolidated deposits: Indiana Geological Survey Regional Geologic Map 8, Fort Wayne Sheet, Part A, scale 1:500,000.
- Jorgensen, D.G., Signor, D.C., and Imes, J.L., 1989a, Accounting for intracell flow in models with emphasis on water table recharge and stream-

- aquifer interaction—1. Problems and concepts: Water Resources Research, v. 25, no. 4, p. 669-676.
- \_\_\_\_\_1989b, Accounting for intracell flow in models with emphasis on water table recharge and stream-aquifer interaction—2. A procedure: Water Resources Research, v. 25, no. 4, p. 677-684.
- Joseph, R.L., and Eberts, S.M., 1994, Selected data on characteristics of glacial-deposit and carbonate-rock aquifers, Midwestern Basins and Arches Region: U.S. Geological Survey Open-File Report 93-627, 43 p.
- Kaatz, M.R., 1955, The Black Swamp, a study in historical geography: Annals of the Association of American Geographers, v. 45, no. 1, 34 p.
- Keller, C.K., and Van Der Kamp, G., 1988, Hydrogeology of two Saskatchewan tills, II. Occurrence of sulfate and implications for soil salinity: Journal of Hydrology, v. 101, p. 123-144.
- Keller, S.J., 1983, Analyses of sub-surface brines of Indiana: Indiana Department of Natural Resources, Division of Geological Survey Occasional Paper 41, 30 p.
- Krouse, H.R., 1980, Sulphur isotopes in our environment, *in* Fritz, P., and Fontes, J.Ch., eds., Handbook of environmental isotope geochemistry, Volume 1: The terrestrial environment, A: New York, Elsevier Scientific Publishing Company, p. 435-471.
- Lamborn, R.E., 1952, Additional analyses of brines from Ohio: Ohio Department of Natural Resources, Division of Geological Survey Report of Investigations 11, 56 p.
- Larsen, G.E., 1991, Development of Silurian and Devonian lithostratigraphic nomenclature, central-western and northwestern Ohio: Ohio Department of Natural Resources, Division of Geological Survey Open-File Report 91-1, 1 pl.
- Leahy, P.P., and Martin, Mary, 1993, Geohydrology and simulation of ground-water flow in the Northern Atlantic Coastal Plain aquifer system: U.S. Geological Survey Professional Paper 1404-K, 81 p.
- Lesney, L.L, 1992, Geochemistry of ground water in glacial aquifers in the Cuyahoga River Basin, northeastern Ohio: Kent, Ohio, Kent State University, unpublished Master's thesis, 177 p.
- Long, D.L., Wilson, T.P., Takacs, M.J., and Rezabek, D.H., 1988, Stable-isotope geochemistry of saline near-surface ground water East-central Michigan Basin: Geological Society of America Bulletin, v. 100, p. 1568-1577
- Lowry, R.M., Faure, Gunter, Mullet, D.I., and Jones, L.M., 1988, Interpretation of chemical and isotopic compositions of brines based on mixing and dilution, "Clinton" sandstones, eastern Ohio, U.S.A.: Applied Geochemistry, v. 3, p. 177-184.
- Lumb, A.M., Kittle, J.L., and Flynn, K.M., 1990, Users manual for ANNIE, a computer program for interactive hydrologic analysis and data management: U.S. Geological Survey Water-Resources Investigations Report 89-4080, 236 p.
- Mazor, E., Drever, J.I., Finley, J., Huntoon, P.W., and Lundy, D.A., 1993, Hydrochemical implications of groundwater mixing – An example from the southern Laramie Basin, Wyoming: Water Resources Research, v. 29, no. 1, p. 193-205.
- McDonald, M.G., and Harbaugh, A.W., 1988, A modular three-dimensional finite-difference ground-water flow model: U.S. Geological Survey Techniques of Water-Resources Investigations, book 6, chap. A1 [variously paginated].
- Melhorn, W.N., and Kempton, J.P., eds., 1991, Geology and hydrogeology of the Teays-Mahomet bedrock valley systems: Geological Society of America Special Paper 258, 128 p.
- Meyer, William, 1978, Hydraulic characteristics of the White River streambed and glacial-outwash deposits at a site near Indianapolis, Indiana: U.S. Geological Survey Journal of Research, v. 6, no. 2, p. 273-283
- Michel, R.L., 1989, Tritium deposition in the Continental United States, 1953-83: U.S. Geological Survey Water-Resources Investigation Report 89-4072, 46 p.

