

Chapter 4 Field Study of CFC Concentrations at the Water Table at the Mirror Lake Site, New Hampshire

4.1 Introduction

4.1.1 CFC's as Environmental Tracers

Chlorofluorocarbons (CFC's; also called Freon, chlorofluoromethane) have emerged as useful age-dating tracers for young ground water (Thompson et al., 1974; Thompson and Hayes, 1979; Plummer et al., 1993). For atmospheric tracers, the age of ground water is defined as the time since the water was in contact with the atmosphere. Conceptually, recharge to the saturated zone is in chemical equilibrium with the atmosphere at the water table, and below in the saturated zone that concentration is maintained. Hence, if the atmospheric concentration changes in time, then different concentrations in ground water presumably correspond to different recharge times, and different ages. Knowledge of the atmospheric source term allows calibration of flow and transport models, yielding estimates of hydraulic and transport properties (e.g. Reilly et al., 1994; Szabo et al., 1996). These methods are most useful where the flow system under investigation is too large or responds too slowly to test through traditional field tracer experiments.

CFC's are useful ground-water tracers because the atmospheric source term is relatively well known and is almost linear in time, and because the CFC concentration of fresh water in equilibrium with the atmosphere is well described as a function of temperature alone (Warner and Weiss, 1985; Bu and Warner, 1995). CFC-12, CFC-11, and CFC-113 are man-made volatile organic compounds widely used as refrigerants and

occurring in many manufactured goods. The atmospheric concentration of CFC's has been increasing since their creation in the 1940's (fig. 4-1). Atmospheric concentrations have been measured for approximately 30 years and concentrations before 1960 are estimated from manufacturing records. Recently, concentrations of CFC's have leveled off and in the case of CFC-11 and CFC-113 have begun to decrease somewhat due to reduced production, atmospheric loss (by reaction) and transfer of CFC's from the atmosphere to the oceans (Khalil and Rasmussen, 1993).

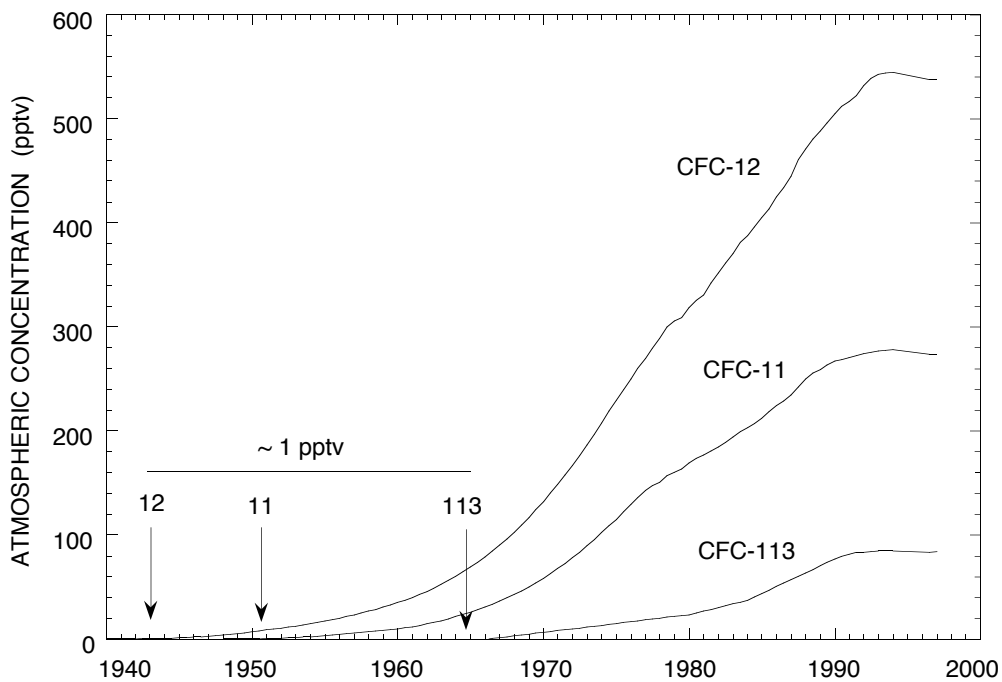


Figure 4-1. Global atmospheric concentration of CFC-12, CFC-11, and CFC-113 (after Plummer et al., 1993)

Assuming that recharging ground water is in CFC equilibrium with the atmosphere, a measured CFC concentration in water can be converted to a corresponding atmospheric concentration, which in turn can be used to compute a corresponding date of recharge from Figure 4-1. The difference between the date of recharge and the date of sampling is the age of the ground water.

The dating of ground water from CFC's depends, in part, on the assumption that CFC's are inert; once isolated from the atmosphere, the CFC concentration in a moving volume of water is constant in time. Processes which may change CFC concentrations include mixing and dispersion, exchange with solids, gases, or immobile waters, and degradation by biotic or abiotic reactions (Busenberg and Plummer, 1992). Degradation of CFC's in water has been identified for anaerobic conditions (Khalil and Rasmussen, 1989; Lovely and Woodward, 1992; Semprini et al., 1990; Terauds et al., 1993; Bullister and Lee, 1995; Oster et al., 1996; Plummer et al., in press). However, in oxygenated waters CFC's appear to be essentially inert. Furthermore, the relatively linear increase in the atmospheric concentrations over time means that CFC concentrations are less affected by mixing and dispersion than tracers with highly variable source terms, such as tritium (Plummer et al., 1993). Exchange processes may be important for CFC's, especially in highly heterogeneous formations, such as fractured rock (Shapiro, 1996; Wood et al., 1996). Sorption of CFC's to most natural aquifer materials is believed to be insignificant (Russell and Thompson, 1983; Lovely and Woodward, 1992). Despite these beneficial factors, CFC concentrations in ground water are not always easy to interpret. The U.S. Geological Survey Mirror Lake, New Hampshire site is one location where CFC's have not been as useful as hoped in characterizing large-scale transport properties (Busenberg and Plummer, 1996; Shapiro et al., 1996).

4.1.2 Mirror Lake Field Site

The U.S. Geological Survey (USGS) is investigating multi-scale flow and transport in a glaciated fractured rock setting at the Mirror Lake site, Grafton County, New Hampshire (fig. 4-2) (Winter, 1984; Shapiro and Hsieh, 1991; Hsieh et al., 1993). These investigations are multi-disciplinary and use tools ranging from detailed geologic and fracture mapping, to surface seismic and borehole radar, to crosshole hydraulic and tracer tests (Hsieh and Shapiro, 1996) and large-scale flow model calibration (Tiedeman et al., 1997). Ground water from both the fractured bedrock and from the overlying

glacially deposited formations has been analyzed for numerous environmental tracers (Busenberg and Plummer, 1996; Drenkard et al., 1996). The Mirror Lake site is within the Hubbard Brook drainage basin that also contains the Hubbard Brook Experimental Forest, a long-term ecological research site of the U.S. Forest Service, the Institute of Ecosystem Studies (IES), and several universities (Bormann and Likens, 1979; Likens, 1985; Federer et al., 1990; USDA Forest Service, 1991; Likens and Bormann, 1995).

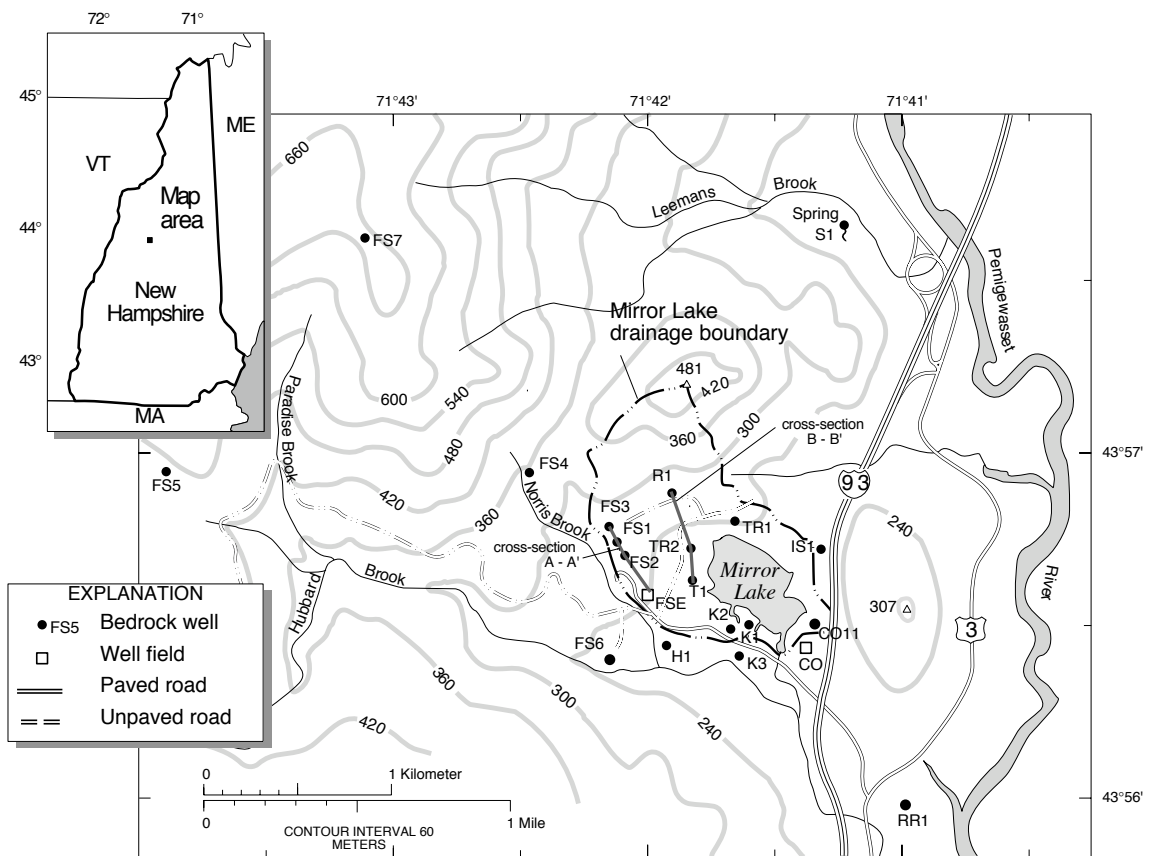


Figure 4-2. Mirror Lake site location and bedrock wells.

The hydrogeologic setting of the Mirror Lake site is glacial drift overlying crystalline bedrock (Winter, 1984; Winter 1985). The glacial drift has a highly variable composition ranging from uniform sandy terraces to fine-grained till filled with large

boulders (Winter, 1984; Harte, 1992; Harte and Winter, 1996). The permeability of the glacial drift is generally low (Wilson, 1991; Harte, 1997). Regional-scale flow modeling indicates that the transmissivities of the glacial drift and the underlying fractured bedrock are low and of the same order of magnitude (Tiedeman et al., 1997). Baseflow to streams in the Mirror Lake drainage basin is significantly higher than in other parts of the Hubbard Brook drainage basin because of the increased thickness of glacial drift (Winter et al., 1989; Mau and Winter, 1997). Sandy terrace deposits located throughout the watershed may have strong local control on ground-water flow and ground-water/surface water interaction (Shattuck, 1991; Harte and Winter, 1996). The climate is humid and long-term average recharge to ground water is on the order of 30 cm/yr (Mau and Winter, 1997).

