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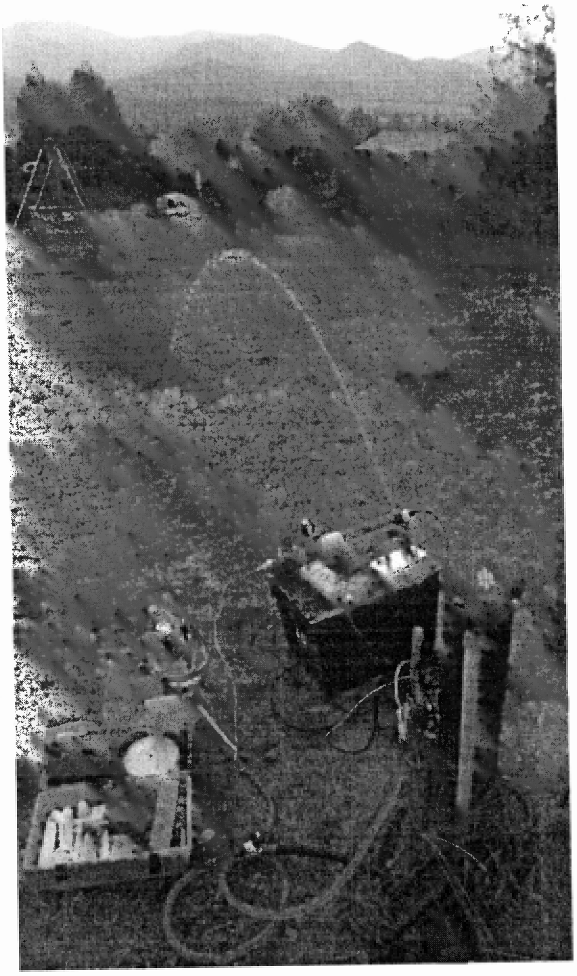
Tracing Ground-Water Flow in the Missoula Valley Aquifer, Southwest Montana



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Tracing Ground-Water Flow in the Missoula Valley Aquifer, Southwest Montana

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Abstract

Major-ion, chlorofluorocarbon (CFC), oxygen-18, deuterium, tritium and noble-gas data were used to evaluate water quality, and as environmental tracers to assess apparent ground-water ages and flow in the Missoula Valley aquifer between the Clark Fork and Bitterroot Rivers. Ground water was sampled at 10 sites, two with nested shallow-deep well pairs, along two transects of ground-water flow; water was also sampled from the Clark Fork River. Calcium and bicarbonate were the dominant ions in all the ground-water samples; total dissolved solids were less than 300 mg/L. Although the ground water is of excellent quality, constituents associated with human activities (sodium, chloride, and nitrate) generally increased along flow path. Seasonal variations of oxygen-18 were detected in surface and ground-water samples. Most of the sampled ground water had CFC concentrations in excess of air-water solubility, rendering the samples unsuitable for age dating; concentrations are markedly greater in unsewered than in sewered areas suggesting that septic effluent is a possible source of the excess CFC's. Tritium was detected in all samples, with concentrations ranging from 8.7 to 13.1 tritium units; tritium/helium-3 age dating shows that ground water in the Missoula Valley aquifer is young, with most of the samples (7 of 12) being less than 2 years old, the oldest age was 4.6 years. In general, the water age increased downgradient along flow path. The noble gas helium-4 is present in surprisingly large concentrations given the young age of the water, and distributed in a pattern opposite of expected flow path trends. Bulk hydraulic conductivity values determined from the age dating are in agreement with values obtained from conventional aquifer tests.

Introduction

Intermontane basins of the Northern Rocky Mountains contain alluvial aquifers that store and yield large quantities of water. In many basins alluvial aquifers represent the most productive aquifers and are important sources of municipal and domestic water (Kendy and Tresch, 1996). The basins also contain perennial streams and associated riparian habitats that are sustained by ground-water discharges. Population growth in the basins is occurring at an unprecedented rate resulting in increased demand for water (municipal/domestic) and a shift in land use from agricultural to residential/urban. The increased demand for water and the land-use shift have created a serious need for information and techniques to evaluate vulnerable hydrologic systems to assure water supplies, and to avid degradation of the ground-water resource.

This report presents the results of a study funded in part by the Montana Water Center and done in conjunction with the Montana Ground-Water Assessment Program at the Montana Bureau of Mines and Geology. The goals were to evaluate the use of environmental tracers, specifically tritium-helium isotopes, chlorofluorocarbons, and oxygen-18 and deuterium to trace ground water flow in the Missoula Valley aquifer. Some study results formed the basis of a University of Montana M.S. thesis to use tracers to refine hydraulic parameters used in ground-water management models for the Missoula Valley aquifer (Pracht, 2001). Previous studies have characterized the physical hydrogeology, modeled ground-water flow, and evaluated the water quality (McMurtrey and others, 1965; Geldon, 1979; Clark, 1986; Woessner, 1988; Miller, 1991).

Surficial glacial outwash and alluvium forms the Missoula Valley aquifer which is the main source of water for the city of Missoula. The primary objective of the study was to develop a better understanding the dynamics of ground-water flow through a part of the aquifer that is heavily utilized, and in a part of the valley that is most susceptible to surface sources of contamination. The report presents a general description of the study area, the geology, the hydrogeology, and the results of the environmental tracer and water-quality analyses.

Acknowledgments

I wish to thank the Missoula Valley Water Quality District for allowing access to their monitor wells, and Jon Harvala for furnishing water-quality and hydrogeologic data; the Montana Water Center for providing funding; Dr. Kip Solomon (University of Utah) for performing the environmental tracer analyses and providing much technical guidance; Dr. William Woessner (University of Montana) for offering insights regarding the Missoula Valley aquifer; Cam Carstarphen for her logistical support and assistance with ground-water sampling; and Don Mason, Mike Richter and Karl Pracht for assistance with ground-water sampling. Reviews by Larry Smith, Tom Patton, and Wayne Van Voast greatly improved the manuscript.

Description of the Study Area

The city of Missoula, home to about 57,000 people, has the second largest population in the state and grew by almost 33 percent between 1990 and 2000 (Montana Department of Commerce, 2001). Missoula is situated in the Missoula Valley, a wedge shaped intermontane basin, that is bounded on the northeast by the Rattlesnake Hills, on the southeast by the Sapphire Mountains and on the southwest by the Bitterroot Mountains (figure 1). The valley is drained by the west-flowing Clark Fork River and the north-flowing Bitterroot River. The part of the valley evaluated for this study lies between the Clark Fork and Bitterroot Rivers; the land use is mostly urban and/or residential. At the time of study, roughly half of the area was serviced by municipal sewer, with residences in the other half relying on septic tank systems (figure 2).

The mountains that surround and underlie the Missoula Valley are composed primarily of metasedimentary rocks of the Belt Supergroup. The basin is filled with up to 2,500 feet of Cenozoic fill, most of it Tertiary in age (McMurtrey and others, 1965). In the study area the Tertiary sediments are mantled by Quaternary alluvium and locally by glacial lake silts.

The climate of the Missoula Valley is characterized by warm summers and cool winters with the wettest months in the winter and spring. At the Missoula airport (altitude 3,200 ft) the average annual temperature is 44.3° F and average annual precipitation is 13.55 in. (Western Climatic Data Center data available online at: http://wrcc.sage.dri.edu/). Average monthly temperatures and monthly rainfall totals for the period of this study are presented on figure 3.

Missoula Valley Aquifer

The city of Missoula is underlain by unconsolidated Pleistocene deposits of the Missoula Valley aquifer, a designated sole-source aquifer by the U.S. Environmental Protection Agency (USEPA). Materials in the aquifer were deposited by glacial melt waters and range in size from fine sand and silt to gravel and cobbles. The aquifer is 100 to 150 feet thick and is bounded below by relatively impermeable, fine-grained Tertiary sediments (figure 4). Three lithologic units have been identified throughout most of the aquifer (Woessner, 1988): the top unit (unit one) is 10 to 30 feet thick, composed of very permeable coarse sand to boulders; the middle unit (unit two) is as much as 40 feet thick and composed of silt and fine sand and is a low permeability horizon within the aquifer; the basal unit (unit three) is composed of 50 to 100 feet of highly permeable, coarse-grained sand and gravel (figure 5). Unit three is the most prolific zone in the aquifer, wells reportedly yield as much as 4,100 gallons per minute (gpm). Few wells penetrate the base of unit three, so the basal configuration of the aquifer is poorly known.

Ground-water in the Missoula Valley aquifer is unconfined, the water table ranges from 10 to 60 feet below the surface. Ground-water flow paths through the aquifer are important because they also describe paths that would likely be taken by contaminants. The potentiometric surface in June 1999 mimics the slope of the land surface; ground water flows from the Clark Fork River southwest toward the Bitterroot River and its confluence with the Clark Fork River; the gradient across the study area was 0.002 (figure 6a). In March 2000, water levels were 5 to 12 feet lower than they were in June 1999 (figure 6b); wells closer to the Clark Fork River show slightly larger declines. The general configuration of the potentiometric was similar to that of June 1999 with the same direction of ground-water flow, although the hydraulic gradient across the study area was slightly smaller.

Leakage from the Clark Fork River is estimated to provide 80 to more than 90 percent of the recharge to the aquifer (Woessner, 1988; Miller, 1991); other sources include underflow through Hellgate Canyon, and precipitation. Water leaves the aquifer as discharge to the Bitterroot River, evapotranspiration, and as pumpage from wells. Water levels fluctuate seasonally and are closely tied to discharge in the Clark Fork River (figure 7). Annual water-level fluctuations in wells are on the order of 5 to 10 feet; however, the fluctuations are more pronounced in wells near the Clark Fork River and become muted downgradient along the flow path.

Sample Collection

Sites for environmental tracer sampling were selected on the basis of location, depth, relative position along flow path, and accessibility. Thirteen monitor wells owned and maintained by the Missoula Valley Water Quality District were sampled for environmental tracers. The wells are completed along two transects of ground-water flow between the Clark Fork and Bitterroot Rivers and include two nested shallow-deep pairs (figure 8 and table 1). The first round of samples were collected in June 1999 for common ions and trace elements, oxygen-18 (^{18}O), deuterium (D), chlorofluorocarbons (CFC's), tritium, and helium (and other noble gases). Samples for common ions and trace elements were collected from seven of the wells, after field measurements of specific conductance, pH and temperature had stabilized and at least three well-casing volumes were removed. Water samples for CFC's and noble gases were initially collected by lowering 0.25-in diameter copper tubes in the well, which were allowed to fill with water and then retrieved; a check valve on the bottom end of the tube prevented water from draining. Upon recovery to the surface the ends of the copper tube were sealed by metal pinch clamps. Water samples for tritium were collected in 1,000 ml glass bottles, samples for ^{18}O and D were collected in 250 ml plastic bottles. Monthly samples for ^{18}O were collected from the Clark Fork River and a nearby well (well 69055[1]) between June 1999 and December 2000; all the other wells (except well 151200) were sampled in June 1999 for ^{18}O and D, and again in March 2000 for ^{18}O by the Missoula Valley Water Quality District.

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[1] Unique Ground-Water Information Center (GWIC) well identification number. The GWIC database is on line at http://mbmggwic.mtech.edu/.

Subsequent samples for noble gases (obtained in December 1999 and from selected wells in August 2001) were collected using in-well diffusion samplers consisting of 1-in long lengths of copper tubing (0.25-in diameter). Each tube had one end sealed and the other end covered by a semi-permeable membrane; the membrane was permeable to gases but not to water. The diffusion samplers were lowered into the wells opposite the well screens and allowed to equilibrate with the dissolved gases in the ground water–generally for a period of about one week. Upon retrieval to the surface the open end of the copper tube was immediately sealed with a specially designed clamp to create a cold weld. Noble gas analyses results from the water samples and diffusion samplers were found to be comparable.

The tritium, CFC, and noble gas samples were analyzed by the University of Utah Noble Gas Laboratory. Tritium was determined using the helium ingrowth method (Clarke and others, 1976). Noble gasses (^{3}He,^{4}He, Ar, Kr, Ne) and reactive gases (O_2, N_2) were determined by mass spectrometer. The University of Waterloo Environmental Isotope Laboratory analyzed the ^{18}O and D samples by mass spectrometry. Analyses of common ions and trace metals were performed by the Montana Bureau of Mines and Geology's (MBMG) Analytical Laboratory. Water-quality data from the wells not sampled by MBMG were obtained from the Missoula Valley Water Quality District (MVWQD).

Discussion of the Results

Major Ions and Trace Metals

Water may be characterized by the type and concentrations of its dissolved constituents. Ground water in the Missoula Valley aquifer has a very consistent chemical make-up and is of very high quality (table 2). All of the sampled ground-water is a calcium-bicarbonate type; there is little variability in water samples (figure 9). The water is safe to drink and suitable for other uses based on USEPA drinking water standards for natural constituents; all total dissolved solids concentrations were less than 300 milligrams per liter (mg/L).

Although the overall composition of the water is consistent and of high quality, total dissolved solids and the concentrations of several constituents commonly associated with human activities increase downgradient along flow path. Figure 10 shows the distribution of specific conductance, used as a proxy for total dissolved solids; concentrations in wells near the Bitterroot River are more than 100 microsiemens per centimeter at 25°C (uS/cm) greater than those in upgradient wells near the Clark Fork River. Similarly, the concentrations of sodium, chloride, and nitrate generally increase downgradient in wells located further from the Clark Fork River (figures 11 - 13).

Water-quality data from the nested well pairs show that there are subtle yet regular differences in water quality with depth. Concentrations of sodium, chloride, and nitrate are all greater in the shallow wells. The increases are consistent with these constituents originating from the land surface. The most likely source of the elevated sodium and chloride is runoff from de-icing chemicals applied to streets, sidewalks and parking lots (MVWQD, 1997), and effluent from septic tanks (Woessner and others, 1995; MVWQD, 1996); likely sources of elevated nitrate include fertilizers applied to lawns and effluent from septic tanks.

The distribution of arsenic shows a different pattern than that of sodium, chloride and nitrate. Arsenic concentrations ranged from below the detection limit to 2.4 micrograms per liter (ug/L), with samples from the upgradient part of the aquifer near the Clark Fork River having larger concentrations than samples from downgradient part of the aquifer (figure 14). Additionally, in samples from the nested well pair closest to the river (Well Pair A, figure 8), arsenic was not detected in the sample from the deep well. A sample collected in June 1999 from the Clark Fork River above Missoula (USGS gaging station 12340500) had an arsenic concentration of 2.2 ug/L (USGS online hydrologic data for Montana: http://mt.water.usgs.gov/), similar to that of the highest concentration measured in the ground water. Arsenic in the Clark Fork River is known to be elevated due to historic mining activity upstream of Missoula. The results suggest that arsenic in the aquifer is derived from the Clark Fork River water that recharges the aquifer.

Oxygen-18 and Deuterium

Oxygen-18 (^{18}O) and deuterium (^{2}H, or D) are the main isotopes that comprise the water molecule. Isotopic analyses are useful in hydrologic studies because waters of different ages, recharge areas, or hydrologic history are often isotopically distinctive which allows them to be used to show hydrologic connections. Variables such as temperature, altitude, distance from the ocean, and latitude have an influence on the isotopic composition of precipitation. Because the isotopic composition of ground water generally reflects the average isotopic composition of precipitation in a recharge area, spatial and temporal variations in the isotopic content of precipitation can be useful in evaluating ground-water recharge sources.

The ^{18}O and D concentrations are reported as δ values, which represent the difference in parts per thousand (per mill, ‰) between the ratios of $^{18}O/^{16}O$ (or D/H) of the water samples and that of standard mean ocean water (SMOW); δ values are calculated by:

$$\text{(in ‰)} = (R_{sample}/R_{SMOW} - 1)1000$$

where "R" is the ratio of the heavy to light isotope. Therefore, the results are interpreted relative to SMOW. A positive δ value means that the sample contains more of the heavy isotope than standard ocean water; a negative δ value means that the sample contains less.

Isotopes of oxygen and hydrogen have been used to determine the sources and flow patterns of ground water (Muir and Coplen, 1981; Taylor and others, 1992), and the seasonal variability of the isotopes in surface water has been used to determine relative quantities and rates of ground-water recharge (McCarthy and others, 1992; Kennedy and others, 1986).

The $\delta^{18}O$ and δ D concentrations were measured in selected surface and ground-water samples (table 3). Monthly samples to assess the seasonal variation in ^{18}O were collected from the Clark Fork River at McCormick Park and a nearby monitor well (well 69055) between June 1999 and December 2000. The river was expected to show a seasonal difference between spring runoff when the river water is derived from snow melt (isotopic signature should be more depleted) and at other times when base flow conditions are predominant. Ground-water samples were collected from wells in June 1999 (peak flow) and March 2000 (low flow) to see if seasonal isotopic variations could be detected in the aquifer. Water from the June 1999 round of sampling, was analyzed for both isotopes (^{18}O and D). Subsequent surface and ground water samples were analyzed for ^{18}O only (table 3).

Seasonal variation of ^{18}O in ground water is typically muted due to relatively slow infiltration and mixing in the unsaturated zone (Clark and Fritz, 1997 and Coplen and others, 2000); however, given the hydrogeologic setting of the Missoula Valley aquifer (most of the recharge is infiltrated river water and the aquifer is highly transmissive) it was hypothesized that a seasonal signal might be detectable in the aquifer and provide an independent means to trace ground-water flow.

The results from the monthly sampling of the Clark Fork River and well 69055 are shown on figure 15. The $\delta^{18}O$ values from the river samples range from -17.86 to -16.46 per mill, the ground-water samples range from -17.86 to -16.29 per mill. In general, the surface and ground water samples show similar seasonal variations, with more depleted values in the cold winter and spring months and more enriched values in the warm summer months. All the surface water samples with $\delta^{18}O$ values greater than -17 per mill occur between June and December.

The $\delta^{18}O$ and δD results from the June 1999 sampling are shown in figure 16 along with the global and North American meteoric water lines (Coplen and others, 2000). The results plot along and between the two lines demonstrating the regular relationship between $\delta^{18}O$ and δD and demonstrating the meteoric origin of the water. The sample from the Clark Fork River plots slightly above the global line and has the most depleted $\delta^{18}O$ value; the ground water samples are all relatively enriched.

The spatial distribution of the June 1999 $\delta^{18}O$ values (figure 17) shows a gradient through the aquifer that reflects the hydraulic gradient of the flow system; values become more enriched (less negative) along flow path; the ground-water values ranged from -18 to -16.94 per mill, with a median of -17.26 per mill.

Figure 18 shows the results from the March 2000 samples. The March 2000 samples from all but one well are enriched relative to the June 1999 samples, the concentrations ranging from -17.52 to -15.82 per mill, with a median of -16.72 per mill. The amount of enrichment ranged from 0.20 to 1.12 per mill, with an average enrichment of 0.67 per mill (median 0.54 per mill). The magnitude of the change is on the same order as the seasonal change observed in the Clark Fork River samples. The $\delta^{18}O$ concentration gradient is greater than in June 1999, especially in the western part of the aquifer (figures 17 and 18), even though the hydraulic gradient is slightly less (figures 6a and 6b).

The overall enrichment and spatial distribution of $\delta^{18}O$ in the March 2000 samples suggests that water recharged from the Clark Fork River during warm months had invaded most of the aquifer. Another explanation of the observed changes is that seasonal pulses of isotopically enriched water move though the aquifer and the sampling frequency and spacing were not sufficient to identify multiple seasonal peaks. Clearly, the results indicate that a seasonal isotopic variability can be recognized throughout the aquifer, not just in the recharge area. Systematic sampling of ground and surface water over one or more years could help trace ground-water flow and assess ground-water residence times in the Missoula Valley aquifer.

