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**The Deep Hydrogeologic Flow
System Underlying the Oak Ridge
Reservation—Assessing the
Potential for Active Groundwater
Flow and Origin of the Brine**

Ronit Nativ
Amy Halleran
Arnold Hunley

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Environmental Sciences Division
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The Deep Hydrogeologic Flow System Underlying the Oak Ridge Reservation—Assessing the
Potential for Active Groundwater Flow and Origin of the Brine

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CONTENTS

	<u>Page</u>
FIGURES	v
TABLES	vii
ACKNOWLEDGMENTS	ix
ABBREVIATIONS	xi
EXECUTIVE SUMMARY	xiii
1. INTRODUCTION	1
2. PROBLEM	4
3. SCOPE	5
4. RESEARCH METHODS	6
5. HYDRAULIC HEAD AND PRESSURE	9
5.1 LATERAL HYDRAULIC CONNECTION	9
5.2 DIRECTION OF POTENTIAL VERTICAL FLOW	9
5.3 CONFINEMENT OF THE DEEP SYSTEM	9
5.4 RESPONSE TO RECHARGE	13
5.4.1 Water-Level Monitoring	13
5.4.2 The Freshwater-Brine Interface	15
6. DISCHARGE POINTS	20
7. EVIDENCE OF HIGH HYDRAULIC CONDUCTIVITY	22
8. TEMPERATURE VARIATIONS AT DEPTH	24
9. CHEMICAL AND ISOTOPIC COMPOSITION	25
9.1 CHEMICAL AND ISOTOPIC FEATURES OF THE ORR BRINE	25
9.2 SPATIAL AND TEMPORAL VARIATIONS OF ORR BRINE CONCENTRATIONS	31
9.3 BRINE OCCURRENCE IN THE APPALACHIAN REGION	32
9.4 GENESIS OF THE BRINE	33
9.4.1 Plausible Mechanisms and Their Signature	33
9.4.2 ORR Brine	34
9.5 EQUILIBRIUM CONSIDERATIONS	37

10. SUMMARY	40
10.1 EVIDENCE FOR STAGNANT GROUNDWATER	40
10.2 EVIDENCE FOR ACTIVE GROUNDWATER	40
10.3 HYDRAULIC CONTINUITY OF THE DEEP SYSTEM	40
10.4 RELATIONSHIPS BETWEEN THE SHALLOW AND DEEP HYDRAULIC SYSTEMS	41
10.5 MISSING ELEMENTS IN THE CONCEPTUAL MODEL	41
11. CONCLUSIONS	42
12. REFERENCES	43
APPENDIX A: Deep Wells Accessed During This Study But Not Monitored	A-1
APPENDIX B: Summary of Project Activities	B-1
APPENDIX C: Variations in Water Levels, Electrical Conductivity, and Temperature with Respect to Rainfall Events, December 1994–May 1995	C-1

FIGURES

<u>Figure</u>	<u>Page</u>
1 Map of the Oak Ridge Reservation	2
2 Stratigraphic column for the Oak Ridge Reservation	3
3 Water levels in the HHMS wells	10
4 Water level in HHMS clusters 3 and 7 during 1990 and 1991, respectively	11
5 Temporal variations in barometric pressure, precipitation, and water levels in the packed intervals of the (a) WOL-2, (b) CH-6, and (c) WCR-2 boreholes	12
6 Precipitation and water-level fluctuations in the deeply cased HHMS-2a and GW-711 wells	16
7 Precipitation data and continuous measurements of water level, electrical conductivity, and temperature in the HHMS-2a well between December 1994 and May 1995	17
8 Temporal variations of the position of interfaces separating the saline and brackish groundwater and the brackish and fresh groundwater in the (a) CH-5, (b) WOL-2, and (c) CH-3 boreholes	18
9 Groundwater flux through fractures in the CH-9 corehole	23
10 Relationships between (a) chloride, (b) sodium, (c) potassium, or (d) magnesium and bromide in the Oak Ridge Reservation deep groundwater	26
11 Relationships between the Carpenter function (a) $CF = Ca + Mg + Sr - SO_4 - HCO_3$, (b) Ca, or (c) Sr and Br concentrations, and (d) Na:Br vs Ca:Mg in the Oak Ridge Reservation deep groundwater.	27
12 Relationship between (a) Na:Cl or (b) Br:Cl and Cl concentrations in the Oak Ridge Reservation deep groundwater	29
13 Oxygen-18 and deuterium data for Oak Ridge Reservation precipitation, the Oak Ridge Reservation deep groundwater, and oil and gas brines sampled outside the reservation	30
14 Relationship between Cl:Br and Cl concentrations in the Oak Ridge Reservation deep groundwater	38

TABLES

<u>Table</u>		<u>Page</u>
1	Chemical and isotopic analyses of groundwater samples obtained from deep wells in the Oak Ridge Reservation	7
2	Shallow boreholes containing groundwater with a Cl content >100 mg/L and a Na:Cl ratio <0.7	21
B.1	Field activities undertaken	B-2

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ABBREVIATIONS

DNAPL	dense nonaqueous-phase liquid
HHMS	hydraulic head monitoring station
pmc	percent of modern carbon
ORNL	Oak Ridge National Laboratory
ORR	Oak Ridge Reservation
TDS	total dissolved solids
TU	tritium units
VOC	volatile organic compound

EXECUTIVE SUMMARY

The deep hydrogeologic system underlying the Oak Ridge Reservation (ORR) contains contaminants such as radionuclides, heavy metals, nitrates, and organic compounds. The groundwater in the deep system is saline and has been considered to be stagnant in previous studies. If the deep system is nearly stagnant, subsurface movement of contaminants on a regional scale is unlikely. Consequently, remediation efforts of known deep-seated contaminants would be of low priority because their migration is likely to be significantly limited. If, however, groundwater circulation within the deep system is active and deep water flows to the shallow, freshwater system or to surface streams, then remediation or control of the deep-seated contaminants should be considered a higher priority. Because deeper systems are likely to develop longer flow paths to natural outlets, discharge points for the deep system may exist beyond the Clinch River and ORR boundaries. This is clearly an undesirable prospect, and one that merits consideration.

This study was designed to address the following questions: Is groundwater in the deep system stagnant? Is contaminant migration controlled by diffusion only or is advection a viable mechanism? Where are the potential outlet points?

On the basis of existing and newly collected data, the nature of saline groundwater flow and potential discharge into shallow, freshwater systems was assessed. Data used for this purpose included (1) spatial and temporal pressures and hydraulic heads measured in the deep system, (2) hydraulic parameters of the formations in question, (3) spatial and temporal temperature variations at depth, and (4) spatial and temporal chemical and isotopic composition of the saline groundwater.

The observations suggest that the saline water contained at depth is old but not isolated (in terms of recharge and discharge) from the overlying active, freshwater-bearing units. Whereas the origin of the salts in the brine may date to the Paleozoic, influx of recent water does occur. The confined water (and dissolved solutes) move along open fractures (or man-made shortcuts) at a relatively high velocity into adjacent, more permeable units. Groundwater volumes involved in this flow are likely to be small.

The origin of the saline groundwater was assessed by using existing and newly acquired chemical and isotopic data. The proposed model that best fits the data is modification of residual brine from which halite has been precipitated. Potential sources for this brine are in the Appalachian Mountains to the east, where bedded halite is documented, and where the hydraulic gradient needed to move the residual brine exists. Other models, such as ultrafiltration and halite dissolution, were also evaluated.

1. INTRODUCTION

The Oak Ridge Reservation (ORR) (Fig. 1) is underlain by a suite of aquifers and aquitards formed in shales, limestone, and dolomite of the Conasauga Group (middle Cambrian) and of the Chickamauga Group (middle Ordovician) (Fig. 2). The Knox aquifer is composed of the Knox Group (upper Cambrian and lower Ordovician) and the Maynardville Limestone (upper Cambrian) (Fig. 2) and forms the only aquifer in the area. Groundwater is fresh [<500 mg/L of total dissolved solids (TDS)], and its flow is controlled by the density of fractures in the aquitards and dissolution channels in the carbonate aquifer (Solomon et al. 1992). Consequently, the bulk of the subsurface flow is believed to be in the 1- to 2-m-deep (3- to 6-ft-deep) storm-flow zone (Moore 1988), and almost all (98%) subsurface flow in areas underlain by aquitards is believed to be at depths of <8 m (~ 90 ft) where fractures and dissolution channels are closely spaced (Solomon et al. 1992). Subsurface flow paths from recharge to discharge zones are presumably short, generally <1.6 km (<1 mile), and do not exceed a few kilometers (Solomon et al. 1992). Consequently, the Clinch River, which surrounds the ORR on three sides (Fig. 1), is the main discharge point for the active flow system and is generally considered to be a hydrologic boundary for the reservation.

The active, shallow groundwater is underlain by a deeper system, referred to as an aquiclude (Solomon et al. 1992), that contains brine water ($\sim 200,000$ mg/L TDS). The groundwater in this system is assumed to be nearly stagnant and not included in the active subsurface circulation (Chapman-Bailey and Lee 1991; Solomon et al. 1992). The stagnancy of the deep groundwater has been inferred from its very high salinity and the low permeability of the host rocks. The assumption is that if active groundwater circulation could take place in this zone, the brine would have been flushed away long ago. A transition zone separates the actively flowing shallow groundwater system from the underlying aquiclude. Groundwater salinity in the transition zone ranges from 500 to tens of thousands of milligrams per liter TDS.

Fig. 1. Map of the Oak Ridge Re

ervation. The framed area is enlarged in Fig. 3.

Fig. 2. Stratigraphic column for the Oak Ridge Reservation: The Kingston thrust sheet (left) and the Copper Creek and White Oak Mountain thrust sheets (right).

Sources: Lemiszki, P. J. 1992. Geology of the Bethel Valley quadrangle - Part of the Department of Energy Oak Ridge Reservation in the southern Appalachian foreland fold-thrust belt and fracture mechanics modeling of extension fracture growth during basin subsidence and buckle folding. Ph.D. dissertation. The University of Tennessee, Knoxville, Tenn.

Hatcher, R. D., P. J. Lemiszki, R. B. Dreier, R. H. Ketelle, R. R. Lee, D. A. Leitzke, W. M. McMaster, J. L. Foreman, and S. Y. Lee. 1992. Status report on the geology of the Oak Ridge Reservation. ORNL/TM-12074. Oak Ridge National Laboratory [for thrust sheet locations].

2. PROBLEM

Groundwater contamination has been observed in several locations within the ORR, and various methods of remediation are currently being tested or evaluated. Evidence exists that contaminants such as radionuclides, nitrates, tritium, heavy metals, dense nonaqueous-phase liquids (DNAPLs), and volatile organic compounds (VOCs) have also reached the transition zone or the underlying deep, presumably inactive groundwater system in several locations (Dreier and Toran 1989; Dreier et al. 1991; Geraghty and Miller Inc. 1987; Haase and King 1990). The presence of contaminants at depth in locations other than where deep-well injection of waste was practiced (Stow and Haase 1986) has been interpreted as density-driven flow rather than as active circulation through the transition zone or the deep system (e.g., Dreier et al. 1991). If the deep system is nearly stagnant, subsurface movement of contaminants on a regional scale is unlikely. Consequently, remediation efforts of known deep-seated contaminants would be of low priority because their migration potential is likely to be limited. If, however, groundwater circulation within the deep system is active and deep water flows to the shallow, freshwater system or to surface streams, then remediation or control of the deep-seated contaminants should be considered a high priority. Because deeper systems are likely to develop longer flow paths to natural outlets (Toth 1963), discharge points for the deep system may exist beyond the Clinch River and the ORR boundaries. This is clearly an undesirable prospect, and one that merits consideration.

