Prepared in cooperation with the Naval Weapons Station Yorktown
Base Civil Engineer
Environmental Directorate

Apparent Chlorofluorocarbon Age of Ground Water of the Shallow Aquifer System, Naval Weapons Station Yorktown, Yorktown, Virginia

By David L. Nelms, George E. Harlow, Jr., and Allen R. Brockman

Open-File Report 01-4179

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Richmond, Virginia
2001

U.S. DEPARTMENT OF THE INTERIOR
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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
	Length	
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
	Area	
acre	4,047	square meter
acre	0.4047	hectare
square mile (mi^2)	259.0	hectare
square mile (mi^2)	2.590	square kilometer
	Volume	
gallon (gal)	3.785	liter
gallon (gal)	.003785	cubic meter
	Velocity	
foot per day (ft/d)	0.3048	meter per day
	Hydraulic conductivity	
foot per day (ft/d)	0.3048	meter per day
	Transmissivity	
foot squared per day (ft^2/d)	0.09290	meter squared per day

Water temperature is reported in degree Celsius (°C), which can be converted to degree Fahrenheit (°F) by the following equation: °F = 1.8 (°C) + 32

Hydraulic conductivity and transmissivity: In this report, hydraulic conductivity is reported in feet per day (ft/d), a mathematical reduction of the unit cubic foot per day per square foot [$(ft^3/d)/ft^2$]. Transmissivity is reported in feet square per day (ft^2/d), a mathematical reduction of the unit cubic feet per day per square foot times feet of aquifer thickness ($[(ft^3/d)/ft^2]ft$).

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

Abbreviated water-quality units: Chemical concentration is reported in milligrams per liter (mg/L) or micrograms per liter (µg/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. For concentrations less than 7,000 mg/L, the numerical value is the same as for concentrations in parts per million. Specific electrical conductance of water is reported in microsiemens per centimeter at 25 degrees Celsius (µS/cm).

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ABSTRACT

Apparent ages of ground water are useful in the analysis of various components of flow systems, and results of this analysis can be incorporated into investigations of potential pathways of contaminant transport. This report presents the results of a study in 1997 by the U.S. Geological Survey (USGS), in cooperation with the Naval Weapons Station Yorktown, Base Civil Engineer, Environmental Directorate, to describe the apparent age of ground water of the shallow aquifer system at the Station. Chlorofluorocarbons (CFCs), tritium (^3H), dissolved gases, stable isotopes, and water-quality field properties were measured in samples from 14 wells and 16 springs on the Station in March 1997.

Nitrogen-argon recharge temperatures range from 5.9°C to 17.3°C with a median temperature of 10.9°C, which indicates that ground-water recharge predominantly occurs in the cold months of the year. Concentrations of excess air vary depending upon geohydrologic setting (recharge and discharge areas). Apparent ground-water ages using a CFC-based dating technique range from 1 to 48 years with a median age of 10 years. The oldest apparent CFC ages occur in the upper parts of the Yorktown-Eastover aquifer, whereas the youngest apparent ages occur in the Columbia aquifer and the upper parts of the discharge area setting, especially springs. The vertical distribution of apparent CFC ages indicates that ground-water movement between aquifers is somewhat retarded by the leaky confining units, but the elapsed time is relatively short (generally less than 35 years), as evidenced by the presence of CFCs at depth. The identification of binary mixtures by CFC-based dating indicates that convergence of flow lines occurs not only at the actual point of discharge, but also in the subsurface.

The CFC-based recharge dates are consistent with expected ^3H concentrations measured in the water samples from the Station. The concentration of ^3H in ground water ranges from below the USGS laboratory minimum reporting limit of 0.3 to 15.9 tritium units (TU) with a median value of 10.8 TU. Water-quality field properties are highly variable for ground water with apparent CFC ages less than 15 years because of geochemical processes within local flow systems. Ground water with apparent CFC ages greater than 15 years represents more stable conditions in subregional flow systems.

The range of apparent CFC ages is slightly greater than the ranges in time of travel of ground water calculated for shallow wells (less than 60-feet deep) from flow-path analysis. Calculated travel times to springs can be up to two orders of magnitude greater than the CFC-based apparent ages. Reasonable assumptions of values for hydraulic parameters can result in substantial overestimates for time of travel to springs.

Recharge rates computed from apparent CFC ages range from 0.29 to 0.89 feet per year (ft/yr) with an average value of 0.54 ft/yr. The analysis of apparent CFC ages in conjunction with geohydrologic data indicates that young water (less than 50 years) is present at depth (nearly 120 feet) and that both local and subregional flow systems occur in the shallow aquifer system at the Station. The addition of the dimension of time to the three-dimensional framework of Brockman and others (1997) will benefit current (2001) and future remediation activities by providing estimates of advective transport rates and how these rates vary

depending upon geohydrologic setting and position within the ground-water-flow system. Estimated ground-water apparent ages and recharge rates can be used as calibration criteria in simulations of ground-water flow on the Station to refine and constrain future ground-water-flow models of the shallow aquifer system.

INTRODUCTION

The U.S. Geological Survey (USGS), in cooperation with the Naval Weapons Station Yorktown, Yorktown, Va., has been investigating the geohydrology of the shallow aquifer system at the 10,624-acre installation since 1995. Brockman and others (1997) described the geohydrology of the shallow aquifer system in terms of geologic setting within the Virginia Coastal Plain Physiographic Province, aquifer and confining units, and conceptual ground-water flow. The production, maintenance, storage, and research and development of ordnance for the U.S. Navy have been the primary mission of the Station since its establishment in 1918. The Station is in an area steeped in historical American events. Not only are the mission of the Station and the local history unique, but the geology and subsequent geohydrology also are unique. Dissolution and erosion of calcareous sediments underlying the Station have formed numerous slump and subsidence features. The relations between ground-water age, chemistry, and flow have contributed to the formation of these unique geomorphic features, which have in turn affected the rich history of the area since colonial times (Brockman and others, 1997).

Estimates of apparent age of ground water are valuable for understanding and conceptualizing flow systems and can be used to refine the conceptualization of the geohydrology of the Station presented in Brockman and others (1997). Determination of apparent ages of ground water also can aid in the definition of potential pathways of contaminant transport on and near the Station and can be used in the calibration and sensitivity analyses of ground-water-flow models of the aquifers underlying the Station.

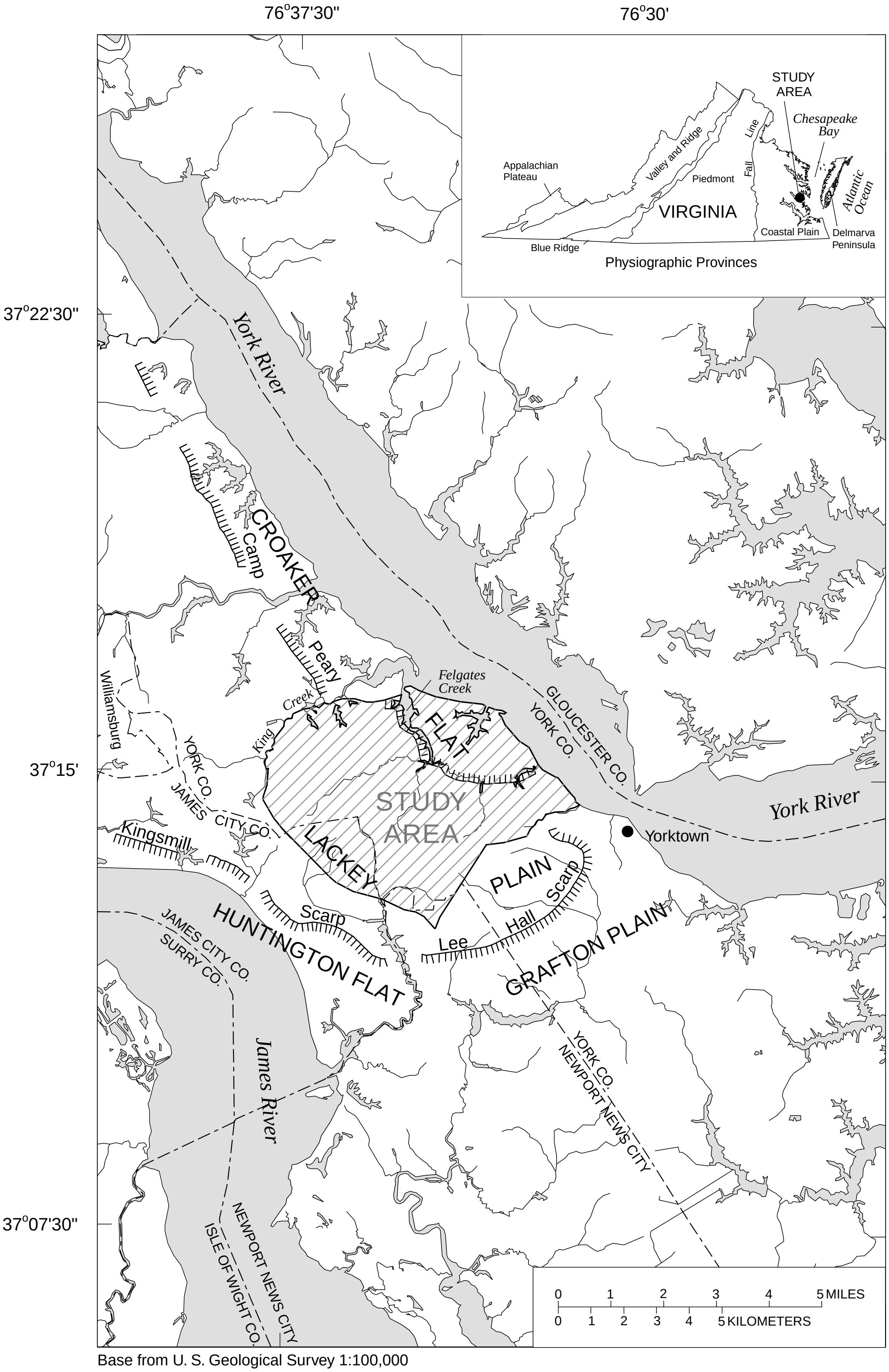
Ground-water dating frequently has been used to aid in the interpretation of ground-water systems in the Coastal Plain Physiographic Province of Virginia. For example, ground-water dating was used (1) to define steady-state conditions and occurrence of selected contaminants in the Delmarva Peninsula (Busenberg and Plummer, 1992; Dunkle and others, 1993; Speiran, 1996); (2) to determine ground-water age distributions in other parts of the Virginia Coastal Plain (Nelms and Ahlin, 1993; McFarland, 1997; Nelms and Brockman, 1997); and (3) to determine ground-water residence times from spring samples, as part of the USGS Chesapeake Bay Ecosystem project (Focazio, 1997; Focazio and others, 1998). This study at the Station uses a similar approach as the other studies in Virginia by using apparent ages of ground water to improve the conceptualization of ground-water flow.

Purpose and Scope

The purpose of this report is to describe the apparent chlorofluorocarbon (CFC) age of ground water in the shallow aquifer system on the Station and to refine the conceptualization of ground-water flow. The report presents the data and findings of a 1-year study that involved the use of environmental tracers and isotopes to estimate and confirm the apparent CFC ages of ground water. The report (1) defines the apparent CFC age of ground water in the shallow aquifer system, (2) compares apparent CFC ages with water-quality field properties and calculated times of travel, and (3) presents estimates of ground-water recharge rates. Water samples were collected in March 1997 from 14 existing observation wells installed by the USGS (Brockman and others, 1997) and from 16 natural springs located throughout the Station. Apparent CFC ages, dissolved gas and stable isotope composition of ground water, and water-quality field properties were determined from the 30 ground-water samples.

Description of Study Area

The study area consists of the Naval Weapons Station Yorktown, which encompasses parts of York and James City Counties and the City of Newport News, Va. (fig. 1). The Station is located on the York-James Peninsula and within the Atlantic Coastal Plain Physiographic Province of Virginia (Fenneman, 1938). An eastward thickening wedge of unconsolidated sediments characterizes the Coastal Plain in Virginia, which extends eastward from the Fall Line to the Atlantic Ocean. The Fall Line marks the boundary between the Coastal Plain and Piedmont Physiographic



Base from U. S. Geological Survey 1:100,000

Figure 1. Location and geomorphic features of the Naval Weapons Station Yorktown (study area), Virginia, and adjacent area, Yorktown, Virginia.

Provinces and is approximately 50 mi west of the Station.

Another prominent feature of the Virginia Coastal Plain is a series of terraces that occur at different elevations and are bounded by scarps cut by shoreline erosion (Johnson and others, 1993a). The Naval Weapons Station Yorktown is divided into two terraces (fig. 1)—the Lackey Plain and the Croaker flat (Brockman and others, 1997). The Lackey Plain (Johnson, 1972) occupies the largest area and the highest elevations of the Station. The Croaker flat is a low-lying terrace located along the base of the Camp Peary scarp along the York River, where coarse to very coarse grained sediments occur at land surface. The terraces are highly dissected by steep valleys formed by stream erosion and ground-water sapping. These terraces and valleys have a major effect on the shallow ground-water-flow system of the Station.

Geohydrologic Setting

The shallow aquifer system at the Station consists of five geohydrologic units that overlay the Eastover-Calvert confining unit: (1) the Columbia aquifer, (2) the Cornwallis Cave confining unit, (3) the Cornwallis Cave aquifer, (4) the Yorktown confining unit, and (5) the Yorktown-Eastover aquifer (fig. 2). All of the geohydrologic units are present beneath the Lackey Plain; the Cornwallis Cave confining unit and aquifer, however, are truncated by the Camp Peary scarp and are not present beneath the Croaker flat. The top of the Eastover-Calvert confining unit defines the base of the shallow aquifer system at the Station.

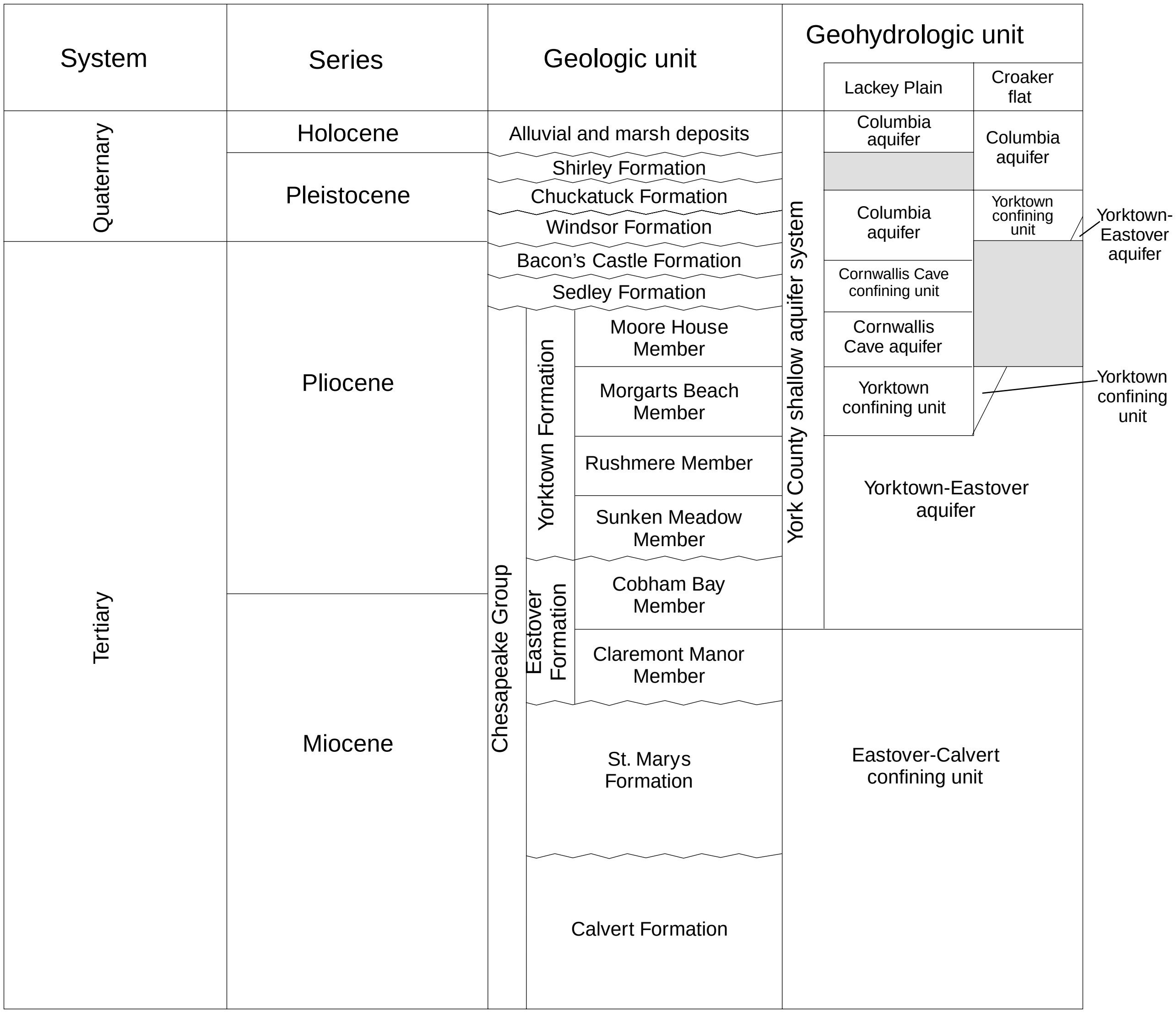
The Columbia aquifer consists of very fine to very coarse grained sands, silty to clayey sand, or sandy clay, and ranges in saturated thickness from 5 to more than 20 ft, seasonally. The Cornwallis Cave confining unit underlies the Columbia aquifer beneath the Lackey Plain and consists of clay, sandy or silty clay, or clayey silt that can be from less than 5- to more than 20-ft thick. The Cornwallis Cave aquifer consists of shell hash, coquina, clay, or silt; clayey or sandy shell hash; very fine to medium grained sand; or shelly clay, and ranges in thickness from less than 5 to more than 60 ft. The Yorktown confining unit consists of clay, clayey silt, sandy clay, or silty clay with or without shell hash or sand stringers that can be from less than 5- to more than 30-ft thick. The Yorktown-Eastover aquifer occurs throughout the Station and consists of very fine to coarse grained sand, silty sand, silt, or sandy clay with or without some conglomerate, clay, and shell hash. The Yorktown-Eastover aquifer ranges in thickness from less than 60 to more than 100 ft. The Eastover-Calvert confining unit consists of silt, clay, and fine-grained sediments and generally is more than 150-ft thick across the Station. A more detailed description of the various geohydrologic units is presented in Brockman and others (1997).

Although the relation between the geomorphology (terraces and steep valleys) and geohydrology is complex, Brockman and others (1997) identified two primary geohydrologic settings on the Station (fig. 3):

Recharge area setting, where the Columbia aquifer is saturated and unconfined, and the Cornwallis Cave and Yorktown-Eastover aquifers are saturated and confined. These areas usually are topographically elevated and flat with minimal stream dissection. Upland wetland areas are scattered about the higher elevations of the Station and are in hydraulic contact with the Columbia aquifer. Fluctuations in water levels and ground-water temperatures are more pronounced in the Columbia aquifer and become progressively more subdued in the deeper aquifers. Ground-water flow tends to be directed downward in response to steep vertical hydraulic gradients between aquifers.

Discharge area setting, where sediments of the Columbia aquifer are unsaturated, but sediments of the Cornwallis Cave and Yorktown-Eastover aquifers are saturated. The Cornwallis Cave aquifer usually is unconfined and the Yorktown-Eastover aquifer generally is confined, but also can be unconfined. These areas are highly dissected with numerous springs and seeps, which are the primary discharge mechanisms along with direct ground-water flow to streams. Field reconnaissance indicates that occurrence of springs is strongly controlled by macropore processes such as ground-water flow along tree roots and rootlets, and dissolution, piping, and/or winnowing of shell material in the Cornwallis Cave aquifer. Seeps and springs normally occur at or slightly above (generally less than 5 ft) the stream and seldom occur up the sides of the valleys. Fluctuations in water levels and ground-water temperatures are more subdued than in the recharge area setting. Ground-water flow tends to be either downward or upward depending on the direction of vertical hydraulic gradients between aquifers; these gradients usually are low (less than 0.2 foot per foot).

The designation of recharge and discharge areas by Brockman and others (1997) is consistent with the geohydrologic framework and conceptual model of the



System	Series	Geologic unit			Geohydrologic unit		
						Lackey Plain	Croaker flat
Quaternary	Holocene	Alluvial and marsh deposits			York County shallow aquifer system	Columbia aquifer	Columbia aquifer
	Pleistocene	Shirley Formation				▨	
		Chuckatuck Formation				Columbia aquifer	Yorktown confining unit
		Windsor Formation					
Tertiary	Pliocene	Bacon's Castle Formation				Cornwallis Cave confining unit	▨ Yorktown-Eastover aquifer
		Sedley Formation					
		Chesapeake Group	Yorktown Formation	Moore House Member		Cornwallis Cave aquifer	
				Morgarts Beach Member		Yorktown confining unit	Yorktown confining unit
				Rushmere Member		Yorktown-Eastover aquifer	
				Sunken Meadow Member			
			Eastover Formation	Cobham Bay Member			
	Miocene			Claremont Manor Member	Eastover-Calvert confining unit		
			St. Marys Formation				
			Calvert Formation				

Figure 2. Relation between geologic and geohydrologic units at the Naval Weapons Station Yorktown, Virginia. Modified from Brockman and others (1997).

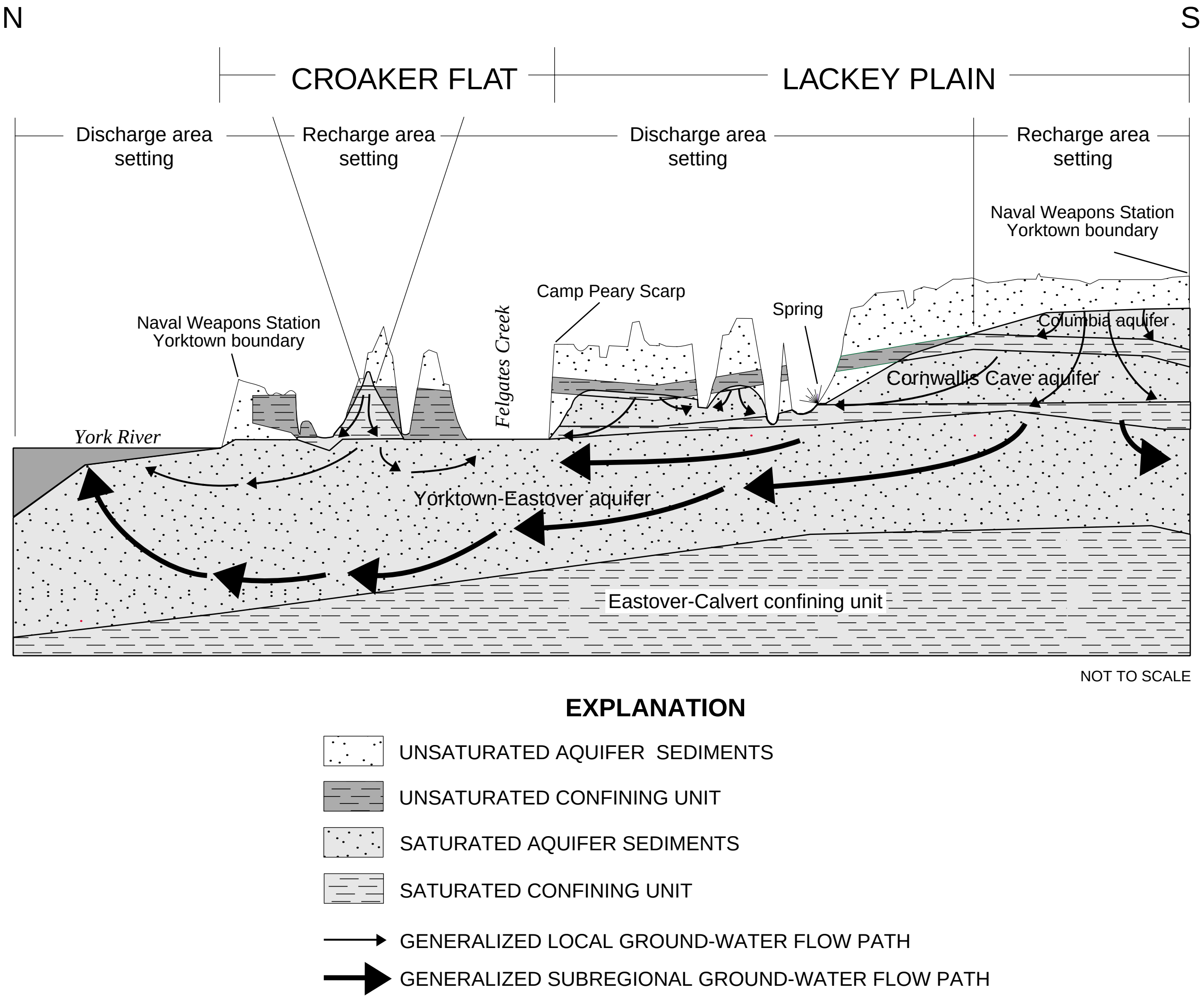


Figure 3. Geohydrologic section showing conceptualized ground-water flow at the Naval Weapons Station Yorktown, Virginia. Modified from Brockman and others (1997).

ground-water-flow system presented in their report, but this designation does not imply that only one of these flow processes occurs in these areas. For example, the discharge area setting occupies a large part of the study area; recharge processes, however, can and do occur in this setting. Furthermore, these two settings are present beneath the Croaker flat, but the sediments and unique features of the Cornwallis Cave aquifer are absent.