- Mickelson, D.M.; Clayton, Lee; Fullerton, D.S.; and Borns, H.W., Jr., 1983, The late Wisconsin glacial record of the Laurentide ice sheet in the United States, *in* Wright, H.E., Jr., ed., Late-Quaternary environments of the United States, v. 1, The Late Pleistocene: Minneapolis, University of Minnesota Press, p. 3-37.
- Mook, W.G., 1980, Carbon-14 in hydrogeological studies, *in* Fritz, P., and Fontes, J.Ch., eds., Handbook of environmental isotope geochemistry, volume 1: The terrestrial environment, A: New York, Elsevier Scientific Publishing Company, p. 49-74.
- Mozola, A.J., 1969, Geology for land and ground-water development in Wayne County, Michigan: Michigan Department of Natural Resources, Geological Survey Report of Investigations 3, 25 p., 5 pl.
- \_\_\_\_\_1970, Geology for environmental planning in Monroe County, Michigan: Michigan Department of Natural Resources, Geological Survey Report of Investigations 13, 34 p., 6 pl.
- Nicholas, J.R., Rowe, G.L., Brannen, J.R., and Gillespie, J.L., 1996, Hydrology, water quality, and effects of drought in Monroe County, Michigan: U.S. Geological Survey Water-Resources Investigations Report 94-4161.
- Nordstrom, D.K., Jenne, E.A., and Ball, J.W., 1979, Redox equilibria of iron in acid mine waters, in Jenne, E.A., ed., Chemical modeling of aqueous systems—Speciation, sorption, solubility, and kinetics: Washington, D.C., American Chemical Society Symposium Series 93, p. 51-79.
- Nordstrom, D.K., and Ball, J.W., 1989, Mineral saturation states in natural waters and their sensitivity to thermodynamic and analytic errors: Scientific Geology Bulletin, v. 42, no. 4, p. 269-280.
- Norris, S.E., 1959, Vertical leakage through till as a source of recharge to a buried-valley aquifer at Dayton, Ohio: Ohio Department of Natural Resources, Division of Water Technical Report 2, 16 p.
- \_\_\_\_\_1974, Regional flow system and ground-water quality in western Ohio: U.S. Geological Survey Journal of Research, v. 2, no., 5, p. 527-531
- \_\_\_\_\_1979, Hydraulic properties of a limestone-dolomite aquifer near Marion, north-central Ohio: Ohio Department of Natural Resources, Division of Geological Survey Report of Investigations 110, 23 p.
- \_\_\_\_\_1986, Draft report on the hydrogeology of the Scioto River valley between Columbus and Shadeville: Unpublished report on file in the library of the Columbus, Ohio office of the U.S. Geological Survey [variously paginated].
- Norris, S.E., Cross, W.P., and Goldthwait, R.P., 1950, The water resources of Greene County, Ohio: Ohio Department of Natural Resources, Division of Water Bulletin 19, p. 23.
- Norris, S.E., and Fidler, R.E., 1973, Availability of water from limestone and dolomite aquifers in southwest Ohio and the relation of water quality to the regional flow system: U.S. Geological Survey Water-Resources Investigations Report 17-73, 42 p.
- Ohio Department of Natural Resources, Division of Water, 1970, Ground water for planning in northwest Ohio—A study of the carbonate rock aquifers: Ohio Water Plan Inventory Report 22, 62 p.
- Ohmoto, Hiroshi, and Rye, R. O., 1979, Isotopes of sulfur and carbon, *in* Barnes, H. L., ed., Geochemistry of hydrothermal ore deposits: New York, John Wiley & Sons, p. 509-567.
- Panno, S.V., and Bourcier, W.L., 1990, Glaciation and saline-freshwater mixing as a possible cause of cave formation in the eastern midcontinent region of the United States—A conceptual model: Geology, v. 18, p. 769-772.
- Pearson, F. J., Jr., and Rightmire, C. T., 1980, Sulfur and oxygen isotopes in aqueous sulphur compounds, in Fritz, P., and Fontes J. Ch., eds., Handbook of environmental isotope geochemistry, volume 1: The terrestrial environment, A: New York, Elsevier Scientific Publishing Company, p. 227-258
- Pearson, F.J., Jr., and White, D.E., 1967, Carbon 14 ages and flow rates of water in Carrizo Sand, Atascosa County, Texas: Water Resources Research, v. 3, no. 1, p. 251-261.

