

# Age of Ground Water in Basalt Aquifers near Spring Creek National Fish Hatchery, Skamania County, Washington

U.S. GEOLOGICAL SURVEY  
Water-Resources Investigations Report 95-4272

Prepared in cooperation with the  
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By STEPHEN R. HINKLE

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Portland, Oregon  
1996

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

U.S. GEOLOGICAL SURVEY  
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## CONVERSION FACTORS AND VERTICAL DATUM

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<b>Multiply</b>	<b>By</b>	<b>To obtain</b>
LENGTH		
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
VOLUME		
gallon (gal)	3.785	liter (L)
PRESSURE		
atmosphere	1.013	bar
TEMPERATURE		
Degrees Fahrenheit (°F) and degrees Celsius (°C) are related by the following equation:		
$^{\circ}\text{F} = 1.8 (^{\circ}\text{C}) + 32$		

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

# Age of Ground Water in Basalt Aquifers near Spring Creek National Fish Hatchery, Skamania County, Washington

By Stephen R. Hinkle

## Abstract

Water samples from four springs and five wells in basalt aquifers near Spring Creek National Fish Hatchery in Skamania County, Washington, were collected and analyzed for selected inorganic ions and stable isotopes. Eight samples were analyzed for carbon-14 ( $^{14}\text{C}$ ), carbon-13 ( $^{13}\text{C}$ ), and either chlorofluorocarbons (CFCs) or tritium. This work was done to estimate the age (residence time, or time elapsed since recharge) of water issuing from springs at the hatchery.

If CFCs are present in ground water, the presence of at least a component of modern (post-1944) water is indicated. CFC-dating suggests that ground water several hundred feet below land surface in the Underwood Heights area north of the hatchery, including ground water discharging from the hatchery springs, contains modern water. In contrast, CFC-dating suggests that deeper ground water such as that withdrawn from the Hatchery Well may contain little or no modern water.

Concentrations of  $^{14}\text{C}$  in water can yield  $^{14}\text{C}$ -based ground-water ages, termed  $^{14}\text{C}$ -model ages. Unadjusted  $^{14}\text{C}$ -model ages ( $^{14}\text{C}$ -model ages unadjusted for carbon mass transfers) for water discharging from the hatchery springs are on the order of several hundred years. Ground-water samples from three wells in the Underwood Heights area yielded  $^{14}\text{C}$ -model ages ranging from modern to several hundred years.

Unadjusted  $^{14}\text{C}$ -model ages for deep ground water pumped by the Hatchery Well indicate an overall age of several thousand years. However,  $^{14}\text{C}$  concentrations may be affected by transfers of carbon into and out of solution. The  $\delta^{13}\text{C}$  values of the downgradient ground waters ranged from  $-16.4$  (per mil) to  $-18.2$  per mil, isotopically heavier than expected for ground water that obtains carbon solely from root respiration in a temperate climate and undergoes no subsequent carbon-isotope fractionation or exchange. Such  $\delta^{13}\text{C}$  values in the ground water near the hatchery suggest the possibility of carbon mass transfers during the evolution of these waters. Geochemical mass-transfer modeling suggests that carbon dioxide may degas and calcite may dissolve during the evolution of the modeled ground waters, but that degassing of carbon dioxide is the dominant carbon mass transfer in these ground waters. In addition, modeling results also suggest that, although some calcite may dissolve during the evolution of the water produced by the Hatchery Well, and possibly during the evolution of the shallower ground waters, the amount of calcite dissolution is small. Model testing suggests that the quantity of  $^{14}\text{C}$ -dead carbon added from calcite dissolution may not be sufficient to greatly affect the  $^{14}\text{C}$ -model ages of these ground waters. In other words, the  $^{14}\text{C}$ -model ages that were adjusted for various modeled carbon mass transfers are similar to the unadjusted  $^{14}\text{C}$ -model ages.

A comparison of CFC data with both adjusted and unadjusted  $^{14}\text{C}$  data suggests that water discharging at the hatchery springs contains a mixture of modern and old water, where old water is defined as water recharged prior to 1944. The CFC data support a component of modern water, whereas the  $^{14}\text{C}$  data suggest a component of old water. Similar results were obtained from a comparison of CFC data with adjusted and unadjusted  $^{14}\text{C}$  data for water collected from Well 3. Well 3 is north of the hatchery springs, on a flow path that appears to be parallel to and similar in length to the flow path leading to the hatchery springs. Water from the Hatchery Well, however, may be devoid of modern water and appears to have an overall age on the order of thousands of years.

## **INTRODUCTION**

Spring Creek National Fish Hatchery is an important hatchery in Washington. Fifteen to 20 million Chinook salmon fry are released from the hatchery each year (Edward LaMotte, Spring Creek National Fish Hatchery, oral commun., 1992).

The hatchery depends on ground water from several large springs that discharge from basalt of the Columbia River Basalt Group. Future residential development upgradient (north) from the hatchery springs could affect their water quality. An estimate of the age (residence time, or time elapsed since recharge) of ground water issuing from the hatchery springs could be used to evaluate the time scale at which any adverse effects of future residential development upgradient from the hatchery springs might be expected to affect the hatchery springs. In recognition of the need to estimate the age of ground water issuing from the hatchery springs, the U.S. Fish and Wildlife Service provided funding to the U.S. Geological Survey in 1991 to collect data that would allow estimation of ground-water age in the vicinity of the hatchery.

### **Purpose and Scope**

The purpose of this report is to discuss efforts to estimate the age of ground water discharging from

springs at Spring Creek National Fish Hatchery. Three major springs at the hatchery were sampled during May 20–24, 1991. In addition to these hatchery springs, one other nearby spring and five wells in the vicinity of the hatchery were sampled to provide comparative data.

Chlorofluorocarbons (CFCs), carbon-14 ( $^{14}\text{C}$ ), and tritium were chosen as dating tools. CFC-dating can be used to date ground water back to 1944, whereas  $^{14}\text{C}$ -dating can be used to date ground water recharged hundreds to tens of thousands of years ago. High concentrations of tritium can serve as a tracer of water recharged since 1953. This combination of dating methods can analyze ground-water ages spanning several orders of magnitude.

Geochemical mass-transfer modeling was done on a representative subset of ground-water samples. Geochemical mass-transfer modeling is a process of using a mass-balance approach to identify geochemically realistic reaction paths describing the geochemical evolution of ground water. The model results were used to adjust  $^{14}\text{C}$ -determined ages for the effects of carbon mass transfers that may be occurring along ground-water flow paths.

### **Hydrogeologic Setting**

Spring Creek National Fish Hatchery is in southern Washington on the north side of the Columbia River, 1 mile west of Underwood (fig. 1). Springs supplying water to the hatchery issue from beneath a talus slope above and north of the hatchery. Combined discharge is reported to be 2,200–2,300 gal/min (gallons per minute) (Edward LaMotte, Spring Creek National Fish Hatchery, oral commun., 1992). Cliffs rise 400 to 500 feet above the springs and merge with gentle slopes of Underwood Mountain, where the Underwood Heights area, which contains scattered houses, orchards, and wooded areas, is located. This area of Skamania County, Washington, containing the Spring Creek National Fish Hatchery springs, the cliffs north of the springs, the Underwood Heights area, and the flanks of Underwood Mountain is, for the purposes of this report, termed the Spring Creek National Fish Hatchery study area (henceforth, the study area).

The geology of the study area is characterized by basalt flows of Pleistocene and Miocene age, commonly separated by interbeds of other rock types and (or) soil horizons. These basalt flows lie approximately



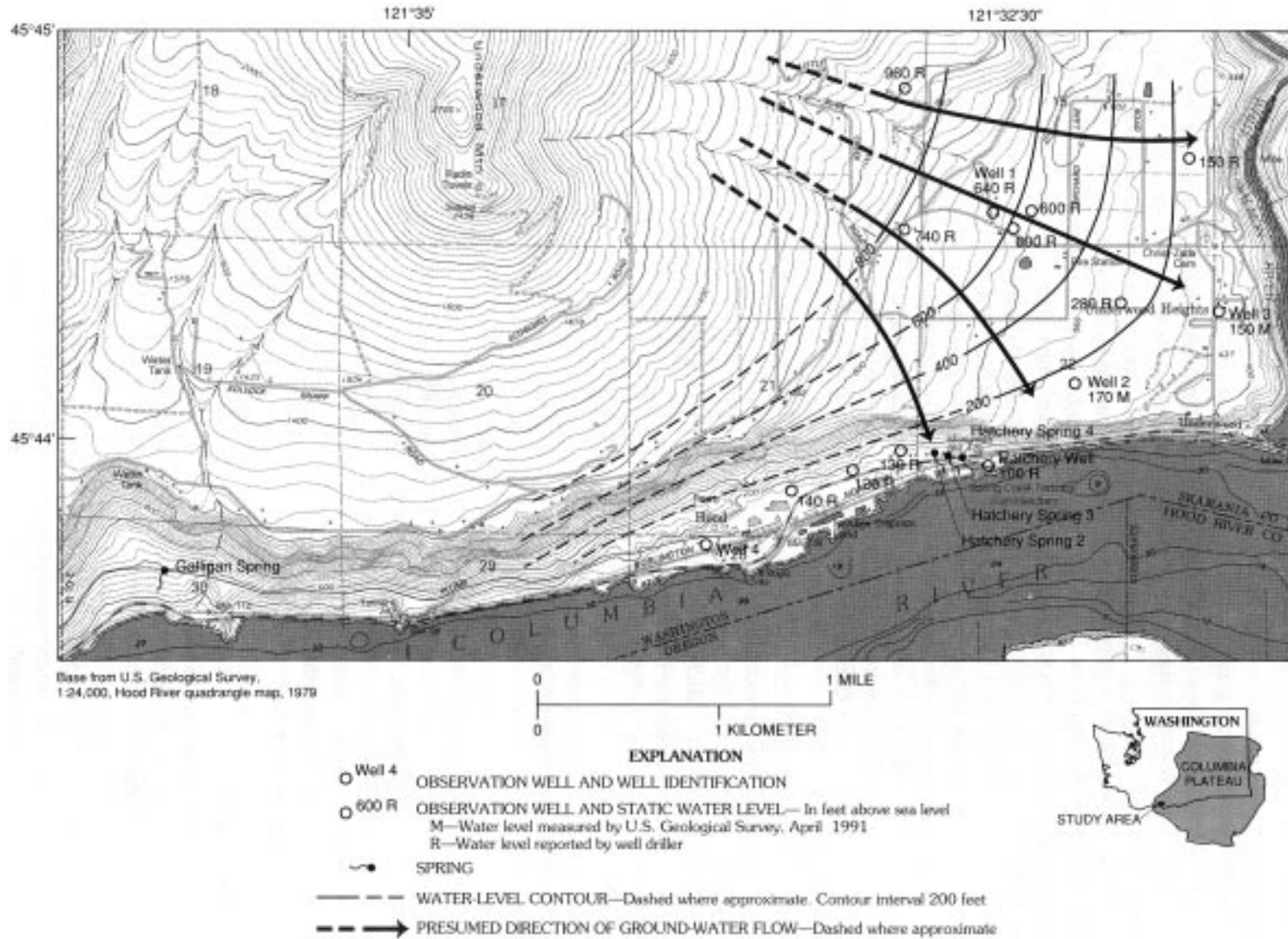


Figure 1. Location of study area, springs and wells, generalized water-level contours, and direction of ground-water flow.

in a horizontal plane, but have been subjected to considerable faulting. Flow centers are generally dense and of low permeability, whereas interflow zones typically are porous, rubbly, and of high permeability. Geologic mapping in the region, compiled by Korosec (1987), identifies three principal geologic units in the study area: Grande Ronde Basalt, Frenchman Springs Member of the Wanapum Basalt, and Basalt of Underwood Mountain.

The Grande Ronde Basalt is composed of Miocene flows of the Columbia River Basalt Group. The Grande Ronde Basalt is the thickest formation in the Columbia River Basalt Group (Korosec, 1987), and it commonly exceeds 1,000 feet in thickness (Swanson and others, 1979). The Grande Ronde Basalt does not crop out at the hatchery but is exposed along cliffs less than 1 mile west of the hatchery. It is not known if the deep well at the hatchery penetrates the Grande Ronde Basalt, nor is the thickness of the Grande Ronde Basalt in the study area known.