Chlorofluorocarbons

Chlorofluorocarbons (CFC-11 and CFC-12) are synthetic organic compounds first produced in the 1930's, they have very low toxicity and have been used primarily as coolants in air conditioners and refrigerators, blowing agents in foams and insulation, propellents in aerosol cans, and as solvents (Plummer and Busenberg, 2000). Atmospheric concentrations of CFC's are uniform across large areas and have been steadily increasing since the 1940's. Atmospheric concentrations of CFC's have been monitored since 1978, and pre-1978 concentrations have been reconstructed from CFC production and rates of release (Cook and Solomon, 1997). Therefore, atmospheric input of CFC's to ground water can be determined for most localities, and CFC's provide excellent tracers and dating tools for young ground water.

In ground water, CFC compounds are soluble and stable. Ground-water ages, or recharge dates, are determined by converting CFC concentrations in ground water to equivalent air concentrations using known solubility relationships and recharge temperature (Cook and Solomon, 1997). The equivalent air concentration is compared to known atmospheric concentrations to determine the recharge year. Limitations to the method include reducing conditions that can degrade CFC's in ground water, and non-atmospheric sources of CFC's (Oster and others, 1996). Under optimal conditions CFC's can be used to estimate ground-water age to within 1- to 2-years; however, accuracy generally decreases as age increases (Szabo and others, 1996; Stoner and others, 1997).

Several studies have used CFC's to age-date ground water and to trace ground-water flow (Busenberg and Plummer, 1992; Busenberg and others, 1993; Dunkle and others, 1993; Reilly and others, 1994; Cook and others, 1995). CFC ages have also been used to assess land-use effects on water quality (Bohlke and Denver 1996; Stoner and others, 1997), evaluate the timing of nitrate impacts to ground water in the Flaxville gravel and underlying aquifers in the northern plains of Montana (Nimick and Thamke, 1998), and to assess ground-water residence times and flow rates in shallow aquifers in west-central Montana (Nimick and others, 1996). Studies that have compared CFC to tritium-helium derived ages have shown generally good agreement between the methods (Ekwurzel and others, 1994; Szabo and others, 1996).

For the Missoula valley, concentrations of CFC-11 and CFC-12 were determined in ground-water samples collected from 12 wells and a sample from the Clark Fork River. The results were variable, ranging from less than 3 to more than 77 picomoles per kilogram (pmoles/kg) for CFC-12, and from less than 4 to 35 pmoles/kg for CFC-11 (table 4). All of the ground-water samples, except for the two closest to the Clark Fork River, were contaminated having CFC concentrations in excess of what would be expected from air-water solubility relationships. The elevated concentrations show that CFC's from non-atmospheric sources have been introduced into the aquifer, rendering the samples unusable for age-dating. The two ground-water samples that did not show elevated CFC concentrations were from wells at McCormick Park (well 69055) and near the Madison St. Bridge (well 151191), the recharge dates were 1989 (10 year old water) and 1999 (recent < 1 year old water), respectively. The sample from the Clark Fork River, collected at McCormick Park, returned a date of 1999 (< 1 year old water).

Although most of the CFC samples were not usable for age dating the ground water, the spatial distribution shows a pattern of increasing concentrations down flow path similar to the other parameters associated with human activities. The land use over a large part of the aquifer is unsewered residential; sewage effluent is a recognized source of CFC contamination to shallow ground water (Schultz and others 1976; Busenberg and Plummer, 1992; Plummer and Busenburg, 2000). Plotting the distribution of CFC-12 in relation to the location of known septic systems shows that concentrations increase markedly downgradient of the high density septic areas (figure 19). CFC concentrations in samples from the unsewered and upgradient parts of the sewered area are less than 10 pmoles/kg; downgradient of the high density septic areas concentrations range up to more than 75 pmoles/kg.

Samples from the shallow-deep well pair (Well Pair A, figure 8) in the upgradient, sewered area showed that there is no significant difference in CFC concentration between the shallow and deep well, the CFC-12 concentrations were 7.5 and 7.94 pmoles/kg, respectively. However, samples from the well pair in the unsewered part of the area (Well Pair B, figure 8) near the end of the flow system showed that concentrations in the shallow well were almost 5 times greater than the deep well, 77.68 and 15.93 pmoles/kg, respectively. These observations suggest that septic effluent is a primary source of the excess CFC's.

Tritium

Tritium (^3H), the radioactive isotope of hydrogen with a half-life of 12.43 yr, is produced naturally in the upper atmosphere. Atmospheric testing of nuclear weapons between 1952 and 1963 injected large amounts of tritium into the atmosphere, overwhelming the natural production. Tritium concentrations in north American rainfall are estimated to have been in the range of 5 to 20 tritium units (TU) prior to above ground nuclear testing; during the early 1960s tritium concentrations in precipitation of more than 5,000 TU were recorded at several North American stations (Solomon and Cook, 2000). Most of the bomb-derived tritium has since been washed from the atmosphere and tritium levels in precipitation are now close to natural levels (Clark and Fritz, 1997). Tritium in precipitation fluctuates seasonally. In Ottawa, Canada where it is monitored monthly, tritium levels in precipitation since 1992 have ranged from about 10 to 30 TU (IAEA/WMO, 2001). Because of its short half life, tritium is an ideal marker of recent (post-1952) ground-water recharge.

Tritium concentrations in ground water and the Clark Fork River ranged from 8.7 to 13.1 TU (table 5 and figure 20). The results show that all the sampled water is modern (i.e. has been recharged since the advent of above ground nuclear testing) and are very consistent, less then 5 TU separate the high and low values. The tight range of values suggests that recharge water flushes through the aquifer relatively rapidly. There are no apparent flow path trends in the tritium data and there is no difference between the ground-water samples and the Clark Fork River sample (figure 20).

Tritium-Helium Ground-Water Ages

Tritium decays to the stable noble gas helium-3 (^3He). After water containing tritium enters the ground-water system and becomes isolated from the atmosphere, ^3He concentrations increase as the ground water becomes older. By determining the amount of tritium and tritiogenic ^3He in a ground-water sample, an age can be calculated according to the relationship (Plummer and others, 1993):

$$t = t_{1/2}/\ln 2 * \ln(1+ {}^3He_{trit}/{}^3H)$$

where t is the tritium-helium age, $^3He_{trit}$ is the helium-3 in the sample derived from tritiogenic decay, ^3H is the tritium concentration, and $t_{1/2}$ is the tritium half life. Ratios of tritium to helium-3 have been used to accurately date shallow ground water with ages ranging from a few months to 50 years (Poreda and others, 1988; Solomon and Sudicky, 1991).

Tritium-helium dating has been used to understand flow constraints in an aquifer recharged by bank infiltration (Stute and others, 1997), and in other studies to determine ground-water recharge, to estimate variations in ground-water recharge, and to trace ground-water age and flow (Poreda and others, 1988; Solomon and Sudicky, 1991; Solomon and others, 1992; Solomon and others, 1993; Cook and others, 1996, Szabo and others, 1996). Tritium-helium dating has also been used to determine aquifer characteristics and to trace solute transport at contaminated sites (Cook and others, 1996; Solomon and others, 1995). More recently tritium-helium ages have been used to improve ground-water flow models, and to estimate and constrain hydraulic parameters used in flow models (Sheets and others, 1998; Shapiro and others, 1998; Portniaguine and Solomon, 1998).

Tritium-helium-3 (^{3}H-^{3}He) apparent ages for the 12 ground-water samples from the Missoula Valley aquifer ranged from less than zero to 4.6 years, with estimated uncertainties of 1 to 1.5 years (table 5 and figure 21).

The results underscore one of the limitations of the ^{3}H-^{3}He method, namely for very young water accurate determinations of the amount of ^{3}He from atmospheric solubility and excess air are very important (Solomon, 2000). Obviously an age less than zero does not make sense. However, there are three main sources of ^{3}He in ground water, the atmosphere, excess air, and tritiogenic decay (^{3}He in ground water can also be derived from mantle and nuclear reactions, but for this study these sources were considered negligible). The total amount of ^{3}He can be expressed as:

$$^3He_{tot} = {}^3He_{atm} + {}^3He_e + {}^3He_{trit}$$

Where $^3He_{atm}$ is the helium-3 derived from dissolution of air in recharging ground water, ^3He_e is the component of helium-3 derived from the supersaturation of air in ground water, and $^3He_{trit}$ is the component derived from tritiogenic decay. What is measured in the laboratory is $^3He_{tot}$, the total amount of helium-3 in the sample. To apply this method the amount of $^3He_{trit}$ must be isolated by subtracting $^3He_{atm}$ and ^3He_e from $^3He_{tot}$. $^3He_{atm}$ is calculated from the recharge temperature, and equilibrium solubility relationships with He in the atmosphere. The excess air component is determined by the degree of neon supersaturation (the only source of neon is the atmosphere), the recharge temperature, and the atmospheric concentration. Once the amounts of $^3He_{atm}$ and ^3He_e have been accounted for the remaining ^{3}He is attributed to tritiogenic decay. The samples that returned "negative ages" are very young water in which the $^3He_{atm}$ and ^3He_e components overwhelm the $^3He_{trit}$ component, not enough time has elapsed to generate a significant amount of $^3He_{trit}$.

In general, the results show expected flow-path trends with ages increasing along flow path. Figure 22 shows the distribution of apparent ages from the samples collected along the eastern transect, the values range from less than 1 year near the river to more than 3 years at the end of the transect. There were no strong correlations with depth below the water table, although most of the samples were obtained near the water table (figure 23). In the nested well pair near the end of the flow system (Well Pair B) the sample from the deep well had the younger age; however, given the uncertainties associated with these determinations the ages can not be considered significantly different.

Using the data from Well Pair B, a horizontal ground-water flow velocity was determined using the equation:

$$\text{velocity} = \text{distance/time}$$

The well pair is approximately 15,000 feet downgradient from the Clark Fork River (figure 8); the apparent ground-water ages were 4.6 years (well 151201) and 3.3 years (well 157210). Assuming most of the ground water is recharged from the river, the velocity through this part of the aquifer ranges from about 7 to 18 feet per day. These velocity estimates can be used in conjunction with the hydraulic gradient and porosity to estimate values of bulk hydraulic conductivity for the aquifer using a form of Darcy's Law:

$$K = (vel*n)/I$$

Where K = hydraulic conductivity, vel = ground-water velocity, n = effective porosity, I = hydraulic gradient. Using the measured hydraulic gradient of 0.002, and an assumed effective porosity value of 0.25, the estimated hydraulic conductivity of the aquifer ranges from about 900 to 2,300 feet per day (ft/d). This range agrees favorably with, although it is slightly lower than, ranges published by McMurtrey and others (1965), 830 - 1,608 ft/d; Woessner (1988), 1,400 - 3,400 ft/d; and Miller (1991), 1,100 - 18,000 ft/d.

Helium-4

Recharging ground water contains atmospheric ^{4}He in an amount that depends on recharge temperature and air-water solubility relationships. As water moves through the subsurface, ^{4}He concentration will rise due to additions of terrigenic ^{4}He produced within the aquifer solids (Solomon, 2000). Terrigenic ^{4}He ($^4He_{ter}$) is derived mostly from the alpha (α) decay of uranium and thorium series elements in rocks and sediments, and has been used to trace ground-water flow. The general theory behind the method is that the longer the ground water is in contact with uranium and thorium bearing minerals the greater the ^{4}He concentration. Therefore, as ground water moves down flow path, ^{4}He concentrations increase; if the release rate is known then ^{4}He concentrations should be proportional to ground-water travel times and can be used to trace ground-water flow (Solomon, 2000). The method has been used to trace ground water in regional bedrock aquifers in the range of 10^3 - 10^8 years (Andrews and Lee, 1979; Torgersen and Clarke, 1985; Stute and others, 1992). However, Solomon and others (1996) observed ^{4}He concentrations increased with travel time in a shallow, unconsolidated aquifer where the ground-water age was less than 50 years, and the concentrations were 300 times greater than what can be supported by in situ decay of uranium and thorium. They postulated that the large concentrations were due to the release of residual helium that had accumulated in the protolith prior to its erosion and deposition as aquifer materials. Furthermore, they showed that by quantifying the release rate, ^{4}He could be used to trace ground water over a time scale of 10 to 10^3 years in some aquifers.

The $^4He_{ter}$ concentrations determined for the ground-water samples and the sample from the Clark Fork River ranged from 0.2×10^{-8} to 5.45×10^{-8} cubic centimeters at standard temperature and pressure per gram (ccSTP/g) (table 5 and figure 24). The sample from the Clark Fork River had a relatively small amount (0.22×10^{-8} ccSTP/g), while samples from wells near the river, in the upgradient part of the flow system, and below the central part of town had the largest concentrations. A plot of the $^4He_{ter}$ concentrations with distance form the Clark Fork River (i.e. down flow path) shows that concentrations decrease down flow path (figure 25), a trend opposite of what has been reported in the literature (Solomon and others, 1996; Solomon, 2000). There were no apparent correlations of $^4He_{ter}$ with depth (figure 26), one of the samples from a deep well near the Clark Fork River had a large concentration (well 157208, $5.45\text{x}10^{-8}$ ccSTP/g), but the other deep well located near the end of the flow system did not (well 157210, $2.10\text{x}10^{-8}$ ccSTP/g). To verify the results, four of the wells were resampled, the results (table 5) confirmed the elevated concentrations and the concentration distribution (figure 27).

The results of the helium analyses indicate a significant source of terrigenic helium in the Missoula Valley aquifer and a concentration distribution that defies conventional interpretation. Large concentrations of terrigenic ^4He have been detected in other aquifers in the region. Plummer and others (2000) observed excess terrigenic helium, believed to be derived from a mantle source, in the eastern Snake River Plain aquifer in south-central Idaho. However, the largest excesses were detected in water with tritium concentrations generally < 1 TU, ground water that contained large fractions of irrigation water (derived from the Snake River) had low excess ^4He. Pope and others (1999) reported significant terrigenic helium in a basin-fill aquifer near Dillon, in southwest Montana. The terrigenic ^4He was shown to increase in relation to depth and ground-water age, however there was insufficient data to determine if the source was diffusion from the mantle or from aquifer solids.

All of the samples from the Missoula Valley aquifer have terrigenic ^4He concentrations well above what could be possible from the in-situ decay of uranium and thorium. If the source is the release of residual helium then it would appear that the release rate is not uniform through the aquifer. Whatever the source, the presence of such large concentrations in ground water less than 5 years old, and a concentration distribution that does not account for known flow paths presents an unsolved problem.

Summary and Conclusions

A study to assess the use of environmental tracers and water quality in the Missoula Valley aquifer was undertaken as part of the Montana Ground-Water Assessment Program and funded in part by the Montana Water Center.

The ground water in the aquifer is a calcium-bicarbonate type with low dissolved solids concentrations; none of concentrations of inorganic constituents exceeded public drinking water standards. However, concentrations of total dissolved solids, sodium, chloride and nitrate were higher in samples from the downgradient wells, indicating that concentrations of these constituents increase as ground water flows from the Clark Fork to the Bitterroot River. Samples from two shallow-deep well pairs show that concentrations of these constituents are slightly greater in the shallow wells (near the water table). Much of the area overlying the aquifer in the study area is urban, or high- and medium density residential (sewered and unsewered), and is covered by streets, driveways, parking lots and lawns. Likely sources of sodium and chloride in this environmental setting include de-icing chemicals and septic effluent; likely sources of the nitrate include fertilizers applied to lawns and gardens, and septic effluent.

Monthly sampling of the Clark Fork River shows that concentrations of $\delta^{18}O$ and δD vary seasonally, generally the water is more isotopically enriched during the warmer months. Ground-water samples from June 1999 show $\delta^{18}O$ increasing fairly uniformly down flow path. The results from a repeat sampling in March 2000, show all of the samples, except one, were enriched relative to the June 1999 samples and the concentration gradient was steeper. The amount of enrichment was on the order of the seasonal variability observed in the Clark Fork River samples. The seasonal variability in the Clark Fork River most likely explains the spatial variability observed within the aquifer and the shift in $\delta^{18}O$ values in the ground water between June 1999 and March 2000 because the river is the primary source of recharge. The observed temporal and spatial variability could be useful for tracing ground-water flow and determining ground-water residence times in the Missoula Valley aquifer.

Evaluation of CFC concentrations in context of the ground-water flow system and land use, specifically the distribution of septic systems, indicate that septic effluent is a probable significant source of CFC's to the Missoula Valley aquifer. The results indicate that CFC's can not be used in this environmental setting to date ground water because of CFC contamination. Although unsuitable for age dating, CFC's may be useful for monitoring the effectiveness of sewering on the ground-water quality. Parts of the study area are scheduled to be sewered, resampling the wells for CFC's after the septic systems are no longer in use may provide a way to document the effect of sewering on ground-water quality.

Ground-water ages determined by the $^{3}H/^{3}He$ method were for the most part hydrologically consistent; ages generally increase with distance down flow path. The oldest apparent age was 4.6 years with an uncertainty of +\- 1 yr. Dating of the ground water was problematic because most of the water is so young. Young water is more sensitive to atmospheric concentrations of ^{3}He which results in increased uncertainty without accurate determinations of atmospheric components of ^{3}He. However, the results are significant because they demonstrate the presence of young water throughout the flow system between the Clark Fork and Bitterroot Rivers, and they are consistent with the high transmissivity of the aquifer as measured by aquifer tests. Comparison of bulk hydraulic conductivity values estimated from $^{3}H/^{3}He$ ages agree favorably with values determined from aquifer tests.

Large concentrations of terrigenic ^{4}He were present in the ground-water samples from the Missoula Valley aquifer. The sample from the Clark Fork River did not contain significant ^{4}He, suggesting that the excess ^{4}He is derived from the aquifer solids or possibly a deep regional flux. However, the spatial distribution of ^{4}He does not show expected flow path trends that would support either of these hypotheses. Ground-water samples very close to the Clark Fork River were highly enriched in ^{4}He and concentrations generally decreased along flow path, samples from the deep wells were not consistently more enriched in ^{4}He than shallow samples.

The water quality trends and the young age of the ground water highlight the overall vulnerability of the Missoula Valley aquifer to contamination. It is recommended that the ongoing monitoring efforts of the Missoula Valley Water Quality District continue in order to preserve the current high-quality ground water in the aquifer.

