SOURCES AND AGES OF GROUND WATER IN UNCONFINED AND CONFINED AQUIFERS BENEATH THE U.S. HIGH PLAINS

Final Technical Report

by

Alan R. Dutton

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Bureau of Economic Geology
W. L. Fisher, Director
The University of Texas at Austin
University Station, Box X
Austin, Texas 78713-7508

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FOREWORD
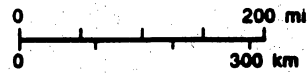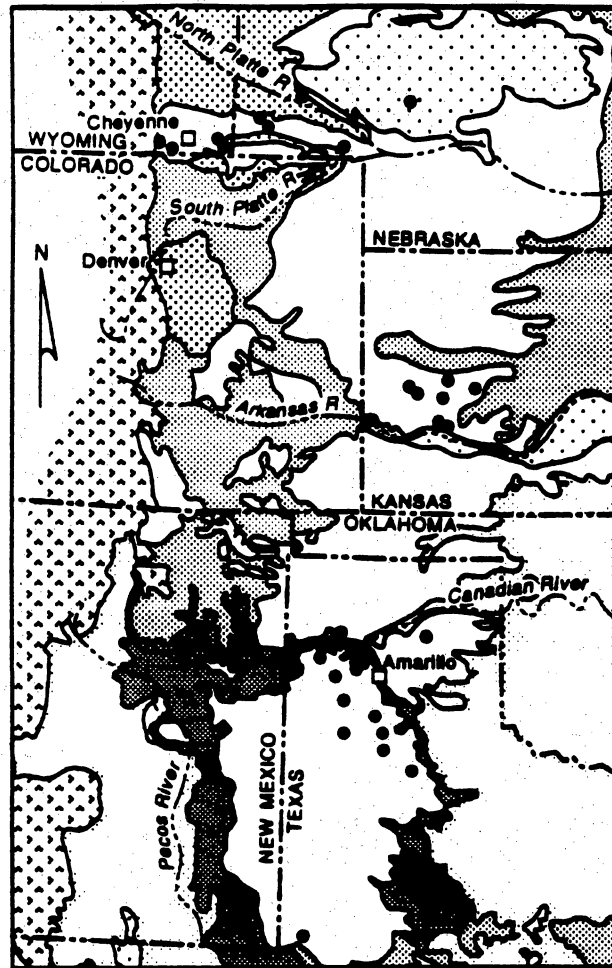
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ABSTRACT

Ground water is a valuable resource in unconfined and confined aquifers beneath the U.S. High Plains, but little is known about its age or hydrologic history. Thirty-two samples of ground water were collected for measurement of δD, $\delta^{18}O$, $\delta^{13}C$, ^{14}C, ^3H, and $^{36}Cl/Cl$ and ionic constituents from the unconfined High Plains aquifer in the Ogallala Formation and from confined aquifers in various hydrostratigraphic units beneath the southern, central, and northern High Plains. All samples of unconfined and confined ground waters plot along the meteoric water line. δD and $\delta^{18}O$ from the unconfined aquifer are consistent with the Modern distribution of meteoric water across North America. δD and $\delta^{18}O$ from the confined aquifer likewise vary from south to north across the High Plains, but beneath the southern and central High Plains mean compositions are lighter in the confined aquifer than in the unconfined aquifer. Beneath the northern High Plains δD and $\delta^{18}O$ are the same or heavier in the confined aquifer than in the overlying unconfined aquifer. In combination, these trends show that the north-to-south range in stable isotopic compositions within the various confined aquifers is smaller than observed in the unconfined aquifer. Although age dates are uncertain, preliminary calculations suggest that unconfined ground waters are probably less than 1,000 yr old and locally as young as 25 yr. Ages of ground waters in the confined aquifers are between 20 and 32 ka and similar in the different study areas. Age of ground water appears to increase along the inferred intrastratal flow path in the confined aquifers but is determined by leakage rate as well as lateral velocity. The range in isotopic composition in confined aquifers supports earlier findings that seawater temperature and patterns of atmospheric circulation during the Late Pleistocene were different from conditions affecting Modern recharge across the High Plains.

INTRODUCTION

Although ground water beneath the U.S. High Plains (fig. 1) is an important resource supplying water to municipalities, industries, and farms, little is known about its age and origin in either the surficial, unconfined aquifer or in deeper, confined aquifers. Knowledge of the distribution of ground-water ages and isotopic compositions of the unconfined and confined ground waters will lead to general insights into paleohydrology and paleoclimatology of the High Plains and will support management of the region's water resources.

The objectives of this research are to (1) determine whether age and source of unconfined and confined ground waters are the same beneath the southern, central, and northern High Plains, (2) determine whether confined ground water is derived from vertical leakage or from lateral inflow from an outcropping recharge area before hydrologic divides are formed, (3) evaluate whether geomorphologic or climatic change during the Quaternary accounts for the isotopically distinct ground water in confined aquifers, and (4) consider the implications of variations in isotopic composition of ground water for Quaternary paleoclimatology of the continental interior.

The approach in this study was to compare hydrology and stable and radioactive isotopic composition between unconfined and confined ground waters in the different regions of the High Plains. As will be shown, hydrologic divides have truncated paleohydrologic flow paths and recharge to confined aquifers beneath the southern and central High Plains. Beneath the so-called Gangplank in the northern High Plains, however, flow paths might have changed little during the Quaternary because the aquifers beneath the High Plains have not been separated by erosion from recharge

Figure 1. Simplified geologic map of U.S. High Plains showing sampled wells.

areas at the east side of the Rocky Mountains. Recharge and ground-water flow patterns in confined aquifers in the northern High Plains might thus serve as a model for paleorecharge beneath the central and southern High Plains before their hydrologic divides formed. By comparing the similarities and differences in hydrology and isotopic composition between the different regions of the High Plains, age and paleohydrology of ground water can be better understood and constrained. Chemical composition of ground water has not been used commonly to interpret paleoclimatic and geomorphologic components of paleohydrology. δD and δ^{18}O were used as main indicators of source and environmental temperature of recharge water. ^{14}C activity was measured to estimate relative ground-water ages in confined and unconfined aquifers. Tritium (^{3}H) was used to evaluate a relatively recent component of recharge in the unconfined aquifer. In addition, the ^{36}Cl isotope was analyzed to constrain any ground-water ages in excess of 30 ka at which ^{14}C values are less than a detection limit of approximately 1 percent Modern carbon (pmc).

HYDROGEOLOGIC SETTING

The High Plains is underlain by Tertiary and Quaternary formations that formed when the Rocky Mountains eroded and were deposited in fan, fluvial, lacustrine, and eolian environments. The Miocene–Pliocene Ogallala Formation (table 1) extends from Texas and eastern New Mexico northward through Kansas and Colorado to Wyoming, Nebraska, and South Dakota (fig. 1). The Ogallala is covered in many places by a thick veneer of Quaternary lacustrine and eolian deposits derived from the Ogallala being reworked.

The term High Plains aquifer refers to hydrologically interconnected parts of the Ogallala and younger (for example, Blackwater Draw) and older (for example, Arikaree Group, Edwards Limestone) formations (table 1) (Weeks and Gutentag, 1981). The principal productive part of the High Plains aquifer, however, lies within the lower part of the Ogallala Formation. The bedrock units beneath the High Plains aquifer vary between the southern, central, and northern High Plains (Weeks and Gutentag, 1981). Ground-water resources in confined aquifers in older stratigraphic units are sparsely developed except where the Ogallala is thin or absent. Beneath the southern Plains, the principal confined aquifer lies in sandstones of the Triassic Dockum Group (table 1) (Dutton and Simpkins, 1986), although locally Permian and Cretaceous deposits underlie the Ogallala and yield potable water (Nativ and Smith, 1987; Nativ and Gutierrez, 1989). The Cretaceous Dakota Sandstone makes up the principal aquifer beneath the High Plains aquifer in the central High Plains (Helgeson and others, 1982; McGovern, 1984; Macfarlane and others, 1991). The Dakota is confined by upper Cretaceous shale and carbonate rocks. In southwestern Kansas the confining layer is less thick than in the center of the Denver Basin toward the north (Belitz and Bredehoeft, 1988). Beneath the northern Plains, a succession of Cretaceous to Tertiary rocks underlie the Ogallala (fig. 2). The Tertiary formations unconformably overlie the Cretaceous deposits (Lowry and Christ, 1967; Swinehart and others, 1985; Swinehart and Diffendal, 1989). Confined ground waters in the Lance and Chadron Formations and upper Pierre Shale (table 1) are locally used in industrial-water supply.

In most areas from New Mexico to Wyoming, the High Plains has been separated from its sediment source areas in the Rocky Mountains. During the late Tertiary and Pleistocene, the termination of Ogallala deposition and continued erosion led to the formation of the Pecos and Canadian River valleys (Gustavson and Finley, 1985). The Colorado Piedmont was formed when the headwaters of the Arkansas and South Platte Rivers eroded (Ostercamp and others, 1987).

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Table 1. Generalized correlation chart of northern, central, and southern High Plains. Modified from Hills and Kottlowski (1983) and Kent and others (1988).

		Northern	Central	Southern
Quat.		Undifferentiated alluvium	Mead Formation	Tule Group
Tertiary	P	Ogallala Group*	Ogallala Formation*	Ogallala Formation*
	M	Arikaree Group		
	O	White River Gp* / Brule / Chadron*		
	E			
	P	Denver Fm.		
Cretaceous	U	Lance Fm.* / Fox Hills Fm. / Pierre Shale / Niobrara Group / Benton Group	Pierre Shale / Colorado Group	
	L	Dakota Group	Dakota Sandstone* / Kiowa Shale / Cheyenne Sandstone	Duck Creek Fm. / Kiamichi Fm. / Edwards Fm. / Comanche Peak Ls. / Paluxy Sandstone
Jurassic	U	Morrison Fm.	Morrison Fm.	
	M	Sundance Fm.		
	L			
Triassic	U			Dockum Group*
	L	Chugwater Fm.		
Permian	U	upper Blaine Gypsum	Guadalupian Series / Nippewalla Group	Ochoan Series / Artesia Group / San Andres Fm.

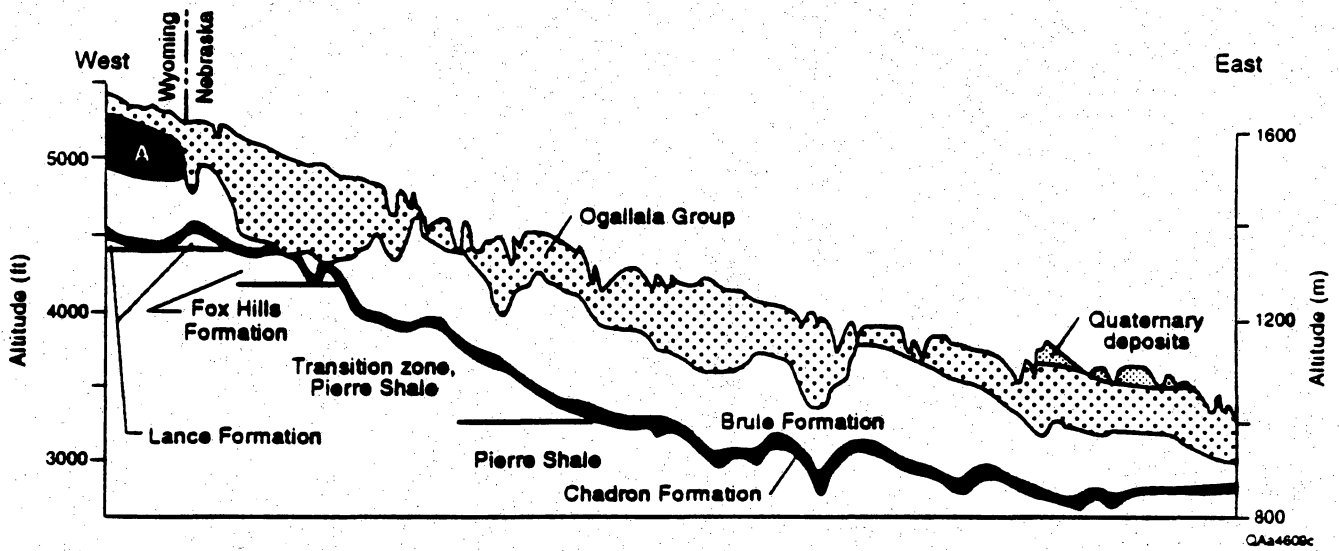* - Aquifers sampled in this study.

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Figure 2. West-east geologic section of Nebraska part of Gangplank in northern High Plains. 'A' is Arikaree Group. The Chadron unconformably overlies and truncates Upper Cretaceous formations (table 1). Modified from Swinehart and others (1985).

Ground water flows in unconfined and confined aquifers beneath all parts of the High Plains generally from west to east, reflecting recharge locations across the High Plains surface and the regional slope of the ground surface to the east. Local and regional variations in the gradient of the potentiometric surface reflect the geometries of discharge areas in river valleys and piedmonts, heterogeneities in aquifer properties, and the amount of cross-formational flow. The potentiometric surface of confined ground water in Dockum sandstones beneath the southern High Plains roughly parallels the topography but generally lies 90 to 210 m below the water table of the High Plains aquifer (Dutton and Simpkins, 1989). Hydraulic head in the confined part of the Dockum Group beneath the southern High Plains stands higher than in the adjacent unconfined part where the Triassic rocks crop out (fig. 3). Dutton and Simpkins (1989) defined a ground-water or hydrologic divide as the narrow zone at the northern and western limits of the southern High Plains, the High Plains escarpment, where inferred flow directions diverge. The inferred hydrologic divide probably reflects vertical leakage of water downward from the unconfined High Plains aquifer into the confined aquifer, lateral flow of confined ground water outward toward discharge areas, and absence of recharge underflow from the outcrop of Triassic deposits in the Pecos River valley.

The potentiometric surface of confined ground water in Dakota sandstones beneath the central High Plains of southeastern Colorado and western Kansas (fig. 4) is oriented east-northeast (Helgeson and others, 1982; Belitz and Bredehoeft, 1988; Macfarlane, 1993). Analogous to the southern High Plains, hydrologic divides might separate ground waters in outcropping Dakota sandstones beneath the Arkansas River valley in southwestern Kansas and beneath the Colorado Piedmont of southeastern Colorado from confined ground waters beneath the High Plains. Macfarlane (1993), however, did not discuss a hydrologic divide at the western limit of the central High Plains. The potentiometric surface suggests a hydrologic divide flanking the north side of the Arkansas River valley where the Dakota crops out (fig. 4). Confined ground water north of the Arkansas River probably derives, therefore, from vertical leakage. In southwestern Kansas the thickness of the confining layer in upper Cretaceous shales and carbonates was thinned by erosion but continues to retard cross-formational flow. Helgeson and others (1982) and Macfarlane (1993) recognized that vertical leakage is the main source of ground water in the confined aquifer beneath the central High Plains, departing from the classic interpretation of Darton (1905).

The northern High Plains in southeastern Wyoming and the Nebraska Panhandle, unlike the southern and central High Plains, has not been cut off from the Rocky Mountains by erosion:

> On the east flank of the Laramie Range is a piece of ground that somehow escaped exhumation. Actually continuous with Miocene remains that extend far into Nebraska, it is the only place between Mexico and Canada where the surface that covered the mountains still reaches to the summit. To the north and south of it, excavation has been deep and wide and the mountain front is of formidable demeanor. Yet this one piece of the Great Plains—extremely narrow but still intact—extends like a finger and, as ever, touches the mountain core: the pink deroofed Precambrian granite, the top of the range. At this place, as nowhere else, you can step off the Great Plains directly onto a Rocky Mountain summit. It is known as the gangplank (McPhee, 1986).