Conceptual Model of Ground-Water Flow

Brockman and others (1997) developed a conceptual model of ground-water flow in the shallow aquifer system at the Station (fig. 3). The model is based on a synthesis of geohydrologic and field reconnaissance data collected during their study, preliminary analysis of apparent age determinations (Nelms, 1997), and previous investigations in neighboring York County (Brockman and Richardson, 1992; Richardson and Brockman, 1992). The shallow aquifer system is recharged by infiltration of precipitation and by leakage of precipitation through the confining units into the underlying aquifers. A majority of the recharge originates from on the Station or nearby adjacent areas. Ranges of vertical hydraulic conductivity for the aquifers and confining units are comparable (table 1); the confining unit thicknesses generally are 8 and 14 ft for the Cornwallis Cave and Yorktown confining units, respectively. The steep vertical hydraulic gradients between aquifers combined with the leaky and thin

Table 1. Ranges and median values for vertical and horizontal hydraulic conductivity by geohydrologic unit at the Naval Weapons Station Yorktown, Virginia

[Data from Brockman and others (1997)]

Geohydrologic unit	Number of analyses	Range (feet per day)	Median (feet per day)
Vertical hydraulic conductivity			
Columbia aquifer	5	1.7×10^{-4}-1.7×10^{-1}	7.1×10^{-2}
Cornwallis Cave confining unit	5	3.1×10^{-5}-1.4×10^{-2}	2.6×10^{-3}
Cornwallis Cave aquifer	12	6.2×10^{-4}-2.4×10^{-1}	4.2×10^{-2}
Yorktown confining unit	6	1.3×10^{-5}-7.4×10^{-3}	1.2×10^{-4}
Yorktown-Eastover aquifer	27	4.0×10^{-6}-4.8×10^{-1}	1.8×10^{-3}
Eastover-Calvert confining unit	11	6.0×10^{-6}-4.3×10^{-4}	8.5×10^{-5}
Horizontal hydraulic conductivity			
Columbia aquifer	4	0.4-8	0.7
Cornwallis Cave aquifer	6	.3-9	4.5
Yorktown-Eastover aquifer	13	.02-.5	.1

confining units allow for relatively rapid vertical movement of ground water. The low vertical hydraulic conductivity (table 1) and large thickness of the Eastover-Calvert confining unit isolates the shallow aquifer system from the deeper regional aquifer systems underlying the Station (Brockman and others, 1997). The vertical isolation of the shallow aquifer system contributes to the development of local and subregional flow paths. Ground water flows from the point of recharge to seeps, springs, and streams located in the highly dissected valleys and estuaries and to the deeply incised York River (incised approximately 60 ft). The relatively shallow incisement (generally less than 30 ft) of the James River to the south creates a different hydrologic response in the shallow aquifer system than does the York River as evidenced by differences in hydraulic gradients determined by Brockman and others (1997).

Geomorphic Features

Stream morphology is strongly affected by the geohydrologic units with stream density increasing as permeability of the underlying unit decreases. Streams tend to be deeply incised and limited to a single stream channel in areas underlain by the Cornwallis Cave aquifer. A common feature in the outcrop areas of this aquifer is the presence and formation of travertine and calcareous tufa deposits, which form by precipitation of carbonate minerals as ground water discharges to the streams. These deposits normally occur in the upper parts of the Cornwallis Cave aquifer and occasionally form a stair-like pattern of small waterfalls along the longitudinal axis of the stream. Old travertine deposits occur at altitudes above the present-day surface of the water table, which may indicate that the water table was higher in the past in response to climatic conditions or changes in sea level. Another possibility is that the water table was lowered locally by the creation of preferred pathways or conduits for ground-water flow because of changes in the aquifer matrix by chemical and/or physical processes.

Areas underlain by the Yorktown confining unit have streams with poorly defined and shallow channels, increased stream density, and broad flood plains. Streams often are braided and flow over organic-rich alluvial deposits that generally are less than a few feet thick. Seeps at the base of the Cornwallis Cave aquifer are readily identified by the occurrence of iron deposits along the margins of the broad flood plains. Discharge from the Yorktown-Eastover aquifer is difficult to identify because it occurs in areas along the tidal marshes of Felgates and King Creeks and in the York River.

Another feature frequently encountered on the Station (predominantly in areas where the Cornwallis

Cave aquifer crops out) is the apparent loss of flow along short segments (generally less than 50 ft in length) of a stream. Streams often disappear into the streambank and re-emerge downstream; these segments easily could be misinterpreted as a spring (fig. 4). Fissures form along the streambanks, and slope creep develops on the valley walls under which the stream is flowing. Stoping and ground-water sapping (erosion) combine to undercut the valley walls resulting in slope instability, which frequently results in rotated and deformed trees.

Numerous subsidence sinkholes or collapse features dot the landscape of the Lackey Plain on the Station. The upland wetland areas usually develop in low relief sinkholes or coalescing collapse features (G.H. Johnson, College of William and Mary, oral commun., 1996). In the discharge area setting, sinkholes or collapse features frequently occur at the heads of streams (fig. 4). Relief on many of these sinkholes can be up to 15 ft, and their formation usually is limited to areas underlain by the Cornwallis Cave aquifer. Evidently, stoping or undercutting processes erode the interstitial shell material of the Cornwallis Cave aquifer; void spaces are created that eventually collapse under the weight of the overlying material. The deposition of shell material and sand that commonly occurs as springs discharge from the Cornwallis Cave aquifer supports the idea of sediment erosion. The relation between sediment removal and dissolution of shell material is not well understood. The formation of subsidence sinkholes, however, may be initiated by the dissolution of shell material that creates voids or openings in the aquifer that probably resemble the structure of a honeycomb. Preferential ground-water flow along these dissolution openings could develop sufficient velocity to transport sediment. Johnson and others (1987; 1993b) provide further information on the origin, distribution and evolution of subsidence sinkholes in the Coastal Plain of southeastern Virginia.

Climate

Climatic data for the Station were obtained from the National Weather Service station 449151 located near Williamsburg, Va. The period of record is 46 years for temperature data and 51 years for precipitation data at this station. The normal values are based on the National Weather Service's current normal climatological period from 1961 to 1990. The mean annual air temperature is 14.6° C with the colder periods of the year between November and March and the warmer periods between April and October (fig. 5). The coldest month is January (2.9°C) and the warmest is July (25.3°C). Precipitation is evenly distributed throughout the year with an average annual value of 47.08 in/yr (fig. 5). Precipitation in an average year would be highest in July, 4.96 in., and lowest in April, 3.01 in.

SAMPLING AND ANALYTICAL METHODS

Samples for analysis of CFCs were collected in March 1997 from 14 observation wells installed by the USGS (Brockman and others, 1997) and from 16 springs located on the Station (fig. 6). The wells were constructed of 4-in.-inside-diameter polyvinyl chloride (PVC) with screen lengths ranging from 4 ft for the wells finished in the Columbia and Cornwallis Cave aquifers to 9.5 ft for the wells finished in the Yorktown-Eastover aquifer. Surface casings and bentonite grout were installed in wells completed in the Cornwallis Cave and Yorktown-Eastover aquifers to prevent leakage of water from the overlying aquifer. Wells were purged prior to sample collection using either a Grundfos Redi-Flo 2 or a Bennett submersible pump. Water-quality field properties (pH, specific conductance, temperature, and dissolved oxygen) and water levels were monitored continuously during purging and sampling. Specific conductance and pH were monitored in a flow-through chamber, whereas dissolved oxygen and temperature were measured downhole within the screened interval. Water-level measurements were made with an electric tape. A minimum of three well volumes was removed during purging with the Grundfos Redi-Flo 2, and then samples were collected with the Bennett pump after stabilization of the field properties. The criteria used to define the stabilization of field properties are shown in table 2.

The springs sampled during this investigation are naturally occurring with no construction improvements. Water samples were collected from springs using a Bennett pump after monitoring the water-quality field properties until measurements stabilized. In most cases, the pump was placed directly into the spring; springs with shallow discharge pools, however, required the temporary installation of a 2-in.-inside-diameter PVC screen to a maximum depth of 2 ft. The pump was placed inside the screen and field properties were monitored directly in the discharge pool. Pertinent site information, water-quality field properties,

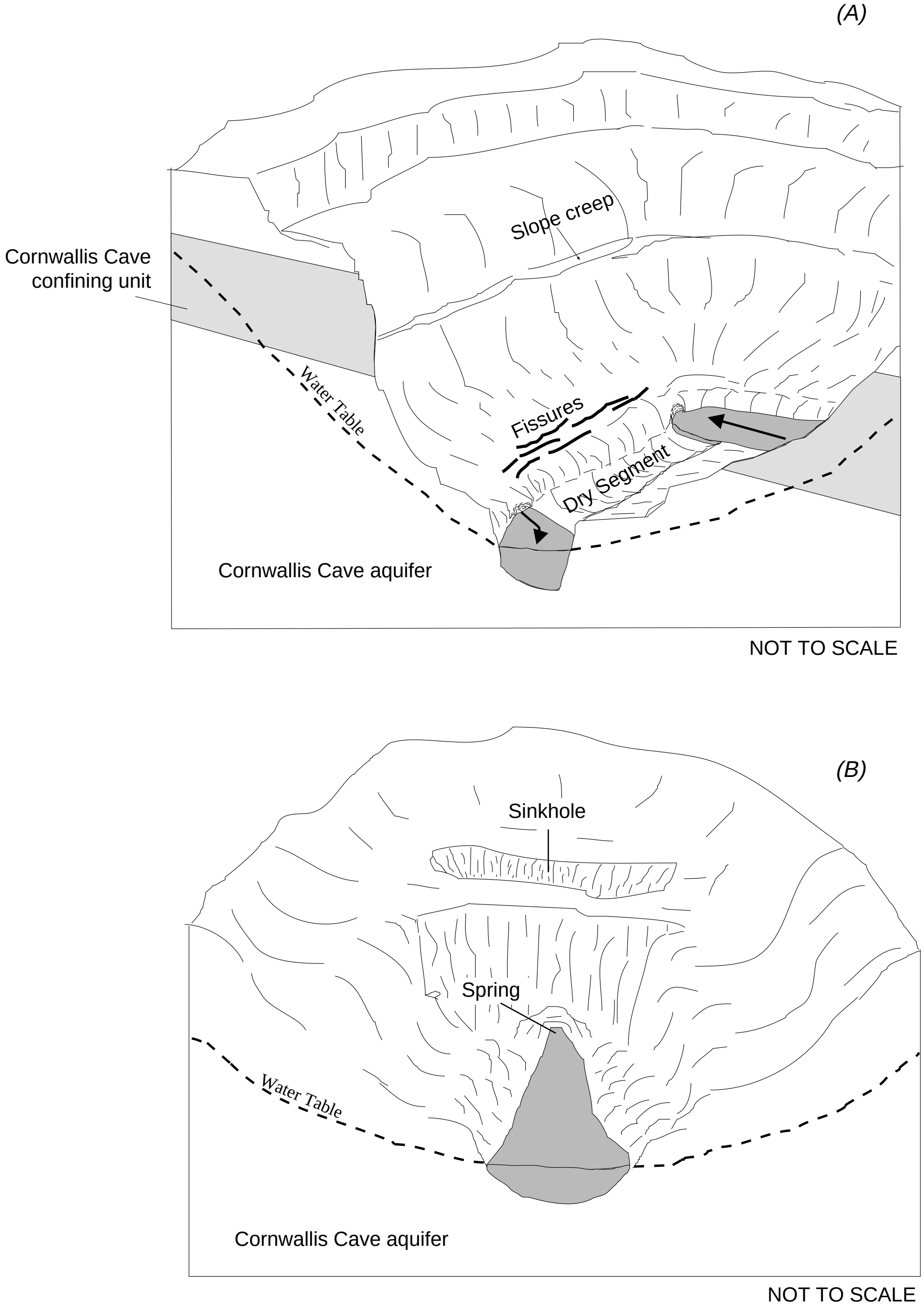


Figure 4. Dry stream segment *(A)* and collapse feature development uphill of spring *(B)* at the Naval Weapons Station Yorktown, Virginia.

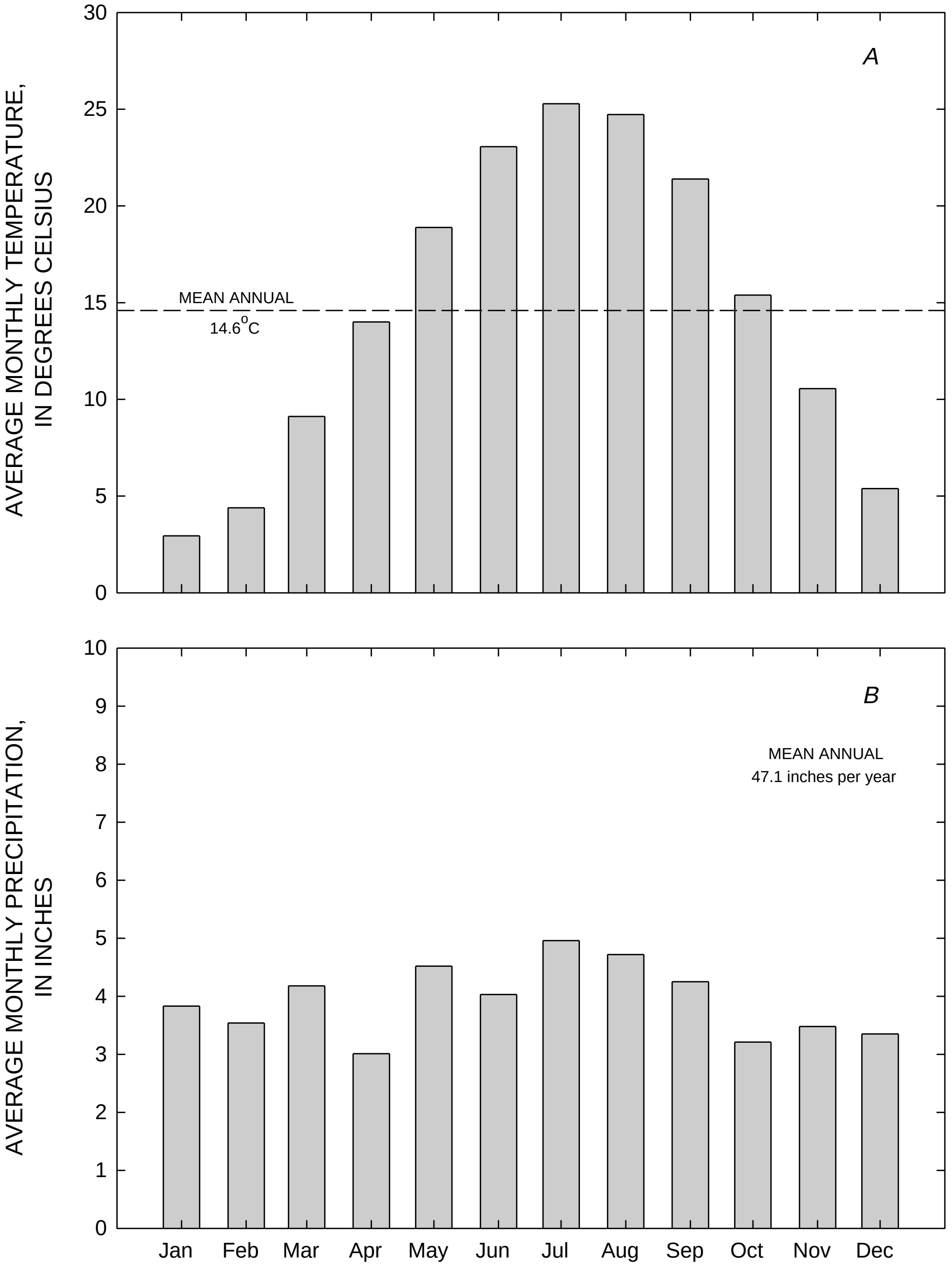
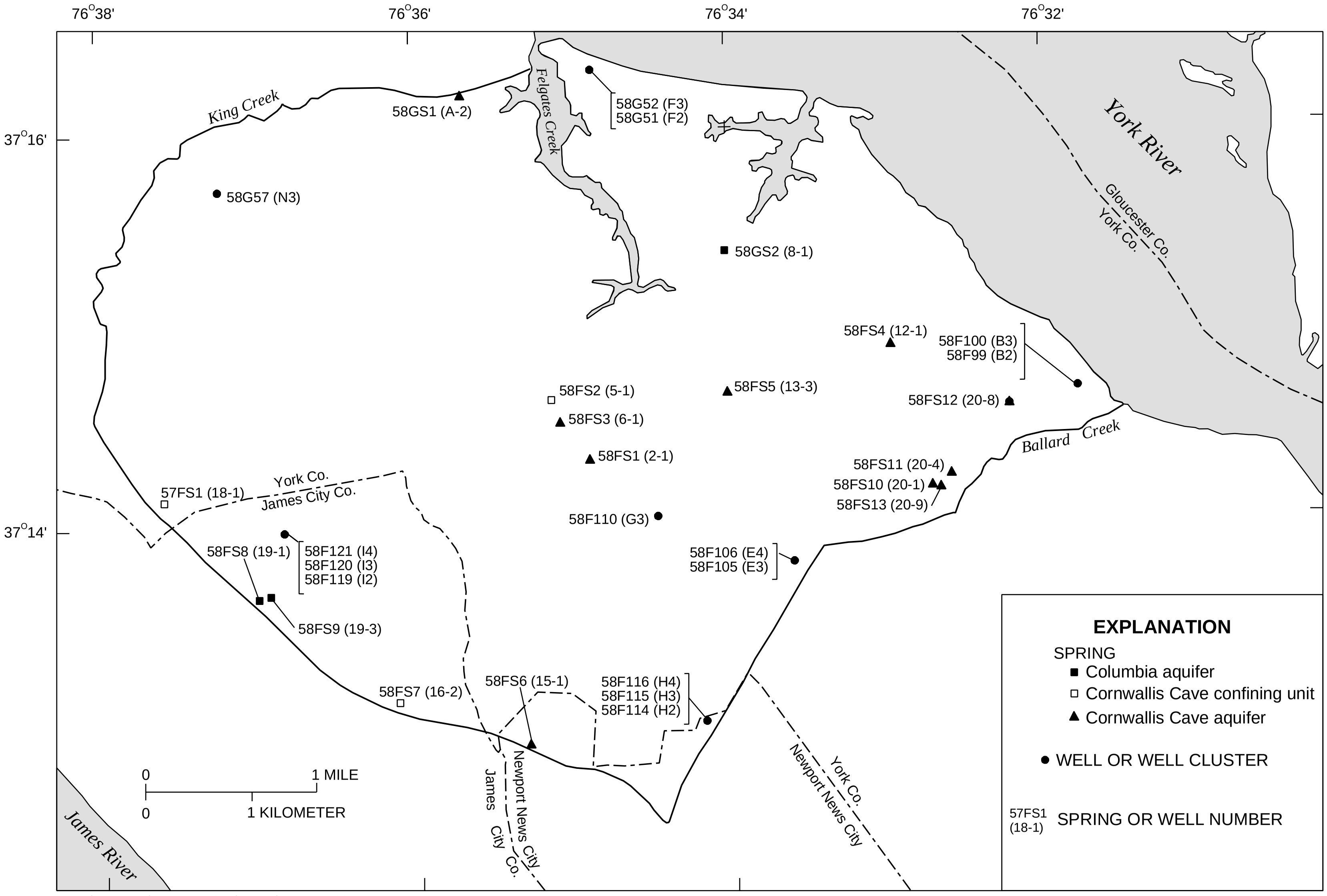


Figure 5. Average monthly temperatures *(A)* and precipitation *(B)* for National Weather Service station 499151 located at Williamsburg, Virginia. (Data from National Oceanic and Atmospheric Administration, 1996).



Base from Naval Weapons Station Yorktown 1:9,600

Figure 6. Location of wells and springs sampled in March 1997 on the Naval Weapons Station Yorktown, Virginia.

Table 2. Measurement accuracy and stability criteria for water-quality field properties during purging

[µS/cm, microsiemens per centimeter; °C, degrees Celsius; mg/L, milligrams per liter; min, minutes; <, less than]

Water-quality field property	Measurement accuracy[1]	Stability criteria[2]
pH	± 0.01 units	0.1 units/min
Specific conductance	± 2.5 µS/cm	0.5 (µS/cm)/min for <500 µS/cm
	± 5.0 µS/cm	1.0 (µS/cm)/min for 500-1000 µS/cm
Temperature	± 0.1°C	0.02°C/min
Dissolved oxygen	± 0.3 mg/L	0.03 (mg/L)/min

[1] From Beckman Instruments, Inc. (1992) and Yellow Springs Instruments, Inc. (1996)

[2] From Gibs and Imbrigiotta (1990)

and isotopic data for the wells and springs sampled in March 1997 also are presented in appendixes 1 and 2.

Samples for CFC analysis were collected through a 0.25-in copper tubing connected to the Bennett pump. The samples were flame-sealed in 62-mL borosilicate-glass ampoules using a special apparatus developed by Busenberg and Plummer (1992) that prevents the water sample from contacting the air. The introduction of air from the time of sampling into the sample could cause erroneous estimates of apparent ground-water age. Five sequential duplicate samples were collected from each well. The samples were analyzed by purge-and-trap gas chromatography with an electron-capture detector in the USGS CFC laboratory in Reston, Va. (Busenberg and Plummer, 1992). The detection limit for the CFCs is less than 1 pg/kg (picogram per kilogram), which is equivalent to less than 1 part per quadrillion (Plummer and Friedman, 1999).

Samples for dissolved gas analysis were collected by filling a 160-mL glass bottle without aerating the sample through a discharge line from the Bennett pump. The 160-mL bottle was submerged in a 7.5-L container filled with water from the well or spring. The sample was then sealed in the 160-mL bottle with a rubber stopper that had a hypodermic needle inserted. The needle was removed from the stopper while the bottle was submerged to prevent gas exchange between the sample and atmospheric air (M.W. Doughten, U.S. Geological Survey, written commun., 1997). Two sequential duplicate samples were collected at each well and spring where CFC samples were collected. The samples were analyzed by gas chromatography in the USGS dissolved gas laboratory in Reston, Va. (Busenberg and others, 1993). Dissolved gas concentrations for nitrogen, argon, oxygen, carbon dioxide, and methane were determined (appendixes 1 and 2).

Samples for tritium (^{3}H) analysis were collected in a 1-L glass bottle capped with a polycone seal. A small headspace was left in the bottle to prevent bottle breakage as a result of expansion of the water upon warming. Following procedures modified from Thatcher and others (1977), the samples were enriched electrolytically and analyzed by liquid scintillation counting in the USGS low-level ^{3}H laboratory in Menlo Park, Calif. Samples for ^{3}H analysis were collected at each well and spring where CFC samples were collected (appendixes 1 and 2).

Additional samples were collected at each site for oxygen and hydrogen isotopic analyses to assist in the interpretation of the CFC, dissolved gas, and ^{3}H analyses. Samples for the determination of stable isotope ratios were collected in 60-mL glass bottles. The samples were analyzed for oxygen-isotopic ratio by the carbon dioxide (CO_2)-equilibration technique of Epstein and Mayeda (1953) and for hydrogen-isotopic ratio by the hydrogen equilibration technique of Coplen and others (1991) in the USGS stable isotope laboratory in Reston, Va. The results of the stable isotope analyses (appendixes 1 and 2) are reported in per mil (parts per thousand or ‰) deviation from the Vienna Standard Mean Ocean Water (VSMOW) with a 2-sigma uncertainty of 0.2 per mil and 2 per mil for oxygen- and hydrogen-isotopic ratios, respectively (T.B. Coplen, U.S. Geological Survey, written commun., 1997).

Acknowledgments

Mr. Jeffrey Harlow of the Naval Weapons Station Yorktown, Environmental Directorate, was of great assistance in arranging permits necessary for sample collection. Mr. Bernard Setterholm and Ms. Carolyn Neill, also of the Directorate, assisted with project logistics. Assistance in the field sampling by R.J. Ahlin, C.F. Bell, J.J. Gildea, and C.W. Reinitz of the USGS is greatly appreciated. G.C. Casile, M.W. Doughten, J.E. Wayland, and P. K. Widman of the USGS National Research Program provided valuable assistance with the preparation and delivery of sample equipment and supplies and performed the laboratory analyses. Eurybiades Busenberg and L. Niel Plummer of the USGS National Research Program assisted with the interpretation of the apparent age determinations.

ESTIMATION OF RECHARGE TEMPERATURE

Recharge temperature is defined as the temperature of ground water when isolated from air in the unsaturated zone. The dissolved concentrations of nitrogen (N_2) and argon (Ar) measured in water samples can be used to determine the temperature at recharge. Air-water equilibrium processes that are dependent upon pressure and temperature (Heaton, 1981; Dunkle and others, 1993) fix the concentrations of N_2 and Ar in waters recharging the ground-water system. Recharge temperature can be calculated from these concentrations because the recharge water is approximately at atmospheric pressure. A graphical representation of the estimation of recharge temperature from the dissolved N_2 and Ar gas concentrations is shown in figure 7 for the 30 ground-water samples from the Station (appendixes 1 and 2). The recharge temperature is determined by projecting from the locus of any sample to the temperature axis (water-air equilibrium) along a line parallel to the temperature lines in figure 7. Busenberg and others (1993) provide a more detailed explanation of the estimation of recharge temperature.