3. SCOPE

Although several previous studies have examined the deep groundwater system at specific locations (e.g., Dreier and Toran 1989; Dreier et al. 1991; Stow and Haase 1986), this study is the first to attempt to directly monitor and evaluate groundwater flow and solute migration in the deep geohydrologic system underlying the entire ORR. The study was designed to address the following questions: Is groundwater in the deep system stagnant? Is contaminant migration controlled by diffusion only or is advection a viable mechanism? Where are the potential outlet points?

These are intriguing questions in a far broader sense (i.e., beyond the immediate remediation needs of the ORR). Saline groundwater can be found at depth anywhere in the eastern and central United States (Brown et al. 1979; Clifford 1973; Goodman 1990; Heck et al. 1964; Kreiger et al. 1957; Lamborn 1952; Milhous 1959; Poth 1962; Price et al. 1937; Startler et al. 1975; Stout et al. 1932). The controlling mechanisms accountable for brine formation and preservation at depths ≤ 200 m (650 ft) in these humid regions are not always clear. The use of subsurface low-permeability brine-containing environments for hazardous and nuclear waste isolation has been proposed and explored at several locations throughout the United States (e.g., Brown et al. 1979). The above questions are generic, to be addressed whenever subsurface isolation of hazardous waste is being considered under similar conditions.

4. RESEARCH METHODS

Groundwater features indicative of active circulation in the deep system and of the potential of hydraulic connections with the shallow hydraulic system include (1) spatial and temporal variations in hydraulic head/pressure of the deep system, (2) evidence of high permeability and temperature variations at depth, and (3) chemical and isotopic composition that suggests the possibility of current recharge and interactions between the shallow and deep systems. Because of the geological complexity of the deep system and the sparsity of data and observation points, attempts were made to assess its activity by using all of these features. This approach provides independent evidence from various angles.

The geologic heterogeneity, the small geographical area, and the limited number of deep wells available for observation account for some of the difficulties encountered during a study of the deep hydrogeological system of the ORR. These problems are typical of almost any study of deep systems. To maximize the representativeness of the samples, data were collected from all possible stratigraphic and lithologic settings (limestone, dolomite, and shale and from all geologic groups), with as much areal coverage as possible within the reservation. Consequently, the studied wells were selected by using screening criteria such as well depth, previously observed salinity anomalies from conductivity/resistivity logs, representation of all major hydrological units in the ORR, and areal coverage.

Twenty-six boreholes in the ORR were accessed during this study; however, for a variety of reasons (listed in Appendix A), only 12 boreholes (Fig. 1) were hydrologically monitored, and 9 of these were sampled for chemical and isotopic analyses. These boreholes included three coreholes in the Oak Ridge National Laboratory (ORNL) area (CH-5, CH-6, and CH-9), which are about 122 m (400 ft) deep in the Chickamauga Group; two boreholes (WCR-2 and GW-711) drilled into the Knox aquifer (Copper Ridge and Maynardville formations, respectively) at ~152 and 201 m (500 ft and 660 ft), respectively; and seven boreholes tapping the Conasauga Group (CH-3, GW-121, GW-211, GW-214, HHMS-6a, HHMS-2a and WOL-2) located along the western part of the ORR. Four of the latter boreholes are ~122 m (400 ft) deep; GW-121, CH-3, and WOL-2 are 183, 201, and 268 m (600, 660, and 880 ft) deep, respectively. These observations were supplemented with a small amount of data from deep wells outside the reservation.

Pressure variations in the deep boreholes were monitored within intervals isolated by packers. The bottom 6 m (~20 ft) of nine deep wells were packed. The water pressure in the packed interval in eight of these boreholes was monitored with high-resolution [34.48 and 17.24 kPa (5 and 2.5 psig)] pressure transducers (Druck) located far above the packer in a tube penetrating the packed interval at its bottom end and extending to land surface. This configuration enabled the measurement of water level variations on the order of 0.003 m (0.01 ft).

Before the beginning of this study, 33 chemical analyses of the ORR brine with a charge-balance error of <10% were available (Haase et al. 1987c; Switek et al. 1987) (Table 1, analyses from 1983 through 1987). Most of these analyses were of grab samples taken from 23 deep wells with no preceding purging. Additional existing analyses were rejected because their charge-balance error exceeded 10%.

Table 1. Chemical and isotopic analyses
on the Oal

Well	Depth	Date	Ca	Mg	Na	K	Sr	Ba	Li	Cl
<i>Historical Data</i>										
DM-1RT	700	1/30/86	13000	2700	30000	740	1300	89	28	98000
DM-3RT	550	1/29/86	11000	2900	35000	140	1300	290	33	93000
DM-1PV	1050	1/31/86	22000	4100	59000	240	2300	680	55	150000
DM-2PV	1050	1/31/86	26000	4400	57000	230	2600	610	51	150000
DM-3PV	875	1/29/86	2800	260	12000	77	210	1.5	11	24000
DM-1RM	1085	1/30/86	11000	1300	37000	330	870	8.6	555	91000
DM-2RM	1250	1/30/86	15000	2300	57000	890	1400	28	88	130000
HF-2E100	650	8/8/85	110	14	3800	82	9.1		2.8	5200
HF-2E200	495	8/12/85	210	63	5100	21	16		3.9	9100
HF-2E400	665	8/9/85	46	13	2400	8	3.8		1.7	2000
HF-2E500	665	8/9/85	280	90	5700	23	21		4.4	9000
HF-2E600	665	8/9/85	35	12	2100	7	3.5		1.5	1800
HF-2W600	800	8/7/85	4900	990	20000	80	440	52	14	48000
HF-2S400	120	9/19/84	85	14	900	8	1.6	0.5	1	1200
	340	9/19/84	20	9	1230	8	2.2	0.2	1.3	1600
RC-N200	400	5/21/86	16000	2900	44000		1600	500		97000
RC-NW400	570	10/83	2820	297	8890	1430	297	119	13.4	23400
RC-NE400	570	10/83	15500	3120	27700	17300	1880	478	53.2	117000
	580	1/16/85	12200	2770	41600	130	1530	463	25.7	100000
	580	5/21/86	16000	3000	44000		1600	530		95000
RC-S200	690	10/83	4810	736	11400	5190	551	162	18.7	33700
	590	1/14/85	2370	331	8630	50	266	58.7		20000
	597	5/22/86	13000	2200	27000		1300	410		71000
RC-SW280	600	1/14/85	25200	5300	60500	180	3020	770	42	155000
	600	5/23/86	23000	3600	48000		2300	650		120000
RC-SE400	690	10/83	12400	3320	33700	8460	1490	516	51	113000
	685	1/14/85	14100	1740	44100	180	1740	547	30	100000
RC-E200	640	10/83	13400	3040	26600	11400	1620	498	40.6	101000
	640	1/16/85	12200	2880	44500	160	1540	599	59.8	120000
	645	5/20/86	19000	3300	48000		2000	660		120000
RC-W200	640	10/83	7410	1110	21200	8830	890	302	37.4	68200
WOL-1	1250	7/30/87	34000	5300	67000	290	3500	470		190000
<i>This Study's Data</i>										
CH-5	427	7/8/93	220	148	3806	23.4	31.6	0.122	1.22	7825
CH-6	380	7/14/93	3.24	1.58	385	4.85	0.27	0.015	0.47	235
CH-9	380	11/9/92	2.35	0.93	338	2.54	0.15	0.01	0.22	296
GW-214	414	7/13/93	2.5	0.73	593	8.39	0.6	0.15	0.45	775
HHMS6a	380	11/9/92	1973	565	12878	81	208	72	3.01	27100
WOL-2	880	11/9/92	7335	1647	22100	101	882	468	3.55	64900
GW-121	590	6/94	1.4	0.02	518	14.2	0.1	0.03	0.1	115
GW-211			160	40	51	14.8	2.24	0.029	0.7	65.5
WCR-2			107	42	7	11.2	5.81	0.017	0.1	BDL
ARM#4		1992	4940	2150	44400	324				77900
B&WMorgan	3975	1992	3120	1830	24200	593				46200
B&W	1672	1992	44100	3240	24100	309				122400
BobyMorgan	1730	1992	4000	2580	31200	276				60700

*Ion concentrations are measured in mg/L. BDL = below detection level. Oxygen-18 and deuterium are expressed in per mill (SMOW). Carbon-13 is c

of groundwater samples obtained from deep wells
Ridge Reservation^a

Br	NO ₃	SO ₄	HCO ₃	TDS	pH	¹⁸ O	D	³ H	¹³ C	¹⁴ C
840	18		3	145740	6.8					
950	442		0	143340	4.6					
400	1991		0	237640	4.4					
100			0	240230	4.3					
210	66	522	60	39347	6.9					
750	9	330	20	141500	8.4					
500			366	206590	10.3					
36		2200		11459	7.8					
60		1700		16280	6.1					
15		2400		6895	6.8					
70		1800		16995	6.7					
14		1900		3965	6.7					
520				74850	5.3					
7	14	100	603	2933	7					
10	82	150	684	3741	7.3					
770	28			162770	5.2					
190			16.3	37646	7.4					
101			0.2	166779	4.4					
300	4		4	159363	4.7					
790	34			160920	5.9					
238			14.3	51597						
220			0	31876	5.3					
580	20			115490	4.9					
300	7		1	251090	4.4					
100	31			198650	4.8					
339			0.3	165265	4.3					
200	5		2	164177	6.3					
333			0	147091	3.5					
330	5		6	182549	4.7					
380	32			193840	4.1					
199			19.2	99611	7.5					
300	3000	16	2	302537	4.6					
2.2		403	169	12669.54	7.04	-5.6	-37.2	83.7	78.85	-8.5
14		291	225	1148.565	8.43	-5.8	-38.1	39	13.14	-6.6
1.5		31.2	286	958.9	8.5	-5.6	-37.6	3576	57.3	-8.7
47		2.68	304	1692.97	9.63	-6.1	-38.4	1.4	2.88	0.9
82		BDL	8.54	43070.55	7.5	-6	-28.6	2.9	98.06	-19.6
05		BDL	36.6	97978.15	5.95	-5.7	-29.2	9.9	78.31	-1.6
1.6		35	2.2		11.6					
DL		631	11.1		7	-6	-38.5	1.8	No Sample	
DL		272	85.7		7.97	-6.1	-38.9	0.4	1.53	-6.1
51	258	638	7.36	131268.4	5.51	-0.99	-25.64	4.6		
98	208	283	10.9	76642.9	4.92	-0.31	-32.18		32.6	
71	197	969	0.96	195587	4.16	-0.86	-19.6	0.8	15.3	
84	200	607	2.62	99949.62	7.35					

expressed in per mill (PDB). Carbon-14 is expressed in percent of modern carbon, and tritium is expressed in tritium units.

5. HYDRAULIC HEAD AND PRESSURE

A comparison of water levels in cased boreholes or piezometers is useful for the assessment of lateral hydraulic connection and the direction of potential vertical flow when data from well clusters are being used. The monitoring of temporal water-level variations may help in evaluating the degree of confinement of the deep system (by using pressure responses to earth tide and barometric pressure) and current recharge of its groundwater.