Comparable hydrological features thus exist in the southern and central High Plains: (1) an unconfined aquifer partly separated from deeper confined aquifers by leaky confining beds, (2) a ground-water divide that under Modern flow conditions cuts off intrastratal recharge to the confined aquifer from the west (the Pecos Plains and the Colorado Piedmont), and (3) an east-west through-cutting river that acts as a local

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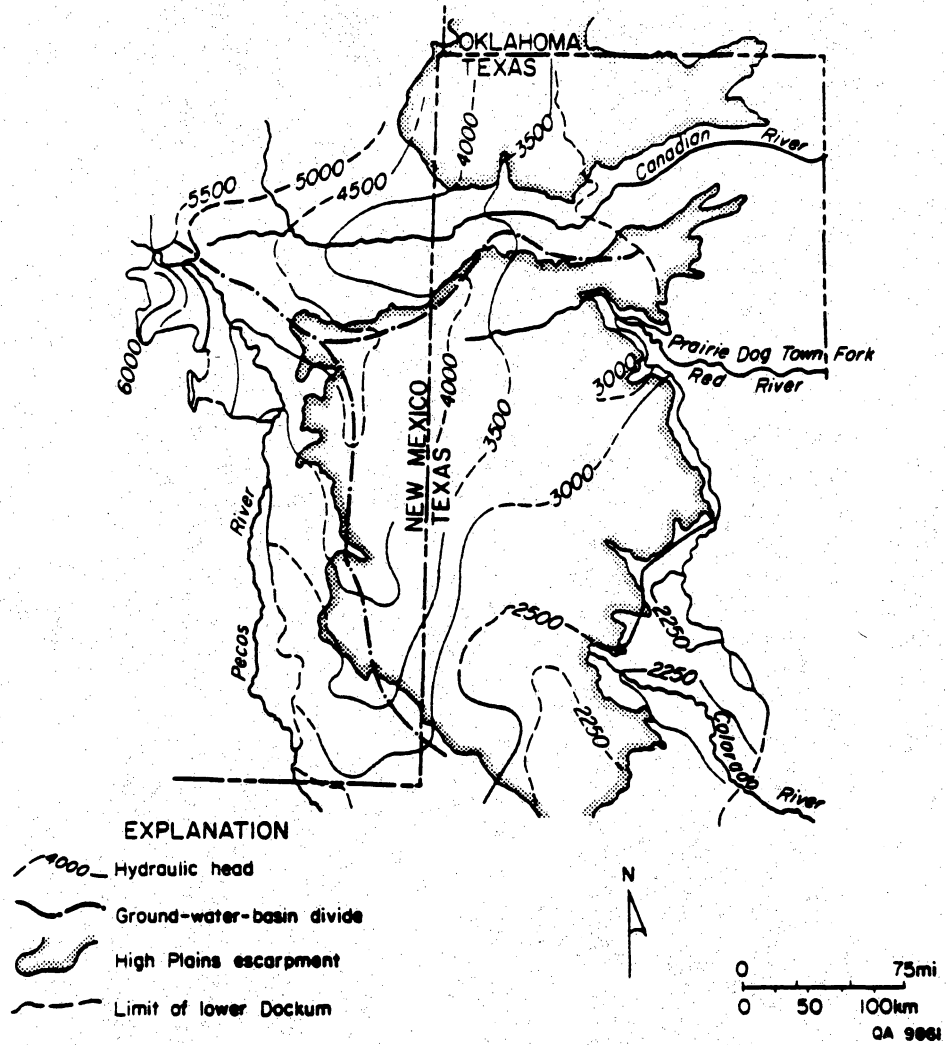
Figure 3. Potentiometric surface of confined ground water in lower Dockum Group beneath southern High Plains. Dashed-line contours (in feet) signify areas of little well control. From Dutton and Simpkins (1989).

103°N
+41°W

N

NEBRASKA

COLORADO

1500
2000
2500
3000
Central High Plains
3500
4000 Arkansas
4500
5000 River
Valley

Wichita

0   30 mi
0   50 km

N.
MEX.|

KANSAS
OKLAHOMA

-3000- Hydraulic head (ft)
Contour interval 250 ft

Limit of Dakota
Sandstone
QAa5814c

Figure 4. Potentiometric surface of ground water in Dakota Sandstone in southeastern Colorado and western Kansas in central Plains. Shaded area represents Arkansas River valley and its headwaters in the Colorado Piedmont. Elevation in feet above sea level. Modified from Macfarlane (1993).

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discharge area for ground water in the regional confined aquifer (the Canadian and Arkansas Rivers). The physiography of the northern High Plains flow system is distinct in that the High Plains might not be divided from the Rocky Mountains and that the breadth of the Gangplank between the North and South Platte Rivers is narrow relative to the north-to-south distance of the central and southern High Plains.

METHODS

The 18 wells in confined aquifers from which samples were taken represent more than 50 percent of the operable wells in the Triassic Dockum Group of the southern High Plains and in the Cretaceous Dakota Sandstone of the central High Plains study areas and more than 90 percent of the accessible wells in the Lance and Chadron Formations, undifferentiated White River Group, and upper (transitional) Pierre Shale beneath the northern High Plains (table 1). The 14 sampled wells in the unconfined High Plains aquifer, however, constitute fewer than 0.01 percent of drilled wells. The difference in proportion of the population of wells that were sampled reflects the extensive preferential development of ground water in the near-surface, high-yield High Plains aquifer. A variety of formations host the confined aquifers included in this study. Wells in the confined aquifer in Dockum Group (Triassic) sandstones beneath the southern High Plains in Texas and New Mexico that were previously sampled by Dutton and Simpkins (1986, 1989) were resampled (fig. 1). The wells were located along a west-to-east transect following Modern and presumed paleohydrologic ground-water flow paths. Wells in the confined aquifer in Dakota (Cretaceous) sandstones beneath the central High Plains in southwestern Kansas were selected to include variations along hydrological strike and dip. The deep (>250-m) wells in confined units that were sampled along the Gangplank in southeastern Wyoming and western Nebraska are completed in various confined hydrostratigraphic units in late Cretaceous to Tertiary rocks (table 1, figure 2). Ground waters in the unconfined High Plains aquifer also were sampled in each of the three study areas to document the extent of differences in isotopic composition and ground-water ages between confined and unconfined hydrostratigraphic units. Wells in the unconfined High Plains aquifer were chosen that were close to the wells in confined aquifers. Sampling locations are shown in figure 1.

Ground waters were collected from municipal, industrial, irrigation, and stock-water supply wells. Most municipal wells had been pumping nearly continuously for weeks before the site visits; other wells were pumped for several hours before sampling to purge a few well-bore volumes of water. Samples were collected for measuring ionic constituents and ^2H (D), ^3H, ^{18}O, ^{13}C, ^{14}C, and ^{36}Cl isotopes. W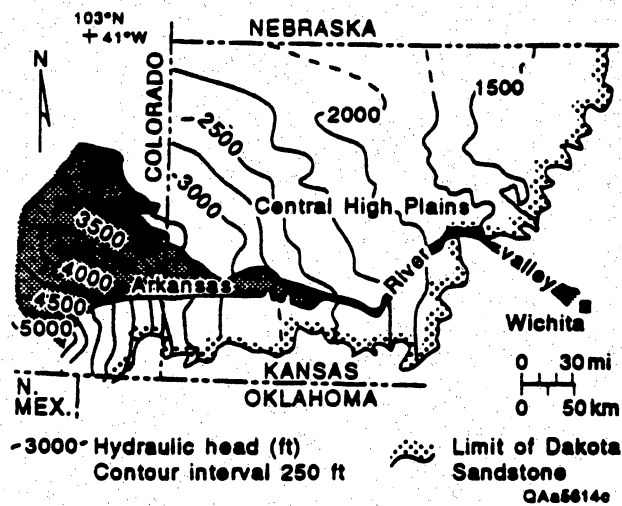ater sampling followed standard techniques (Brown and others, 1970; Wood, 1976). Temperature, pH, and Eh were measured in a flow cell. Titrated alkalinity was measured at well sites using unfiltered samples. Water samples for determining cationic concentrations were filtered through 0.45-μm cartridge filters and acidified at well sites using 6N HCl or 6N HNO$_3$. Waters to be analyzed for anionic concentrations and δD, $\delta^{18}O$, tritium and ^{36}Cl isotopic compositions were likewise filtered and sealed in sample bottles without other treatment.

Dissolved carbon to be used in ^{14}C and $\delta^{13}C$ analyses was collected by a direct precipitation method (appendix A). Polypropylene carboys (50 L) were filled and rinsed at well sites to ensure displacement of atmospheric CO$_2$. Fill rates of 10 L/min were typical of municipal and irrigation wells but were as slow as 1.5 L/min at low-yield windmills and test wells and as high as 100 L/min at one artesian well. After the carboys were flushed, 500 mL of a 30-percent ammonium hydroxide solution saturated with

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SrCl$_2$ (Gleason and others, 1969; Hassan, 1982) was added to precipitate SrCO$_3$. The SrCO$_3$ was then collected from the carboys in a slurry and later filtered and washed in the laboratory. The SrCO$_3$ powder was analyzed by liquid scintillation counting for ^{14}C and by mass spectrometry for δ^{13}C at Beta Analytic, Inc. ^{14}C results are reported in a unit of pmc (percent modern carbon).

Tritium was determined by low-level proportional counting of water samples that had undergone electrolytic enrichment at the University of Miami Tritium Laboratory. The ^{36}Cl samples were analyzed using a tandem Van de Graaff accelerator mass spectrometer at the University of Rochester Nuclear Structure Laboratory. Data on tritium, ^{14}C, δ^{13}C, and ^{36}Cl isotopic composition of ground waters are reported in table 2. Oxygen and hydrogen isotope measurements followed common methods; values are reported relative to SMOW using familiar del notation and are uncorrected for effects of dissolved salts (Sofer and Gat, 1972). Measurements were made at two laboratories for comparison (table 3). Within a given laboratory, duplicate analyses indicate that δ^{18}O measurements are highly reproducible within ±0.3‰; analytical scatter is higher for δD data, ±5‰. Cations and silica were analyzed using inductively coupled plasma-optical emission spectrometry. In the 1991 DOC (table 4), Cl was determined by argentometric autotitration, SO$_4$ by turbidimetric spectrophotometry, and Br by UV-visible spectrophotometry. In other samples, anions were analyzed using ion chromatography except I, which was determined by spectrophotometry.

RESULTS

All samples of unconfined and confined ground waters plot with minor scatter along the meteoric water line defined by Craig (1961) (fig. 5a and b). In the unconfined aquifer, samples from the southern High Plains are isotopically heaviest, samples from the northern High Plains are lightest, and samples from the central High Plains are intermediate (fig. 5a). The relative and absolute values of δD and δ^{18}O from the unconfined aquifer are consistent with the isotopic composition of meteoric water in central North America (Taylor, 1974; Lawrence and White, 1991). δD and δ^{18}O from the confined aquifer likewise decrease from south to north across the High Plains, the heaviest isotopic composition being from the southern High Plains and the lightest from the northern High Plains (fig. 5b).

Isotopic compositions of δD and δ^{18}O differ, however, between unconfined and confined aquifers within each geographic region of the High Plains. For example, mean δD and δ^{18}O values of ground water in the confined aquifer beneath the southern High Plains are 17‰ and 2‰, respectively, lighter than those in the overlying High Plains aquifer (fig. 6a). This is the same finding made by Dutton and Simpkins (1989), who interpreted the isotopically depleted ground water in the confined aquifer as residual meteoric water that had been recharged under environmental temperatures that were cooler by as much as 5.6°C, as compared with present recharge across the southern High Plains surface. Dutton and Simpkins (1989) called on an elevation effect to explain the differences in apparent environmental temperature. They thought that the confined ground water had been recharged at altitudes of 1,600 to 2,200 m in eastern New Mexico before the hydrologic divide completely formed more than 300 ka ago. But because data on ground-water ages and paleoclimatic conditions (Holliday, 1987) across the southern High Plains were sparse, their interpretations were poorly constrained. Young ground-water ages of less than 50 ka would be inconsistent with recharge before the Pecos River valley was fully incised.

Table 2. Tritium, ^{14}C, ^{13}C, and ^{36}Cl isotopic composition of ground waters.

Lab no.	Sample no.	Date	Name (unit)	Tritium (TU)	^{14}C (pmc)	$\delta^{13}C$ (‰DB)	$^{36}Cl/Cl$ ($\times 10^{-15}$)
91–262	DOC15	6/18/91	Boy's Ranch Magenta (Dockum)	nm	2.7 ± 0.2	–3.8	96.9 ± 9.6
91–263	DOC101	6/19/91	Hereford Well 18 (Dockum)	0.00 ± 0.09	3.1 ± 0.2	–7.9	57.9 ± 6.8
91–264	DOC111	6/19/91	Ralls Ranch (Dockum)	nm	1.5 ± 0.2	–7.1	326 ± 52
91–265	DOC110	6/19/91	Richardson (Dockum)	0.00 ± 0.09	12.3 ± 0.2	–8.7	171 ± 13
92–761	PAL23	8/19/92	Richardson (Dockum)	nm	13.1 ± 0.2	–8.7	nm
91–266	DOC122	6/20/91	Caprock Amphitheatre (Dockum)	nm	4.8 ± 0.2	–8.7	60.2 ± 5.9
91–267	DOC114	6/21/91	Tulia Well 13 (Dockum)	0.09 ± 0.09	4.9 ± 0.3	–9.6	181 ± 46
91–269	DOC102	6/20/91	Happy Well 6 (Dockum)	–0.14 ± 0.09	2 ± 0.1	–8.5	187 ± 28
91–270	DOC118	6/21/91	Amoco WT Ford (Dockum)	nm	<1	–9.7	49.6 ± 5.5
91–268	DOC123	6/21/91	Muleshoe Refuge (Ogallala)	nm	nm	nm	nm
92–758	PAL20	8/17/92	Pampa (Ogallala)	0.82 ± 0.09	20.8 ± 0.7	–7.30	nm
92–759	PAL21	8/18/92	Bushland (Ogallala)	–0.02 ± 0.09	32.4 ± 0.2	–6.90	562 ± 54
92–760	PAL22	8/18/92	Adrian (Ogallala)	0.01 ± 0.09	61.1 ± 0.4	–6.00	nm
92–762	PAL24	8/19/92	Dimmit (Ogallala)	1.50 ± 0.09	46.5 ± 0.4	–7.60	nm
92–763	PAL25	8/20/92	Floydada (Ogallala)	–0.04 ± 0.09	45.2 ± 0.5	–8.40	nm
92–764	PAL26	8/20/92	Plainview (Ogallala)	5.39 ± 0.18	35.7 ± 0.3	–8.00	nm
91–722	KS01	11/5/91	Coolidge (Dakota)	–0.11 ± 0.09	11.8 ± 0.2	–8.0	1521 ± 89
91–723	KS02	11/6/91	Leoti (Dakota)	0.02 ± 0.09	2.1 ± 0.1	–8.4	406 ± 27
91–725	KS04	11/7/91	Poky Feeders (Dakota)	5.56 ± 0.18	21.1 ± 0.2	–8.2	nm
91–727	KS06	11/8/91	Ranger Feeders (Dakota)	–0.03 ± 0.09	1.8 ± 0.2	–7.1	32.3 ± 7.1
91–728	KS07	11/9/91	Garden City (Dakota)	–0.02 ± 0.09	6.4 ± 0.2	–7.1	623 ± 32
91–724	KS03	11/6/91	Leoti (Ogallala)	6.44 ± 0.21	72.6 ± 0.9	–7.6	960 ± 48
91–726	KS05	11/8/91	Scott City (Ogallala)	0.92 ± 0.10	60.2 ± 0.8	–4.3	nm
91–729	KS08	11/9/91	Garden City (Ogallala)	0.0 ± 0.09	67.4 ± 1.0	–5.8	514 ± 26
91–731	PAL10	11/13/91	Lodgepole (Lance)	nm	2.2 ± 0.3	–7.4	1245 ± 54
91–733	PAL12	11/13/91	Coastal Chem (Lance)	nm	3.1 ± 0.5	–12.0	1393 ± 59
91–734	PAL13	11/14/91	Hall Artesian (Chadron)	nm	2.2 ± 0.3	–12.8	73.1 ± 11
91–736	PAL16	11/16/91	U.S. Air Force ("trans. Pierre")	nm	<0.6	–8.9	0 ± 9.7
91–737	PAL17	11/22/91	Oshkosh Stop (White River)	nm	<0.6	–16	32.5 ± 10
91–738	PAL18	11/23/91	Whitewater Ranch (Ogallala)	32.2 ± 1.10	34 ± 0.5	–8.8	5
91–730	PAL09	11/12/91	Cheyenne 18 (Ogallala)	–0.06 ± 0.09	107 ± 1	–12.3	nm
91–732	PAL11	11/12/91	Pine Bluffs 11 (Ogallala)	6.39 ± 0.23	88.3 ± 1	–11.1	1062 ± 102
91–735	PAL14	11/15/91	Kimball 78–2 (Ogallala)	0 ± 0.09	47.9 ± 1	–8.9	1247 ± 53
91–738A	PAL15	11/15/91	Levine Ranch (Ogallala)	nm	nm	nm	nm

nm   Not measured

Table 3. δD and δ¹⁸O isotopic composition (‰) of ground waters.