4.1.3 Ground-Water Ages from CFC Data at Mirror Lake

In contrast to results from some relatively homogeneous coastal plain sediments (e.g. Reilly et al., 1994; Szabo et al., 1996), ground-water ages derived from CFC concentrations in samples from site bedrock wells do not follow a readily apparent spatial distribution. Figure 4-3 shows cross-sections of ground-water ages determined from samples collected from packer-isolated portions of open bedrock boreholes at the Mirror Lake site (Busenberg and Plummer, 1996; Shapiro et al., 1996). In homogeneous formations, ground-water age is expected to increase gradually from recharge to discharge locations, as shown in Chapter 2. However, in the highly heterogeneous fractured rock at Mirror Lake, in which the small-scale hydraulic conductivity varies over at least 7 orders of magnitude (Hsieh and Shapiro, 1996), complex patterns such as those shown in Figure 4-3 may be expected. This is consistent with ground-water age simulation results shown in, for example, Figure 2-8.

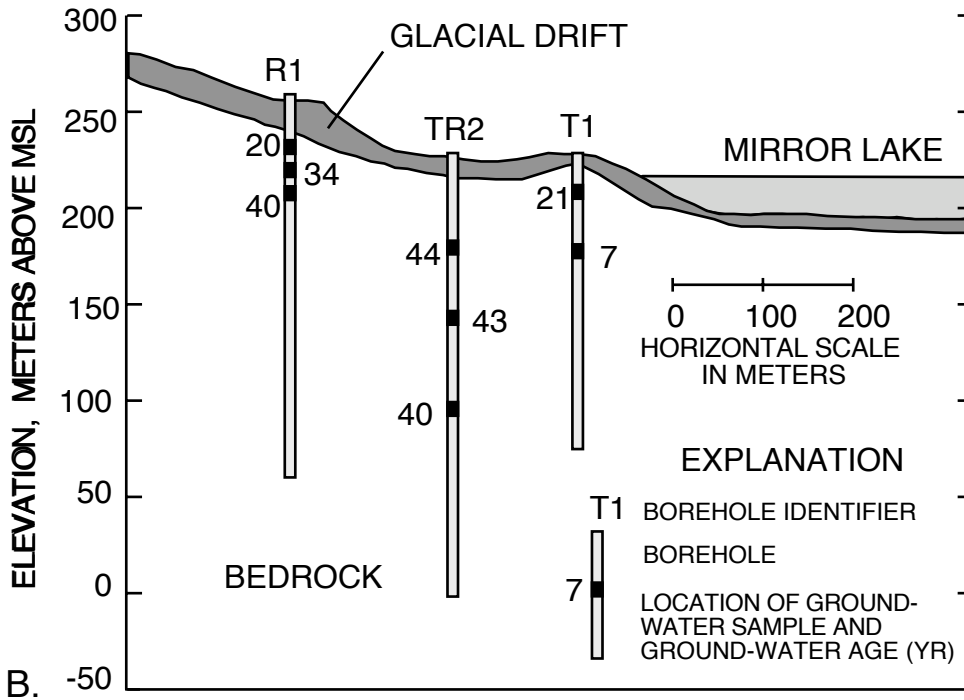
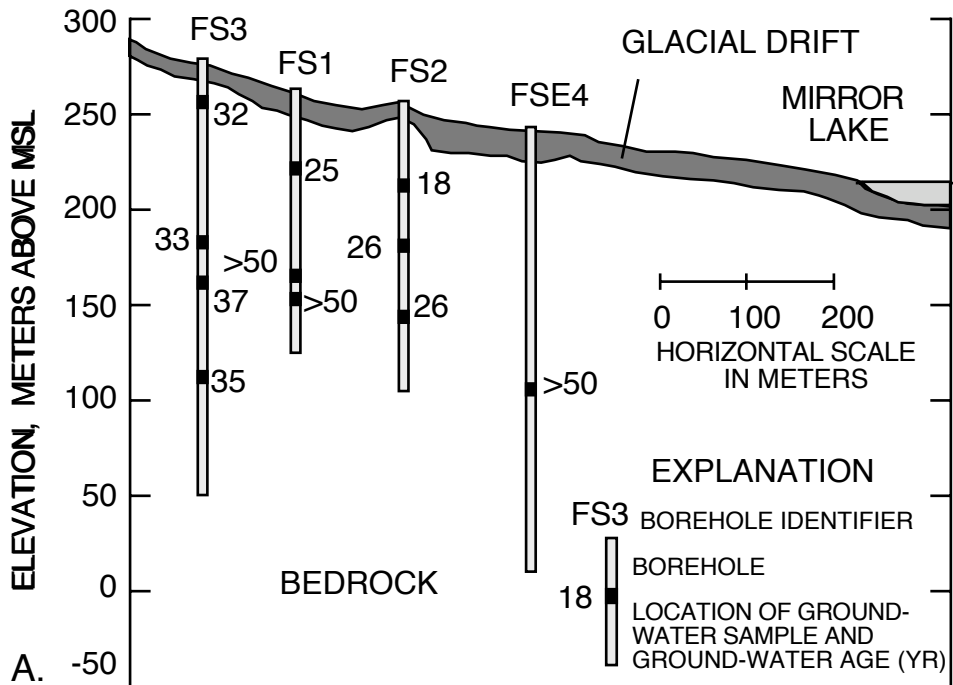


Figure 4-3. Ground-water ages in bedrock estimated from CFC-12 concentrations in 1990 & 1991 along projected cross-sections (a) A-A' (data from Busenberg and Plummer, 1996), and (b) B-B' (Shapiro et al., 1996).

Other possible causes of the complex age spatial pattern at Mirror Lake, and the corresponding CFC concentration pattern, involve in situ processes that modify CFC concentrations. Possible processes include, but may not be limited to, sorption, exchange, and degradation. Furthermore, seasonal temperature cycles may cause corresponding cycles in CFC concentrations in recharging waters (Chapter 3). These cycles may lead to variability in CFC concentrations along a flow path that may be misinterpreted as highly variable ages. Previous and concurrent work indicates that CFC's, particularly CFC-11 and CFC-113, are degraded under anaerobic conditions in ground water (Semprini et al., 1990; Terauds et al., 1993; Plummer et al., in press).

4.1.4 Scope and Objectives

The goals of this field study are to characterize the concentrations of CFC's in water recharging the saturated zone at Mirror Lake, to identify the processes that control those concentrations, and to describe the source function for CFC's in infiltrating waters that recharge the saturated zone. The field program investigates the following properties and processes: CFC concentrations at or near the water table, and in the unsaturated zone; temperature cycles where CFC air/water equilibrium is occurring; biogeochemical factors that may be related to CFC concentrations; and hydraulic properties of the unsaturated zone. Section 4.2 describes methods used in this field study, and results are presented in section 4.3. These results are discussed and processes controlling CFC in recharge water at the Mirror Lake site are identified in section 4.4. Preliminary summaries of the findings here have been presented at scientific meetings (see abstracts: Goode, 1997; Goode et al., 1997).

4.2 Methods

Some of the data used in this study were obtained from previous and ongoing research at Mirror Lake and at Hubbard Brook Experiment Forest conducted by U.S. Forest Service, Institute of Ecosystems Studies (IES), U.S. Geological Survey, and numerous universities. Geochemical data, including CFC results from bedrock wells and isolated piezometers were provided by USGS. Water level measurements are also provided by USGS and IES. Barometric pressure data were provided by IES. Precipitation and air temperature data were provided by USFS, Radnor Pa. Hydrogen concentrations in water reported here were provided by USGS (Don A. Vroblesky, written communication, 1997).

4.2.1 Moisture Content and Pressure

Unsaturated zone hydraulic conditions were monitored during 1996 and 1997, with most data collected during the summers. A Time-Domain-Reflectometry (TDR) system from CSI and Tektronix was used to measure soil moisture near W2 (fig. 4-4). The system consists of a CR10 datalogger with special TDR PROM chips, a Tektronix 1502B cable tester, a CSI multiplexer, coax cable, and CSI model 605 3-rod TDR probes. TDR measures the reflection time of an electrical pulse, which is a function of the moisture content around the 3-rod 30-cm probe. The measurement is the average moisture content within an elliptical cylinder 30 cm long, about 10 cm maximum cross-section and about 5 cm minimum cross-section. One of the first long-term field applications of automated TDR was performed at Hubbard Brook Experimental Forest by Herkelrath and others (1991).

Soil suction pressure head was measured at four depths near the TDR system, near W2. Soil Moisture Inc. tensiometers were used with depths of approximately 30, 60, and 90 cm. These tensiometers consist of a porous ceramic cup at the end of a clear plastic rigid tube of the appropriate length. A calibrated pressure gage is installed near

the top of the tensiometer, and a water reservoir with 'quick-fill' system is mounted on the top. The gage reading was recorded periodically by field personnel.

A secondary automatic measure of soil suction pressure head was obtained during the last part of this study using gypsum blocks. These gypsum blocks were also installed near the TDR system, near W2. Gypsum blocks were installed at depths ranging from 10 to 90 cm. The CSI datalogger of the TDR system was additionally programmed to measure the electrical resistance of the gypsum blocks which is a function of the moisture content in the block. The block's moisture content depends in turn on the prevailing soil pressure head in the surrounding material. These gypsum blocks were not calibrated in the laboratory and give only qualitative measures of pressure, but were used because the measurements are continuous, and supplement the direct tensiometer measurements.

Well water levels were measured throughout this study using manual electrical tape, and using continuous pressure transducer measurements. The water level indicator used was a Slope Indicator Inc. model 51453 which is marked in 0.01 ft (about 0.3 cm) intervals. Druck submersible pressure transducers were used with CSI dataloggers, and these were continuously calibrated in the field from manual water level measurements.

4.2.2 Soil Temperature

Average hourly soil temperature was monitored from June 1996 through September 1997 at several depths at two locations in the study area: near the FS3 and FS3C well clusters, and near FS4 and FS4-WT. Campbell Scientific Inc. (CSI) model 107B soil temperature probes were installed in natural backfill in hand augered boreholes. The average hourly temperature was recorded from measurements made every 5 minutes. Data collection was automated with CSI CR10 dataloggers. At the FS3C site, one temperature probe was installed in the bottom of piezometer FS3C-14, which was dry throughout the monitoring period. At each location, a CSI model 107U air temperature probe was installed on the ground in a small plastic box. At the FS3C site,

the depths of measurement of soil temperature were 0, 0.8 m, 1.9 m, and 3.5 m. At the FS4 site, the measurements depths were 0, 42 cm and 75 cm.