The N_2-Ar recharge temperatures for the 30 ground-water samples collected in March 1997 range from 5.9°C to 17.3°C with a median temperature of 10.9°C (table 3). Uncertainty in the estimation of N_2-Ar recharge temperatures is ±1.0°C (L.N. Plummer, U.S. Geological Survey, oral commun., 2001). Estimated N_2-Ar recharge temperatures for 28 of the 30 ground-water samples were colder than the mean annual air temperature of 14.6° C, which indicates recharge predominantly occurs in the colder months of the year when plants are dormant and evapotranspiration is minimal. Although precipitation generally is highest in the summer months, dissolved gas concentrations indicate that only a small percentage of this rainfall recharges the ground-water system.

Dissolved concentrations of N_2 and Ar can also be used to determine the amount of excess air in ground water (Heaton and Vogel, 1981). Excess air is defined as air in the unsaturated zone that is in excess of solubility equilibrium (Plummer and Busenberg, 1999). As the water table rises, excess air is entrained in ground water and is eventually dissolved by increasing hydrostatic pressures with depth. The presence of excess air will cause the sample to plot to the right (higher concentration of gases than expected) of the water-air equilibrium line along a given temperature line (fig. 7). Plummer and Busenberg (1999) reported that excess air in ground water typically is less than 6 cm^3/L (cubic centimeters per liter).

Nelms (1997) noted that excess air concentrations vary depending upon geohydrologic setting. The highest concentrations of excess air occur in water samples from wells located in the recharge area setting of the Station, where seasonal water-level fluctuations are large (table 3). Excess air increases as the saturated thickness above the screened interval increases. Low excess air concentrations are characteristic of wells and springs located in the discharge area setting where seasonal water-level fluctuations are more subdued and saturated thicknesses are less than in the recharge area setting.

Temperature differentials can be used to indicate relative ground-water flow paths on the Station. Comparisons of ground-water and recharge temperatures to mean annual air temperature indicate that recharge and ground-water temperatures usually were colder than mean annual air temperature (fig. 8), which indicates short and shallow flow paths for water discharging to springs. If the ground water had flowed deeper, the measured water temperatures of the springs should be warmer. Water from wells has followed deeper flow paths. Variations in seasonal ground-water temperatures generally are less than 1°C in the discharge area setting, and the warmest temperatures occur in the late winter and early spring months (Brockman and others,

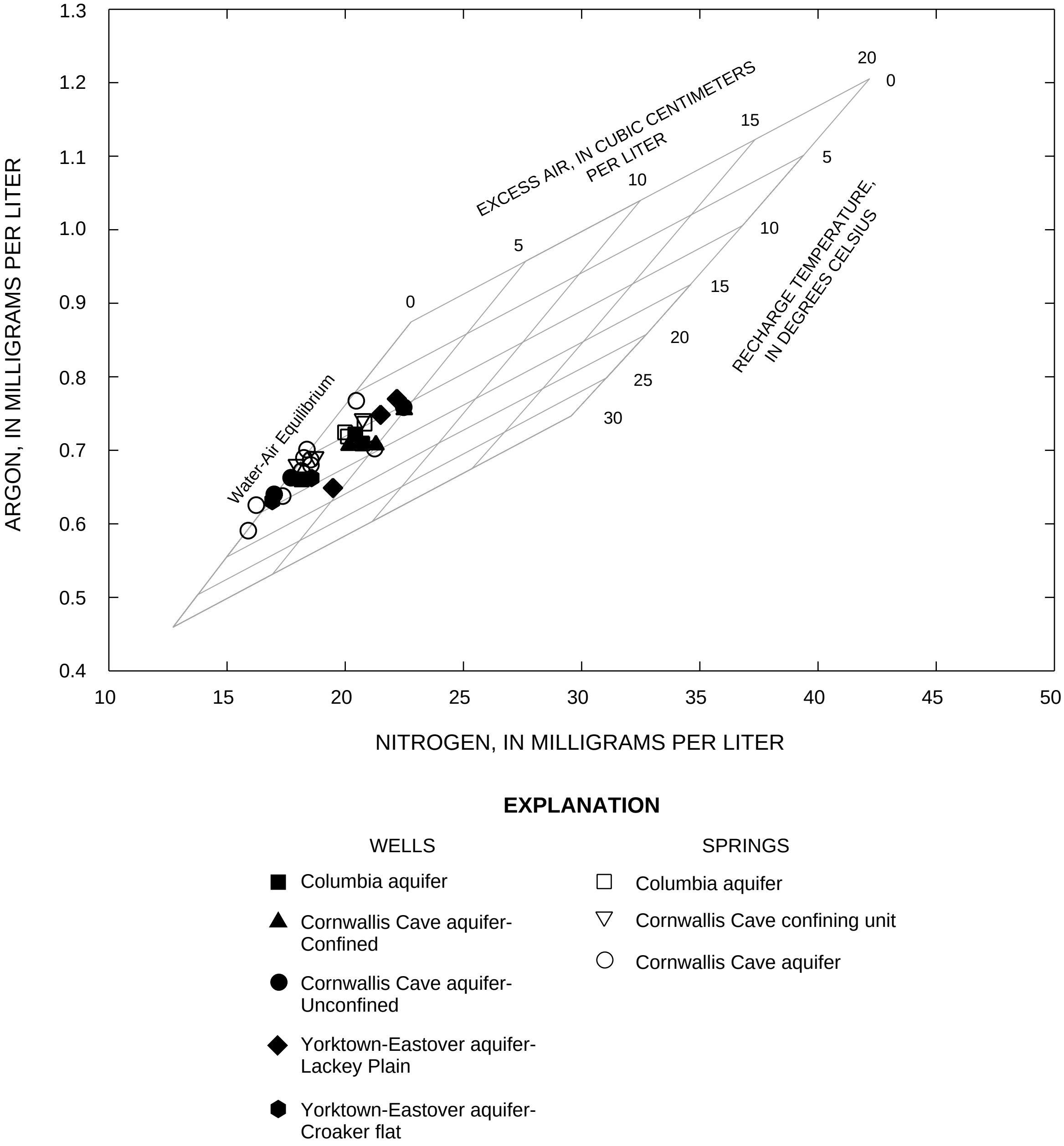


Figure 7. Dissolved nitrogen and argon compositions of ground water and estimates of recharge temperature at the Naval Weapons Station Yorktown, Virginia, March 1997.

Table 3. Range and median values for dissolved-gas compositions of ground water and for estimates of recharge temperature at the Naval Weapons Station Yorktown, Virginia, March 1997

[Gas concentrations are in milligrams per liter. Median values in parenthesis if sufficient number of sites (at least 5) available to calculate. °C, degrees Celsius; cm^3/L, cubic centimeters per liter]

Sample location	Number of sites	Recharge temperature (°C)	Excess air (cm^3/L)	Nitrogen	Argon	Oxygen	Carbon dioxide	Methane
Columbia aquifer	6	9.3-13.0 (10.3)	1.1-3.4 (2.2)	18.1-20.8 (20.3)	0.660-0.736 (0.720)	0.1-2.9 (1.2)	42.6-132.3 (85.7)	0.00-0.00 (0.00)
Cornwallis Cave confining unit	3	8.7-10.5	-0.2-2.1	17.9-20.7	.681-.743	1.6-6.0	37.4-61.1	.00-.01
Cornwallis Cave aquifer	16	5.9-17.1 (11.5)	-.8-4.6 (.6)	15.9-22.5 (18.5)	.591-.767 (.689)	.0-7.0 (2.8)	4.5-199.6 (47.1)	.00-.01 (.00)
Yorktown-Eastover aquifer	5	8.4-17.3 (13.5)	.2-3.8 (3.1)	16.9-22.2 (19.5)	.631-.770 (.662)	.0-5.9 (.0)	12.4-32.2 (20.8)	.00-.02 (.00)
Wells	14	8.4-17.3 (12.2)	-.1-4.6 (2.9)	16.9-22.5 (20.3)	.631-.770 (.707)	.0-5.9 (.1)	9.6-199.6 (24.8)	.00-.02 (.00)
Springs	16	5.9-17.1 (10.4)	-.8-4.6 (.6)	15.9-21.2 (18.5)	.591-.767 (.691)	.1-7.0 (2.9)	4.5-94.0 (52.2)	.00-.01 (.00)
Recharge area setting	8	8.4-13.9 (10.9)	1.1-4.6 (3.3)	18.1-22.5 (21.0)	.660-.770 (.715)	.0-2.9 (.1)	9.6-132.3 (23.8)	.00-.02 (.00)
Discharge area setting	22	5.9-17.3 (11.0)	-.8-4.6 (.6)	15.9-22.5 (18.5)	.591-.767 (.684)	.0-7.0 (2.8)	4.5-199.6 (43.9)	.00-.01 (.00)
Shallow aquifer system	30	5.9-17.3 (10.9)	-.8-4.6 (1.3)	15.9-22.5 (19.1)	.591-.770 (.696)	.0-7.0 (2.0)	4.5-199.6 (41.4)	.00-.02 (.00)

1997). The temperature differentials depicted on figure 8 represent minimums because sampling occurred in March, during the period when ground-water temperatures are the warmest. The springs with water temperatures warmer than mean annual air temperature (fig. 8) have a large percentage of their drainage areas in the urbanized sections of the Station. The effect of urban land use on recharge and ground-water temperatures is not well understood. Heat retention by pavement and buildings or leaking water and sewer lines could contribute to these temperature differentials.

The temperature differentials for wells and springs indicate that recharge predominantly occurs in the colder months of the year. Ground water, however, equilibrates with the temperature of the aquifer material as it moves deeper in the flow system (Mazor, 1991), which explains the positive temperature differentials between ground-water and mean annual air temperatures. Ground-water temperatures varied by 3°C seasonally in the Columbia aquifer and usually varied less than 1°C in the deeper aquifers beneath the recharge area setting of the Station (Brockman and others, 1997).

The stable isotopes of oxygen and hydrogen—expressed as δ^{18}O and δD—can be used to trace the origin and movement of local ground water (Mazor, 1991). Compositions of the stable isotopes in ground water (fig. 9) at the Station tend to parallel the global meteoric water line (Craig, 1961). The δ^{18}O values range from -7.2 to -5.5 ‰ and δD values range from -41.2 to -29.7‰. Deuterium excess (*d*) is a measure of the local shift from the global meteoric water line and is defined as $d = \delta D - 8\delta^{18}O$ (Clark and Fritz, 1997). Values of *d* range from 13.3 to 16.8‰ with a median value of 14.8‰ for the Station. These *d* values are indicative of late winter to early spring recharge (Dunkle and others, 1993). The estimate of recharge season based on stable isotope data yields results consistent with the estimates of recharge temperature based on dissolved gas analyses.

APPARENT CHLOROFLUOROCARBON AGE OF GROUND WATER

Estimates of the apparent age of ground water aid in the conceptualization and subsequent evaluation

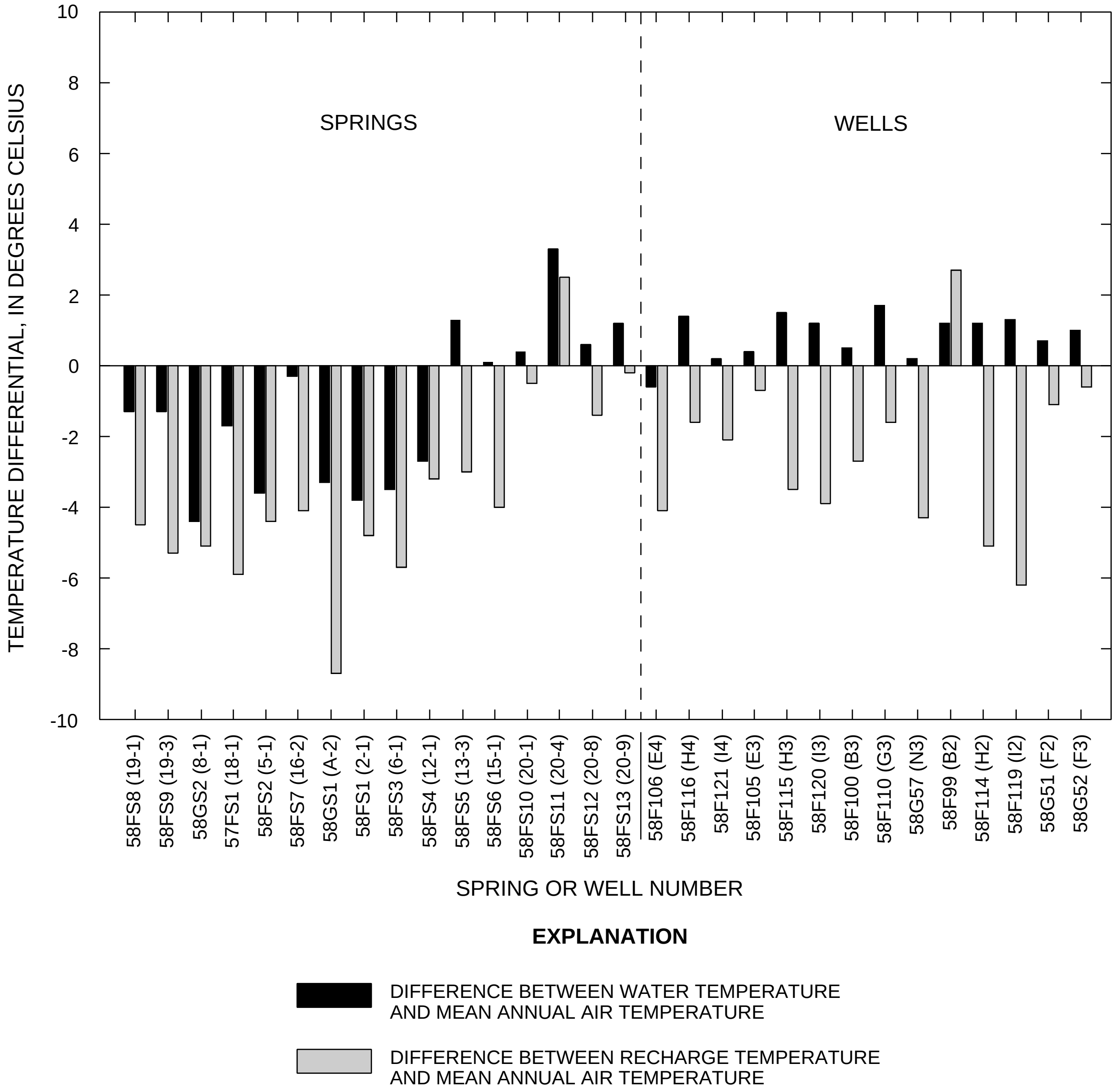


Figure 8. Relation between ground-water temperature and mean annual air temperature and between ground-water recharge temperature and mean annual air temperature at the Naval Weapons Station Yorktown, Virginia.

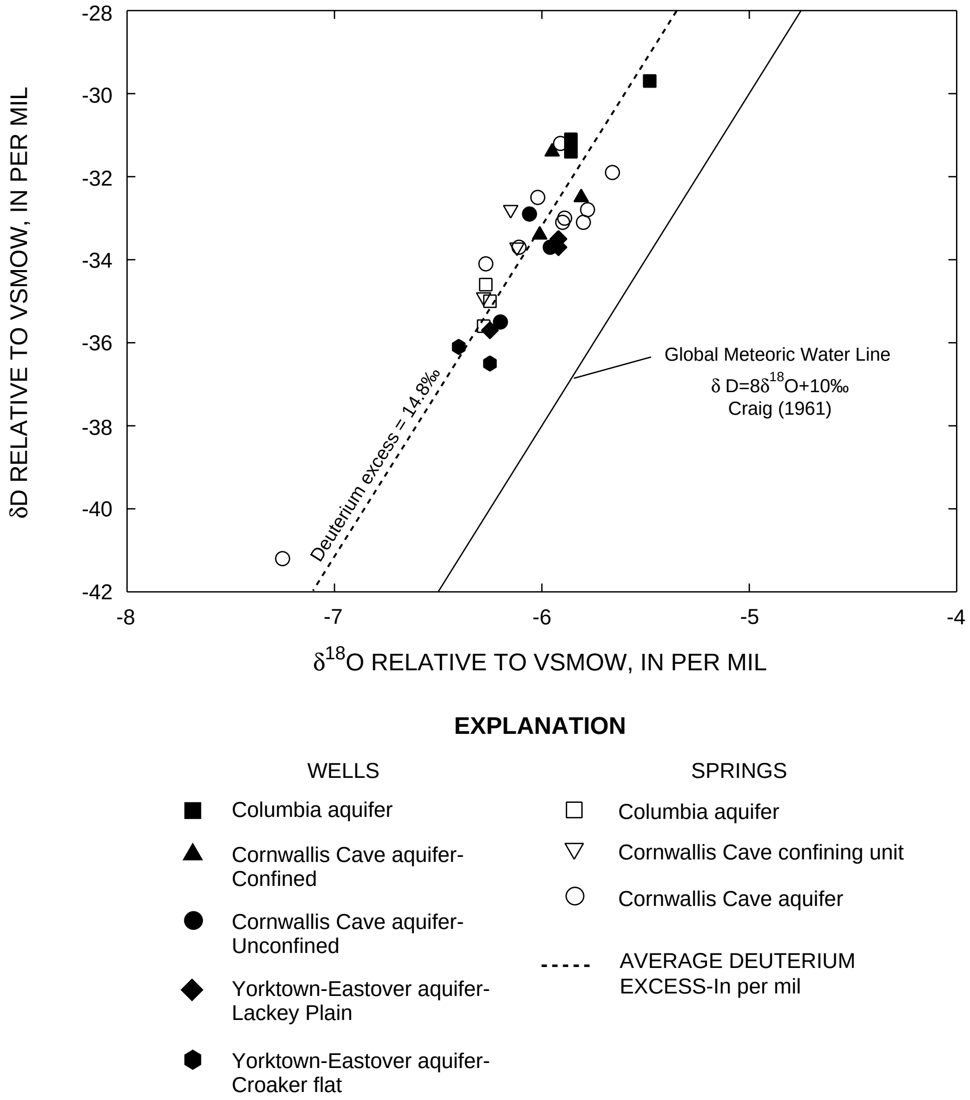


Figure 9. Relation between ^{18}oxygen ($\delta^{18}O$) and deuterium (δD) in ground water at the Naval Weapons Station Yorktown, Virginia, March 1997. Oxygen and hydrogen isotope values for water are reported relative to Vienna Standard Mean Ocean Water (VSMOW).

of ground-water-flow systems. Ground-water velocities and recharge rates can be estimated using the apparent ground-water ages. Two types of transient environmental tracers—CFCs and ^3H—were used in the determination of apparent age of ground water at the Station. The CFC-based dating technique (Busenberg and Plummer, 1992) was the primary method for dating ground water in this study; the concentration of ^3H in the water was used to confirm the CFC-based apparent age determinations.

Dating Methods

Chlorofluorocarbons (CFCs) are stable synthetic organic compounds that were first manufactured in the 1930's and used as refrigerants, aerosol propellants, cleaning agents, solvents, and blowing agents in the production of foam rubber and plastics (Busenberg and Plummer, 1992). CFCs eventually are released to the atmosphere and hydrosphere, where concentrations have increased over time. Depletion of the Earth's ozone layer has been attributed to the rapid atmospheric accumulation of these compounds (Molina and Rowland, 1974). The most widely used CFCs are trichlorofluoromethane (CCl_3F, CFC-11, Freon 11), dichlorodifluoromethane (CCl_2F_2, CFC-12, Freon 12), and trichlorotrifluoroethane ($C_2Cl_3F_3$, CFC-113). CFC-11 and CFC-12 made up 77 percent of total global production of CFCs (Derra, 1990). Busenberg and Plummer (1992) developed a method for dating ground water using concentrations of these major CFCs.

Atmospheric partial pressures of CFCs that were in equilibrium with the measured concentrations of CFCs in the ground-water samples are determined by Henry's law from the N_2-Ar recharge temperature estimates. The calculated equilibrium partial pressures are compared to the atmospheric mixing ratios of CFCs (fig. 10) to determine the apparent CFC recharge date, which equates to the time that the tracer (CFCs) was isolated from air/soil gas in the unsaturated zone at the water table. The apparent CFC age is the difference between the date of sample collection and the apparent CFC recharge date.

The term “apparent CFC age,” as defined by Szabo and others (1996) and Plummer and Busenberg (1999), is used throughout this report to qualify the ground-water age determinations. “Apparent age” is used because ground-water samples usually represent a mixture of waters of varying ages, whereas the dating method developed by Busenberg and Plummer (1992) is based on the simplifying assumption of piston or plug flow, which presumes that the tracer (CFCs) is transported as a plug through the aquifer with no dispersive mixing in the direction of flow. “Apparent CFC age” is used because the age determinations are based on the time since the CFCs were equilibrated with recharge entering the ground-water system. Because chemical and physical processes can affect the transport of CFCs through the unsaturated zone and into the ground water, the apparent CFC age may not equate to the actual travel time of the water (Plummer and Busenberg, 1999).

Tritium (^3H) is the radioactive isotope of hydrogen with a half-life of 12.43 years (International Atomic Energy Agency, 1981) and is an indicator of ground water recharged since 1952 (Clark and Fritz, 1997). Production of ^3H in the atmosphere naturally occurs by cosmic ray spallation, but the principal source of ^3H since about 1952 was the atmospheric testing of thermonuclear weapons. The standard unit of measure for ^3H is a tritium unit (TU) for which one TU is equivalent to one ^3H atom per 10^{18} atoms of hydrogen or, in terms of radioactivity, 3.2 picocuries per liter (Clark and Fritz, 1997). Tritium content in precipitation in the northern hemisphere reflects world events during the Cold War years with a maximum concentration occurring in 1963, commonly referred to as the “bomb peak” (fig. 10). Atmospheric concentrations gradually have declined since 1963 and present-day ground water typically contains less than 1 to 10 TU, seldom exceeding 50 TU (Clark and Fritz, 1997).

Apparent Age of Ground Water Based on Chlorofluorocarbons

The presence of CFCs in water from the 30 sites sampled in March 1997 (table 4) indicates that at least some parts of the shallow aquifer system on the Station contain ground water that is younger than 50 years. CFC apparent ages range from 1 to 48 years with a median age of 10 years (fig. 11). The oldest apparent ages occur in the upper parts of the Yorktown-Eastover aquifer, whereas the youngest apparent ages occur in samples from the Columbia and Cornwallis Cave aquifers, and in the discharge area setting, especially in springs, where apparent CFC ages range from 1 to 14 years. Ground water in the recharge area setting has a wide distribution of apparent CFC ages (6 to 48 years),

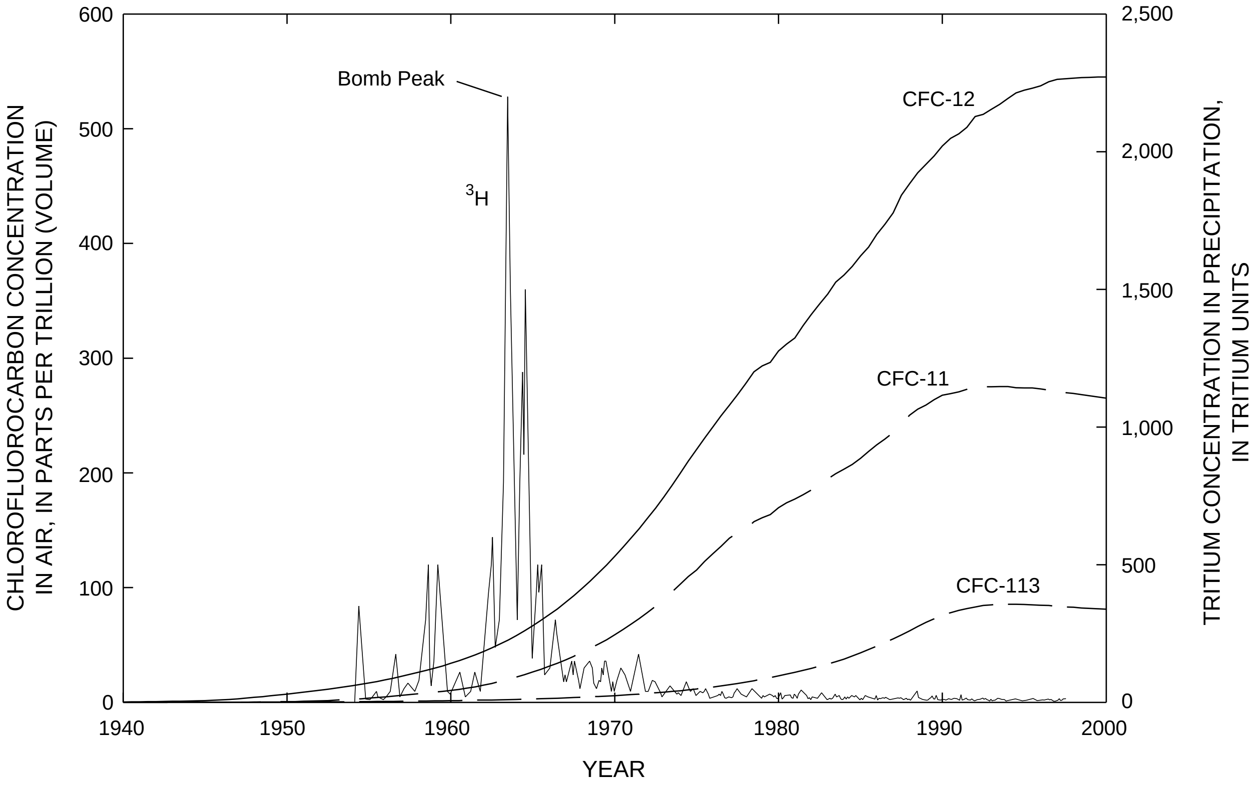


Figure 10. Atmospheric mixing ratios of chlorofluorocarbon-11 (CFC-11), chlorofluorocarbon-12 (CFC-12), and chlorofluorocarbon-113 (CFC-113) for North American air and estimated monthly concentration of tritium (^3H) in precipitation for the Naval Weapons Station Yorktown, Virginia. Tritium data derived from estimation technique of Michel (1989) and are not corrected for radioactive decay. Modified from Plummer and Busenberg (1999).

which is expected because of steep, downward vertical hydraulic gradients between aquifers. Although the range in apparent ages (1 to 44 years) for samples from the discharge area setting is similar to the range for the recharge area setting, nearly 75 percent of the samples from the discharge area setting contain water that was recharged since 1987.