5.1 LATERAL HYDRAULIC CONNECTION

For the assessment of hydraulic connectivity across the deep system and the potential for lateral groundwater flow, wells that penetrated the same geologic group, had small open intervals, and were relatively close to each other were used. The selected wells were those that penetrated the shale and limestone of the Conasauga Group in Melton Valley (Fig. 3). The similar water levels [228–241 m (748–790 ft)] in the wells that had completely recovered from the purging following their drilling may suggest hydraulic continuity between them (Fig. 3). The very long recovery of the water level in the hydraulic head monitoring station (HHMS) wells -4a, -5a, -8a, and -9a after drilling suggests an extremely restricted flow, whereas the relatively fast recovery observed in the other HHMS wells may suggest high connectivity. These conflicting observations may be related to the presence of contributing fractures in some of the wells and the lack of them in others.

5.2 DIRECTION OF POTENTIAL VERTICAL FLOW

A comparison of water levels in the deep and shallow systems in well clusters allows a definition of potential vertical flow. Hydraulic heads in the deep system were lower than those in the shallow system in well clusters HHMS-1, -6, and -7 (shown in Fig. 3), suggesting the potential for recharge from above (as shown in well cluster HHMS-7, Fig. 4). In other wells (well clusters HHMS-2, -3, -10, and -13, shown in Fig. 3), water levels in the deep system were higher, suggesting the potential for upward leakage from below (well cluster HHMS-3, Fig. 4). Similar observations were documented in packed deep wells in the Conasauga and Chickamauga formations, where water levels measured in a deep packed interval were higher than those measured above them. The documented higher hydraulic heads in some of the deep wells suggest that, at least in these areas, recharge into the deep system cannot come directly from above but may reach this zone from more remote, higher elevation areas.

5.3 CONFINEMENT OF THE DEEP SYSTEM

The degree of confinement of the deep system from the overlying unconfined freshwater system and from the atmosphere was estimated by using water-level variations. Confined groundwater with little connection to the atmosphere displays minute pressure variations in response to loading by moisture accumulation near land surface, earth tide, and barometric pressure (Bredehoeft 1967; Geiske and de Vries 1985; Gilliland 1969; Jacob 1940; van der Kamp and Gale 1983; van der Kamp and Maathuis 1991). Slight confinement may result in a pressure response to earth tide but will not result in any response to barometric pressure (Nativ and Weisbrod 1994; Salama et al. 1993).

HYDRAULIC HEAD MONITORING STATIONS

Fig 3. Water levels (feet above sea level) in the HHMS wells (measurements were taken on June 25, 1992). The area is an inset from Fig. 1.

Fig. 4. Water level (feet above sea level) in HHMS clusters 3 (bottom) and 7 (top) during 1990 and 1991, respectively. The open intervals in the A, B, and C wells in cluster 3 are 380–400 ft, 190–212 ft, and 62–81 ft. The open intervals in the A, B, and C wells in cluster 7 are 380–400 ft, 275–295 ft, and 158–178 ft.

Source: Drier, R. B., and L. E. Toran. 1989. Hydrogeology of Melton Valley determined from head measuring station data. ORNL/TM-11216. Oak Ridge National Laboratory.

Fig. 5. Temporal variations in barometric pressure (in.), precipitation (in.), and water levels (ft) in the packed intervals (measured by pressure transducers) of the (a) WOL-2, (b) CH-6, and (c) WCR-2 boreholes. Water level dropped below the pressure transducer in the WCR-2 borehole starting June 18, 1992.

The pressure observations (measured with the pressure transducers) suggested varying degrees of confinement of the deep system (Fig. 5). The smallest head variations were observed in the WOL-2 borehole tapping the Rogersville Shale (Conasauga Group) at its base, amounting to <0.03 m (0.1 ft) on a daily scale (Fig. 5a). These variations were unrelated to either barometric pressure or precipitation (Fig. 5). Small daily fluctuations were also observed in the HHMS-6a and GW-211 boreholes (completed in the Pumpkin Valley Shale and Rome formations, respectively, and not shown in Fig. 5). Similar patterns have been observed in aquifers that are only slightly confined (Salama et al. 1993; Nativ and Weisbrod 1994).

Daily (tide-related) variations of 0.15 m (0.5 ft) with some response to barometric pressure variations were documented in coreholes CH-6 (Fig. 5b), CH-5, and CH-9 (not shown) completed in the Chickamauga Group (limestone) and in the GW-214 borehole (not shown) completed in the Maynardville Limestone. In these boreholes, no water-level response to precipitation events was observed.

The greatest response was observed in the WCR-2 borehole, completed in the Copper Ridge Dolomite (Knox Group) and packed between 155 and 163 m (510 and 535 ft) below land surface. Both large daily fluctuations [exceeding 0.3 m (1 ft) on some days] and longer-term fluctuations [exceeding 1.2 m (4 ft)] (Fig. 5c) were observed. The longer-term fluctuations may both reflect barometric pressure variations and be a direct response to recharge during rain events (June 4–6, 1992), as well as to water-level depletion during the following dry period.

The karst features of the Copper Ridge Dolomite documented at shallow depths might also be occurring at greater depths. Similar pressure responses to rainfall events have been observed at depth in both the Maynardville [up to 213 m (700 ft)] and the Nolichucky Shale [up to 91 m (300 ft)] formations, although the response is dampened in the latter (David Watson, ORNL, personal communication).

With these observations in mind, note that wells in unconfined aquifers having very small porosity and vertical diffusivity values, or very large saturated thicknesses, may also display small water-level fluctuations in response to earth tides (Bredehoeft 1967; Galloway and Rojstaczer 1988). Under such circumstances, although the water table is largely insensitive to rock deformation, the aquifer at depth can be largely isolated from water-table influences. In fact, Richardson (1956) reported tidal fluctuations in a well on the ORR that penetrated an unconfined aquifer and exhibited a semidiurnal tidal fluctuation with an amplitude of ~2 cm (0.78 in.). The tidal response is generally less efficient in a well that taps unconfined systems. Therefore, the larger fluctuations observed in most of the packed wells are considered to represent a confined system, whereas the small water-level fluctuations observed in the WOL-2 and HHMS-6a boreholes could suggest either slight confinement or unconfined groundwater in a low-porosity aquitard. This observation in the WOL-2 borehole is particularly intriguing because the packed interval was located 268 m (880 ft) below land surface.

5.4 RESPONSE TO RECHARGE

5.4.1 Water-Level Monitoring

Water-level variations in deep wells [>45 m (150 ft)] cased close to their bottoms may imply seasonal or event-based recharge into the deep system. Water levels in some deep wells in Melton Valley were monitored on a monthly basis for several years, enabling the detection of seasonal variation. Although groundwater levels in some of these deep wells did not display any temporal variations (Fig. 4a), those in other wells may suggest seasonal recharge (Fig. 4b). For

the latter wells, the highest water levels were observed during April and May (HHMS-2a, -3a, and -6a wells) or during the fall and early winter months (HHMS-1a and -7a wells). Note that some of the wells that displayed seasonal variations also had higher water levels than those documented at the nearby shallower wells (e.g., HHMS-2a, -3a, and -10a). Hence, the seasonal response cannot be attributed to direct percolation of water from above and has to be related to recharge from an unknown distance.

The researchers van der Kamp and Maathuis (1991) discussed annual water-level fluctuations in deep confined aquifers in Saskatchewan, Canada, suggesting that often these have no relationship to actual recharge. Instead, the fluctuations represent moisture accumulation in the overlying shallow aquifers, separated from the deep aquifers by thick (tens of meters) aquitards (glacial till). The actual recharge into the deep aquifers is in fact constant. Is it possible that the seasonal variations in water levels observed in some of the ORR deep boreholes are mere reflections of moisture accumulation at a shallow depth during the recharge season? The deep system in the ORR deviates from the case model discussed by van der Kamp and Maathuis (1991) because (1) it is better described as a fractured aquitard (as will be further discussed in Chap. 7), rather than a deep aquifer; (2) the water-level response in this aquitard is nonuniform (i.e., some of the deep wells display seasonal response whereas others do not), unlike the loading effects documented in all the monitored wells in the Canadian deep aquifer; (3) the groundwater in some of the "responding wells" has higher hydraulic head than that in the shallow aquifer, whereas the lower water levels in the Canadian deep aquifers required recharge from the overlying shallow systems; (4) in contrast to observations in the Canadian deep wells, the seasonal response observed in some of the deep wells in the ORR is not lagging behind that observed in the shallow system; and (5) the event-based water-level responses documented in the ORR deep system (to be described later in this chapter) cannot be explained by the annual loading found in Canada. These deviations suggest that the seasonal water-level fluctuations in the deep system in the ORR may imply actual water movement, as will be further discussed in this chapter.

Water-level measurements were taken on a weekly basis in the deeply cased HHMS-2a and GW-711 wells during 1992 and 1993, respectively. These wells were completed in the Conasauga and Knox groups, respectively, with open intervals at 116–122 m (380–400 ft) and 188–203 m (616–666 ft), respectively. The measurements in these two wells revealed a few event-based responses of the water level to specific rainstorms (Figs. 6a,b). In both wells, the water-level fluctuations were very rapid, and the observed increase [exceeding 33 cm (1 ft) in the HHMS 2a borehole, and 3 m (10 ft) in the GW-711 borehole] had dissipated by the following week. Because of the rapid water-level response, many more undocumented fluctuations may have occurred between the weekly measurements. Similar event-based fluctuations have been documented in other boreholes at depths of up to 220 m (721 ft) in the Maynardville Formation (David Watson, ORNL, personal communication, Oct. 1994).

Although the diameter of the HHMS 2a and GW-711 wells is large [20 and 16 cm (8 and 6.25 in.), respectively], the rapid water-level fluctuations may not represent actual water flow near the well. Instead they may be merely a manifestation of a pressure wave moving across the formation. The pressure may result from recharge taking place in the outcrop area of the same formation. However, instead of flowing deeper into the formation, where fracture density decreases (resulting in a vertical decrease of hydraulic permeability), the recharged water may discharge at a nearby stream at a shallow depth. To assess the possibility of actual recharge (as opposed to water-level responses to pressure), continuous monitoring of water levels, temperature, and electrical conductivity was carried out in the HHMS-2a well from December

1994 to May 1995. These parameters were measured by using an in situ continuous logging and recording system. The monitoring results are shown in Fig. 7 and Appendix C. Fourteen large [>0.76 cm (0.3 in)] rainfall events were documented during the monitoring period, but measurements from only 12 events were recorded. Although 11 of the 12 large precipitation events were accompanied by small water-level increases, these never exceeded 4 cm (1.6 in.) (Fig. 7). Because the water level in the well was seasonally increasing throughout the entire measurement period, its response to heavy rainfall events was reflected by a steeper slope of increasing water level. However, steeper slopes were also observed on February 20 and March 17, 1995 with no accompanying rainfall, and the large precipitation event of April 17 to April 21, 1995, [4 cm (1.59 in)] had no effect whatsoever on the water levels (perhaps because of the increasing water demand of the blooming trees and vegetation). Only 9 of the 11 rainfall events that induced increases in water level were accompanied by electrical conductivity increases. Temperature decrease was observed in 5 of these 11 events, and the temperature increased in 1 event. Some of the observed fluctuations in temperature and electrical conductivity had no association with rainfall events (e.g., March 17 and April 28, 1995). In conclusion, the large water-level fluctuations observed in 1992 in the HHMS-2a well were not documented during the late 1994–95 monitoring period. However, (1) the increasing water level throughout the rainy season, (2) its enhanced response to 11 rainfall events, and (3) the accompanying variations in electrical conductivity and temperature in 9 and 6 of those events, respectively, suggest that groundwater is actually flowing in the deep hydrogeological system tapped by this well.