Lab no.	Sample no.	δD CS 1985	δD CS 1991	δD MSL 1991	δ¹⁸O CS 1985	δ¹⁸O CS 1991	δ¹⁸O MSL 1991
91–262	DOC15	–67.	–68.	–58.	–9.2	–10.1	–9.54
91–263	DOC101	–55.		–58.	–7.4		–7.96
91–264	DOC111	–47.		–50.	–6.85		–7.48
91–265	DOC110	–76.	–70.,–73.	–71.	–10.8	–11.7	–9.54
92–761	PAL23			–67.*			–10.5*
91–266	DOC122	–72.5.	–59.	–53.	–10.7	–8.6,–8.4	–8.16
91–267	DOC114	–72.		–68.	–10.4		–9.5
91–269	DOC102	–74.5	–78.,–82.	–81.	–10.75	–11.7	–11.4
91–270	DOC118	–48.	–51.,–47.	–46.	–7.4	–7.2,–7.2	–6.46
91–268	DOC123			–34.			–5.57
92–758	PAL 20			–42.*			–6.73*
92–759	PAL 21			–54.*			–8.24*
92–760	PAL 22			–38.*			–6.57*
92–762	PAL 24			–34.*			–6.39*
92–763	PAL 25			–41.*			–6.86*
92–764	PAL 26			–31.*			–5.35*
91–722	KS01			–88.			–12.8
91–723	KS02		–92.	–83.		–12.2	–11.9
91–725	KS04			–52.			–7.93
91–727	KS06		–96.	–90.		–13.	–12.9
91–728	KS07		–87.	–81.		–11.8	–11.3
91–724	KS03		–64.	–60.		–9.5,–9.6	–8.92
91–726	KS05		–64.	–57.		–9.7,–9.5	–9.20
91–729	KS08		–75.	–74.		–10.4	–9.82
91–731	PAL10		–100.	–96.		–13.2	–13.1
91–733	PAL12		–107.	–105.		–14.4	–14.3
91–734	PAL13		–98.,–97.	–91.		–13.7	–13.2
91–736	PAL16		–89.,–92.	–85.		–13.	–12.3
91–737	PAL17		–98.	–89.		–13.4	–12.8
91–738	PAL18		–78.	–72.		–11.	–10.3
91–730	PAL09		–110.,108.	–100.		–14.3	–5.3
91–732	PAL11		–106.	–101.		–14.2	–13.7
91–735	PAL14		–114.,–112.	–107.		–15.2,–15.4	–15.1
91–738A	PAL15			–99.			–13.8

*1992 samples

12

Table 4. Ionic composition of ground waters in milligrams per liter (mg/L).

Lab no.	Sample no.	Temp (°C)	Eh (mv)	pH	Na	K	Ca	Mg	SiO$_2$	Cl	SO$_4$	HCO$_3$
91-262	DOC15	nm	nm	nm	489	5.46	24.3	18.8	15.8	64.3	280	982
91-263	DOC101	21	-190	8.02	863	2.09	4.93	1.5	11	477	346	977
91-264	DOC111	22.5	nm	8.33	1115	1.91	5.85	2.54	10.9	587	961	630
91-265	DOC110	nm	-130	8.01	235	1.93	7.85	5.62	11.9	55.5	111	426
92-761	PAL23	19.4	350.32	8.26	240	2.3	8.0	5.4	11.5	51.8	102	429
91-266	DOC122	22.5	nm	9.4	1224	0.75	9.9	2.75	10.5	836	740	926
91-267	DOC114	24	nm	8.04	347	3.87	9.9	7.07	17	129	246	484
91-269	DOC102	21.5	-120	8.31	320	1.83	32.3	2.31	11	75.8	188	513
91-270	DOC118	28.1	nm	8.27	815	6.94	4.07	12.7	12.6	451	679	571
91-268	DOC123	20.8	nm	7.68	73.7	8.49	12.4	30.7	41.7	58	92	242
92-758	PAL20	18.6	408.08	7.49	208	8.1	115	44.5	26.8	302	286	214
92-759	PAL21	17.8	419.84	7.38	36.9	5.3	46.5	29.3	50.5	7.2	45.3	301
92-760	PAL22	17.6	434.28	7.85	30.7	5.2	32.4	30.4	20.6	7.6	48.3	253
92-762	PAL24	17.7	462.06	7.56	18.3	7.7	53.6	31.1	35.6	16.8	22.1	298
92-763	PAL25	18.5	855.30	7.69	37.7	7.4	38.0	30.5	55.2	23.4	25.2	286
92-764	PAL26	19.4	500.32	7.59	32.4	9.7	42.3	41.9	52.6	13.1	29.7	352
91-722	KS01	17.2	118	6.97	43.7	6.22	63.9	21.8	9.6	13.5	159	198
91-723	KS02	15.6	-55	8.5	346	4.28	5.17	2.29	10.3	54.2	380	334
91-725	KS04	19.8	107	7.4	156	8.79	86.8	65.2	59.5	123	284	367
91-727	KS06	25.6	-11	7.92	388	7.21	6.54	3.37	10.3	392	139	265
91-728	KS07	19.7	131	7.61	38.3	3.1	41.2	12.4	12.8	6.18	73	180
91-724	KS03	15.4	318	7.65	21	4.39	55.7	24.1	51.1	37.5	42	194
91-726	KS05	15.3	255	7.85	30	6.26	51	22.6	58.2	27.9	54.1	209
91-729	KS08	17.5	407	7.78	21.2	3.04	50	9.76	20	6.52	48.9	175
91-731	PAL10	17.2	73	8.61	93.7	3.16	5.6	1.97	11.1	7.29	38.1	211
91-733	PAL12	18.6	208	7.88	49.8	5.68	19.8	4.69	24.6	3.25	25.8	169
91-734	PAL13	18.2	nm	8.18	327	6.21	11.6	3.31	12	156	207	362
91-736	PAL16	20.9	-72	8.67	469	5.04	4.22	1.52	12.7	216	2.81	851
91-737	PAL17	15.2	-20	7.87	277	9.3	22.4	3.53	15.4	262	60.8	352
91-738	PAL18	11.9	26	7.74	9.43	8.1	51.5	7	60.1	1.62	37.9	168
91-730	PAL09	16.5	460	7.58	8.87	4.1	70.6	11.4	32.3	7.73	22.2	240
91-732	PAL11	12.5	432	7.59	36.1	6.91	74.5	19.7	58.8	26.6	42.9	279
91-735	PAL14	13.5	410	7.83	14.1	4.73	36.2	8.58	49.8	3.73	13.5	150
91-738	PAL15	14.0	nm	7.85	12.7	7.02	40.4	11	56.7	3.93	11.8	181

nm Not measured
* Near detection limit

Table 4 (cont.)

| Lab no.	Sample no.	F	Li	NO$_3$	Br	B	U	Sr	I	Ba	Se
91–262	DOC15	nm	0.24	nm	<0.25	nm	<6.1	0.53	<1.0	nm	nm
91–263	DOC101	nm	0.07	nm	*0.36	nm	<6.1	0.19	<1.0	nm	nm
91–264	DOC111	nm	0.27	nm	3.19	nm	<6.1	0.38	<1.0	nm	nm
91–265	DOC110	nm	0.08	nm	<0.25	nm	<6.1	0.31	<1.0	nm	nm
92–761	PAL23	2.2	0.08	<0.1	<0.1	0.87	nm	0.32	nm	0.03	nm
91–266	DOC122	nm	0.29	nm	1.39	nm	<6.1	0.67	<1.0	nm	nm
91–267	DOC114	nm	0.08	nm	*0.25	nm	<6.1	0.41	<1.0	nm	nm
91–268	DOC123	nm	0.08	nm	<0.25	nm	<6.1	1.91	<1.0	nm	nm
91–269	DOC102	nm	0.18	nm	<0.25	nm	<6.1	0.14	<1.0	nm	nm
91–270	DOC118	nm	0.08	nm	2.48	nm	<6.1	0.42	<1.0	nm	nm
92–758	PAL20	<0.7	0.05	<0.1	<0.1	0.19	nm	1.86	nm	0.02	nm
92–759	PAL21	3.7	0.13	8.3	<0.1	0.19	nm	0.95	nm	0.06	nm
92–760	PAL22	2.0	0.05	1.4	<0.1	0.14	nm	1.20	nm	0.10	nm
92–762	PAL24	2.3	0.06	8.8	<0.1	0.13	nm	1.26	nm	0.18	nm
92–763	PAL25	4.5	0.10	1.5	<0.1	0.17	nm	1.12	nm	0.13	nm
92–764	PAL26	4.8	0.11	4.1	<0.1	0.23	nm	1.32	nm	0.10	nm
91–722	KS01	1.15	*0.05	<0.1	<0.01	0.11	nm	1.41	<1.0	*0.02	<0.77
91–723	KS02	4.79	*0.07	<0.1	0.46	0.74	nm	0.14	<1.0	*0.02	<0.77
91–724	KS03	1.74	<0.04	16.7	<0.1	0.1	nm	1.29	<1.0	0.12	<0.77
91–725	KS04	4.14	0.14	20.8	<0.1	0.47	nm	3.46	<1.0	*0.03	<0.77
91–726	KS05	2.44	*0.05	14.8	<0.1	0.15	nm	1.03	<1.0	0.08	<0.77
91–727	KS06	4.2	*0.05	<0.1	<0.1	0.34	nm	0.1	<1.0	<0.02	<0.77
91–728	KS07	1.19	<0.04	0.53	<0.1	0.1	nm	0.67	<1.0	*0.04	<0.77
91–729	KS08	0.56	<0.04	7.62	<0.1	<0.04	nm	0.62	<1.0	*0.05	<0.77
91–730	PAL09	0.45	<0.04	3.01	<0.1	<0.04	nm	0.59	<1.0	0.17	<0.77
91–731	PAL10	0.76	<0.04	<0.1	<0.1	0.11	nm	0.15	<1.0	*0.02	<0.77
91–732	PAL11	0.45	<0.04	25.7	<0.1	0.09	nm	1.03	<1.0	0.16	<0.77
91–733	PAL12	0.79	<0.04	2.2	<0.1	0.13	nm	0.3	<1.0	*0.02	<0.77
91–734	PAL13	1.98	<0.04	<0.1	1.44	1.22	nm	0.36	<1.0	*0.02	<0.77
91–735	PAL14	0.56	<0.04	11.9	<0.1	*0.05	nm	0.35	<1.0	0.09	<0.77
91–738	PAL15	0.44	<0.04	8.81	<0.1	*0.05	nm	0.44	<1.0	0.13	<0.77
91–736	PAL16	3.46	<0.04	<0.1	1.66	3.61	nm	0.25	<1.0	*0.06	<0.77
91–737	PAL17	1.92	<0.04	<0.1	1.67	1.61	nm	0.41	<1.0	0.08	<0.77
91–738	PAL18	0.15	<0.04	1.48	<0.1	*0.04	nm	0.27	<1.0	*0.06	<0.77