The predominance of young apparent CFC ages (less than 10 years) for the samples in the discharge area setting is a function of site selection and time of sampling. Most of the sites (11 out of 15) in the discharge area setting for which apparent CFC ages could be determined were springs. In addition, the time of sampling coincided with the seasonal high in water levels for the shallow aquifer system. One would expect the apparent ages to be young because the dissolved gas data suggest shallow flow of late winter/early spring recharge from areas intermediate of the recharge area setting. The intermittent occurrence and flow of many of the springs sampled during this investigation further imply that apparent ages should be young.

Patterns in the spatial distribution of apparent CFC ages are not readily apparent (fig. 12). The most obvious pattern is the relatively young apparent ages determined for the samples from the springs located throughout the Station. Similar apparent CFC ages have been determined for springs sampled in Colonial National Historic Park, which is adjacent to the Station (Focazio and others, 1998). The simplifying assumption of piston flow for CFC-based dating is valid for the samples from springs on and near the Station. The discharge from springs, therefore, probably represents horizontal convergence of flow lines that contain young waters recharged at approximately the same time. The resolution of the CFC dating method precludes identification of these waters as mixtures. The results from CFC-based dating, however, support the concept of local flow systems within the shallow aquifer system proposed by Brockman and others (1997).

Table 4. Averages for calculated atmospheric partial pressure of chlorofluorocarbons, recharge date, and apparent age of ground water for wells and springs sampled on the Naval Weapons Station Yorktown, Virginia, in March 1997

[T_R, nitrogen-argon recharge temperature in degrees Celsius; pptv, parts per trillion by volume; CFC, chlorofluorocarbon; F-11, F-12, and F-113— trichlorofluoromethane (CCl_3F, CFC-11, Freon 11), dichlorodifluoromethane (CCl_2F_2, CFC-12, Freon 12), and trichlorotrifluoroethane ($C_2Cl_3F_3$, CFC-113), respectively; CNT, CFC may be contaminated and not representative of an atmospheric source because CFC-calculated atmospheric partial pressure is greater than modern and sample cannot be dated; M, modern; <, actual recharge date older than CFC-recharge date shown; >, actual age younger than CFC-recharge date shown; *Mix*, analyses indicate water sample represents a possible mixture of different age waters; –, no data]

			Average calculated atmospheric partial pressure (pptv)[1]			Average apparent CFC recharge date			Average apparent CFC age[1]			Average apparent CFC-		
Site number	Sample date	T_R	F-11	F-12	F-113	F-11	F-12	F-113	F-11	F-12	F-113	Date	Age[1]	CFCs used
Wells														
58F99 (B2)	03/28/97	17.3	12±1.5	44±4.0	37±9.7	1960.5	1961.5	1983.5	36.5±0.7	35.5±0.7	13.5±2.0	[2]<1962 >1983	Mix?	12, 113
58F100 (B3)	03/19/97	11.9	222±21	493±42	81±9.6	1985.5	1990.5	1991	11.5±1.9	6.5±1.7	6±1.4	1991	6±1.6	12, 113
58F105 (E3)	03/07/97	13.9	3.9±.4	57±5.9	0.0±0.0	1955	1963.5	<1955	42±.4	33.5±.8	>42±.0	1955	42±.4	11, 113
58F106 (E4)	03/07/97	10.5	154±15	445±41	52±6.4	1978	1987.5	1986.5	19±1.6	9.5±2.4	10.5±1.0	1987	10±2.0	12, 113
58F110 (G3)	03/11/97	13	210±19	559±46	63±7.2	1984.5	M	1988	12.5±2.0	M	9±1.1	1988	9±1.1	113
58F114 (H2)	03/26/97	9.5	2.2 ±.2	11±1.7	.0±.0	1953	1952	<1955	44±.4	45±.9	>42±.0	1953	44±.9	11, 12, 113
58F115 (H3)	03/05/97	11.1	1.8±.4	262±23	.0±.0	1952.5	1977	<1955	44.5±.6	20±1.3	>42±.0	1977	20±1.3	12
58F116 (H4)	03/05/97	13	167±15	437±41	83±9.8	1979.5	1987	1991.5	17.5±1.7	10±2	5.5±3.0	1991	6±3.2	12, 113
58F119 (I2)	03/27/97	8.4	.8±.1	5.0±.9	.0±.0	1950.5	1948.5	<1955	46.5±.5	48.5±.7	>42±.0	1949	48±1.4	11, 12, 113
58F120 (I3)	03/06/97	10.7	1.3±.2	18±4.9	.0±.0	1952	1955	<1955	45±.5	42±1.8	>42±.0	1953	44±2.2	11, 12, 113
58F121 (I4)	03/06/97	12.5	96±20	402±34	42±8.0	1973	1985.5	1984.5	24±1.6	11.5±1.9	12.5±1.6	1985	12±1.7	12, 113
58G51 (F2)	03/25/97	13.5	3.4±.4	12±5.2	.0±.0	1954.5	1952.5	<1955	42.5±.4	44.5±2.5	>42±.0	1953	44±2.1	11, 12, 113
58G52 (F3)	03/10/97	14	930±89	517±48	79±8.9	CNT	1993	1990.5	CNT	4.0±2.8	6.5±1.6	1991	6±1.8	12, 113
58G57 (N3)	03/11/97	10.3	2.9±.6	81±7.5	14±1.9	1954	1966	1976	43±.7	31±3.7	21±1.0	[2]<1966 >1976	Mix	12, 113
Springs														
57FS1 (18-1)	03/20/97	8.7	133±13	423±39	58±6.4	1976	1986.5	1987	21±1.2	10.5±2.0	10±1.0	1987	10±1.4	12, 113
58FS1 (2-1)	03/20/97	9.8	257±25	984±96	80±8.8	1988.5	CNT	1990.5	8.5±2.6	C	6.5±1.1	1989	8±2.2	11, 113
58FS2 (5-1)	03/14/97	10.2	193±19	469±41	65±7.6	1982.5	1989	1988	14.5±2.1	8.0±3.0	9.0±1.1	1989	8±2.3	12, 113
58FS3 (6-1)	03/13/97	8.9	159±16	426±41	58±7.2	1978.5	1986.5	1987	18.5±1.8	10.5±2.3	10±1.1	1987	10±1.7	12, 113
58FS4 (12-1)	03/17/97	11.4	222±21	524±46	65±7.7	1985.5	1994.5	1988	11.5±1.8	2.5±3.3	9.0±1.3	1995	2±3.3	12
58FS5 (13-3)	03/17/97	11.6	2,376±223	5,800±2,317	–	CNT	CNT	CNT	CNT	CNT	CNT	CNT	–	–
58FS6 (15-1)	03/21/97	10.6	2,493±238	148,397±14,318	136±55	CNT	CNT	CNT	CNT	CNT	CNT	CNT	–	–
58FS7 (16-2)	03/21/97	10.5	179±17	476±43	52±5.5	1981	1989	1986.5	16±2.2	8.0±2.6	10.5±.8	1988	9±2.3	12, 113
58FS8 (19-1)	03/20/97	10.1	147±14	401±37	46±5.2	1977	1985.5	1985.5	20±1.5	11.5±1.9	11.5±9	1985	12±1.4	12, 113
58FS9 (19-3)	03/20/97	9.3	121±12	334±31	37±4.2	1975	1981.5	1983.5	22±1.0	15.5±1.8	13.5±.9	1983	14±1.7	12, 113
58FS10 (20-1)	03/12/97	14.1	2,136±191	33,521±4,921	381,770±418,330	CNT	CNT	CNT	CNT	CNT	CNT	CNT	–	–
58FS11 (20-4)	03/12/97	17.1	2,707±228	5,402±537	47,725±35,567	CNT	CNT	CNT	CNT	CNT	CNT	CNT	–	–
58FS12 (20-8)	03/13/97	13.2	256±24	533±45	133±41	1988.5	1996.5	CNT	8.5±3.0	.5±4.1	CNT	1996	1±4.1	12
58FS13 (20-9)	03/12/97	14.4	393±35	30,773±2,551	81,022±8,299	CNT	CNT	CNT	CNT	CNT	CNT	CNT	–	–
58GS1 (A-2)	03/18/97	5.9	113±12	454±43	48±6.2	1974.5	1988	1985.5	22.5±.9	9.0±2.5	11.5±1.0	1987	10±2.4	12, 113
58GS2 (8-1)	03/17/97	9.5	134±14	502±47	60±7.4	1976	1991.5	1987.5	21±1.2	5.5±3.4	9.5±1.0	1991	6±3.2	12, 113

[1] Error calculations based on an uncertainty of ±2°C in nitrogen-argon recharge temperature.

[2] Young fraction is less than recharge date shown and old fraction is greater than recharge date shown

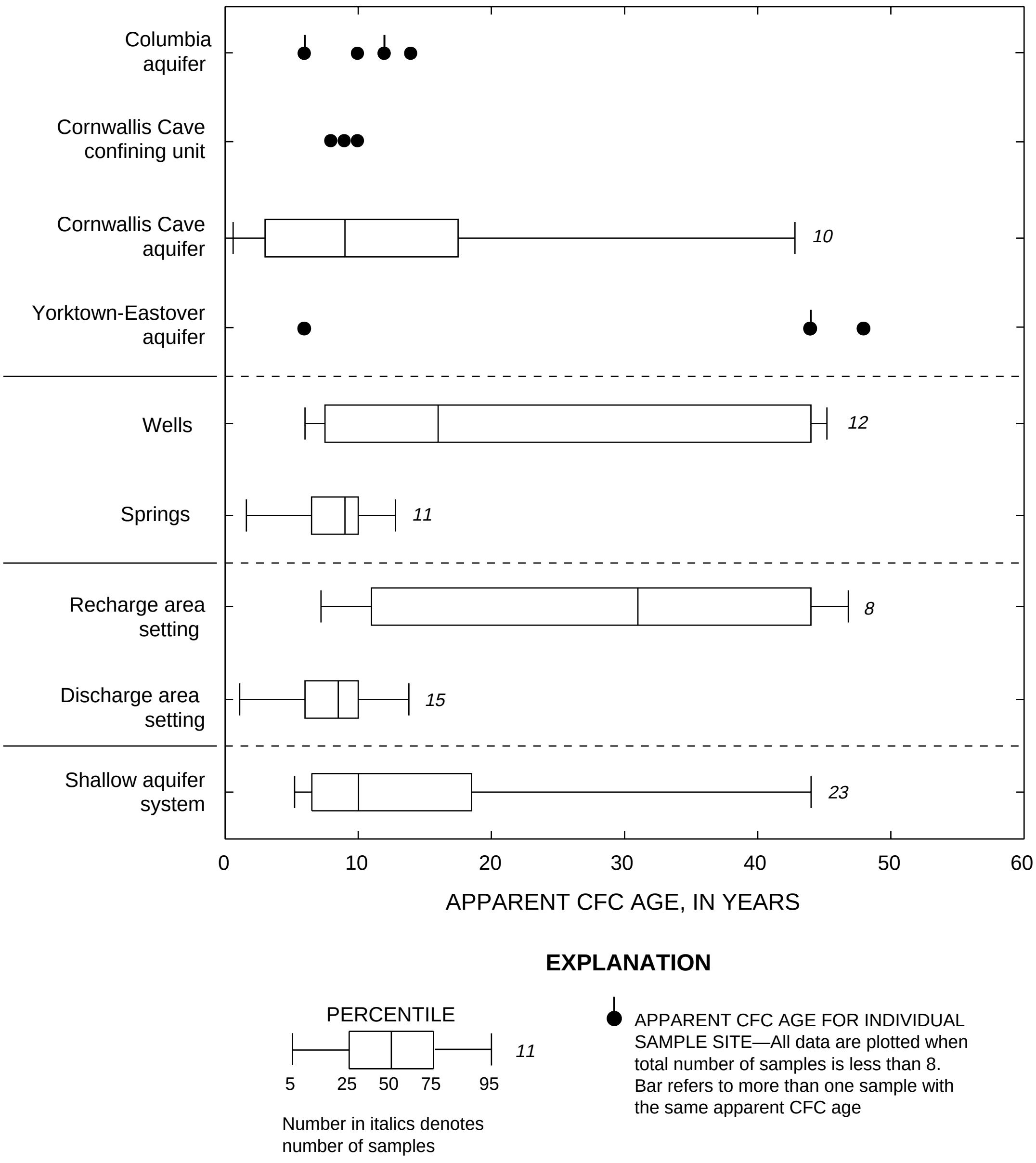
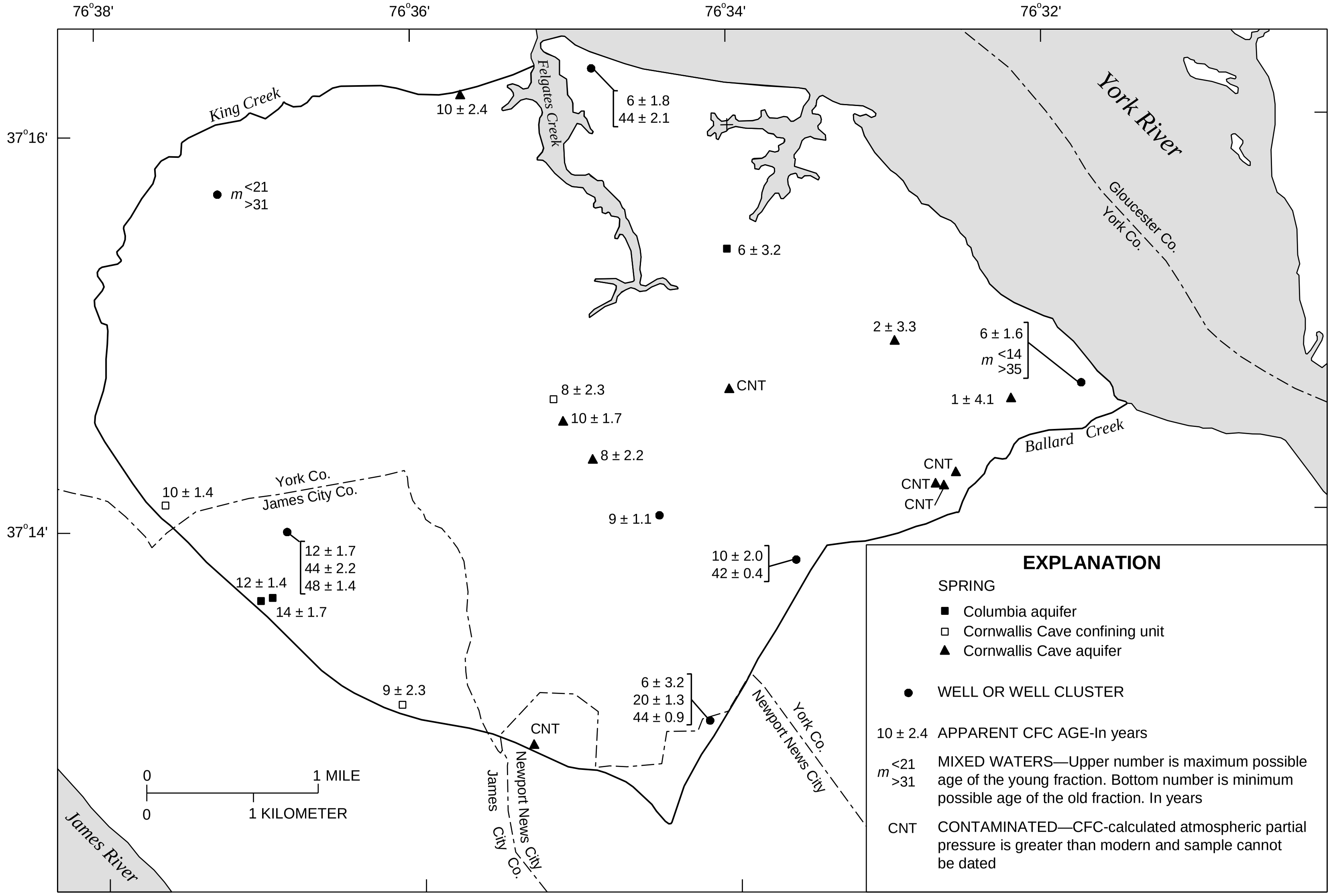


Figure 11. Distribution of apparent chlorofluorocarbon (CFC) age of water in shallow aquifer system at the Naval Weapons Station Yorktown, Virginia, March 1997. Uncertainties in apparent CFC age range from 0.4 to 4.1 years.



Base from Naval Weapons Station Yorktown 1:9,600

Figure 12. Apparent chlorofluorocarbon (CFC) age of water in the shallow aquifer system, Naval Weapons Station Yorktown, Virginia.

Binary Mixtures of Water

Some of the samples from the discharge area setting are interpreted, using the ratios of the CFCs, to represent a binary mixture of young (less than 50 years) and old (greater than 50 years) waters. Plummer and Busenberg (1999) describe a method for identifying binary ground-water mixtures based on the ratios of CFC-11/CFC-12 and CFC-113/CFC-12. These ratios have changed over time in response to the varying input of the individual CFCs into the atmosphere. Binary mixtures of young and old waters are readily identifiable by the disparity between the apparent ages estimated for the individual CFCs. For example, the apparent CFC recharge dates for well 58G57 (N3) are 1976 and 1966 for CFC-113 and CFC-12, respectively (table 4). The distribution of these recharge dates, as described in Plummer and Busenberg (1999), indicates that the sample represents a binary mixture of young water that was recharged after 1976 and old water that was recharged prior to 1966. The presence of mixed waters in the discharge areas is expected because flow lines generally converge in these settings and the potential for convergence increases in the lower reaches.

Position within the shallow aquifer system is an important criterion in determining whether the water sample represents plug flow or a binary mixture. Well 58G57 (N3) is the farthest site sampled in the Cornwallis Cave aquifer downgradient of the ground-water divide. The measured concentrations of CFC-113 and CFC-12 indicate that the binary mixture in the sample from this well contains between 10 and 20 percent of water recharged in the past 21 years. The remainder of the water in the mixture was recharged before 31 years ago. Evaluation of the ratio of CFC-11/CFC-12 indicates that the measured concentrations of CFC-11 have been modified by sorption or degradation processes, which are described later in the report. The actual apparent age of the young fraction in well 58G57 (N3) is unknown; but the interpretation that the young fraction was recharged less than 21 years ago is within the range of apparent CFC ages (1 to 14 years) determined for the samples from springs. The actual apparent age of the old fraction is also unknown; the old fraction, however, could represent water recharged prior to the introduction of CFCs into the atmosphere (greater than 50 years) based on the position of well 58G57 (N3) within the shallow aquifer system. The stable seasonal fluctuation of ground-water temperatures in this well of 0.2°C, as measured by Brockman and others (1997), indicates that enough time has elapsed after recharge for the ground water to equilibrate with the temperature of the aquifer sediments.

The sample from well 58F99 (B2), which is finished in the Yorktown-Eastover aquifer, also appears to represent a binary mixture of water (table 4). The assumption that the young fraction in this well was recharged in the past 14 years seems unlikely because the Yorktown confining unit is relatively thick at well cluster B. Evaluation of the ratio of CFC-113/CFC-12 suggests that the measured concentrations of CFC-113 have been modified by contamination during sampling or as an artifact of the well drilling process.

Vertical Distribution of Apparent CFC Ages

The vertical distribution of apparent CFC ages indicates that, in the recharge area setting, ground water becomes progressively older with depth (fig. 13). The apparent absence of mixed waters in the recharge area setting indicates that ground-water movement is by piston or plug flow downward in response to the relatively steep vertical hydraulic gradients between aquifers. Cluster I is located at a ground-water divide (Brockman and others, 1997) where the vertical hydraulic gradient between the water table and the base of the Yorktown-Eastover aquifer is nearly 3.5 times greater than those at the other clusters shown on figure 13. Clusters E and H are located downgradient from the ground-water divides.

The thickness of the geohydrologic units and the ratio of horizontal to vertical hydraulic conductivity (K_h/K_v) also are important controls on the vertical distribution of ages. The thicknesses of the different geohydrologic units vary greatly and the ratio of K_h/K_v ranges from 6:1 to greater than 56,000:1, with the lowest ratios occurring in the aquifers and the highest occurring between the Cornwallis Cave aquifer and the Yorktown confining unit (fig. 13). The distribution of these ratios indicates that a majority of the downward flow of ground water moves laterally away from the divides. Sufficient recharge is available, however, to move young water down to relatively deep depths (nearly 120 ft below land surface).

The vertical distribution of apparent CFC ages depicted on figure 13 represents the time interval of the initial stages of ground-water flow along a subregional flow path. Water-level mapping by Brockman and others (1997) shows that ground water flows away from well clusters E, H, and I. The age of ground water,

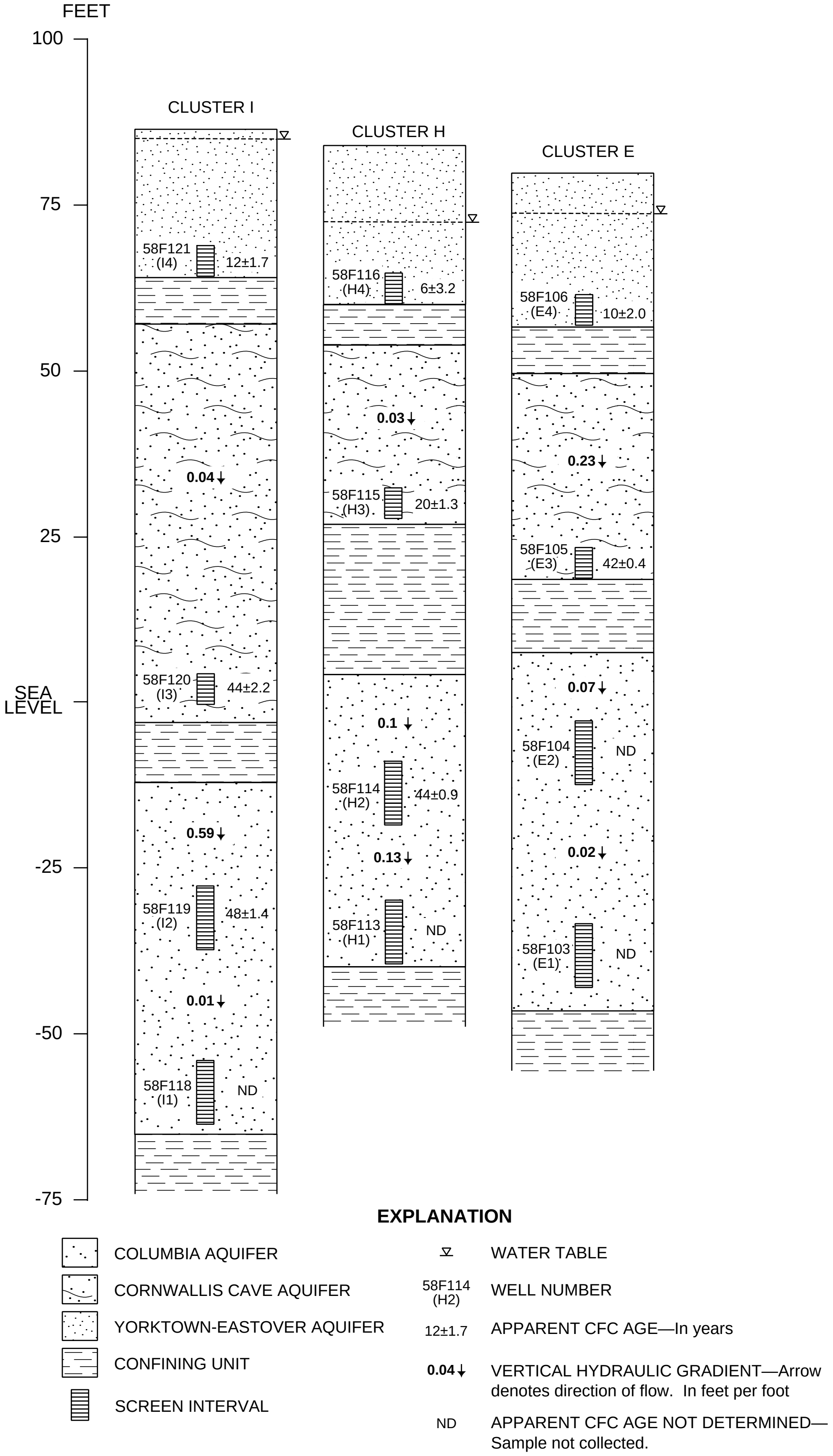


Figure 13. Vertical distribution of apparent chlorofluorocarbon (CFC) ages for well clusters E, H, and I located in the recharge area setting on the Naval Weapons Station Yorktown, Virginia, March 1997.

therefore, should increase downward and outward as the distance from the ground-water divides increases. Apparent ages that are greater than 40 years, however, approach the limits of CFC-based dating and complicate the identification of whether a sample represents piston flow or a binary mixture. The apparent CFC ages that are greater than 40 years (fig. 13) were determined with the assumption of piston flow because the measured concentrations of CFC-11 and CFC-12 yield similar ages, and CFC-113 was not detected in these samples (table 4). The absence of CFC-113 in these water samples is consistent with recharge prior to 1955, when CFC-113 was introduced (Plummer and Busenberg, 1999).