5.4.2 The Freshwater–Brine Interface

The position of the freshwater–brine interface is believed to represent the lower boundary of the actively flushed zone and is presumably controlled by fracture density, aperture, and interconnectedness (Solomon et al. 1992). Fluid resistivity logs in open boreholes display a relatively sharp transition zone in some boreholes and a gradual salinity increase in others. Periodic logging was initiated in the CH-5 (Chickamauga Group), WCR-2 (Knox Group), and WOL-2 and CH-3 (Conasauga Group) open boreholes. This activity began long before the chemical analyses of these wells became available. Boreholes where anomalies in existing resistivity and conductivity logs had been observed were selected as monitoring wells. When the chemical analyses became available, it was apparent that the interface with the brine had been monitored only in the WOL-2, CH-5, and (possibly) CH-3 boreholes. The interface monitored in the WCR-2 borehole and the upper sections of the CH-3 and WOL-2 boreholes separated the freshwater in the shallow system and the brackish water in the underlying transition zone.

The brine interface was located 60 m (195 ft) below land surface in the CH-5 corehole (Chickamauga Group) and 137 and 177 m (450 and 580 ft) below land surface in the WOL-2 and CH-3 boreholes, respectively (Conasauga Group) (Fig. 8a,b,c). The temporal variations documented in the location of this interface in the CH-5 corehole were small (Fig. 8a). Maximum conductivity values (175,000 micromhos/cm) were observed at the bottom of this corehole during the summer and the minimum values were observed during the winter (160,000 micromhos/cm). The conductivity gradient at the interface in the CH-5 corehole varied over time and was greatest in late summer (August and September 1993) and smallest in winter (October, November, and December 1993). The dilution by winter precipitation percolating through the overlying shallow aquifers probably accounts for these observations.

Fig. 6. Precipitation and water-level fluctuations in the deeply cased HHMS-2a and GW-711 wells. Water-level variations were monitored weekly.

Fig. 7. Precipitation data and continuous measurements of water level, electrical conductivity, and temperature in the HHMS-2a well between December 1994 and May 1995.

Fig. 8. Temporal variations of the position of the interfaces separating the saline and brackish groundwater and the brackish and fresh groundwater in the (a) CH-5, (b) WOL-2, (c) CH-3, and (d) WCR-2 boreholes.

Temporal variations in the location of the brine-brackish water interface in the WOL-2 borehole amounted to 6 m (20 ft). The interface was highest [at 134 m (440 ft) below land surface] during the summer and lowest [at 140 m (460 ft)] during the winter (Fig. 8b). Two of the six temperature profiles run simultaneously with the conductivity logs for the WOL-2 borehole showed temperature increases near the brine-brackish water interface.

Because the deeper section of CH-3 became blocked and therefore could not be reached more than once, no information exists from this borehole on possible temporal variations of the brine interface. However, at 91 m (300 ft), conductivity logs from different months seem to combine into roughly one line (Fig. 8c). Temperature profiles from this corehole revealed no major increases near the conductivity interface.

The interfaces between the fresh and brackish groundwater in the WOL-2 and CH-3 boreholes (Conasauga Group) were each located at about 61 m (200 ft) below land surface. The interfaces fluctuated and 30-, 14-, and 23-m (100-, 45-, and 75-ft) variations in their position were observed in the WOL-2, CH-3, and WCR-2 boreholes, respectively (Fig. 8b,c,d). In the WOL-2 and CH-3 boreholes, the freshwater-brackish water interface was higher in the summer (August 1994) than at the end of the winter (similar to the brackish water-brine interface variations observed in the WOL-2 borehole), correlating with the decreases in water level of 0.5 m (1.64 ft; summer) and 2.5 m (8 ft; winter). This correlation could result from either an increased contribution of the deep brine as the hydraulic head of the overlying freshwater system decreases or from reduced dilution of the same brine by the overlying freshwater. In the WOL-2 borehole, temperature increases were observed near the conductivity interface between fresh and brackish groundwater. However, when plotted on a monthly basis, in four out of five profiles (April, May, August, and November) the temperature increase was observed 15–30 m (50–100 ft) above the conductivity increase.

An opposite conductivity pattern was observed in the WCR-2 borehole, where the highest interface was observed in April and December 1993 and the lowest in August and September 1993. No correlation between the location of the interface and water level could be documented.

The fluctuations occurred over a short time. For instance, the 14-m (45-ft) change in the location of the interface in the WCR-2 borehole was observed within the 3 weeks separating the measurements (September 29 and October 20, 1993).

Significant temporal variations were observed in the electrical conductivity of the upper section of these uncased boreholes. For instance, in the WOL-2 borehole, conductivity increased by 900 micromhos/cm between April and August 1994. Generally, conductivity increased throughout the summer.

6. DISCHARGE POINTS

Potential outlets for the brine may be either saline springs or upward leakage into more permeable zones. Hundreds of springs issue inside the ORR and along its boundaries. Topographic maps dating back to 1940, before the Tennessee Valley Authority constructed the dams on the Clinch River, show additional springs that were later flooded by the higher water stage. A year-long springs survey along two transects [covering (21 km²)] in the eastern area of the ORR was begun in the spring of 1992 to identify these outlets. The survey included measurements of electrical conductivity, temperature, and dissolved oxygen in more than 200 springs along these transects, as well as chemical and isotopic analyses of selected springs (Jones 1995). No temperature anomalies were observed, and only a few springs had electrical conductivity values >0.6 mmhos/cm or anoxic water. However, three springs showed helium peaks, which could reflect some contribution from a deeper flow component (more details in Chap. 9) (Jones 1995). Sampling of Oliver Spring north of the ORR, reported to have a high mineral content (Killbrew 1874), and Sulphur Spring northeast of the ORR revealed chemically reduced water containing low salt concentrations (2.53 and 0.89 mmhos/cm, respectively).

The absence of documented outlet points for the brine implies that it either seeps into adjacent, more permeable formations or is stagnant. Water-level fluctuations observed in the deep system, and chemical and isotopic data discussed in Chap. 9, do not support the latter explanation. On the other hand, seepage into adjacent permeable formations must be small in volume, as the water salinity in the Knox aquifer is generally low. A survey of salinity anomalies in wells tapping the shallow system yielded a list of about 43 shallow [<30 m (100 ft)] wells, containing groundwater with Cl concentrations >100 mg/L (background salinity is ~5 mg/L) and a Na:Cl mole ratio <0.7, typical of the underlying brine (further discussion on the brine chemistry in Chap. 9) (Table 2). However, many of these wells are located in sites that could be affected by waste-disposal facilities (David Watson and Tom Zondlo, Oak Ridge National Laboratory, personal communication, Oct. 1994), and groundwater in some of them is already contaminated (Table 2). The observed increased salinity could, therefore, be a result of surface processes, rather than of brine discharge. Access to most of these wells for sampling and logging was denied because they are included in the U.S. Environmental Protection Agency sampling program at the ORR. Monthly monitoring of the groundwater's electrical conductivity in one of these wells, GW-057, began in March 1995. The three available profiles have not produced any meaningful conclusions regarding the temporal salinity variations in this well.

Table 2. Shallow boreholes containing groundwater with a Cl content >100 mg/L and a Na:Cl ratio <0.7

Well	Area ^a	Depth (ft)	Cl content (mg/L)	Documented contaminants ^b
985	X-10 WAG3	35	255–267	
986	X-10 WAG3	62.5	326–415	
997	X-10 WAG3	33.5	102–11	
BRW-015	K-25	60	107	
BRW-054	K-25	72	110	Mn
BRW-056	K-25	73	100	Mn
TMW-006	K-25	38	100	Mn, alpha, beta
TSW-004	K-25	15	259	As, alpha, beta
UNP-002	K-25	27	529	Ba, B, Cr, Pb, Mn, PCB, alpha
UNW-001	K-25	20	345	Mn
UNW-002	K-25	12.3	290	B, Mn, alpha, beta
UNW-003	K-25	11.5	618	Ba, Cd, Cr, Mn
UNW-004	K-25	17	157	Cd, Mn
UNW-005	K-25	11	478	B, Mn
UNW-009	K-25	13	200	Cr, Pb, Mn
UNW-028	K-25	51	152	Cr, Mn, beta
UNW-052	K-25	32	363	Mn
GW-014	Y-12 BG	3.2	110	Ba, B, Mn, VOC
GW-027	Y-12 BG	0.5	290	Ba, B, VOC
GW-039	Y-12 BG	2.5	119	Cr, Fe, Pb, Mn
GW-053	Y-12 BG	9.7	100	As, VOC
GW-057	Y-12 BG	5	149	As, Cr, Fe, Mn
GW-127	Y-12 S3 ponds	4	339	Cr, Ti, U, Mn, alpha, beta, NO3
GW-148	Y-12 NHP	1.1	101	Cr, Fe, Mn
GW-152	Y-12 NHP	7.3	100	Fe, Pb, Ti, Mn
GW-153	Y-12 NHP	53	110	As, Fe, Mn, Rad
GW-154	Y-12 NHP	1.2	168	Fe, Pb, Ti, V, Mn, alpha, beta
GW-222	Y-12 NHP	5	103	Fe, Ag, U, Mn, alpha, beta, coliform
GW-229	Y-12 OSL	55	154	Ba, Fe, Mn, VOC
GW-240	Y-12 NHP	29.5	128	Cd, alpha, beta, coliform
GW-277	Y-12 S3 pond	77.4	225	Ba, Fe, Pb, Ti, Mn, alpha, beta, NO3
GW-283	Y-12 Fuel Station	20	115	Ba, Cr, Fe, Mn
GW-284	Y-12 Fuel Station	18	202	Cr, Fe, Ni, Mn, beta, coliform
GW-335	Y-12 WCF	15.7	113	Cr, Fe, Mn, coliform
GW-380	Y-12 NHP	15.5	271	Cr, Fe, Mn

^aBG = burial grounds; K-25 = Oak Ridge K-25 Site; NHP = New Hope Pond; OSL = Old Sanitary Landfill; WAG = Waste Area Grouping; WCF = waste coolant factory; X-10 = Oak Ridge National Laboratory; Y-12 = Oak Ridge Y-12 Plant.

^bNO3 = nitrate; VOC = volatile organic compound.

7. EVIDENCE OF HIGH HYDRAULIC CONDUCTIVITY

A variety of borehole techniques, including packer, slug, and slow-recovery tests, were used to measure the hydraulic conductivity of the rocks (Dreier and Toran 1989; King et al. 1988; Solomon et al. 1992). These tests were run primarily in the Conasauga aquitards, but some were also run in the Chickamauga aquitards (Environmental Restoration Program 1992). Estimated values of hydraulic conductivity obtained through the use of these techniques ranged from 10^{-5} to 10^{-9} cm/s, with mean values of 10^{-7} or 10^{-8} cm/s for most areas (Solomon et al. 1992). The low permeability values may reflect the hydraulic properties of the unfractured matrix. These properties are difficult to measure in fracture zones, but the few available measurements suggest the presence of locally increased fracture density resulting in potentially enhanced flow. Although the number of permeable fractures generally decreases with depth, their presence at depth has been documented in many of the deep coreholes and wells (Dreier and Caldenaro 1993; Haase et al. 1987a; King et al. 1988). Of the 15 wells drilled into the Maynardville Formation during 1991 and 1992, 12 had water-producing fractures at depths of >50 m (164 ft) (Shevenell et al. 1992). Fractures have been assumed to account for increases in permeability, as well as pressure, temperature, and hydrochemical anomalies and the presence of contaminants in many boreholes (Dreier and Toran 1989; Dreier et al. 1991; Haase and King 1990; King et al. 1988).