The Frenchman Springs Member of the Wanapum Basalt overlies the Grande Ronde Basalt. In the study area, the Frenchman Springs Member crops out in the cliffs above the hatchery, and the hatchery springs discharge from the member of the Wanapum Basalt. The Frenchman Springs Member is a series of Miocene flows of the Columbia River Basalt Group. The thickness of these flows in the study area is unknown, but in its type locality, the Frenchman Springs Member is 250 feet thick (Swanson and others, 1979).

Basalt of Underwood Mountain overlies the Frenchman Springs Member and is widely exposed on Underwood Mountain and Underwood Heights. Basalt of Underwood Mountain is a Pleistocene unit composed of numerous blocky, jointed flows, each about 10 to 30 feet thick. The total thickness of the Basalt of Underwood Mountain reaches at least 590 feet (Korosec, 1987).

The Columbia River Basalt Group consists of Miocene flood basalts. These basalts consist of plagioclase feldspar, pyroxene, and magnetite in a glassy groundmass; olivine occurs as an accessory mineral (Newcomb, 1972; Hearn and others, 1985). Pyroxene minerals present include augite and pigeonite (Long and Strobe, 1983). Important secondary phases present in basalts of the Columbia River Basalt Group are smectite, clinoptilolite (a zeolite mineral), amorphous iron oxide, and silica (Hearn and others, 1985).

The Basalt of Underwood Mountain is an olivine basalt (Korosec, 1987) and thus is probably similar to the Columbia River Basalt Group in terms of general mineralogy.

Water-level measurements from U.S. Geological Survey files were used to construct a generalized water-level contour map (fig. 1). This map indicates that flow of shallow ground water (ground water in the upper several hundred feet of aquifer material) is largely controlled by local topography; ground water flows from the flanks of Underwood Mountain downward towards the Columbia River to the south, and beneath Underwood Heights and downward towards the White Salmon River to the east. Local precipitation recharges shallow ground water in the study area. Several intermittent streams on Underwood Mountain lose their surface expressions without discharging to other streams or to lakes, suggesting that vertical movement of recharge water is important in the study area. Discharge occurs at seepage faces along cliffs above the Columbia and White Salmon Rivers, as well as into bank-edge parts of the Columbia and White Salmon Rivers.

Deeper, more regional ground-water flow exists and is likely controlled by higher topography to the north of the Underwood Mountain area. Ground water recharged from precipitation in these more distant areas probably migrates towards the Columbia River, and likely discharges through upward flow beneath the Columbia River, which is the regional sink for ground water in the Columbia Basin. Deep, flowing wells along the banks of the Columbia River, such as the Hatchery Well and Well 4 (fig. 1), may tap this regional ground water.

The presence of flowing wells in the study area indicates that at least some study-area ground water exists under confined conditions. The conditions under which ground water in the study area becomes confined are not known.

## **Acknowledgments**

Spring Creek National Fish Hatchery personnel provided site access, logistical assistance, and relevant site information. The cooperation of the U.S. Fish and Wildlife Service and the assistance of Spring Creek National Fish Hatchery personnel are gratefully acknowledged.

## GROUND-WATER DATING

The age of a parcel of ground water is defined as the amount of time that has elapsed since the water became isolated from the Earth's atmosphere (Freeze and Cherry, 1979, p. 135). This age usually approximates the time elapsed since recharge (Busenberg and Plummer, 1992).

Knowledge of the age of ground water can aid in delineation of ground-water flow paths and can be used in assessing susceptibility of ground water to anthropogenic contamination. For example, old ground water is likely to be farther along a flow path than is young ground water along the same flow path, and ground water recharged hundreds of years ago is less likely to contain anthropogenic contamination than is ground water recharged within the last several years.

Three dating tools— $^{14}\text{C}$ , tritium, and CFCs—were used to estimate the age of ground water; the three different methods allowed coverage of a range of ground-water ages and sampling conditions. Of particular interest was determination of the presence or absence of modern water in various study-area ground waters. The definition of modern water is a function of the dating tool used. Although different dating tools rely on different dates in defining the boundary between modern and old water, the range of these dates is small. Modern water is essentially water containing at least some water recharged since 1944.

Carbon-14 dating is a common method of dating ground water and is appropriate for ground-water ages in the range of hundreds to tens of thousands of years. The principles and methodology of  $^{14}\text{C}$ -dating are well documented in the literature (for example, Faure, 1986). The concept of  $^{14}\text{C}$ -dating of ground water is to measure the concentration of  $^{14}\text{C}$  in dissolved inorganic carbon (DIC) in a water sample, and to relate that concentration to a ground-water age. Carbon-14-determined ages are usually expressed in terms of years before present (B.P.), where the present is defined as the year 1950 (Faure, 1986, p. 392). Water with an adjusted (adjusted for carbon mass transfer along a flow path)  $^{14}\text{C}$  concentration of 100 percent modern carbon or greater is considered to be modern (post-1950).

Carbon-14-determined ground-water ages may be influenced by carbon mass transfers along a flow path and by ground-water mixing. Carbon mass

transfers along a flow path can result in a change in DIC and  $^{14}\text{C}$  concentrations in the water. If this occurs, the  $^{14}\text{C}$  concentration in the sample will no longer represent the time elapsed since recharge. Numerous geochemical models have been developed in an attempt to facilitate the process of accounting for carbon mass transfers along flow paths and the resultant effects on  $^{14}\text{C}$  concentrations in ground water (for example, Pearson and White, 1967; Tamers, 1967; Mook, 1976; Fontes and Garnier, 1979; Cheng and Long, 1984; Plummer and others, 1991). The assumptions inherent in the application of such geochemical models introduce uncertainty in the resultant  $^{14}\text{C}$ -determined ages. Mixing of different ground waters along flow paths or in well bores prior to sample collection also may affect  $^{14}\text{C}$ -determined ages. Because  $^{14}\text{C}$  undergoes radioactive (exponential) decay, a  $^{14}\text{C}$ -determined age of a mixed ground-water sample does not represent a mean age of a ground-water sample, and in the absence of supplemental data from other dating tools, identification of components of different age may not be possible. These limitations result in  $^{14}\text{C}$ -determined ages that only approximate the true ages of the water. Thus, a  $^{14}\text{C}$ -determined age should be considered a model age. The term "model age" implies that there are uncertainties associated with the age determination.

Tritium has long been used as a tracer of modern water. High tritium concentrations in natural waters represent anthropogenic contributions from above-ground testing of hydrogen bombs. Bomb tritium first entered the global water cycle in detectable concentrations in 1953. The term "modern water" is applied to water containing bomb tritium, and thus implies that at least part of the water is no older than 1953 (Drever, 1988, p. 379).

CFCs recently have gained widespread attention as dating tools (Thompson and others, 1974; Randall and Schultz, 1976; Schultz and others, 1976; Thompson and Hayes, 1979; Busenberg and Plummer, 1992; Dunkle and others, 1993; Plummer and others, 1993; Ekwurzel and others, 1994; Reilly and others, 1994). Two CFCs that have been used to date ground water are trichlorofluoromethane ( $\text{CCl}_3\text{F}$ ) and dichlorodifluoromethane ( $\text{CCl}_2\text{F}_2$ ), stable synthetic compounds that have been produced since the 1930s ( $\text{CCl}_2\text{F}_2$ ) and 1940s ( $\text{CCl}_3\text{F}$ ). The lag time between production of these compounds and their release to the

atmosphere is short; once in the atmosphere, CFCs undergo equilibrium partitioning with water in contact with the atmosphere. This partitioning is a function of temperature. The CFC solubility relations of Warner and Weiss (1985) describe this partitioning. Atmospheric CFC concentrations have increased steadily over time. Atmospheric CFC concentrations, as a function of time, have been reconstructed (Busenberg and Plummer, 1992), so by measuring the  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  concentrations of a ground-water sample, and determining or estimating the recharge temperature of the ground water, a CFC-determined age can be assigned to the sample. The current detection limit of 1pg/kg (picogram per kilogram) for CFCs allows water to be dated back to approximately 1948 with  $\text{CCl}_3\text{F}$  and to approximately 1944 with  $\text{CCl}_2\text{F}_2$ . Water containing detectable concentrations of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  has, therefore, at least a component of modern water, where modern water would be water recharged no earlier than 1948 or 1944 for  $\text{CCl}_3\text{F}$  or  $\text{CCl}_2\text{F}_2$ , respectively.

The accuracy of CFC-determined ground-water ages can be limited by processes that contribute CFCs to water, other than CFC exchange between recharge water and the atmosphere, by processes that alter CFC concentrations along flow paths, and by ground-water mixing. Local point sources of CFC contamination may increase CFC concentrations in ground water, although such environmental contamination usually is indicated by large differences between  $\text{CCl}_3\text{F}$ - and  $\text{CCl}_2\text{F}_2$ -model ages. CFC contamination may also occur during sampling or analysis; however, in a comparison between CFC and tritium concentrations at six sites in the Portland Basin using field and laboratory methods identical to those used in this study, non-detections and detections of CFCs matched pre- and post-1953 tritium concentrations (Hinkle and Snyder, in press), suggesting that the CFC-dating method can be implemented with little or no contamination. If CFC contamination occurs, CFC-determined ages will be smaller (younger) than actual ages. CFCs are relatively nonreactive in oxic hydrogeologic systems with low concentrations of organic matter, but may undergo biodegradation in anoxic environments or partition into organic matter (Plummer and others, 1993, p. 277). Biodegradation or sorption will cause CFC-determined ages to be greater (older) than actual ages. If the unsaturated zone immediately above the ground water contains old air (air with low CFC concentra-

tions), partial CFC loss may occur from recharge water or ground water to the unsaturated zone. This would result in CFC-determined ages greater (older) than actual ages. Finally, mixing of different ground waters along flow paths or in well bores prior to sample collection may also affect CFC-determined ages. Atmospheric concentrations of CFCs, and therefore concentrations of CFCs in recharge water, increase nonlinearly with increasing time; as a consequence, a CFC-determined age of a mixed ground-water sample does not represent the mean age of the ground-water sample. These limitations result in CFC-determined ages that may or may not accurately estimate the true ages of the waters. Thus, as with  $^{14}\text{C}$ -determined ages, a CFC-determined age should be considered a model age. The term "model age" implies a degree of uncertainty associated with the age determination.

## SAMPLING SITES

Nine ground-water sites (wells and springs) in the study area (table 1) were sampled for selected inorganic ions and stable isotopes of water between May 20 and May 24, 1991. Eight of the nine sites also were sampled for  $^{13}\text{C}$  and  $^{14}\text{C}$  content in DIC. Six of the sites that were sampled for  $^{14}\text{C}$  were sampled for CFCs, but access problems at the other two sites made collection of CFC samples impossible, so tritium samples were collected at these two sites. CFC samples, when collected, were collected in triplicate. Samples for analysis of  $^{13}\text{C}$  and  $^{14}\text{C}$  were collected in duplicate at one site.

Sampling sites were selected to yield information on the hatchery springs and on other ground water in the study area. Three of the five major springs at the hatchery were chosen to represent ground water discharging at the hatchery (Springs 2, 3, and 4). They were sampled as close to their sources as possible; the sampling points were 140 feet above sea level.

Three of the sampled wells (1, 2, and 3) are domestic wells in the Underwood Heights area. Well 1, at 95 feet deep, is the shallowest. It was sampled to gain insight into the geochemical character of recently recharged, upgradient ground water in the Underwood Heights area. Wells 2 and 3 draw water from a hydrogeologic interval with elevation about equal to or slightly lower than the surface expression of the hatchery springs (table 1).