The Cornwallis Cave and Yorktown confining units in the recharge area setting tend to retard ground-water movement between aquifers. The maximum difference in apparent CFC ages between the base of the Columbia aquifer and the base of the Cornwallis Cave aquifer is 32 years (fig. 13), whereas the differences in apparent CFC ages between the base of the Cornwallis Cave aquifer and the upper parts of the Yorktown-Eastover aquifer at well clusters H and I are 24 and 4 years, respectively. The vertical distribution of apparent CFC ages indicates that ground-water movement between aquifers is somewhat retarded by the confining units, but the elapsed time is relatively short (generally less than 35 years), as evidenced by the presence of CFCs at depth. The vertical distribution of apparent CFC ages is consistent with the conceptual model of Brockman and others (1997) where the confining units in the shallow aquifer system are considered to be leaky.

As in the recharge area setting, the vertical distribution of apparent CFC ages in samples from wells located in the discharge area setting also increases with depth. The assumption of plug flow is valid for some parts of the shallow aquifer system in the discharge area setting. The apparent ages determined for samples from wells finished in the Cornwallis Cave aquifer at well clusters B and G (fig. 14) are young and similar to the ages determined for samples located at the base of the Columbia aquifer in the recharge area setting. This similarity in apparent ages suggests that water in the Cornwallis Cave aquifer at well clusters B and G did not originate from the recharge area setting where well clusters E, H, and I are located; the similarity in ages can be explained by the presence of local flow systems in the discharge area setting. CFC-based dating indicates that a majority of the samples from wells and springs in the discharge area setting could be interpreted as piston or plug flow, which further confirms the presence of local flow systems in the shallow aquifer system at the Station.

The major difference between the two geohydrologic settings is the occurrence of mixed waters in the discharge area setting, as indicated by the CFC ratios. The occurrence of mixed waters is expected because flow lines from the local and subregional flow systems generally converge in discharge areas. The vertical hydraulic gradients are less than those in the recharge area setting and can be upward rather than downward as illustrated at cluster G (fig. 14). The earlier discussion of N_2-Ar recharge temperatures for the spring samples indicated that flow can be shallow and that recharge occurred between the point of discharge and where the Columbia aquifer sediments become unsaturated. The relatively high excess air concentration for well 58G57 (N3) (4.37 cm^3/L) indicates that the old fraction of the mixture could have originated from an area where the seasonal water-level fluctuations are large (recharge area setting). The presence of samples that represent both piston flow and mixtures of young and old waters, diminished and reversed vertical head gradients, and multiple origins of recharge in the discharge area setting suggests that both local and subregional flow systems compose the shallow aquifer system at the Station under Lackey Plain.

Well cluster F is located in a unique discharge area beneath the Croaker flat where the Yorktown-Eastover aquifer is unconfined and both the Columbia and Cornwallis Cave aquifers are absent (Brockman and others, 1997). The vertical head gradient between wells 58G52 (F3) and 58F51 (F2) is practically nonexistent (0.002 ft/ft). The relatively young apparent age (6 years) determined for the sample from well 58G52 (F3) is a function of the shallow depth (8 ft) below the water table of the screened interval (fig. 14). On the basis of water-level mapping, Brockman and others (1997) suggest that recharge to well 58G52 (F3) probably occurs in proximity to the well. The low vertical head gradient and high K_h/K_v ratio of 1,500:1 in this area results in lateral flow of water towards the York River in the upper parts of the Yorktown-Eastover aquifer. The relatively old apparent age (44 years old) that was determined for the sample from 58G51 (F2) is the result of ground-water movement along a deep flow path. The apparent ages of the water from these two wells are significantly different although these wells intercept the same equipotential line. The absence of mixed waters

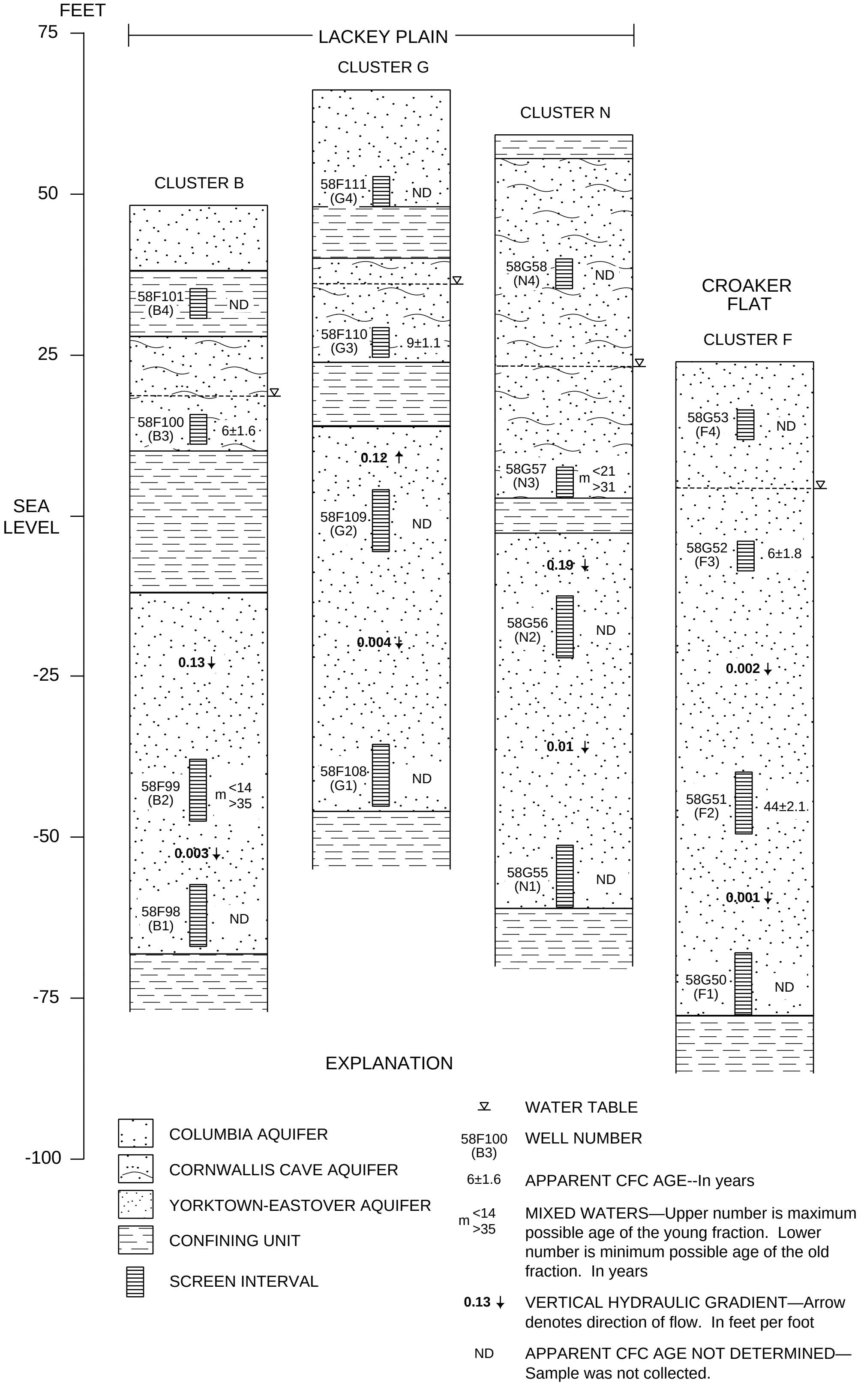


Figure 14. Vertical distribution of apparent chlorofluorocarbon (CFC) ages for well clusters B, G, N, and F located in the discharge area setting on the Naval Weapons Station Yorktown, Virginia, March 1997.

at well cluster F indicates that ground-water recharge to the Columbia and Yorktown-Eastover aquifers beneath the Croaker flat predominantly originates within the areal extent of this particular geomorphic feature on the Station.

Limitations of CFC-Based Dating

Apparent age determinations using the CFC-based technique for ground water recharged between the mid- to late-1990s are extremely sensitive to uncertainties in estimates of recharge temperature (Plummer and Busenberg, 1999). For ground water recharged prior to 1990, apparent CFC age uncertainties generally are less than 3 years for an uncertainty of ±2°C in recharge temperature (Plummer and Busenberg, 1999). In order to minimize uncertainty, the recharge temperature estimated for a particular sample site was used in the age determination rather than an average or median value for the entire Station. The uncertainties in apparent CFC ages presented in table 4 were calculated by adjustment of the recharge temperature by ±2°C. Samples containing water recharged prior to 1990 had apparent CFC age uncertainties that ranged from 0.4 to 2.4 years, whereas samples containing waters recharged since 1990 had uncertainties that ranged from 1.6 to 4.1 years.

Additional processes can affect the transport of CFCs in ground water and thereby modify the apparent age determinations. Plummer and Busenberg (1999) identify 10 such processes. Review of the CFC analyses (table 4) indicates that some of these processes have affected the samples collected during this study. Sorption of CFCs to sediments and organic matter and biodegradation of the CFCs can decrease the concentrations of CFCs in ground water. This decrease results in the apparent age determined from measured concentrations of one CFC appear to be older than the ages determined from the other CFCs (fig. 15). CFC-11 and CFC-113 are more susceptible to sorption and biodegradation processes than CFC-12 (Plummer and Busenberg, 1999). Column experiments conducted by Ciccioli and others (1980) indicate that transport through ground or pulverized limestone caused significant sorption of CFC-11 and CFC-113. Water samples from the Cornwallis Cave aquifer frequently yield different apparent ages from the measured concentrations of each individual CFC. This disparity may be attributed to sorption of CFC-11 and CFC-113 to shell material in this aquifer. For example, spring 58FS3 (6-1) discharges from the Cornwallis Cave aquifer, and the apparent CFC ages are 18.5±1.8, 10.5±2.3, and 10±1.1 years from CFC-11, CFC-12, and CFC-113, respectively. The abundance of shell material in the shallow aquifer system (especially the Cornwallis Cave aquifer) and organic matter in the soil zone may enhance sorption primarily of CFC-11 and occasionally of CFC-113 (table 4). In anoxic environments, CFC-11 and CFC-113 are more susceptible to microbial degradation than CFC-12 (Plummer and Busenberg, 1999).

Apparent ages of water from springs sampled in the more urbanized parts of the Station frequently could not be determined by CFC-based dating because calculated CFC atmospheric partial pressures for these samples were greater than modern (1997) CFC atmospheric mixing ratios. The elevated concentrations of CFCs in the water indicate that sources other than the atmosphere have introduced CFCs into the ground-water system. Sewage effluent, for example, commonly contains elevated concentrations of CFCs (Plummer and Busenberg, 1999). The five sites for which the apparent ages could not be determined (58FS5 (13-3), 58FS6 (15-1), 58FS10(20-1), 58FS11 (20-4), and 58FS13 (20-9)) are identified as “contaminated” in table 4 and figure 12. The term “contaminated” is applied here only relative to the CFC-based method for ground-water dating, which is based on extremely low atmospheric ratios (measured in parts per trillion by volume), and the unit of measure for the water samples is approximately equivalent to parts per quadrillion. The elevated concentrations of CFCs identified in the water at the five sites generally are less than 0.05 µg/L.

Comparison of Apparent CFC Ages with Tritium Concentrations

The concentration of ^{3}H in ground water at the Station in March 1997 ranged from below the USGS reporting limit of 0.3 to 15.9 TU with a median value of 10.8 TU (table 5). Tritium concentrations have similar ranges and median values for the different geohydrologic units with the lowest concentrations present in the water samples from the Yorktown-Eastover aquifer. Samples from springs tended to have higher ^{3}H concentrations than those from wells. Ranges in ^{3}H concentrations for the recharge and discharge area setting are similar.

Precise dating of ground water by means of ^{3}H is difficult because of five factors: (1) radioactive decay

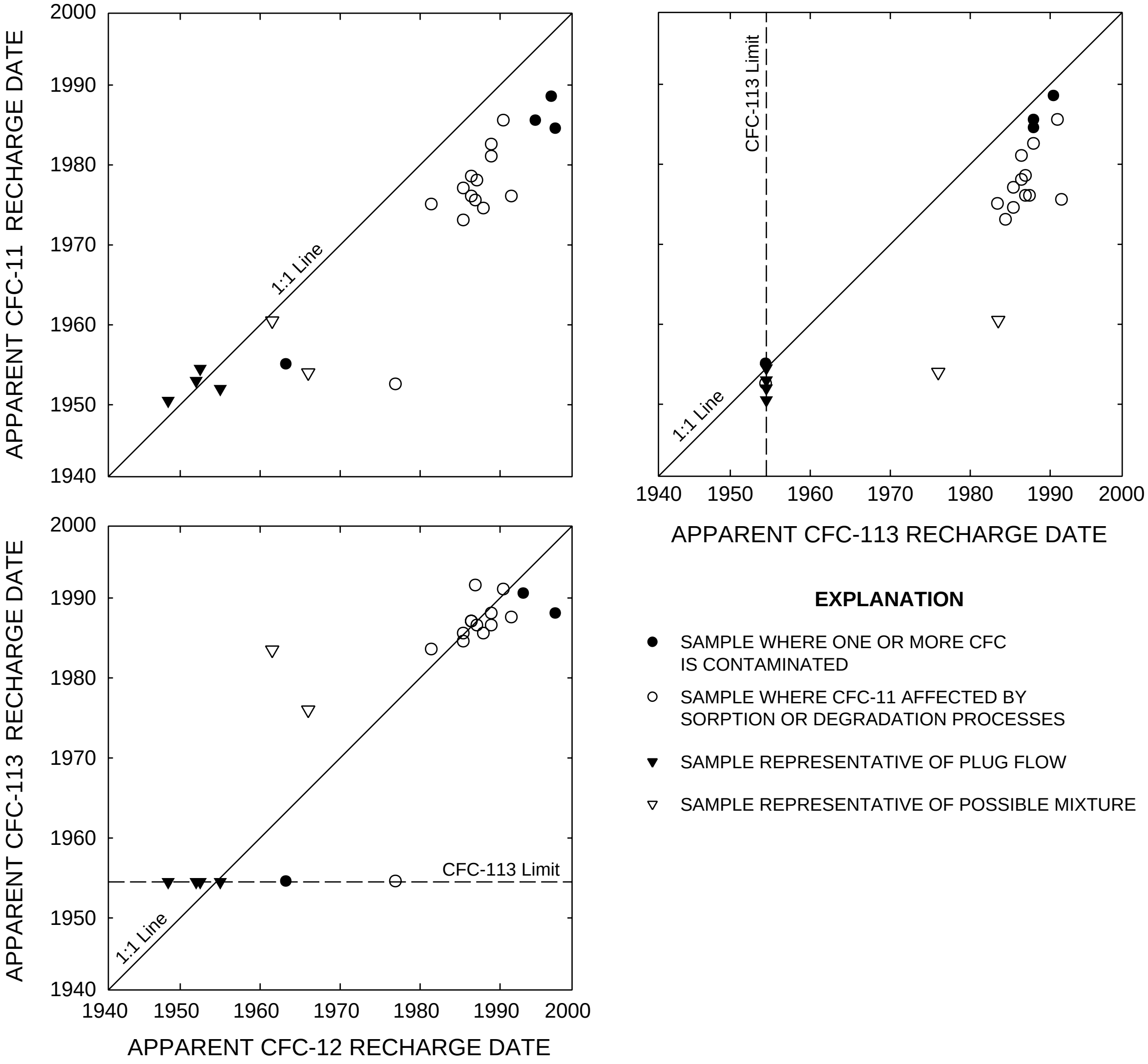


Figure 15. Variations in apparent chlorofluorocarbon (CFC) recharge date of ground water grouped by sample characteristics.

Table 5. Range and median values for tritium concentrations in ground water on the Naval Weapons Station Yorktown, Virginia, March 1997.

[All tritium concentrations are reported for March 1997. Median values in parenthesis if sufficient number of sites available to calculate. pCi/L, picocuries per liter; TU, tritium units, <, less than]

Sample location	Number of sites	Tritium (pCi/L)	Tritium 2 sigma error (pCi/L)	Tritium (TU)	Tritium 2 sigma error (TU)
Columbia aquifer	6	26.0-45.0 (38.5)	2.6-3.2 (2.6)	8.1-14.1 (12.0)	0.8-1.0 (.8)
Cornwallis Cave confining unit	3	27.0-36.0	1.9-2.6	8.4-11.3	.6-.8
Cornwallis Cave aquifer	16	<1.0-51.0 (36.0)	1.0-5.1 (2.9)	<0.3-15.9 (11.3)	.3-1.6 (.9)
Yorktown-Eastover aquifer	5	<1.0-31.0 (<1.0)	1.0-1.9 (1.0)	<.3-9.7 (<.3)	.3-.6 (.3)
Wells	14	<1.0-48.0	1.0-3.2 (1.9)	<.3-15.0 (9.8)	.3-1.0 (.6)
Springs	16	26.0-51.0 (35.5)	1.9-5.1 (2.9)	8.1-15.9 (11.1)	.6-1.6 (.9)
Recharge area setting	8	<1.0-45.0 (23.0)	1.0-3.2 (1.8)	<.3-14.1 (7.2)	.3-1.0 (.6)
Discharge area setting	22	<1.0-51.0 (34.5)	1.0-5.1 (2.6)	<.3-15.9 (10.8)	.3-1.6 (.8)
Shallow aquifer system	30	<1.0-51.0 (34.5)	1.0-5.1 (2.6)	<.3-15.9 (10.8)	.3-1.6 (.8)

of initial ^3H levels, (2) latitudinal effects, (3) seasonal variations of ^3H concentrations in precipitation, (4) variation in ^3H concentrations with distance from the ocean, and (5) the series of spikes for the ^3H precipitation input function (Dunkle and others, 1993; Plummer and others, 1993). Tritium concentrations, however, can be useful to refine the apparent CFC ages by comparing the measured concentration in ground water sampled in March 1997 to the ^3H input function. The ^3H input function (fig. 16) was reconstructed for the Station using the geographic distribution and historical ^3H concentrations from a national network of USGS precipitation stations (Michel, 1989). The initial ^3H concentrations were adjusted to account for radioactive decay to the time of the sampling period (March 1997) by use of a modified version of the radioactive decay law (Coplen, 1993) and given as

$$A_t = A_o e^{-0.693t/t_{1/2}} \quad (1)$$

where A_t is the activity or concentration at time t, A_o is initial activity, and $t_{1/2}$ is the half-life of ^3H (12.43 years). A plot of ^3H concentration and apparent CFC recharge date determined for each sample with the adjusted ^3H input function for the Station is shown on figure 16. The apparent recharge date determined with CFCs and the measured ^3H concentration for a majority of the samples correspond to the expected ^3H concentration on the ^3H input curve. Plummer and Busenberg (1999) suggest that the tritium/helium-3 dating method (Schlosser and others, 1988; Solomon and others, 1992) could be used to date the young fraction of binary mixtures if the older fraction of water was recharged prior to the bomb peak in 1963.

The ^3H concentrations for water samples from the Yorktown-Eastover aquifer are low because recharge occurred prior to sufficient input of ^3H from the atmospheric testing of thermonuclear weapons. Natural ^3H concentrations from cosmogenic sources were estimated to range from 2 to 8 TU (Thatcher, 1962); after adjustment for radioactive decay, these concentrations would range from 0.2 to 0.6 TU in March 1997. The high ^3H concentrations in the water samples from the springs and other sites in the discharge area setting are a result of high initial ^3H concentrations after the bomb peak, which were not substantially reduced by radioactive decay because

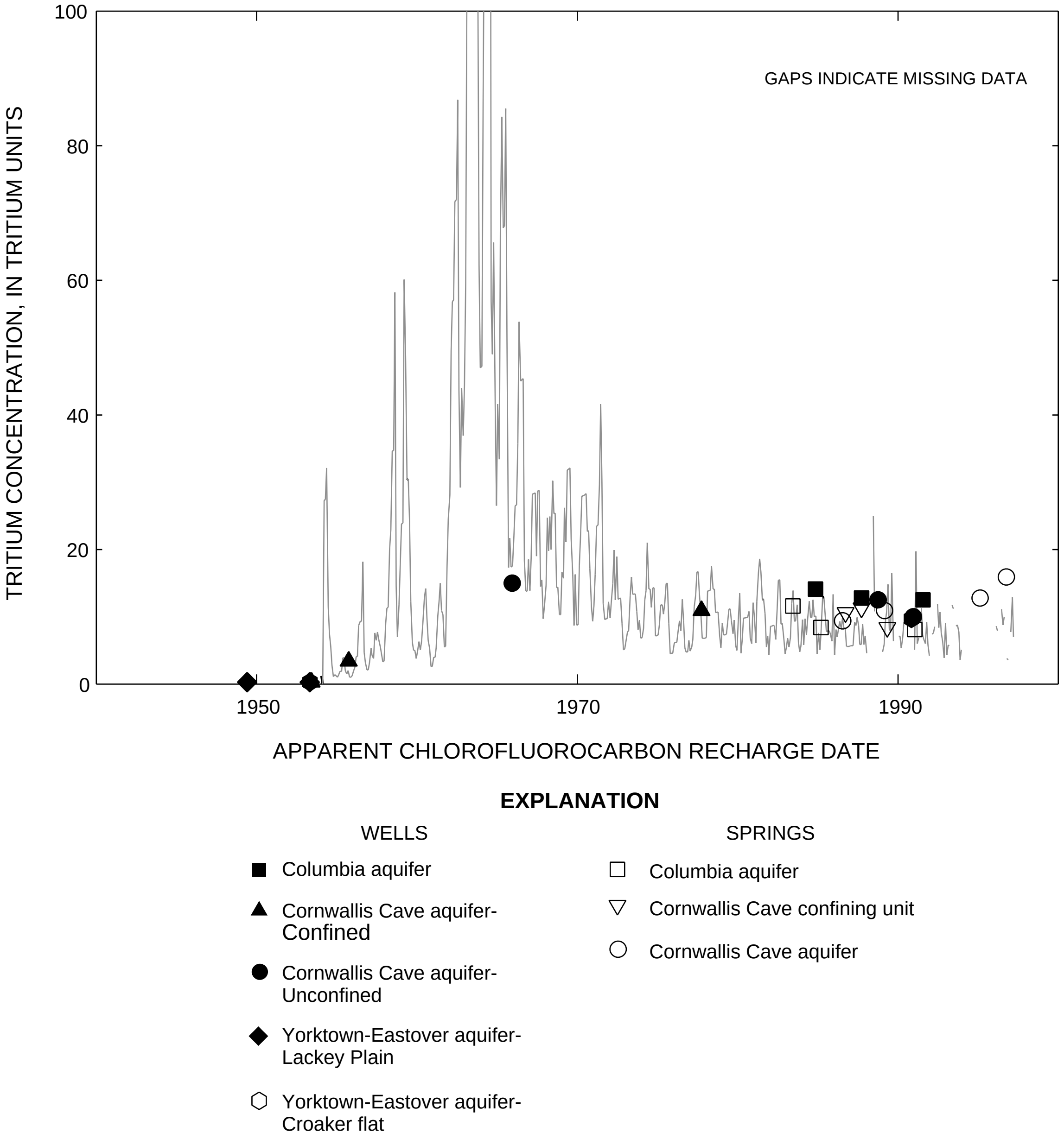


Figure 16. Relation between apparent chlorofluorocarbon recharge date and tritium concentration in ground water and in precipitation (from Michel, 1989) at the Naval Weapons Station Yorktown, Virginia. Tritium concentrations in precipitation are decayed to March 1997. Uncertainties in apparent chlorofluorocarbon recharge dates range from 0.4 to 4.1 years.

elapsed time was short (generally less than 10 years) since the water was recharged.

Relation to Water-Quality Field Properties

Water-quality field properties are highly variable for ground water with apparent CFC ages less than 15 years but have similar ranges for ground water with apparent ages greater than 15 years (fig. 17). The apparent wide ranges in water-quality field properties (table 6) for the different geohydrologic units and settings are the result of interaction of water with the sediments along local and subregional flow paths and the relative position of the sample sites within these flow systems. The young waters represent the local flow systems where: (1) biochemical and chemical reactions are actively weathering the sediments of the shallow geohydrologic units and (2) the potential for contaminants to be introduced from near-surface sources is high. The older apparent CFC ages in the deepest geohydrologic units indicate longer residence times along subregional flow paths during which the ground water chemically equilibrates with the sediments in these units.

pH

Water in the Columbia aquifer is acidic with pH values between 4.8 and 6.9, predominantly less than 6.0. Water in the remaining geohydrologic units is slightly acidic or more likely alkaline in response to the abundance of shell material. The upper parts of the shallow aquifer system contain waters with low values of pH because of (1) acidic precipitation, (2) short residence times as interpreted from the young apparent CFC ages, (3) lack of neutralizing capacity of the quartz-rich sediments, and (4) presence of dissolved carbon dioxide (CO_2) gas.