nm Not measured
*   Near detection limit
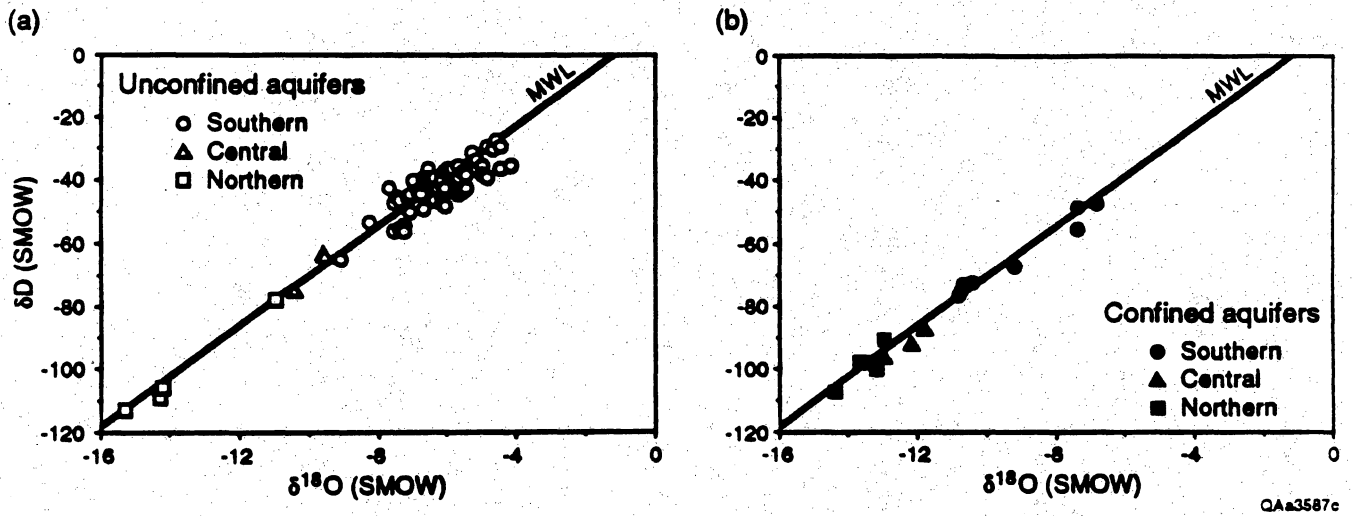
Figure 5. δD and δ^{18}O in (a) unconfined and (b) confined ground water beneath the High Plains. Data given in concentration units. MWL is meteoric water line defined by Craig (1961).
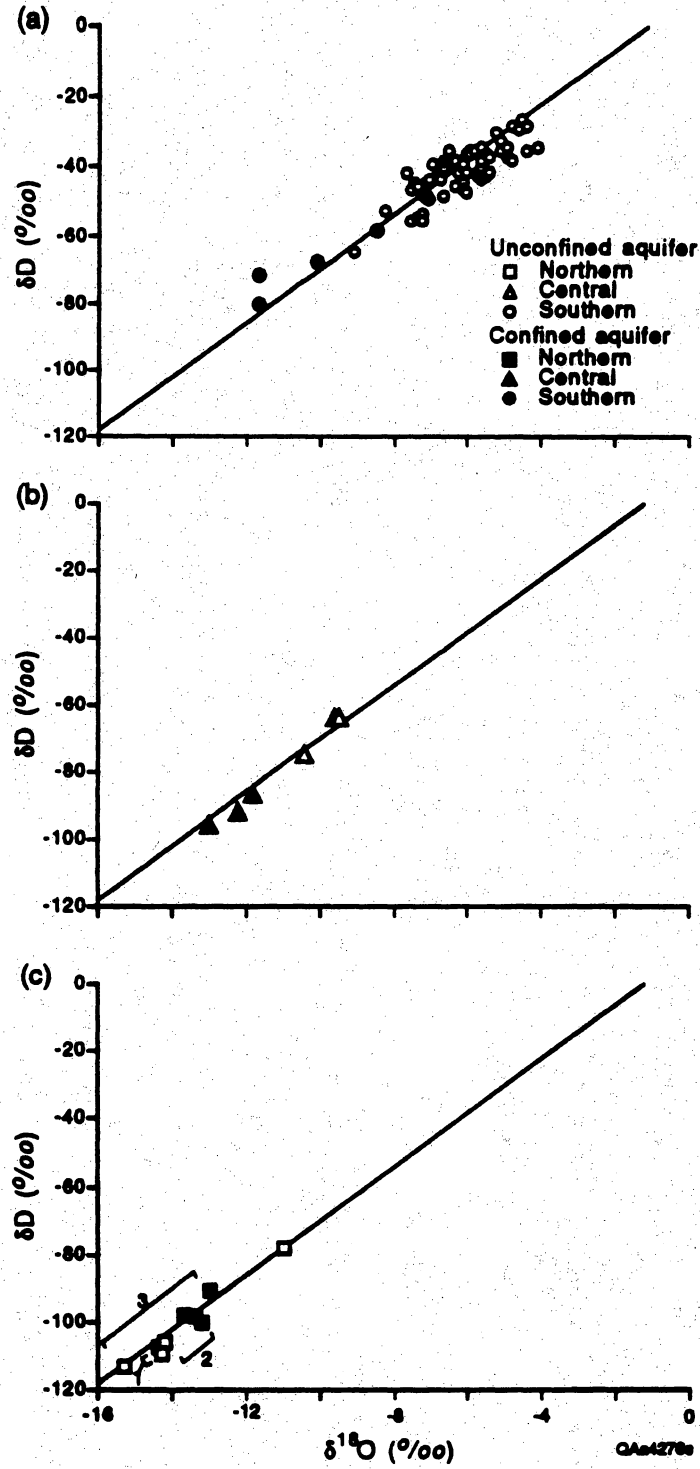
Figure 6. δD and δ¹⁸O in unconfined and confined ground water from beneath (a) southern, (b) central, and (c) northern High Plains. MWL is meteoric water line defined by Craig (1961).

Differences in isotopic composition between the pairs of unconfined and confined ground-water samples in the central High Plains appear to be comparable to the differences seen in the southern High Plains, although sample size is small (fig. 6b). In the northern High Plains, however, isotopic composition of ground waters from the confined aquifer is generally heavier than that of the overlying High Plains aquifer (fig. 6c). One exception is the least depleted sample, which comes from a test well in the unconfined High Plains aquifer beneath the Sand Hills of central Nebraska (PAL18, table 3). This unpaired sample is located farther east along the Gangplank and at lower ground-surface elevation than any sample from the confined aquifer (fig. 1). Isotopic composition in the confined aquifer becomes heavier with distance from the mountain front. In consequence, the difference in isotopic composition between the three pairs of unconfined and confined ground waters beneath the northern High Plains increases with west-to-east distance from the mountain front (fig. 6c). $\delta^{18}O$ is essentially identical (~−14.3‰) in the paired samples from confined (PAL12, table 3) and unconfined (PAL09) aquifers nearest the mountain front (set 1, fig. 6c). At a distance of approximately 75 km to the east down the Gangplank, $\delta^{18}O$ differs by 1‰ (samples PAL10 and PAL11 [table 3] in confined and unconfined aquifers, respectively) (set 2, fig. 6c). At a distance of approximately 110 km down the Gangplank from the mountain front, $\delta^{18}O$ differs by at least 2‰ (samples PAL16 and PAL14 [table 3] in confined and unconfined aquifers, respectively) (set 3, fig. 6c).

Tritium was not measured in all samples from the confined aquifers, but it is below background in all measured samples except one in the Dakota Sandstone in Kansas (KS04, table 2). This water-supply well at a cattle feedlot also has elevated NO_3 concentration, which suggests possible contamination by movement of water along an inadequately sealed casing. Tritium was above background in half of the samples from the High Plains aquifer, and in these it ranged from 6.4 to 32.2 TU (table 2). The highest value is from the test well in the Sand Hills of Nebraska, where recharge is rapid (PAL18, table 2). Nativ and Smith (1987) found that tritium in ground water in the High Plains aquifer in the southern High Plains was between 4.2 and 73 TU where the overlying unsaturated zone was thin but was between 0 and 2.8 TU where the depth to water was greater, reflecting the greater travel time to the water table.

The difference between average ^{14}C content in unconfined (57.8 pmc [standard deviation of ± 25.1 pmc]) and confined (<5.1 ± 5.5 pmc) ground waters was statistically significant. No significant differences in ^{14}C content emerged, however, between unconfined ground waters in the southern, central, and northern parts of the High Plains or between the confined ground waters in the different regions. ^{14}C values in unconfined ground waters averaged 47.4 ± 22.7 pmc beneath the southern High Plains, 66.7 ± 6.2 pmc beneath the central High Plains, and 69.3 ± 34.1 pmc beneath the northern High Plains (table 2). ^{14}C values in confined ground waters averaged 5.0 ± 4.5 pmc beneath the southern High Plains, 8.6 ± 8.1 pmc beneath the central High Plains, and <1.7 ± 1.1 pmc beneath the northern High Plains.

The $^{36}Cl/Cl$ ratio varies among all samples from 0 to $1,521 \times 10^{-15}$ and decreases with increasing chloride content (fig. 7). Ground waters in the confined aquifer beneath the southern High Plains have the highest chloride content and the lowest $^{36}Cl/Cl$ ratio, possibly related to "dead" chloride from Permian halite (Dutton, 1989; Dutton and Simpkins, 1989). Ground waters in unconfined aquifers tend to have the lowest chloride content and the highest $^{36}Cl/Cl$ ratio, probably influenced by evaporative concentration of rainfall. The $^{36}Cl/Cl$ ratio is positively correlated with $^{36}Cl/L$ concentrations (fig. 8), but the regressions differ in slope between regions. Confined ground waters beneath the southern High Plains make up two groups. The group that has low (56 to 129 mg/L) chloride concentrations (fig. 8) has a slope of about 7×10^{-22}
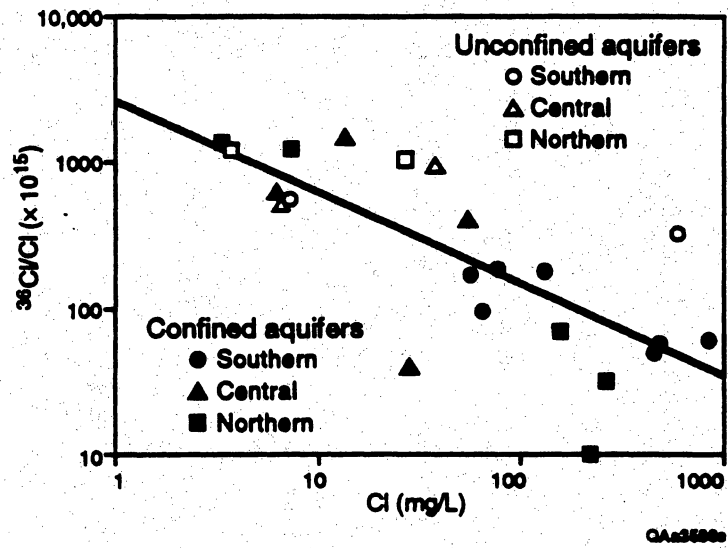
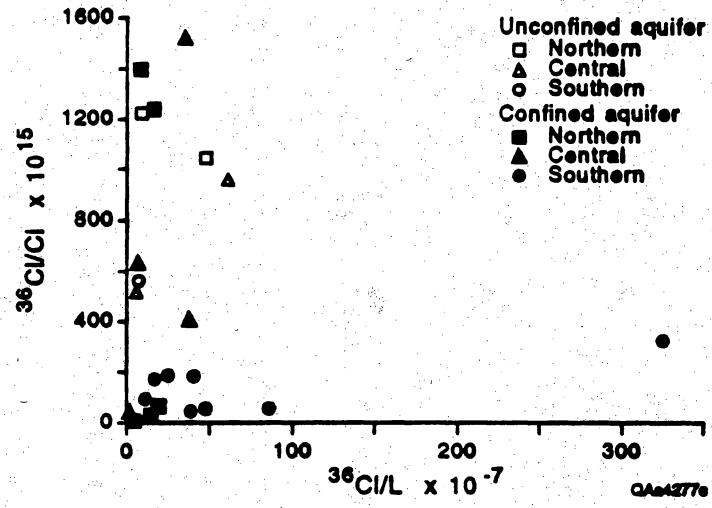Figure 7. Variation of $^{36}Cl/Cl$ ratio with chloride ionic concentration in ground waters beneath the High Plains.

Figure 8. Variation of $^{36}Cl/Cl$ ratio with ^{36}Cl concentration in ground waters beneath the High Plains.

(atoms/L)$^{-1}$, and the group that has high (451 to 836 mg/L) concentrations has a slope of about 1×10^{-22} (atoms/L)$^{-1}$. Confined ground waters from the central and northern Plains lie along lines having slopes of either 80×10^{-22} or 7×10^{-22} (atoms/L)$^{-1}$, whereas some unconfined ground waters lie along an intermediate line. In contrast, Bentley and others (1986) determined slopes of 12.1×10^{-22} and 3.4×10^{-22} (atoms/L)$^{-1}$ of low- and high-chloride samples, respectively, from the Great Artesian Basin, Australia. The ^{36}Cl/Cl ratio decreases from updip to downdip positions in flow paths beneath the central and northern High Plains (fig. 8).

DISCUSSION

The distinction in isotopic compositions between confined and unconfined ground waters beneath the southern High Plains that was reported by Dutton and Simpkins (1989) was again documented in this study but was extended to the central and northern High Plains. Three central questions are raised by these data. What was the source of isotopically light water in confined aquifers in the central and southern High Plains, that is, is the isotopic difference related to geomorphologic change or to climatic change? Why is isotopic composition of confined ground water beneath the northern High Plains enriched relative to unconfined ground water? What do the ages and residence times of isotopically distinct ground waters in the confined aquifers imply about persistence of paleohydrologic or paleoclimatic conditions? The following discussion constrains ages of ground waters beneath the High Plains, interprets possible flow paths between unconfined and confined aquifers, and offers preliminary interpretations of the paleohydrological significance of isotopic composition.

Estimates of Ground-Water Ages

Judging from the absolute values of ^{14}C and ^{3}H, the confined ground waters are significantly older than the overlying unconfined ground waters. Preliminary calculated ages suggest that waters in the High Plains aquifer are young, probably less than 1,000 yr and locally as young as 25 yr. Age of ground water in the confined aquifers appears to be statistically similar across the High Plains and on the order of 15 to 35 ka. Several problems, however, make accurate age-dating difficult: estimating the amount of dissolved calcite or dolomite and other subsurface sources of dissolved carbon, assuming δ^{13}C of paleorecharge waters, documenting the history of ^{14}C and ^{3}H in precipitation, and estimating ^{36}Cl/Cl ratio of recharge water and the subsurface generation of ^{36}Cl. δ^{13}C is very enriched in low-HCO_3 ground water but becomes less so as HCO_3 increases. The commonly assumed model of dilution of ^{14}C by calcite solution does not obviously apply in these siliciclastic aquifers. For the purpose of this report, however, comparison of absolute ^{14}C, ^{3}H, and ^{36}Cl values was sufficient to define relative differences in ground-water ages.

^{14}C activities in confined ground water beneath the southern High Plains (fig. 9) tend to decrease along the northwest-to-southeast intrastratal flow path inferred from the potentiometric surface, with the one exception of 4.9 pmc (DOC114, table 2) at the southeast end of the transect (compare figs. 3 and 9). Dutton and Simpkins (1989) cited results of a finite-element simulation that predicted vertical travel time of approximately 310 ka downward across the confining layer in the upper Dockum Group. Model results also showed that more than 90 percent of the lateral flow in the confined aquifer derives from vertical leakage under present conditions. Vertical
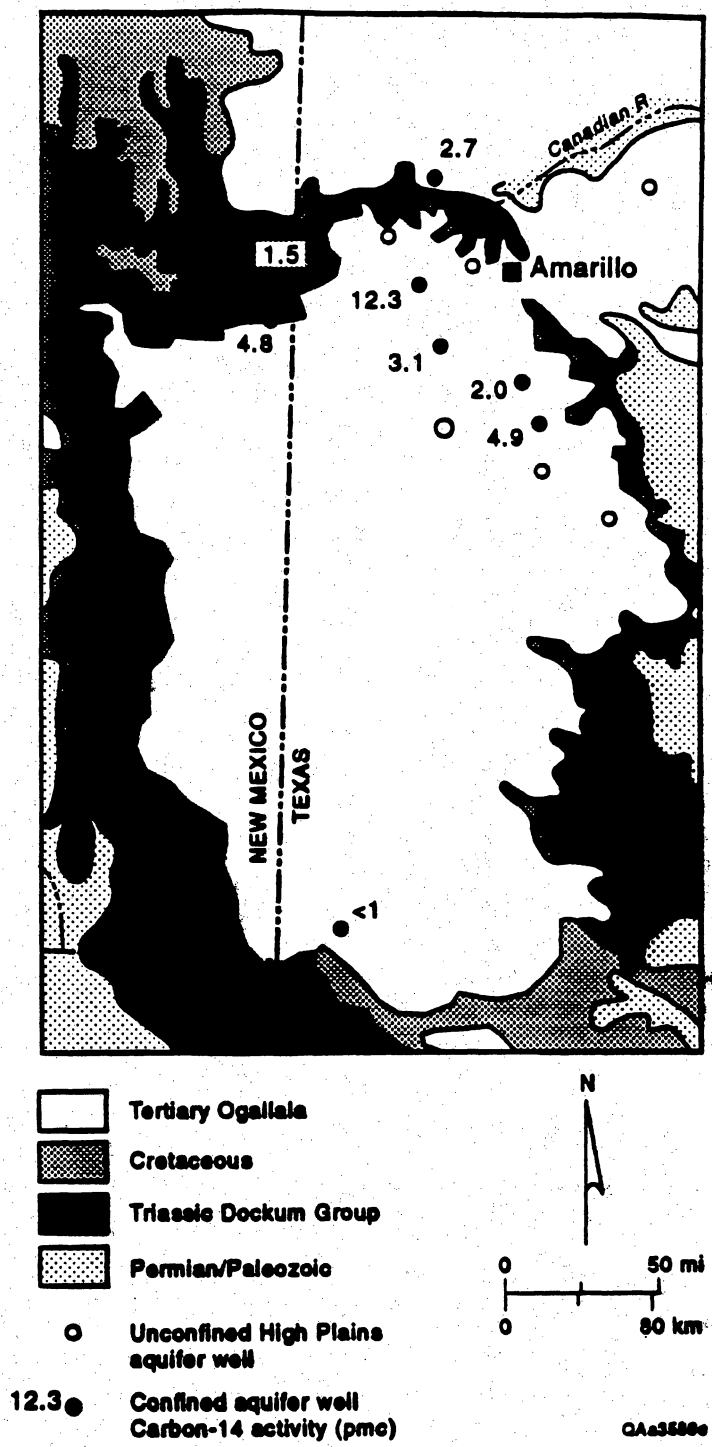
Legend:

Tertiary Ogallala

Cretaceous

Triassic Dockum Group

Permian/Paleozoic

O Unconfined High Plains aquifer well

12.3● Confined aquifer well
Carbon-14 activity (pmc)

Figure 9. Distribution of ^{14}C in confined ground water (Dockum Group) beneath the southern High Plains.

hydraulic conductivity in the model was set to 8×10^{-6} m/d ($\sim 10^{-8}$ cm/s). Using a 10- to 20-fold larger value of vertical hydraulic conductivity in the confining layer decreases the vertical travel time to less than 30 ka and increases the proportion of lateral flow derived from vertical leakage. Average ^{14}C age of confined ground water beneath the southern High Plains is estimated to be 25 ± 1 ka, assuming that δ^{13}C of recharge water was -12.6% and using the age-correction method of Pearson and White (1967). If ^{14}C was determined only by radioactive decay, that is, if "dead" carbon has not diluted the material, the limit of average ^{14}C-based ground-water age is calculated to be 28 ± 1 ka. These estimates of ground-water ages are consistent with model results using the vertical hydraulic conductivity of 1.6×10^{-4} to 8×10^{-5} m/d ($\sim 2 \times 10^{-6}$ to 9×10^{-8} cm/s) for upper Dockum mudstones, but are considerably younger than the minimum 300-ka age predicted by Dutton and Simpkins (1989). The absolute ^{14}C value appears to be too high to support the interpretation that recharge from the unconfined aquifer west or north of the hydrologic divide was the source of water in the confined aquifer. With ground-water flux downward across the aquitard possibly taking 15 to 30 ka and lateral transport through the confined aquifer across the southern High Plains taking 300 ka (Dutton and Simpkins, 1989), radioactive decay along the lateral flow path in the confined aquifer could account for the trend of decreasing ^{14}C activity (fig. 9). The greater ^{14}C activity in one sample at the east end of the transect might reflect more cross-formational flow near the High Plains escarpment (Senger and Fogg, 1987).

^{14}C activity in the confined aquifer beneath the central High Plains decreases toward the northeast away from the Dakota Formation outcrop in the Arkansas River valley (fig. 10) and decreases from west to east in each pair of samples (11.8 to 6.4 pmc; 2.1 to 1.8 pmc) aligned along inferred flow paths (fig. 4). Distribution of higher ^{14}C activities nearer the Arkansas River valley might reflect shorter travel time downward across the confining layer and greater vertical leakage where the upper Cretaceous confining layer is thin near the Arkansas River valley. Lower ^{14}C activities farther from the Arkansas River valley might reflect greater travel time across the confining layer, less vertical leakage where the upper Cretaceous confining layer is thick, and a component of ground water that has traveled longer and farther within the confined aquifer.

Ground-water flow paths are undoubtedly complex within the unconformable succession of heterogeneous, Cretaceous- and Tertiary-age stratigraphic units that make up the confined aquifer system beneath the Gangplank in the northern High Plains (fig. 2). No regional potentiometric-surface map has been compiled. Confined ground water beneath the Gangplank flows mostly eastward (Lowry and Christ, 1967), parallel to the regional slope of ground surface, but flow paths most likely bend to the north and south toward discharge areas in the North Platte and South Platte River valleys. Vertical flow must also vary longitudinally and transversely along the Gangplank. Vertical and horizontal hydraulic conductivities probably are highest along the mountain front. Near the mountain front, ground water probably moves vertically downward through the proximal, permeable deposits to recharge the semiconfined and confined aquifers in Cretaceous rocks (for example, the Lance Formation, table 1). Similarity in isotopic composition most likely reflects the great vertical recharge that occurs. However, even there, ^{14}C activity differs significantly between unconfined (88.3 to 107 pmc) and confined aquifers (2.2 and 3.1 pmc, respectively) (fig. 11). To the east, local, upward-directed, vertical flow is suggested by the presence of an artesian well (PAL13, table 2) in the North Platte River valley. ^{14}C activity in confined aquifers decreases from west to east along the Gangplank (fig. 11). Because deep recharge occurs through proximal, coarsely permeable rocks at the west end of the Gangplank, intrastratal flow within the succession of confined aquifers in Cretaceous and Tertiary rocks is probably more important than beneath the southern and central High Plains.
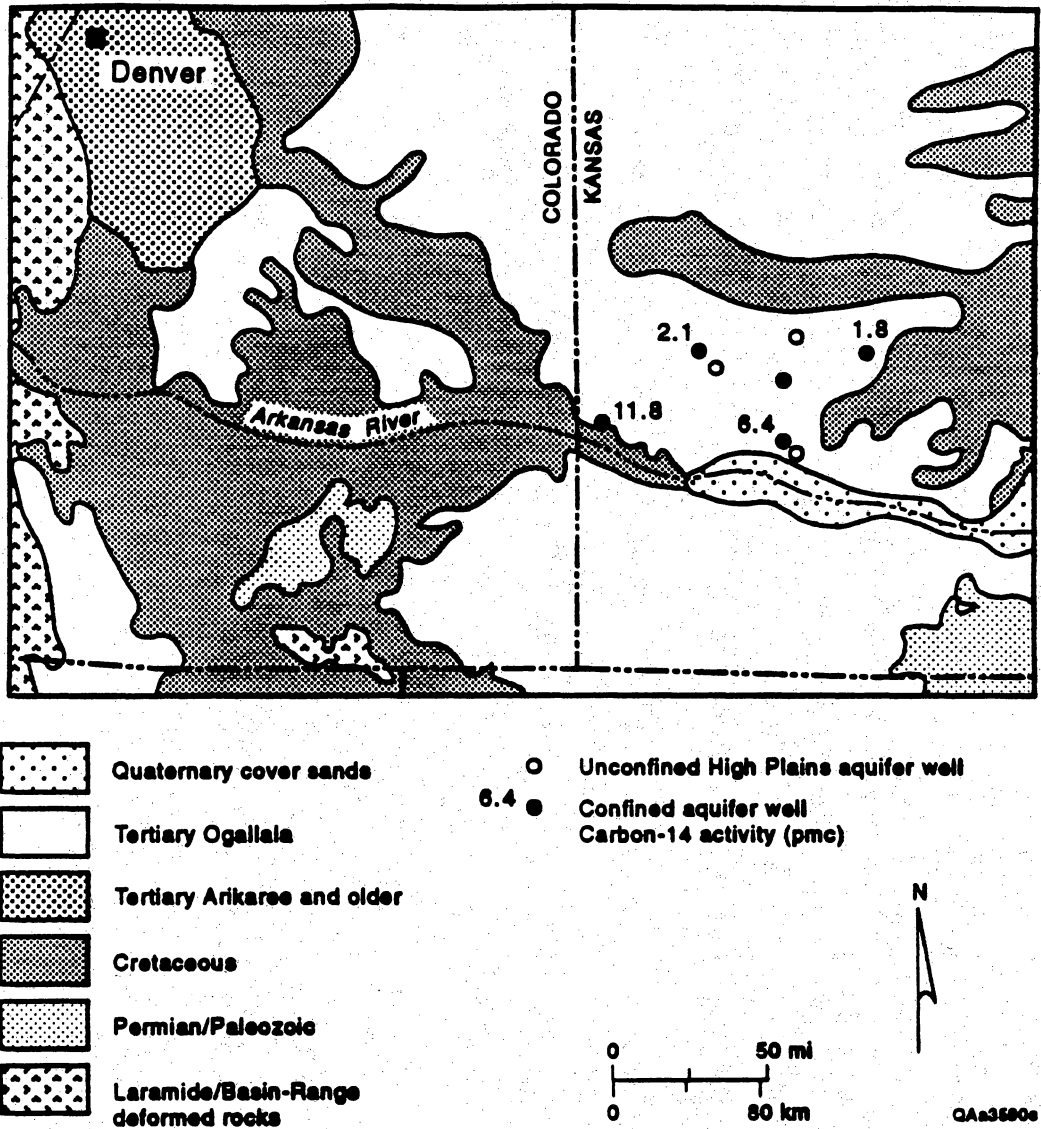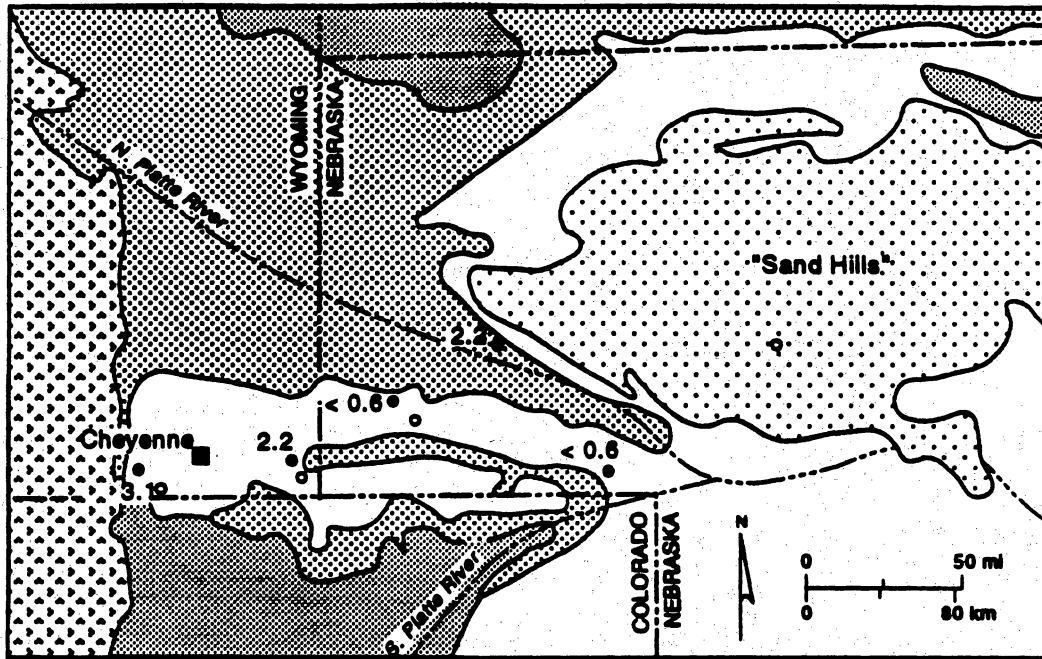
22

Quaternary cover sands

Tertiary Ogallala

Tertiary Arikaree and older

Cretaceous

Permian/Paleozoic

Laramide/Basin-Range
deformed rocks

O   Unconfined High Plains aquifer well

6.4 ● Confined aquifer well
Carbon-14 activity (pmc)

N

0   50 mi
├────┼────┤
0   80 km   QAa3590c

Figure 10. Distribution of ^{14}C in confined ground water (Dakota Formation) beneath the central High Plains.

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Figure 11. Distribution of ^{14}C in confined ground water (Lance and Chadron Formations and "transitional" Pierre Shale) beneath the northern High Plains.

Such a strong water drive might have existed in the confined aquifers beneath the southern and central High Plains during the late Tertiary. After Pleistocene erosion of the Pecos Plains and Colorado Piedmont, this recharge source was cut off and vertical leakage of ground water would have been the main source of recharge to the confined aquifers.

Implications of Stable Isotopic Composition

Across the continental interior, average ^{14}C of <5.1 ± 5.5 pmc suggests that confined ground waters were most likely recharged approximately 15 to 35 ka ago during the Wisconsinan (Late Pleistocene) glaciation. These ground waters are isotopically distinct from unconfined ground waters in the High Plains aquifer. Recharge during the past 11 to 18 ka displaced and flushed older water from the unconfined aquifers, in which ground water might have had a short residence time of approximately 1 ka. Time or recharge have apparently been insufficient to flush the older ground waters in the confined aquifers with water of typical Modern isotopic composition. Ground-water ages in confined aquifers beneath the southern and central High Plains appear more consistent with vertical leakage than with intrastratal flow from formation outcrops because of the age and origin of ground-water divides and the short vertical flow path and large area for cross-formational flow. The elevation effect hypothesized by Dutton and Simpkins (1989) is unsupported by ground-water age data because of the presumed age of the Pecos River basin and the related hydrologic divide. The long travel distance from outcrops of confined aquifers, stratigraphic heterogeneity (Domenico and Robbins, 1985), and probability of effective hydrologic divides at the High Plains escarpment make intrastratal flow an unlikely source of ground water in the confined aquifers.

Climatic rather than geomorphologic change, therefore, must account for the distinct isotopic composition of old ground water in confined aquifers. The north-to-south range in isotopic composition of confined ground water (fig. 5b) is smaller than that of either unconfined ground water (fig. 5a) or meteoric water (Taylor, 1974; Lawrence and White, 1991). δD and $\delta^{18}O$ compositions are more depleted in confined than in unconfined ground water beneath the southern and central High Plains but more enriched beneath the northern High Plains, indicating the smaller range. Yapp and Epstein (1977) showed that δD of cellulose from ^{14}C-dated trees also reflects a smaller range in isotopic composition during the glacial maximum from 14 to 22 ka. δD of cellulose was 20 to 30‰ more enriched than modern meteoric water in the northern nonglaciated plains. Siegel (1992) also reported on samples from confined aquifers in Iowa that were isotopically enriched relative to Modern meteoric waters.

For climatic change to account for the differences in isotopic composition between unconfined and confined ground water requires (1) regional climate to have been cool and wet during the Wisconsinan, (2) ground water in the confined aquifer to have been derived from vertical leakage of ground water downward from the High Plains aquifer, (3) the pluvial climate to have persisted long enough for its recharge to replace older ground waters in both the unconfined and deeper confined aquifers and in the intervening confining layer, (4) the High Plains aquifer to have since been flushed by recharge under a warm and dry Holocene climate, and (5) transport or recharge rates not to have been high enough during the past 11 to 18 ka to replace the Wisconsinan-age ground water in the confined aquifers.

Complex effects of glaciation that could account for the observed stratigraphic and inferred temporal variations in isotopic composition include (1) changed seasonal or

average annual temperature and effective precipitation in the different parts of the High Plains, (2) modified jet stream and storm trajectories (COHMAP Members, 1988), (3) changed amounts of winter and summer precipitation (COHMAP Members, 1988; Lawrence and White, 1991), (4) changed amounts of moisture derived from Pacific and Atlantic Oceans and the Gulf of Mexico (Gat, 1983), and (5) temperature or amount effects (Dansgaard, 1964; Lawrence and White, 1991). In the central and southern High Plains, the isotopically light ground water might simply reflect a pluvial climate during the Wisconsinan, estimated to range from an average of 3°C to as much as 5.6°C cooler than the Modern climate (Dutton and Simpkins, 1989). The enriched isotopic composition in confined aquifers beneath the northern High Plains, however, probably does not represent the presence of warm tropical air, as suggested by Siegel (1992), because no evidence of its presence exists between the northern plains and the Gulf Coast. Isotopic enrichment of ocean water would have the effect of enriching D and O in precipitation over the northern plains during times of maximum continental ice (Yapp and Epstein, 1977; Friedman and Hardcastle, 1988). Paleoclimatic weather simulations at the time of glacial maximum (~18 ka) show bifurcation of the North American jet stream and anticyclonic circulation (COHMAP Members, 1988) that might account for cold, isotopically heavy, North Atlantic moisture being drawn across the continental interior as hypothesized by Yapp and Epstein (1977).