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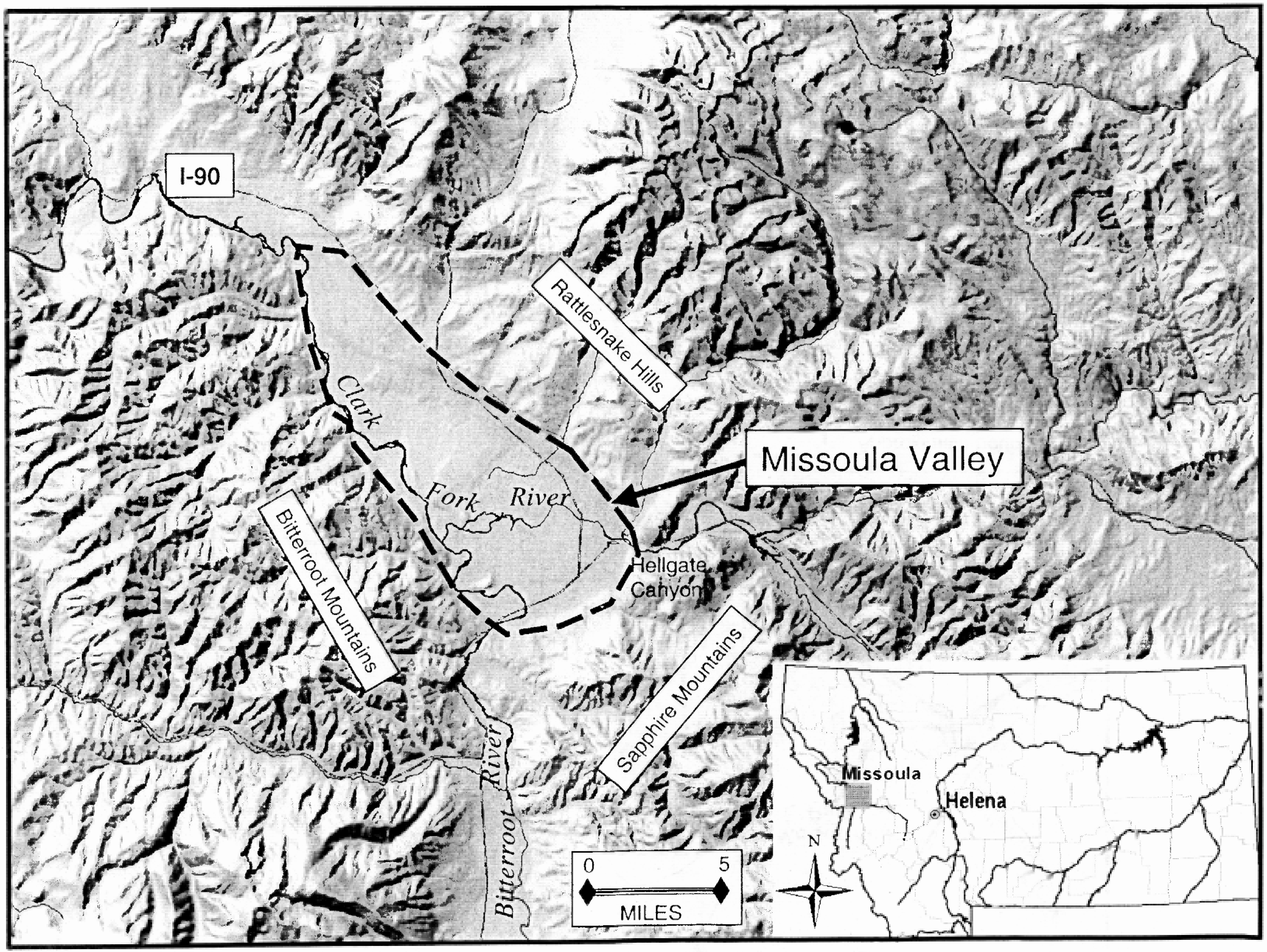

Figure 1. The Missoula Valley is located in southwest Montana near the confluence of the Clark Fork and Bitterroot rivers.

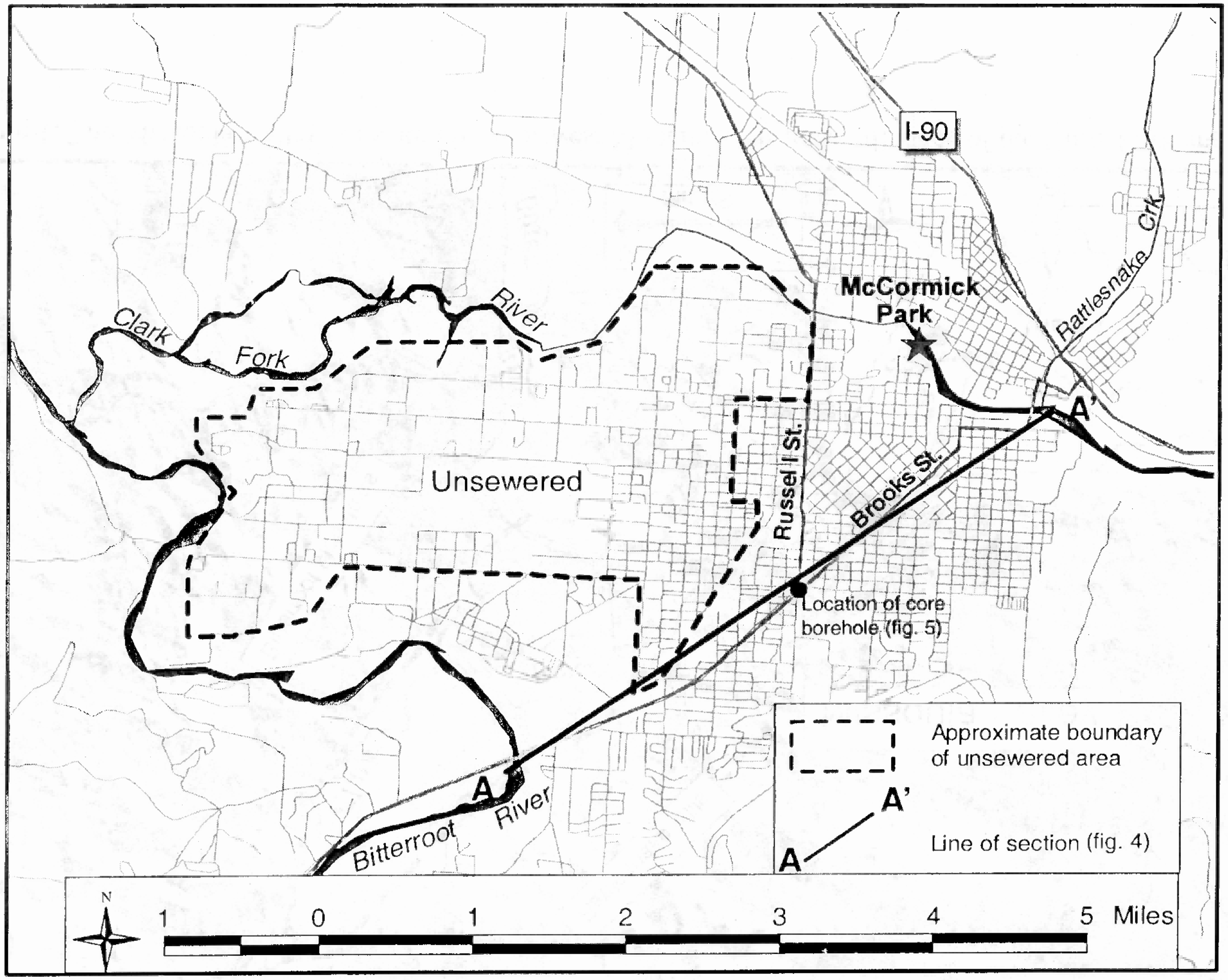

Figure 2. The study area includes the part of the basin between the Clark Fork and Bitterroot Rivers; land use is predominately urban and residential. A large part of the study area is not serviced by municipal sewer.

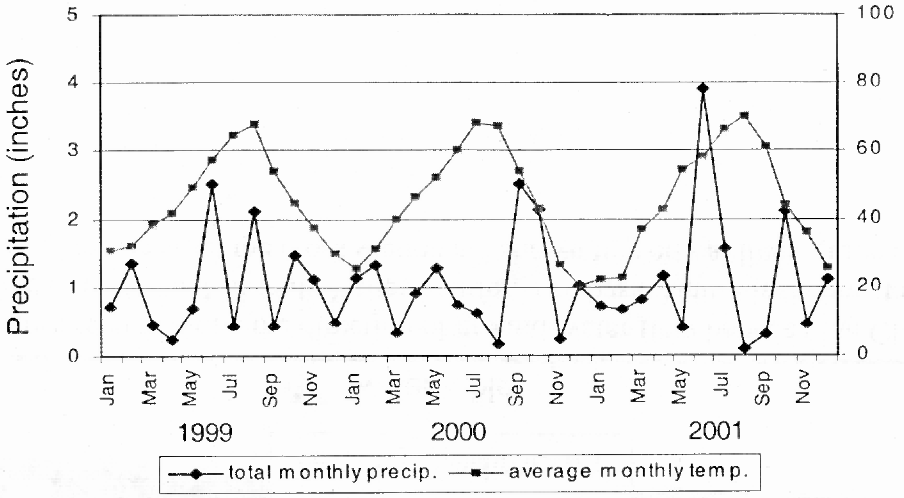

Figure 3. Monthly temperature averages and rainfall totals recorded at the Missoula airport during the study period.

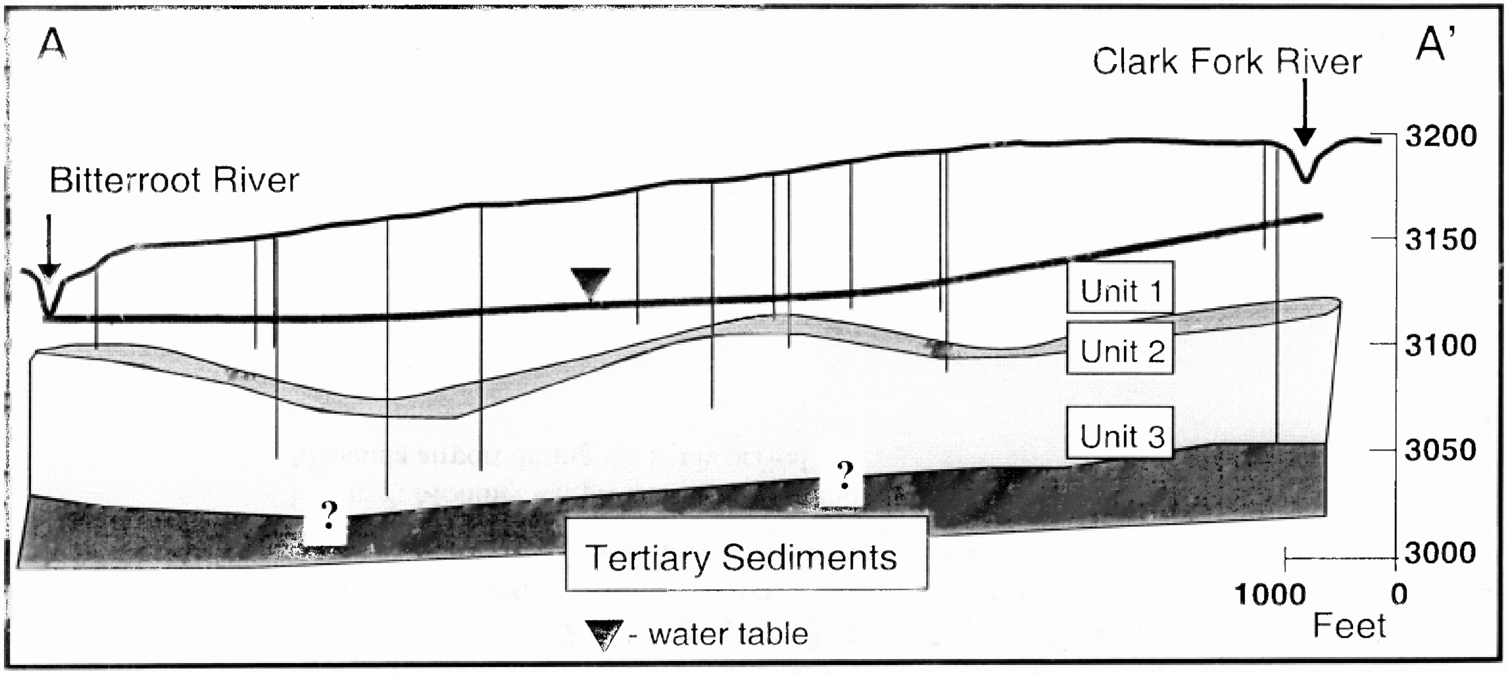

Figure 4. Generalized cross section along the direction of ground-water flow between the Clark Fork and Bitterroot Rivers, showing the three units of the Missoula Valley aquifer. The basal Unit 3 is the most productive part of the aquifer. Borehole data used to construct the cross section are shown by vertical lines. (Line of section A-A' is shown on figure 2.)

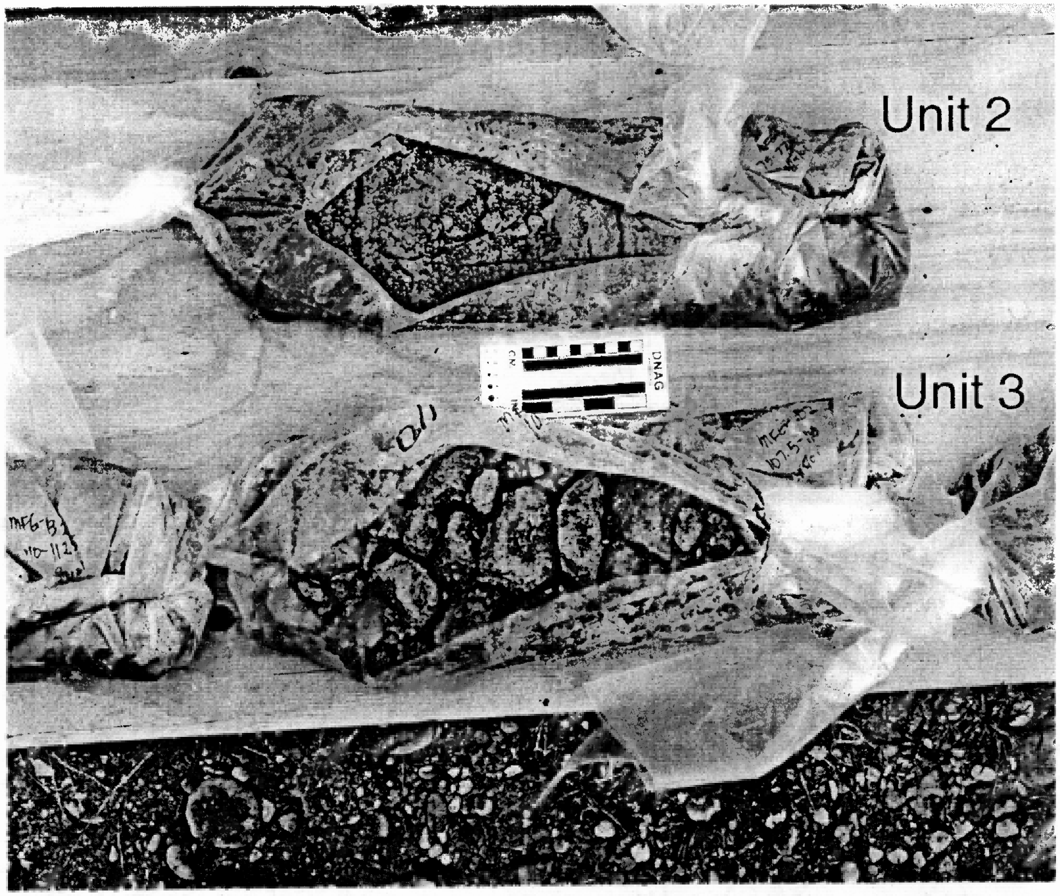

Figure 5. Photograph of core samples showing the fine sand of Unit 2, and the coarse gravels and cobbles of Unit 3. Core came from borehole drilled near the intersection of Russell and Brooks Streets (figure 2). Unit 2 sample is from 75 to 77 feet below land surface. Unit 3 sample is from 107.5 to 110 feet below land surface.

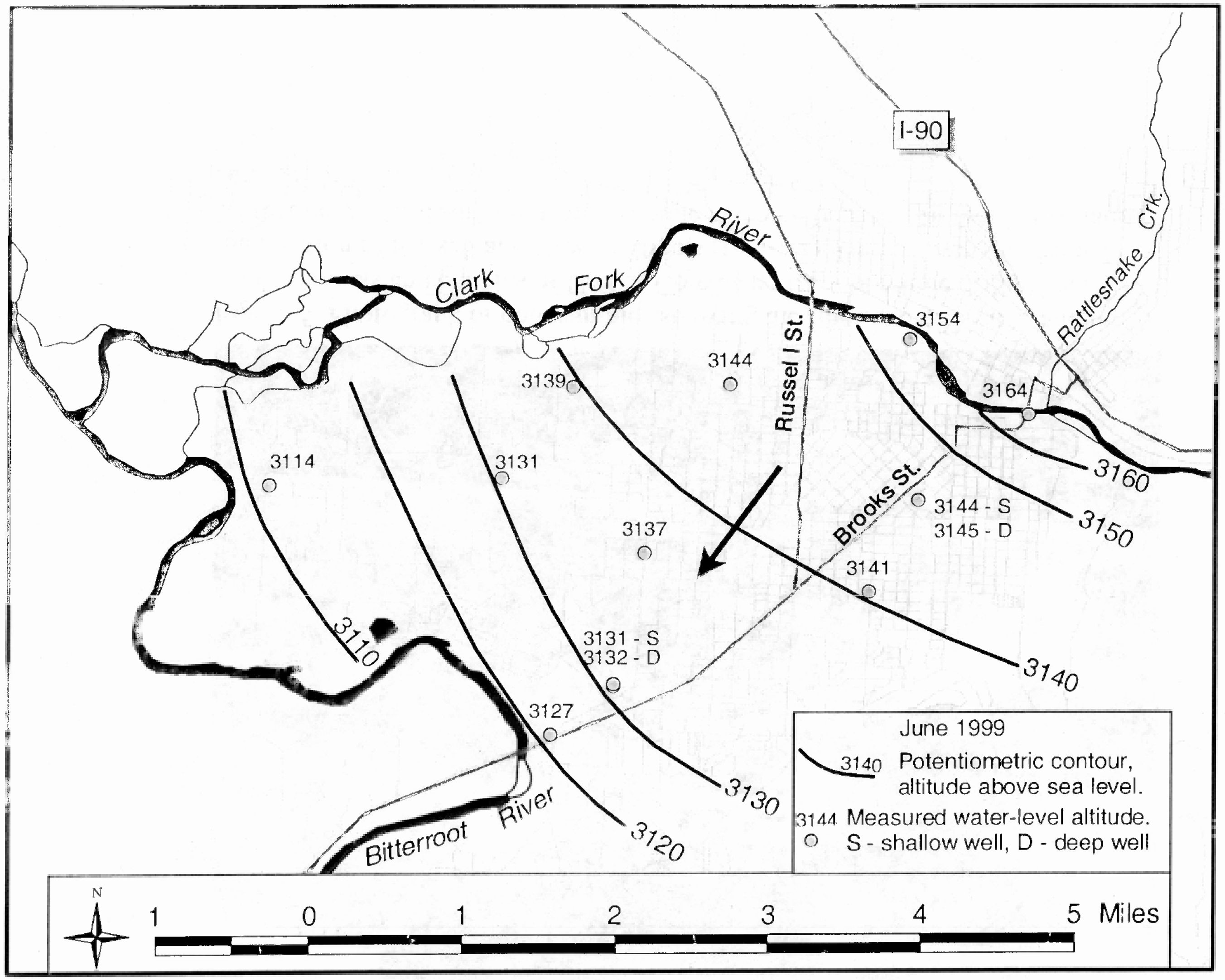

Figure 6a. Potentiometric surface of the Missoula Valley aquifer, June 1999. Ground-water flows to the southwest (arrow), roughly parallel to Brooks St., between the Clark Fork and Bitterroot Rivers.