The pH of water increases with decreasing P_{CO_2} (partial pressure of CO_2) in the shallow aquifer system (fig. 18). The CO_2 gas reacts with the water molecule to form carbonic acid (H_2CO_3), which dissolves shell material in the shallow aquifer system (especially sediments of the Cornwallis Cave aquifer). Dissolution reactions tend to consume H_2CO_3, which causes the pH to rise. The upper or shallow parts of the recharge and discharge area settings on the Station are open systems where the pH values are low and the P_{CO_2} values are high (fig. 18). Parts of the recharge area setting below the Columbia aquifer likely are closed systems for which the supply of CO_2 is small and the supply of H_2CO_3 is quickly depleted.

Specific Conductance

The specific conductance of ground water in the shallow aquifer system on the Station ranges from 40 to 960 µS/cm with a median value of 438 µS/cm (table 6). The lowest values of specific conductance were measured in water samples from the Columbia aquifer. The extremely dilute water in the Columbia aquifer is a result of an abundance of minerals (silicates) in the aquifer sediments that tend to be resistant to chemical weathering. The remaining geohydrologic units primarily consist of soluble minerals (calcite and aragonite) and have high values for specific conductance, which is consistent with the composition of the sediments within these units. The dissolution of shell material causes the specific conductance to increase as a result of an increase in the concentration of dissolved species in solution. Comparison of apparent CFC ages and results of specific conductance measurements indicate that the dissolution of shell material is likely a relatively rapid process (fig. 17). The variability of ranges and median values of specific conductance between the recharge and discharge area settings is partly related to the availability of P_{CO_2}. The dissolution reactions in the geohydrologic units below the Columbia aquifer in the recharge area setting are moderated because the supply of CO_2 is depleted, which is typical of subregional flow systems. The opposite is true in the upper parts of the discharge area setting, especially for springs, where the supply of CO_2 is abundant in the open system and dissolution of shell material can proceed until equilibrium or even supersaturated states are achieved.

Analysis of specific conductance values measured at well 58F100 (B3) and spring 58FS1 (2-1) appears to contradict the concept of increasing concentration of dissolved constituents in ground water along a flow path as the residence time increases. When the position of well 58F100 (B3) within the local flow system is considered, however, the sample is consistent with this concept; only when compared to the entire data set does it appear to be contradictory. The time of travel can be as important as the length of the flow path. The low value of specific conductance and high pH at spring 58FS1 (2-1) illustrate the importance of understanding the effect of geochemical processes on

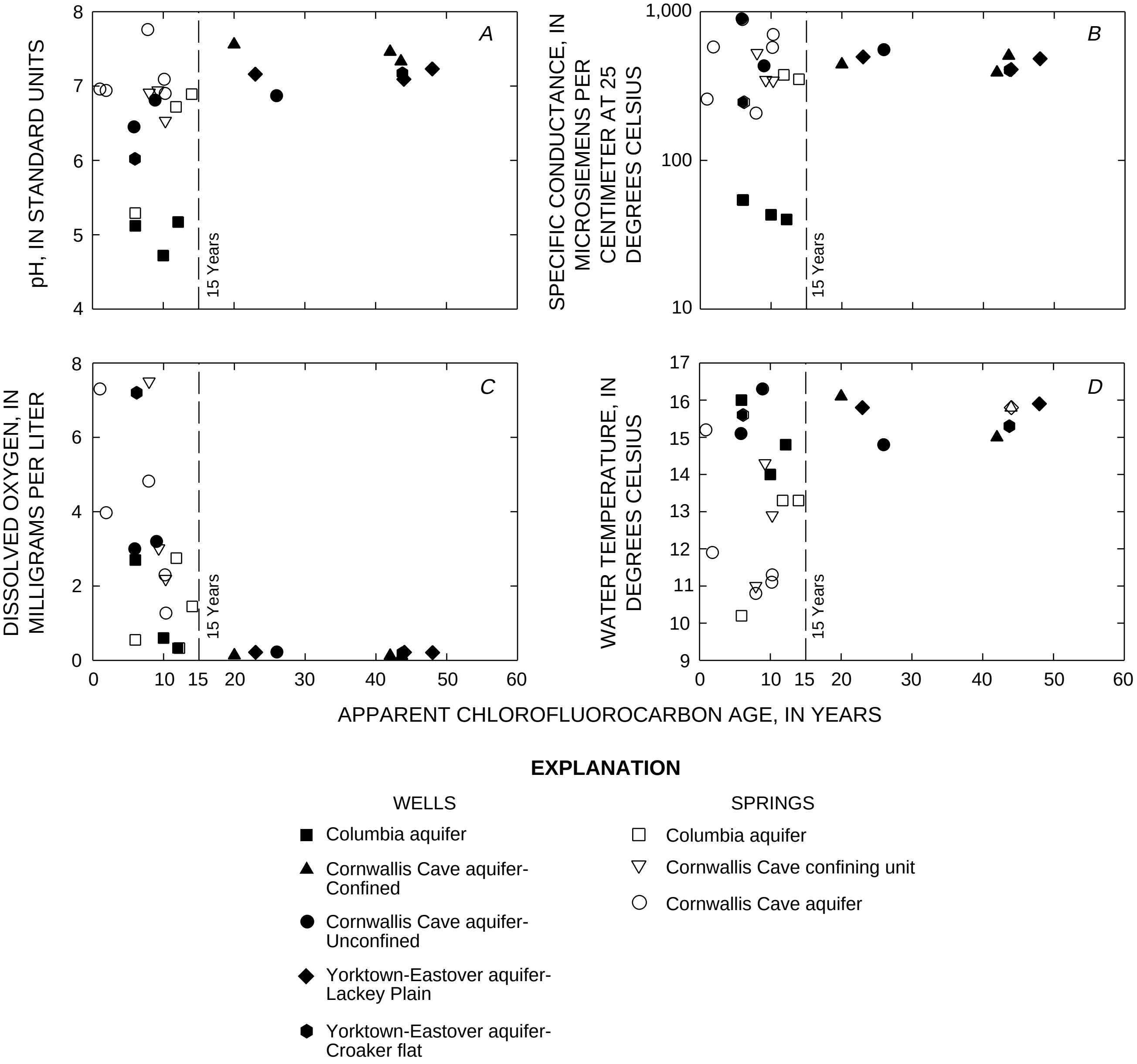


Figure 17. Relation between apparent chlorofluorocarbon age and pH *(A)*, specific conductance *(B)*, dissolved oxygen *(C)*, and water temperature *(D)* of ground water in March 1997 at the Naval Weapons Station Yorktown, Virginia. Uncertainties in apparent chlorofluorocarbon age range from 0.4 to 4.1 years.

Table 6. Range and median values for water-quality field properties of ground water on the Naval Weapons Station Yorktown, Virginia, March 1997.

[Median values in parenthesis if sufficient number of sites available to calculate; °C, degrees Celsius; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

Sample location	Number of sites	Water temperature (°C)	Dissolved oxygen (mg/L)	pH (Standard units)	Specific conductance (µS/cm)
Columbia aquifer	6	10.2-16.0 (13.6)	0.3-2.8 (1.0)	4.8-6.9 (5.3)	40-378 (54)
Cornwallis Cave confining unit	3	11.1-14.3	2.2-7.5	6.5-7.0	343-525
Cornwallis Cave aquifer	16	10.8-17.9 (15.0)	0.0-9.3 (2.9)	6.4-7.7 (6.9)	208-960 (516)
Yorktown-Eastover aquifer	5	15.3-15.9	.0-7.2 (.0)	6.2-7.2 (7.2)	249-495 (408)
Wells	14	13.8-16.3 (15.5)	.0-7.2 (.1)	4.8-7.6 (7.0)	40-960 (422)
Springs	16	10.2-17.9 (13.3)	.6-9.3 (2.9)	5.3-7.7 (6.9)	54-730 (486)
Recharge area setting	8	13.8-16.3	.0-2.7 (.1)	4.8-7.6 (7.1)	40-498 (399)
Discharge area setting	22	10.2-17.9 (14.8)	.0-9.3 (2.9)	5.3-7.7 (6.9)	54-960 (477)
Shallow aquifer system	30	10.2-17.9 (14.9)	.0-9.3 (2.3)	4.8-7.7 (6.9)	40-960 (438)

the concentration of dissolved constituents. Knowledge of the ground-water-flow system and the geochemical processes is critical in interpreting trends in hydrologic and water-quality data, and in estimating apparent ages of ground water.

The interaction of young waters that contain an abundant supply of CO_2 with the shell material in the Cornwallis Cave aquifer probably contributes to the formation of (1) travertine and tufa deposits and (2) subsidence sinkholes or collapse features on the Station. Burmester (1987) and Burkhart and Autrey (1993) discuss the occurrence and hydrochemistry of travertine deposits in the Coastal Plain of Virginia. These deposits occur at springs and seeps where ground water contains high concentrations of calcium carbonate from the dissolution of shell material in the Moore House member of the Yorktown Formation (Hubbard and Herman, 1990; Herman and Hubbard, 1990). This geologic formation is the unit that comprises the Cornwallis Cave aquifer. Travertine deposits occur where ground water discharges from the Cornwallis Cave aquifer on the Station, especially in the upper parts of the aquifer. Abundant travertine deposits occur at spring 58FS1 (2-1), which had the lowest P_{CO_2} (0.002 atm) and highest pH (7.7) values of the water samples from the Cornwallis Cave aquifer (fig. 18). These values for P_{CO_2} and pH, when combined with the low value for specific conductance (208 µS/cm), indicates that outgassing of CO_2 is occurring at this spring. Lorah and Herman (1990) suggest that outgassing of CO_2 causes a rapid rise in pH, and ground water becomes supersaturated with respect to calcite. The abundance of travertine deposits along the seepage face adjacent to spring 58FS1 (2-1) and the low specific conductance indicate that initial precipitation of calcite occurs prior to discharge at the spring. Excavation during sampling indicated that the travertine deposits extended at least 3 to 5 ft into the seepage face. Travertine deposits form small waterfalls (generally less than 2 ft high) along streams on the Station. The turbulent flow of streams over these falls causes increased CO_2 outgassing, which in turn causes additional precipitation of calcite (Lorah and Herman, 1990).

Formation of subsidence sinkholes or collapse features on the Station, especially in the discharge area setting, is initiated by the dissolution of shell material in the Cornwallis Cave aquifer from the circulation of young ground water through these sediments. The presence of the travertine and tufa deposits indicates that these dissolution reactions are occurring in the shallow

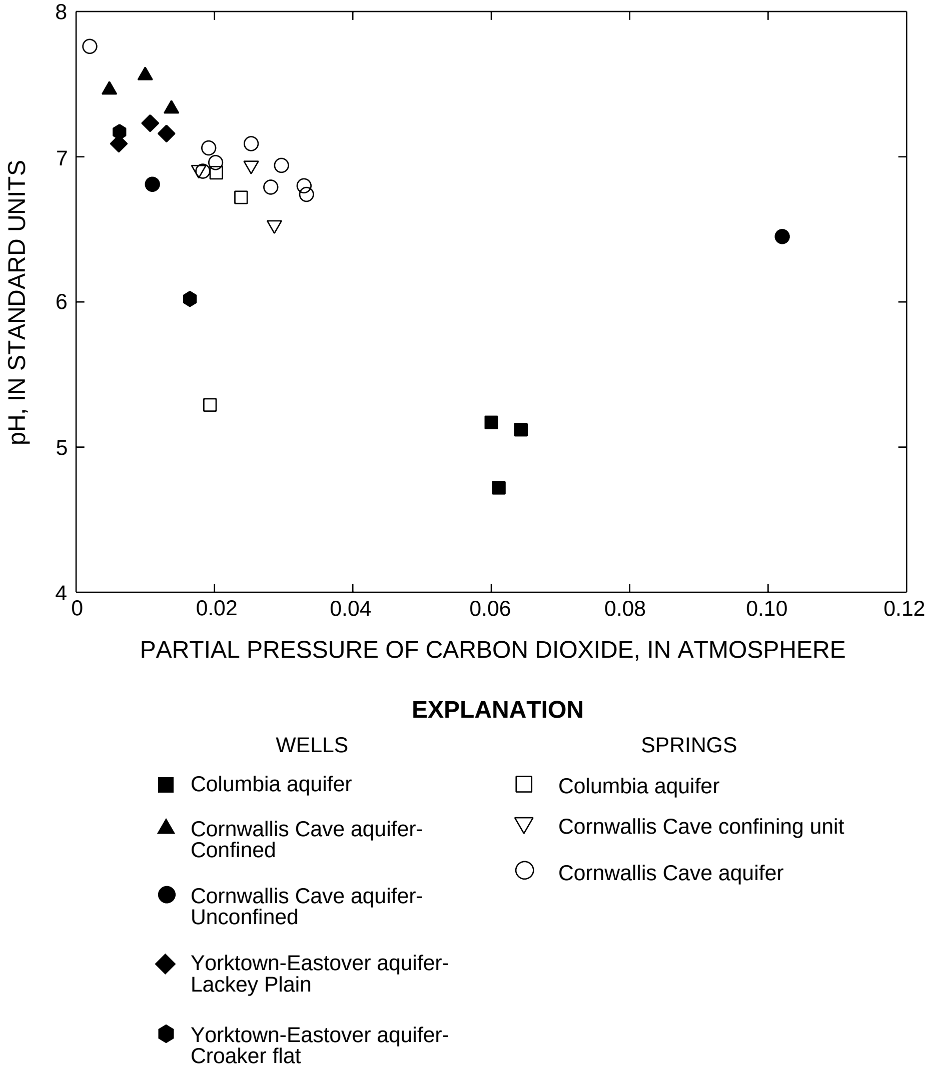


Figure 18. Relation between partial pressure of carbon dioxide and pH in ground water at the Naval Weapons Station Yorktown, Virginia, March 1997.

aquifer system on the Station. Chemical removal of the shell material can create void spaces within the aquifer. The potential for preferential flow along these void spaces can facilitate additional erosion of aquifer material. As more material is removed, the weight of the overlying material causes the collapse feature to form.

Dissolved Oxygen

The upper parts of the shallow aquifer system at the Station tend to be oxic environments. One would expect dissolved oxygen concentrations in the Columbia aquifer in the recharge area setting to be high in response to shallow depths to the water table and relatively young apparent ages. The highest dissolved oxygen concentrations, however, occur in the springs. The dissolved oxygen saturation concentration of precipitation at the Station is approximately 10 mg/L at the mean annual air temperature of 14.6°C. As ground water moves through the flow system, biochemical and chemical reactions involving organic material and oxidizable minerals deplete dissolved oxygen in ground water (Hem, 1985). The high dissolved oxygen concentrations in the springs sampled during this investigation (table 6), especially in the Cornwallis Cave confining unit, indicate:

1. Ground water discharging at springs has followed a short or local flow path over a short time period (less than 15 years).

2. The point of recharge may be between the recharge and discharge area settings.
3. Preferential flow along voids associated with changes in the aquifer matrix by chemical and/or physical processes or fracturing associated with slope instability reduces the time of travel and the surface area for biochemical and chemical reactions to occur.

Dissolved oxygen concentrations in the deeper aquifers beneath the recharge area settings generally are low. The occurrence of iron bacteria and the precipitation of iron in seeps along the base of the aquifers in the discharge areas are consistent with low dissolved oxygen concentrations in ground water. Dissolved oxygen concentrations are depleted by up to an order of magnitude between the Columbia and Cornwallis Cave aquifers in the recharge area settings. Results of CFC-based dating are consistent with geochemical evolution of water in which dissolved oxygen is consumed within a period of about 15 years.

APPLICATION OF APPARENT CFC AGES TO GEOHYDROLOGY OF THE STATION

The apparent CFC ages determined for the wells and springs sampled during this investigation can be used to constrain the wide range of hydraulic parameters that are assumed to be valid for the shallow aquifer system at the Station. Advective transport rates are frequently estimated from these hydraulic parameters through calculations of time of travel of ground water. The apparent CFC ages also can be used to estimate ground-water recharge rates to the shallow aquifer system.

Comparison of Apparent CFC Ages to Calculated Ranges in Time of Travel

The extent of the Columbia aquifer is contiguous to the extent of the recharge area setting at the Station, with the dominant direction of ground-water flow being downward through intervening confining units, recharging the underlying Cornwallis Cave and Yorktown-Eastover aquifers (Brockman and others, 1997). The time required for ground water to move downward from the water table to a given depth in the aquifer is calculated from hydraulic parameters for the shallow aquifer system. These calculated travel times may be compared to the apparent ages derived from environmental tracers such as CFCs. Solomon and others (1992) and Reilly and others (1994) noted that the vertical velocity of ground water at the water table is a function of the recharge rate and the porosity and given as

$$v = \frac{R}{\theta} \qquad (2)$$

where v is vertical velocity, R is recharge rate, and θ is porosity. The time of travel for vertical movement from the water table to a point at a given depth is a function of the depth and the vertical velocity as

$$t = \frac{d}{v} = \frac{d \cdot \theta}{R} \qquad (3)$$

where t is time of travel and d is depth.

Richardson (1994) estimated that the average ground-water discharge from geohydrologic units in the Coastal Plain of Virginia ranged from 0.66 to 0.93 ft/yr, and averaged 0.82 ft/yr (9.8 in/yr) for the entire Coastal Plain. Assuming that the average ground-water discharge equals the average ground-water recharge, over the span of a year, recharge in the vicinity of the Station is estimated to be about 0.82 ft/yr. The range of porosity (0.25 to 0.45) was estimated from methods that use median grain size (D_{50}) and specific yield derived from grain-size analyses of core samples (Johnson, 1967). The calculated ranges in time of travel, based on these parameter estimates, are given in table 7. The apparent CFC ages are slightly older than the ranges in time of travel calculated for the six shallow wells examined (fig. 19). Three of the wells (58F106 (E4), 58F116 (H4), and 58F121 (I4)) are screened in the Columbia aquifer, and three (58F99 (B3), 58F110 (G3), and 58G57 (N3)) are screened in unconfined parts of the Cornwallis Cave aquifer, where the overlying Columbia aquifer is missing. The slightly older apparent CFC ages may indicate that the average annual ground-water recharge at the Station is less than the 0.82 ft/yr estimated by Richardson (1994).

The process by which dissolved substances are transported by the bulk motion of ground-water flow is referred to as advection. Because of advection, conservative environmental tracers (like CFCs) that are dissolved in ground water are transported at the rate of the average linear velocity of the water (Freeze and Cherry, 1979). To calculate average linear velocity requires

Table 7. Calculated range of travel time for six shallow wells based on estimated recharge rate and ranges of porosity and the apparent chlorofluorocarbon age at the Naval Weapons Station Yorktown, Virginia

[Recharge rate is 0.825 feet/year; CFC, chlorofluorocarbon]

Well number	Well depth (feet)	Depth to water table (feet)	Depth below water table of center of well screen (feet)	Range of porosity (dimensionless)	Range of estimated time of travel (years)	Apparent CFC age (years)
58F106 (E4)	24	7.7	13.3	0.25-0.45	4.0-7.3	10±2.0
58F116 (H4)	24	12.9	7.9	.25-.45	2.4-4.3	6±3.2
58F121 (I4)	22	2.3	16.7	.25-.45	5.1-9.1	12±1.7
58F99 (B3)	37	29.3	4.5	.25-.45	1.4-2.5	6±1.6
58F110 (G3)	42	30.7	8.3	.25-.45	2.5-4.5	9±1.1
58G57 (N3)	57	37.0	16.8	.25-.45	5.1-9.2	[1]21±

[1] CFC analyses indicate that water represents a possible mixture of different age waters. The apparent CFC age presented is the oldest possible age of the young fraction.

knowledge of the effective porosity of an aquifer. Lohman (1972) noted

$$\bar{v} = \frac{-K\frac{dh}{dl}}{\theta} \tag{4}$$

where $\bar{v}$ is average linear velocity, K is horizontal hydraulic conductivity**,** dh/dl is hydraulic gradient, and θ is effective porosity.

Average linear velocity may range from less than to more than the actual velocity between two points in the aquifer (Lohman, 1972). The time of travel for horizontal movement from the water table to a point a given distance downgradient is a function of the distance traveled and the average linear velocity

$$t = \frac{l}{\bar{v}} \tag{5}$$

where t is time of travel and l is length of flow.

Time of travel was calculated for hydrologic basins contributing to springs sampled on the Station. The basins were delineated from the water-level maps presented in Brockman and others (1997), and travel distances were assumed to be the maximum distance between the springs and the edge of their contributing basins. For velocity calculations in the hydrologic basins, the hydraulic gradient was estimated from water-level maps (Brockman and others, 1997), and the effective porosity was assumed to range from 0.25 to 0.45. Based on the estimated hydraulic gradients, assumed porosity ranges, and horizontal hydraulic conductivity values from slug tests, ground-water-flow rates range from a low of 0.3 ft/yr to a high of 350 ft/yr. The calculated ranges in time of travel, based on these estimated parameters, are given in table 8.

Spatial and seasonal differences in water levels will cause changes in head and, thus, velocity and direction of flow. Seasonal changes in water levels generally will be small because velocities are generally low. Spatial differences in water levels, however, can be substantial. Because the rate of ground-water flow is controlled by hydraulic conductivity, hydraulic gradient, and effective porosity, variations in these parameters will result in changes in the average linear velocity.

The apparent CFC ages of water from the springs on the Station range from 1 to 14 years. Of the 11 springs examined (fig. 20), the apparent CFC ages of 7 springs lie within the range of calculated times of travel, 3 springs have apparent CFC ages slightly below (less than 6 years) the minimum calculated times of travel, and 1 spring (57FS1 (18-1)) has an apparent CFC age well below (66 years) the minimum calculated time of travel. These relatively young apparent ages indicate that shallow ground water recharged at the water table in these small hydrologic basins moves quickly to the spring discharges. These results have important implications with respect to estimates of ground-water flow and the transport of conservative contaminants that are based upon reasonable ranges of geotechnical and hydraulic parameters. As evidenced

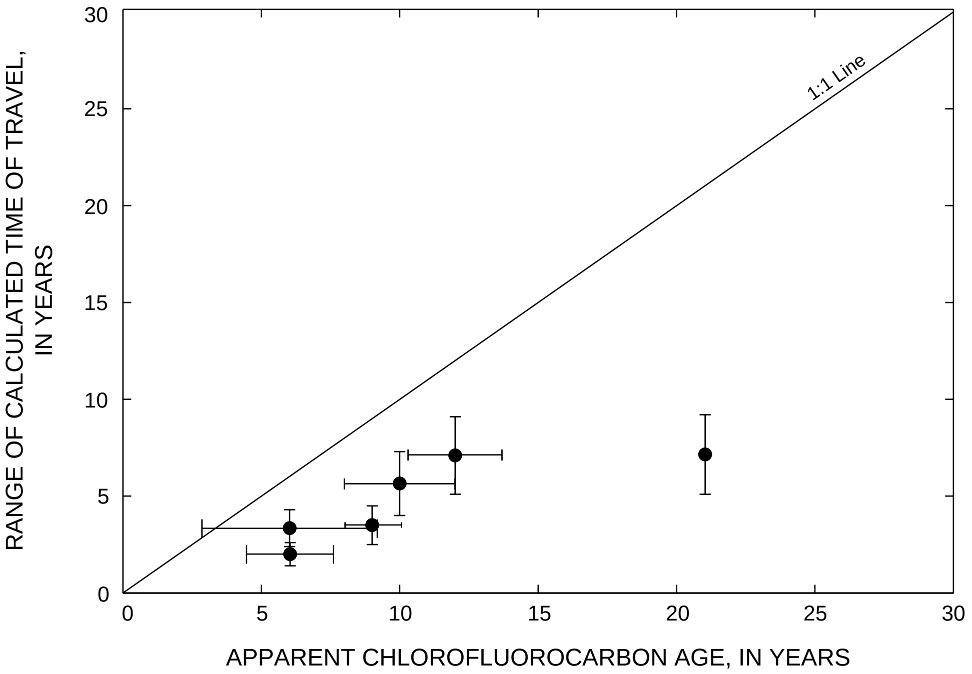


Figure 19. Relation of apparent chlorofluorocarbon age and range of calculated time of travel for ground water from six shallow wells at the Naval Weapons Station Yorktown, Virginia, March 1997. Horizontal error bars represent uncertainty in apparent chlorofluorocarbon ages and vertical error bars represent uncertainty in range of calculated time of travel.

by the apparent CFC ages for spring discharges, calculated travel times can be up to two orders of magnitude greater than the actual observed for a transient environmental tracer.