The climatic imprint on isotopic composition of confined ground water is made through vertical leakage, at least in the southern and central High Plains. Therefore, climatic conditions must have persisted long enough for the Pleistocene ground water to percolate through the confining layers and flush out older water from the confined aquifers. If age of confined ground water is 15 to 35 ka, if age is assumed to be similar to residence time, and if several pore volumes must pass through the heterogeneous strata to displace older ground water, then pluvial climatic conditions had to have persisted for at least 45 to 105 ka for the confined aquifers to have their present composition. Since the end of the Pleistocene, enough time has elapsed for recharge to replace older ground water only in the unconfined aquifer, in which ground water has a shorter residence time.

CONCLUSIONS

Isotopic composition of ground water in confined aquifers can be used to interpret paleoclimatic conditions in the continental interior of the United States. Comparison of age and isotopic composition of ground water in confined and unconfined aquifers suggests that a Wisconsinan pluvial climate was as much as 5.6°C cooler than Modern average temperature in recharge areas across the southern and central High Plains. Isotopically enriched ground water in confined aquifers beneath the northern High Plains probably reflects the bifurcation of the jet stream during glaciations and the precipitation of water derived from cold ocean water at northern latitudes. Additional work needs to be done to constrain interpretations of ground-water ages. In particular, information is needed on the $\delta^{13}C$ composition of soil gas and shallow ground waters, which are surprisingly heavy, and on the $^{36}Cl/Cl$ ratio of ground waters derived from both atmospheric fallout during the past 40 yr and from equilibration with subsurface sources of ^{36}Cl.

ACKNOWLEDGMENTS

REFERENCES

Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geological Survey Water-Supply Paper 1535-H, 17 p.

Belitz, Kenneth, and Bredehoeft, J. D., 1988, Hydrodynamics of Denver Basin: explanation of subnormal fluid, pressures: American Association of Petroleum Geologists Bulletin, v. 72, no. 11, p. 1334–1359.

Bentley, H. W., Phillips, F. M., Davis, S. N., Habermehl, M. A., Airey, P. L., Calf, G. E., Elmore, David, Gove, H. E., and Torgersen, Thomas, 1986, Chloride 36 dating of very old groundwater 1. The Great Artesian Basin, Australia: Water Resources Research, v. 22, no. 13, p. 1991–2001.

Brown, E., Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: U.S. Geological Survey Techniques of Water-Resources Investigations, bk. 5, ch. A1, 160 p.

COHMAP Members, 1988, Climatic changes of the last 18,000 years: observations and model simulations: Science, v. 241 (26 August), p. 1043–1052.

Craig, Harmon, 1961, Isotopic variations in meteoric waters: Science, v. 133, no. 3465, p. 1702–1703.

Dansgaard, W., 1964, Stable isotopes in precipitation: Tellus, v. 16, p. 436–468.

Darton, N. H., 1905, Geology and underground water resources of the central Great Plains: U.S. Geological Survey Professional Paper No. 32, 433 p.

Domenico, P. A., and Robbins, G. A., 1985, The displacement of connate water from aquifers: Geological Society of America Bulletin, v. 96, p. 328–335.

Dutton, A. R., 1989, Hydrogeochemical processes involved in salt-dissolution zones, Texas Panhandle, U.S.A.: Hydrological Processes, v. 3, no. 1, p. 75–89.

Dutton, A. R., and Simpkins, W. W., 1986, Hydrogeochemistry and water resources of the Triassic lower Dockum Group in the Texas Panhandle and eastern New Mexico: The University of Texas at Austin, Bureau of Economic Geology Report of Investigations No. 161, 51 p.

_____ 1989, Isotopic evidence for paleohydrologic evolution of ground-water flow paths, Southern Great Plains, U.S.A.: Geology, v. 17, no. 7, p. 653–656.

Feltz, H. R., and Hanshaw, B. B., 1963, Preparation of water samples for carbon-14 dating: U.S. Geological Survey Circular 480, 3 p.

Fontes, J.-C., 1980, Environmental isotopes in groundwater hydrology, *in* Fritz, P., and Fontes, J.-C., eds., Handbook of environmental isotope geochemistry, Volume 1: Amsterdam, Elsevier, p. 179–226.

Friedman, I., and Hardcastle, K., 1988, Deuterium in interstitial water from deep-sea cores: Journal of Geophysical Research, v. 93, p. 8248–8263.

Gat, J. R., 1983, Precipitation, groundwater, and surface waters; control of climatic parameters on their isotopic composition and their utilization as palaeoclimatological tools, *in* Palaeoclimates and palaeowaters; a collection of environmental isotope studies: Vienna, International Atomic Energy Agency, p. 3–12.

Gleason, J. D., Friedman, I., and Hanshaw, B. B., 1969, Extraction of dissolved carbonate species from natural water for carbon-isotope analysis: U.S. Geological Survey Professional Paper 650-D, p. D248–D250.

Gustavson, T. C., and Finley, R. J., 1985, Late Cenozoic geomorphic evolution of the Texas Panhandle and Northeastern New Mexico—case studies of structural controls on regional drainage development: The University of Texas at Austin, Bureau of Economic Geology Report of Investigations No. 148, 42 p.

Hassan, A., 1982, Methodologies for extraction of dissolved inorganic carbon for stable carbon isotope studies: evaluation and alternatives: U.S. Geological Survey, Water Resources Investigations 82-6, 51 p.

Helgeson, J. O., Jorgensen, D. G., Leonard, R. B., and Signor, D. C., 1982, Regional study of the Dakota aquifer (Darton's Dakota revisited): Ground Water, v. 20, no. 4, p. 410–414.

Hem, J. D., 1985, Study and interpretation of the chemical characteristics of natural water: U.S. Geological Survey Water-Supply Paper 1473, 269 p.

Hills, J. M., and Kottlowski, F. E., 1983, Southwest/southwest mid-continent region: Correlation of stratigraphic units of North America (COSUNA) project: American Association of Petroleum Geologists, Correlation Chart Series.

Holliday, V. T., 1987, Re-examination of late-Pleistocene boreal forest reconstruction for the southern High Plains: Quaternary Research, v. 28, p. 238–244.

Kent, H. C., Couch, E. L., and Knepp, R. A., 1988, Central and southern Rockies region: Correlation of stratigraphic units of North America (COSUNA) project: American Association of Petroleum Geologists, Correlation Chart Series.

Lawrence, J. R., and White, J. W. C., 1991, The elusive climate signal in the isotopic composition of precipitation, *in* Taylor, H. P., Jr., O'Neil, J. R., and Kaplan, I. R., eds., Stable isotope geochemistry: a tribute to Samuel Epstein: The Geochemical Society, Special Publication No. 3, p. 169–185.

Lowry, M. E., and Christ, M. A., 1967, Geology and ground-water resources of Laramie County, Wyoming: U.S. Geological Survey, Water-Supply Paper 1834, 71 p.

Macfarlane, P. A., 1993, The effect of topographic relief and hydrostratigraphy on the upper part of the regional ground-water flow system in southeastern Colorado and western and central Kansas, with emphasis on the Dakota aquifer: University of Kansas, Ph.D. dissertation, 197 p.

Macfarlane, P. A., Whittemore, D. O., Townsend, M. A., Butler, J. J., Jr., Doveton, J. H., Hamilton, V. J., Coleman, Janet, Chu, T. M., Wade, A., and Macpherson, G. L., 1991, The Dakota aquifer program: annual report, FY91: Kansas Geological Survey, Open-File Report 91-1, 42 p.

McGovern, H. E., 1984, Overview of the Dakota aquifer in Kansas, in Jorgensen, D. G., and Signor, D. C., eds., Geohydrology of the Dakota aquifer, First C. V. Theis Symposium Proceedings, Lincoln, Nebraska: Dublin, Ohio, National Water Well Association, p. 58–61.

McPhee, J. A., 1986, Rising from the plains: New York, Farrar, Straus, Giroux, 213 p.

Nativ, Ronit, and Gutierrez, G. N., 1989, Hydrogeology and hydrochemistry of Cretaceous aquifers, southern High Plains: Journal of Hydrology, v. 108, p. 79–109.

Nativ, Ronit, and Smith, D. A., 1987, Hydrogeology and geochemistry of the Ogallala aquifer, southern High Plains: Journal of Hydrology, v. 91, p. 217–253.

Ostercamp, W. R., Fenton, M. M., Gustavson, T. C., Hadley, R. F., Holliday, V. T., Morrison, R. B., and Toy, T. J., 1987, Great Plains, in Graf, W. L., ed., Geomorphic systems of North America: Boulder, Colorado, Geological Society of America, Centennial Special Volume 2, p. 163–210.

Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N., 1982, PHREEQE, a computer program for geochemical calculations: U.S. Geological Survey Water Resources Investigations 80-96, 210 p.

Pearson, F. J., Jr., and White, D. E., 1967, Carbon-14 ages and flow rates of water in Carrizo Sand, Ataskosa County, Texas: Water Resources Research, v. 3, no. 1, p. 251–261.

Senger, R. K., and Fogg, G. E., 1987, Regional underpressuring in deep brine aquifers, Palo Duro Basin, Texas. 1. Effects of hydrostratigraphy and topography: Water Resources Research, v. 23, no. 8, p. 1481–1493.

Siegel, D. I., 1992, Isotopic evidence from regional ground water and calcite cements that Late Wisconsin continental ice lobes were sustained by tropical air masses (abs.): Geological Society of America Abstracts with Programs, v. 24, no. 7, p. A240.

Sofer, Zvi, and Gat, J. R., 1972, Activities and concentrations of oxygen-18 in concentrated aqueous salt solutions: analytical and geophysical implications: Earth and Planetary Science Letters, v. 15, no. 3, p. 232–238.

Swinehart, J. B., and Diffendal, R. F., Jr., 1989, Geology of pre-dune strata, in Bleed, Ann, and Flowerday, Charles, eds., An atlas of the Sand Hills: Lincoln, University of Nebraska–Lincoln, Conservation and Survey Division, Resource Atlas No. 5a, p. 29–42.

Swinehart, J. B., Souders, V. L., DeGraw, H. M., and Diffendal, R. F., Jr., 1985, Cenozoic paleogeography of western Nebraska, in Flores, R. M., and Kaplan, S. S., eds., Cenozoic paleogeography of West-Central United States: Society of Economic Paleontologists and Mineralogists, Rocky Mountain Section, Rocky Mountain Paleogeography Symposium No. 3, p. 209–229.

Taylor, H. P., Jr., 1974, The application of oxygen and hydrogen isotope studies to problems of hydrothermal alterations and ore deposition: Economic Geology, v. 69, no. 6, p. 843–883.

Turner, J. V., 1982, Kinetic fractionation of carbon-13 during calcium carbonate precipitation: Geochimica et Cosmochimica Acta, v. 46, p. 1183–1191.

Weeks, John, and Gutentag, Edwin, 1981, Hydrological atlas of the Ogallala aquifer: U.S. Geological Survey Hydrologic Investigations Atlas HA-648.

Wigley, T. M. L., 1975, Carbon-14 dating of ground water from closed and open systems: Water Resources Research, v. 11, p. 324–328.

_____ 1976, Effect of mineral precipitation on isotopic composition and ^{14}C dating of ground water: Nature, v. 263, p. 219–220.

Wood, W. W., 1976, Guidelines for collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water-Resources Investigations, bk. 1, ch. D2, 24 p.

Yapp, C. J., and Epstein, Samuel, 1977, Climatic implications of D/H ratios of meteoric water over North America (9500–22,000 B.P.) as inferred from ancient wood cellulose C-H hydrogen: Earth and Planetary Science Letters, v. 34, p. 333–350.

APPENDIX A. FIELD METHOD FOR DIRECT PRECIPITATION OF DISSOLVED HCO₃ IN ¹⁴C DATING

APPENDIX A. FIELD METHOD FOR DIRECT PRECIPITATION OF DISSOLVED HCO_3 IN ^{14}C DATING

Abstract

A practical method for direct precipitation of dissolved inorganic carbon in ^{14}C dating of ground water was devised on the basis of collecting multiple aliquots of 50-L samples to yield carbon mass sufficient to perform radiometric analysis. In the method, polypropylene carboys containing treated water samples are held upside down on modified heavy-duty hand trucks, and the precipitated carbonate salt is collected in glass sample jars attached to the carboy by means of a special transfer valve. $SrCO_3$ settling time of 8 h should yield at least 50 percent of total dissolved inorganic carbon with insignificant bias of contamination in ^{14}C or $\delta^{13}C$. The number of 50-L aliquots that is collected should be chosen on the basis of an assumed 50 percent recovery to ensure an adequate mass of analyzable dissolved inorganic carbon.

Introduction

Age dating of ground waters on the basis of activity of the ^{14}C isotope (Pearson and White, 1967; Wigley, 1975, 1976) requires field treatment of samples to avoid their contamination by uptake of atmospheric CO_2. Direct precipitation (Gleason and others, 1969) and gas evolution (Feltz and Hanshaw, 1963) are the two methods generally applied to recover and preserve dissolved inorganic carbon (DIC). In the direct precipitation method, inorganic carbon dissolved in ground water is precipitated in a sample container by adding a high-pH-buffered solution rich in barium or strontium. Few researchers have described field-sampling techniques used in ground-water age-dating studies, but most direct-precipitation samples have probably been collected using a 42-gallon steel drum to which the reagent is added. In the field the precipitate is drawn off using a bung tap, or the entire sample is returned to the laboratory to extract DIC there. Gas evolution is impractical in most field settings for treating a large volume of water in order to recover a large mass of DIC, especially from waters that have low HCO_3 concentration.

By either method, the crux of collecting a high-quality, uncontaminated sample of dissolved carbon for ^{14}C analysis is to reduce the volume and weight of water that must be handled. Typical concentrations of dissolved HCO_3 in ground waters range from as low as 10 mg/L in carbonate-depleted sandstones to more than 1,000 mg/L in limestones and formations low in calcium and magnesium but that have a subsurface source of CO_2 (Hem, 1985). Figure A1 gives the volume of water of varying HCO_3 concentration that must be collected to provide a minimum of 1 g of carbon for isotopic analysis by scintillation counting (SC). Ground water that has 100 mg/L HCO_3, for example, requires 50 L of sample when assuming 100-percent recovery but more than 100 L of sample when assuming 50-percent recovery. The advanced laboratory technique of accelerator mass spectrometry (AMS) lowers the mass of carbon required for analysis to as little as 0.002 g. This can be helpful during analyses of waters having an HCO_3 concentration of much less than 100 mg/L, but the 1992 AMS cost of more than $500 per sample is more than twice the cost of scintillation counting and analytic turnaround time can be more
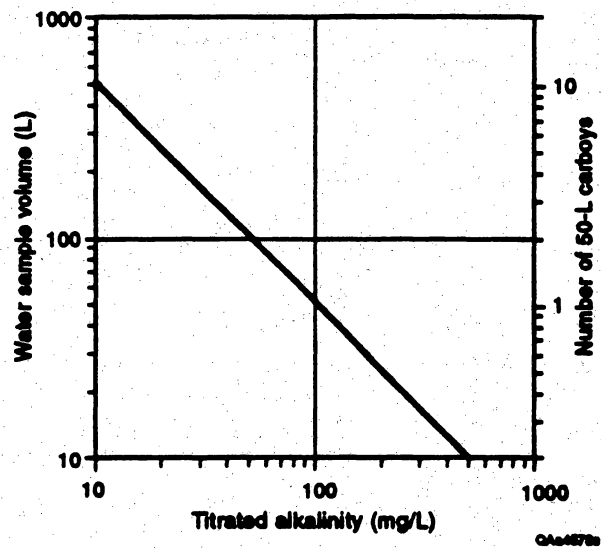
Figure A1. Relation of dissolved HCO_3 concentration, number of 50-L carboys needed, and volume of water to yield 1 g of carbon, assuming 100-percent recovery.

than 3 times as long. Therefore, investigators most commonly use SC and try to recover a large mass of carbon sufficient for analysis.