**Table 1.** Sites sampled May 20–24, 1991

[Latitude given as a six-digit number representing degrees, minutes, and seconds; longitude given as a seven-digit number representing degrees, minutes, and seconds. NA, not applicable. Zones of contribution and open intervals for wells determined from well logs]

Site	Latitude	Longitude	Well depth (feet)	Estimated elevation of the spring discharge point (*), or bottom of the zone of contribution or open interval of a well (**) (in feet above sea level)	Estimated elevation of the spring discharge point (*), or top of the zone of contribution or open interval of a well (**) (in feet above sea level)
Hatchery Spring 2	454347	1213249	NA	140*	140*
Hatchery Spring 3	454347	1213246	NA	140*	140*
Hatchery Spring 4	454347	1213245	NA	140*	140*
Well 1	454427	1213232	95	565**	656**
Well 2	454357	1213228	408	105**	107**
Well 3	454408	1213135	400	40**	140**
Well 4	454327	1213346	373	–231**	–219**
Hatchery Well	454342	1213233	656	–556**	–335**
Galligan Spring	454324	1213604	NA	360*	360*

Both of these wells lie on flow paths that are approximately parallel and similar in length to the flow path ending at the hatchery springs (fig. 1). Assuming similar ground-water velocities, the model ages of the water samples drawn from these two wells should be of similar magnitude to the model ages of the water samples collected at the hatchery springs. The model ages of ground water associated with Wells 2 and 3 could represent corroborative evidence for the reasonableness of the model ages of the ground water discharging from the hatchery springs. This constraining information is important for evaluation of the CFC data, as the potential exists for atmospheric-CFC enrichment of the water in the hatchery springs.

Two industrial wells near the Columbia River also were sampled. These are deep, flowing wells near the hatchery springs, tapping hydrogeologic units and intervals considerably deeper than those transmitting water to the hatchery springs. One of these wells belongs to the hatchery and is referred to in this report as the “Hatchery Well”; the other is identified as “Well 4.” Water samples collected from these wells represent deeper, more regional water.

One additional site, Galligan Spring, was sampled. It is several miles west of the hatchery springs, at approximately 360 feet above sea level. Although not hydraulically connected with the other sites, it was sampled to provide additional information on the geochemistry of local, downgradient ground water in the study area.

## METHODS

A variety of samples were collected in this study to address different time scales of ground-water age and to facilitate comprehensive geochemical interpretation of processes occurring in the study area. Several sample-collection and laboratory analytical methods were used to obtain these data.

### Sample-Collection Methods

Water samples from wells were collected before passage through pressure tanks, chlorinators, filters, and water softeners. Water samples from springs were collected as close to the points of discharge as possible. Procedures for collection and processing of samples for inorganic ions are defined by Wood (1976) and Claassen (1982), with the exception that samples were filtered with 0.10- $\mu\text{m}$  (micron) instead of 0.45- $\mu\text{m}$  filters; the filters were cellulose-nitrate membrane. Triplicate samples for CFC analysis were collected in the field under a nitrogen atmosphere, where they were welded shut in borosilicate glass ampules for later analysis. Details of the collection technique are given by Busenberg and Plummer (1992). Samples for isotopes of hydrogen and oxygen, and some samples for  $^{13}\text{C}$  and  $^{14}\text{C}$ , were collected as aqueous samples; some samples for  $^{13}\text{C}$  and  $^{14}\text{C}$  were collected as  $\text{BaCO}_3$  precipitate. Procedures for collection of samples for isotopes are described as follows.

Samples for oxygen-18 ( $^{18}\text{O}$ ), deuterium, tritium, and aqueous samples for  $^{13}\text{C}$  and  $^{14}\text{C}$  were collected as follows: Tygon or Teflon tubing was connected to a hose bibb affixed at the wellhead or as close to the wellhead as possible. A peristaltic pump was used to collect samples from springs. The tubing was placed at the bottom of a glass bottle [one 125-mL (milliliter) bottle for  $^{18}\text{O}$  and deuterium, one 1-L (liter) bottle for tritium, two 1-L bottles for  $^{13}\text{C}$  and  $^{14}\text{C}$ ], the bottle was filled, and several volumes were allowed to overflow. Sufficient sample volume was removed to leave a small air bubble (about 0.5 mL) in the capped bottle. This air bubble allowed the sample to expand upon exposure to changes in temperature and pressure without breaking the bottle or cap. Bottles were capped with conical-seal caps and sealed with electrical tape. Sampling lines were then rinsed with deionized water.

Precipitation of  $\text{BaCO}_3$  for analysis of  $^{13}\text{C}$  and  $^{14}\text{C}$  was accomplished as follows: The alkalinity of the aqueous sample was determined in the field (Wood, 1976), and the sample volume required to recover 3 to 4 g (grams) of elemental carbon was calculated. One gram of elemental carbon is the minimum mass required for analysis by liquid scintillation counting, but 3 to 4 g provides more accurate analytical results. The required number of 50-L low-density polyethylene carboys with polypropylene caps were thoroughly rinsed with sample water. The drain tubes in the caps were similarly rinsed. Carboys were flushed with nitrogen. A carboy was filled with sample, taking care to introduce as few bubbles as possible. The time required to fill one volume was recorded, and the carboy was allowed to overflow for one to two additional volumes, based on the time required for filling the first volume. A small space in the neck of the carboy was left to add reagents. High-purity NaOH pellets were added to achieve a pH of 11 or greater, and 20 g of  $\text{BaCl}_2$  was added to each carboy for each 100 milligrams per liter of  $\text{HCO}_3^-$ . Carboys were capped and hoses clamped. Enough carboys were filled to obtain 3 to 4 g of elemental carbon. Carboys were inverted, and the supernatant was allowed to settle overnight. After settling, carboys were tilted and gently rocked in all directions to allow precipitate to settle into cap. One-liter glass bottles were flushed with nitrogen, and the precipitated slurry was drained into the bottle. If necessary to induce flow into the bottle, a positive

head of nitrogen was provided in the carboy through a second cap vent. After filling the first bottle, the carboys were rocked a second time to allow remaining precipitate to collect in the cap. After 15 to 20 minutes of settling, a second 1-L bottle was filled with the aid of nitrogen pressure. The precipitate in the 1-L bottles was allowed to settle for at least 2 hours, the supernatant was gently decanted, and nitrogen was used to flush air from the headspace. For each pair of bottles, one bottle was vigorously swirled and its entire contents quickly transferred into the second bottle. Remaining headspace was flushed with nitrogen, and conical-seal caps were secured with electrical tape. Carboys, caps, and tubing were then rinsed with deionized water.

### Laboratory Analytical Methods

Inorganic ions were analyzed at the U.S. Geological Survey National Water Quality Laboratory in Arvada, Colorado. Calcium, magnesium, sodium, iron, manganese, and strontium were analyzed by inductively coupled plasma atomic emission spectrometry. Potassium was analyzed by atomic absorption spectrometry. Chloride and sulfate were analyzed by ion-exchange chromatography. Silica was analyzed by molybdate blue colorimetry. Aluminum was analyzed by d-c plasma atomic emission spectrometry.

Deuterium and  $^{18}\text{O}$  were analyzed by mass spectrometry at the U.S. Geological Survey Stable Isotope laboratory in Reston, Virginia. The amounts of deuterium and  $^{18}\text{O}$  present in a sample are expressed as a deviation from the reference standard Standard Mean Ocean Water (SMOW) using standard delta ( $\delta$ ) notation:

$$\delta = [(R_{\text{sample}} / R_{\text{standard}}) - 1] \times 1,000 \quad (1)$$

where

$\delta$  is reported in units of per mil (‰, or parts per thousand) for D or  $^{18}\text{O}$ , and

R is D/H or  $^{18}\text{O}/^{16}\text{O}$ .

Tritium was analyzed at the University of Miami Tritium Laboratory by electrolytic enrichment with gas counting. Tritium concentrations are reported in tritium units.

Samples for CFC analysis were collected and analyzed in triplicate. Analyses were performed by purge-and-trap gas chromatography with an electron capture detector (Busenberg and Plummer, 1992) and are reported in units of picograms per kilogram. Analytical uncertainty for this method is approximately  $\pm 3$  percent at concentrations exceeding 50 pg/kg. As concentrations approach the method detection limit of 1 pg/kg, analytical uncertainty approaches  $\pm 50$  percent (Ekwurzel and others, 1994). This level of analytical uncertainty corresponds to approximately 1 year in a CFC-model age.

Carbon-13 analyses were done by the University of Arizona Laboratory of Isotope Geochemistry by mass spectrometry on  $\text{CO}_2$  evolved from submitted  $\text{BaCO}_3$  precipitate and aqueous samples. Results are reported in units of per mil relative to the Pee Dee belemnite (PDB) standard, using standard delta ( $\delta$ ) notation:

$$\delta = [(R_{\text{sample}} / R_{\text{standard}}) - 1] \times 1,000 \quad (2)$$

where

$\delta$  is reported in units of per mil (‰, or parts per thousand) for  $\delta^{13}\text{C}$ , and

R is  $^{13}\text{C}/^{12}\text{C}$ .

Analytical uncertainty is approximately 0.11‰.

One  $^{14}\text{C}$  sample was analyzed by liquid scintillation counting by the University of Arizona Laboratory of Isotope Geochemistry. The sample was run on benzene reduced from  $\text{CO}_2$  evolved from the submitted  $\text{BaCO}_3$  sample. The remaining  $^{14}\text{C}$  samples were analyzed by tandem accelerator mass spectrometry by the University of Arizona National Science Foundation-Arizona Accelerator Mass Spectrometry Facility. Samples were run on graphite reduced from  $\text{CO}_2$  evolved from submitted  $\text{BaCO}_3$  precipitate and aqueous samples. Carbon-14 values from both laboratories are reported as percent modern carbon. Both University of Arizona laboratories use two primary carbon standards: National Institute of Standards and Technology oxalic acid I and oxalic acid II. Analytical uncertainty for  $^{14}\text{C}$  analyses in this paper ranged from 0.4 to 0.6 percent modern carbon.

## AGE OF GROUND WATER

### Chlorofluorocarbons and Tritium

Calculation of a CFC-model age requires determination or estimation of the recharge temperature for the water being dated. Direct measurements of recharge temperatures in the study area were not made, but an estimate of recharge temperature was obtained by extrapolating results from calculations of recharge temperatures in Clark County, Washington. Nitrogen- and argon-gas analyses from eight ground-water samples in alluvial and basalt aquifers in Clark County indicate a mean recharge temperature of  $7^\circ\text{C}$  for ground water in the uppermost several hundred feet of aquifer material (Hinkle and Snyder, in press). Clark County is west of the study area, and lies primarily in the Puget-Willamette lowland. Recharge in Clark County has a seasonal pattern similar to that of the study area, occurring mainly during late fall, winter, and early spring. Air temperatures in Clark County are generally warmer than in the study area because of the maritime influence of the Pacific Ocean and the relatively lower elevation of Clark County. Annual mean air-temperature data (National Oceanic and Atmospheric Administration, 1987, 1988, 1989, 1990, 1991) were used to shift the calculated recharge temperature in Clark County to an estimated recharge temperature in the study area. Data from the Battle Ground, Washington, station were compared with data from the Carson Fish Hatchery, Washington, station. The Battle Ground station is located near the center of Clark County, 48 miles west of the study area. The Carson Fish Hatchery station is located in Skamania County, 13 miles west of the study area. Long-term mean annual air-temperature data were unavailable for the Carson Fish Hatchery station, so the most recent 5-year period of record was used for this comparison. The mean annual air temperature at the Carson Fish Hatchery station for this period of record was  $2^\circ\text{C}$  lower than the mean annual air temperature at the Battle Ground station for the same period of record. Thus, a recharge temperature of  $5^\circ\text{C}$  ( $2^\circ\text{C}$  less than the  $7^\circ\text{C}$  recharge temperature determined for Clark County) was used in calculating CFC-model ages in the study area. This estimate of recharge temperature is realistic, because a recharge temperature between the  $7^\circ\text{C}$  recharge temperature determined for

Clark County (Hinkle and Snyder, in press) and the 0°C temperature at which water freezes would be expected for the study area. Given these constraints on recharge temperatures, any errors in the estimate of recharge temperature would not significantly affect the results. For example, a 2°C increase in recharge temperature would result in a decrease in the calculated CFC-model ages ranging from 0 to 1 year for the study-area waters.

CFC data are presented in table 2. CFC-model ages are represented in table 2 as CFC-model recharge dates, where the CFC-model recharge date is equal to the difference between the year of sample collection (1991) and the CFC-model age of the water. The data indicate CFC-model ages corresponding to recharge in the early- to mid-1970s for the water in the hatchery springs. Data for Well 2 and Well 3 give CFC-model ages corresponding to recharge in the 1960s. Water in the Hatchery Well represents recharge prior to 1944. Note that although the CCl<sub>3</sub>F concentrations for Well 3 indicate CFC-model ages corresponding to recharge in the 1960s, the high CCl<sub>2</sub>F<sub>2</sub> concentrations for Well 3 are greater than those expected for water in equilibrium with 1991 air. These concentrations may reflect small environmental contributions of CCl<sub>2</sub>F<sub>2</sub> from landfill

leachate, sewage effluent, or other non-atmospheric sources of CCl<sub>2</sub>F<sub>2</sub>. The water cannot be dated with CCl<sub>2</sub>F<sub>2</sub>, but the presence of CCl<sub>2</sub>F<sub>2</sub> indicates at least a component of water recharged since 1944.