Estimated Ground-Water-Recharge Rates Based on Apparent CFC Age

Ground-water dating techniques can be used to estimate ground-water recharge rates. For instance, Robertson and Cherry (1989) used the depth of the ^{3}H bomb peak to approximate the ground-water recharge rate in a shallow unconfined sand aquifer. This method assumes uniform downward flow through the aquifer, which is analogous to a plug flow model. Because apparent CFC ages represent a continuum of time since the mid-1940s, they can provide a better approximation of recharge rates in more diverse geohydrologic environments than the ^{3}H bomb peak. Ground-water recharge rates for the shallow aquifer system at the Station are estimated by rearranging equation 3 as

$$R = \frac{d \cdot \theta}{t} \qquad (6)$$

where *d* is depth to the center of the screened interval, θ is the median porosity (0.35), and *t* is the assigned apparent CFC age. Recharge rates were not calculated for wells 58F99 (B2) and 58G57 (N3) because the CFC analysis indicated that water samples from these wells represent mixtures and the assumption of plug flow, therefore, is not valid. The calculated recharge rates range from 0.29 to 0.89 ft/yr with a median value of 0.54 ft/yr; this value is lower than the recharge rate estimated by Richardson (1994) of 0.82 ft/yr, which represents the integration of multiple recharge rates over a large drainage area as measured by a single streamflow-gaging station. The use of a uniform porosity (0.35) in the estimation of recharge rates based on the apparent CFC ages can be a major source of difference in estimated recharge rates. Another possible source of uncertainty in the calculation of recharge rates is the apparent CFC ages. The uncertainty in recharge rates associated with the apparent CFC age uncertainties is less than ±0.20 ft/yr for all of the wells but one. The uncertainty in the estimated recharge rate for well 58F116 (H4), with an apparent CFC age uncertainty of 3.2 yrs, is ±0.57 ft/yr. Discrepancies in estimates of recharge rates derived from different methods, therefore, are to be expected.

The relatively flat landscape of the recharge area setting in the Lackey Plain and Croaker flat at the Sta-

Table 8. Calculated range of travel time to 11 springs based on estimated hydraulic gradient, maximum basin length, ranges of horizontal hydraulic conductivities and porosities, and the apparent chlorofluorocarbon age at the Naval Weapons Station Yorktown, Virginia

[Porosity ranges from 0.25 to 0.45; CFC, chlorofluorocarbon]

Spring number	Estimated hydraulic gradient (feet/feet)	Maximum hydrologic basin length (feet)	Range of horizontal hydraulic conductivity (feet/day)	Range of estimated time of travel (years)	Apparent CFC age (years)
57FS1 (18-1)	0.014	1,400	0.03-0.9	76-4,100	10±0.4
58FS1 (2-1)	.027	1,110	.3-9	3.1-170	6±.8
58FS2 (5-1)	.054	460	.03-.9	6.5-350	9±.5
58FS3 (6-1)	.016	830	.3-9	3.9-210	10±.9
58FS4 (12-1)	.016	1750	.3-9	8.3-450	4±1.0
58FS7 (16-2)	.045	590	.03-.9	10-540	9±1.4
58FS8(19-1)	.003	390	.4-8	11-400	12±.6
58FS9 (19-3)	.007	770	.4-8	9.4-340	15±1.3
58FS12 (20-8)	.008	660	.3-9	6.3-340	3±.4
58GS1 (A-2)	.006	1,270	.3-9	16-870	10±1.3
58GS2 (8-1)	.019	1,040	.4-8	4.7-170	7±2.1

tion is more conducive to ground-water recharge than is the highly dissected landscape with steep valleys of the discharge area setting, where overland and subsurface runoff (interflow) are increased. The cross-sectional area of the different geohydrologic units decreases as the distance from the ground-water divides increases, which further reduces the available volume of the aquifer where recharge can occur.

The relation between recharge rates and seasonal water-level fluctuations also varies depending on geohydrologic setting (fig. 21). Recharge causes greater seasonal water-level fluctuations for sites in the recharge area setting than those for sites in the discharge area setting. For example, wells 58F121 (I4) and 58G52 (F3) have similar recharge rates (0.51 and 0.57 ft/yr, respectively), but the seasonal water-level fluctuation in well 58F121 (I4) is nearly 6.5 times larger than the fluctuation in well 58G52 (F3). The relation between the amount of recharge and the magnitude of seasonal fluctuation is not only a result of geohydrologic setting but also of factors such as the heterogeneity and anisotropy (K_h/K_v) of the aquifer sediments, distance from the discharge outlet, and land use.

Revised Conceptual Model of Ground-Water Flow

The analysis of apparent CFC ages confirms the validity of the conceptual model of ground-water flow in the shallow aquifer system of the Station proposed by Brockman and others (1997). The revised conceptual model of ground-water flow presented in figure 22 adds the dimension of time. The age of ground water increases downward and outward as the distance from the ground-water divides increases. Young ground water (less than 50 years) is present in the upper parts of the Yorktown-Eastover aquifer in the recharge area setting. The vertical distribution of apparent CFC ages indicates that ground-water movement between aquifers is somewhat retarded by the confining units, but the elapsed time is relatively short (generally less than 35 years), as evidenced by the presence of CFCs at depth. Convergence of flow lines from local and subregional flow systems occurs in the discharge areas, and the binary mixtures identified by CFC-based dating indicate that flow lines converge not only at the actual point of discharge, but also in the subsurface (for example, well 58G57 (N3)). The analysis of N_2-Ar recharge temperatures indicates that discharge from springs during the seasonal high of the water levels in the shallow aquifer system has followed a short and probably shallow flow path. The assumption of piston or plug flow

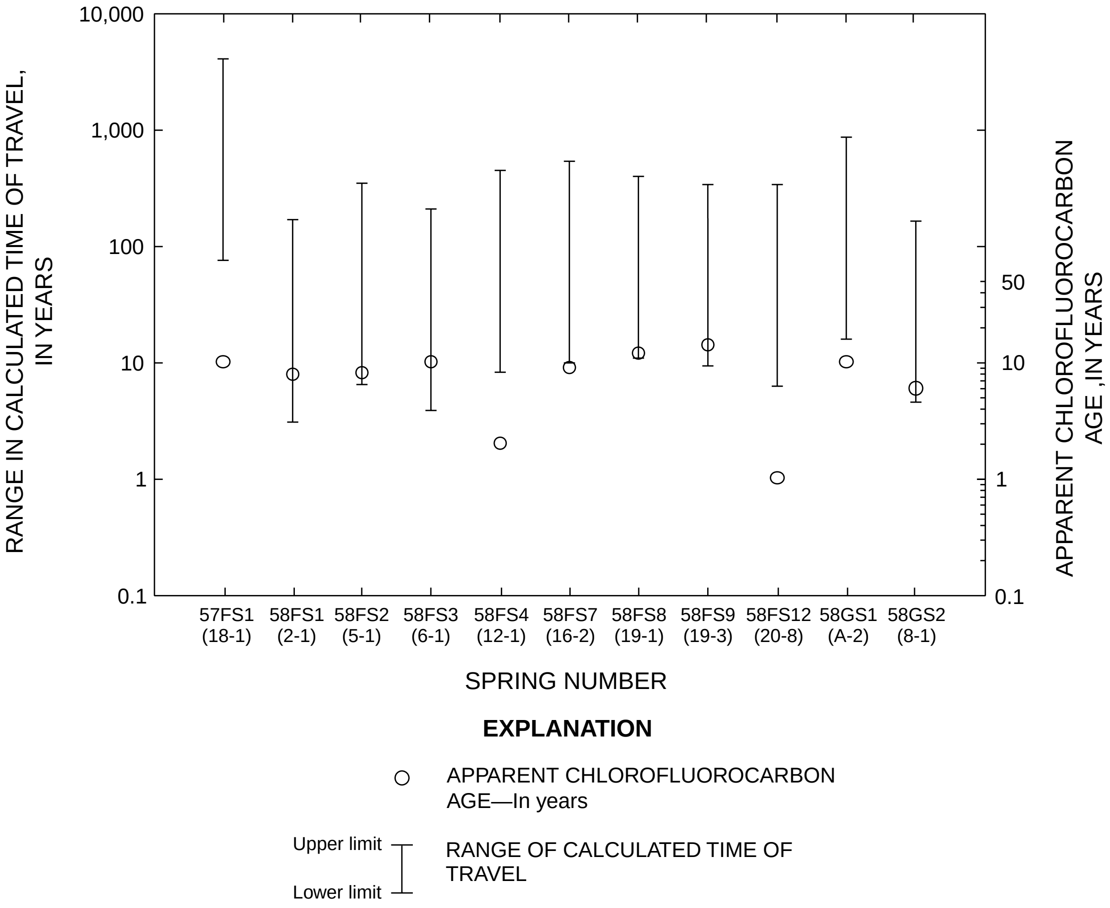


Figure 20. Relation of apparent chlorofluorocarbon age and calculated time of travel for ground water from 11 springs at the Naval Weapons Station Yorktown, Virginia, March 1997. Errors in apparent chlorofluorocarbon age range from 0.4 to 4.1 years.

seems valid for the springs, at least for that time of the year that the springs were sampled. The fact that binary mixtures were not identified by CFC-based dating suggests that the springs sampled during this study represent flow from a local system.

STUDY IMPLICATIONS FOR REMEDIATION ACTIVITIES

The findings of this study support the geohydrologic framework and the conceptualization of the shallow aquifer system at the Station developed by Brockman and others (1997). The determination and evaluation of the apparent age of ground water add the dimension of time to the three-dimensional framework of Brockman and others (1997). The findings from this study can be applied to ongoing remediation and engineering activities at the Station and the adjacent area. Additionally, these findings also have implications for other areas within the Coastal Plain of Virginia. McFarland (1997) reported similar ranges of apparent CFC ages in a highly dissected area of the upper Coastal Plain along the James River. Similar age distributions in the shallow aquifers of both the upper and lower Coastal Plain indicate that the shallow ground-water-flow system in a particular area is directly related to the landscape or geomorphic setting of that area and contributes to the development of the present-day landscape.

The occurrence of subsidence sinkholes and other collapse features on the Station is related to interaction of young ground water with shell material in the Cornwallis Cave aquifer. The relation between apparent age and field water-quality properties indicates that dissolution of the shell material in the Cornwallis Cave aquifer is relatively rapid and ongoing. Therefore, renovation and new construction projects on the Station

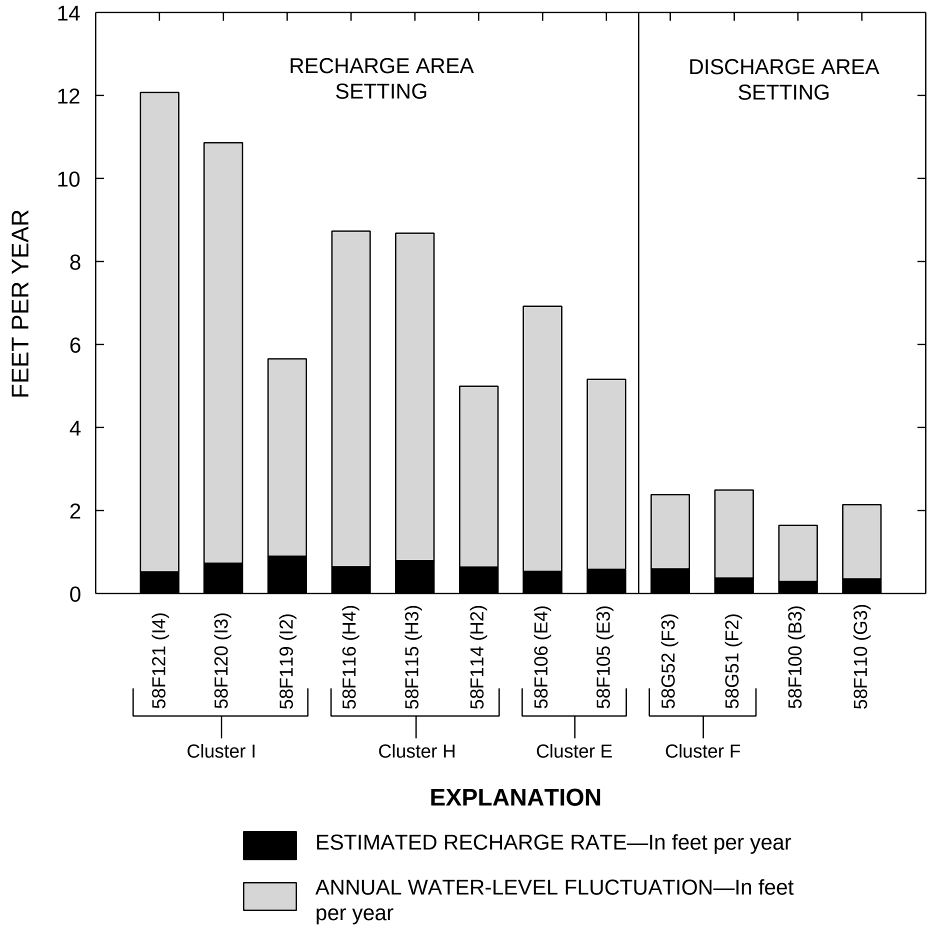


Figure 21. Relation between estimated recharge rate based on apparent chlorofluorocarbon age in March 1997 and annual water-level fluctuations at the Naval Weapons Station Yorktown, Virginia. Porosity for all wells is assumed to be 35 percent. Distance from ground-water divides increases to the right between clusters. Wells within a cluster are plotted from shallow to deep.

and the nearby adjacent area may require geotechnical investigation to assess the potential effects of subsidence in these areas. Numerous slope stabilization structures have been constructed on the Station. Future structures in areas underlain by the Cornwallis Cave aquifer could be designed to eliminate or minimize the effects of ground-water sapping. In both of the cases described above, the maps constructed by Brockman and others (1997) can be used as a guide for planning future engineering activities at the Station.

Analysis of apparent CFC ages will benefit remediation strategies and activities at the Station. The apparent ages determined from this study can be used to estimate rates of advective transport. The analysis also indicates that (1) these rates of transport vary depending upon geohydrologic setting and position within the ground-water-flow system; (2) the rate of transport and fate of contaminants in the local and subregional flow systems may be completely different; and (3) flow in the upper parts of the shallow aquifer system can be rapid and extremely sensitive to seasonal and climatic effects, which could cause temporal variations in the distribution of contaminants at the Station.

Organic compounds, like trichloroethylene (TCE), have been detected in the subsurface at the Station (Baker Environmental, Inc., and Roy F. Weston, Inc., 1993) and the transport and fate of these compounds are a major concern of the Station. The rate-limiting factor in the reductive dehalogenation of TCE is the accumulation of vinyl chloride. Reductive dehalogenation of TCE occurs in anaerobic environments, whereas conversion of vinyl chloride to CO_2 requires the addition of oxygen (Chapelle, 1993). If a sufficient microbial community is present, it is feasible that TCE

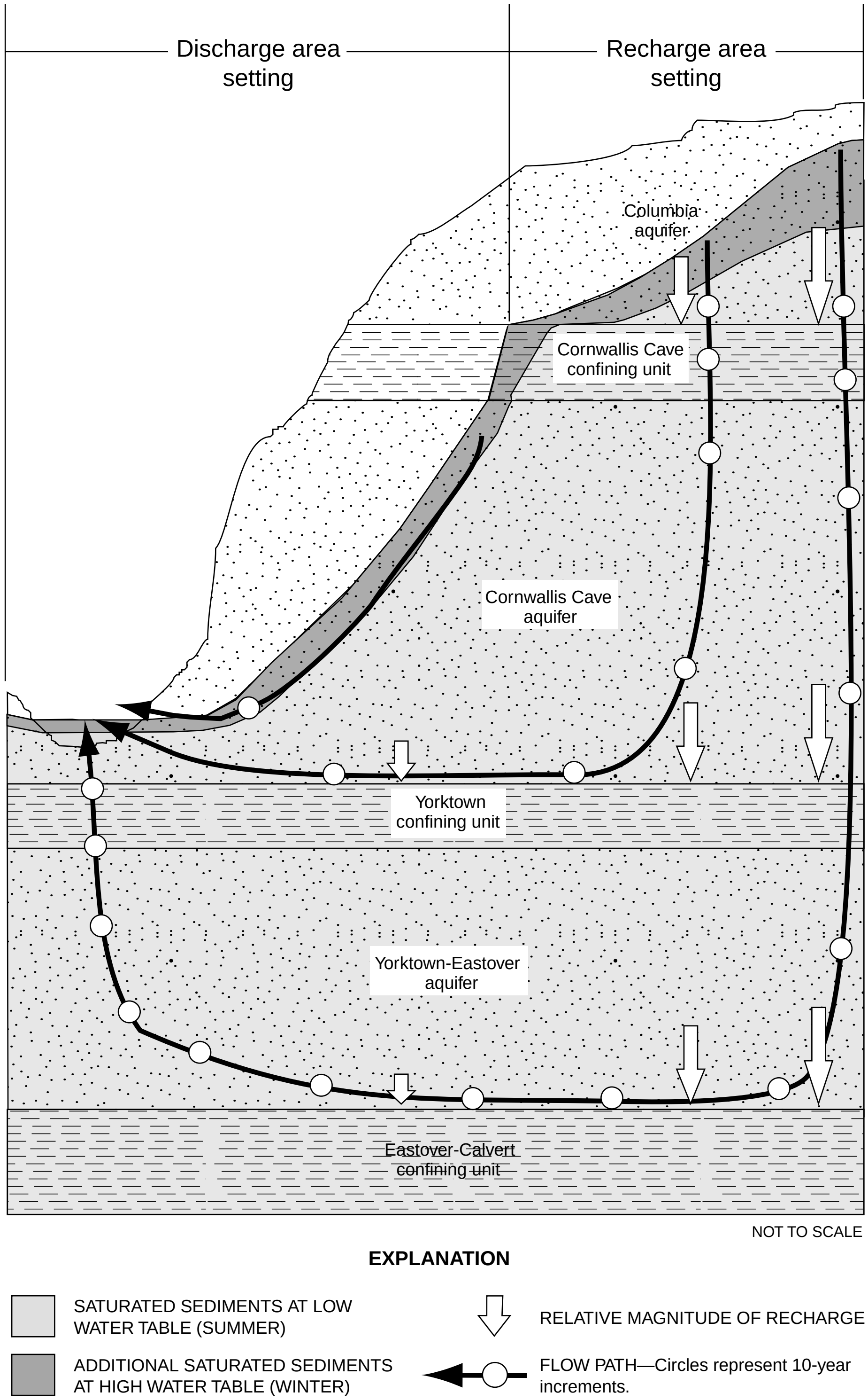


Figure 22. Revised conceptual model of ground-water flow at the Naval Weapons Station Yorktown, based on apparent chlorofluorocarbon ages of ground water in March 1997.

will degrade along a long, deep flow path within either a local or subregional flow system. Concentrations of dissolved oxygen decrease with increasing depth and apparent age of the ground water. Mixing of young ground water containing abundant oxygen from the upper parts of the shallow aquifer system with old water could provide the mechanism for the conversion of vinyl chloride to CO_2. The identification during this study of mixed waters at some distance away from the point of discharge may indicate that sufficient time would be available for this conversion to occur. The scenario described above is dependent upon the location of a contaminated site in the shallow aquifer system at the Station. Potential remediation activities on the Station can be evaluated in the light of potential rates of advective transport at various locations in the ground-water-flow system as determined by the apparent CFC ages.

The apparent age determinations and estimated ground-water recharge rates can be used as calibration criteria in simulations of ground-water flow on the Station to refine and constrain future ground-water-flow models of the shallow aquifer system. Apparent CFC ages illustrate that seemingly valid assumptions of hydraulic parameters can result in substantial overestimates for time of travel calculations. Realistic simulation results will aid in the evaluation of remediation alternatives such as pump-and-treat technologies. Solute transport modeling, based on these flow simulations, can be used to estimate the transport and fate of contaminants in the ground water.

SUMMARY

The USGS, in cooperation with the Naval Weapons Station Yorktown, Base Civil Engineer, Environmental Directorate, has been investigating the shallow aquifer system on the 10,624-acre installation in Yorktown, Va., since 1995. This report presents the data and findings of a 1-year study using multi-tracer methods to estimate apparent chlorofluorocarbon (CFC) ages of ground water. The report (1) defines the apparent CFC age of ground water in the shallow aquifer system, (2) compares apparent CFC ages with water-quality field properties and calculated times of travel, and (3) presents estimates of ground-water recharge rates. CFCs, tritium (^3H), dissolved gases, stable isotopes, and water-quality field properties were measured in samples from 14 wells and 16 springs in March 1997.

Two environmental tracers—CFCs and ^3H—were used to determine the apparent age of ground water of the shallow aquifer system on the Station. CFC-based dating was the primary method for dating ground water in this study, and the concentrations of ^3H in ground water were used to confirm the apparent CFC age determinations. Recharge temperatures, estimated from dissolved nitrogen (N_2) and argon (Ar) concentrations in ground water, range from 5.9°C to 17.3°C with a median temperature of 10.9°C. Concentrations of excess air vary depending upon geohydrologic setting (recharge and discharge areas). Water samples from springs and wells located in the discharge area setting have low values of excess air, whereas wells located in the recharge area setting have high values. The $\delta^{18}O$ values range from -7.2 to -5.5‰ and δD values range from -41.2 to -29.7‰. Deuterium excess (*d*) ranges from 13.3 to 16.8‰ with a median value of 14.8‰ for the Station. Precipitation generally is highest in the summer months, yet the N_2-Ar recharge temperatures and stable isotope data indicate that ground-water recharge predominantly occurs in the cold months of the year.

Apparent CFC ages range from 1 to 48 years with a median age of 10 years. The oldest apparent ages occur in the upper parts of the Yorktown-Eastover aquifer, whereas the youngest apparent ages occur in samples from the Columbia aquifer and the upper parts of the discharge area setting, especially springs. The vertical distribution of apparent CFC ages indicates that ground-water movement between aquifers is somewhat retarded by the leaky confining units, but the elapsed time is relatively short (generally less than 35 years), as evidenced by the presence of CFCs at depth. The assumption of plug or piston flow applies in the recharge area setting on the Station, but only applies to parts of the shallow aquifer system in the discharge area setting, where binary mixtures of young and old waters were identified. Convergence of flow lines occurs not only at the actual point of discharge, but also occurs in the subsurface as evidenced by CFC-based dating.

The concentration of ^3H in ground water ranges from below the USGS laboratory minimum reporting limit of 0.3 to 15.9 TU with a median value of 10.8 TU. The CFC-based recharge dates are consistent with expected ^3H concentrations. Tritium concentrations in samples from wells finished in the upper parts of the Yorktown-Eastover aquifer are indicative of ground water recharged prior to atmospheric testing of thermonuclear weapons. Spring samples have high ^3H concentrations as a result of high initial ^3H levels after the "bomb peak" in 1963 and the short time that has elapsed since the water was recharged.

Water-quality field properties for ground water with apparent CFC ages less than 15 years are highly variable because of geochemical processes within local flow systems. Ground water with apparent CFC ages greater than 15 years represents subregional flow systems where field properties tend to be stable. Ground water in the Columbia aquifer is acidic and dilute, whereas ground water in the remaining geohydrologic units is slightly acidic to alkaline with high values of specific conductance in response to dissolution of shell material. The formation of travertine and tufa deposits along streams on the Station and the development of subsidence sinkholes and collapse features are probably related to the circulation and interaction of young water with the shell material in the Cornwallis Cave aquifer. The upper parts of the shallow aquifer system at the Station tend to be oxic environments, whereas deeper parts generally are anoxic. High concentrations of dissolved oxygen in springs are related to flow of young ground water along short or local flow paths.

The apparent CFC ages are slightly older than the range in time of travel calculated for shallow wells sampled during this study, which may indicate that the average annual ground-water recharge at the Station is less than the 0.82 ft/yr estimated by Richardson (1994). Calculated travel times to springs can be up to two orders of magnitude greater than the determined apparent CFC ages. Reasonable assumptions of values for hydraulic parameters can result in substantial overestimates for time of travel for springs. The relatively young apparent ages (less than 15 years) indicate that shallow ground water recharged at the water table in small hydrologic basins moves quickly to the spring discharges. CFC-based recharge rates range from 0.29 to 0.89 ft/yr with an average value of 0.54 ft/yr. Recharge causes greater seasonal water-level fluctuations for sites in the recharge area setting than for sites located in the discharge area setting.

The analysis of apparent CFC ages confirms the validity of the conceptual model of ground-water flow in the shallow aquifer system underlying the Station proposed by Brockman and others (1997). The revised conceptual model of ground-water flow adds the dimension of time. The findings from this study can be applied to ongoing remediation activities at the Station and adjacent areas. The apparent CFC ages can be used to estimate rates of advective transport, refine and constrain future ground-water-flow models of the shallow aquifer system, and aid in the evaluation of remediation alternatives such as pump-and-treat technologies.

REFERENCES CITED

Baker Environmental, Inc., and Roy F. Weston, Inc., 1993, Final round one remedial investigation report for sites 1-9, 11, 12, 16-19, and 21, Naval Weapons Station, Yorktown, Virginia: Baker Environmental, Inc., Coraopolis, Pa., [variously paged].

Beckman Instruments, Inc., 1992, Beckman Φ12 pH/ISE meter: Beckman Instructions 015-246800-F.

Brockman, A.R., Nelms, D.L., Harlow, G.E., Jr., and Gildea, J.J., 1997, Geohydrology of the shallow aquifer system, Naval Weapons Station Yorktown, Yorktown, Virginia: U.S. Geological Survey Water-Resources Investigations Report 97-4188, 61 p.

Brockman, A.R., and Richardson, D.L., 1992, Hydrogeologic framework of the shallow aquifer system of York County, Virginia: U.S. Geological Survey Water-Resources Investigations Report 92-4111, 36 p.

Burkhart, P.A., and Autrey, P.I., 1993, Hydrogeochemistry of the Burwell Bay travertine deposits, *in* Johnson, G.H., Beach, T.A., Burkhart, P.A., Harris, M.S., Herman, J.D., and Autrey, P.I., The geology along the lower James estuary, Virginia: Southeastern Friends of the Pleistocene, Field Trip Guidebook, p. 21-22.