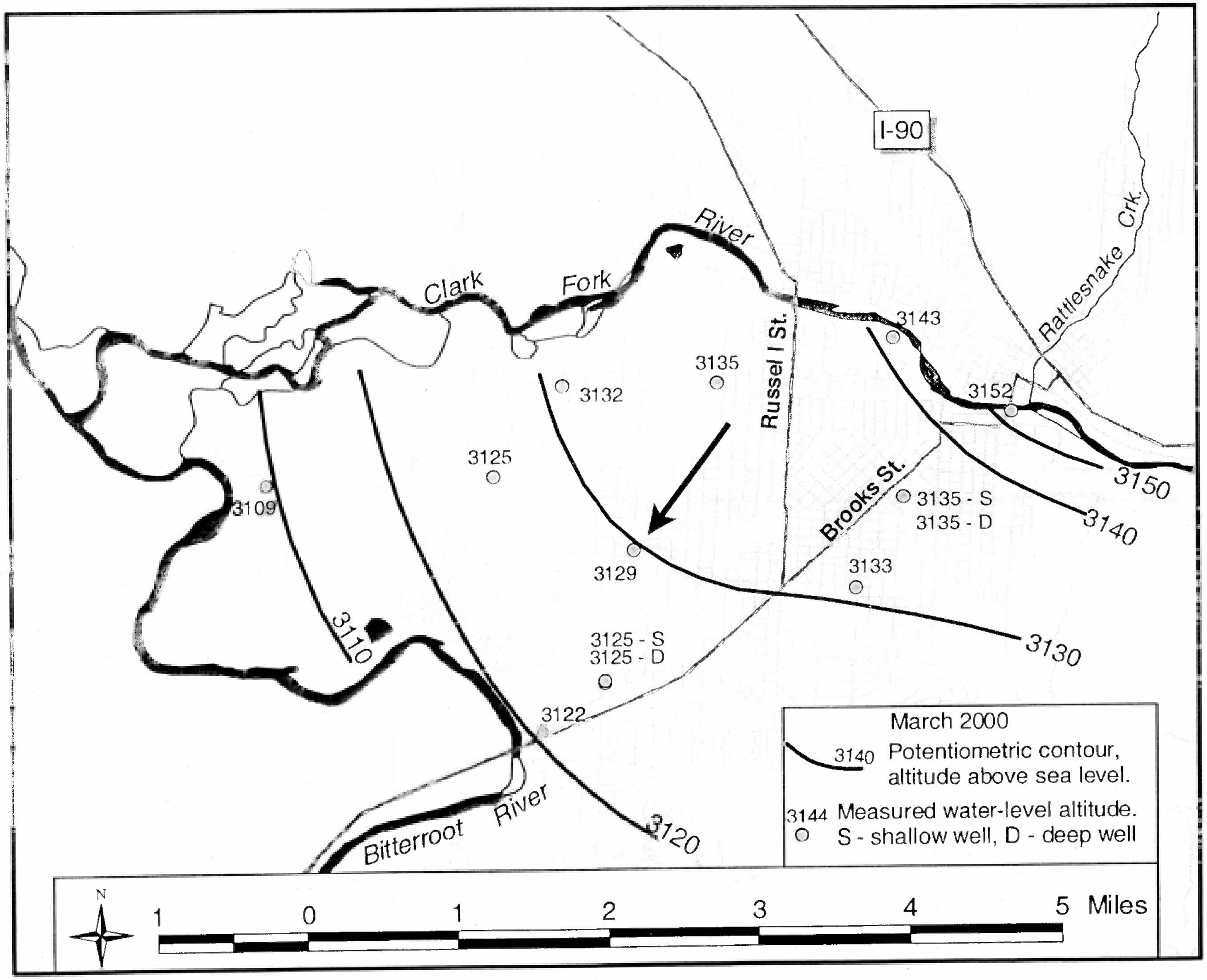

Figure 6b. Potentiometric surface of the Missoula Valley aquifer, March 2000. Ground-water flow direction (arrow) was similar to June 1999, however water levels were lower and the hydraulic gradient across the area was slightly less.

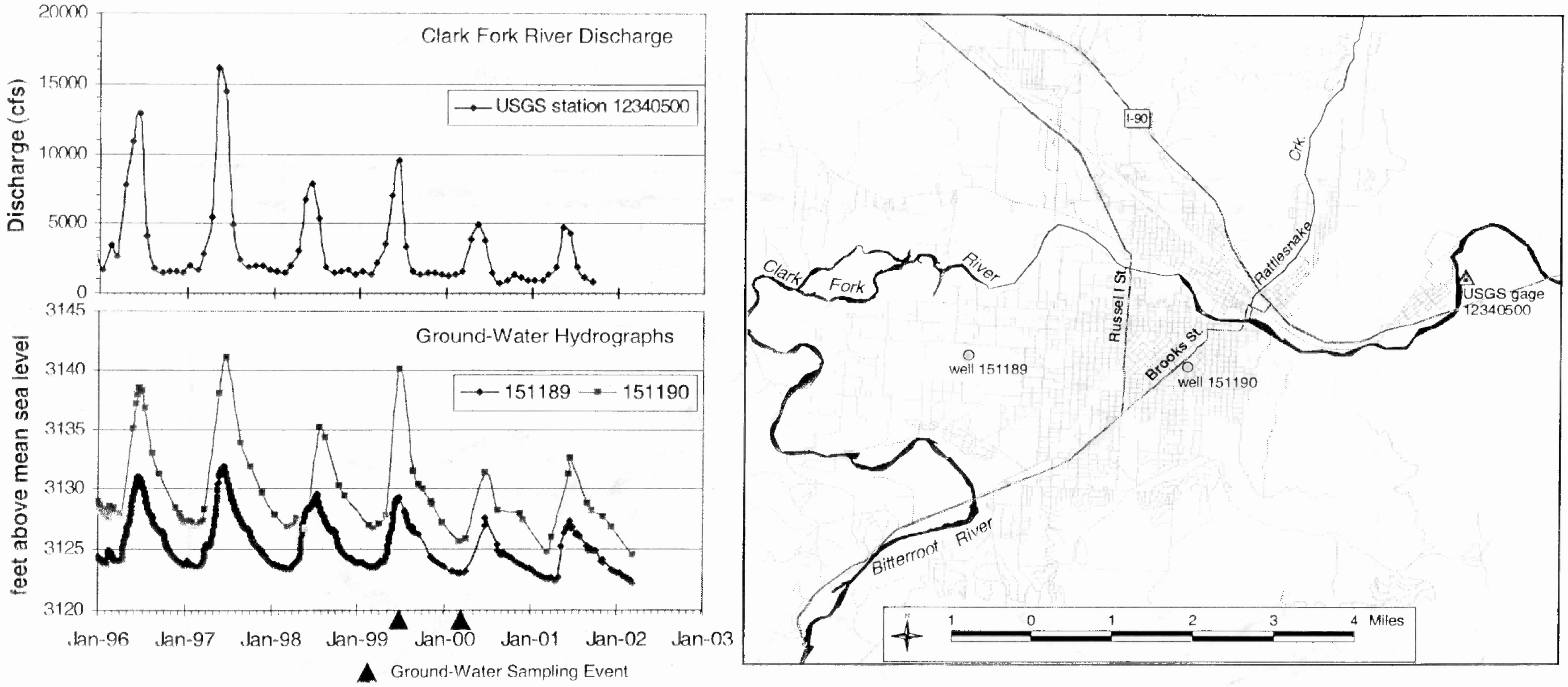

Figure 7. Ground-water levels in the Missoula Valley aquifer closely follow variations in the Clark Fork River discharge highlighting the interconnection of the surface and ground water. Major ground-water sampling events occurred during peak and low flow periods.

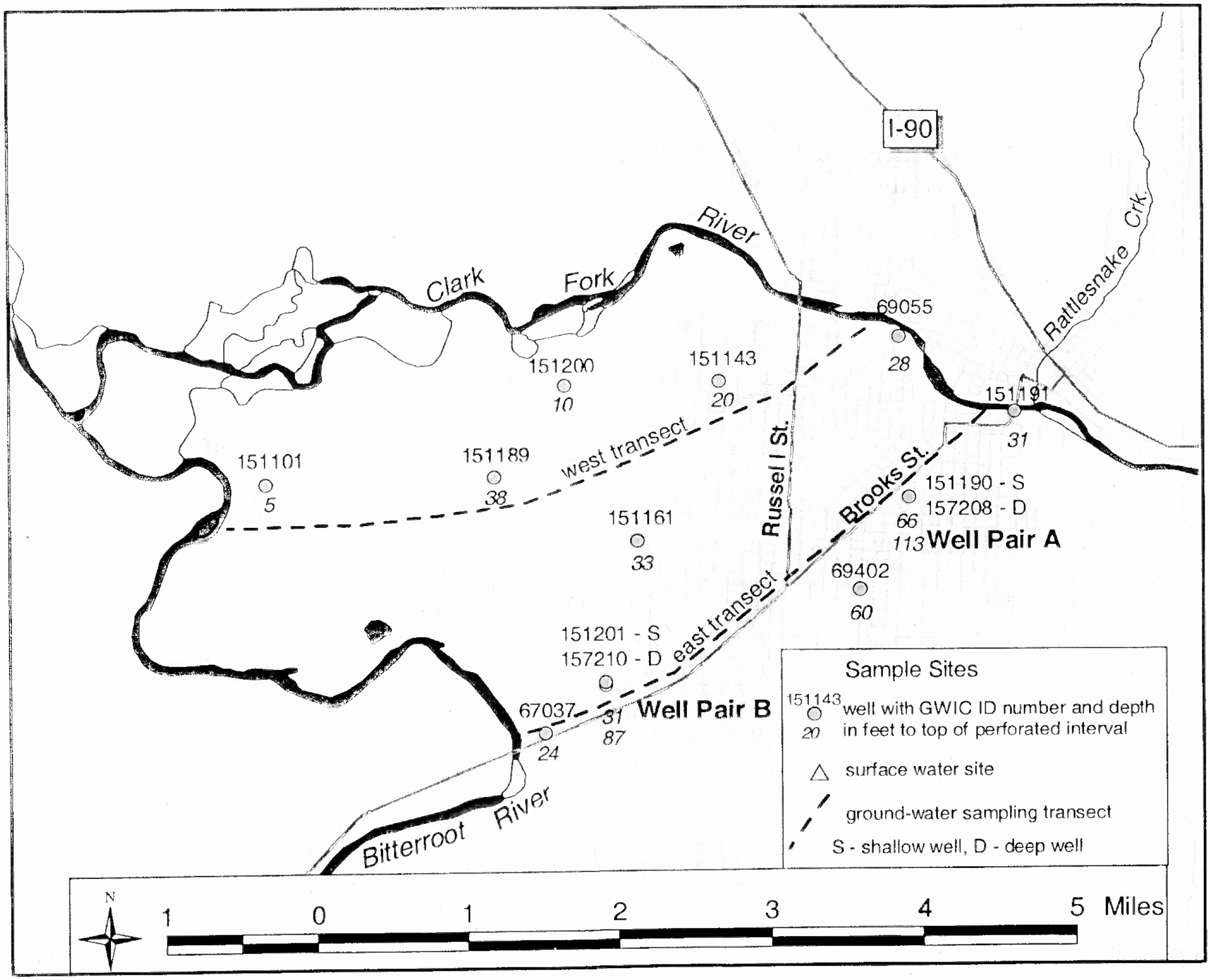

Figure 8. Ground-water samples were collected from monitor wells located along two transects of ground-water flow, surface water samples were collected near the boat ramp at McCormick Park. Ground Water Information Center (GWIC) identification numbers and depths to the top of perforated intervals are shown.

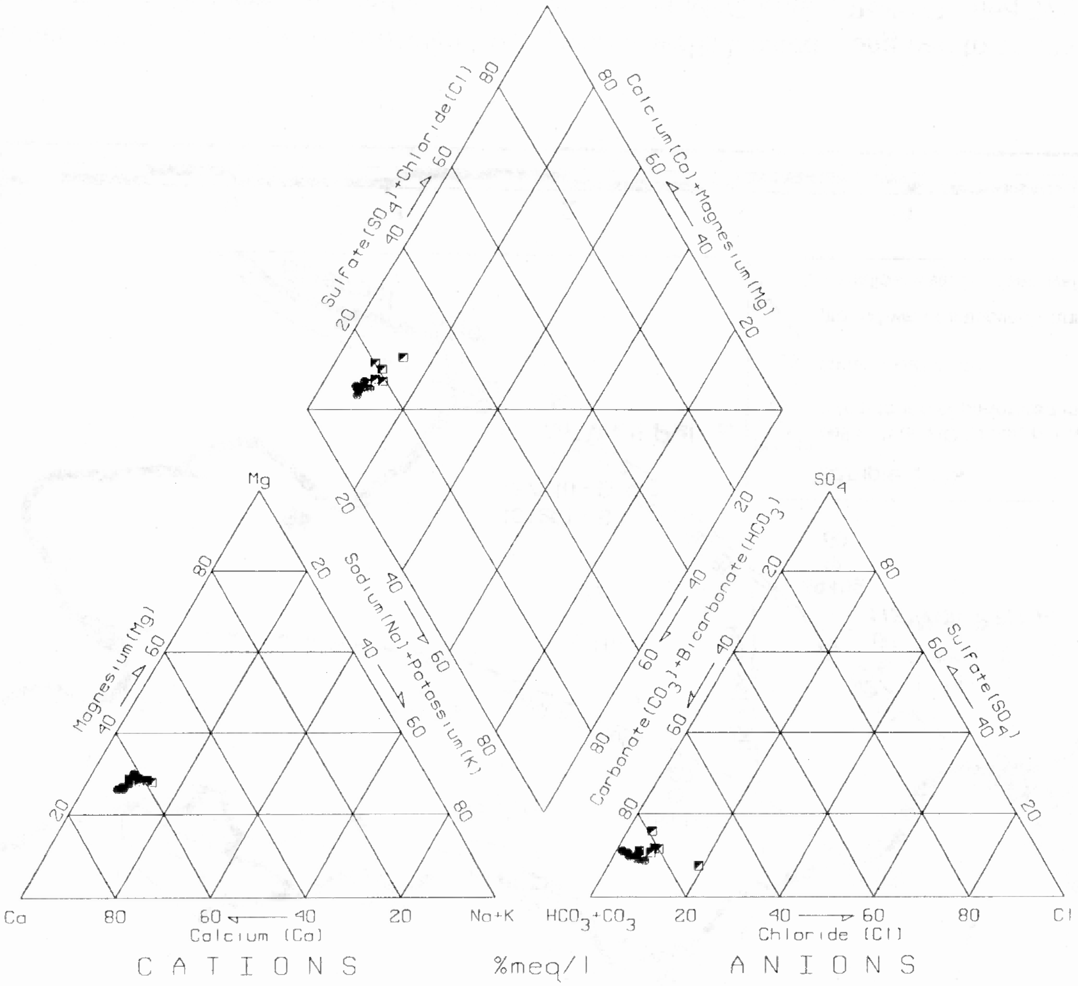

Figure 9. The Missoula Valley aquifer contains a consistent calcium-bicarbonate type water. Samples collected in June, 1999; squares represent data from the Missoula Valley Water Quality District.

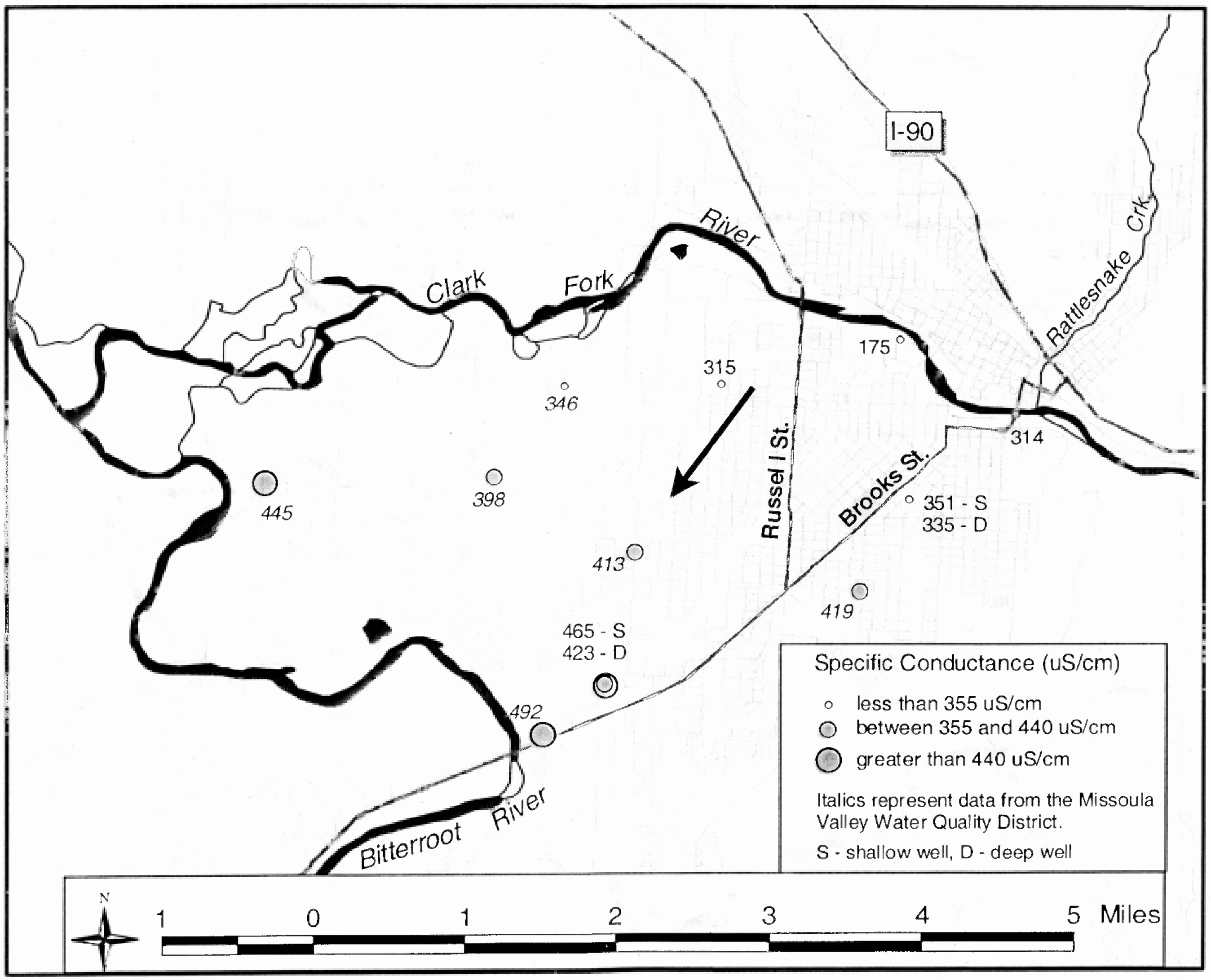

Figure 10. The distribution of specific conductance shows that the concentration of dissolved solids in the aquifer increases along ground-water flow path (arrow) between the Clark Fork and Bitterroot Rivers.