An improved field technique of the direct-precipitation method is herein described. Rather than facing the logistically difficult and physically dangerous task of handling one or several hundred liters of water in one bulky and heavy container, workers can subdivide the water sample into smaller aliquots, for example, 50 L (50 L of water weighs 50 kg [~110 lb]). This technique is also inexpensive in its use of equipment, accurate and reproducible, easily handled by one person, and applicable to ground waters of varying HCO_3 concentrations. Gleason and others (1969) stated that the direct precipitation method can give correct values of $\delta^{13}C$ in 1-L water samples but not in large samples because of kinetic problems and coprecipitation of gelatinous flocs of Mg and Al hydroxides. Gleason and others (1969) did not specify the volume limit or explain the kinetic problem. Findings of this study suggest that accurate ^{14}C and $\delta^{13}C$ values can be obtained using large-volume samples needed when extracting DIC for ^{14}C dating.

Equipment

A polypropylene carboy in which to collect water samples is suitable for ^{14}C dating because it is (1) semitranslucent, allowing carbonate precipitate to be seen, (2) three times less permeable to CO_2 than polyethylene, (3) cheaper and lighter than stainless steel, and (4) more durable than glass. Polypropylene is more permeable to CO_2 than glass or stainless steel, but the solution remains in the carboy for only 8 to 12 h, before much gas can be exchanged through the polypropylene wall. Polypropylene carboys are available in 25- and 50-L capacities.

We use pint-size (0.47-L), wide-mouth, glass canning jars to catch and store the decanted slurry of precipitate, reagent, and ground water. These inexpensive glass jars are readily available in most grocery stores. This size generally holds all of the carbonate precipitate that can be recovered from a 50-L water sample, leaving a minimum of excess reactive supernatant.

Connecting the glass sample jar to the polypropylene carboy requires adapting the unique thread of the carboy to the thread of the glass jar. To solve this problem we drill out the center of an extra carboy cap and connect it to the metal canning-lid ring using a series of PVC fittings and a brass ball valve (fig. A2). To bond the polyethylene cap and the metal ring to the PVC we use a self-leveling adhesive–sealant (E6000, Eclectic Company) that creates a high-strength bond between the nonporous, dissimilar materials after 24 h of curing. Because the soft metal canning ring must be replaced when its threads become rusted or stripped by overtightening, we should stress that the bond is not permanent. The ring can be pulled free using pliers, and residual adhesive–sealant can be rubbed and scraped off the PVC base, leaving a clean surface for bonding a replacement ring.

A two-wheel, heavy-duty hand truck is used both to move the full carboy and to invert it to decant the precipitate (fig. A3). The carboy full of water must be held upside down long enough for sufficient $SrCO_3$ to settle (fig. A4). Modifications to the hand truck include replacing a cross bar with one shaped and positioned to hold the inverted carboy and drilling holes through which U-bolts can be bolted for attaching nylon web straps (fig. A3). The heavy-duty hand truck has a large foot plate (12 inches × 16 inches) for stability.

Two additional items needed are a length of garden hose, through which to fill the carboy from the wellhead, and a 1-m-long (3-ft) section of 2-inch, schedule-40 PVC pipe
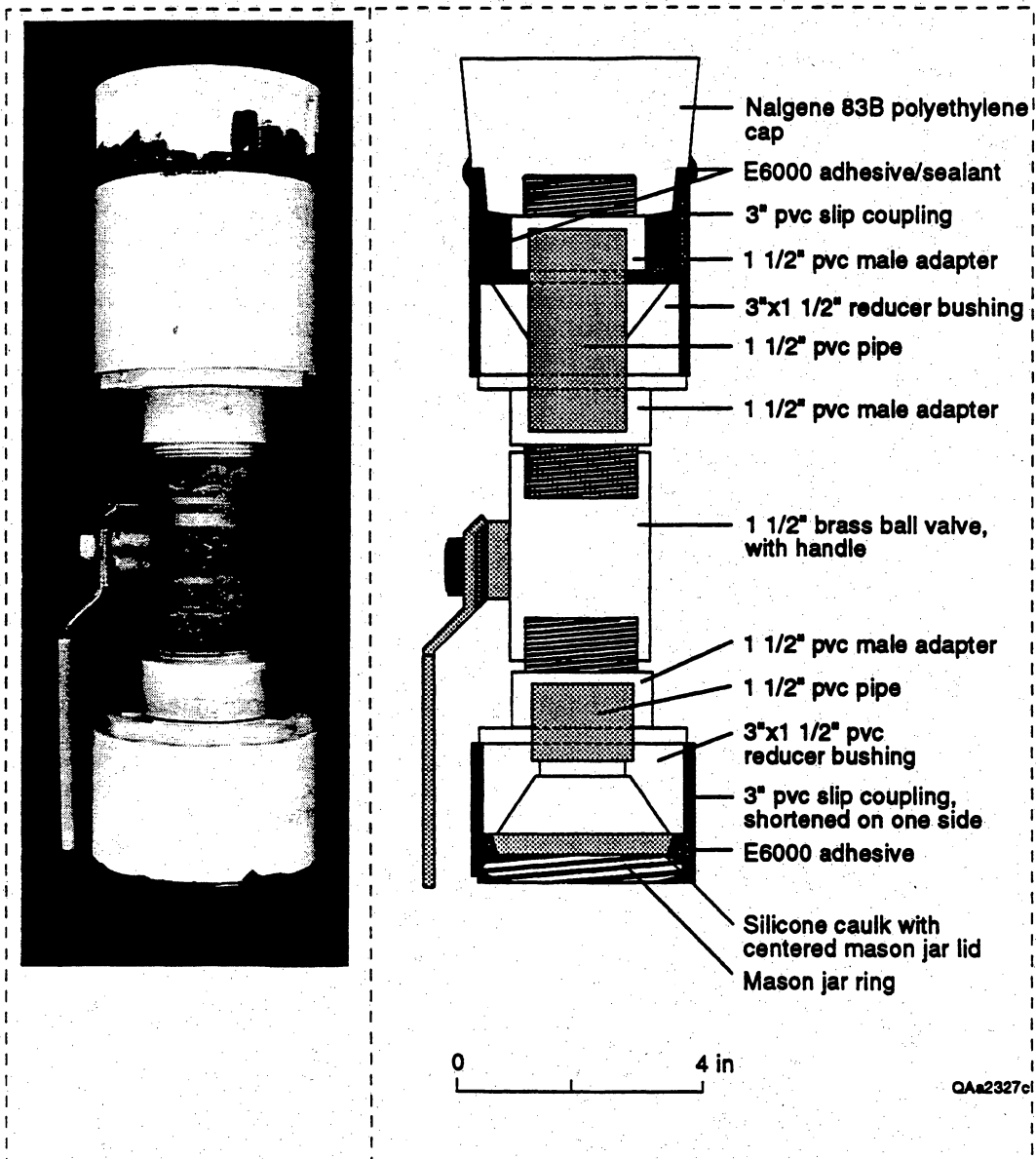
Nalgene 83B polyethylene cap

E6000 adhesive/sealant

3" pvc slip coupling

1 1/2" pvc male adapter

3"x1 1/2" reducer bushing

1 1/2" pvc pipe

1 1/2" pvc male adapter

1 1/2" brass ball valve, with handle

1 1/2" pvc male adapter

1 1/2" pvc pipe

3"x1 1/2" pvc reducer bushing

3" pvc slip coupling, shortened on one side

E6000 adhesive

Silicone caulk with centered mason jar lid

Mason jar ring

0   4 in

QAa2327c

Figure A2. (a) Photograph and (b) schematic drawing of component parts of transfer valve for connecting 50-L carboy to glass sample jar.

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Install 1.5" U-bolts at these points. 10-ft web-strap mini-rachet load-huggers are used to hold the 50-liter carboy in place. The U-bolts are pivoted to permit the carboy to rest against the dolly frame.
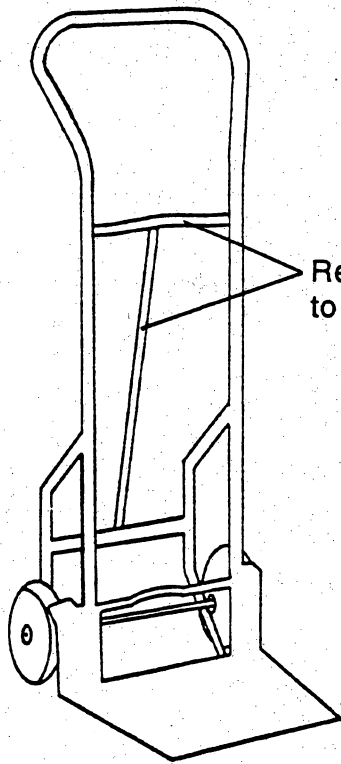
Reinforcement bars to be removed

25"

No scale
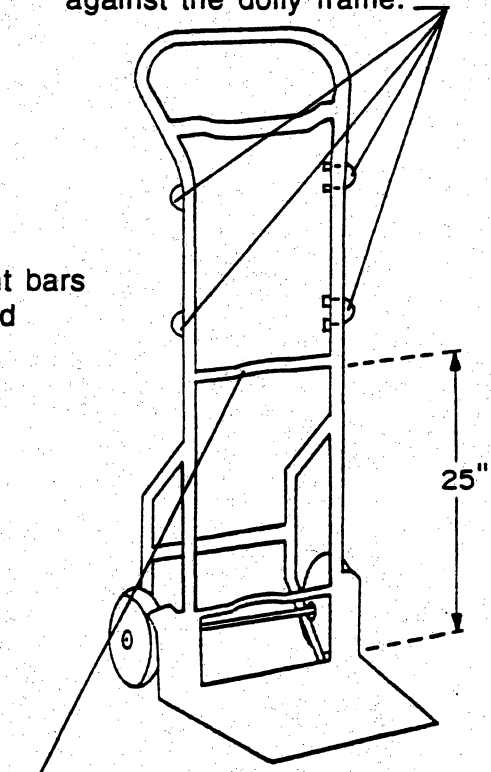
Install 1" steel pipe 25" above the base plate.

QAa 2328r

Figure A3. Illustrations of modifications of a heavy-duty hand truck for inverting a 50-L carboy.
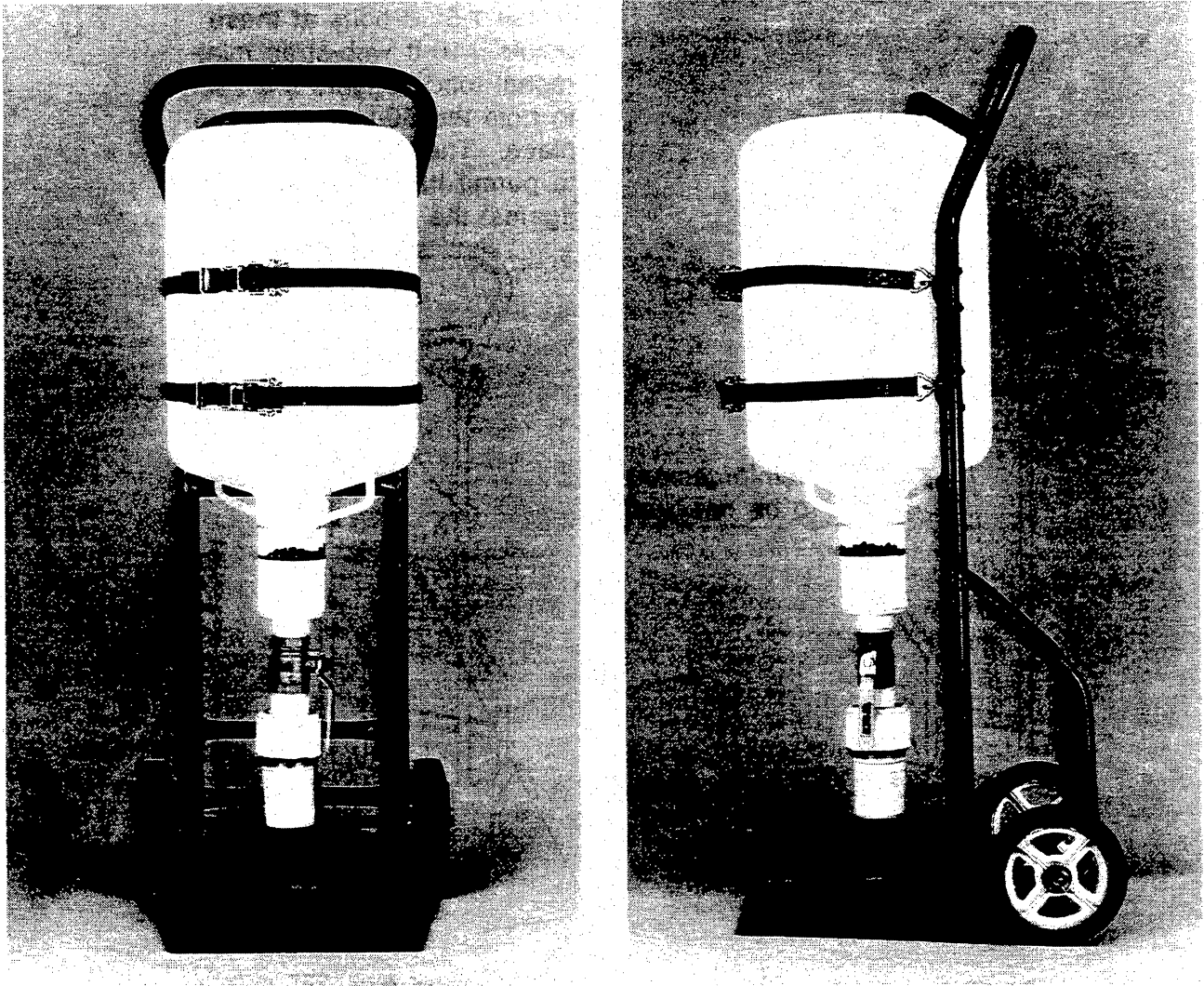
Figure A4. (a) Front and (b) side views of a heavy-duty hand truck holding an inverted 50-L carboy with sample jar.

with cap. The latter is used to displace somewhat more than 500 mL of sample from the carboy to make room for the reagent.