4.2.3 Water Sample Collection and Analysis

Water samples were collected from 31 shallow piezometers during the summers of 1995, 1996, and 1997. Figure 4-4 shows the locations of these wells within the Mirror Lake watershed, Grafton County, New Hampshire. These wells were constructed by the U.S. Geological Survey over approximately 20 years as part of ground-water/lake interaction studies (Winter, 1984) and of fractured rock research (Shapiro and Hsieh, 1996). Wells are constructed of either steel or PVC (Table 4-1) and are almost all screened over 0.6 to 0.9 m long intervals. This sampling effort focused primarily on wells screened near the water table, but also included some wells screened in the glacial drift beneath the water table. New wells constructed for the present study are W16A, W33, W34, W35, W36, and FS4-WT. These wells were installed by the USGS New Hampshire District drill rig crew under supervision by the author. These boreholes were power augered without adding any water during drilling, and the wells were constructed of threaded PVC to minimize CFC contamination. Except where the borehole caved during auger withdrawal, coarse sand was placed in the annulus around the screen, followed by natural backfill, followed by a layer of ground silica flour, and natural backfill to the surface. The purpose of the fine-grained ground silica is to minimize vertical flow within the borehole annulus.

The general procedures for sampling (Table 4-2) consisted of pumping at least 1 borehole volume and then collecting water samples using standard procedures and equipment developed by USGS. CFC samples were collected using procedures and equipment developed at the USGS CFC Lab, Reston Virginia (Busenberg and Plummer, 1992).

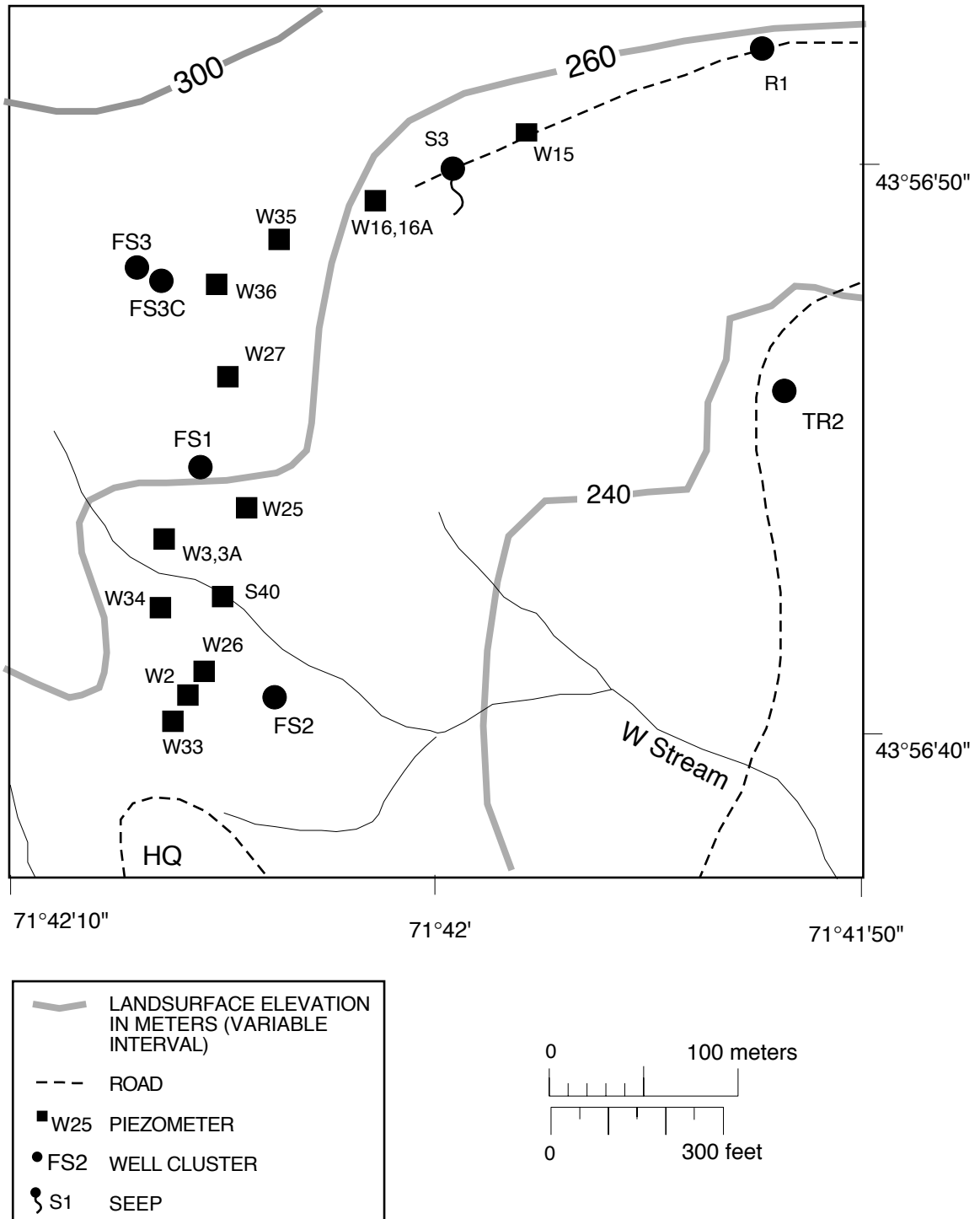


Figure 4-4. Locations of individual piezometers, well clusters, and seep sampled for this study.

Table 4-1. Selected piezometer construction data. [Primary references: W84, Winter, 1984; W94, T.C. Winter, personal commun., 1995; H91, P.T. Harte, written commun., 1991; H97, Harte, 1997; S91, Shattuck, 1991]

Well ID	Date installed	Casing material	Casing Diam. (cm)	Screen type	Screen Length (cm)	Screen top depth (m)	Top of casing elevation (m)	Land surface elevation (m)	Primary reference
W2	Nov-78	PVC	5.1	PVC wound	91	4.6	256.78		W84
W3	Nov-78	PVC	3.2	PVC slotted	76	5.9	258.56		W84
W3A	Nov-78	PVC	5.1	PVC slotted	76	1.7	259.11		W84
W6	Jul-82	Steel	5.1	Steel wound	91	9.4	239.27		W84
W11	Jul-82	ABS	5.1	PVC wound	61	7.3	240.97	240.1	W84
W15	Jul-82	Steel	3.2	Steel wound	91	0.9	263.26		W84
W16	Jul-82	Steel	3.2	Steel wound	91	5.5	264.82		W84
W16A	Jul-96	PVC	5.1	PVC wound	61	2.1		263.8	this study
W25	Oct-88	PVC	5.1	PVC wound	61	6.7	262.34	261.0	W94
W26	Oct-88	PVC	5.1	PVC wound	61	4.9	258.05	256.8	W94
W27	Aug-90	PVC	5.1	PVC slotted	152	4.9	266.93	265.9	H91
W33	Jul-96	PVC	5.1	PVC wound	61	5.2		256.0	this study
W34	Jul-96	PVC	5.1	PVC wound	61	4.5		258.0	this study
W35	Jul-96	PVC	5.1	PVC wound	61	2.4		271.0	this study
W36	Jul-96	PVC	5.1	PVC wound	61	5.2		272.0	this study
FS1-17	Jul-82	Steel	5.1	Steel wound	91	4.9	262.64	261.3	W84
FS1-25	Aug-79	PVC	5.1	PVC wound	61	6.9	262.35	261.2	W94
FS1-35	Aug-79	PVC	5.1	PVC wound	61	9.5	262.22	260.7	W94
FS3-11		PVC	5.1		61	2.7	275.04	274.0	
FS3-22		PVC	5.1		61	6.1	275.05	274.0	
FS3-29		PVC	5.1		61	8.2	275.02	274.0	
FS3C-14	Aug-91	PVC	5.1	PVC slotted	15	3.9	273.81	273.6	H97
FS3C-19	Aug-91	PVC	5.1	PVC slotted	15	5.5	274.27	273.7	H97
FS3C-24	Aug-91	PVC	5.1	PVC slotted	15	7.2	274.32	273.7	H97
FS3C-29	Aug-91	PVC	5.1	PVC slotted	15	8.8	274.13	273.7	H97
FS4-WT	Jul-96	PVC	5.1	PVC wound	61	1.1		349.7	this study
R1-36	Aug-90	PVC	5.1	PVC slotted	152	9.6	257.30	256.5	H91
R1-55		PVC	5.1		61	15.5	257.32	256.2	
S40	Aug-88	PVC	5.1	PVC slotted	24	0.5	255.30	254.3	S91
T1-8	Jul-82	Steel	5.1	Steel wound	91	1.5	229.62	228.9	W84
TR1-63	Sep-83	PVC	5.1	PVC wound	183	17.4	249.30	248.4	W94

Table 4-2. Overview of water sampling procedures.

Step	Procedures and Parameters	Equipment	Notes
1	measure water level and total well length	electric tape	compute volume of water in well
2	install submersible piston pump, or intake tubing for peristaltic pump	stainless steel piston pump or peristaltic pump	either copper or nylon tubing
3.	purge well of at least 1 well volume		monitor pH, specific conductivity, temperature, and dissolved oxygen; collect discharge for volume measurements; intermittent water level measurements
4	Tritium	1 L poly bottle	overflow at least 1 volume
5	Carbon Isotopes	1 L brown or clear glass bottle with polyseal cap	overflow at least 1 volume; small air bubble at top
6	Alkalinity	50 ml in graduated cylinder	analyze in field by titration
7	Total Organic Carbon	4 oz brown glass bottle with Teflon cap	store on ice and express mail to USGS Lab
8	Deuterium and Oxygen-18	2 oz glass bottle with polyseal cap	no air bubble
9	Dissolved Gases	200 ml clear glass bottles with rubber septum	duplicate samples; no air bubble; store on ice and express mail to USGS Lab
10	Sulfur Hexafluoride	1 L clear glass bottle with polyseal cap	no air bubble, store on ice and express mail to USGS Lab
11	CFC's	75 ml clear glass ampules	collect and seal in ultra-pure apparatus provided by USGS Lab; 3-6 samples
12	shutdown		record final field parameters

Field water quality parameters included temperature, pH, specific conductivity, dissolved oxygen, and alkalinity. Specific conductivity and pH were measured with separate Orion probes, both of which also measured temperature. In some cases the probes were lowered into the piezometer prior to sampling to record in situ values. Dissolved oxygen was measured in the field using the Winkler titration method (Hach kit) or a YSI self-stirring BOD probe (model 5905). Alkalinity was measured using 0.16 N sulfuric acid titration of 50 ml samples. Collected samples were analyzed at the following USGS laboratories: CFC Lab and Isotope Lab in Reston; National Water Quality Lab in Denver; and Tritium Lab in Menlo Park.