The 1970s CFC-model recharge dates for the hatchery springs and the 1960s CFC-model recharge dates for water from Wells 2 and 3 are only estimates of actual recharge dates. The springs and wells could be yielding mixtures of older and younger ground water. For example, assuming equilibrium conditions, a recharge temperature of 5°C, and using the atmospheric growth curves of Busenberg and Plummer (1992), a ground-water sample containing 5 percent 1990-recharged water and 95 percent pre-1944-recharged water would yield a CCl<sub>3</sub>F-model recharge date of 1961, and a CCl<sub>2</sub>F<sub>2</sub>-model recharge date of 1958. CCl<sub>3</sub>F- and CCl<sub>2</sub>F<sub>2</sub>-model recharge dates of a mixed-water sample are not always equal because the atmospheric ratio of CCl<sub>2</sub>F<sub>2</sub> to CCl<sub>3</sub>F decreased between 1944 and the present (Busenberg and Plummer, 1992). The CCl<sub>2</sub>F<sub>2</sub>-model recharge dates were consistently older than the CCl<sub>3</sub>F-model recharge dates in sampled study-area waters; this can be explained in terms of mixing of younger and older waters, and suggests that these ground waters could be mixtures of

**Table 2.** Chlorofluorocarbon data for ground-water samples collected May 20–22, 1991  
 [Triplicate analyses were run for samples from each site. pg/kg, picograms per kilogram; \*, samples that contained CCl<sub>2</sub>F<sub>2</sub> concentrations greater than would be found in water at equilibrium with average global 1991 air; <, less than]

Site	CCl <sub>3</sub> F concentration (pg/kg)	CCl <sub>2</sub> F <sub>2</sub> concentration (pg/kg)	CCl <sub>3</sub> F-model recharge date	CCl <sub>2</sub> F <sub>2</sub> -model recharge date
Hatchery Spring 2	463	141	1975	1972
Hatchery Spring 2	460	135	1975	1972
Hatchery Spring 2	469	131	1975	1972
Hatchery Spring 3	401	116	1973	1971
Hatchery Spring 3	417	119	1974	1971
Hatchery Spring 3	415	115	1974	1971
Hatchery Spring 4	485	134	1975	1972
Hatchery Spring 4	493	144	1975	1973
Hatchery Spring 4	524	153	1976	1973
Well 2	200	54	1969	1965
Well 2	206	52	1969	1964
Well 2	195	54	1968	1965
Well 3	78	2,078	1963	*
Well 3	77	2,062	1963	*
Well 3	76	2,068	1963	*
Hatchery Well	19	3	1956	1947
Hatchery Well	16	3	1955	1947
Hatchery Well	13	<1	1954	<1944



ground waters older and younger than the CFC-model recharge dates. Such mixing is common in wells and springs, where multiple flow paths commonly converge. In the absence of atmospheric-CFC enrichment, sampling contamination, or analytical error, the presence of CFCs in the water from the hatchery springs and Wells 2 and 3, does, however, indicate the presence of at least a component of modern water.

The possibility of atmospheric-CFC enrichment of hatchery springwater deserves consideration. Water from the hatchery spring is exposed to the atmosphere and starts exchanging gases with the atmosphere when it discharges from the aquifer into the talus slope above the hatchery. Exposure to the atmosphere constitutes a potential source of CFC enrichment. Although it is not possible to determine the extent of this enrichment, surface-water CFC sampling by Busenberg and Plummer (1992) illustrates the magnitude of the problem by demonstrating slow CFC exchange between surface water and the atmosphere.

Busenberg and Plummer (1992) found 18 surface-water sites in Oklahoma (of 53 sites sampled) with significantly lower than equilibrium concentrations of CFCs. Many of the CFC-model ages were more than 20 years. The anomalous concentrations were attributed to discharge of old ground water to surface-water bodies. Surface waters did not exchange CFCs with the atmosphere quickly enough to maintain modern levels of CFCs. This slow exchange suggests that CFC equilibration is not a rapid process. In a similar example, CFC-model ages of 6 years were determined for surface-water samples from Chesterville Branch, Maryland (Dunkle and others, 1993). The low CFC concentrations were attributed to discharge of ground water (with CFC-model ages of up to nearly 20 years) to surface water, accompanied by slow equilibrium of CFCs between surface water and atmosphere (Dunkle and others, 1993).

Thus, although the possibility of atmospheric contamination of samples from the hatchery springs suggests that the CFC-model ages for water from the springs should be treated as minimum ages, the possibility of slow CFC exchange and the fact that springwaters were sampled close to their discharge points may have minimized atmospheric-CFC enrichment of the water. Furthermore, the partial pressures of CO<sub>2</sub> [calculated from field measurements of alkalinity with WATEQF (Plummer and others, 1976) in the water

samples drawn from the hatchery springs ranged from 10<sup>-2.67</sup> to 10<sup>-2.73</sup> atmospheres. These levels of CO<sub>2</sub>, which are substantially above those expected for water in equilibrium with an atmospheric partial pressure of CO<sub>2</sub> of 10<sup>-3.48</sup> atmospheres (Stumm and Morgan, 1981, p. 172), suggest minimal contact time with the atmosphere.

Although CFC-dating of water from the hatchery springs suggests that the springwater contains at least a component of modern water upon discharge from the aquifer, additional data to support or refute this conclusion would be desirable. As discussed previously, it was for this reason that Wells 2 and 3 were sampled. These two wells are believed to have ground-water contributions from a part of the aquifer similar to, but as much as 100 feet lower in elevation than, the surface expression of the springs (table 1). The 1960s CFC-model recharge dates for water from Wells 2 and 3 are similar to, but slightly older than, the CFC-model recharge dates for the hatchery springs, suggesting that the hatchery springs indeed contain modern water.

The Hatchery Well contains predominantly pre-1944 ground water. Only one sample contained no detectable CCl<sub>3</sub>F, and all samples contained CCl<sub>2</sub>F<sub>2</sub>; however, all CFC concentrations were low. The one nondetect suggests that the bulk of the water being tapped by this well is older than 1944. The detections of CFCs in the Hatchery Well samples could represent sample contamination or analytical error, or could represent the existence of small amounts of modern water in the Hatchery Well. The extreme depletion of divalent cations in this water (see the section "Inorganic Constituents and Stable Isotopes of Water") not only suggests the presence of old water, but also suggests negligible modern contributions to the water—because it is unlikely that modern water would be depleted in divalent cations to such an extent.

Two sites with restricted access, Wells 1 and 4, could not be sampled for CFCs and were therefore sampled for tritium. The tritium concentration in water from Well 1 was 15 tritium units, and in water from Well 4, 1.1 tritium units. The tritium concentration of Well 1 is clearly a modern tritium concentration. The tritium concentration of Well 4 is borderline modern. Prebomb tritium (from cosmic-ray production) in precipitation is estimated to have been approximately 10 tritium units (Bowen, 1988, p. 265; Drever, 1988, p. 379). Given a half-life of 12.43 years (International

Atomic Energy Agency, 1981, p. xiii), these ground-water samples (collected in 1991) should have tritium levels of approximately 1.1 tritium units if they were recharged entirely in 1952. A more recent recharge date would yield greater tritium concentration, whereas an older recharge date, due to radioactive decay, would yield less than 1.1 tritium units. Because of the uncertainty of the estimate of prebomb tritium concentrations in precipitation, the tritium concentration of Well 4 could represent prebomb or bomb tritium, but for the purposes of this study, the tritium concentration was considered to be modern. It is more likely, however, that the water in Well 4 is a mixture of old and modern water.

### Carbon-14

Concentrations of  $^{14}\text{C}$  in samples from seven of the eight sites sampled for  $^{14}\text{C}$  ranged from 93.2 to 114 percent modern carbon (table 3). The occurrence of  $^{14}\text{C}$  concentrations greater than 100 percent modern carbon indicates the presence of nuclear bomb  $^{14}\text{C}$  (Mook, 1980, p. 52). Waters from some of these seven sites, such as water from the hatchery springs, have unadjusted  $^{14}\text{C}$ -model ages of several hundred years (table 3). Such waters could actually be on the order of several hundred years old. Alternatively, such waters could be mixtures of waters both younger and older than indicated by these unadjusted  $^{14}\text{C}$ -model ages.

The eighth site—the Hatchery Well—did not yield a high  $^{14}\text{C}$  concentration (table 3). Its  $^{14}\text{C}$  concentration, 57.7 percent modern carbon, represents an unadjusted  $^{14}\text{C}$ -model age of about 4,500 years B.P. This  $^{14}\text{C}$ -model age is old relative to other ground waters sampled in the study area but is relatively young compared to some other  $^{14}\text{C}$ -model age ages determined for ground waters in the Columbia River Basalt Group. For instance, Newcomb (1972, p. 40) reports  $^{14}\text{C}$ -model ages of up to 32,000 years B.P. for ground water in the Columbia River Basalt Group.

### Inorganic Constituents and Stable Isotopes of Water

Field parameters (table 4), inorganic constituents (table 5 and fig. 2), and stable isotopes of water (table 6 and fig. 3) are useful data for identifying ground waters of different sources, and for understanding the evolution of natural waters, including the evolution of carbon chemistry of ground water. The isotopic data presented in table 6 are nearly identical, suggesting similarity of recharge conditions for all of the waters. The inorganic data, however, suggest differences in geochemical evolution among some of the waters. As shown in figure 2, eight of the nine water samples analyzed as part of this study are mixed-cation/bicarbonate waters, whereas water from the Hatchery Well is a monovalent-cation/bicarbonate type.

**Table 3.** Carbon-isotope data for ground-water samples collected May 20–23, 1991

[Unadjusted  $^{14}\text{C}$ -model ages were calculated using a half-life of 5,730 years. The two samples for Hatchery Spring 2 represent serial replicates run on different sample types. The analytical method and sample type used for  $^{14}\text{C}$  analysis are indicated as follows: \* = method, tandem accelerator mass spectrometry; sample, water. \*\* = method, tandem accelerator mass spectrometry; sample,  $\text{BaCO}_3$ . \*\*\* = method, liquid scintillation; sample,  $\text{BaCO}_3$ ]

Site	$\delta^{13}\text{C}$ (‰)	$^{14}\text{C}$ (percent modern carbon)	Unadjusted $^{14}\text{C}$ -model age (years before present)
Hatchery Spring 2	-17.6	96.2 **	325
Hatchery Spring 2	-16.4	93.2 *	585
Hatchery Spring 3	-17.4	97.9 **	177
Hatchery Spring 4	-18.2	98.0 **	163
Well 1	-22.5	114 ***	Modern
Well 2	-17.1	100 **	Modern
Well 3	-18.2	94.4 **	473
Well 4	-16.5	93.9 *	522
Hatchery Well	-16.8	57.7 *	4,540

**Table 4.** Field parameters for waters sampled May 20–24, 1991

[Alkalinity was measured on samples filtered through a 0.10-micron nominal-pore-size filter. °C, degree Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; --, parameter not measured]

Site	Sample collection date	Temperature (°C)	Specific conductance (µS/cm)	pH	Dissolved oxygen (mg/L)	Alkalinity (mg/L as CaCO <sub>3</sub> )
Hatchery Spring 2	May 20, 1991	8.0	147	7.6	11.8	74
Hatchery Spring 3	May 20, 1991	8.5	146	7.6	9.4	74
Hatchery Spring 4	May 20, 1991	8.0	137	7.5	11.6	68
Well 1	May 22, 1991	10.5	122	6.2	9.3	68
Well 2	May 21, 1991	10.5	121	7.8	11.0	63
Well 3	May 22, 1991	10.0	130	8.3	10.8	66
Well 4	May 23, 1991	11.5	197	7.6	--	107
Hatchery Well	May 21, 1991	14.0	207	8.8	2.4	107
Galligan Spring	May 24, 1991	8.0	133	7.6	--	67

**Table 5.** Data on selected inorganic ions for samples collected May 20–24, 1991

[Concentrations reported in units of milligrams per liter. <, less than]