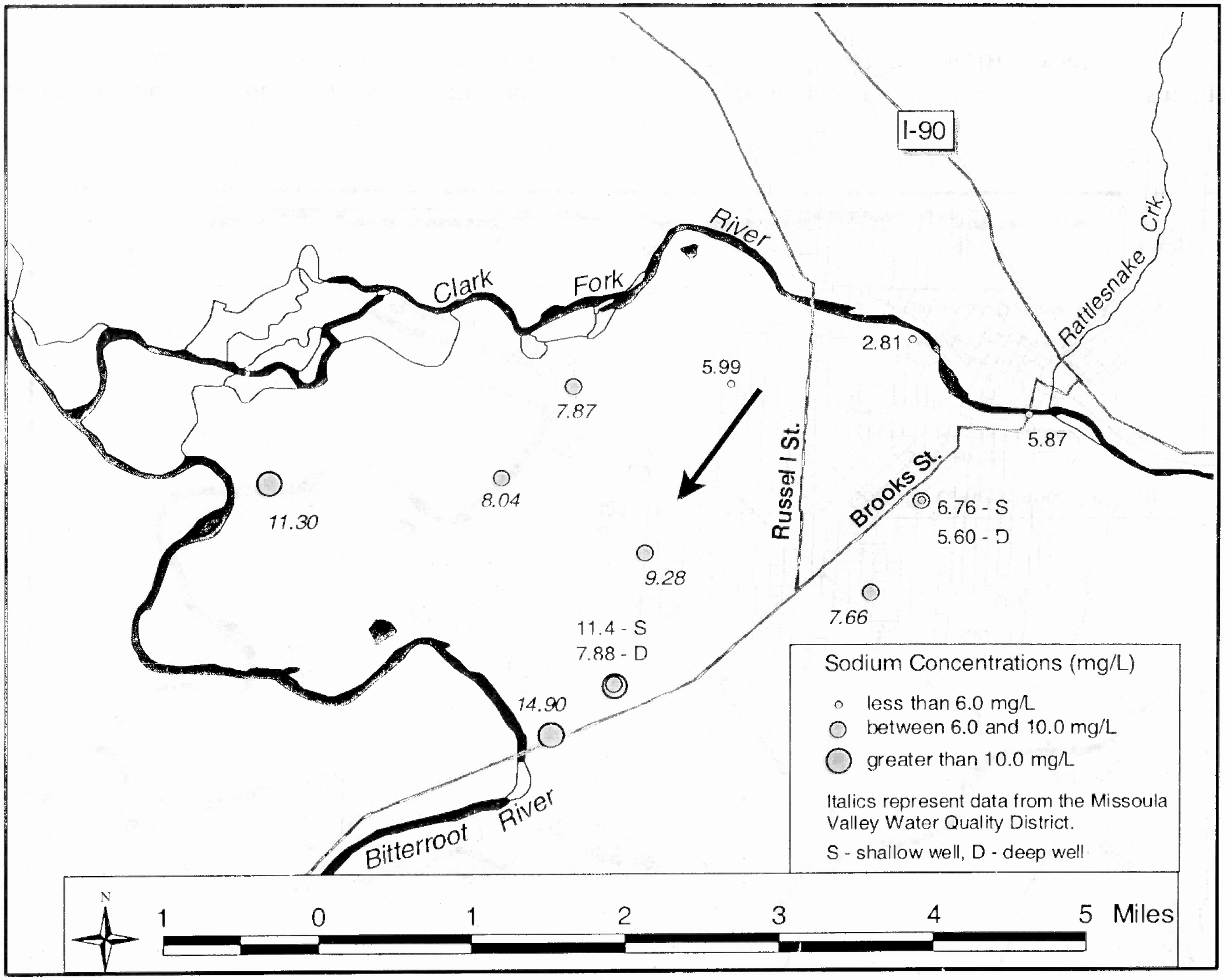

Figure 11. The concentration of sodium in the aquifer increases along ground-water flow path (arrow) between the Clark Fork and Bitterroot Rivers.

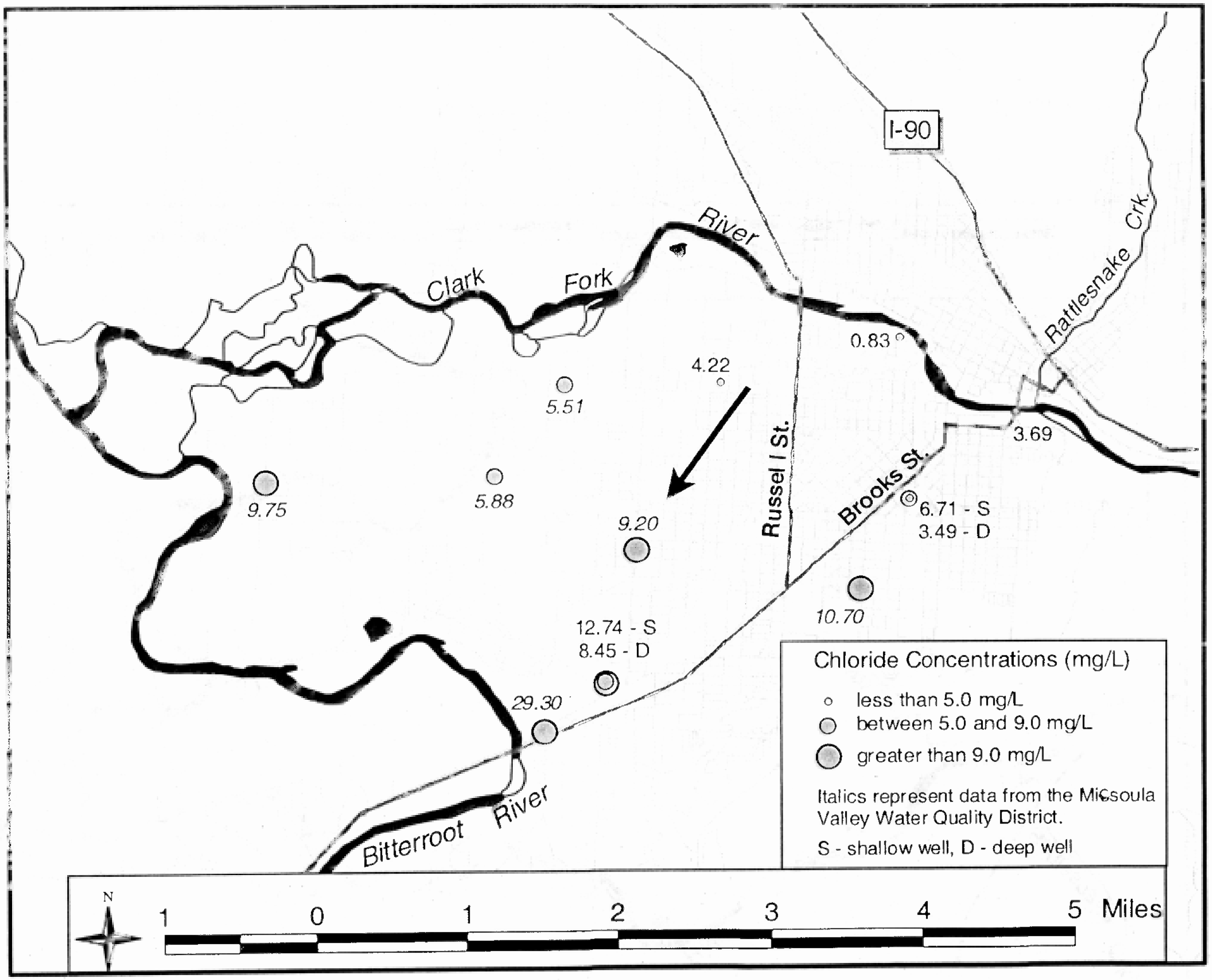

Figure 12. The concentration of chloride in the aquifer increases along the ground-water flow path (arrow) between the Clark Fork and Bitterroot Rivers.

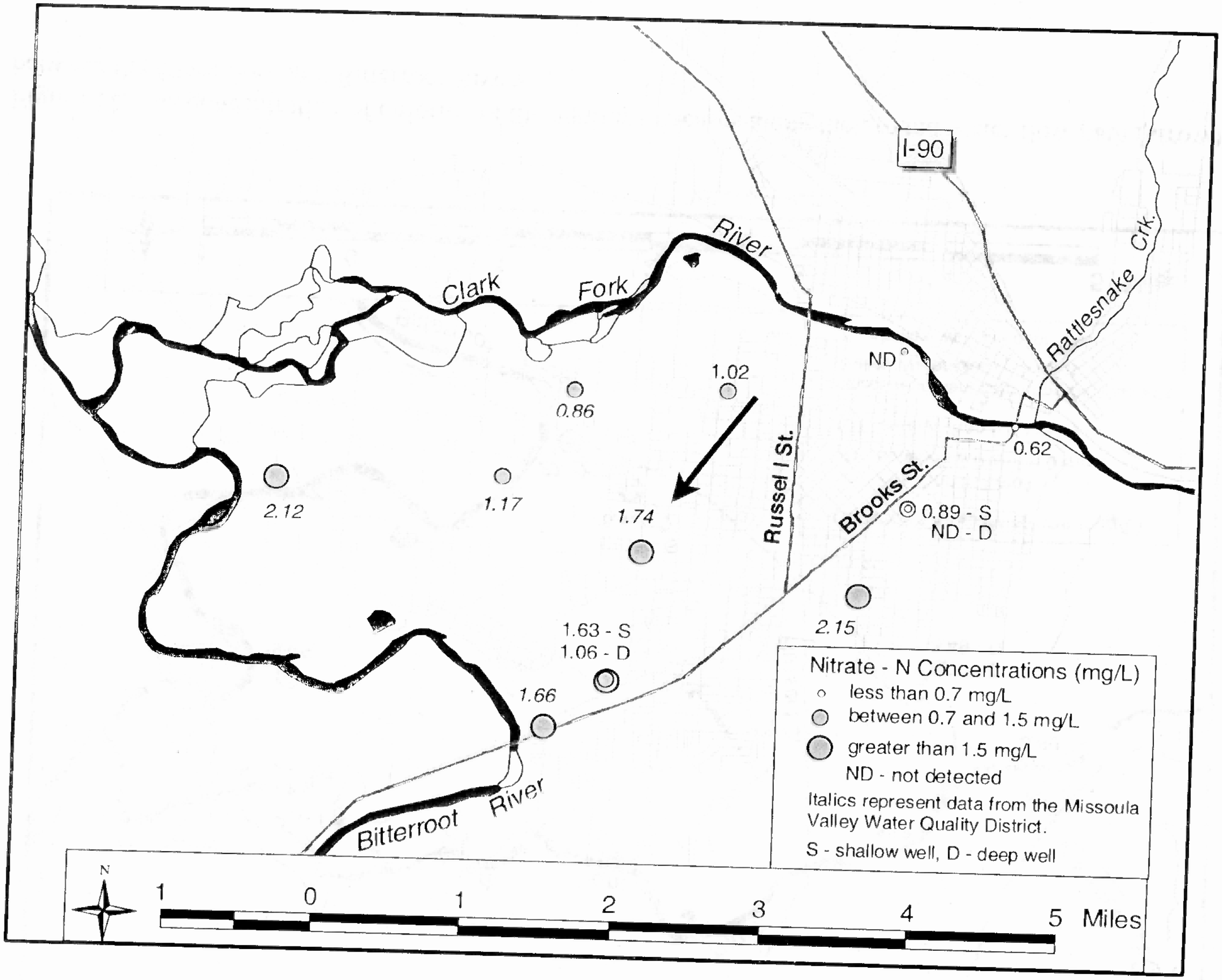

Figure 13. The concentration of nitrate in the aquifer increases along ground-water flow path (arrow) between the Clark Fork and Bitterroot Rivers.

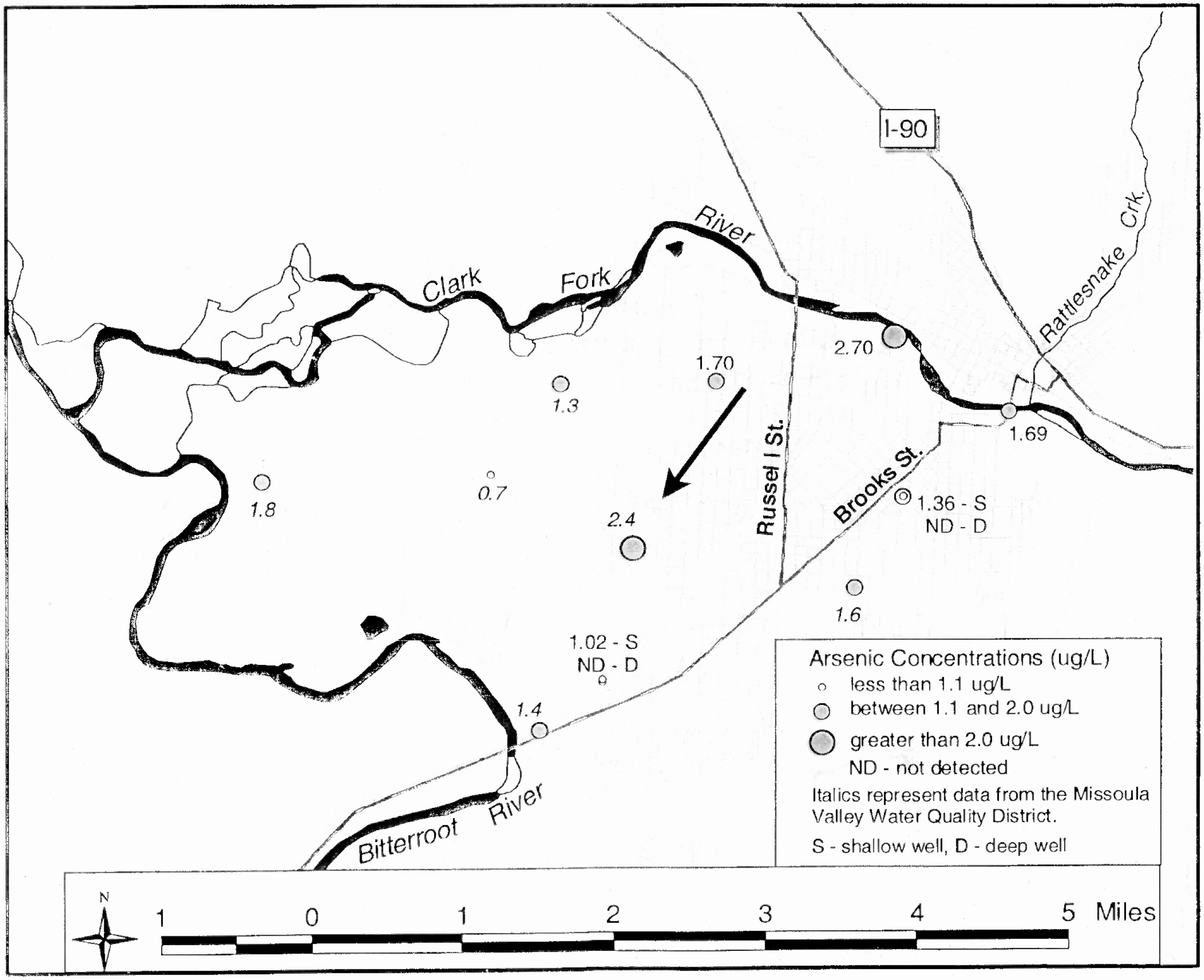

Figure 14. Arsenic concentrations (shown in micrograms per liter) in the upgradient part of the aquifer are slightly greater than concentrations near the end of the flow system. Arrow shows direction of ground-water flow.

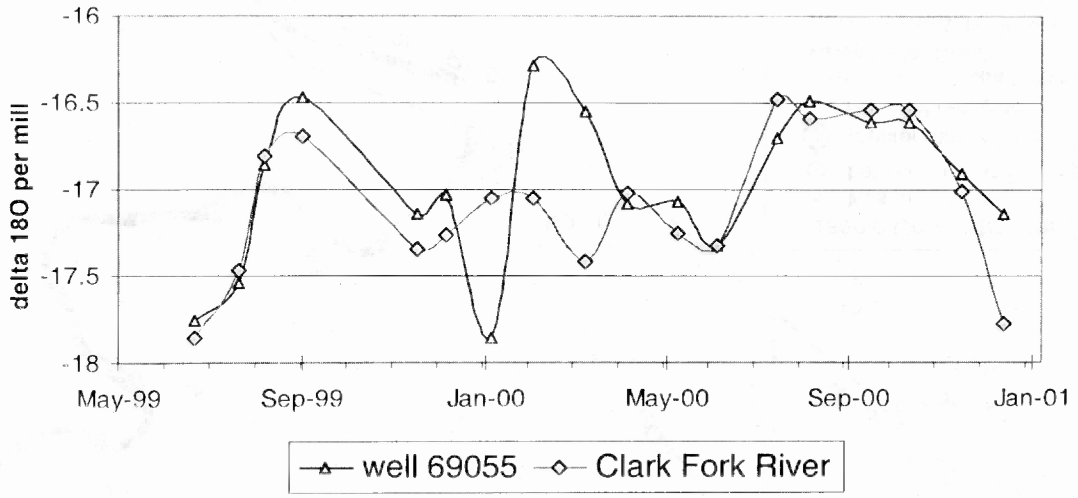

Figure 15. The $\delta^{18}O$ in the ground water (well 69055) tracks the surface water fairly closely. The values are generally more enriched during the warmer months. The variation in the well signal for Jan.- March 2000 is unexplained.

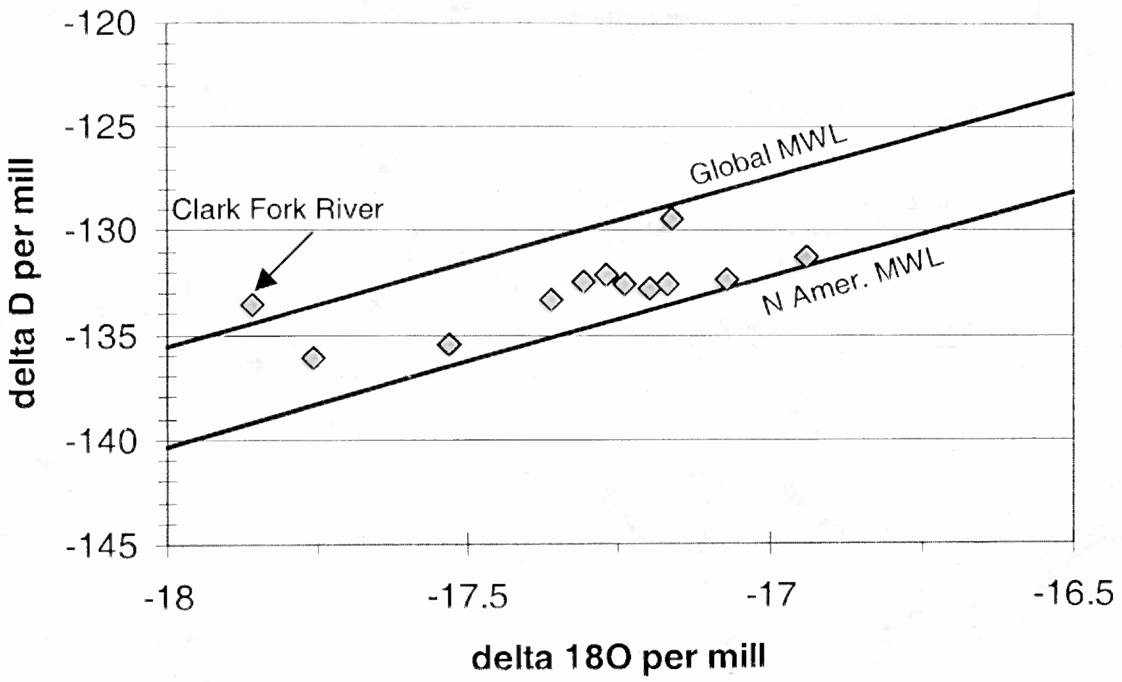

Figure 16. The $\delta^{18}O$ and δD of the June 1999 surface and ground-water samples plot along the global and North American meteoric water lines (MWL's).