- Pettyjohn, W.A., and Henning, R.J., 1979, Preliminary estimate of groundwater recharge rates, related streamflow and water quality in Ohio: Columbus, Ohio State University, Water Resources Center, Project Completion Report 553, 323 p.
- Piper, A.M., 1944, A graphic procedure in the geochemical interpretation of water analyses: American Geophysical Union, v. 25, p. 914-923.
- Plummer, L.N., 1977, Defining reactions and mass transfer in part of the Floridan aquifer: Water Resources Research, v. 13, no. 5, p. 801-812.
- Plummer, L.N., Jones, B.F., and Truesdell, A.H., 1976, WATEQF—A Fortran IV version of WATEQ, a computer program for calculating chemical equilibria of natural waters: U.S. Geological Survey Water-Resources Investigations Report 76-13, 61 p.
- Plummer, L.N., Michel, R.L., Thurman, E.M., and Glynn, P.D., 1993, Environmental tracers for age dating young ground water, *in* Alley, W.M., ed., Regional ground-water quality: New York, Van Nostrand Reinhold, p. 255-294.
- Pollock, D.W., 1989, Documentation of computer programs to compute and display pathlines using results from the U.S. Geological Survey modular three-dimensional finite-difference ground-water flow model: U.S. Geological Survey Open-File Report 89-381, 188 p.
- Richards, R.P., 1990, A study of water quality in private rural wells in the limestone ridge area near Carey, Ohio—Preliminary report of first year results: Tiffin, Ohio, Heidelberg College Water Quality Laboratory, 23 p.
- Roadcap, G.S., Cravens, S.J., and Smith, E.C., 1993, Calculating ground-water recharge rates to the Silurian dolomite aquifer in northeastern Illinois [abs.], in 38th Annual Midwest Ground Water Conference, Program and Abstracts, p. 53.
- Rosenshein, J.S., 1963, Recharge rates of principal aquifers in Lake County, Indiana: Ground Water, v. 1, no. 4, p. 4-20.
- Rowland, M.R., and Kunkle, G.R., 1970, Cones of influence developed in the Silurian-Devonian aquifer, Maumee River Basin, Ohio: Ground Water, v. 8, no. 3, p. 37-43.
- Rupp, J.A., and Pennington, Dean, 1987, Determination of the 10,000 mg/l TDS surface within the bedrock aquifers of Indiana: Proceedings of the Indiana Academy of Science, v. 97, p. 383-389.
- Rye, R.O.; Back, William; Hanshaw, B.B.; Rightmire, C.T.; and Pearson, F.J., Jr., 1981, The origin and isotopic composition of dissolved sulfide in groundwater from carbonate aquifers in Florida and Texas: Geochimica et Cosmochimica Acta, v. 45, p. 1941-1950.
- Schmidt, J.J., 1979, Ground-water resources of Delaware County: Ohio Department of Natural Resources, Division of Water, 1 sheet.
- Schneider, W.J., 1957, Relation of geology to streamflow in the upper Little Miami Basin: Ohio Journal of Science, v. 57, no. 1, p. 11-14.
- Scott, J.C., 1990, A statistical processor for analyzing simulations made using the modular finite-difference ground-water flow model: U.S. Geological Survey Water-Resources Investigations Report 89-4159, 218 p.
- Searcy, J.K., 1959, Flow-duration curves: U.S. Geological Survey Water-Supply Paper 1542-A, 33 p.
- Seber, G.A.F. and Wild, C.J., 1989, Nonlinear regression: New York, John Wiley & Sons, 768 p.
- Shaver, R.H., regional coordinator, 1985, Midwestern Basin and Arches Region—Correlation of stratigraphic units of North America (COSUNA) project: American Association of Petroleum Geologists, 1 sheet.
- Sherwood, J.M., Rogers, J.C., and Pickens, J.B., 1991, Ohio, floods and droughts, in Paulson, R.W., and others, comps., National water summary 1988-89—Hydrologic events and floods and droughts: U.S. Geological Survey Water-Supply Paper 2375, p. 443-450.
- Shindel, H.L., Klingler, J.H., Mangus, J.P., and Trimble, L.E., 1991a, Water resources data, Ohio, water year 1990: U.S. Geological Survey Water-Data Report OH-90-1, v. 1, 305 p.
- \_\_\_\_\_1991b, Water resources data, Ohio, water year 1990: U.S. Geological Survey Water-Data Report OH-90-2, v. 2, 281 p.