4.2.4 Soil Gas Sampling and Analysis

Soil gas samples were collected during the summers of 1996 and 1997, and in January 1997 from steel dry wells installed by hand or power auger, or manual drive point in one case (fig. 4-5; Table 4-3). Figure 4-6 shows a schematic of the a steel gas well consisting of 0.6 cm diameter stainless steel tubing, stainless steel or brass swagelok compression fittings, a stainless steel screen, and glass wool. The borehole annulus around the sampling port is filled with coarse sand, followed by natural backfill, followed by ground silica flour, and natural backfill to the surface.

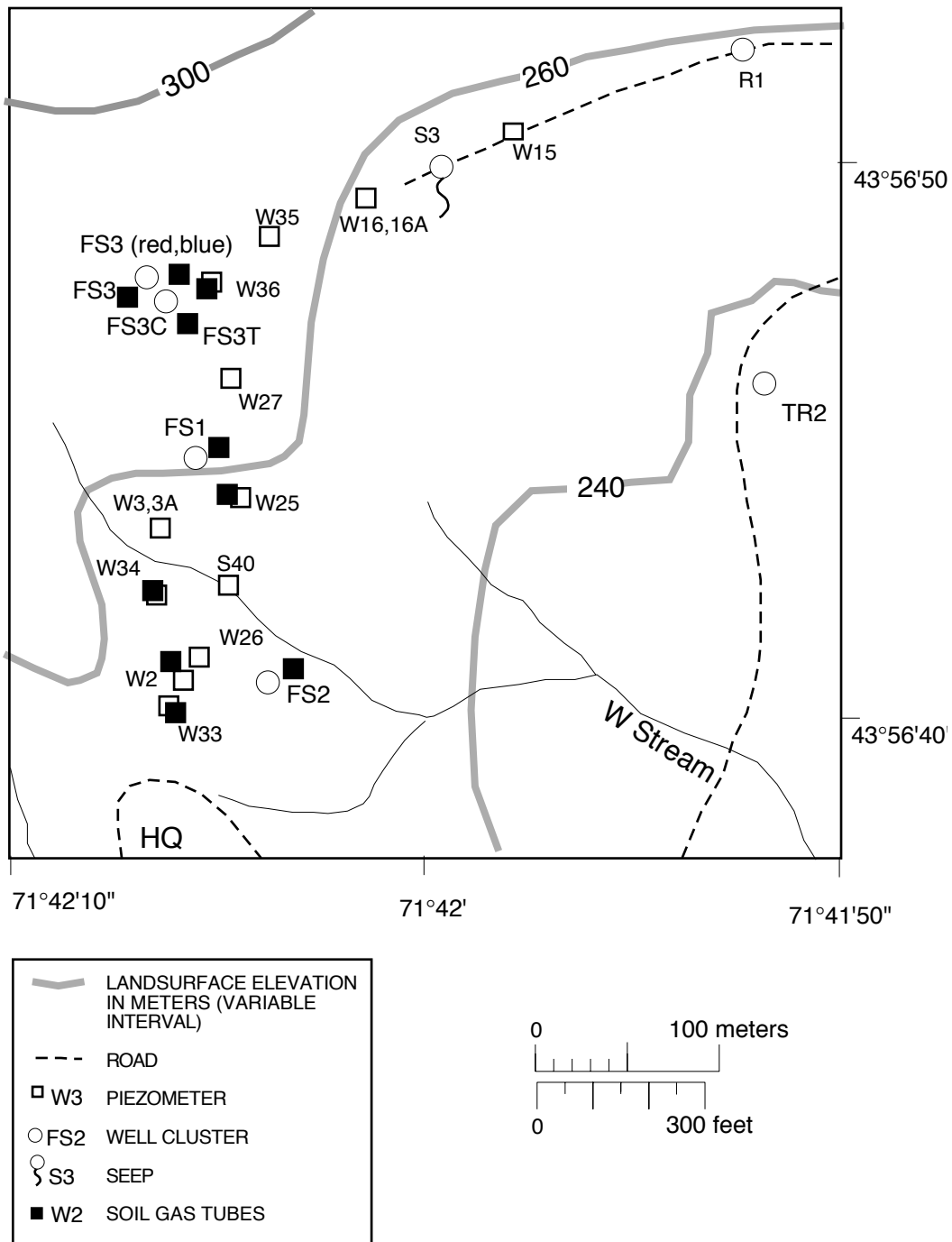


Figure 4-5. Locations of soil gas sampling tubes installed for this study.

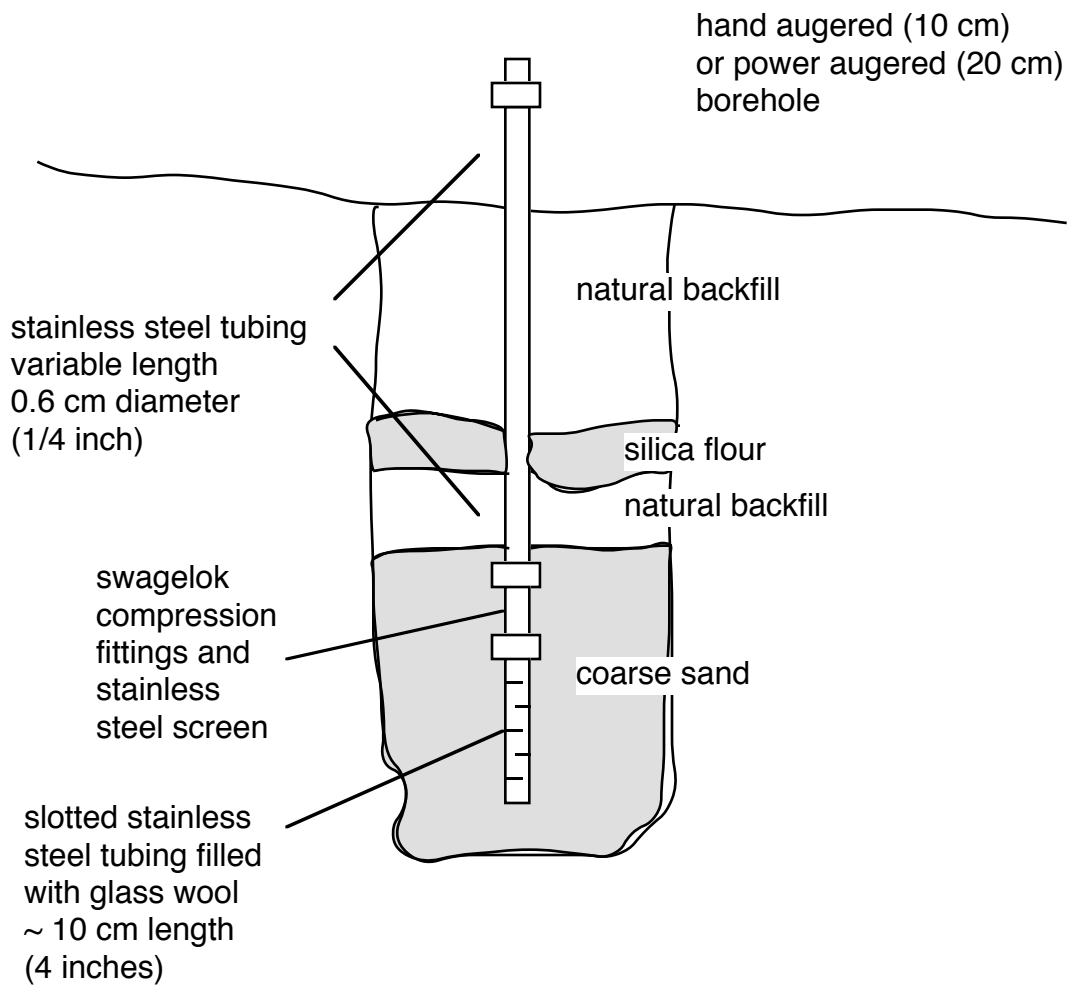


Figure 4-6. Schematic of typical soil gas well.

Soil gas samples were pumped from the dry well into glass ampules which were sealed by welding. A Rasmussen stainless steel gas pump with Teflon diaphragm (40 psig model) was attached to the dry well and pumped for 2-3 minutes to purge the well. All metal (aluminum and stainless steel) tubing was used. Samples were collected after purging in 150 ml glass ampules which were sealed by welding the ampule neck closed with a MAP gas torch. Three samples were normally collected from each dry well. All CFC gas samples were analyzed at the USGS CFC Lab in Reston.

Air samples were also collected to ascertain the local CFC gas concentrations. Samples were collected using the Rasmussen pump with aluminum tubing and a stainless steel cylinder provided by the USGS CFC Lab in Reston. Additional samples were collected using the same apparatus and sample ampules as the soil gas, but with the pump intake in air, 1-2 m above ground. These samples provide further information on local CFC air concentrations, and possible sample apparatus contamination.

4.3 Results

4.3.1 Moisture Content and Pressure

Soil moisture was relatively high from late fall through early summer, and was relatively low in the summer, except immediately after rainfall (fig. 4-7). Overall, the moisture content was significantly higher at the shallower depth. Moisture content at 18 cm is 0.2 - 0.25 in late spring and falls to as low as 0.09 during late summer. Average moisture content over the 50-80 cm depth range is 0.12 - 0.17 in spring and fell to 0.07 in mid-September 1997. When the 18-cm moisture content is above about 0.2, then the 50-80 cm moisture content responds relatively quickly to rainfall, although the response is smaller in magnitude than at the shallower depth. However, when the shallow moisture content falls below about 0.2, the deeper moisture content responds only very gradually to rainfall.

Precipitation during 1996 was very high, but 1997 precipitation was below average through September (U.S. Forest Service files, 1997). However, this difference in precipitation is not reflected by soil moisture differences. Overall, the ranges of soil moisture contents during the wet summer of 1996 and the dryer summer of 1997 are similar. Some differences are apparent. For example, moisture contents in July 1996 are significantly higher than in July 1997. However, even in the dryer July 1997, recharge of soil moisture is occurring at the 50-80 cm depth following sufficient precipitation.

Moisture content was relatively constant in time under snow cover during February 1997 (fig. 4-7), increasing during a partial melt at the end of February and again during final melt at the end of March and beginning of April 1997. The relatively small changes in moisture content during winter are consistent with previous observations in other parts of the Hubbard Brook drainage basin (Herkelrath et al., 1991).