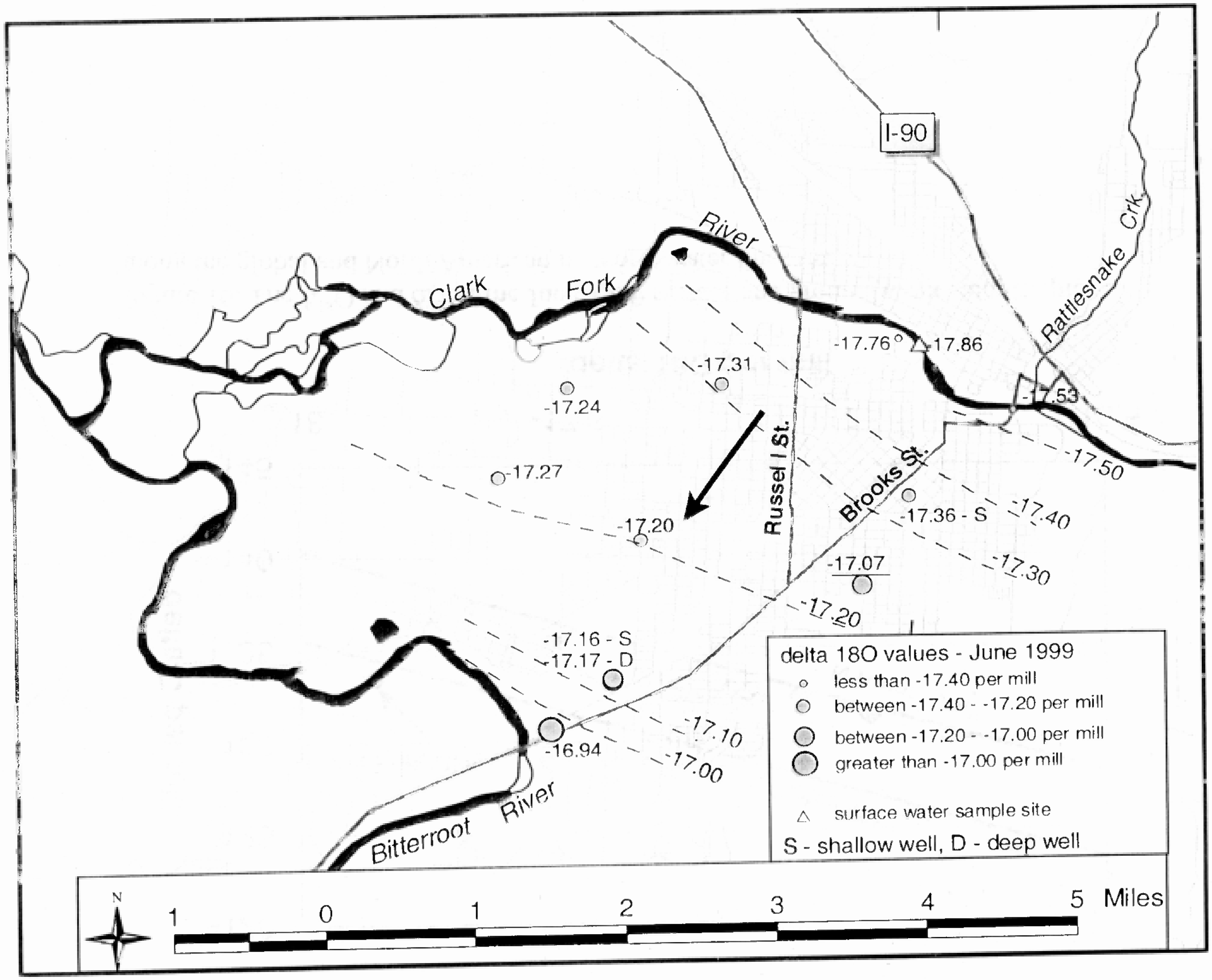

Figure 17. The $\delta^{18}O$ values from the June 1999 samples become enriched along the ground-water flow path (arrow).

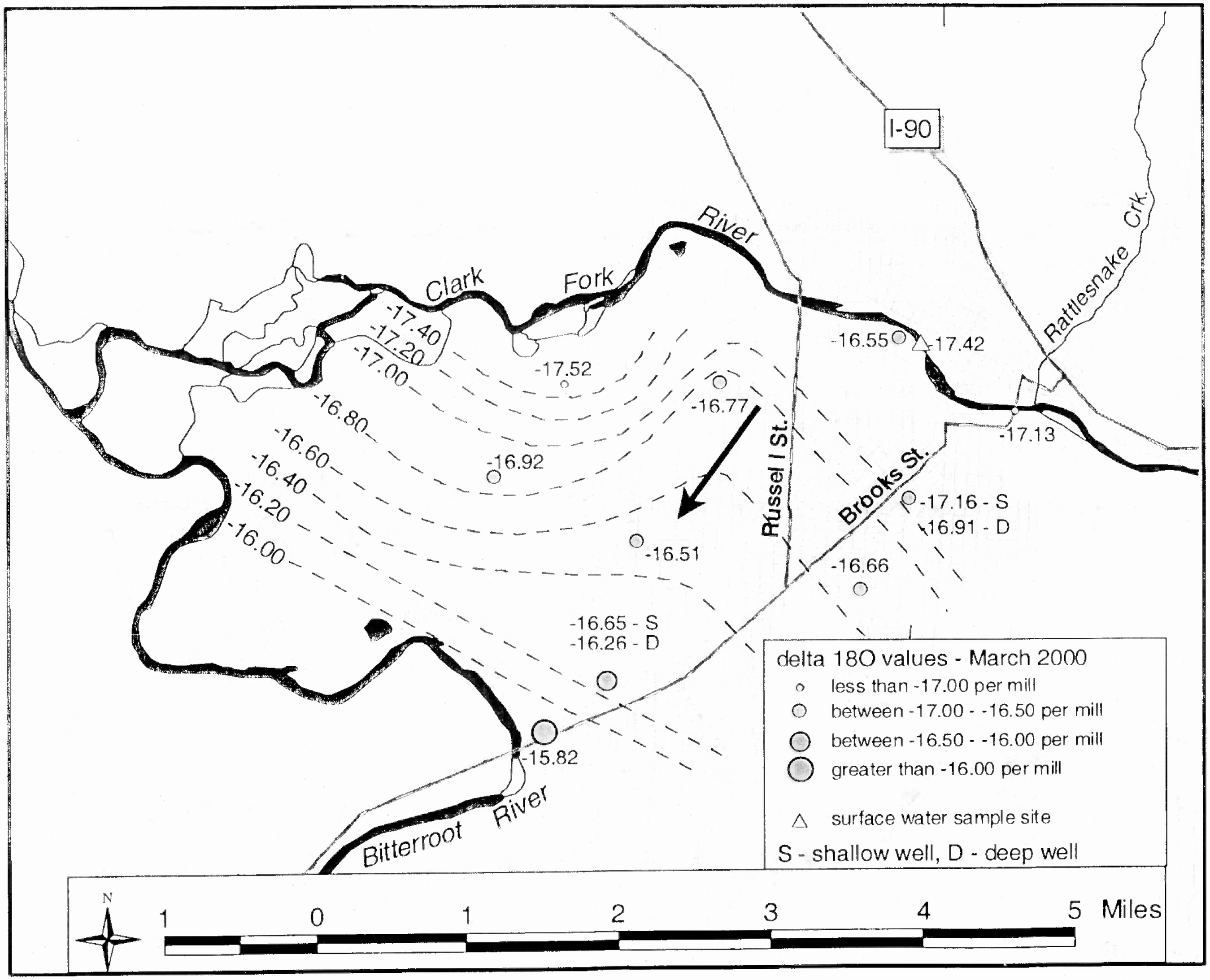

Figure 18. The $\delta^{18}O$ values from March 2000 are enriched relative to the June 1999 samples and the concentration gradient is greater (Figure 17). Arrow shows the direction of ground-water flow.

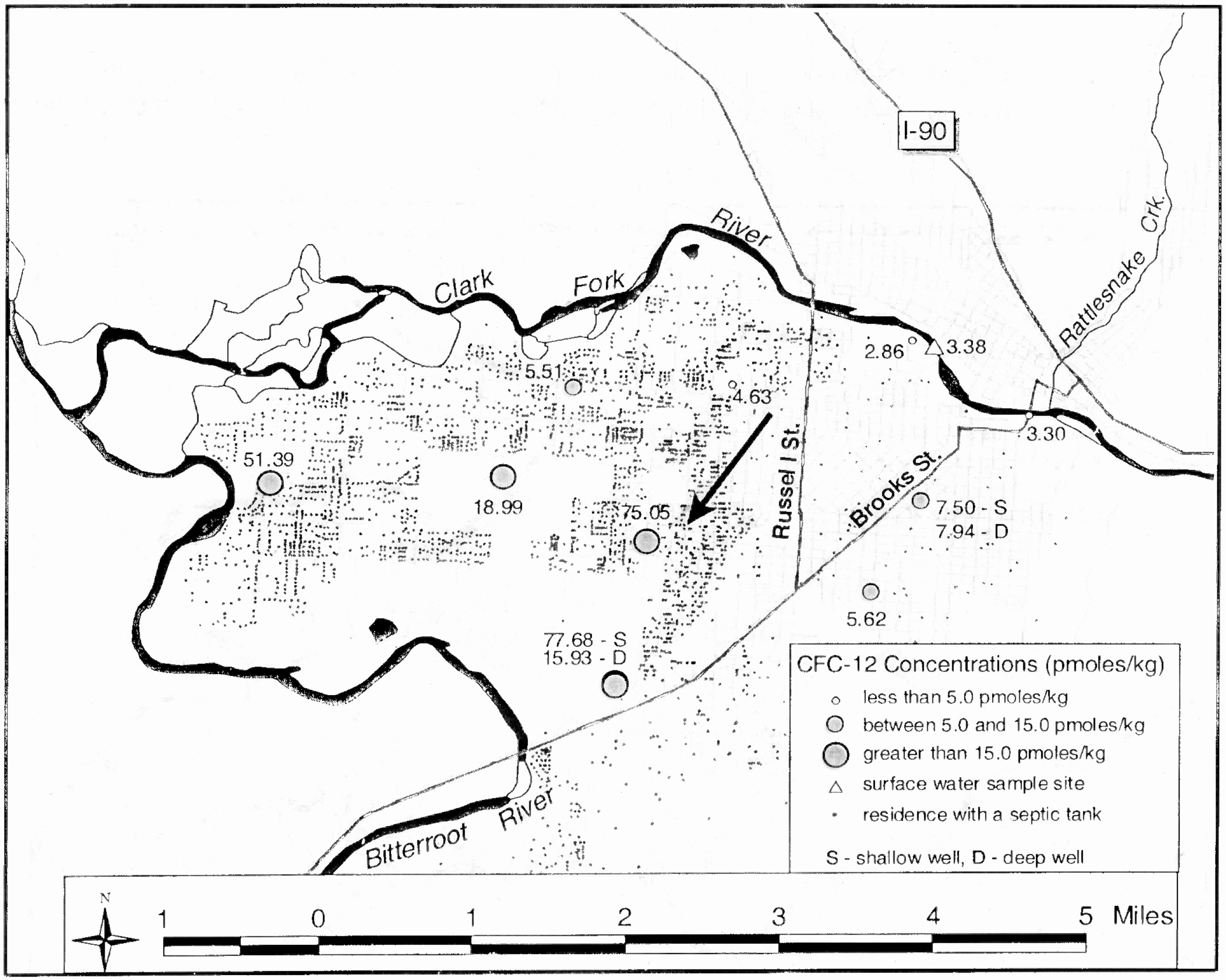

Figure 19. The ground-water concentrations of CFC-12 increase markedly in areas downgradient (arrow) of high density septic areas. (Septic tank location data from the Missoula Valley Water Quality District)

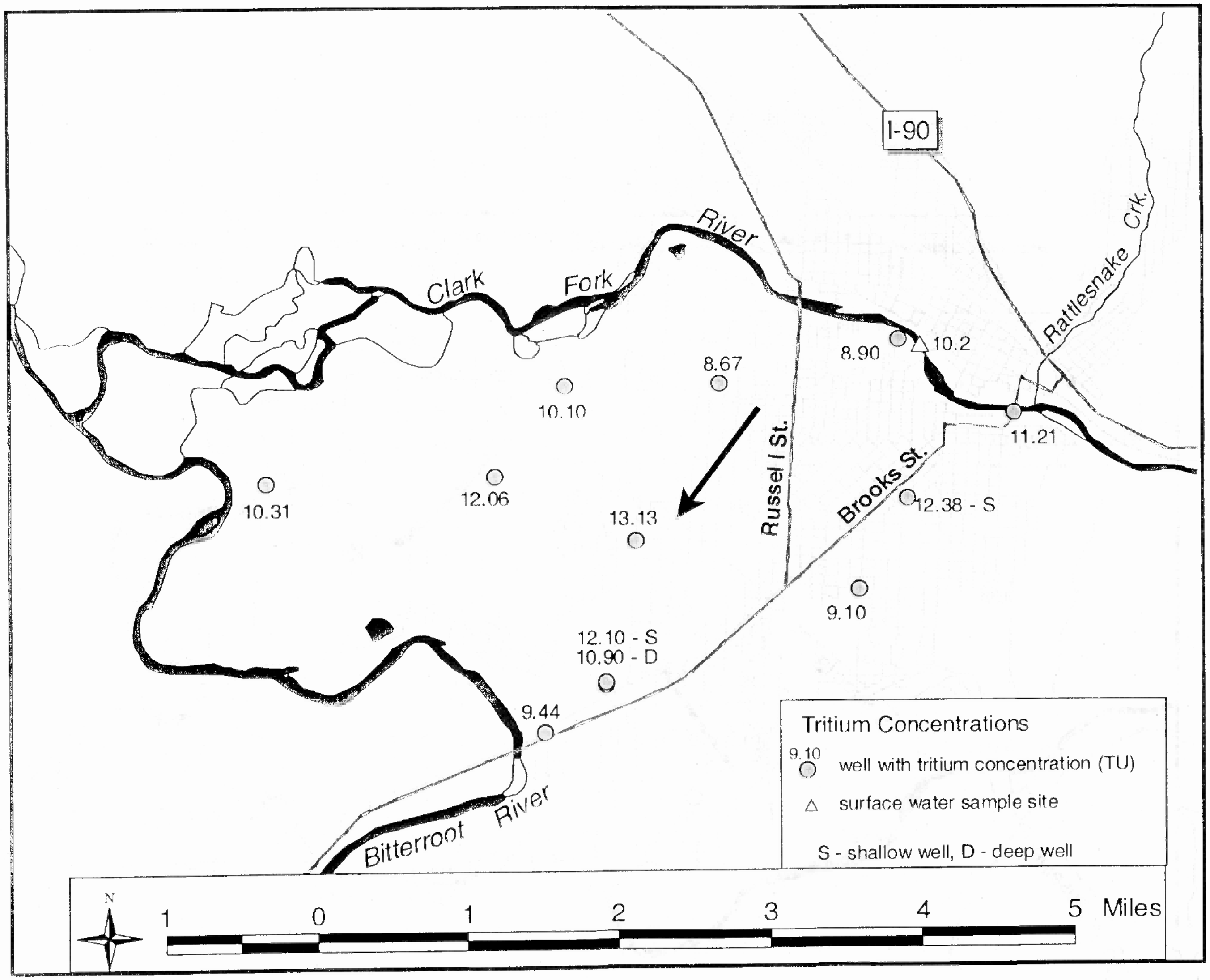

Figure 20. Tritium concentrations are fairly uniform through the aquifer. Arrow shows the direction of ground-water flow.

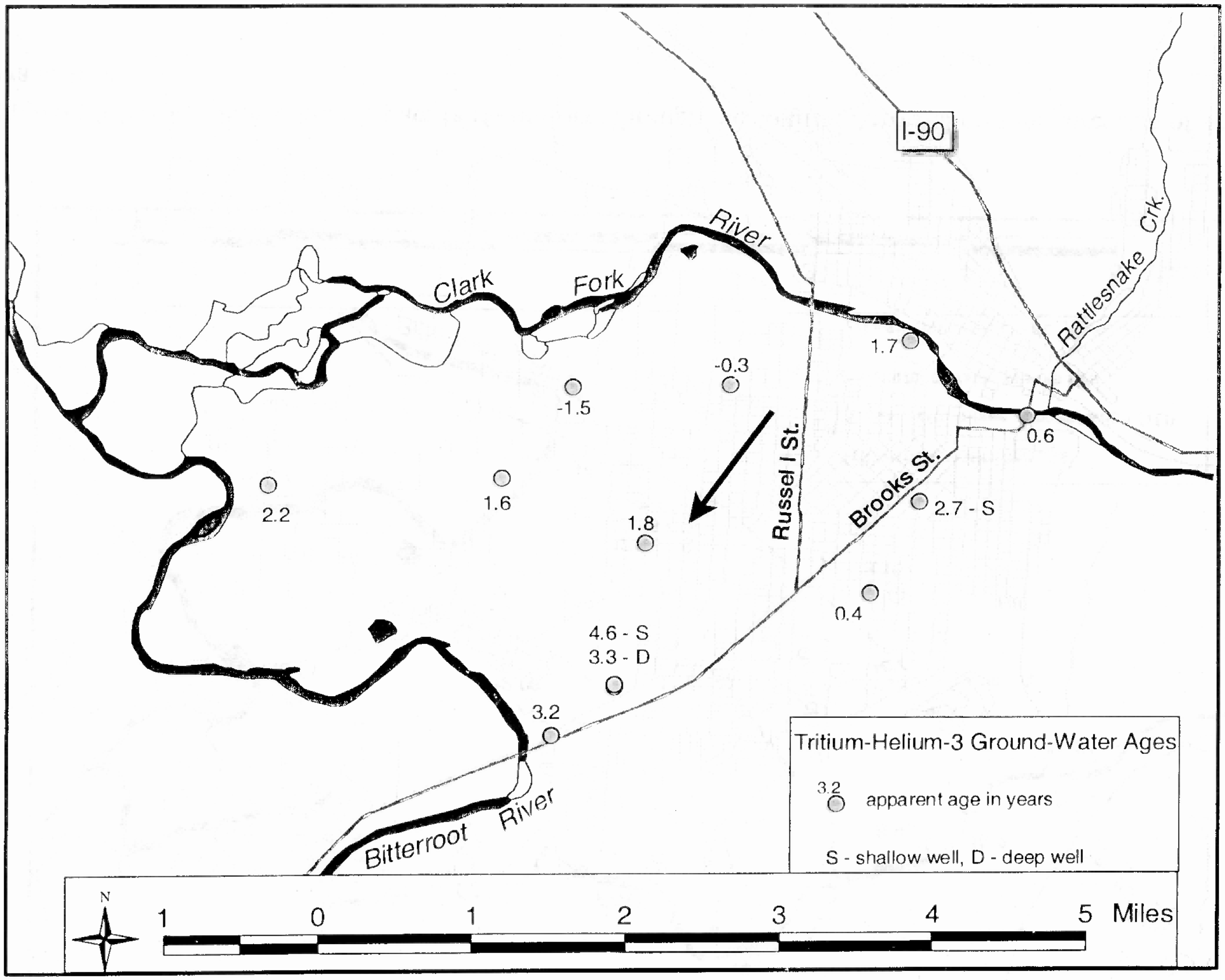

Figure 21. In general, the $^3H/^3He$ apparent ages increase along the ground-water flow path (arrow). For an explanation of negative ages see text.

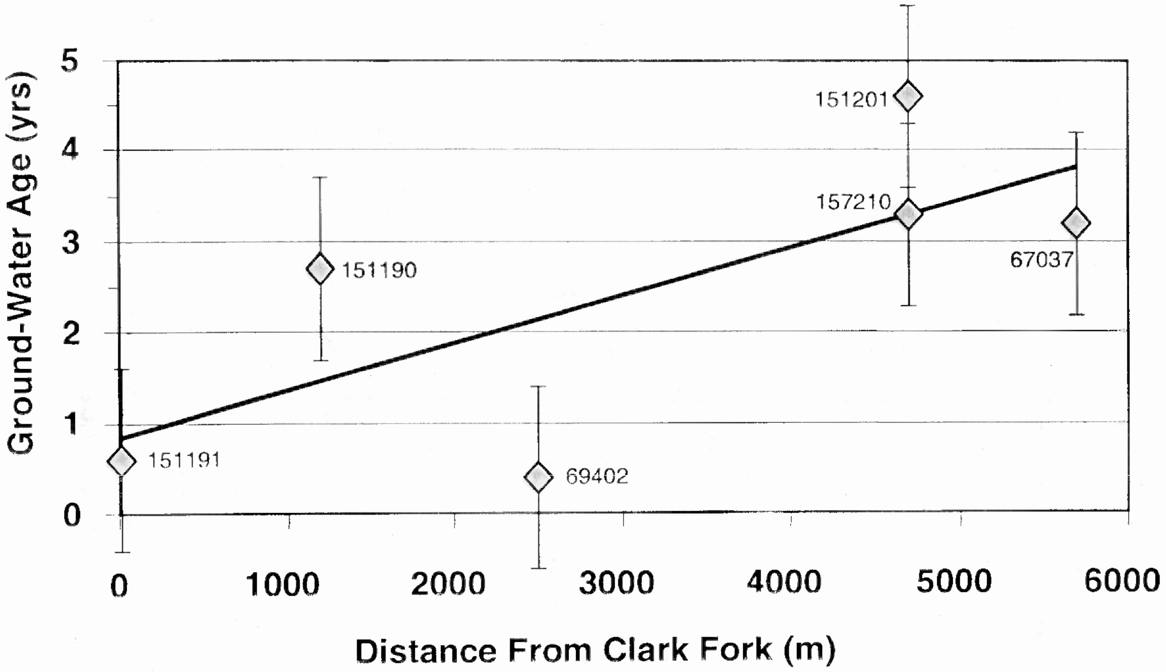

Figure 22. In general, apparent $^3H/^3He$ ages increase with distance from Clark Fork River along the east transect. GWIC identification numbers and error bars are shown.