These observations suggest that characterization of the deep system with extremely low estimates of hydraulic conductivity may be an oversimplification. Groundwater flow and solute transport in this zone are greatly affected by the discontinuities in the low-permeability environment, and those features may occur more abundantly than previously assumed, especially in the karst-affected formations of the Knox Group. This conclusion calls for parameter-estimation techniques that are more suitable for fractured media than the ones practiced in the past on the ORR. Borehole methods that use concentration gradients in space and time (Ronen et al. 1986; Tsang et al. 1990) or accurate flow-meter measurements in packed intervals (Moore and Young 1992) were designed specifically for dual-porosity, dual-permeability environments and hence, could be more successful. One of the few flow measurements carried out in the deep flow system at corehole CH-9 (where saline water was documented) revealed high flux at a depth exceeding 100 m (328 ft) (Moore and Young 1992) (Fig. 9). Indeed, high tritium levels found later in a packed interval at the bottom of this corehole (Table 1) suggest contamination from the land surface assisted by deep active flow.

Fig. 9. Groundwater flux through fractures in the CH-9 corehole. The flux was measured by means of a flowmeter. The test was performed on November 15, 1991. *Source:* Moore, G. K., and S. C. Young. 1992. Identification of groundwater-producing fractures by using an electromagnetic borehole flowmeter in monitoring wells on the Oak Ridge Reservation, Oak Ridge, Tennessee. ORNL/ER-91. Oak Ridge National Laboratory.

8. TEMPERATURE VARIATIONS AT DEPTH

Temperature anomalies recorded in temperature logs (Dreier and Toran 1989; Dreier et al. 1991) are an effective means of identifying fractures and groundwater conduits in boreholes that have no cores. They are also useful for the detection of vertical flow gradients where well clusters are unavailable. Temperature deflections in two deep wells (HHMS-8a and -3a, locations shown in Fig. 3) showed an increase of up to 2.5°C, which was interpreted as resulting from the influx of water that had been transported from a deeper source [at least 152 m (500 ft) below the logging interval] along a fault zone (Dreier and Toran 1989).

Periodic logging may help identify recharge-related temperature effects (Shuster and White 1971; Winslow et al. 1965) and assess the relationships between the shallow and deep systems. During 1993 and 1994, temperature profiles were logged monthly in the WOL-2, WCR-2, and CH-3 boreholes. In the WOL-2 borehole, temperature variations among the profiles logged from April through November 1994 did not exceed 1°C. Temperature increases were observed near the freshwater-brackish water and brackish water-brine interfaces. The only major temperature increase, by as much as 3°C, was observed near the lower brine-brackish water interface in the November measurement. In the CH-3 corehole, the temporal variations among the profiles logged from December 1993 through September 1994 did not exceed 0.5°C. The seasonal temperature variations observed in the WCR-2 borehole did not exceed 0.3°C, and no consistent temperature pattern could be identified at the freshwater-brackish water interface near the bottom of the hole.

9. CHEMICAL AND ISOTOPIC COMPOSITION

Nine wells inside the ORR were sampled for chemical and isotopic analyses as part of this study. These boreholes included the three coreholes in the ORNL area (CH-5, CH-6, and CH-9), which are about 122 m (400 ft) deep in the Chickamauga Group; one borehole in the western ORR (WCR-2) drilled into the Knox Copper Ridge Formation at ~152 m (500 ft); and five wells, which are bored into the Conasauga Group (GW-121, GW-211, GW-214, HHMS-6a, and WOL-2) located along the western part of the ORR, in Melton Valley, and near Melton Lake. Three of these five boreholes are ~122 m (400 ft) deep; the GW-121 and WOL-2 boreholes are 183 and 268 m (600 and 880 ft) deep, respectively. Four additional oil wells outside the ORR were also sampled, and their brine was analyzed. Despite the screening process, designed to select monitoring wells containing brine which had diversified lithological and areal coverage, only three of the nine wells sampled in the ORR appeared to contain highly salinized water (7,800 to 64,900 mg/L Cl). The other wells contained water with elevated salinity (a few hundred milligrams per liter TDS) and probably tap the transition zone between the brine and the shallow fresh groundwater.

9.1 CHEMICAL AND ISOTOPIC FEATURES OF THE ORR BRINE

Groundwater salinity in the deep system ranged in the various deep wells from a few thousand to >200,000 ppm TDS, possibly as a result of a mixing between diluted and very saline end members (Table 1). The freshwater end member is typical of the shallow groundwater system, as evidenced by the regression lines shown in Fig. 10 that lead to the origin. The saline end member is represented by the halite-saturated groundwater sampled from the WOL-1 borehole (Table 1, Fig. 3).

The major ions in the brine were sodium and chloride (Table 1). Sulfate and bicarbonate concentrations were extremely small, except in the more dilute water (<20,000 ppm TDS) (Table 1). Consequently, although sodium was the dominant cation, the more saline waters were Ca-Cl brines. The dominant ions in the six dilute groundwater samples were Na, Ca, Cl, and SO₄, resulting in a Na-Cl facies in three samples (the CH-6, GW-121, and GW-214 boreholes), Ca-SO₄ in another two samples (the WCR-2 and GW-211 boreholes), and Na-Cl-SO₄ in one sample (the CH-9 corehole). From the chemical facies of the water samples, some of the boreholes apparently tapped the top of the brine zone in the Chickamauga Group (the CH-6 corehole) and Conasauga Group (the GW-121 and GW-214 boreholes), whereas the other boreholes were within the transition zone containing Ca-SO₄ water in the Maynardville Formation (the WCR-2 and GW-211 boreholes). Ca-SO₄ water is typical of the transition zone in the Knox aquifer (Toran and Saunders 1992). Water from the CH-9 corehole with Na-Cl-SO₄ appears to have been sampled from the interface between the brine and the transition zone.

The more dilute groundwater samples followed the seawater evaporation line (Figs. 10 and 11). The concentrated groundwater samples deviated from this line and were enriched with divalent ions, as indicated by the very high Carpenter function (CF) values (Carpenter 1978) with respect to seawater (Table 1) (Fig. 11a). Among the divalent ions, Ca and Sr were enriched relative to evaporating seawater by factors of 2.8 and 10.1, respectively (Fig. 11b,c), whereas Mg was depleted to 0.15 of that found in seawater (Fig. 10d), resulting in Ca:Mg values that were always >1 (Fig. 11d).

Fig. 10. Relationships between (a) chloride, (b) sodium, (c) potassium, or (d) magnesium and bromide in the Oak Ridge Reservation deep groundwater. Sodium, chloride, magnesium and potassium are depleted with respect to evaporating seawater (arrow, McCaffrey et al. 1987). Analyses from Haase et al. (1987) and from Switek et al. (1987) are marked as circles; analyses of samples collected during the study from the Oak Ridge Reservation and from oil wells outside the reservation are marked as triangles and squares, respectively.

Sources:

- Haase, C. S., J. Switek, and S. H. Stow. 1987. Geochemistry of formation waters in the lower Conasauga Group at the new hydrofracture facility: Preliminary data from the deep monitoring (DM) wells. ORNL/RAP-6. Oak Ridge National Laboratory.
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Fig. 11. Relationships between the Carpenter function (a) ($CF = Ca + Mg + Sr - SO_4 - HCO_3$), (b) Ca, (c) Sr and Br concentrations, and (d) Na:Br vs Ca:Mg in the Oak Ridge Reservation deep groundwater. High CF, Ca, and Sr values with respect to evaporating seawater (arrow, McCaffrey et al. 1987) suggest divalent ion (Ca and Sr) enrichment. Analyses from Haase et al. (1987) and from Switek et al. (1987) are marked as circles; analyses of samples collected during the study from the Oak Ridge Reservation and from oil wells outside the reservation are marked as triangles and squares, respectively. Source: McCaffrey, M. A., B. Lazar, and H. D. Holland. 1987. The evaporation path of seawater and the coprecipitation of Br and K with halite. *J. Sediment. Petrol.* 57:928–37.

The ORR brine is either enriched in Br with respect to evaporating seawater or, alternatively, depleted in Na and Cl (Fig. 10a,b). The mean values for the Cl:Br and Na:Br weight ratios were only 93 and 34, respectively, whereas these values for seawater are 291 and 163, respectively. If the ORR brine composition is taken to be the result of the depletion of certain constituents rather than of the enrichment of Br (which is more problematic to account for, as is discussed later), then Na and Cl are depleted to 0.38 and 0.43 of their relative concentrations in seawater. Potassium was depleted in the more dilute samples and enriched in the more saline groundwater samples (Fig. 10c).

Na:Cl values varied from 1.85 to 0.36 (mean value 0.58). Nonmarine values (above 0.86 molal ratio) were documented in the less-concentrated samples, whereas the low values were observed in the higher brine concentrations (Fig. 12a). Br:Cl values varied from 0.0062 to 0.0026, with slightly increasing values in the more concentrated water (Fig. 12b).

In a preliminary survey, ORR brine appeared to contain a high concentration of helium. For instance, in the multiport wells GW-726 and GW-722 in Bear Creek Valley, dissolved helium concentrations varied from near atmospheric solubility values (50 $\mu\text{cc/kg}$) at shallow depths to nearly 10,000 and 3,000 times greater than atmospheric values at depths of 152 and 175 m (500 and 575 ft), respectively (Kip Solomon, University of Utah, personal communication, May 1995).

The ^{18}O and deuterium values of the more dilute water (<10,000 ppm TDS) varied from -5.57 to -6.10‰ and from -37.20 to -38.86‰, respectively. These samples were aligned with the meteoric line and plotted on the basis of 39 precipitation events sampled during 1992 and 1993 (Halleran 1995) (Fig. 13). Two water samples with higher salinity had similar ^{18}O values but were enriched in deuterium (-28.6 and -29.2‰), causing them to shift slightly above the meteoric water line (Fig. 13). Four analyses of brine sampled during this study from oil and gas wells outside the reservation [tapping the Knox Group and the Monteagle Limestone (Mississippian)] showed a deviation from the meteoric line to the right, which is typical of oil-field brines (Kharaka and Carothers 1986; Richter and Kreitler 1986) (Fig. 13).

The saline groundwater sampled during this study contained tritium [83.7 tritium units (TU) in the CH-5 corehole, 2.9 TU in the HHMS-6a borehole, and 9.9 TU in the WOL-2 borehole; the analytical precision was 0.1 TU], suggesting the influx of post-bomb water to depths exceeding 268 m (880 ft). No tritium should have been found in a system hydraulically disconnected from the active, shallow aquifers. This result was shown to be real, as possible contamination resulting from exchange with the tritiated atmosphere in the ORR was evaluated by similarly processing tritium-free water from Jackson City, Tennessee, as a blank. Among the more dilute samples, except for that from the WCR-2 borehole (Copper Ridge Formation, Knox aquifer), which had only 0.4 TU (a value that can be considered 0), all the other samples had tritium values ranging from 1.4 to 3576 TU. The samples from the GW-214 (Maynardville) and GW-211 (Conasauga Group/Rome Formation contact) boreholes had the lowest tritium values, 1.4 and 1.8 TU, respectively. The sample from the CH-6 corehole (Chickamauga Group) had 39 TU. The sample from the CH-9 corehole (Chickamauga Group), containing 3576 TU, appeared to be contaminated by wastewater from a nearby storage pond.