- Siegel, D.I., 1989, Geochemistry of the Cambrian-Ordovician aquifer system in the northern Midwest, United States: U.S. Geological Survey Professional Paper 1405-D, 76 p.
- \_\_\_\_\_1991, Evidence for dilution of deep, confined ground water by vertical recharge of isotopically heavy Pleistocene water: Geology, v. 19, p. 433-436.
- Siegel, D.I., and Mandle, R.J., 1984, Isotopic evidence for glacial meltwater recharge to the Cambrian-Ordovician aquifer, north-central United States: Quaternary Research, v. 22, p. 328-335.
- Smith, B.S., Hardy, M.A., and Crompton, E.J., 1985, Water resources of Wildcat Creek and Deer Creek basins, Howard and parts of adjacent Counties, Indiana, 1979-82: U.S. Geological Survey Water-Resources Investigations Report 85-4076, 92 p.
- Soller, D.R., 1986, Preliminary map showing the thickness of glacial deposits in Ohio: U.S. Geological Survey Miscellaneous Field Studies Map 1862, scale 1:500,000.
- Steiger, J.R., and Holowaychuk, Nicholas, 1971, Particle size and carbonate analysis of glacial till and lacustrine deposits in western Ohio in, Goldthwait, R. P., ed., Till, a symposium: Ohio State University Press, p. 275-289.
- Stith, D.A., 1979, Brine analyses, 1972-1974: Ohio Department of Natural Resources, Division of Geological Survey Open-File Report 79-1 [no page numbers].
- Stoertz, M.W., 1989, A new method for mapping groundwater recharge areas and for zoning recharge for an inverse model: Madison, Wis., University of Wisconsin, Ph.D. dissertation, p. 178.
- Stoertz, M.W., and Bradbury, K.R., 1989, Mapping recharge areas using a ground-water flow model—A case study: Ground Water, v. 27, no. 2, p. 220-228.
- Stout, Wilbur, Lamborn, R.E., and Schaaf, Downs, 1932. Brines of Ohio: Geological Survey of Ohio Bulletin 37, Fourth Series, 123 p.
- Strobel, M.L., 1990, Characteristics affecting the vertical flow of ground water through selected glacial deposits in Ohio: Ohio State University, unpublished Master's thesis, 185 p.
- \_\_\_\_\_1993, Hydraulic properties of three types of glacial deposits in Ohio: U.S. Geological Survey Water-Resources Investigations Report 92-4135, 41 p.
- Strobel, M.L., and Faure, Gunter, 1987, Transport of indicator clasts by ice sheets and the transport half-distance—A contribution to prospecting for ore deposits: Journal of Geology, v. 95, p. 687-697.
- Stueber, A.M., Pushkar, Paul, and Heatherington, E.A., 1987, A strontium isotopic study of formation waters from the Illinois Basin, U.S.A.: Applied Geochemistry, v. 2, p. 477-494.
- Stueber, A.M., and Walter, L.M., 1991, Origin and chemical evolution of formation waters from Silurian-Devonian strata in the Illinois Basin, U.S.A.; Geochimica et Cosmochimica Acta, v. 55, p. 309-325.
- Stueber, A.M., Walter, L.M., Huston, T.J., and Pushkar, Paul, 1993, Formation waters from Mississippian-Pennsylvanian reservoirs, Illinois Basin, U.S.A.—Chemical and isotopic restraints on evolution and migration: Geochemica et Cosmochimica Acta, v. 57, p. 763-784.
- Sun, R.J., and Johnston, R.H., 1994, Regional aquifer-system analysis program of the U.S. Geological Survey, 1978-92: U.S. Geological Survey Circular 1099, 126 p.
- Thatcher, L.L., 1962, The distribution of tritium fallout in precipitation over North America: Bulletin of the International Association of Scientific Hydrology, v. 7, no. 2, p. 48-58.
- Thorstenson, D.C., Fisher, D.W., and Croft, M.G., 1979, The geochemistry of the Fox Hills-Basal Hell Creek aquifer in southwestern North Dakota and northwestern South Dakota: Water Resources Research, v. 15, no. 6, p. 1479-1498.
- Thelin, G.P., and Pike, R.J.. 1991, Landforms of the conterminous United States—A digital shaded-relief portrayal, U.S. Geological Survey Miscellaneous Investigations Series Map I 2206, scale 1:3,500,000