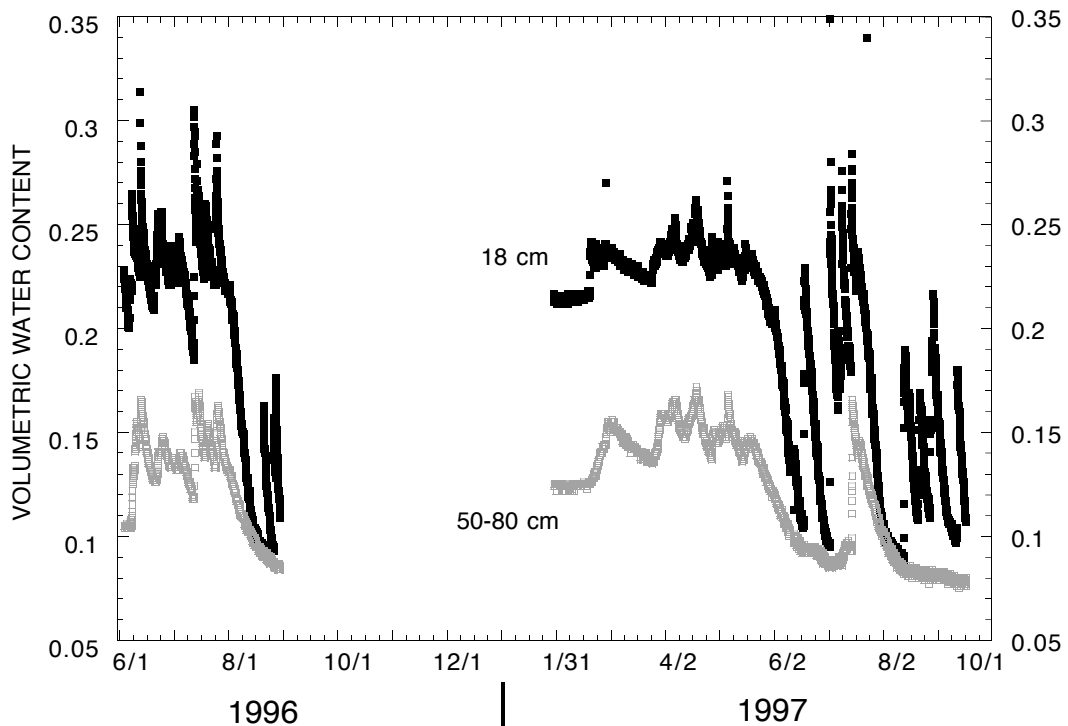


Figure 4-7. Moisture content during 1996 and 1997 near W2 at depth of 18 cm and average over depth range 50-80 cm.

Tensiometer measurements of pressure head in the unsaturated zone are similar to the soil moisture results, although tensiometer results are available only for the summers of 1996 and 1997 (fig 4-8). Suction head (negative pressure head) is low in the early summer at all depths but increases significantly at the 30 cm depth as the upper soil zone dries out. Fluctuations in suction head at 30 cm generally mirror soil moisture fluctuations, with high moisture content and low suction head after rainfall, and then falling moisture content and increasing suction head as drying proceeds. The deeper 60- and 90-cm suction pressure heads changed much less during the monitored period. The 90-cm results were essentially constant in the range 10-14 centibars, while the 60-cm suction head increased somewhat only after extended drying, and then increased only to about 30 centibars.

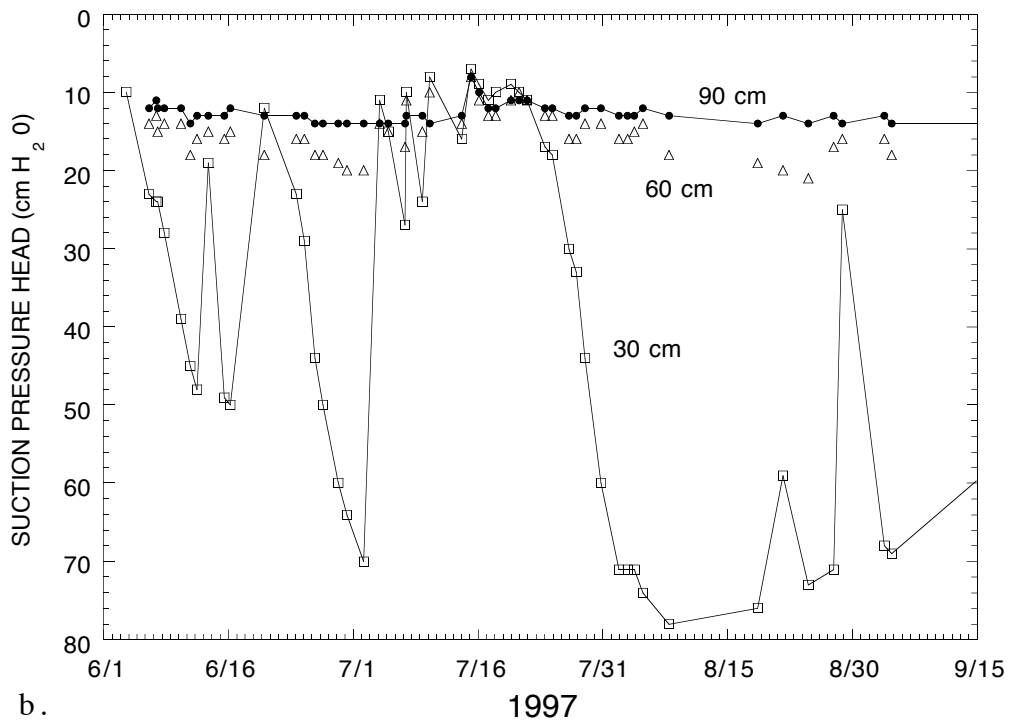
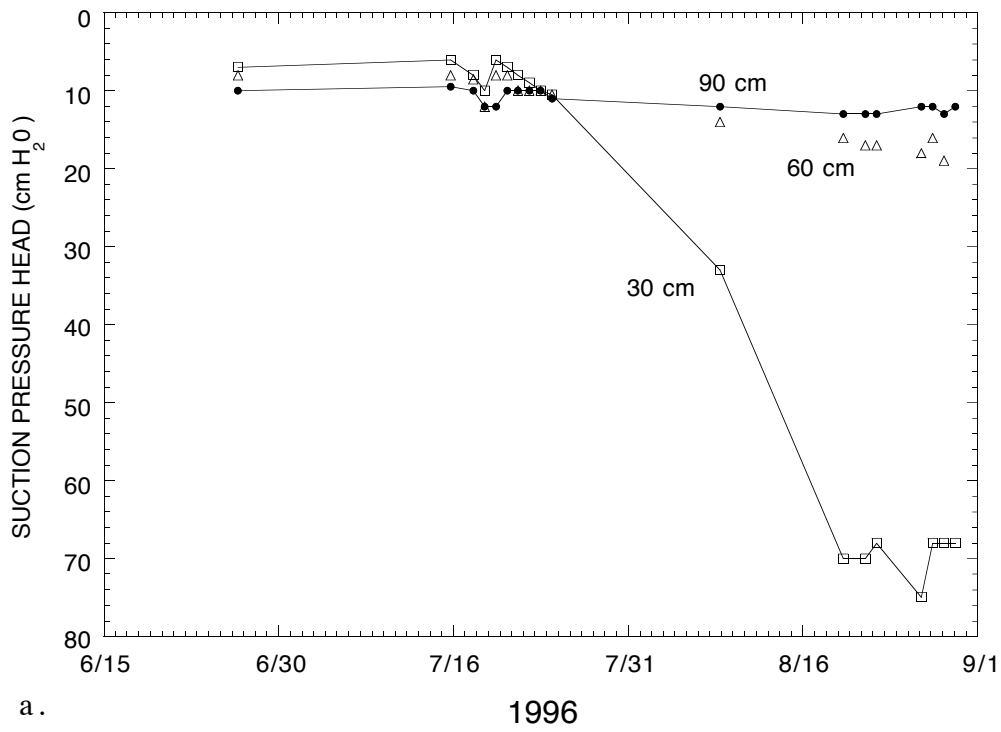


Figure 4-8. Suction pressure head at W2 TDR site during (a) the summer of 1996, and (b) the summer of 1997.

Although uncalibrated, the gypsum block results provide a continuous record of relative fluctuations of suction pressure head during the summer of 1997. The 3 blocks installed with the tensiometers show similar, but not identical, responses (fig. 4-9a). The deepest probe (90 cm) shows a very slow decrease in resistance, corresponding to increasing wetness. The resistance change at 60 cm is similar in pattern to the observed suction pressure head (fig. 4-8b). The significant decreases in suction pressure head at 30 cm depth during the early part of the summer of 1997 correspond to only minor changes in electrical resistance at 30 cm. However, the subsequent drying in the latter part of the summer is represented similarly by both suction pressure head and electrical resistance changes. Notably, the electrical resistance changes following recharge are more gradual than the tensiometer data, suggesting a time-lag in the gypsum block, probably due to moisture diffusion.

The temporal fluctuations are more rapid for the 5 gypsum blocks installed in a separate shallow hole (fig. 4-9b). The overall pattern of the electrical resistance in the gypsum block at 20 cm depth is very similar to the pressure head fluctuations measured at 30 cm (fig. 4-8b). However, the block at 10 cm apparently has much lower resistance, relative to the other gypsum blocks, but has a similar temporal pattern. The rapid decrease in resistance in the first week of August 1997 is observed only for the 10 cm block, suggesting that wetness increased very near the surface, but infiltration did not occur to 20 cm. The resistance changes also appear to be most rapid at the 10 cm depth. The 30 and 40 cm block respond very similarly to each other, and their response slightly lags that at 20 cm. The 58 cm block responds most slowly, but indicates significant drying at that depth during August 1997.