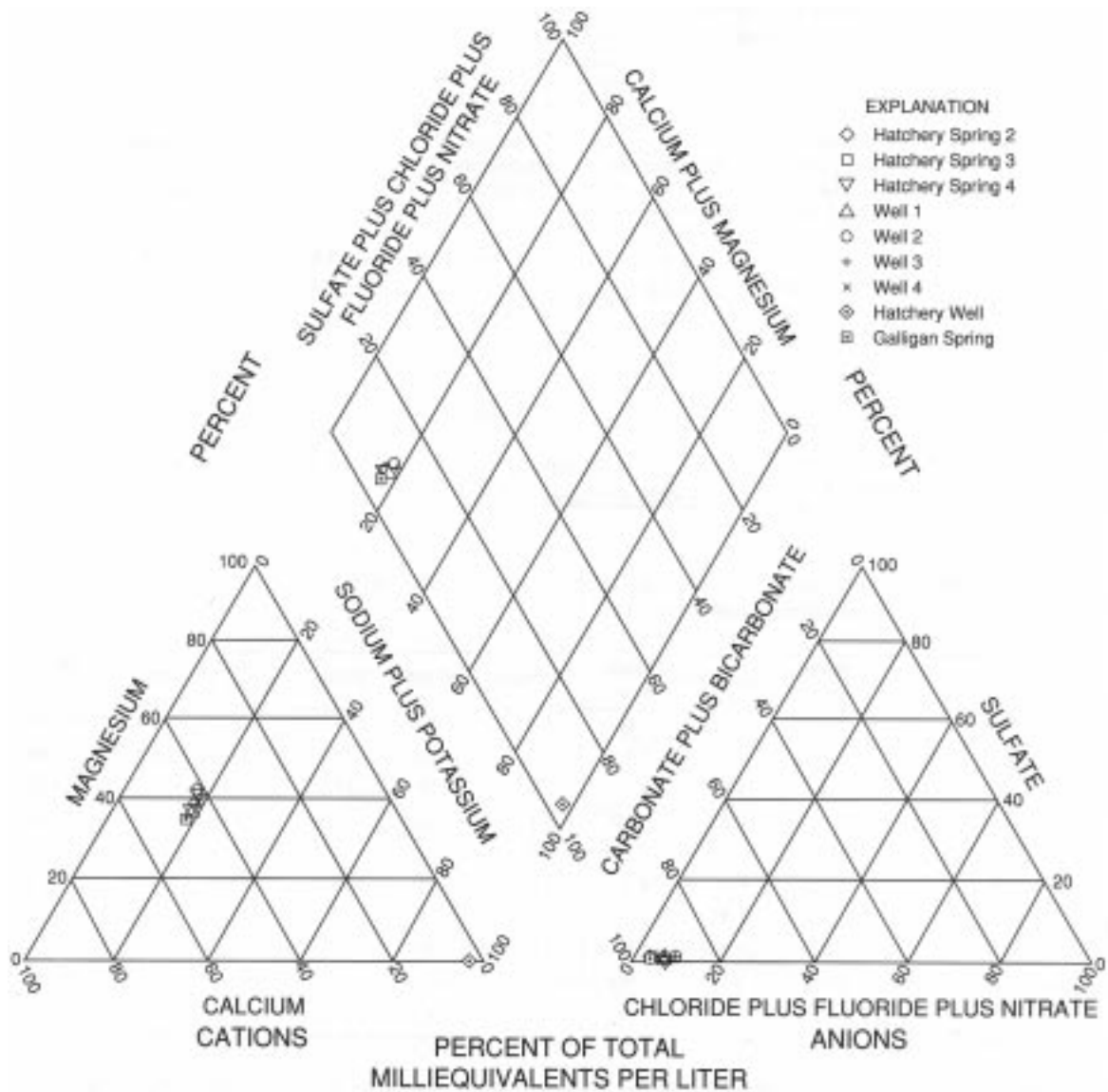
Site	Calcium	Magnesium	Sodium	Potassium	Chloride	Sulfate	Silica	Aluminum	Iron	Manganese	Strontium
Hatchery Spring 2	13	7.9	5.0	1.0	3.0	0.30	38	<0.01	0.005	<0.001	0.059
Hatchery Spring 3	13	7.4	5.0	1.1	2.7	.30	39	<.01	<.003	<.001	.058
Hatchery Spring 4	12	6.3	4.8	1.0	2.6	.30	37	<.01	<.003	<.001	.061
Well 1	12	5.6	4.8	.70	3.1	.40	41	<.01	.017	<.001	.11
Well 2	12	6.4	4.6	1.2	2.9	.80	34	<.01	.005	<.001	.072
Well 3	13	5.6	5.0	1.4	2.9	.40	32	.01	<.003	<.001	.068
Well 4	18	10	7.3	2.2	.80	1.2	40	<.01	<.003	<.001	.070
Hatchery Well	1.2	<.01	45	5.1	3.1	.30	58	<.01	.014	<.001	.003
Galligan Spring	13	5.6	4.8	.70	.80	.20	37	<.01	<.003	<.001	.060

The Hatchery Well water, strongly depleted in the divalent cations, calcium, magnesium, and strontium, and enriched in the monovalent cations, sodium and potassium, has probably undergone a long geochemical evolution. The Hatchery Well water also has the lowest dissolved-oxygen concentration of the nine water samples. These data are consistent with the greater <sup>14</sup>C- and CFC-model ages assigned to this water relative to the other ground water in the study area. Furthermore, the extreme depletion of divalent cations in this water suggests not only the presence of old water, but also negligible contributions of modern water because it is unlikely that modern water would be so depleted in divalent cations. The similarity of inorganic data between water from the hatchery springs, downgradient water in the Underwood Heights area (Wells 2 and 3), and recently recharged water in Well 1, on the other

hand, suggests a chemically similar flow system and short residence times within this local flow system.

### Geochemical Mass-Transfer Modeling

Geochemical mass-transfer modeling is a form of mass-balance modeling in which changes in the geochemical character of water along a flow path are accounted for by modeling phase dissolution, phase precipitation, gas exchange, cation exchange, redox reactions, isotopic fractionation, and (or) mixing of waters along flow paths. This modeling can provide insight into hydrologic systems by allowing the testing of hypotheses for the geochemical evolution of waters. It is described in detail by Plummer and Back (1980), Plummer and others (1983), and Plummer and others (1990).



**Figure 2.** Major-ion data for study-area ground-water samples collected May 20–24, 1991.

An important application of geochemical mass-transfer modeling is its relevance to  $^{14}\text{C}$ -dating. By modeling geochemical processes that may be occurring along ground-water flow paths, an understanding of plausible carbon mass transfers can be developed. Carbon-14 model ages can then be adjusted for the effects of carbon mass transfers that, on the basis of the modeling, appear to be occurring along modeled ground-water flow paths.

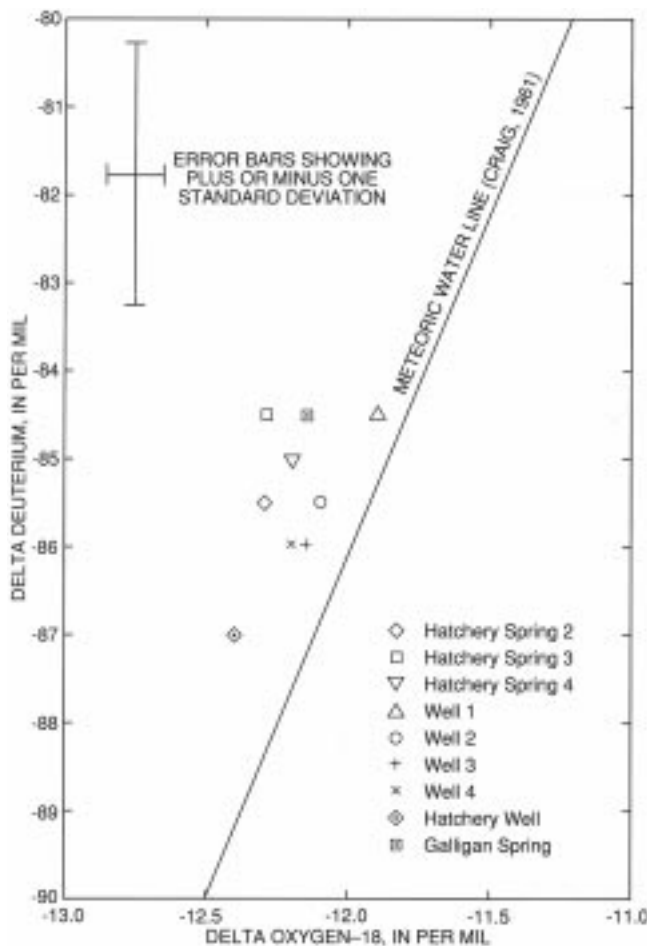
A limitation of geochemical mass-transfer models is that a number of models can usually be generated for one particular model reaction path. Thus, geochemical mass-transfer models are not unique,

and they cannot be used to validate hypotheses for geochemical evolution. Geochemical mass-transfer models, however, can be constrained by incorporating only those phases that are likely to be reactive along model flow paths. Phase reactivity is a function of relative phase abundances, weathering kinetics, and thermodynamic constraints. Knowledge of phase abundances, combined with knowledge of precipitation and dissolution kinetics, is usually used to constrain the selection of phases modeled as undergoing mass transfer. For instance, it is believed that dissolution of basaltic glass generally occurs more than an order of magnitude faster than does dissolution of plagioclase in basalt (Gislason and Eugster, 1987).

**Table 6.** Stable isotopes of water for samples collected May 20–24, 1991

[Values reported in units of per mil relative to Standard Mean Ocean Water. Standard deviations for delta deuterium ( $\delta D$ ) and delta oxygen-18 ( $\delta^{18}O$ ) are 1.5 per mil and 0.1 per mil, respectively.]

Site	$\delta D$	$\delta^{18}O$
Hatchery Spring 2	-85.5	-12.30
Hatchery Spring 3	-84.5	-12.30
Hatchery Spring 4	-85.0	-12.20
Well 1	-84.5	-11.90
Well 2	-85.5	-12.10
Well 3	-86.0	-12.15
Well 4	-86.0	-12.20
Hatchery Well	-87.0	-12.40
Galligan Spring	-84.5	-12.15



**Figure 3.** Relation between delta oxygen-18 ( $\delta^{18}O$ ) and delta deuterium ( $\delta D$ ) in ground-water samples.

To reflect these apparent differences in dissolution kinetics, realistic models in basaltic systems would probably include dissolution of basaltic glass, whereas dissolution of plagioclase might not be warranted. Thermodynamic data are also used to constrain models. Minerals modeled as precipitating should be thermodynamically supersaturated, and those modeled as undergoing dissolution must be undersaturated.

Geochemical mass-transfer models can be further evaluated with isotopic calculations. Isotopic calculations are valuable because they facilitate an independent evaluation of the feasibility of mass-transfer models. An independent evaluation results because the inclusion of isotopes in mass-transfer models can add mass-balance constraints without adding chemical elements or phases to the mass-transfer model. Isotopes can provide, therefore, an important check on the plausibility of geochemical mass-transfer models (Plummer and others, 1983; Plummer and others, 1990).

Geochemical mass-transfer modeling may be warranted in this study area. The downgradient ground waters (ground waters sampled from sources other than Well 1) are more enriched in  $^{13}C$  ( $\delta^{13}C$  values of  $-16.4$  to  $-18.2\%$ ; table 3) than would be expected for ground water that obtains DIC solely from biogenic  $CO_2$  ( $CO_2$  generated by root respiration and decay of organic matter) in a temperate climate ( $\delta^{13}C$  values of about  $-25\%$ ; Mook, 1980, p. 60) and that is not subjected to subsequent carbon-isotope fractionation or exchange. This observation suggests that carbon mass transfers may be occurring in the study-area ground waters. Two carbon mass-transfer reactions that likely could cause enrichment of  $^{13}C$  in study-area ground waters are hypothesized. One hypothesis is that calcite dissolution occurs during the evolution of these ground waters. Calcite dissolution would be expected to enrich these ground waters in  $^{13}C$  (Craig, 1953) and to dilute the  $^{14}C$  content (Mook, 1976, p. 214). The second hypothesis is that degassing of  $CO_2$  has occurred during the evolution of these ground waters. Degassing of  $CO_2$  from water would be expected to enrich ground water in  $^{13}C$  and  $^{14}C$  (Mook, 1980, p. 63; Craig, 1954). Geochemical mass-transfer modeling allows evaluation of the plausibility of such carbon mass transfers during the evolution of these ground waters.