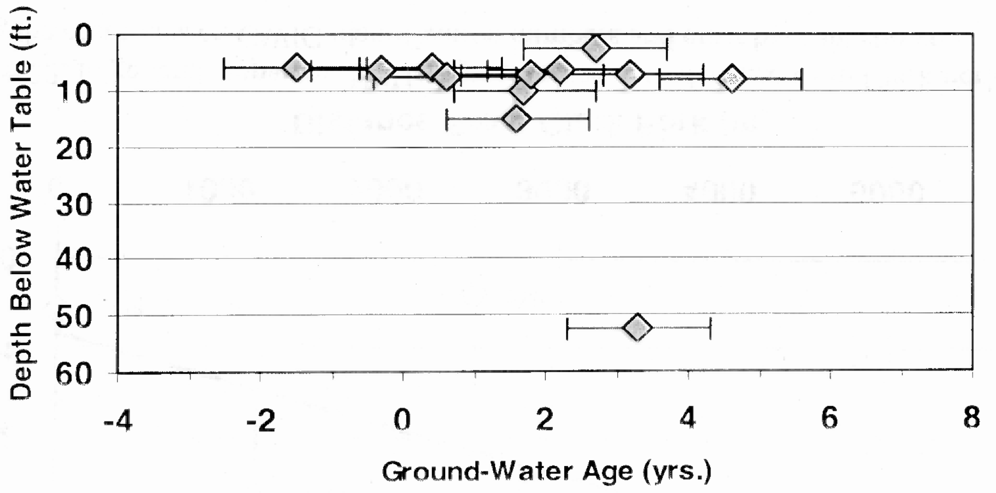

Figure 23. Most of the samples for $^3H/^3He$ age dating were collected within 10 feet of the water table, there were no apparent trends in ground-water age with depth. Error bars are shown.

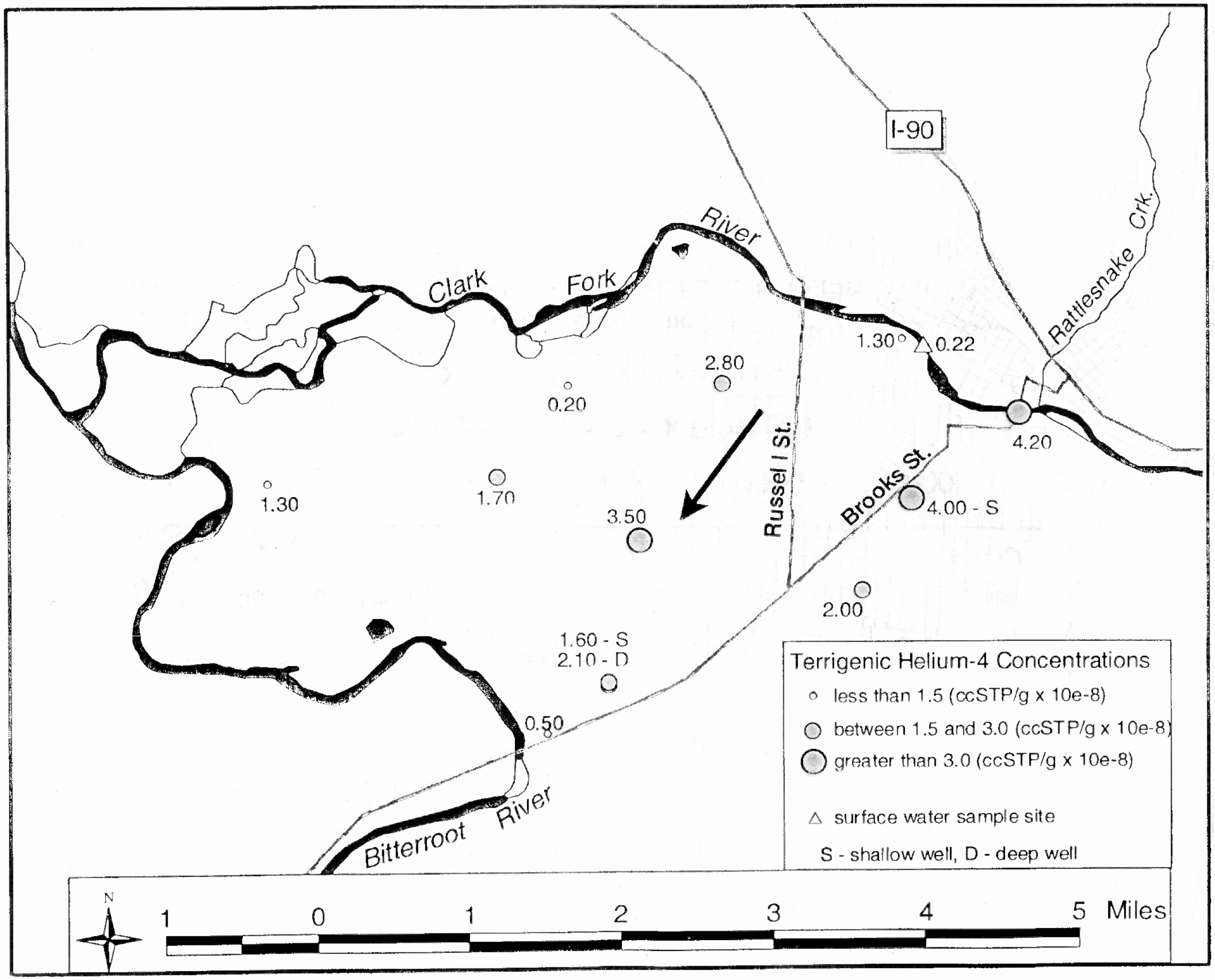

Figure 24. Elevated concentrations of terrigenic ^{4}He occur in the upgradient part of the flow system. Arrow shows the direction of ground-water flow.

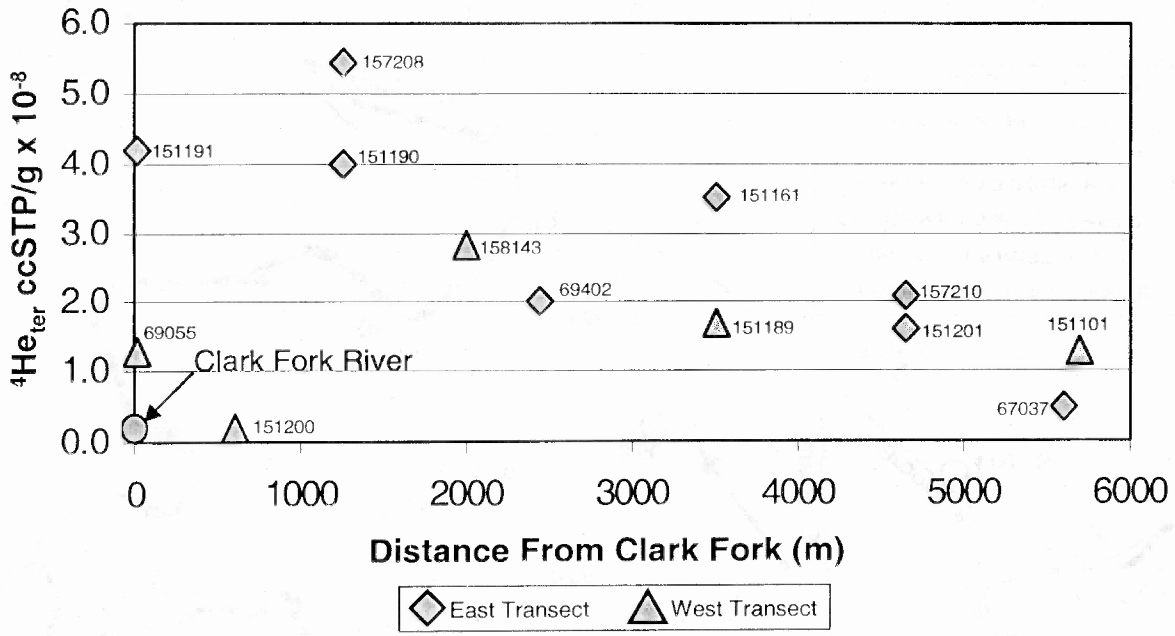

Figure 25. Plot of terrigenic ^{4}He with distance from the Clark Fork River. In general, terrigenic ^{4}He decreases with distance from the Clark Fork, down flow path. GWIC identification numbers are shown.

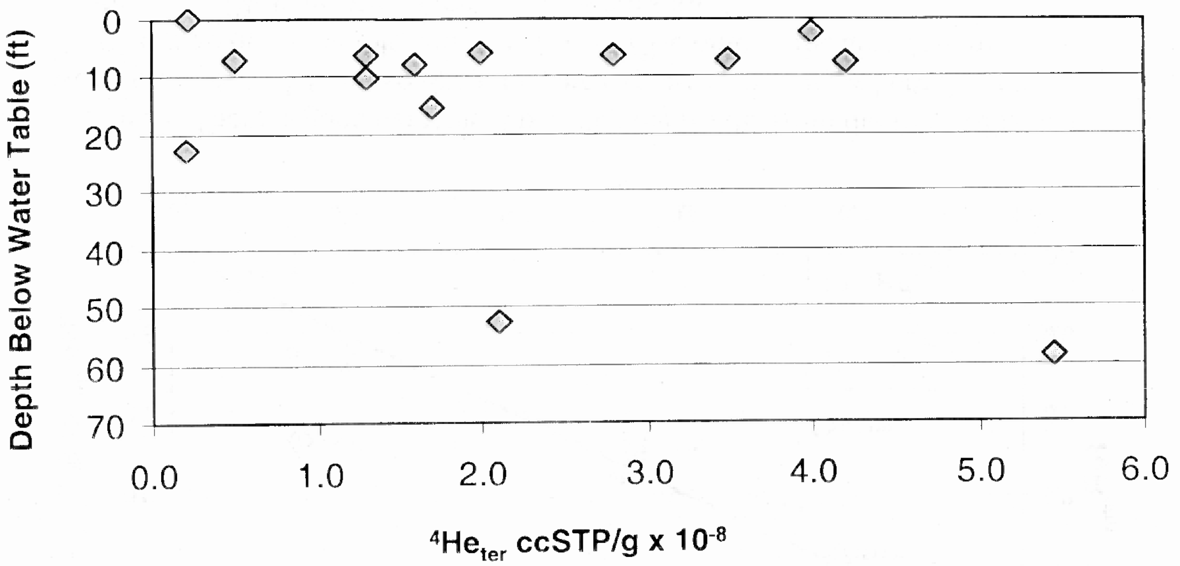

Figure 26. There are no clear trends in the terrigenic ^{4}He concentrations with depth below the water table.

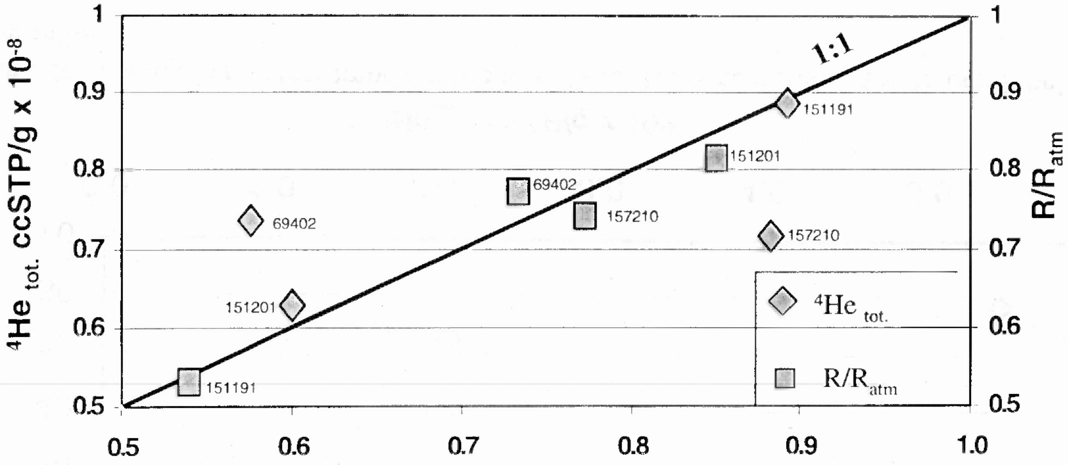

Figure 27. There is good agreement between the results from the four wells that were resampled. Helium isotope ratios are expressed as R/R_a, where R is the $^3He/^4He$ ratio of the sample and R_a is the $^3He/^4He$ ratio of the air standard ($1.36x10^{-6}$). GWIC identification numbers are shown.

Table 1. Well records, sample site information, and water-level data, Missoula Valley Montana.

Site ID	Longitude	Latitude	Site Name	Water Quality District Number	Township	Range	Sec.	Tract	Altitude mp (ft above sea level)	Total Depth (ft)	Top of open interval (ft below land surface)	Bottom of open interval (ft below land surface)
67037	-114.0508	46.8334	Buckhouse Bridge	WQD-35 U122001A	12N	20W	1	ABAD	3149.09	38	24	36
69055	-114.0023	46.8732	McCormick Park	WQD-30 U131921A	13N	19W	21	DABC	3179.29	57	28	48
69402	-114.0072	46.8491	South/Bancroft	WQD-32 U131933B	13N	19W	33	BAAA	3193.56	76.3	60	70
151101	-114.0916	46.8558	Humble/Mount	WQD-7 W132026D	13N	20W	26	DBBB	3122.57	25	5	25
151143	-114.0291	46.8680	Emma Dickinson	WQD-10 W131920C	13N	19W	20	CDDA	3165.08	45	20	45
151161	-114.0394	46.8513	C.S.Porter School	WQD-8 W131930D	13N	19W	30	DDDA	3169.67	53	33	53
151189	-114.0597	46.8577	Tower Street (DSL)	WQD-33 U132025D	13N	20W	25	ADAD	3154.43	50	38	48
151190	-114.0021	46.8578	Blaine/Crosby (shallow)	WQD-31 U131928A	13N	19W	28	ACDAA	3204.27	76.3	66	76
151191	-113.9878	46.8666	Madison Street	WQD-29 U131922C	13N	19W	22	CDABD	3191.38	53	31	51
151200	-114.0507	46.8668	Hawthorne School	WQD-5 W131919C	13N	19W	19	CDAAC	3151.14	35	10	35
151201	-114.0426	46.8383	Larchmont (shallow)	WQD-6 W131931D	13N	19W	31	DDBA	3163.19	51	31	51
157208	-114.0021	46.8578	Blaine/Crosby (deep)	WQD-21 W131928A2	13N	19W	28	ACDAA	3204.10	113	113	118
157210	-114.0426	46.8386	Larchmont (deep)	WQD-20 W131931D2	13N	19W	31	DDBA	3163.56	97	87	97
182632	-114.0029	46.8734	Clark Fork- McCormick		13N	19W	21	ADBC	3160.00	na	na	na

Site ID	Longitude	Latitude	Site Name	Water Quality District Number	Township	Range	Sec.	Tract	Static water level (ft) below mp June 1999	Altitude of water level (ft above sea level) June 1999	Static water level (ft) below mp March 2000	Altitude of water level (ft above sea level) March 2000
67037	-114.0508	46.8334	Buckhouse Bridge	WQD-35 U122001A	12N	20W	1	ABAD	22.28	3126.81	27.32	3121.77
69055	-114.0023	46.8732	McCormick Park	WQD-30 U131921A	13N	19W	21	DABC	25.43	3153.86	36.55	3142.74
69402	-114.0072	46.8491	South/Bancroft	WQD-32 U131933B	13N	19W	33	BAAA	52.49	3141.07	61	3132.56
151101	-114.0916	46.8558	Humble/Mount	WQD-7 W132026D	13N	20W	26	DBBB	8.78	3113.79	13.9	3108.67
151143	-114.0291	46.8680	Emma Dickinson	WQD-10 W131920C	13N	19W	20	CDDA	20.77	3144.31	30	3135.08
151161	-114.0394	46.8513	C.S.Porter School	WQD-8 W131930D	13N	19W	30	DDDA	32.47	3137.20	40.28	3129.39
151189	-114.0597	46.8577	Tower Street (DSL)	WQD-33 U132025D	13N	20W	25	ADAD	23.2	3131.23	29.55	3124.88
151190	-114.0021	46.8578	Blaine/Crosby (shallow)	WQD-31 U131928A	13N	19W	28	ACDAA	59.89	3144.38	69.34	3134.93
151191	-113.9878	46.8666	Madison Street	WQD-29 U131922C	13N	19W	22	CDABD	27.2	3164.18	39.15	3152.23
151200	-114.0507	46.8668	Hawthorne School	WQD-5 W131919C	13N	19W	19	CDAAC	12.01	3139.13	19.15	3131.99
151201	-114.0426	46.8383	Larchmont (shallow)	WQD-6 W131931D	13N	19W	31	DDBA	31.71	3131.48	38	3125.19
157208	-114.0021	46.8578	Blaine/Crosby (deep)	WQD-21 W131928A2	13N	19W	28	ACDAA	59.45	3144.65	68.84	3135.26
157210	-114.0426	46.8386	Larchmont (deep)	WQD-20 W131931D2	13N	19W	31	DDBA	32.03	3131.53	38.37	3125.19

Table 2. Inorganic constituents and trace metals in ground-water samples, June 1999, Missoula Valley, Montana.