Reagent

The carbonate precipitate is decanted to minimize the volume and weight of solution being transported and to limit the volume of the pH-buffered ground-water–reagent solution that might react with atmospheric CO_2. To precipitate dissolved HCO_3 we favor using a solution of 30-percent NH_4OH saturated with $SrCl_2$ (Gleason and others, 1969; Hassan, 1982). The solution, made in the laboratory in batches of 2.5 L, is filtered (0.45 µ) into 500-mL, narrow-mouth, glass bottles to remove $SrCO_3$ and excess $SrCl_2$. CO_2 that might be adsorbed in the reagent bottle precipitates as white $SrCO_3$ crystals later. The field technician avoids using any reagent from a bottle in which precipitate is visible, regardless of whether it is of $SrCO_3$ or $SrCl_2$. We prefer an NH_4OH solution to NaOH pellets for adjusting sample pH in the field. Besides being slow to dissolve, NaOH pellets are hydrophilic, adsorbing water and atmospheric CO_2 that cannot be detected. We prefer a strontium-based reagent to a barium base. $BaSO_4$, more than 3,000 times less soluble than $SrSO_4$, would contaminate a $BaCO_3$ precipitate and interfere with the efficiency of carbon recovery and accuracy of ^{14}C analysis—a particular problem in sulfate-rich ground water.

Sampling Technique

Glass sample jars are prepared and labeled in advance of sampling at the well according to applicable quality assurance–quality control guidelines. Information on well construction, pumping rate, and well-bore storage is obtained and evaluated. Measurements of pH, Eh, and water temperature may be made in a flow cell (Wood, 1976), which also serve to track the purging of well-bore storage. Flow-cell readings or well-bore calculations indicate when discharge is coming from the formation rather than mostly out of well storage. Alkalinity is then measured by potentiometric titration of a water sample (Barnes, 1964; Wood, 1976), and water samples are collected for analyses of ^{14}C and other ionic and isotopic constituents of interest. Measured alkalinity is used as a basis for estimating the number of 50-L carboys to be filled with ground water to ensure an adequate recovery of DIC (fig. A1). For example, two 50-L carboys should be collected to obtain at least 1 g of carbon from ground water having a titrated alkalinity of 100 mg/L, given a yield of 50 percent.

After the carboys to be filled are set near the wellhead, the hose is set at the bottom of one carboy and the time it takes to fill the carboy is noted. Atmospheric CO_2 is displaced as the carboy is filled, and we allow the carboy to overflow at least 3 times that initial filling time to expel sample that was exposed to atmospheric CO_2. Fill and flush times of 10 to 15 min are typical of sampling at municipal and irrigation wells but can range from a few minutes to more than 1 h. Municipal and irrigation well operators usually allow the 150 L (~40 gal) of spilled water per carboy to run off. At hazardous waste sites, however, special efforts must be made to minimize and capture all wastewater overflow.

Once the carboy is purged, the following steps are made in quick succession: (1) the filling hose is removed and the PVC pipe is pushed into the full carboy to displace just over 500 mL of water, (2) the cap of the 500-mL bottle holding the ammoniacal $SrCl_2$ reagent is removed and the reagent is poured into the carboy, (3) the

carboy is topped off with water from the hose if necessary, (4) a cap is screwed onto the carboy and tightened, and (5) the carboy is shaken to mix the water sample and reagent. To minimize exposure of the reagent to atmospheric CO_2 and to avoid inhalation of ammonia vapor, the reagent bottle should be inverted and seated on the carboy mouth. A white cloud of $SrCO_3$ precipitate immediately forms in the water sample when the reagent is added.

The ratio of 500 mL reagent to 50 L sample of ground water is sufficient to raise the sample pH and provide excess strontium for precipitation of $SrCO_3$. This was confirmed using PHREEQE (Parkhurst and others, 1972) to simulate the titration of typical ground waters by the reagent. The pH of the sample and reagent mixture is approximately 10.4.

A sample of ground water is also collected in a 1-L, narrow-mouth glass bottle, and 25 mL of the $SrCl_2$ reagent is added by pipette to precipitate $SrCO_3$. The precipitate is decanted in the laboratory, with 100-percent DIC recovery. The $\delta^{13}C$ of the 1-L sample is determined in order to compare it with the larger sample from the carboy.

Filling and treatment of each additional carboy follow the above procedures. Each filled carboy can be rolled to the field vehicle using the two-wheel hand truck. At least 8 h should be allowed for the reagent to react with the water sample to precipitate DIC as $SrCO_3$ and for the $SrCO_3$ crystals to grow. Full carboys are loaded into the field vehicle and taken to the next sampling site. The drive to the next site or to the base of operations at the end of the day agitates the reagent and sample to mix them thoroughly.

To attach the transfer valve (fig. A2) to the glass sample jar, we cover threads of the jar with teflon tape and then attach the jar to the end of the transfer valve using the metal ring. We carefully ensure that the jar is tight enough to avoid a leak, but not so tight that the threads of the soft metal ring are stripped. N_2 gas can be used to displace air out of the sample jar before the ball valve is closed, isolating the CO_2-free sample jar. A sample jar is attached to a transfer valve for each carboy collected.

To decant the sample, we (1) remove the carboy cap and replace it quickly and tightly with the assembled transfer valve and sample jar, (2) set the carboy on the horizontal hand truck and carefully tip the carboy over—the sample bottle toward the footplate of the hand truck, (3) fasten and tighten the web straps around the carboy, and (4) raise the hand truck, inverting the carboy (fig. A4). The $SrCO_3$ powder immediately begins to settle to the inverted "top" of the carboy. To prevent small leaks, we sometimes use a pipe wrench to tighten the transfer valve before the carboy is inverted. Force should be applied, however, only to the carboy cap and not to the attached parts of the transfer valve so as not to shear any connections. The ball valve is slowly opened, letting a slurry of precipitate and solution into the sample jar; the bottle can be carefully tightened to stop leaks around the jar's threads. As the soft metal ring is reused, leaks become inevitable and the ring should be replaced. We assume that any leakage of sample must greatly exceed any inward diffusion of CO_2 so as not to affect sample quality. It generally takes 15 to 90 min for the precipitated $SrCO_3$ to settle in the sample jar, although most settles in the first 5 to 10 min. The hand truck and carboy must be periodically shaken to move the precipitate inward toward the neck of the carboy and down the transfer valve. A rocking motion that gathers the precipitate in a radial wave is most effective. In the pint-size (0.47-L) sample jar, 1 cm of settled precipitate equals approximately 1 g of carbon for analysis.

When collection is complete, the ball valve is closed and the sample jar removed. Immediately the metal dome lid is placed on the jar and a ring screwed on and tightened. Sealing tape is placed over the ring as a final barrier to CO_2 exchange. The sample jars are stored in a cooler under ice. When the jar is removed from the transfer valve, because a small amount of solution is spilled, suitable gloves should be worn as part of standard hygiene.

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The final step in the field is to dispose of the 50 L of treated water remaining in each carboy. If it is uncontaminated, dilute ground water, a property owner ought to permit the sample to be poured on the ground or into a ditch. The NH_4 should be a nutrient in plant growth. Precipitation of $SrCO_3$ might leave a thin white crust or stain on soil or pavement until rainfall washes it away, to which property owners might object. Strontium and chloride in the discarded sample have concentrations of approximately 630 and 510 mg/L, respectively, discounting the contribution of the ground water. Brines or samples from hazardous waste sites, of course, require that other arrangements be made to dispose of each 50-L waste-water sample properly.

Laboratory Treatment

Laboratory treatment yields a washed and filtered $SrCO_3$ powder that is free of the ammonium $SrCl_2$ solution and therefore safe from atmospheric contamination. Some ^{14}C laboratories will carry out this procedure as part of their service. A siphoning device (constructed from common laboratory supplies including an aspirator, tubing, a canning jar sealing lid, gas drying tube filled with CO_2 absorbent, and a 5-cc syringe body with plunger modified to seal around the polypropylene siphon tube) is used to remove as much as possible of the clear supernatant without also siphoning the $SrCO_3$ powder. Carbonate-free distilled water is added and mixed into the remaining slurry, and after the $SrCO_3$ powder settles, the clear liquid once again is siphoned off. These steps are repeated until the pH of the liquid nears pH 7, which requires at least three full rinses. The near-neutral pH indicates the absence of OH^- ions from the ammoniacal reagent such that the powder is finally safe from potential contamination by atmospheric CO_2. Powders from different carboys can be composited for laboratory analysis of ^{14}C and $\delta^{13}C$.

Results

The rate of precipitation decreases exponentially, requiring as much as 72 h to approach 100-percent recovery. The main controls on recovery efficiency appear to be (1) reaction time before decanting, which determines $SrCO_3$ crystal size and settling rate, (2) time allowed for settling, and (3) effort applied to shaking precipitate out of the carboy and into the sample jar. As noted by Gleason and others (1969), to recover 100 percent of DIC is difficult. The last 10 percent or so of total carbon forms very fine, possibly colloidal, $SrCO_3$ that is difficult to capture in the sample jar; agitation of the carboy resuspends the accumulated sediment. Yield of DIC in 90 ground-water samples collected by four investigators averaged 22 percent (fig. A5). Settling time among the 90 samples varied from 1 to 12 h.

To evaluate whether lack of 100-percent recovery affects isotopic data, in one experiment we collected samples after settling times of 1, 2, 4, 8, 16, and 24 h. In another test, the initial settling time was varied and then additional precipitate was repeatedly decanted from each carboy. Results show that $\delta^{13}C$ of precipitated $SrCO_3$ powder becomes as much as 0.4 to 0.8‰ enriched during the first few hours before reaching a steady value (fig. A6). One possible explanation is that $\delta^{13}C$ of $SrCO_3$ is affected by precipitation rate as it is in $CaCO_3$ (Turner, 1982). The initially formed, rapidly precipitated $SrCO_3$ is isotopically lighter than the later, more slowly precipitated $SrCO_3$. Sufficient reaction and settling time must be allowed, therefore, for total
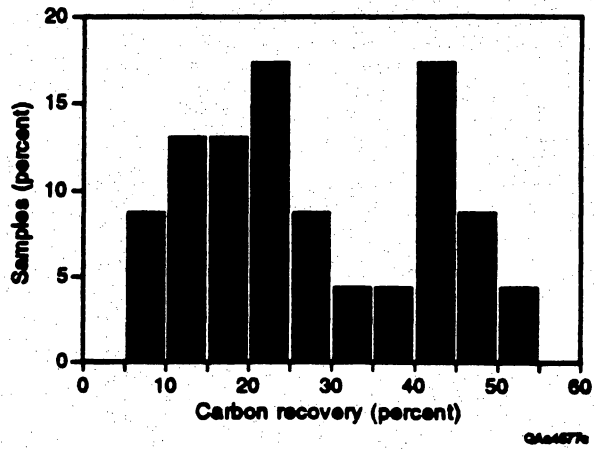
Figure A5. Histogram of percent DIC recovered from ground water by different technicians from various hydrostratigraphic units. Histogram represents 90 samples.
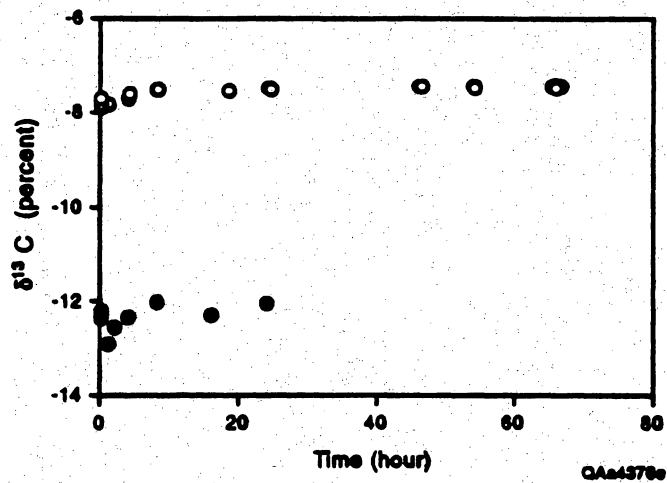
Figure A6. Results of two experiments for studying variation in $\delta^{13}C$ using $SrCO_3$ settling time in 50-L carboy. Open circles plotted at time = 0 represent $\delta^{13}C$ of 1-L control samples.

precipitated DIC to average out the effect of the early precipitation. Figure A6 suggests that a settling time of approximately 8 h yields a consistent value of $\delta^{13}C$.

Comparison of $\delta^{13}C$ from 50-L and 1-L samples shows that at least 75 percent of the samples agree very well, within 4 percent (fig. A7). Two of the three 50-L samples that are more enriched than the reference 1-L sample had low percent recovery. Comparison of $\delta^{13}C$ values between the 50-L samples and other measurements made at various times at the same wells show variable agreement. Four of 12 samples differ by an average of 2 percent. Too many variables make explaining the discrepancies of the other samples difficult. These data compare 50-L samples with 1-L samples collected by direct precipitation several years earlier, 1-L samples collected without field treatment 1 yr later than the 50-L samples and sent to a laboratory for DIC extraction, and 200-L samples collected using $BaCl_2$ and NaOH. The data include analyses by liquid scintillation counting as well as accelerator mass spectrometry.

Few data exist for evaluating the effect of sampling technique on ^{14}C. If $\delta^{13}C$ is unbiased, we assume ^{14}C is also unbiased. Data obtained using the carboy direct-precipitation method distinguish old and young waters ranging from <0.6 to 109 pmc, indicating that atmospheric contamination is insignificant. Reasonably reproducible ^{14}C values of 12.3 ± 0.2 pmc and 13.1 ± 0.2 pmc were obtained in analyses of samples collected 14 months apart from one well. Another comparison is of samples collected during 1 yr at four wells and analyzed by different methods at different laboratories. Samples to be analyzed by scintillation counting were collected by direct precipitation following the methods of this report, but samples to be used in accelerator mass spectrometry were collected untreated in 1-L glass bottles and DIC was extracted in the laboratory (L. Davisson, 1993, personal communication). Two samples differ by less than 2 pmc but the others differ by 13 and 23 pmc.

Conclusions

Scintillation counting remains a popular method for analyzing ^{14}C in ground water because it is cheap and fast. Using 50-L polypropylene carboys in direct precipitation of DIC allows workers to collect sufficient quantities (>1 g) of high-quality material efficiently. Depending on DIC and sample recovery, two to six carboys yield the 1 to 2 g of carbon needed for scintillation counting. This inexpensive method allows one person to sample two to three wells per day, cover dozens of wells across hundreds of miles in a regional aquifer, and then ship back to the laboratory only two to six small jars of $SrCO_3$ slurry from each well. Weight of full sample containers is not excessive or dangerous. Settling time of 8 h ensures at least 50-percent recovery, which minimizes fractionation effects. Precautions make contamination by atmospheric CO_2 insignificant, but potential for degassing of sample CO_2 and its effect on isotopic composition remains a concern.

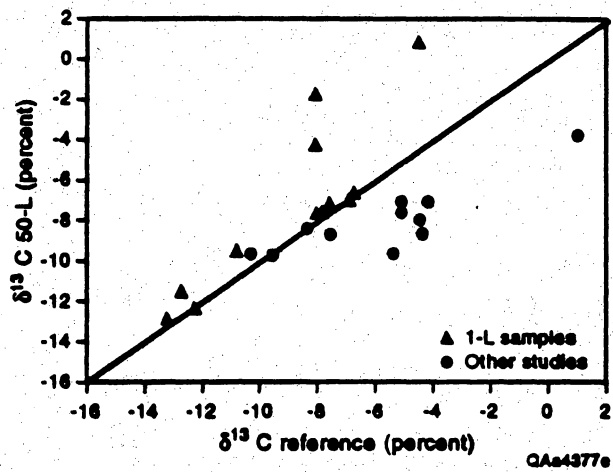Figure A7. Comparison of $\delta^{13}C$ in samples collected in 50-L carboys with reference $\delta^{13}C$ data— samples collected during this study in 1-L glass bottles using direct precipitation and samples collected during other studies in a 200-L steel tank using direct precipitation and in 1-L glass bottles without field treatment.