The low tritium values in some of the more dilute samples, in contrast to the high tritium values in the saline groundwater samples, are intriguing. The saline groundwater is suggested to come from the less-permeable zones, which may still preserve some residual (tritiated) drilling fluids (RaNaye Dreier, ORNL, personal communication, Oct. 1994). The one-time purging of the sampled interval might not suffice for the complete flushing of these fluids. Conversely, the more dilute groundwater samples were taken from zones likely to have higher

Fig. 12. Relationship between (a) Na:Cl and (b) Br:Cl and Cl concentrations in the Oak Ridge Reservation deep groundwater. Low values of the ion ratios suggest both Na and Cl depletion with respect to evaporating seawater (arrow, McCaffrey et al. 1987). Analyses from Haase et al. (1987) and from Switek et al. (1987) are marked as circles; analyses of samples collected during this study from the Oak Ridge Reservation and from oil wells outside the reservation are marked as triangles and squares, respectively.
Source: McCaffrey, M. A., B. Lazar, and H. D. Holland. 1987. The evaporation path of seawater and the coprecipitation of Br and K with halite. *J. Sediment. Petrol.* 57:928-37.

Fig. 13. Oxygen-18 and deuterium data for Oak Ridge Reservation precipitation (open circles) (Halleran 1995), the Oak Ridge Reservation deep groundwater (triangles), and oil and gas brines sampled outside the reservation (squares) (this study). The plotted line is the world meteoric water line (Craig 1961). The local meteoric line does not deviate much from the global line (Halleran 1995).

Sources:

Craig, H. 1961. Isotopic variations in meteoric waters. *Science* 133:1702-03.

Halleran, A. 1995. Comparison of hydrologic cycle components for pre-storm and storm conditions, Walker Branch Watershed, Oak Ridge Reservation. M.Sc. thesis. The University of Tennessee, Knoxville, Tenn.

permeability, resulting in complete flushing of all residual drilling fluids before their packing and sampling. According to this hypothesis, the tritium values from these zones are the only reliable and representative values.

To assess this hypothesis, electric logs available from the deep [~427 m (1400 ft)] WOL-1 borehole were examined. This borehole is located ~300 m (~1000 ft) away from the WOL-2 borehole (Fig. 3) where a value of 9.9 TU was documented, and both holes tap similar Conasauga Group formations. The documented spacings between the lateral, long-normal, and short-normal logs were negligible, suggesting no significant invasion of drilling fluids (Dewan 1983). In addition, 6 to 7 years have elapsed since the drilling of the WOL-2, CH-5, and HHMS 6a boreholes, a reasonable time to allow for natural flushing of the residual fluids away from the vicinity of the boreholes. Finally, tritium contamination observed in the CH-9 corehole suggests that pathways for recent water are available from land surface to at least 122 m (400 ft). Because no other contaminants have been detected in this well, the observation cannot be related to the contaminant's higher density. Because the corehole is located far from any hydrofracture facility, these pathways to the deep system are natural. In light of this contamination case, the geophysical observations, and the time elapsed since the drilling of these boreholes, the tritium data appear to be representative of the formations sampled.

The ^{14}C concentrations support the tritium results, as the saline samples contained recent water [98 percent of modern carbon (pmc) in the HHMS-6a borehole, 78.9 pmc in the CH-5 borehole, and 78.3 pmc in the WOL-2 borehole]. The presence of tritium in these samples suggests the mixing of recent water with another type of water having longer residence time. Under these circumstances, the calculated age of the groundwater samples (160 years in HHMS-6a, 1910 years in CH-5, and 1960 years in WOL-2), determined by using ^{14}C and ^{13}C data, is meaningless. In the more dilute samples, ^{14}C was lowest in the WCR-2 borehole, amounting to only 1.53 pmc, an equivalent of ~17,000 years (after correction with ^{13}C data). Because this is the only sample that had no tritium, an indicator of mixing, this is also the only sample for which groundwater residence time could be calculated. The calculated residence time for the other samples is only a minimum value, and the residence time of the older component could be much longer.

The sample from the GW-214 borehole (Maynardville), which had a higher percentage of modern carbon (2.88 pmc), yielded a longer residence time, exceeding 28,000 years, as a result of its high ^{13}C value (+0.9 per mil). Because only low tritium activity was observed in this sample (1.4 TU), the dilution with recent water must have been small, and the calculated residence time may be considered a good approximation. The sample from the GW-211 borehole, which had a low tritium value, had insufficient amounts of carbon for the ^{14}C analysis. The samples from the GW-121, CH-6, and CH-9 boreholes had 27, 13, and 57 pmc, respectively, resulting in calculated residence times of ~10,000, 16,000, and ~4,000 years, respectively. These are minimum residence times for the older water component in these samples because of the high tritium concentrations observed in these wells.

9.2 SPATIAL AND TEMPORAL VARIATIONS OF ORR BRINE CONCENTRATIONS

The large variations in concentration observed in the ORR brine could not be tied to chemical evolution along a probable flow path because of the sparse areal coverage of the data and the complex geology. In the past, when the sampling of deep wells revealed only brackish water, it was generally assumed that in that location brine water was present in deeper, untapped zones (Dreier et al. 1991; Solomon et al. 1992). However, groundwater sampling in the

monitoring wells surrounding the hydrofracture facility [where low-level radioactive liquid had been mixed with cement to a slurry and injected into the subsurface (Haase et al. 1987c)] resulted in large spatial variations in chemical composition in the same area, formations, and depth. For instance, the DM-1RM and DM-2RM wells are located about 640 m (2100 ft) apart, and their uncased interval in the Rome Formation is similar [333 to 350 m (1092 to 1149 ft) and 330 to 389 m (1084 to 1275 ft), respectively]. However, chloride concentrations in their sampled groundwater differ by almost 40,000 ppm (91,000 vs 130,000 ppm, respectively) (Haase et al. 1987c) (Table 1).

The difference in groundwater salinity in these wells could be attributed to waste injection activities in the area. Because the chloride concentration of the injected waste did not exceed 5000 ppm (Switek et al. 1987), the injected water would not have contributed significantly to the overall chloride concentrations. However, the injected water could have diluted the original brine to a variable, unknown extent. Although injected water reached the DM-1RM and DM-2RM wells (as evidenced by the presence of ^{90}Sr in their groundwater) and could account for the spatial salinity variations, similar salinity variations were also observed in the monitoring wells penetrating the formation overlying the injection zone where no contamination (i.e. dilution) was documented. Chloride concentrations observed in two of these wells (RC-S200 and RC-SW280) located <122 m (400 ft) apart and tapping the same open interval [top at 150 to 180 m (490 to 590 ft) and bottom at 180 to 210 m (590 to 689 ft)] and the same formations (Rutledge Limestone and Rogersville Shale) were 71,000 and 120,000 ppm, respectively, a 49,000 ppm difference (Switek et al. 1987) (Table 1). Because these wells were sampled in the past on three different occasions (Switek et al. 1987), these salinity variations appear to be real. The implied lack of spatial hydraulic connection and circulation is, in fact, typical of fractured aquitards containing fracture sets that do not connect on a small scale (Nativ and Nissim 1992).

In addition to spatial variations in salinity, temporal changes were also observed in wells that had been sampled several times in the past. The difference in chloride concentrations between two subsequent samplings at the same depth amounted to 35,000, 37,300, and 19,000 ppm in three monitoring wells near the hydrofracture facility (RC-SW280, RC-S200, and RC-E200) (Switek et al. 1987) (Table 1). The observed salinity variations were related to groundwater movement within the strata surrounding the wells (Switek et al. 1987). This conclusion, however, does not conform with the large spatial variations among these wells, suggesting that groundwater movement is restricted to small, disconnected enclaves. A possible explanation that could link both observations is active groundwater circulation along hydraulically separated fracture nets.

9.3 BRINE OCCURRENCE IN THE APPALACHIAN REGION

The occurrence of brine and salt beds has been documented throughout the Appalachian region. Beds of Silurian-age rock salt underlie southern New York, much of western Pennsylvania, eastern Ohio, and northern West Virginia. Mississippian-age rock salt is found in southwestern Virginia. In addition, natural brine is found in wells in strata ranging in age from Cambrian to Pennsylvanian in Ohio, Pennsylvania, West Virginia, Kentucky, and Tennessee (Kreiger et al. 1957).

The Silurian salt beds (consisting primarily of halite) are part of a sequence of shale, dolomite, and evaporites. This sequence is referred to as the Salina Group in New York and in most of the subsurface in Ohio and Pennsylvania. To the southeast and southwest, rocks of the Salina Group grade into limestone and shale, and equivalent rocks in the Valley and Ridge

Province, called the Tonoloway Limestone, Wills Creek Shale, and McKenzie Formation, do not include salt beds. In Ohio, salt beds thin and disappear but reappear as a thick sequence in the Great Lakes region (Kreiger et al. 1957).

Brine-bearing sands occur throughout the Pennsylvanian system, but the most important are the Salt Sand and Maxton Sand in the Pottsville Formation. In the Mississippian system, the most important brine-producing sand is the Big Injun Sand, a part of the Pocono Formation. Many drilling logs from oil-producing Mississippian formations in the Cumberland Plateau, Tennessee, report the occurrence of brine at depth (Milhous 1959). The Upper Devonian shale sequence contains many sand beds that yield brines in Pennsylvania and West Virginia. The Oriskany Sandstone of the Lower Devonian contains concentrated brine in Pennsylvania, Maryland, Ohio, and West Virginia. Brine also occurs in the Silurian- and Devonian-age limestone sequence in Kentucky (referred to as coniferous by drillers). In Kentucky, below the Silurian Salina Group lies the brine-bearing Newburg Sand. Brines have been recorded in the Ordovician Trenton Formation, St. Peter Sandstone, and Knox Dolomite (Upper Cambrian and Lower Ordovician).

9.4 GENESIS OF THE BRINE

During the past 30 years, researchers have suggested that several processes could generate brine, including (1) rock-water interactions (e.g., dissolution, recrystallization, and ion exchange), (2) subareal evaporation of seawater, and (3) shale-membrane filtration. Proposed origins of brines imply the degree to which groundwater circulates in the deep basins. The rock-water interaction model postulates that the original groundwater (connate water) has been thoroughly flushed and replaced, requiring a large water-to-rock volume ratio. The evaporated seawater model implies that connate or modified connate water is still present. The first two models are not necessarily mutually exclusive because both may apply where displacement of modified connate brine by meteoric water moving into the basin is incomplete (Bein and Dutton 1993). The geologic history of the basin, the abundance of minerals, plausible hydrodynamic conditions, and chemical and isotopic composition of the brine serve as constraints on these brine-generating processes.

9.4.1 Plausible Mechanisms and Their Signature

The activation of shale-membrane filtration requires a high shale content and a high pressure differential. This process results in heavier values for ^{18}O and deuterium with increasing salinity in the residual brine (Graf et al. 1966; Kharaka and Carothers 1986). However, the increase in ion concentration in the original formation water is limited (Egeberg and Aagaard 1989), and its importance in natural systems has been challenged (Fontes and Matray 1993; Knauth and Beeunas 1986). An inverse relationship between salinity and ^{18}O and deuterium, or the presence of constituents that should be transferred to the effluent water rather than remain in the residual brine, suggests that membrane filtration is not the controlling salinization process.

Evaporation of seawater to a point beyond halite precipitation results in a residual brine having low Na:Cl and high Br:Cl values (Eugster and Jones 1979; Holser 1979; McCaffrey et al. 1987) and enriched values of ^{18}O and deuterium (Fontes and Matray 1993; Knauth and Beeunas 1986). An inverse relationship between salinity and heavier isotopes precludes evaporation as a potential salinization process and suggests that the saline end member is isotopically depleted.

Brine originating from halite dissolution results in relatively high Na:Cl values (~1) (Eugster and Jones 1979) and low Br:Cl values (Holser 1979; McCaffrey et al. 1987). Its ^{18}O and deuterium values are not necessarily enriched and depend on the isotopic composition of the dissolving water (Knauth and Beeunas 1986).