Sample ID	Site ID	Sample date	Lab pH	Field pH	Lab specific conductance (uS/cm)	Field specific conductance (uS/cm)	Water temperature degrees C	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Iron (mg/L)
Health Standard										250**		0.3**
1999Q0850	151143	6/28/1999	7.6	7.6	315	250	10.3	50.3	12.5	5.99	1.59	<.005
1999Q0840	151190	6/21/1999	7.8	7.3	351	357	10.4	52.7	12.9	6.76	1.84	<.005
1999Q0825	151191	6/22/1999	7.3	7.3	314	270	10.1	44.8	10.9	5.87	1.52	<.005
1999Q0821	151201	6/21/1999	7.5	7.3	465	465	11.3	63.5	18.4	11.4	2.33	<.01
1999Q0832	157208	6/21/1999	7.7	7.4	335	334	9.9	51.2	12.2	5.6	1.55	0.017
1999Q0835	157210	6/21/1999	7.6	7.4	423	418	11.5	55.4	14.5	7.88	2.01	<.01
1999Q0841	69055	6/22/1999	8.0	7.3	175	246	12.3	20.7	6.14	2.81	1.02	0.015
MVWQD Data												
WQD-35 U122001A	67037	6/28/1999	7.5	NR	NR	492	7.5	61.5	17.8	14.9	2.38	0.009
WQD-32 U131933B	69402	6/23/1999	7.5	7.5	NR	419	11.1	57.4	15.9	7.66	2.1	0.009
WQD-7 W132026D	151101	6/21/1999	7.4	7.4	NR	445	11.1	53.2	15.5	11.3	2.38	0.008
WQD-8 W131930D	151161	6/22/1998	7.0	7.0	NR	413	10.6	53.2	15.2	9.28	2.15	0.007
WQD-33 U132025D	151189	6/22/1999	7.2	7.2	NR	398	10.7	53.8	14.5	8.04	1.82	0.01
WQD-5 W131919C	151200	6/28/1999	7.2	7.2	NR	346	12.8	44.7	12.5	7.87	1.96	0.008

uS/cm - microsiemens per centimeter at 25 degrees C
mg/L - milligrams per liter
ug/L - micrograms per liter
NR - Not Reported

* USEPA Primary Maximum Contaminant Level
**USEPA Secondary Maximum Contaminant Level

Table 2. Inorganic constituents and trace metals in ground-water samples, June 1999, Missoula Valley, Montana. - *Continued*

Sample ID	Site ID	Manganese (mg/L)	Silica (mg/L)	Bicarbonate (mg/L)	Carbonate (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Nitrate as N (mg/L)	Phospahate, ortho as P (mg/L)	Fluoride (mg/L)	Aluminum (ug/L)	Antimony (ug/L)	Arsenic (ug/L)
Health Standard		0.05**				250**	250**	10*		4*		6*	50*
1999Q0850	151143	<.001	12.7	192.8	0	17.13	4.216	1.02	<.05	0.13	<30	<2	1.7
1999Q0840	151190	<.001	13.3	200.32	0	19.71	6.707	0.885	<.05	0.13	<30	<2	1.36
1999Q0825	151191	<.001	13.7	167.1	0	15.03	3.69	0.618	<.05	0.117	<30	<2	1.69
1999Q0821	151201	<.002	15.5	257.2	0	20.75	12.74	1.628	<.05	0.129	<30	<2	<1
1999Q0832	157208	<.001	13.6	192.5	0	18.3	3.493	<.5	<.05	0.149	<30	<2	<1
1999Q0835	157210	<.002	14.2	233.3	0	19.33	8.446	1.06	<.05	0.145	<30	<2	1.02
1999Q0841	69055	0.004	9.44	94.2	0	9.25	0.83	<.5	<.05	0.083	<30	<2	2.7
MVWQD Data													
WQD-35 U122001A	67037	<0.001	NR	196	NR	15.8	29.3	1.66	NR	NR	NR	NR	1.4
WQD-32 U131933B	69402	<0.001	NR	171	NR	19.3	10.7	2.15	NR	NR	NR	NR	1.6
WQD-7 W132026D	151101	<0.001	NR	176.8	NR	20.1	9.75	2.12	NR	NR	NR	NR	1.8
WQD-8 W131930D	151161	<0.001	NR	176	NR	18	9.2	1.74	NR	NR	NR	NR	2.4
WQD-33 U132025D	151189	<0.001	NR	174.4	NR	18	5.88	1.17	NR	NR	NR	NR	0.7
WQD-5 W131919C	151200	<0.001	NR	146.8	NR	22.9	5.51	0.86	NR	NR	NR	NR	1.3

uS/cm - microsiemens per centimeter at 25 degrees C
mg/L - milligrams per liter
ug/L - micrograms per liter
NR - Not Reported

* USEPA Primary Maximum Contaminant Level
**USEPA Secondary Maximum Contaminant Level

Table 2. Inorganic constituents and trace metals in ground-water samples, June 1999, Missoula Valley, Montana. - *Continued*

Sample ID	Site ID	Barium (ug/L)	Beryllium (ug/L)	Boron (ug/L)	Bromide (ug/L)	Cadmium (ug/L)	Chromium (ug/L)	Cobalt (ug/L)	Copper (ug/L)	Lead (ug/L)	Lithium (ug/L)	Molybdenum (ug/L)	Nickel (ug/L)	Selenium (ug/L)
Health Standard		2000*				5*	100*		1,300*	15*				50*
1999Q0850	151143	158	<2	<30	<50	<2	<2	<2	<2	<2	<50	<10	<2	<1
1999Q0840	151190	219	<2	<30	<50	<2	<2	<2	2.81	<2	<50	<10	<2	<1
1999Q0825	151191	153	<2	<30	<50	<2	<2	<2	<2	<2	<50	<10	<2	<1
1999Q0821	151201	268	<2	<30	<50	<2	<2	<2	<2	<2	<100	<10	<2	<1
1999Q0832	157208	190	<2	<30	<50	<2	<2	<2	<2	<2	<50	<10	<2	<1
1999Q0835	157210	243	<2	<30	<50	<2	<2	<2	<2	<2	<100	<10	<2	<1
1999Q0841	69055	102	<2	<30	<50	<2	<2	<2	<2	<2	<50	<10	<2	<1
MVWQD Data														
WQD-35 U122001A	67037	235	NR	NR	NR	<1	<5	NR	NR	<4	NR	NR	<1	NR
WQD-32 U131933B	69402	249	NR	NR	NR	<1	<5	NR	NR	<4	NR	NR	<1	NR
WQD-7 W132026D	151101	204	NR	NR	NR	<1	<5	NR	NR	<4	NR	NR	<1	NR
WQD-8 W131930D	151161	220	NR	NR	NR	<1	<5	NR	NR	<4	NR	NR	<1	NR
WQD-33 U132025D	151189	213	NR	NR	NR	<1	<5	NR	NR	<4	NR	NR	<1	NR
WQD-5 W131919C	151200	161	NR	NR	NR	<1	<5	NR	NR	<4	NR	NR	<1	NR

uS/cm - microsiemens per centimeter at 25 degrees C
mg/L - milligrams per liter
ug/L - micrograms per liter
NR - Not Reported

* USEPA Primary Maximum Contaminant Level
**USEPA Secondary Maximum Contaminant Level

Table 2. Inorganic constituents and trace metals in ground-water samples, June 1999, Missoula Valley, Montana. - *Continued*

Sample ID	Site ID	Strontium (ug/L)	Silver (ug/L)	Thallium (ug/L)	Titanium (ug/L)	Vanadium (ug/L)	Zinc (ug/L)	Zirconium (ug/L)	Total Dissolved Solids (mg/L)	Lab
Health Standard			100*				5,000**		500**	
1999Q0850	151143	133	<1	<5	<10	<5	<2	<5	201	MBMG
1999Q0840	151190	141	<1	<5	<10	<5	<2	<5	214	MBMG
1999Q0825	151191	117	<1	<5	<10	<5	2.39	<5	179	MBMG
1999Q0821	151201	195	<1	<5	<20	<5	2.55	<10	273	MBMG
1999Q0832	157208	141	<1	<5	<10	<5	<2	<5	201	MBMG
1999Q0835	157210	167	<1	<5	<20	<5	<2	<10	238	MBMG
1999Q0841	69055	67.4	<1	<5	<10	<5	3.34	<5	97	MBMG
MVWQD Data										
WQD-35 U122001A	67037	NR	NR	NR	NR	NR	4.0	NR	NR	UofM
WQD-32 U131933B	69402	NR	NR	NR	NR	NR	2.0	NR	NR	UofM
WQD-7 W132026D	151101	NR	NR	NR	NR	NR	1.0	NR	NR	UofM
WQD-8 W131930D	151161	NR	NR	NR	NR	NR	1.0	NR	NR	UofM
WQD-33 U132025D	151189	NR	NR	NR	NR	NR	2.0	NR	NR	UofM
WQD-5 W131919C	151200	NR	NR	NR	NR	NR	4.0	NR	NR	UofM

uS/cm - microsiemens per centimeter at 25 degrees C
mg/L - milligrams per liter
ug/L - micrograms per liter
NR - Not Reported

* USEPA Primary Maximum Contaminant Level
**USEPA Secondary Maximum Contaminant Level

Table 3. Results of oxygen-18 and deuterium analyses

Sample ID	Sample Date	delta O18	delta D	Sample Date	delta O18
69037	6/28/99	-16.94	-131.30	3/6/00	-15.82
69055	6/22/99	-17.76	-136.10	3/8/00	-16.55
69402	6/28/99	-17.07	-132.30	3/9/00	-16.66
151143	6/28/99	-17.31	-132.40	3/9/00	-16.77
151161	6/22/99	-17.20	-132.80	3/7/00	-16.51
151189	6/22/99	-17.27	-132.10	3/7/00	-16.92
151190	6/21/99	-17.36	-133.30	3/6/00	-17.16
151191	6/22/99	-17.53	-135.50	3/9/00	-17.13
151200	6/28/99	-17.24	-132.50	3/7/00	-17.52
151201	6/21/99	-17.16	-129.40	3/9/00	-16.65
157208	6/21/99	-18.00	-135.54	3/6/00	-16.91
157210	6/21/99	-17.17	-132.50	3/9/00	-16.26
182632	6/22/99	-17.86	-133.50	3/8/00	-17.42

Sample Date	69055 delta O18	182632 delta O18
6/22/99	-17.76	-17.86
7/21/99	-17.54	-17.47
8/7/99	-16.86	-16.81
9/1/99	-16.47	-16.69
11/17/99	-17.14	-17.35
12/6/99	-17.03	-17.27
1/6/00	-17.86	-17.05
2/3/00	-16.29	-17.05
3/8/00	-16.55	-17.42
4/6/00	-17.08	-17.02
5/10/00	-17.07	-17.26
6/5/00	-17.33	-17.33
7/15/00	-16.7	-16.48
8/7/00	-16.49	-16.59
9/17/00	-16.61	-16.54
10/12/00	-16.61	-16.54
11/16/00	-16.91	-17.01
12/14/00	-17.14	-17.78

delta O18 and delta D results in per mill

Table 4. Chlorofluorocarbon (CFC) data for the Missoula Valley, Montana

Sample ID	Sample Date	CFC-11 (pmoles/kg)	CFC-12 (pmoles/kg)	CFC-11-average* (pmoles/kg)	CFC-12-average* (pmoles/kg)	Apparent CFC-12 recharge year**
69055-1	6/22/1999	4.05	2.96			
69055-2	6/22/1999	4.39	2.76			
69055-3	6/22/1999	5.62	5.62	4.22	2.86	1989
182632-1	6/22/1999	3.94	3.88			
182632-2	6/22/1999	3.78	3.38			
182632-3	6/22/1999	3.85	3.38	3.55	3.38	1999
151101-1	6/21/1999	na	na			
151101-2	6/21/1999	34.06	47.56			
151101-3	6/21/1999	35.99	55.21	35.03	51.39	contaminated
151143-1	6/28/1999	na	4.73			
151143-2	6/28/1999	6.68	4.53			
151143-3	6/28/1999	6.53	6.83	6.61	4.63	contaminated
151161-1	6/22/1999	na	na			
151161-2	6/22/1999	6.72	61.33			
151161-3	6/22/1999	6.16	68.76	6.45	75.05	contaminated
151189-1	6/22/1999	na	19.9			
151189-2	6/22/1999	13.79	16.08			
151189-3	6/22/1999	na	23.08	13.79	18.99	contaminated
151190-1	6/21/1999	na	7.56			
151190-2	6/21/1999	6.27	7.57			
151190-3	6/21/1999	6.33	7.38	6.3	7.5	contaminated
151191-1	6/22/1999	6.75	2.92			
151191-2	6/22/1999	na	3.68			
151191-3	6/22/1999	na	na	6.75	3.3	1999
151200-1	6/28/1999	na	na			
151200-2	6/28/1999	na	14.7			
151200-3	6/28/1999	9.85	5.51	9.85	5.51	contaminated
151201-1	6/21/1999	na	na			
151201-2	6/21/1999	10.56	75.01			
151201-3	6/21/1999	10.81	80.35	10.69	77.68	contaminated
157208-1	6/21/1999	na	7.77			
157208-2	6/21/1999	5.35	7.99			
157208-3	6/21/1999	5.46	8.06	5.4	7.94	contaminated
157210-1	6/21/1999	na	na			
157210-2	6/21/1999	9.25	15.99			
157210-3	6/21/1999	9.44	15.87	9.34	15.93	contaminated
69402-1	6/28/1999	na	na			
69402-2	6/28/1999	6.84	5.74			
69402-3	6/28/1999	6.73	5.51	6.78	5.62	contaminated

* - Outliers removed.

** - Assumes 6 C recharge temperature at an elevation of 1500 m.

na - Concentration was outside of calibration.

Table 5. Noble gas, tritium, tritium-helium-3 age data.

Water Samples Concentrations in ccSTP/g

Utah RunID	Sample ID	sample date	N28	Ar40	Ne20	He4	R/Ra	Comment
09219914	69055	6/22/1999	1.94E-01	2.43E-03	4.16E-06	1.47E-06	0.899	Large bubble in sample
09169905	69402	6/23/1999	1.75E-02	4.28E-04	2.54E-07	4.69E-08	0.662	Helium data is approximate
09219905	151101	6/21/1999	1.71E-02	4.63E-04	2.30E-07	6.67E-08	0.882	
09219910	151143	6/28/1999	1.57E-02	4.45E-04	1.87E-07	5.55E-08	0.873	
09219907	151161	6/22/1999	1.56E-02	4.22E-04	2.11E-07	8.49E-08	0.640	
09179903	151189	6/22/1999	1.68E-02	4.35E-04	2.51E-07	7.46E-08	0.721	
09219911	151190	6/21/1999	Leaked	Leaked	Leaked	Leaked	Leaked	
09219908	151191	6/22/1999	2.17E-02	5.35E-04	3.09E-07	8.45E-08	0.859	Moderate amount of excess air
09219913	151200	6/28/1999	1.61E-02	4.57E-04	2.07E-07	5.71E-08	0.981	
09169907	151201	6/21/1999	1.43E-02	4.04E-04	2.00E-07	5.72E-08	0.878	
09219904	157208	6/21/1999	1.66E-02	4.05E-04	2.15E-07	1.17E-07	0.479	
09179904	157210	6/21/1999	1.64E-02	4.20E-04	2.27E-07	7.89E-08	0.737	
09169908	182632	6/22/1999	1.37E-02	3.70E-04	1.84E-07	4.83E-08	0.963	

Diffusion Samplers Values below are dry volume fractions in equilibrium with water sample

Utah RunID	Sample ID	depth to water	depth deployed	date deployed	date retrieved	N28	Ar40	O32	Kr84	Ne20	He4	R/Ra
04130007	67037	26.98	34	11/20/1999	12/13/1999	8.53E-01	9.89E-03	1.34E-01	6.45E-07	1.67E-05	5.73E-06	0.965
05170004	69055	33.53	45	11/10/1999	12/13/1999	9.85E-01	1.13E-02	1.35E-05	7.91E-07	2.00E-05	8.20E-06	0.798
04130004	69402	58.00	65	11/9/1999	12/13/1999	8.63E-01	9.46E-03	1.27E-01	7.03E-07	1.78E-05	7.90E-06	0.733
04130006	151101	13.70	20	11/10/1999	12/13/1999	8.52E-01	9.55E-03	1.34E-01	6.54E-07	1.74E-05	6.89E-06	0.843
02170003	151143	27.66	35	11/10/1999	12/13/1999	9.74E-01	1.10E-02	1.49E-02	6.16E-07	2.06E-05	1.01E-05	0.656
03090006	151161	38.21	46	11/10/1999	12/13/1999	8.78E-01	9.87E-03	1.12E-01	7.14E-07	1.81E-05	9.66E-06	0.634
03090004	151189	28.31	44	11/10/1999	12/13/1999	8.91E-01	9.78E-03	9.88E-02	7.51E-07	1.87E-05	7.84E-06	0.802
02170005	151190	66.27	70	11/9/1999	12/13/1999	9.65E-01	1.10E-02	2.44E-02	7.76E-07	1.94E-05	1.12E-05	0.593
05170003	151191	36.25	45	11/10/1999	12/13/1999	8.97E-01	1.08E-02	9.17E-02	7.41E-07	1.84E-05	1.11E-05	0.540
03090003	151200	17.48	24	11/10/1999	12/13/1999	9.06E-01	1.00E-02	8.38E-02	7.30E-07	1.91E-05	6.38E-06	0.941
05170009	151201	36.70	45	11/10/1999	12/13/1999	8.86E-01	9.96E-03	1.04E-01	5.44E-07	1.74E-05	7.26E-06	0.851
03090007	157208	65.88	115	11/10/1999	12/13/1999	9.64E-01	1.10E-02	2.55E-02	7.99E-07	1.98E-05	1.36E-05	0.486
02170002	157210	37.03	90	11/10/1999	12/13/1999	9.11E-01	1.02E-02	7.91E-02	5.11E-07	1.86E-05	8.30E-06	0.773

Repeat Samples Values below are dry volume fractions in equilibrium with water sample

Utah RunID	Sample ID			date deployed	date retrieved	N28	Ar40	O32	Kr84	Ne20	He4	R/Ra
7050105	69402			4/6/2001	4/30/2001	8.44E-01	9.73E-03	1.45E-01	6.85E-07	1.71E-05	7.05E-06	0.773
7050106	157210			4/6/2001	4/30/2001	8.96E-01	1.01E-02	9.38E-02	7.24E-07	1.99E-05	8.23E-06	0.741
7050104	151201			4/6/2001	4/30/2001	8.78E-01	1.01E-02	1.12E-01	6.95E-07	1.70E-05	7.28E-06	0.816
7050103	151191			4/6/2001	4/30/2001	8.87E-01	1.02E-02	1.03E-01	7.25E-07	2.00E-05	1.09E-05	0.532

Age Summary

Utah Run ID	Sample ID	Computed Age (yr)	plus/minus (estimated)	Terigenic 4He (ccSTP/g)	Rech. Temp. Used (C)	Computed Tritiogenic 3He (TU)	Tritium (TU)	Error +	-	Excess Air (ccSTP/g)	Computed N2 (ccSTP/g)	Computed 40Ar (ccSTP/g)	Computed 20Ne (ccSTP/g)	Computed Total 4He (ccSTP/g)
4130007	67037	3.2	1	5.00E-09	4	1.8	9.44	0.47	0.47	0.0004	1.51E-02	3.88E-04	1.78E-07	4.89E-08
4130003	67037	2.5	1	3.50E-09	4	1.4	9.44	0.47	0.47	0.0011	1.56E-02	4.05E-04	1.93E-07	5.21E-08
5170004	69055	1.7	1	1.30E-08	4	0.9	8.90	0.40	0.40	0	1.48E-02	3.81E-04	1.71E-07	5.42E-08
4130004	69402	0.4	1	2.00E-08	4	0.2	9.10	0.50	0.50	0.0023	1.66E-02	4.02E-04	2.08E-07	7.36E-08
4130006	151101	2.2	1	1.30E-08	4	1.3	10.31	0.52	0.52	0.0018	1.62E-02	4.03E-04	2.03E-07	6.42E-08
2170003	151143	-0.3	1	2.80E-08	4	-0.1	8.67	0.43	0.43	0.0019	1.63E-02	4.09E-04	2.06E-07	8.05E-08
3090006	151161	1.8	1	3.50E-08	4	1.3	13.13	0.72	1.43	0.0019	1.63E-02	4.06E-04	2.04E-07	8.69E-08
3090004	151189	1.6	1	1.70E-08	4	1.1	12.06	1.00	0.60	0.0026	1.68E-02	4.09E-04	2.15E-07	7.21E-08
2170005	151190	2.7	1	4.00E-08	4	2.0	12.38	0.62	0.62	0.001	1.56E-02	3.95E-04	1.89E-07	8.68E-08
5170003	151191	0.6	1	4.20E-08	4	0.4	11.21	0.56	0.56	0.0005	1.52E-02	4.07E-04	1.86E-07	8.87E-08
3090003	151200	-1.5	1.5	2.00E-09	4	-0.8	10.10	0.50	0.50	0.0025	1.68E-02	4.10E-04	2.14E-07	5.71E-08
5170009	151201	4.6	1	1.60E-08	4	3.5	12.10	0.60	0.60	0.0011	1.56E-02	3.89E-04	1.87E-07	6.27E-08
12229905	182632	--	--	--	--	--	10.20	0.50	0.50	--	--	--	--	--
2170002	157210	3.3	1	2.10E-08	4	2.2	10.90	0.50	0.50	0.0018	1.62E-02	4.02E-04	2.01E-07	7.17E-08