The geochemical mass-transfer model used in this study was NETPATH (Plummer and others, 1991). Calculations of thermodynamic stability of phases, important for model testing, are performed in NETPATH by the aqueous speciation code WATEQF (Plummer and others, 1976), which exists as a NETPATH subroutine. NETPATH also allows development of models that include carbon-isotope fractionation and carbon-isotope exchange. Equations used in NETPATH to describe carbon isotopic fractionation are given by Wigley and others (1978, 1979). Fractionation factors for  $^{13}\text{C}$  fractionations can be chosen to be those of Deines and others (1974) or Mook (1980). Fractionation factors used in this modeling were those of Mook (1980). Fractionation factors for  $^{14}\text{C}$  were assumed to be twice those of  $^{13}\text{C}$  (Craig, 1954).

### Conceptual Models

Most geochemical mass-transfer models are based on conceptual models. The conceptual models used in this study draw largely from the conceptual model developed by Hearn and others (1985) to describe the geochemical evolution of ground water in the Columbia River Basalt Group in the Columbia Plateau. Hearn and others (1985) developed their conceptual model on the basis of regional hydrochemical trends and the abundance, location, and qualitative thermodynamic evaluation of primary and secondary minerals and volcanic glass. The model calls for dissolution of volcanic glass and pyroxene, and precipitation of smectite, ferrihydrite, calcite, silica, and the zeolite mineral clinoptilolite. Apparently, clinoptilolite begins to precipitate only after the ground water evolves to a composition enriched in silica, sodium, and potassium (Hearn and others, 1985). Consumption of dissolved oxygen is attributed to oxidation of ferrous iron (Hearn and others, 1985).

The conceptual models used in this study are generally consistent with the conceptual model of Hearn and others (1985). Dissolution of volcanic glass was included in all models. Dissolution of pyroxene and precipitation of smectite, ferrihydrite, and silica, were included in most models. Clinoptilolite was included in the models of the water from the Hatchery Well, which is a monovalent-cation water.

Quantitative thermodynamic evaluation of the appropriateness of the previously mentioned phases in the models for this study area is problematic for two reasons. First, thermodynamic data for non-end-member smectite and clinoptilolite present in Columbia River Basalts are not available (Hearn and others, 1985). Second, most aluminum and many iron analyses in this study (table 5) were reported as censored data (values falling below the detection limit), thereby limiting thermodynamic evaluation of phases containing aluminum and iron. Some thermodynamic constraints, however, are apparent. It is known that volcanic glass and pyroxene minerals are thermodynamically unstable at surface temperatures and that these phases are kinetically more susceptible to dissolution than other important primary basalt minerals (Gislason and Eugster, 1987; White and Hochella, 1992). The widespread presence of secondary smectite, ferrihydrite, silica, and clinoptilolite in Columbia River Basalts (Hearn and others, 1985) supports their inclusion in these models. Finally, thermodynamic calculations performed with WATEQF (Plummer and others, 1976) suggest that all sampled ground waters were supersaturated with respect to amorphous silica or were within 0.1 log unit of saturation with amorphous silica, further supporting the inclusion of silica precipitation in these models.

Although the conceptual models for this study largely follow the conceptual model of Hearn and others (1985), some additions and modifications to their conceptual model were needed. One such change involved calcite. The conceptual model of Hearn and others (1985) includes precipitation of calcite in down-gradient ground water. Thermodynamic calculations performed with WATEQF (Plummer and others, 1976) suggest that all of the waters analyzed in this study were undersaturated with respect to calcite. Thermodynamic calculations indicate, therefore, that calcite precipitation is unlikely to occur and, assuming its availability, calcite dissolution would be expected in these waters. One might not expect significant dissolution of calcite in a noncarbonate-bedrock aquifer, where carbonate minerals are present in small volumetric proportion to other minerals but calcite dissolution is a function not only of available mass but also of the rate of dissolution, which is fast for carbonates. For example, Bassett and others (1992) studied the geochemical evolution of ground water in the upper reaches of the Geneva Creek drainage in Colorado.

The upper Geneva Creek drainage is underlain primarily by gneiss and granite, and calcite is present in only trace amounts. Using mass-balance calculations, Bassett and others (1992) estimated that more than 50 percent of the calcium leaving the upper Geneva Creek drainage was derived from calcite dissolution.

Similar results were obtained by Katz (1989). Using mass-balance calculations, Katz (1989) suggested that dissolution of calcite was a significant component in the evolution of ground water in contact with carbonate-poor metabasalt and soils derived from metabasalt in the Catoctin Mountains in Maryland.

These examples suggest that dissolution of calcite may be an important process in carbonate-poor geologic media. It is not known if calcite is present in the study area, but calcite is present in small amounts in Columbia River Basalt east of the study area (Benson and Teague, 1982). Because a reasonable potential exists for calcite dissolution in the study area, calcite dissolution was considered in some of the models.

Another change to the conceptual model of Hearn and others (1985) was the inclusion of CO<sub>2</sub> as a phase. The partial pressure of CO<sub>2</sub>, calculated from field measurements of alkalinity using WATEQF (Plummer and others, 1976), at Well 1 was 10<sup>-1.35</sup> atmospheres; at Well 3, the hatchery springs, and the Hatchery Well, the values were 10<sup>-3.48</sup>, 10<sup>-2.74</sup>, and 10<sup>-3.77</sup> atmospheres, respectively. Total inorganic carbon at Well 1 was 3.70 millimoles per liter; at Well 3, the hatchery springs, and the Hatchery Well, the values were 1.32, 1.54, and 2.05 millimoles per liter, respectively. On the basis of the concentrations of DIC in upgradient and downgradient ground water, degassing of CO<sub>2</sub> appears to occur in the evolution of these ground waters. Part of the decrease in CO<sub>2</sub> partial pressures results from the increase in pH along the flow paths, but a loss of CO<sub>2</sub> also is evident from the loss of carbon mass between Well 1 and downgradient ground water. Water from Well 1 appears to receive CO<sub>2</sub> from biogenic processes during recharge of precipitation, as shown by the high concentration of CO<sub>2</sub> and the depleted δ<sup>13</sup>C signature. This CO<sub>2</sub> is probably lost to the unsaturated-zone atmosphere above the ground water prior to aquifer confinement.

The mechanism by which degassing of CO<sub>2</sub> may occur in the study area is not known. Degassing of CO<sub>2</sub> is not a rare phenomenon; for example, degassing of CO<sub>2</sub> is considered to be an important geochemical process in basalts in the Snake River Plain in Idaho (McLing and Smith, 1993). It is possible that in a thick unsaturated zone, a high ratio of air-filled voids to plant matter (CO<sub>2</sub> source) in the unsaturated zone could result in the unsaturated zone having a low partial pressure of CO<sub>2</sub>, relative to the partial pressure of CO<sub>2</sub> that would be in equilibrium with the partial pressure of CO<sub>2</sub> in many ground waters. In such a case, degassing of CO<sub>2</sub> into the unsaturated zone atmosphere would be plausible. The unsaturated zones above Wells 2 and 3 are thick (approximately 300 feet), and the unsaturated zone in the Snake River Plain is nearly 1,000 feet thick (Wood and Low, 1988); however, the distribution of partial pressures of CO<sub>2</sub> in these unsaturated zones is not known.

Another possible mechanism for degassing of CO<sub>2</sub> is related to fluid flow in fractured basalts. The surface of fluid flowing in fractured basalts may be exposed to large volumes of air in the fractures directly above the water surface. The air in these fractures could conceivably be well connected to the atmosphere at ground surface, where one would expect the partial pressure of CO<sub>2</sub> to be low. In such a setting, degassing of CO<sub>2</sub> would be plausible.

A third change to the conceptual model of Hearn and others (1985) was inclusion of ion exchange. Ion exchange in this study was modeled as an exchange of 2 millimoles of sodium per millimole of calcium sorbed. Ion exchange is a common geochemical reaction in natural systems, but it is possible that the modeled ion exchange acts, in part, to adjust the models for the fact that the phase compositions used in the modeling are average compositions. The phases actually undergoing mass transfer are certain to differ from these average compositions.

Geochemical mass-transfer models for the evolution of water collected from Well 3 could not be constructed with the phases listed previously, until precipitation of small amounts (approximately 0.03 to 0.04 millimole per liter of water) of illite were modeled. This result suggested that the conceptual models needed reevaluation with respect to illite.

Although illite was not included in the conceptual model of Hearn and others (1985), inclusion of minor illite precipitation may be warranted because secondary illite is present in Columbia River Basalts (Benson and Teague, 1982). Furthermore, thermodynamic calculations of illite stability using the speciation program WATEQ4F (Ball and Nordstrom, 1991) suggest that water from Well 3 is supersaturated with respect to illite. If the analytical result for aluminum at Well 3 is in error [it was reported as 10 µg/L (micrograms per liter), but all of the other analyses in table 5 were reported to have aluminum concentrations of less than the detection limit of 10 µg/L], thermodynamic calculations of illite stability using WATEQ4F (Ball and Nordstrom, 1991) suggest that the water should remain supersaturated with respect to illite at aluminum concentrations as low as 1 µg/L. Although the chemical analysis for aluminum in the water of Well 3 is certainly accurate to better than an order of magnitude, the possibility of sample contamination or inaccurate thermodynamic data is significant.

The unit-cell chemical formulas for glass and crystalline phases used in the modeling are listed in table 7, along with the references for the chemical analyses. All of the glass and crystalline phase compositions, except illite, were calculated from chemical analyses of minerals from the Columbia River Basalt Group.

Information on the chemical composition of illite in Columbia River Basalt Group was not available. Other phases used in this modeling exercise are idealized, end-member compositions. The unit-cell chemical formulas, when not presented in the original papers, were calculated by the method of Deer and others (1966, p. 515–517). The distributions of iron between ferrous and ferric forms for phases listed in table 7 were not given in the original analyses, so for this study, these distributions were calculated to yield optimal charge balance within each phase.

### Construction of Mass-Transfer Models

Geochemical mass-transfer models were constructed to model the evolution of selected ground waters in the study area. The initial water used in the models was shallow, upgradient ground water representing recently recharged ground water; the final waters were various downgradient ground waters, representing chemically evolved ground waters. Water from Well 1, an upgradient well, was chosen to represent initial or recently recharged water. Water in Well 1 is dilute, contains a modern <sup>14</sup>C signature, and has a δ<sup>13</sup>C value of –22.5‰, close to that expected for a recharge-zone water that has obtained DIC from biogenic CO<sub>2</sub> in a temperate climate (about –25‰; Mook, 1980, p. 60).