Water-rock interactions may modify the original composition of the brine generated by any of the above processes. Kerogen maturation and halite recrystallization preferentially release Br to solution (Land and Macpherson 1992; Land and Prezbindowski 1981; Stoessel and Carpenter 1986; Wilson and Long 1984) and increase Br:Cl values. Ion exchange with clay minerals or albitization of plagioclase or K-feldspars could account for low Na:Cl values and increased Ca concentrations in brines (Land and Prezbindowski 1981). Dolomitization of limestone could also account for high Ca and Sr concentrations and low Mg:Ca values (Carpenter 1978; Stoessel and Moore 1983). However, high CF values with respect to the evaporating seawater trajectory suggest enrichment of divalent cations, unaffected by dolomitization, recrystallization, or precipitation of CaCO_3 or CaSO_4 (Carpenter 1978). In that case, the enrichment of divalent ions and the depletion of sodium can be attributed to the formation of sodic clays, illite, and authigenic potassium-feldspar from kaolinite. During these reactions, hydrogen ions are released and available to react with carbonate minerals (Stueber and Walter 1991). Modification of brine by water-rock interactions should not result in major variations with regard to the isotopic composition, unless large volumes of deuterium have been exchanged, resulting in depleted deuterium values in the water phase (Kharaka and Carothers 1986). Interaction with H_2S gas may result in deuterium enrichment (Friedman and O'Neil 1977; Fritz and Frape 1982).

9.4.2 ORR Brine

The origin of the deep brine in various study areas in the Appalachian region has been discussed extensively by previous researchers, and they seem to generally agree that the brine is derived mainly from ancient seawater entrapped during sedimentation (N. S. Davis, Oak Ridge National Laboratory, personal communication, 1991; Price et al. 1937; Rose and Dresel 1990; Stout et al. 1932; Toran and Saunders 1992). According to Poth (1962) and Davis (1991), the compaction and stresses [mentioned by Rose and Dresel (1990)] resulted in ultrafiltration that produced the brine. According to Toran and Saunders (1992), the brine encountered in the ORR might have occupied a structurally higher position in the past and is continuously being flushed out by the fresh groundwater system. Where flushing becomes inefficient, brine can be found. All the studies support the concept that the deep system containing the brine is hydraulically inactive. It has been recognized (Price et al. 1937), however, that in many instances Appalachian brines seem to include, along with water of marine origin, greater or lesser proportions of groundwater of meteoric source.

9.4.2.1 Halite dissolution model

Although all the afore-listed studies suggest an extremely long residence time for the brine [Rose and Dresel (1990) proposed an age of 300 million years], another alternative, the solution of halite by modern water, needs to be evaluated in the context of the ORR. If halite dissolution is a viable mechanism, brine may be currently formed by actively circulating fresh groundwater that dissolves halite crystals. In that case, the high salinity of the brine does not imply stagnant water but rather an active system that can transport contaminants from land surface to unidentified discharge points.

Halite crystals have been found only in the Rome Formation (Lemiszki 1992; Samman 1975), and whether they can account for the large brine reservoir observed in the ORR is unclear. However, the absence of massive halite deposits in the ORR subsurface does not necessarily eliminate halite dissolution in the past as a brine-generating mechanism. Ranganathan (1991) demonstrated, in the Illinois Basin (where halite beds have never been documented), that if a basal halite bed had been deposited during Cambrian times, at least 60 to 130 m (197 to 426 ft) of the halite could have been dissolved and removed by vertical diffusion during the history of the basin. Consequently, the absence of halite in the basin today does not preclude halite dissolution as the mechanism responsible for brine evolution in the past.

Another alternative is that halite dissolution is not an In Situ process. Bedded halite in the Silurian Salina Group in New York and in most of the subsurface in Ohio and Pennsylvania, as well as the halite in the Early Cambrian Rome Formation southeast of the ORR (Diegel 1988), could be the source of this brine. Brine migration (along several hundred kilometers from the original basin) was probably gravity-driven as a result of the hydraulic gradients caused by Paleozoic orogenies (Oliver 1986), as modeled by Garven et al. (1993). This brine migration was tied to Mississippi Valley-type (MVT) ore formation (zinc, barite, fluorite, and lead) in East Tennessee and adjacent states (Garven and Freeze 1984; Garven et al. 1993; Haynes et al. 1989; Nakai et al. 1993; Ohle 1980). MVT minerals have been dated by $^{40}\text{Ar}/^{39}\text{Ar}$ on low-temperature authigenic K-feldspar (Hearn et al. 1987) and by $^{87}\text{Rb}/^{86}\text{Sr}$ on sphalerite (Branon et al. 1992; Nakai et al. 1990, 1993), providing upper- and lower-limit constraints on the migration time of the ore-forming brine [380 and 280 million years (MA), respectively]. The suggested "time window" is post-Silurian, after bedded salt was deposited as the Salina Group, and can be tied to the Alleghenian orogeny (270 MA) or to the earlier Acadian orogeny (380 MA) which could provide the driving mechanism needed for the brine's migration (Garven et al. 1993).

The process of simple halite dissolution by modern (or ancient) meteoric water discussed herein, however, cannot account for the high CF and Br:Cl values (Figs. 11a and 12b) and the low Na:Cl values (Fig. 12a). In simple halite dissolution (1) high Ca and Sr concentrations (Figs. 11b,c) would not occur, (2) Na:Cl values would have been closer to 1 rather than the mean value of 0.59 and the minimum value of 0.46 approached by the samples with higher salinity (Fig. 12a), and (3) the typical Br:Cl (weight) values would have been around 4×10^{-4} (Richter and Kreitler 1986; Whittemore and Pollock 1979) rather than ranging from 69×10^{-4} to 140×10^{-4} (Fig. 12b). Not only do the ranges of these ion ratios deviate from the typical values of brine formed by halite dissolution but so do their patterns: Na:Cl ratio values decrease with increasing salinity, whereas Br:Cl and Ca:Na ratio values increase with it, suggesting a saline end member depleted in Na and enriched in Br and Ca. Consequently, if halite dissolution is actually the mechanism producing the brine, then aside from this process, a major modification of this brine by a variety of water-rock interactions has to be invoked to account for all its observed features.

Albitization and formation of sodic clays, in combination with recrystallization of halite could (1) decrease the Na:Cl ratio in the formation water as a result of Na incorporation into the rock phase, (2) increase the Ca in the water as a result of its release from the minerals, and (3) increase the Br content in the solution, following the dissolution and reprecipitation of halite. These mechanisms can account not only for the depleted value of Na:Cl in the ORR brine but also for the low values of Na:Cl (0.6 to 0.7) in brines from adjacent states in which halite beds are abundant (Kreiger et al. 1957; Price et al. 1937; Rose and Dresel 1990; Stout et al. 1932). However, except for two samples from the Conasauga Group (Kopp et al. 1988) and a few samples from the Rome Formation (Siribhakdi 1976), the significant presence of albite was not documented in several studies that used a variety of techniques and described the mineralogy of

the Nolichucky and Pumpkin Valley shale in the Conasauga Group (Foreman 1991; Lee et al. 1987; Maher 1973; Weber 1988).

9.4.2.2 Evaporated seawater model

The ion-ratio ranges and patterns of ORR brine fit the model of modified evaporated seawater, which has precipitated halite, better than they fit the model of freshwater-dissolving halite (Figs. 10 and 12). Given the abundance of halite deposits in the Silurian section, it is reasonable to consider the fate of the evaporatively concentrated Silurian seawater. It seems possible that the extremely dense residual brine may have migrated downward thousands of feet and displaced older seawater from the predominantly marine section. Following the aforementioned Paleozoic orogenies and on the basis of tectonic interpretation, the brine was first driven to the west of the Appalachians, where later uplift in the southern Appalachians drove brine in a northwesterly direction (Garven et al. 1993).

The mean values of the various ion ratios of the saline groundwater samples suggest that the residual brine was evaporated to 22 to 24 times the initial concentration of seawater (McCaffrey et al. 1987) into the range between halite and epsomite precipitation (Fig. 14). The high magnesium content of such brine favored dolomitization and reactions with silicates. Diagenetic reactions with carbonate rocks seem to be responsible for the concentration levels of divalent cations currently observed in the ORR deep waters. Ca:Br relations (Fig. 11b) show a significant enrichment over evaporated seawater, whereas the Mg:Br relations (Fig. 10d) illustrate Mg depletion. The complementary diagenetic relationships shown by these two cations strongly suggest that the ORR brine was affected by dolomitization of limestone (Carpenter 1978). Relations between strontium and bromide reveal very large increases in strontium concentration relative to evaporated seawater (Fig. 11c), also suggesting recrystallization and dolomitization of carbonate minerals. Indeed, dolomite is abundant in both the ORR aquitards and aquifer (Fig. 2). The extremely low concentrations of sulfate in the brine suggest sulfate reduction. This is supported by the unique odor of sulfuric gas emitting from many of the sampled wells. The interaction with the H₂S gas may explain the observed enriched deuterium in the more saline groundwater samples (Friedman and O'Neil 1977; Fritz and Frape 1982) (Fig. 13). The saline end member of the brine was eventually diluted by freshwater, which did not alter the ionic ratios but reduced the formation water concentrations, as evidenced by the horizontal shift shown in Fig. 14 (Fontes and Matray 1993). The freshwater must be modern, as evidenced by its measurable tritium and high ¹⁴C content.

The modified evaporated seawater model has been challenged, however, by Garven et al. (1993), who suspected that the pool of residual brine resulting from the precipitation of halite must have been exhausted by the extensive groundwater circulation predicted by their model. Consequently, they favor halite dissolution as the brine-generating mechanism because of the larger salt reservoir.

9.4.2.3 Ultrafiltration model

The high shale content in the ORR aquitards may support the third mechanism proposed to account for the origin of the brine. Under a suitable pressure differential (which has disappeared over the years of erosional unloading), the shale could act as a membrane, sieving out the water and leaving behind the salts and heavy isotopes. However, the expected positive correlation between salinity and ¹⁸O or deuterium, typical of membrane filtration, was not documented. The

high concentrations of lithium in the ORR brine (up to 88 mg/L), which should be enriched in the membrane effluent rather than in the residual solution, also does not support this mechanism. Whether past pressure distribution at the subsurface could have activated shale-membrane formation is unclear because the current pressure distribution does not provide any supporting evidence.

9.4.2.4 Proposed model

On the basis of our preliminary results, we determined that the salt composition of the brine clearly did not originate from simple halite solution by recent water. Clay-water reactions cannot explain all of the observed data. Shale-membrane filtration does not contradict most of the observed data, but evidence for the required pressure differential throughout the geological past is not available. The chemical composition of the saline end member of the ORR brine closely resembles that of a residuum of original saline water that underwent extensive evaporation and subsequent dolomitization and sulfate reduction. Similar brine features are typical of oil-field brines, which can be found in adjacent basins (Richter and Kreitler 1986). Indeed, hydrocarbons were documented in some ORR deep wells in the Chickamauga Group (CH-4) and in the Knox Group (JOY-2) as well as in deep wells outside the reservation. On the basis of major element composition, high salinity, stable isotope composition, and temperature, Garven et al. (1993), Oliver (1986), and Sverjensky (1984, 1986) linked large-scale brine migration to oil occurrence and ore formation. Both phenomena were observed in or near the ORR.