Burmester, J.L., 1987, A travertine deposit on the Coastal Plain in Isle of Wight, Virginia [unpublished senior thesis]: Williamsburg, Virginia, College of William and Mary, 55 p.

Busenberg, Eurybiades, and Plummer, L.N., 1992, Use of chlorofluorocarbons (CCl_3F and CCl_2F_2) as hydrologic tracers and age-dating tools: The alluvium and terrace system of central Oklahoma: Water Resources Research, v. 28, no. 9, p. 2257-2283.

Busenberg, Eurybiades, Weeks, E.P., Plummer, L.N., and Bartholomay, R.C., 1993, Age dating ground water by use of chlorofluorocarbons (CCl_3F and CCl_2F_2) and distribution of chlorofluorocarbons in the unsaturated zone, Snake River Plain aquifer, Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Water-Resources Investigations Report 93-4054, 47 p.

Chapelle, F.H., 1993, Ground-water microbiology and geochemistry: New York, John Wiley and Sons, Inc., 424 p.

Ciccioli, P., Cooper, W.T., Hammer, P.M., and Hayes, J.M., 1980, Organic solute-mineral surface interactions: A new method for the determination of groundwater velocities: Water Resources Research, v. 16, no. 1, p. 217-223.

Clark, I.D., and Fritz, Peter, 1997, Environmental isotopes in hydrogeology: New York, Lewis Publishers, 328 p.

Coplen, T.B., 1993, Uses of environmental isotopes, *in* Alley, W.M., ed., Regional ground-water quality: New York, Van Nostrand Reinhold, p. 227-254.

Coplen, T.B., Wildman, J.D. and Chen, J., 1991, Improvements in the gaseous hydrogen-water equilibration technique for hydrogen isotope ratio analysis: Analytical Chemistry, v. 63, p. 910-912.

Craig, Harmon, 1961, Isotopic variations in meteoric waters: Science, v. 133, p. 1702-1703.

Derra, S., 1990, CFCs—No easy solutions: Research and Development, v. 32, p. 54-66.

Dunkle, S.A., Plummer, L.N., Busenberg, Eurybiades, Phillips, P.J., Denver, J.M., Hamilton, P.A., Michel, R.L., and Coplen, T.B., 1993, Chlorofluorocarbons (CCl_3F and CCl_2F_2) as dating tool and hydrologic tracers in shallow groundwater of the Delmarva Peninsula, Atlantic Coastal Plain, United States: Water Resources Research, v. 29, no. 12, p. 3837-3860.

Epstein, S. and Mayeda, T., 1953, Variation of ^{18}O content of water from natural sources: Geochimica et Cosmochimica Acta, v. 4, p. 213-224.

Fenneman, N.M., 1938, Physiography of Eastern United States: New York, McGraw-Hill, 534 p.

Focazio, M.J., 1997, Ground-water residence times in shallow aquifers of the Chesapeake Bay watershed [abs.]: Geological Society of America Abstracts with Programs, v. 29, no. 6, p. 76.

Focazio, M.J., Plummer, L.N., Böhlke, J.K., Busenberg, Eurybiades, Bachman, L.J., and Powars, D.S., 1998, Preliminary estimates of residence times and apparent ages of ground water in the Chesapeake Bay Watershed, and water-quality data from a survey of springs: U.S. Geological Survey Water-Resources Investigations Report 97-4225, 75 p.

Freeze, R. A., and Cherry J. A., 1979, Groundwater: New Jersey, Prentice-Hall, 604 p.

Gibs, Jacob, and Imbrigiotta, T.E., 1990, Well-purging criteria for sampling purgeable organic compounds: Ground Water, v. 28, no. 1, p. 68-78.

Heaton, T.H.E., 1981, Dissolved gases: Some applications to ground-water research: Transactions of the Geological Society of South Africa, v. 84, p. 91-97.

Heaton, T.H.E., and Vogel, 1981, Excess air in groundwater: Journal of Hydrology, v. 50, p. 201-216.

Hem, J.D., 1985, Study and interpretation of chemical characteristics of natural waters (3d ed.): U.S. Geological Survey Water-Supply Paper 2254, 263 p.

Herman, J.S., and Hubbard, D.A., Jr., eds., 1990, Travertine-marl: Stream deposits in Virginia: Virginia Division of Mineral Resources Publication 101, 184 p.

Hubbard, D.A., Jr., and Herman, J.S., 1990, Overview of travertine-marl volume, *in* Herman, J.S., and Hubbard, D.A., Jr., eds., Travertine-marl: Stream deposits in Virginia: Virginia Division of Mineral Resources Publication 101, p. 1-2.

International Atomic Energy Agency (IAEA), 1981, Statistical treatment of environmental isotope data in precipitation: Vienna, IAEA, Technical Report Series No. 206.

Johnson, A.I., 1967, Specific yield—Compilation of specific yields for various materials: U.S. Geological Survey Water-Supply Paper 1662-D, 74 p.

Johnson, G.H., 1972, Geology of the Yorktown, Poquoson West, and Poquoson East quadrangles, Virginia: Virginia Division of Mineral Resources Report of Investigations 30, 57 p.

Johnson, G.H., Beach, T.A., Harris, M.S., and Herman, Julie, 1993a, Late Cenozoic environments along the James River of southeastern Virginia: College of William and Mary, Virginia Field Conference, 1993, Guidebook, 36 p.

Johnson, G.H., Beach, T.A., Harris, M.S., and Hodges, R.L., 1993b, Evolution of subsidence sinkholes, southeastern Virginia Coastal Plan, U.S.A. [abs.]: Geological Society of America Abstracts with Programs, v. 25, no.4, p. 24.

Johnson, G.H., Burmester, J.L., McKay, W.A., and Walliser, W.G., 1987, Origin and distribution of sinkholes in the Atlantic Coastal Plain of southeastern Virginia [abs.]: Geological Society of America Southeastern Section, 36th Meeting, Abstracts with Programs, v. 19, p. 91.

Lohman, S.W., 1972, Ground Water Hydraulics: U.S. Geological Survey Professional Paper 708, 70 p.

Lorah, M.M, and Herman, J.S., 1990, Geochemical evolution and calcite precipitation rates in Falling Spring Creek, Virginia, *in* Herman, J.S., and Hubbard, D.A., Jr., eds., Travertine-marl: Stream deposits in Virginia: Virginia Division of Mineral Resources Publication 101, p. 17-32.

Mazor, Emanuel, 1991, Applied chemical and isotopic groundwater hydrology: New York, Halsted Press, John Wiley and Sons, Inc., 274 p.

McFarland, E.R., 1997, Hydrogeologic framework, analysis of ground-water flow, and relations to regional flow in the Fall Zone near Richmond, Virginia: U.S. Geological Survey Water-Resources Investigations Report 97-4021, 56 p.

Michel, R.M., 1989, Tritium deposition in the Continental United States, 1953-1983: U.S. Geological Survey Water-Resources Investigations Report 89-4072, 46 p.

Molina, M., and Rowland, F.S., 1974, Stratospheric sink for chlorofluoromethanes: Chlorine atom catalyzed destruction of ozone: Nature, no. 249, p. 810-812.

National Oceanic and Atmospheric Administration (NOAA), 1996, Climatological data annual summary—Virginia 1996: National Climatic Data Center, Asheville, North Carolina, v. 106, no. 13, 19 p.

Nelms, D.L., and Ahlin, R.J., 1993, Use of chlorofluorocarbons to age date ground water in Prince William County, Virginia [abs.]: Collected abstracts of the 1993 Virginia Water Resources Conference, Richmond, Virginia, April 12-14, 1993, p. 67.

Nelms, D.L., and Brockman, A.R., 1997, Hydrogeology of, quality and recharge ages of ground water in, Prince William County, Virginia, 1990-91: U.S. Geological Survey Water-Resources Investigations Report 97-4009, 58 p.

Nelms, D.L., 1997, Use of chlorofluorocarbons to delineate ground-water-flow systems, Naval Weapons Station Yorktown, Yorktown, Virginia [abs.]: Geological Society of America Abstracts with Programs, v. 29, no. 6, p. 76.

Nuckels, E.H., and Prugh, B.J., Jr., 1991, National Water Summary 1988-89—Floods and droughts, *with a section on* General climatology, by P.J. Michaels: U.S. Geological Survey Water-Supply Paper 2375, p. 543-550.

Plummer, L.N., and Busenberg, Eurybiades, 1999, Chlorofluorocarbons, *in* Cook, P.G., and Herczeg, Andrew, eds., Environmental tracers in subsurface hydrology: Boston, Kluwer Academic Publishers, 552 p.

Plummer, L.N., Busenberg, Eurybiades, McConnell, J.B., Drenkard, S., Schlosser, Peter, and Michel, R.L., 1998, Flow of river water into a karstic limestone aquifer. 1. Tracing the young fraction in groundwater mixtures in the Upper Floridan aquifer near Valdosta, Georgia: Applied Geochemistry, v. 13, no. 8, p. 995-1015.

Plummer, L.N., and Friedman, L.C., 1999, Tracing and dating young ground water.: U.S. Geological Survey Fact Sheet-134-99, 4 p.

Plummer, L.N., Michel, R.L., Thurman, E.M., and Glynn, P.D., 1993, Environmental tracers for age dating young ground water, *in* Alley, W.M., ed., Regional ground-water quality: New York, Van Nostrand Reinhold, p. 255-294.

Reilly, T.E., Plummer, L.N., Phillips, P.J., and Busenberg, E., 1994, The use of simulation and multiple environmental tracers to quantify groundwater flow in a shallow aquifer: Water Resources Research, v. 30, No. 2, pp. 421-433.

Richardson, D.L., 1994, Ground-water discharge from the Coastal Plain of Virginia: U.S. Geological Survey Water-Resources Investigations Report 93-4191, 15 p.

Richardson, D.L., and Brockman, A.R., 1992, Hydrogeology and water quality of the shallow ground-water system in eastern York County, Virginia: U.S. Geological Survey Water-Resources Investigations Report 92-4090, 41 p.

Robertson, W.D., and Cherry, J.A., 1989, Tritium as an indicator of recharge and dispersion in a groundwater system in Central Ontario: Water Resources Research, v. 25, no. 6, p. 1097-1109.

Schlosser, Peter, Stute, M., Dorr, H., Sonntag, C., and Munnich, K.O., 1988, Tritium/^{3}He dating of shallow groundwater: Earth and Planetary Science Letters 89, p. 245-256.

Solomon, D.K., Poreda, R.J., Schiff, S.L., and Cherry, J.A., 1992, Tritium and helium 3 as groundwater age tracers in the Borden aquifer: Water Resources Research, v. 28, no. 3, p. 741-755.

Speiran, G.K., 1996, Geohydrology and geochemistry near coastal ground-water-discharge areas of the Eastern Shore of Virginia: U.S. Geological Survey Water-Supply Paper 2479, 73 p.

Szabo, Zoltan, Rice, D.E., Plummer, L.N., Busenberg, Eurybiades, Drenkard, S. and Schlosser, Peter, 1996, Age-dating of shallow groundwater with chlorofluorocarbons, tritium/helium 3, and flow path analysis, southern New Jersey coastal plain: Water Resources Research, v. 32, no. 4, p. 1023–1038.

Thatcher, L.L, 1962, The distribution of tritium fallout in precipitation over North America: Bulletin of the International Association of Scientific Hydrology, v. 7, no. 2, p. 48-58.

Thatcher, L.L., Janzer, V.J., and Edwards, K.W., 1977, Methods for determination of radioactive substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A5, 95 p.

Yellow Springs Instruments, Inc., 1996, Operations manual YSI Model 85 Handheld, 36 p.

APPENDIXES

Appendix 1. Site and well-construction information, field properties, isotope and dissolved gas data for wells sampled in March 1997 at the Naval Weapons Station Yorktown, Virginia

[Well and screen interval depths and water-level measurements are in feet below land surface. ft, feet; T_W, water temperature; °C, degrees Celsius; DO, dissolved oxygen; mg/L, milligrams per liter; SC, specific conductance at 25°C; µS/cm, microsiemens per centimeter; NTU, nephelometric turbidity units; COL AQ, Columbia aquifer; CC AQ, Cornwallis Cave aquifer; YE AQ, Yorktown-Eastover aquifer]

	Site information				Well-construction					Field properties						
Well number	Site identifier	Geohydrologic		Altitude (ft above sea level)	Well depth	Screen interval		Water level		Sample date	Sample time	T_W (°C)	DO (mg/L)	pH (standard units)	SC (µS/cm)	Turbidity (NTU)
		Unit	Setting			Top	Bottom	Static	Pumping							
58F 99 (B2)	371440076314702	YE AQ	Discharge	47.2	94.79	85.10	94	36.03	48.42	03/28/97	1524	15.8	0.1	7.2	495	0.77
58F100 (B3)	371440076314703	CC AQ	Discharge	47.4	36.56	31.59	36	28.93	31.85	03/19/97	1613	15.2	3.0	6.4	960	3.63
58F105 (E3)	371348076333503	CC AQ	Recharge	80.2	61.80	57.08	61	15.15	20.30	03/07/97	1515	15.0	.1	7.4	390	.31
58F106 (E4)	371348076333504	COL AQ	Recharge	79.8	23.79	19.04	23	5.97	10.12	03/07/97	1613	13.8	.6	4.8	43	1.50
58F110 (G3)	371403076342803	CC AQ	Discharge	65.6	41.98	37.05	41	30.03	33.24	03/11/97	1607	16.3	3.2	6.8	435	.49
58F114 (H2)	371300076341002	YE AQ	Recharge	83.1	95.55	85.55	95	15.14	43.16	03/26/97	1618	15.8	.0	7.1	408	1.88
58F115 (H3)	371300076341003	CC AQ	Recharge	83.0	56.80	51.80	56	11.27	17.59	03/05/97	1309	16.3	.0	7.6	440	.26
58F116 (H4)	371300076341004	COL AQ	Recharge	83.0	23.55	18.55	23	10.42	18.06	03/05/97	1645	16.0	2.7	5.1	54	3.78
58F119 (I2)	371359076365002	YE AQ	Recharge	86.7	114.80	105.00	114	20.13	35.57	03/27/97	1413	15.9	.0	7.2	482	3.88
58F120 (I3)	371359076365003	CC AQ	Recharge	86.3	86.80	81.85	86	3.57	17.85	03/06/97	1551	14.5	.1	7.3	498	1.38
58F121 (I4)	371359076365004	COL AQ	Recharge	86.6	21.78	17.02	21	1.27	7.66	03/06/97	1715	14.8	.3	5.2	40	2.11
58G 51 (F2)	371619076345102	YE AQ	Discharge	24.2	73.78	63.97	73	20.21	35.95	03/25/97	1657	15.3	.0	7.2	406	.48
58G 52 (F3)	371619076345103	YE AQ	Discharge	24.0	32.79	28.01	32	19.93	23.66	03/10/97	1246	15.6	7.2	6.2	249	.49
58G 57 (N3)	371544076371403	CC AQ	Discharge	58.9	56.55	51.57	56	35.85	51.30	03/11/97	1241	14.8	.2	6.9	562	1.07

Appendix 1. Site and well-construction information, field properties, isotope and dissolved gas data for wells sampled in March 1997 at the Naval Weapons Station Yorktown, Virginia—Continued

[Stable isotope data reported in per mil relative to VSMOW (Vienna Standard Mean Ocean Water). ^3H, tritium; pCi/L, picocuries per liter; TU, tritium unit; $\delta^{18}O$, oxygen isotopic ratio; δD, hydrogen isotopic ratio; *d*, deuterium excess; N_2, nitrogen; Ar, argon; O_2, oxygen; CO_2, carbon dioxide; CH_4, methane; T_R, N_2-Ar recharge temperature; °C, degrees Celsius; cm^3/L, cubic centimeters per liter; <, less than]

	Isotope data							Dissolved gas data						
Well number	**^3H (pCi/L)**	**^3H 2 sigma (pCi/L)**	**^3H (TU)**	**^3H 2 sigma (TU)**	**$\delta^{18}O$ (per mil)**	**δD (per mil)**	**d (per mil)**	**N_2 (mg/L)**	**Ar (mg/L)**	**O_2 (mg/L)**	**CO_2 (mg/L)**	**CH_4 (mg/L)**	**T_R (°C)**	**Excess air (cm^3/L)**
58F 99 (B2)	<1.0	1.0	<0.3	0.3	-6.25	-35.7	14.3	19.5	0.649	0.0	25.4	0.00	17.3	3.81
58F100 (B3)	32	1.9	10.0	.6	-6.20	-35.5	14.1	17.7	.663	3.2	199.6	.00	11.9	0.21
58F105 (E3)	11	1.0	3.4	.3	-6.01	-33.4	14.7	21.3	.707	.0	9.6	.00	13.9	4.48
58F106 (E4)	41	2.6	12.8	.8	-5.86	-31.4	15.5	20.4	.722	.6	132.3	.00	10.5	2.41
58F110 (G3)	40	2.6	12.5	.8	-5.96	-33.7	14.0	16.9	.640	3.3	21.1	.00	13.0	-.07
58F114 (H2)	1	1.0	.3	.3	-5.92	-33.7	13.7	21.5	.748	.0	12.9	.00	9.5	3.14
58F115 (H3)	35	2.6	10.9	.8	-5.95	-31.4	16.2	20.2	.707	.0	19.1	.01	11.1	2.61
58F116 (H4)	40	2.6	12.5	.8	-5.48	-29.7	14.1	18.2	.660	2.9	124.2	.00	13.0	1.06
58F119 (I2)	<1.0	1.0	<.3	.3	-5.92	-33.5	13.9	22.2	.770	.1	20.8	.02	8.4	3.40
58F120 (I3)	<1.0	1.0	<.3	.3	-5.81	-32.5	14.0	22.5	.755	.1	26.8	.01	10.7	4.55
58F121 (I4)	45	3.2	14.1	1.0	-5.86	-31.1	15.8	20.7	.709	.1	121.1	.00	12.5	3.43
58G 51 (F2)	<1.0	1.0	<.3	.3	-6.25	-36.5	13.5	18.6	.662	.0	12.4	.01	13.5	1.71
58G 52 (F3)	31	1.9	9.7	.6	-6.40	-36.1	15.1	16.9	.631	5.9	32.2	.00	14.0	.16
58G 57 (N3)	48	3.2	15.0	1.0	-6.06	-32.9	15.6	22.5	.759	.3	24.1	.00	10.3	4.37

Appendix 2. Site information, field properties, isotope and dissolved gas data for springs sampled in March 1997 at the Naval Weapons Station Yorktown, Virginia

[ft, feet; mi^2, square miles; T_W, water temperature; °C, degrees Celsius; DO, dissolved oxygen; mg/L, milligrams per liter; SC, specific conductance at 25°C; µS/cm, microsiemens per centimeter; NTU, nephelometric turbidity units; COL AQ, Columbia aquifer; CC AQ, Cornwallis Cave aquifer; CC CU, Cornwallis Cave confining unit; YE AQ, Yorktown-Eastover aquifer]

Spring number	Site information					Field properties						
	Site identifier	Geohydrologic		Altitude (ft above sea level)	Drainage area (mi^2)	Sample date	Sample time	T_W (°C)	DO (mg/L)	pH (standard units)	SC (µS/cm)	Turbidity (NTU)
		Unit	Setting									
57FS 1 (18-1)	371406076373901	CC CU	Discharge	70	0.041	03/20/97	0907	12.9	2.2	6.5	343	8.1
58FS 1 (2-1)	371413076345701	CC AQ	Discharge	25	.022	03/20/97	1544	10.8	4.8	7.7	208	4.3
58FS 2 (5-1)	371434076351401	CC CU	Discharge	35	.006	03/14/97	0936	11.1	7.5	7.0	525	6.2
58FS 3 (6-1)	371424076351301	CC AQ	Discharge	25	.015	03/13/97	1525	11.2	2.3	7.1	575	6.4
58FS 4 (12-1)	371450076325301	CC AQ	Discharge	25	.038	03/17/97	1152	11.9	4.0	7.0	580	29
58FS 5 (13-3)	371436076340001	CC AQ	Discharge	35	.040	03/17/97	1722	15.9	5.0	7.0	519	3.4
58FS 6 (15-1)	371252076351701	CC AQ	Discharge	40	.034	03/21/97	0915	14.7	2.3	6.7	459	3.4
58FS 7 (16-2)	371307076360401	CC CU	Discharge	50	.006	03/21/97	1125	14.3	3.0	6.9	347	7.9
58FS 8 (19-1)	371338076370101	COL AQ	Discharge	70	.004	03/20/97	1315	13.3	2.8	6.7	378	3.3
58FS 9 (19-3)	371338076365601	COL AQ	Discharge	70	.007	03/20/97	1113	13.3	1.5	6.9	349	12.1
58FS 10 (20-1)	371409076324401	CC AQ	Discharge	50	.021	03/12/97	1442	15.0	4.3	6.8	544	1.2
58FS 11 (20-4)	371411076323601	CC AQ	Discharge	40	.015	03/12/97	1213	17.9	9.2	6.9	605	2.7
58FS 12 (20-8)	371434076321401	CC AQ	Discharge	30	.012	03/13/97	1140	15.0	7.0	6.9	258	31.5
58FS 13 (20-9)	371409076324301	CC AQ	Discharge	50	.062	03/12/97	1550	15.8	2.7	6.8	513	3.5
58GS 1 (A-2)	371611076354101	CC AQ	Discharge	25	.037	03/18/97	0955	11.2	1.2	6.9	730	20
58GS 2 (8-1)	371522076340301	COL AQ	Discharge	20	.020	03/17/97	1525	10.2	.6	5.3	54	12

Appendix 2. Site information, field properties, isotope and dissolved gas data for springs sampled in March 1997 at the Naval Weapons Station Yorktown, Virginia—Continued

[Stable isotope data reported in per mil relative to VSMOW (Vienna Standard Mean Ocean Water). ^{3}H, tritium; pCi/L, picocuries per liter; TU, tritium unit; δ^{18}O, oxygen isotopic ratio; δD, hydrogen isotopic ratio; *d*, deuterium excess; N_2, nitrogen; Ar, argon; O_2, oxygen; CO_2, carbon dioxide; CH_4, methane; T_R, N_2-Ar recharge temperature; °C, degrees Celsius; cm^3/L, cubic centimeters per liter]

	Isotope data							Dissolved gas data						
Spring number	**^{3}H (pCi/L)**	**^{3}H 2 sigma (pCi/L)**	**^{3}H2 (TU)**	**^{3}H 2 sigma (TU)**	**δ^{18}O (per mil)**	**δD (per mil)**	**d (per mil)**	**N_2 (mg/L)**	**Ar (mg/L)**	**O_2 (mg/L)**	**CO_2 (mg/L)**	**CH_4 (mg/L)**	**T_R (°C)**	**Excess air (cm^3/L)**
57FS 1 (18-1)	34	2.6	10.6	0.8	-6.12	-33.7	15.3	20.7	0.743	1.6	61.1	0.00	8.7	2.06
58FS 1 (2-1)	35	3.2	10.9	1.0	-7.25	-41.2	16.8	18.2	.690	7.0	4.5	.00	9.8	0.01
58FS 2 (5-1)	27	1.9	8.4	.6	-6.15	-32.8	16.4	17.9	.681	6.0	40.2	.01	10.2	-.15
58FS 3 (6-1)	32	1.9	10.0	.6	-6.27	-34.1	16.1	18.4	.701	3.9	57.0	.00	8.9	-.23
58FS 4 (12-1)	41	3.8	12.8	1.2	-6.11	-33.7	15.2	18.6	.680	5.0	65.3	.00	11.4	.94
58FS 5 (13-3)	34	2.6	10.6	.8	-5.78	-32.8	13.4	18.2	.672	3.5	37.2	.00	11.6	.59
58FS 6 (15-1)	42	3.8	13.1	1.2	-5.91	-31.2	16.1	18.5	.687	1.4	66.9	.00	10.6	.61
58FS 7 (16-2)	36	2.6	11.3	.8	-6.28	-34.9	15.3	18.7	.691	3.6	37.4	.00	10.5	.80
58FS 8 (19-1)	27	2.6	8.4	.8	-6.25	-35.0	15.0	20.1	.719	2.3	50.2	.00	10.1	2.00
58FS 9 (19-3)	37	3.2	11.6	1.0	-6.27	-34.6	15.6	19.9	.724	1.7	42.6	.00	9.3	1.56
58FS 10 (20-1)	40	2.6	12.5	.8	-5.80	-33.1	13.3	17.4	.638	2.3	56.1	.00	14.1	.63
58FS 11 (20-4)	43	3.2	13.4	1.0	-5.66	-31.9	13.4	15.9	.591	6.7	54.2	.00	17.1	.10
58FS 12 (20-8)	51	5.1	15.9	1.6	-5.90	-33.1	14.1	16.2	.625	6.2	40.1	.00	13.2	-.75
58FS 13 (20-9)	37	3.2	11.6	1.0	-5.89	-33.0	14.1	21.2	.702	2.3	64.0	.00	14.4	4.60
58GS 1 (A-2)	30	3.2	9.4	1.0	-6.02	-32.5	15.7	20.5	.767	0.8	93.9	.00	5.9	.56
58GS 2 (8-1)	26	2.6	8.1	.8	-6.28	-35.6	14.6	20.8	.736	0.1	45.1	.00	9.5	2.48