- Todd, D.K., 1969, Ground water resources of the Upper Great Miami River basin and the feasibility of their use for streamflow augmentation: Dayton, Ohio, Miami Conservancy District, 142 p.
- Toth, Jozsef, 1963, A theoretical analysis of groundwater flow in small drainage basins: Journal of Geophysical Research, v. 68, no. 16, p. 4795-4812.
- Turner, W.S., 1977, A geochemical study of some Silurian dolomites in northwestern Ohio: Toledo, Ohio, University of Toledo, unpublished Master's thesis, 82 p.
- U.S. Environmental Protection Agency, 1984, National secondary drinking water regulations: EPA-570/9-76-000, Appendix A [no pagination].
- U.S. Geological Survey, 1987, Digital elevation models, data users guide: U.S. Geological Survey National Mapping Program Technical Instructions Data Users Guide 5, 38 p.
- \_\_\_\_\_1989, Digital line graphs from 1:100,000-scale maps: U.S. Geological Survey National Mapping Program Technical Instructions Data Users Guide 2, 88 p.
- U.S. Geological Survey, 1970, Hypsography of Indiana: U.S. Geological Survey State Base Map, scale 1:500,000.
- U.S. Geological Survey, 1971, Hypsography of Ohio: U.S. Geological Survey State Base Map, scale 1:500,000.
- Van Metre, P.C., 1990, Structure and application of an interface program between a geographic-information system and a ground-water flow model: U.S. Geological Survey Open-File Report 90-165, 68 p.
- Walker, F.H., 1959, Natural brines of Indiana and adjoining parts of Illinois and Kentucky: Indiana Geological Survey Report of Progress 13, 58 p.
- Walter, L.M., Stueber, A.M., and Huston, T.J., 1990, Br-Cl-Na systematics in Illinois basin fluids—Constraints on fluid origin and evolution: Geology, v. 18, p. 315-318.
- Walton, W.C., and Scudder, G.D., 1960, Ground-water resources of the valley-train deposits in the Fairborn area, Ohio: Ohio Department of Natural Resources, Division of Water Technical Report 3, 57 p.
- Watkins, F.A., Jr., and Rosenshein, J.S., 1963, Ground-water geology and hydrology of the Bunker Hill Air Force Base and vicinity, Peru, Indiana: U.S. Geological Survey Water-Supply Paper 1619-B, 32 p.
- Wayne, W.J., and Zumberge, J.H., 1965, Pleistocene geology of Indiana and Michigan, *in* Wright, H.E., Jr., and Frey, D. G., eds., The Quaternary of the United States: Princeton, N.J., Princeton University Press, p.63-83.
- Weist, W.G., Jr., 1978, Summary appraisals of the Nation's ground-water resources—Great Lakes Region: U.S. Geological Survey Professional Paper 813-J, 28 p.
- Western Michigan University, Department of Geology, 1981, Hydrogeologic atlas of Michigan: Kalamazoo, Mich., plate 14, scale 1:500,000.
- Wigley, T.M., 1975, Carbon-14 dating of ground water from closed and open systems: Water Resources Research, v. 11, p. 324-328.
- Wilding, L.P., Drees, L.R., Smeck, N.E., and Hall, G.F., 1971, Mineral and elemental composition of Wisconsin-age till deposits in west-central Ohio *in*, Goldthwait, R.P., ed., Till, a symposium: Ohio State University Press p. 290-317.
- Williams, T.A., and Williamson, A.K., 1989, Estimating water-table altitudes for regional ground-water flow modeling, U.S. Gulf Coast: Ground Water, v. 27, no. 3, p. 333-340.
- Williamson, A.K., Grubb, H.F., and Weiss, J.S., 1990, Ground-water flow in the Gulf Coast aquifer systems, south-central United States—A preliminary analysis: U.S. Geological Survey Water-Resources Investigations Report 89-4071, 124 p., 4 pls.
- Willman, H.B., and others, comps., 1967, Geologic map of Illinois: Illinois State Geological Survey, scale 1:500,000.
- Wilson, T.P., and Long, D.T., 1993a, Geochemistry and isotope chemistry of Michigan Basin brines—Devonian formations: Applied Geochemistry, v. 8 p. 81-100.
- \_\_\_\_\_1993b, Geochemistry and isotope chemistry of Ca-Na-Cl brines in Silurian strata, Michigan Basin, U.S.A.: Applied Geochemistry, v. 8, p. 507-524.