None of the previously mentioned models preclude recharge of the brine with modern water, as documented by its tritium content and high percentage of modern carbon. The chemical composition of the brine may have been controlled by mid-Paleozoic mineralization of halite and late-Paleozoic migration of the halite-dissolving or residual brine. Modern water subsequently mixed with the brine and diluted it to some extent. However, because of the brine's high ion concentrations, ion ratios would not be easily modified. Consequently, the scenario of an ancient source for the salts, combined with a small volume of recently recharged water, is proposed.

9.5 EQUILIBRIUM CONSIDERATIONS

Geochemical modeling was used to assess equilibrium between the rock matrix and secondary mineralization and the contained fluids. In the absence of highly soluble minerals, chemical and isotopic equilibrium between the rock minerals and the rock fluids may indicate a long residence time. Using the EQ6/EQ3 speciation model, Haase et al. (1987b) found that the water in the Rome Formation and in the lower Conasauga Group with low ionic strength (<1) is saturated with respect to carbonates (calcite, dolomite, strontianite, and smithsonite) as well as to some sulfate minerals (barite and celestite) and aluminosilicates. Their modeling of the water with higher ionic strength suggested that groundwater is also saturated with celestite, strontianite, and halite. In Bear Creek Valley, water in the Maynardville and Maryville

Fig. 14. Relationship between Cl:Br and Cl concentrations in the Oak Ridge Reservation deep groundwater. Analyses from Haase et al. (1987) and from Switek et al. (1987) are marked as circles; analyses of samples collected during this study from the Oak Ridge Reservation and from oil wells outside the reservation are marked as triangles and squares, respectively. SW = sea water; G = gypsum; H = halite; E = epsomite; S = sylvite; C = carnallite; and B = bischofite.

Sources:

Haase, C. S., J. Switek, and S. H. Stow. 1987. Geochemistry of formation waters in the lower Conasauga Group at the new hydrofracture facility: Preliminary data from the deep monitoring (DM) wells. ORNL/RAP-6. Oak Ridge National Laboratory.

Switek, J., C. S. Haase, and S. H. Stow. 1987. Geochemistry of formation water in the lower Conasauga Group at the new hydrofracture facility: Preliminary data from the Rock Cover (RC) wells. ORNL/RAP-5. Oak Ridge National Laboratory.

Limestone was also saturated with respect to carbonates but undersaturated with respect to gypsum, when evaluated with SOLMINEQ.88 (Toran and Saunders 1992) and WATEQF (Chapman-Bailey and Lee 1991).

10. SUMMARY

In this study, existing data from the deep system in the ORR were compiled with newly collected field data and interpreted in light of environmental protection and restoration. Decision-makers need guidance now, even though the conceptual model is incomplete. Given that reality, the following is the best conceptual model of the deep system that the current data will support, together with some possible residual uncertainties.

10.1 EVIDENCE FOR STAGNANT GROUNDWATER

Some evidence exists that supports the concept of stagnant brine at depth and its hydraulic disconnection from the overlying shallow, fresh and active flow zone. The deep system is evidently confined, as indicated by the daily pressure variations. The slow recovery of water level in some boreholes following their purging suggests restricted flow. The location of the interface between the brine and the overlying brackish water, as observed in two boreholes, does not fluctuate much. The high salinity of the water could not have been preserved under intensive deep groundwater circulation. The large spatial variations in the salinity of its contained brine may support an extremely restricted flow in portions of the deeper system. The ion ratios suggest the presence of residual brine, which may have been in the subsurface since the Paleozoic era. Finally, defined outlets of the deep system have not yet been identified, also suggesting the absence of flow.

10.2 EVIDENCE FOR ACTIVE GROUNDWATER

Other evidence supports the potential for groundwater flow in the deep system. Fractures were observed at great depth in many cores, locally enhancing the permeability of the aquitards. Temperature anomalies are tied to some of these fractures, suggesting that they may be hydraulically active. Actual flow through these fractures was measured in some boreholes with a flow meter. Fast (advective) flow and preferential dilution through these fractures may account for the observed recent water component of the brine (evidenced by tritium and high pmc) and spatial variations in salinity. Temporal variations in brine salinity were also related to active groundwater flow. Seasonal water-level variations were observed in some deep wells, suggesting active recharge of the deep system. In the Knox aquifer and in the Conasauga aquitard [at depths of 213 m (700 ft) and 116 m (380 ft), respectively] water-level variations could even be tied to individual precipitation events.

10.3 HYDRAULIC CONTINUITY OF THE DEEP SYSTEM

Similar (but not identical) hydraulic head values in adjacent, deep wells suggest the potential for lateral hydraulic continuity (as opposed to stagnant water). However, the spatial variations in water salinity documented in another set of nearby wells suggest the opposite. The similar water levels can mimic similar topography, without necessarily implying hydraulic connectivity (Toth 1963); however, this situation is more typical of unconfined aquifers than of the confined system in question. In addition, seasonal variations in water levels in some deep wells were observed where water levels in the deep wells were higher than those measured in nearby, shallow wells of the same clusters. This observation suggests that the seasonal variations

could not have resulted from water percolation from the overlying shallow system. Instead, they probably reflect a contribution from outcrops of unknown distance, requiring lateral hydraulic continuity between the outcrops and the wells. The presence of fractures at depth in some boreholes connected to a large, perhaps regional, fracture net, in contrast to a lack of fractures in others, could explain the conflicting observations of (1) slowly recovering water levels in some boreholes with no seasonal response vs (2) seasonal/event variations of water levels in other, nearby boreholes. The spatial variations in salinity can thus be explained either (1) by different, disconnected fracture nets feeding the wells with water having distinct concentrations of solutes or (2) by different fracture densities allowing for various degrees of flushing.

10.4 RELATIONSHIPS BETWEEN THE SHALLOW AND DEEP HYDRAULIC SYSTEMS

Vertical flow between the deep and shallow hydrogeological systems seems possible. Upward flow potential from the deep hydrogeologic system into the shallow one is supported by a large array of observations, including salinity and temperature anomalies in the shallow system, water levels in some well clusters in the Conasauga Group, and water levels measured below and above packed intervals in boreholes in the Chickamauga and Knox groups. Downward flow potential from the shallow to the deep system was documented in some of the wells completed in the Conasauga Group and confirmed by the presence of contaminated water at a depth exceeding 200 m (656 ft) or recent groundwater (with measurable tritium and a high percentage of ^{14}C) at depths of up to 268 m (880 ft).

10.5 MISSING ELEMENTS IN THE CONCEPTUAL MODEL

The geometry of the deep hydrological system and the flow net within it have not yet been defined. Brine has been encountered at depth in each lithological unit in the ORR [except within the explored upper 200 m (~656 ft) of the Knox aquifer]. Its documented depth varies, however, between 52 and 137 m (170 and 450 ft) below land surface. The number of observation points is insufficient to spatially map the brine top over space and time. The horizontal distribution of the brine and its preferred pathways have not yet been assessed. The spatial distribution of major faults and fractures needs to be mapped as they control the pathways and rate of solute/contaminant migration and can potentially enhance dissolution and thus increase permeability. Work in multiport wells that was funded outside the Oak Ridge Reservation Hydrology and Geology Study provides additional information regarding the deep system (e.g., hydraulic head and hydraulic conductivity values, chemical and isotopic compositions) which can be combined in the future with results from this study.

11. CONCLUSIONS

On the basis of existing data, the following description for the deep system addresses most of the afore-listed comments: The deep hydraulic system contains confined brine, whose residence time in the subsurface is probably very long. The brine contained in the deep system originated from an evaporating water body, from which halite had precipitated. The brine was pushed westward following the orogeneses that formed the Appalachian Mountains. Processes such as oil and ore formation and accumulation may have accompanied this brine migration. Although the salts in the ORR brine are very old, a recent contribution of water is evidenced by contamination and by the high percentage of modern carbon and tritium in the sampled saline groundwater. The modern water probably moves along a limited number of active, open fractures at relatively high velocities. However, because of small fracture volume, the total volume of water moving through these fractures is also small. The nonuniform mixing of fresh, recent water with the old pool of brine accounts for the large spatial and temporal variations in brine salinity. Groundwater discharge is probably through adjacent, more-permeable units, where the brine is considerably diluted. Groundwater at great depth is currently recharged, but the volume of water moving through the fracture network is likely to be small. The brine is not isolated from the overlying shallow system, and groundwater flow as well as solute (and contaminant) transport between systems takes place wherever pathways are naturally or artificially provided, but again, the water volumes involved are likely to be small.

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APPENDIX A

Deep Wells Accessed During This Study But Not Monitored

	Well	Area ^a	Borehole depth (ft)	Depth penetrated by EC probes (ft)	Group ^b	Comments
A-1	CH-1	WAG 1	385	390	Chick.	Gradual salinity increase
	CH-2	WAG 1	472	300	Chick.	Gradual salinity increase
	CH-3	WAG 1	400	105	Chick.	Blocked at 105 ft
	CH-12	WAG 1	500	495	Chick.	Brackish water
	WOL-1	South of SWSA 6	1440	1440	Con.	Logged (Kennard), sampled (Switek), Stuck packer
	JOY-2	Melton Valley Access Rd. 2	718	656	Con.	Stuck packers (straddle), thin oil film on top
	CH-143	Kerr Hollow	600	55	Knox	Restriction at 55 ft
	CH-157	Sed. Disp. Basin	540	540	Knox	Freshwater with Radon
	CH-166	Bear Creek Valley	385	385	Knox	Freshwater
	CH-185	Rogers quarry	841.7	841	Chick.	High salinity water from 330 ft down, alpha and beta
	GW-185	Rogers quarry	471	471	Chick.	No water but mud at the bottom
	GW-189	Rogers quarry	210	210	Chick.	Freshwater (planned as substitute for GW-185)

^aSWSA = solid waste storage area; WAG = waste area grouping.

^bChick. = Chickamauga Group; Con. = Conasauga Group.

APPENDIX B

Summary of Project Activities

Data Evaluation

1. Screening geologic, hydrologic, chemical and engineering (borehole construction) information from all the deep (>400 ft) boreholes in the Oak Ridge Reservation (ORR).
2. Screening chemical information from all the shallow (<100 ft) boreholes in the ORR to assess brine contribution to the shallow aquifers.
3. Gathering, screening, and processing chemical information about saline groundwater in the Appalachian Region.
4. Evaluation of the logs and chemical analyses from the Rock Cover wells sampled by CH2M-Hill during the summer of 1994.
5. Processing and evaluation of newly generated data collected during this study.

Field Activities

The field activities that were undertaken at the various boreholes are summarized in Table B.1.

APPENDIX C

Variations in Water Levels, Electrical Conductivity, and Temperature with Respect to Rainfall Events, December 1994–May 1995

Rainfall date	Rainfall amount (in.)	Water-level increase (cm) ^{a, b}	Electric-conductance change (μ s/cm) ^b	Temperature change (°C)
Dec.10	1.24	+0.7 ^b	+15	-0.02
Jan.6	1.65	No data	No data	No data
Jan.11	0.71	+0.6 ^b	-6	-0.02
Jan.14–15	2.81	2.100 ^b	+47	x
Jan.28	1.02	0.700 ^b	x	x
Feb.15–16	2.24	1.400 ^b	x	x
Feb.27–28	0.99	0.860 ^b	-17	x
March 5–8	2.08	2.000 ^b	x	+0.008
March 20	0.82	0.007 ^b	+59	x
April 12	0.49	No data	No data	No data
April 17–21	1.59	x	+33	x
April 23	0.32	0.004	+33	-0.01
May 1	0.89	0.003	+17	-0.01
May 9–19	5.18	+3.7	+115	-0.012

^aThe seasonal increase in water level was not subtracted.

^bObserved response; "x" signifies that no response was observed.

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