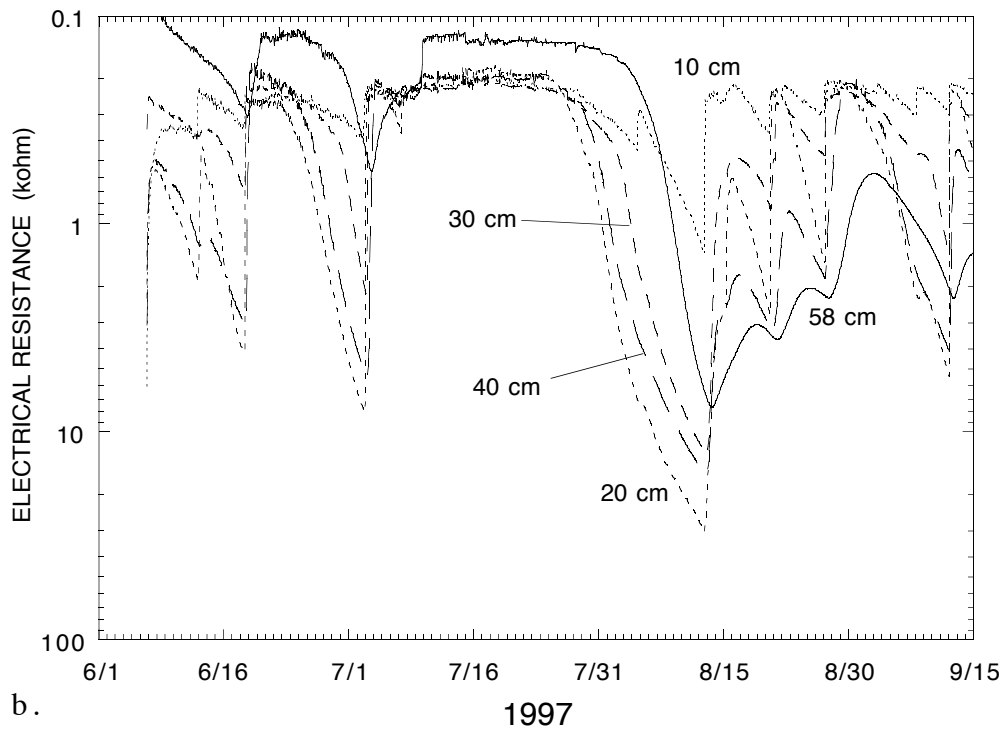
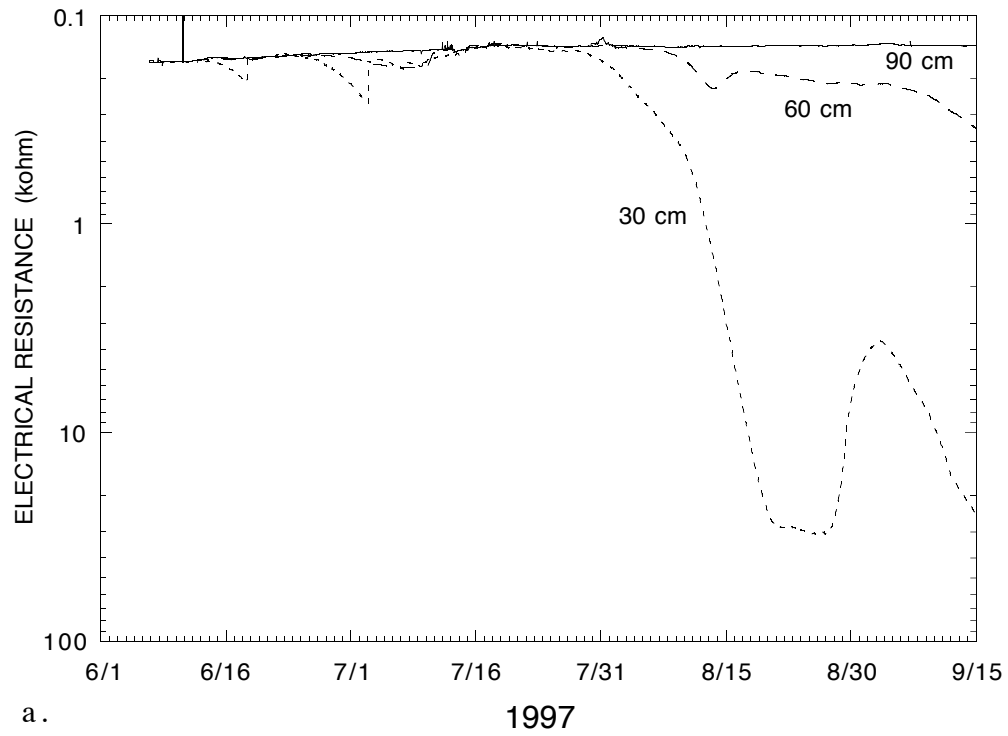


Figure 4-9. Gypsum block electrical resistance during summer 1997: (a) at W2 TDR site, and (b) in separate borehole at W2 TDR site.

Overall, these soil moisture, tensiometer, and gypsum block data indicate that a dynamic unsaturated zone exists at Mirror Lake. Although moisture contents are generally constant during the winter, significant infiltration can occur during temporary warm periods. The summer is not characterized by very low moisture contents and high soil moisture suction. Rather several drying/wetting cycles occur during the summer to depths of at least 60 cm. The unsaturated zone is not in static equilibrium with zero recharge during the summer. Soil moisture and suction pressure data show that infiltration to depths of at least 60 cm routinely occurs following sufficient precipitation, even during the peak evapotranspiration period. These data are consistent with observations of static and occasionally increasing hydraulic head in saturated-zone wells during the summer (fig. 4-10). Without this recharge during the 3-to-4-month growing season, water levels in these wells would be expected to drop throughout the summer due to discharge to streams.

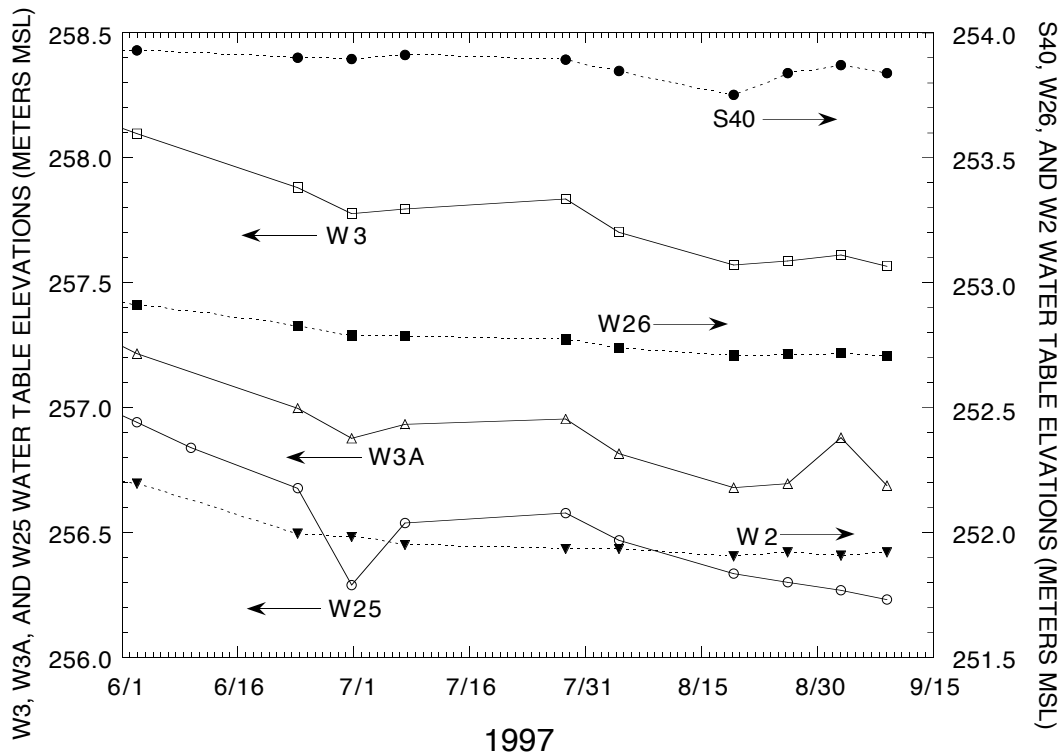


Figure 4-10. Water table elevations during summer 1997 in six piezometers near W2 TDR, tensiometer, and gypsum block sites. Arrows point to the corresponding elevation axis.

4.3.2 Soil Temperature

Soil temperature at FS3 was monitored continuously from early June 1996 until mid-September 1997. All of the soil temperatures change gradually from hour to hour (fig. 4-11). The most rapid changes are associated with infiltration events during heavy storms or snowmelt. The surface temperature changes rapidly except when the surface is covered by snow in the winter.

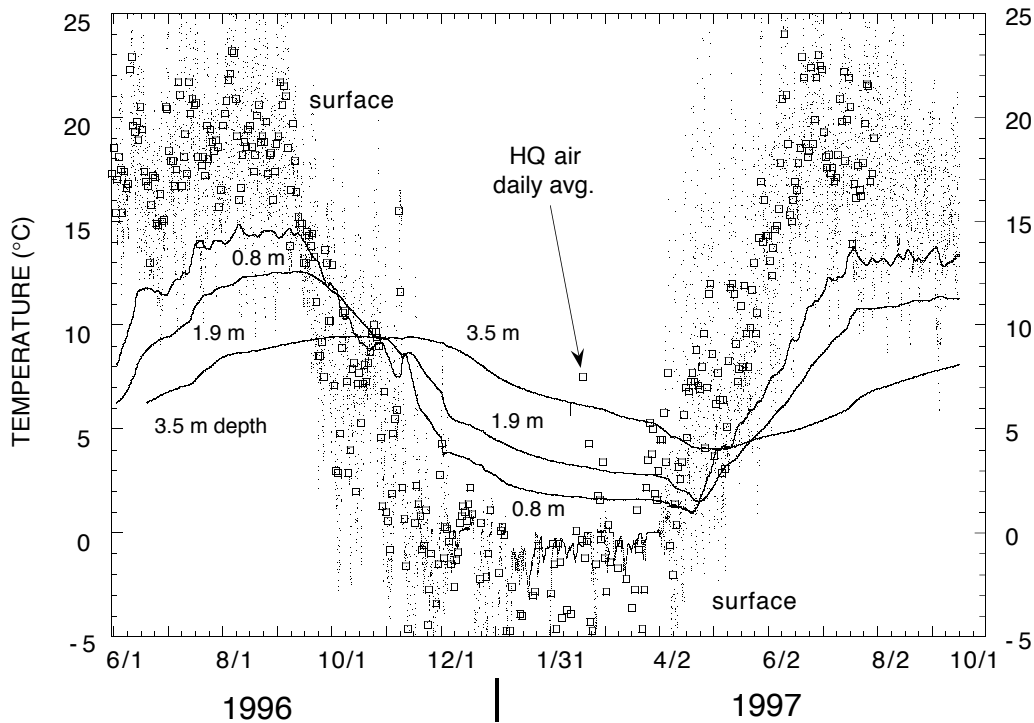


Figure 4-11. Air, surface and soil temperature near FS3. Hourly soil temperatures at 0.9 and 1.8 m depth and at 3.5 m depth at bottom of dry well FS3C-14 are solid lines. Hourly surface temperatures are dots. Daily average air temperature at Forest Service Headquarters (HQ) is squares.

The general temporal and spatial trends in temperature follow the classic diffusion controlled profile, as reported by Federer (1973) for other parts of the Hubbard Brook drainage basin. The lag and dampening of temperature fluctuations increases with depth. Surface temperatures range from about $-5\text{ }^{\circ}\text{C}$ to over $25\text{ }^{\circ}\text{C}$ with minimum temperatures in November-April and maximum in June-August. At 3.5 m depth, the temperature range is only 4 to $9.5\text{ }^{\circ}\text{C}$ with the minimum in April and the maximum in November. The mean temperature at the 3.5 m depth is about $7\text{ }^{\circ}\text{C}$. At intermediate soil depths the cycle in temperature is not symmetric. Cooling in the fall and winter is more gradual than the rapid heating that occurs for about 3.5 months after snow melt.

Soil temperatures at the FS4 site (fig. 4-12) are similar to those as FS3. FS4 is higher in the watershed and this elevation change is reflected in the slightly lower summer temperatures at FS4. The maximum temperature at 75 cm at FS4 is 13°C, whereas the maximum temperature at 80 cm at FS3 is 14 °C. Conversely, the minimum temperature at 75 cm at FS4, 3.5°C, is higher than that at 80 cm at FS3, 1°C.