**Table 7.** Chemical compositions of volcanic glasses and aluminosilicate minerals used to model the geochemical evolution of selected ground waters  
[NA, not applicable]

Glass or mineral	Mean chemical composition	Reference or origin	Number of analyses
Entablature glass	Si <sub>8.804</sub> Ti <sub>0.169</sub> Al <sub>2.272</sub> Fe <sub>0.918</sub> Mg <sub>0.105</sub> Ca <sub>0.558</sub> Na <sub>1.254</sub> K <sub>0.466</sub> P <sub>0.083</sub> O <sub>24</sub>	Allen and Strope (1983)	60
Colonnade glass	Si <sub>9.769</sub> Ti <sub>0.082</sub> Al <sub>2.000</sub> Fe <sub>0.264</sub> Ca <sub>0.088</sub> Na <sub>0.798</sub> K <sub>0.963</sub> P <sub>0.023</sub> O <sub>24</sub>	Allen and Strope (1983)	57
Augite	Si <sub>1.951</sub> Ti <sub>0.021</sub> Al <sub>0.072</sub> Fe <sub>0.380</sub> Mg <sub>0.852</sub> Ca <sub>0.698</sub> Na <sub>0.008</sub> Mn <sub>0.010</sub> O <sub>6</sub>	Long and Strope (1983)	4
Pigeonite	Si <sub>1.974</sub> Ti <sub>0.014</sub> Al <sub>0.035</sub> Fe <sub>0.774</sub> Mg <sub>0.974</sub> Ca <sub>0.200</sub> Na <sub>0.004</sub> Mn <sub>0.020</sub> O <sub>6</sub>	Long and Strope (1983)	4
Pyroxene	Si <sub>1.962</sub> Ti <sub>0.018</sub> Al <sub>0.054</sub> Fe <sub>0.575</sub> Mg <sub>0.913</sub> Ca <sub>0.450</sub> Na <sub>0.006</sub> Mn <sub>0.015</sub> O <sub>6</sub>	(Average of augite and pigeonite compositions)	NA
Smectite	Si <sub>3.67</sub> Al <sub>0.76</sub> Fe <sub>1.11</sub> Mg <sub>0.71</sub> Ca <sub>0.15</sub> Na <sub>0.07</sub> K <sub>0.09</sub> O <sub>10</sub> (OH) <sub>2</sub>	Hearn and others (1985)	40
Illite	Si <sub>3.50</sub> Al <sub>2.30</sub> Mg <sub>0.25</sub> K <sub>0.60</sub> O <sub>10</sub> (OH) <sub>2</sub>	Default NET-PATH formula	NA
Clinoptilolite	Si <sub>14.34</sub> Al <sub>3.66</sub> Fe <sub>0.20</sub> Mg <sub>0.10</sub> Ca <sub>0.48</sub> Na <sub>0.88</sub> K <sub>0.94</sub> O <sub>36</sub>	Hearn and others (1985)	30



Final (chemically evolved) waters modeled were (1) water representing the mean geochemical and isotopic composition of the three hatchery springs, (2) water from Well 3, and (3) water from the Hatchery Well. Well 3 is downgradient from Well 1, and the hatchery springs and Hatchery Well are approximately down-gradient from Well 1.

The total number of phases that can be included in any given geochemical mass-transfer model in NETPATH is constrained to the number of elemental constituents used in the models. In this modeling exercise, the chemical constraints are calcium, magnesium, sodium, potassium, carbon, aluminum, iron, silica, and redox state. Manganese, phosphorus, and titanium, although present in small amounts in the mineral and glass phases considered to be reactive in this system, were not used in this modeling exercise. Chloride and sulfate concentrations were virtually unchanged along flow paths and are not components of the reacting phases discussed previously; therefore they were not included as constraints or components of phases modeled as undergoing mass transfer. Eight phases, plus dissolved oxygen (included in the geochemical mass-transfer models as the electron acceptor in the oxidation of ferrous iron), therefore can be modeled as undergoing mass transfer in any given geochemical mass-transfer model.

In modeling the isotopic evolution of the ground waters in the study area, the following commonly used assumptions regarding the isotopic composition of the reacting phases were used: Carbon dioxide was assumed to have a  $\delta^{13}\text{C}$  value of  $-25\text{‰}$  (Mook, 1980, p. 60). Carbon-14 concentrations in  $\text{CO}_2$  and calcite were assumed to be 100 percent modern carbon and 0 percent modern carbon, respectively (Mook, 1976, p. 214).

Assigning a model value for the  $\delta^{13}\text{C}$  of the calcite was less straightforward. Freshwater and marine carbonates tend to have median  $\delta^{13}\text{C}$  values close to  $0\text{‰}$ , but values for freshwater carbonates have a wide range, typically from  $+4$  to  $-10\text{‰}$  (Craig, 1953). A value of  $0\text{‰}$  was used in the present modeling. Where modeled calcite mass transfers were significant, values of  $+4$  and  $-10\text{‰}$  also were used for comparative purposes.

The downgradient ground waters were recharged over an unknown period of time in the past, and were associated with an unknown initial  $^{14}\text{C}$  concentration.

It was assumed, therefore, that the  $^{14}\text{C}$  concentration of upgradient ground water was 100 percent modern carbon at the time of recharge.

### Model Limitations

There are several limitations to the geochemical mass-transfer models. One of these limitations results from the fact that the modeled glass and silicate-mineral dissolution is an approximation, and it is unlikely that the chemical compositions of the glasses and silicate minerals utilized in the models exactly represent the phases reacting along the flow paths. For example, the volcanic-glass samples analyzed by Allen and Strope (1983) by microprobe analysis (table 7) were obtained from the Umtanum flow in the Grande Ronde Basalt and are unlikely to exactly represent volcanic glass in other study-area basalts. Within this one flow itself, there is a considerable range in chemical composition of the glasses from sample to sample (Allen and Strope, 1983). Similarly, Long and Strope (1983), in analyzing pyroxene samples from the Cohasset and Umtanum flows of Grande Ronde Basalt by microprobe analysis (table 7), report variable compositions of pigeonite within single basalt flows. Furthermore, assuming that the model chemical compositions of the phases were exactly representative of the phases existing in the study area, the phases might not dissolve in exact stoichiometric proportion to the compositions of the phases. Allen and Strope (1983) caution that reported average chemical compositions for glasses in the Columbia River Basalt Group are not necessarily representative of the glasses most susceptible to dissolution.

Another limitation of the geochemical mass-transfer modeling is the small size of the aqueous data set, a result of only a few wells being available for sampling. The limited data set allows for only gross evaluation of spatial patterns in geochemistry; furthermore, the temporal variability of water chemistry was not measured. The geochemistry of the water in Well 1, an upgradient ground water assumed to represent recently recharged ground water, may undergo seasonal fluctuations not accounted for in these models.

A third limitation concerns isotopic values for carbon in  $\text{CO}_2$  and calcite. Values for these phases in the study area were unavailable, and assumed typical values were used.

Geochemical mass-transfer modeling, and hydrologic modeling in general, is always accompanied by uncertainty. The limitations previously discussed must be kept in mind when interpreting model results.

### Selected Models

Geochemical mass-transfer models were generated following the model considerations discussed previously. The models represent an attempt to combine existing knowledge concerning primary and secondary phases likely to be present in the ground-water system with knowledge of kinetic and thermodynamic limitations to constrain the geochemical mass-transfer models. Comparison of measured and modeled  $\delta^{13}\text{C}$  values further constrains models. As expected, however, multiple models were generated; the solutions are not unique.

Nevertheless, the resulting models for individual sites are similar in their overall theme—a fact that increases confidence in the models. All models constructed for the evolution of these ground waters involve dissolution of primary mineral and glass phases, precipitation of secondary phases, degassing of  $\text{CO}_2$ , and ion exchange. In addition to these mass transfers, some models included calcite dissolution. Selected examples of plausible geochemical mass-transfer models for the modeled waters are presented in table 8.

Models A and B (table 8) are examples of models that describe the geochemical evolution of water from the hatchery springs; models C and D (table 8) are examples of models that describe the geochemical evolution of Well 3 water. These models are dominated by one mass-transfer reaction—degassing of  $\text{CO}_2$ . Other modeled mass transfers are small.

**Table 8.** Mass transfers, observed and modeled delta carbon-13 values, and unadjusted and adjusted carbon-14 model ages from selected geochemical mass-transfer models for the evolution of Spring Creek National Fish Hatchery springs, Well 3, and the Spring Creek National Fish Hatchery well

[Initial water for all flow paths is water from Well 1. Mass transfers are given in units of millimoles per liter. A positive mass transfer indicates dissolution or addition to the water; a negative mass transfer indicates precipitation or removal (for example, degassing) from the water. Positive ion exchange is defined as removal from solution of 1 millimole of calcium per liter of water, for which 2 millimoles of sorbed sodium are released. ‰, per mil; --, phase not included in model]

	Model A Hatchery springs	Model B Hatchery springs	Model C Well 3	Model D Well 3	Model E Hatchery Well	Model F Hatchery Well	Model G Hatchery Well	Model H Hatchery Well
$\text{CO}_2$ gas	-2.15558	-2.15558	-2.37719	-2.37719	-1.64621	-1.64621	-1.97088	-1.97138
$\text{O}_2$ gas	.07119	.06579	.05268	.05177	.02320	-.01834	-.10625	-.11461
Entablature glass	.00986	--	.00355	.00345	.99289	.72000	.46082	.40641
Colonnade glass	.00852	.01123	.03614	.04192	.42535	.25206	.29147	.25724
Augite	--	.01774	--	--	--	--	--	--
Pigeonite	.10798	.07743	--	--	--	--	--	--
Pyroxene	--	--	.02708	.01059	--	.36838	--	.07232
Smectite	-.05687	-.03479	-.02583	--	-.36235	-.84628	-.33983	-.43480
Illite	--	--	-.02703	-.04011	--	--	--	--
Ferrihydrite	-.03205	-.03132	--	-.02062	-.62160	--	-.12281	--
$\text{SiO}_2$	-.22440	-.21938	-.39782	-.47008	-.19118	-.19270	--	--
Ion exchange	-.00563	-.00131	-.01147	-.01457	.43531	.53336	.64609	.66567
Clinoptilolite	--	--	--	--	-.77354	-.41439	-.37476	-.30363
Calcite	--	--	--	--	--	--	.32467	.32517
$\delta^{13}\text{C}$ observed (‰)	-17.4	-17.4	-18.2	-18.2	-16.8	-16.8	-16.8	-16.8
$\delta^{13}\text{C}$ modeled (‰)	-18.3	-18.3	-17.4	-17.4	-19.7	-19.7	-16.8	-16.8
Unadjusted $^{14}\text{C}$ -model age (years)	311	311	473	473	4,540	4,540	4,540	4,540
Adjusted $^{14}\text{C}$ -model age (years)	382	382	558	558	4,590	4,590	3,640	3,640

Differences among models for one particular site are minor. In model A, entablature glass, colonnade glass, and pigeonite dissolve, but augite does not dissolve (table 8). In model B, colonnade glass, pigeonite, and augite dissolve, but entablature glass does not dissolve. In other respects, models A and B are nearly identical. A more refined model might include dissolution of all four phases (entablature glass, colonnade glass, pigeonite, and augite), but the total number of phases undergoing mass transfer in the models cannot exceed the number of constraints (chemical elements) in the models; therefore, all phases that might be undergoing mass transfer cannot be accounted for in all models. As a consequence, these models are only approximations of real hydrochemical systems. Models A and B (table 8) are merely attempts to model the important reactions that might be occurring in these systems. Other models generated for the evolution of the water from the hatchery springs yielded similar results. It is apparent from these models that mass transfers of glass and mineral phases in the geochemical evolution of this water are small.

Models C and D are also similar to each other (table 8). In model C, smectite precipitates, while in model D, ferrihydrite precipitates. Other models for the water at Well 3 yielded similar results. Mass-transfers of glass and mineral phases in this system appear to be small.

The (small) modeled increases in dissolved oxygen along the flow paths modeled in models A through D (table 8) represent a combination of (1) consumption of dissolved oxygen by oxidation of ferrous iron in dissolving phases, and (2) an apparent increase in dissolved oxygen between the upgradient ground water (9.6 mg/L of O<sub>2</sub>) and downgradient ground water (10.9 mg/L of O<sub>2</sub> for the hatchery springs and 10.8 mg/L of O<sub>2</sub> for Well 3). The apparent increases in dissolved oxygen between upgradient and downgradient sites are probably artifacts of flow-path approximations.

The significant result of the geochemical mass-transfer modeling is that degassing of CO<sub>2</sub> appears to be important in the evolution of the water in the hatchery springs and Well 3. This type of mass transfer, which was modeled using Rayleigh distillation calculations, has an important effect on the residual aqueous carbon pool, enriching the residual carbon pool in the isotopically heavier isotopes, <sup>13</sup>C and <sup>14</sup>C.

Degassing of CO<sub>2</sub> appears to be the process responsible for the relatively <sup>13</sup>C-enriched nature of these two downgradient ground waters.

Independent evidence to support the models for evolution of the ground water at the hatchery springs and at Well 3 comes from the modeled <sup>13</sup>C evolution. Mass transfers of <sup>13</sup>C were calculated using the isotope subroutine in NETPATH. The modeled  $\delta^{13}\text{C}$  signature of the final waters can be compared with the measured  $\delta^{13}\text{C}$  values as a check of the plausibility of the models. For models A through D, modeled and measured  $\delta^{13}\text{C}$  values differ by less than 1.0‰ (table 8), suggesting that the models are plausible.