REFERENCES CITED C103

- Winter, T.C., 1983, The interaction of lakes with variably saturated porous media: Water Resources Research, v. 19, no. 5, p. 1203-1218.
- Wood, W.W., 1976, Guidelines for collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water-Resources Investigations, book 1, chap. D2, 24 p.
- Yager, R.M., 1993, Simulated three-dimensional ground-water flow in the Lockport Group, a fractured dolomite aquifer near Niagara Falls, New York: U.S. Geological Survey Water-Resources Investigations Report 92-4189, 43 p.
- Yapp, C.J., and Epstein, Samuel, 1977, Climatic implications of D/H ratios of meteoric water over North America (9500-22,000 B.P.) as inferred from ancient wood cellulose C-H hydrogen: Earth and Planetary Science Letters, v. 34, p. 333-350.
- Young, G.M., Sharpe, D.R., and McKenzie, G.S., 1985, Quaternary and Proterozoic glacial deposits of the central Great Lakes: Columbus, Ohio, Sixth Gondwana Symposium, August, 19-23, 1985, Ohio State University, Field Excursion 7, Guidebook, 119 p.

# Selected Series of U.S. Geological Survey Publications

#### **Books and Other Publications**

**Professional Papers** report scientific data and interpretations of lasting scientific interest that cover all facets of USGS investigations and research.

**Bulletins** contain significant data and interpretations that are of lasting scientific interest but are generally more limited in scope or geographic coverage than Professional Papers.