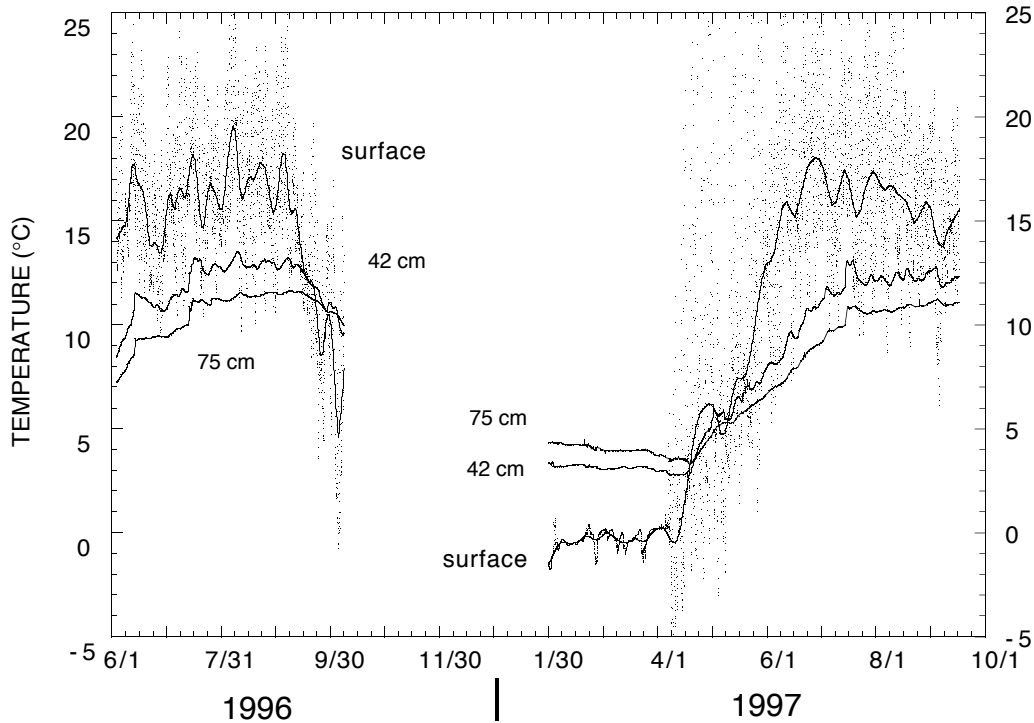


Figure 4-12. Air, surface and soil temperature near FS4: Hourly soil temperatures at 42 and 75 cm depth (solid lines); Hourly surface temperature (dots) with smoothed curve (solid line).

Rapid air and surface temperature fluctuations are often associated with precipitation or melting events which serve to advect relatively hot or cold water down with infiltrating water. For example, very rapid soil temperature increases in 1996 are associated with a moving cold front that caused rapid drops in air and surface temperature (hail was observed at the site). Even though the precipitation was cold, the result of the heavy precipitation (mostly rain) was to carry relatively warm water down into the soil

column. Inflections in soil temperature at 3.5 m in July 1996, April 1997, and July 1997 are caused by heat advection in moving water during significant infiltration events.

Snow cover in winter insulates the surface from air temperature fluctuations. During November-December 1996 snow cover was minimal and surface temperatures closely followed air temperature. January-March 1997 was a period with more snow cover and stable surface temperature near zero. A melt in February 1997 led to subsequent decreased surface temperatures because of the loss of the insulating snow cover. Gradual cooling occurs at the intermediate depths while snow cover is present. Snow melt in April 1997 caused rapid decreases in soil temperature as large amounts of nearly frozen water infiltrated. These dynamics cause the upper soil column to experience minimum temperatures during the spring snow melt event. The minimum temperatures in April 1997 were 1°C at 0.8 m and 1.5°C at 1.9 m depth.

4.3.3 General Chemistry

Field water-quality parameters exhibit significant variability in water-table piezometers at the Mirror Lake site (Table 4-4). In general, specific conductance values are relatively low compared to bedrock wells at the site (Shapiro et al., 1998). The pH ranges from 5 to 11 with most values between 5 and 7. High pH has been associated with cement grout installed at older piezometers (P.T. Harte, written commun., 1991).

Dissolved oxygen (DO) concentrations are significantly below saturation levels in many samples from water-table piezometers at the Mirror Lake site (Table 4-3). In several areas the water table is apparently anaerobic, or nearly so (fig. 4-13). This corresponds with the wide-spread observation of low-DO in bedrock wells (Busenberg and Plummer, 1996).

Table 4-4. Geochemical data from water samples.

Well ID	Date	Pumping Rate (L/min)	Temp. (°C)	pH	Sp. Cond. (µS/cm)	Field DO (mg/L)	Ca2+ (mg/L)	Mg2+ (mg/L)	Sr2+ (mg/L)	SiO2 (mg/L)
FS1-17	18-Jul-95	0.05	15	6.6	77	0.01	5.5	1.24	0.034	9.24
FS1-17	19-Jul-96	0.1		6.8	74	0.1-0.7	5.3	1.20	0.034	10.7
FS1-25	20-Jul-96	0.1		11	370	3	32.3	0.51	0.069	14.2
FS1-35	20-Jul-96	0.7		5.3	24	4	1.6	0.24	0.011	6.50
FS3C-19	14-Jul-95	0.05	24	5.6	25	9.5	1.56	0.26	0.015	5.65
FS3C-19	18-Jul-96	0.34		5.4	24	8	1.6	0.32	0.014	6.90
FS3C-24	15-Jul-95	0.1	18	5.8	30	8.8	2.19	0.55	0.015	8.17
FS3C-24	18-Jul-96	0.13		5.8	28	6.8	2.1	0.50	0.015	8.80
FS3C-24	12-Jun-97	0.11	8-9	5.5	26	7	1.77	0.44	0.013	7.47
FS3C-29	17-Jul-96	0.1-0.2		6.5	29	6.2	1.5	0.37	0.013	7.20
FS3C-29	11-Jun-97	0.04	7-12	5	22	5.8	1.38	0.37	0.012	5.93
FS4-WT	8-Jul-97	0.06	10.6	4.5	54-76	4.7	4.02	0.36	0.025	9.26
R1-36	10-Jul-95	0.3	8	6.4	23	10.6	1.88	0.31	0.016	4.09
R1-55	11-Jul-95	0.05	18	10.2	190	0				
RR1-PZ	21-Aug-95	0.74	13.5	6.6	575	0.8	30	5.16	0.42	13.0
S1 spring	6-Aug-97		7.7	4.8	10.5	6	2.78	0.48	0.020	8.58
S3 seep	7-Aug-97	0.07	14	5	23-40	0.8-1.6	0.68	0.16	0.007	4.32
S40	1-Jan-96									
S40	25-Jul-97	0.05					0.92	0.21	0.007	8.43
T1-8	12-Jul-95		20	6.4	35	5.3	1.42	0.28	0.015	6.25
T1-8	26-Jun-97	0.07	13-15	6	28	2	1.27	0.27	0.017	5.73
TR1-63	8-Jul-95	0.1	19	7.8	47	9	4.64	0.75	0.026	17.4
TR1-63	25-Jun-97	0.15	9-16	6.1	46	9.2	4.08	0.79	0.023	18.0
W11	25-Jul-97	0.2	10-13	5.5	38	6.9	3.73	0.44	0.019	9.05
W15	28-Jul-97	0.03	17-20	6.2	50-70	1.9	1.56	0.41	0.014	5.33
W16	28-Aug-96	0.1	13	7	120-180	0.1	14.7	6.50	0.131	24.4
W16	13-Jul-97	0.08	10-20	6.6-8	140-170	0.5	14.3	6.21	0.134	25.5
W16A	27-Aug-96	0.1	15	7	80	3	4.30	1.80	0.039	16.5
W16A	8-Jul-97	0.07	12	6	62-86					
W16A	12-Jul-97	0.09	13	6.3	50-72		3.69	1.41	0.031	12.8
W2	20-Jun-95	0.06	17	6.4	74	0	5.16	1.18	0.031	18.7
W2	26-Aug-96	0.2	21	6.3	68	0.2-2.0				
W2	7-Jun-97	0.07	9-12	7	75	0.5-1.0	5.22	1.34	0.027	19.7
W25	21-Jun-95	0.13	11	6.8	85	0.5	7.17	1.84	0.036	16.7
W25	13-Jul-97	0.09	14-17	6.7	93	0.1	7.53	2.02	0.034	18.5
W26	21-Jun-95	0.1	15	6.9	83	0	5.80	1.44	0.032	19
W26	16-Aug-95						6.10	1.48	0.032	19.1
W26	26-Aug-96	0.2		6.4	80	0.05				
W26	8-Jun-97	0.08	10-12	6.7	85	0.5-0.7	5.99	1.62	0.030	20.3
W26	26-Jul-97									
W27	16-Jul-95	0.05	20	6.3	54	5.1	5.55	1.19	0.033	12
W27	19-Jun-97	0.11	10	5.8	50	4	5.16	1.16	0.027	12.6
W3	23-Jun-95	0.1	16	6.3	47	3	3.85	0.89	0.025	16.5
W3	14-Jul-97	0.26	11-20	6	52	2.5	4.30	1.10	0.027	18.6
W3A	23-Jun-95	0.2	19	5.4	23	6.8	1.33	0.25	0.014	7.57
W3A	14-Jul-97	0.09	12-22	5	20-29	5.6	1.45	0.28	0.013	7.30
W33	22-Aug-96	0.4	24	6.8	74	0.04	5	1.3	0.025	21
W33	7-Jul-97	0.15	10	6.4	78	0				
W34	22-Aug-96	0.05		7	55	2.7	3.5	0.79	0.021	15.7
W34	10-Jun-97	0.06	9-14	6.3	37	6-7	3.04	0.61	0.016	13.9
W34	14-Jul-97									
W34	14-Jul-97									
W35	27-Aug-96	0.1	15		60	0.2	1.9	0.72	0.028	15.4
W35	11-Jul-97	0.03	9.3	5-5.8	35	4.6				
W36	26-Aug-96	0.05-0.1	15	6	39	3	2.2	0.71	0.027	10.8
W36	27-Aug-96	0.1	15		40	3				
W36	17-Jun-97	0.1	8	5.4	23	7.8	1.55	0.33	0.017	8.54
W6	26-Jul-97	0.07	10-16	6-6.4	140	0.3-0.8	1.85	0.4	0.017	18.9

Table 4-4. Geochemical data from water samples (continued).