Dissolution of calcite was not included in models A through D (table 8). In order to assess the potential effects that dissolution of calcite might have on the these geochemical mass-transfer models, additional geochemical mass-transfer models for the evolution of water from the hatchery springs and from Well 3 were constructed. These additional models were similar to models A through D (table 8), but calcite was allowed to replace one of the previously included dissolving phases. A total of seven new solutions converged. In all models, small amounts (generally less than 0.01 millimole per liter) of calcite dissolved. Values of  $\delta^{13}\text{C}$  differed by no more than 0.1‰ between the models that included calcite and those that did not. Even if geochemical mass-transfer models that included significant calcite dissolution could be generated for the evolution of these two waters, measured  $\delta^{13}\text{C}$  values would not support the models. This is because calcite dissolution would add <sup>13</sup>C-rich carbon into solution. It appears, therefore, that significant calcite dissolution does not occur along these two modeled flow paths.

Models E, F, G, and H (table 8) are examples of models that describe the geochemical evolution of the Hatchery Well water. Models E and F are conceptually similar to models A through D, but the mass transfers of glasses and minerals are greater, ion exchange becomes significant, and clinoptilolite precipitation has been included. There is, as in models A through D, significant degassing of CO<sub>2</sub>. In model E, ferrihydrite precipitates, and in model F, pyroxene dissolves. Models E and F are reasonable representations of the conceptual model of Hearn and others (1985). The modeled  $\delta^{13}\text{C}$  values, however, are almost 3.0‰ lower (more negative) than the measured value.

Thus, models E and F do not appear to accurately represent the geochemical evolution of Hatchery Well water.

Models G and H are similar to models E and F (table 8). Calcite dissolution is included, and silica mass transfers are omitted so that calcite can be included in these models. In model G, ferrihydrite precipitates, and in model H, pyroxene dissolves. Again, there is a significant mass transfer of CO<sub>2</sub> out of solution, which is important in the carbon-isotope evolution of this ground water. Modeled mass transfers of calcite, although present, are small compared to modeled mass transfers of CO<sub>2</sub> through degassing. The modeled losses of dissolved oxygen along the flow paths represent that portion of the dissolved oxygen decrease along the flow path unaccounted for by oxidation of ferrous iron. This dissolved oxygen is probably consumed by other oxidation processes, such as oxidation of organic matter and oxidation of manganese. If one assumes that all of the dissolved-oxygen loss along the flow path not attributable to oxidation of ferrous iron in models G and H is assumed to oxidize organic matter, this dissolved-oxygen consumption would yield only 0.11 millimole per liter of inorganic carbon—about 5 percent of the total inorganic carbon in the water at this site. This suggests that oxidation of organic carbon along the modeled flow path between Well 1 and the Hatchery Well is, at most, of minor importance.

The model  $\delta^{13}\text{C}$  values of models G and H match the measured  $\delta^{13}\text{C}$  values (table 8). The agreement between modeled and measured  $\delta^{13}\text{C}$  values suggests that models G and H are plausible approximations of the evolution of water at the Hatchery Well. When the assumed  $\delta^{13}\text{C}$  value of 0‰ was varied between +4 and -10‰ (the typical range of values for freshwater carbonates; Craig, 1953), the differences between measured and modeled  $\delta^{13}\text{C}$  values ranged up to 1.1‰. Apparently, the models are not particularly sensitive to the model  $\delta^{13}\text{C}$  value of the calcite.

## Evaluation of Ground-Water Age

Ground-water ages for representative samples from selected sites in the study area are evaluated by first analyzing the results of geochemical mass-transfer modeling and then considering the combined CFC and <sup>14</sup>C data. Geochemical mass-transfer modeling

allows estimation of the effects of modeled carbon mass transfers on <sup>14</sup>C-model ages. Evaluation of CFC and <sup>14</sup>C data in tandem allows evaluation of the extent of ground-water mixing.

The adjusted <sup>14</sup>C-model age for the hatchery springs is 382 years B.P. in models A and B, and the adjusted <sup>14</sup>C-model age for water from Well 3 is 558 years B.P. in models C and D (table 8). These adjusted <sup>14</sup>C-model ages are similar to the unadjusted <sup>14</sup>C-model ages (table 8). As discussed in the section describing the results of the geochemical mass-transfer modeling, alternative models for these two model flow paths could include calcite dissolution. Modeled calcite dissolution was not significant, however, and adjusted <sup>14</sup>C-model ages calculated by these alternative models averaged only 20 years younger than adjusted <sup>14</sup>C-model ages calculated by models that did not include calcite dissolution.

The adjusted <sup>14</sup>C-model ages for the water from the Hatchery Well are 3,640 years B.P. for models F and G (table 8), 900 years younger than the unadjusted <sup>14</sup>C-model age of 4,540 years B.P. (table 8). The difference between the adjusted and unadjusted <sup>14</sup>C-model ages for the Hatchery Well water are probably not significant compared to the inherent errors associated with <sup>14</sup>C-dating.

The greater adjusted <sup>14</sup>C-model age of the deep water from the Hatchery Well, compared with the adjusted <sup>14</sup>C-model ages of the ground water in the hatchery springs and Well 3, is consistent with the work of Hearn and others (1985), Steinkampf and others (1985), and Bortleson and Cox (1986). In these regional studies of ground water in the Columbia River Basalt Group in Washington, percent modern carbon steadily decreased (apparent age of ground water increased) as ground-water chemistry progressed from a mixed-cation ground water towards a monovalent-cation ground water. The greater adjusted <sup>14</sup>C-model age of the Hatchery Well water also is consistent with the CFC data, and with the depth of its zone of contribution or open interval relative to the elevation of the springs and the zones of contribution or open intervals of other wells in the study area.

The purpose of conducting geochemical mass-transfer modeling on selected waters in the study area was to attempt to improve estimates of ground-water ages. Although the adjusted <sup>14</sup>C-model ages

for ground waters in the study area may be better estimates than unadjusted  $^{14}\text{C}$ -model ages, the adjusted  $^{14}\text{C}$ -model ages remain only gross estimates of overall ground-water age. Most importantly perhaps, adjusted and unadjusted  $^{14}\text{C}$ -model ages do not, by themselves, indicate whether or not ground-water mixing has occurred. For example, waters from the hatchery springs and Well 3 are probably mixtures of waters both older and younger than their adjusted  $^{14}\text{C}$ -model ages would indicate. This is supported by the presence of CFCs in these two waters. The CFC data demonstrate that water from the hatchery springs and from Well 3 contain at least a component of modern water. The  $^{14}\text{C}$  data also suggest that some of the water from the hatchery springs and from Well 3 is not modern and that the bulk of the water may be on the order of hundreds of years old. It is also possible that these waters consist of modern water mixed with small amounts of very old water (water significantly older than the adjusted  $^{14}\text{C}$ -model ages). Although the CFC-model ages do not match the  $^{14}\text{C}$ -model ages, the CFC and  $^{14}\text{C}$  data are consistent with each other when interpreted with respect to ground-water mixing. CFC- and  $^{14}\text{C}$ -model ages are only estimates. Ground-water mixing must be taken into account when CFC and  $^{14}\text{C}$  data are interpreted.

Results of geochemical mass-transfer modeling suggest that the bulk of the water from the Hatchery Well may be on the order of several thousand years old. Because of the possibility of ground-water mixing along flow paths and in the well bore, this water may also be a mixture of water both significantly younger and older than the ages indicated by the adjusted  $^{14}\text{C}$ -model ages calculated in models G and H (table 8). The CFC data suggest, however, that there is little or no modern water in the Hatchery Well.

## SUMMARY AND CONCLUSIONS

Water samples from four springs and five wells in basalt aquifers in the vicinity of Spring Creek National Fish Hatchery in Skamania County, Washington, were collected and analyzed for geochemical and isotopic constituents. The purpose of the analyses was to estimate the age (residence time, or time elapsed since recharge) of water issuing from springs at the hatchery. All samples were analyzed

for selected inorganic ions and stable isotopes of water. Samples from eight of the nine sites were analyzed for carbon-14 ( $^{14}\text{C}$ ), carbon-13 ( $^{13}\text{C}$ ), and either chlorofluorocarbons (CFCs) or tritium.

The presence of CFCs in ground water indicates the presence of at least a component of modern (post-1944) water. CFC-dating suggests that water from the hatchery springs contains a component of modern water. Although atmospheric contributions of CFCs to the springwater may have occurred, CFC-dating of water from two wells (Well 2 and Well 3) in the Underwood Heights area north of the hatchery, which lie on flow paths thought to be approximately parallel and similar in length to the flow paths to the hatchery springs, also indicates the presence of modern water. Therefore, ground water several hundred feet below land surface in the Underwood Heights area north of the hatchery, including ground water discharging from the hatchery springs, appears to contain modern water. On the other hand, CFC-dating suggests that deeper ground water such as that withdrawn from the Hatchery Well may be devoid of modern water.

Concentrations of  $^{14}\text{C}$  can be used to estimate the age of ground water. A  $^{14}\text{C}$ -based ground-water age is termed a  $^{14}\text{C}$ -model age. Unadjusted  $^{14}\text{C}$ -model ages ( $^{14}\text{C}$ -model ages unadjusted for carbon mass transfers) for the water from the hatchery springs suggest an overall age of several hundred years. Unadjusted  $^{14}\text{C}$ -model ages for the three wells sampled in the Underwood Heights area ranged from modern to several hundred years old. Unadjusted  $^{14}\text{C}$ -model ages for deep ground water from the Hatchery Well indicate an overall age of several thousand years. However,  $^{14}\text{C}$  concentrations can be affected by transfers of carbon into and out of solution. Evidence suggesting carbon mass transfers during the evolution of these ground waters lies in the  $^{13}\text{C}$  signatures of these ground waters. The  $\delta^{13}\text{C}$  values of downgradient ground water ranged from  $-16.4\text{‰}$  to  $-18.2\text{‰}$ , isotopically heavier than expected for ground water that obtains carbon solely from root respiration in a temperate climate and undergoes no subsequent carbon-isotope fractionation or exchange. In order to account for possible mass transfers of carbon during the evolution of these ground waters, geochemical mass-transfer modeling was conducted on selected study-area ground waters. An existing conceptual model for the geochemical

evolution of ground water in the Columbia River Basalt Group in the Columbia Plateau was modified and applied to study-area aqueous chemical and isotopic data to account for the effects of plausible carbon mass transfers on  $^{14}\text{C}$ -model ground-water ages. Two hypotheses for the apparent enrichment of  $\delta^{13}\text{C}$  values in downgradient ground water were considered: degassing of  $\text{CO}_2$  and dissolution of calcite. Degassed  $\text{CO}_2$  would be expected to be enriched in  $^{12}\text{C}$ , whereas the residual (aqueous) carbon should be enriched in the heavier carbon isotopes  $^{13}\text{C}$  and  $^{14}\text{C}$ . Degassing of  $\text{CO}_2$  should have only a small effect on  $^{14}\text{C}$ -model ages. Calcite dissolution would be expected to enrich aqueous carbon in  $^{13}\text{C}$  and to add  $^{14}\text{C}$ -dead carbon to solution. Significant calcite dissolution, therefore, could have a large effect on  $^{14}\text{C}$ -model ages.

The results of the geochemical mass-transfer modeling suggest that  $\text{CO}_2$  degassing and calcite dissolution both may occur during the evolution of the modeled ground waters in the study area, but that degassing of  $\text{CO}_2$  is the dominant carbon mass transfer in these ground waters. The results of the modeling also suggest that although some calcite dissolution may occur during the evolution of the water produced by the Hatchery Well, and possibly during the evolution of the shallower ground waters, calcite dissolution does not occur to a great extent. The results of the geochemical mass-transfer modeling suggest that the quantity of  $^{14}\text{C}$ -dead carbon added from calcite dissolution may not be sufficient to greatly affect the  $^{14}\text{C}$ -model ages of these ground waters. In other words, the  $^{14}\text{C}$ -model ages that were adjusted for various modeled carbon mass transfers are similar to the unadjusted  $^{14}\text{C}$ -model ages.

A comparison of CFC data with both adjusted and unadjusted  $^{14}\text{C}$  data suggests that water discharging at the hatchery springs appears to contain a mixture of modern and old water, where old water is defined as water recharged prior to 1944. The CFC data support a component of modern water, whereas the  $^{14}\text{C}$  data suggest a component of old water. Similar results were obtained from a comparison of CFC data with adjusted and unadjusted  $^{14}\text{C}$  data for water collected from Well 3. Water from the Hatchery Well, on the other hand, appears to contain little or no modern water and to have an overall age of thousands of years.

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