Water-Supply Papers are comprehensive reports that present significant interpretive results of hydrologic investigations of wide interest to professional geologists, hydrologists, and engineers. The series covers investigations in all phases of hydrology, including hydrogeology, availability of water, quality of water, and use of water.

**Circulars** are reports of programmatic or scientific information of an ephemeral nature; many present important scientific information of wide popular interest. Circulars are distributed at no cost to the public.

Fact Sheets communicate a wide variety of timely information on USGS programs, projects, and research. They commonly address issues of public interest. Fact Sheets generally are two or four pages long and are distributed at no cost to the public.

Reports in the **Digital Data Series (DDS)** distribute large amounts of data through digital media, including compact discread-only memory (CD-ROM). They are high-quality, interpretive publications designed as self-contained packages for viewing and interpreting data and typically contain data sets, software to view the data, and explanatory text.

Water-Resources Investigations Reports are papers of an interpretive nature made available to the public outside the formal USGS publications series. Copies are produced on request (unlike formal USGS publications) and are also available for public inspection at depositories indicated in USGS catalogs.

**Open-File Reports** can consist of basic data, preliminary reports, and a wide range of scientific documents on USGS investigations. Open-File Reports are designed for fast release and are available for public consultation at depositories.

# Maps

Geologic Quadrangle Maps (GQ's) are multicolor geologic maps on topographic bases in 7.5- or 15-minute quadrangle formats (scales mainly 1:24,000 or 1:62,500) showing bedrock, surficial, or engineering geology. Maps generally include brief texts; some maps include structure and columnar sections only.

Geophysical Investigations Maps (GP's) are on topographic or planimetric bases at various scales. They show results of geophysical investigations using gravity, magnetic, seismic, or radioactivity surveys, which provide data on subsurface structures that are of economic or geologic significance.

Miscellaneous Investigations Series Maps or Geologic Investigations Series (I's) are on planimetric or topographic bases at various scales; they present a wide variety of format and subject matter. The series also incudes 7.5-minute quadrangle photogeologic maps on planimetric bases and planetary maps.

# **Information Periodicals**

Metal Industry Indicators (MII's) is a free monthly newsletter that analyzes and forecasts the economic health of five metal industries with composite leading and coincident indexes: primary metals, steel, copper, primary and secondary aluminum, and aluminum mill products.

Mineral Industry Surveys (MIS's) are free periodic statistical and economic reports designed to provide timely statistical data on production, distribution, stocks, and consumption of significant mineral commodities. The surveys are issued monthly, quarterly, annually, or at other regular intervals, depending on the need for current data. The MIS's are published by commodity as well as by State. A series of international MIS's is also available.

Published on an annual basis, **Mineral Commodity Summaries** is the earliest Government publication to furnish estimates covering nonfuel mineral industry data. Data sheets contain information on the domestic industry structure, Government programs, tariffs, and 5-year salient statistics for more than 90 individual minerals and materials.

The Minerals Yearbook discusses the performance of the worldwide minerals and materials industry during a calendar year, and it provides background information to assist in interpreting that performance. The Minerals Yearbook consists of three volumes. Volume 1, Metals and Minerals, contains chapters about virtually all metallic and industrial mineral commodities important to the U.S. economy. Volume 11, Area Reports: Domestic, contains a chapter on the minerals industry of each of the 50 States and Puerto Rico and the Administered Islands. Volume 11I, Area Reports: International, is published as four separate reports. These reports collectively contain the latest available mineral data on more than 190 foreign countries and discuss the importance of minerals to the economies of these nations and the United States.

### **Permanent Catalogs**

"Publications of the U.S. Geological Survey, 1879–1961" and "Publications of the U.S. Geological Survey, 1962–1970" are available in paperback book form and as a set of microfiche.

"Publications of the U.S. Geological Survey, 1971–1981" is available in paperback book form (two volumes, publications listing and index) and as a set of microfiche.

**Annual supplements** for 1982, 1983, 1984, 1985, 1986, and subsequent years are available in paperback book form.