Well ID	Date	Na+ (mg/L)	K+ (mg/L)	Fe2+ (mg/L)	Mn2+ (mg/L)	Al3+ (mg/L)	Alkalinity as		Cl- (mg/L)	S042- (mg/L)
							HCO3- (mg/L)	lab field		
FS1-17	18-Jul-95	2.58	1.54	3.84	0.118	<0.005	31.9	40.8	0.69	2.52
FS1-17	19-Jul-96	2.8	1.8	4.51	0.117	0.008	29		0.71	2.87
FS1-25	20-Jul-96	3.4	2.2	0.023	<0.004	0.241	47.4		0.52	6.33
FS1-35	20-Jul-96	0.8	<0.3	0.039	0.019	0.225	2.5		0.56	3.97
FS3C-19	14-Jul-95	1.17	0.28	0.085	0.023	0.02	5.25	4.39	0.9	4.85
FS3C-19	18-Jul-96	1.3	<0.3	0.012	0.014	0.14	3.1		0.68	5.02
FS3C-24	15-Jul-95	1.46	0.45	0.027	0.019	0.007	7.53	9.29	0.99	5.75
FS3C-24	18-Jul-96	1.4	0.3	<0.010	0.016	0.015	7		0.7	4.61
FS3C-24	12-Jun-97	1.33	0.5	0.010	0.012	0.016	4.5		1.16	5.06
FS3C-29	17-Jul-96	1.2	0.3	0.046	0.037	0.093	4.5		1.04	5.1
FS3C-29	11-Jun-97	1.09	0.4	0.01	0.028	0.061	2.0		1.16	5.06
FS4-WT	8-Jul-97	1.12	1.0	0.79	0.114	0.564	<2		1.21	18.3
R1-36	10-Jul-95	0.81	0.15	0.01	<0.005	0.02	1.8	2.93	0.98	6.19
R1-55	11-Jul-95									
RR1-PZ	21-Aug-95	57.4	11.9	1.46	1.47	0.071	71.1	53.7	115.3	23.6
S1 spring	6-Aug-97	1.42	0.4	<0.007	0.004	0.050	5.0		1.15	5.80
S3 seep	7-Aug-97	0.98	0.2	2.02	0.054	0.192	5.6		1.29	2.95
S40	1-Jan-96									
S40	25-Jul-97	0.93	0.3	0.352	0.062	0.262	3.6		1.12	3.89
T1-8	12-Jul-95	1.1	0.43	1.39	0.074	<0.005	16	22.7	1.14	1.72
T1-8	26-Jun-97	1.01	0.50	2.41	0.072	0.01	10.1		1.29	1.65
TR1-63	8-Jul-95	2.89	1.1	0.017	0.012	0.01	19.5	19	0.98	5.82
TR1-63	25-Jun-97	2.88	1.2	0.009	0.005	0.008	16.9		1.23	5.22
W11	25-Jul-97	2.18	0.6	0.008	0.009	0.022	9.4		2.65	4.05
W15	28-Jul-97	1.11	0.6	10.4	0.215	0.003	28.9		1.18	4.67
W16	28-Aug-96	4.7	3.9	5.65	1.03	0.003	96.9		0.61	1.62
W16	13-Jul-97	4.39	3.5	5.05	1.07	0.003	94		1.11	2.81
W16A	27-Aug-96	2.3	2.1	<0.010	0.463	0.01	27		0.64	5.80
W16A	8-Jul-97									
W16A	12-Jul-97	1.99	1.1	<0.006	0.119	0.007	18.9		1.18	5.60
W2	20-Jun-95	3.28	1.06	4.77	0.085	<0.005	20.1	25.9	0.67	11.1
W2	26-Aug-96									
W2	7-Jun-97	3.33	1.2	3.42	0.092	0.007	19.8		1.25	13.9
W25	21-Jun-95	3.79	1.82	2.45	0.108	<0.005	33.4	33.7	0.71	11.2
W25	13-Jul-97	3.87	2.0	2.2	0.086	0.003	31.3		1.16	14.2
W26	21-Jun-95	3.43	1.33	4.83	0.114	<0.005	22.5	29.3	0.71	12.4
W26	16-Aug-95	3.48	1.34	5.07	0.097	0.006	23.4		1.26	12.1
W26	26-Aug-96									
W26	8-Jun-97	3.63	1.5	3.09	0.089	0.002	22.7		1.14	15.3
W26	26-Jul-97									
W27	16-Jul-95	1.75	1.23	0.2	0.164	0.007	22	22	0.77	6.87
W27	19-Jun-97	1.73	1.3	0.154	0.096	0.007	18.8		1.19	6.11
W3	23-Jun-95	2.69	1.09	0.014	<0.005	<0.005	16	14.2	0.67	8.52
W3	14-Jul-97	2.80	1.3	0.021	<0.003	0.004	16.5		1.12	8.35
W3A	23-Jun-95	1.36	0.14	0.024	0.012	0.092	4.5	6.83	0.63	4.36
W3A	14-Jul-97	1.14	0.2	0.009	0.009	0.131	2.5		1.18	4.31
W33	22-Aug-96	3.4	1.4	3	0.217	0.009	16.1		0.67	13.7
W33	7-Jul-97									
W34	22-Aug-96	3.4	2.1	<0.010	0.209	0.015	15.4		0.66	7.87
W34	10-Jun-97									
W34	14-Jul-97	2.09	1.4	0.023	0.021	0.028	11.4		1.22	5.66
W34	14-Jul-97									
W35	27-Aug-96	3.60	3.6	0.054	1.55	0.006	22.2		0.73	4.31
W35	11-Jul-97									
W36	26-Aug-96	1.80	1.6	<0.010	1.06	0.013	11.3		0.78	6.05
W36	27-Aug-96									
W36	17-Jun-97	1.32	0.6	<0.007	0.042	0.046	3.3		1.19	4.74
W6	26-Jul-97	3.60	2.5	21.5	0.355	0.002	37.9		12.3	6.14

Table 4-4. Geochemical data from water samples (continued).

Well ID	Date	NO ₃ - (mg/L)	F- (mg/L)	Br- (mg/L)	Total Cations meq	Total Anions (meq) lab alk.	Total Anions (meq) field alk.	Charge Bal % lab alk.	Charge Bal % field alk.	Si (mg/L)
FS1-17	18-Jul-95	0.14		0	0.671	0.597	0.743	11.63	-10.21	
FS1-17	19-Jul-96	0.06	0.04	<0.01	0.71	0.56		23.7		5.01
FS1-25	20-Jul-96	0.13	0.06	0.02	1.89	0.93		68.11		6.64
FS1-35	20-Jul-96	0.01	0.06	<0.01	0.16	0.14		14.08		3.02
FS3C-19	14-Jul-95	0.15		0	0.164	0.215	0.201	-26.99	-20.3	
FS3C-19	18-Jul-96	0.02	0.06	<0.01	0.19	0.18		7.14		3.24
FS3C-24	15-Jul-95	0.08		0	0.232	0.272	0.301	-15.85	-25.81	
FS3C-24	18-Jul-96	0.03	0.04	<0.01	0.23	0.23		-0.41		4.12
FS3C-24	12-Jun-97	0.13	<0.05	<0.02	0.2	0.214		-6.68		3.49
FS3C-29	17-Jul-96	0.1	0.08	<0.01	0.21	0.22		-2.61		3.38
FS3C-29	11-Jun-97	0.16	0.01	<0.02	0.166	0.174		-4.27		2.77
FS4-WT	8-Jul-97	<0.10	0.06	<0.02	0.401	0.418		-4.11		4.33
R1-36	10-Jul-95	0.13		0	0.161	0.188	0.207	-15.33	-24.62	
R1-55	11-Jul-95									
RR1-PZ	21-Aug-95	10.5		0	4.846	5.078	4.793	-4.68	1.1	
S1 spring	6-Aug-97	0.62	0.05	<0.02	0.258	0.248		4.09		4.01
S3 seep	7-Aug-97	<0.10	0.05	<0.02	0.192	0.192		0.00		2.02
S40	1-Jan-96									
S40	25-Jul-97	<0.10	0.06	<0.02	0.156	0.174		-10.8		3.94
T1-8	12-Jul-95	0.18		0	0.206	0.333	0.443	-47.3	-73.2	
T1-8	26-Jun-97	<0.10	<0.05	<0.02	0.239	0.236		1.1		2.68
TR1-63	8-Jul-95	0.37		0	0.45	0.474	0.466	-5.31	-3.57	
TR1-63	25-Jun-97	0.30	0.06	<0.02	0.433	0.428		1.16		8.43
W11	25-Jul-97	0.89	0.04	<0.02	0.338	0.33		2.45		4.23
W15	28-Jul-97	<0.10	<0.05	<0.02	0.607	0.604		0.43		2.49
W16	28-Aug-96	<0.01	0.49	<0.01	1.82	1.66		8.99		11.4
W16	13-Jul-97	0.73	0.49	<0.02	1.734	1.668		3.87		11.9
W16A	27-Aug-96	0.09	0.1	<0.01	0.54	0.59		-9.04		7.7
W16A	8-Jul-97									
W16A	12-Jul-97	0.25	0.12	<0.02	0.421	0.470		-11.1		6.0
W2	20-Jun-95	0.08		0	0.699	0.581	0.676	18.5	3.38	
W2	26-Aug-96									
W2	7-Jun-97	<0.10	0.11	<0.02	0.675	0.655		3.03		9.2
W25	21-Jun-95	0.08		0	0.813	0.802	0.807	1.39	0.77	
W25	13-Jul-97	<0.10	0.22	<0.02	0.845	0.853		-1.01		8.66
W26	21-Jun-95	0.08		0	0.769	0.648	0.76	17.04	1.22	
W26	16-Aug-95	0.02		0	0.798	0.671		17.29		
W26	26-Aug-96									
W26	8-Jun-97	<0.10	0.15	<0.02	0.745	0.730		2.00		9.5
W26	26-Jul-97									
W27	16-Jul-95	0.17		0	0.497	0.528	0.528	-6.04	-6.04	
W27	19-Jun-97	<0.10	0.05	<0.02	0.471	0.472		-0.10		5.9
W3	23-Jun-95	0.09		0	0.411	0.46	0.43	-11.17	-4.55	
W3	14-Jul-97	<0.10	0.09	<0.02	0.466	0.481		-2.99		8.7
W3A	23-Jun-95	0.05		0	0.162	0.183	0.221	-12.53	-31.23	
W3A	14-Jul-97	<0.10	0.08	<0.02	0.166	0.168		-1.19		3.41
W33	22-Aug-96	<0.01	0.13	<0.01	0.66	0.57		13.61		9.8
W33	7-Jul-97									
W34	22-Aug-96	0.02	0.08	0.01	0.45	0.44		2.94		7.34
W34	10-Jun-97	0.25	0.05	<0.02	0.335	0.346		-3.06		6.52
W34	14-Jul-97									
W34	14-Jul-97									
W35	27-Aug-96	<0.01	0.07	<0.01	0.46	0.48		-3.07		7.2
W35	11-Jul-97									
W36	26-Aug-96	0.02	0.05	<0.01	0.33	0.34		-2.23		5.03
W36	27-Aug-96									
W36	17-Jun-97	<0.10	0.05	<0.02	0.183	0.192		-4.37		3.99
W6	26-Jul-97	1.79	0.05	0.02	1.141	1.128		1.2		8.85

Table 4-4. Geochemical data from water samples (continued).

Well ID	Date	B3+ (mg/L)	Ba2+ (mg/L)	Li+ (mg/L)	Cu (mg/L)	Zn (mg/L)	trace NO2	trace PO4	trace oxalate	Deuterium (per mil VSMOW)
FS1-17	18-Jul-95									-66.14
FS1-17	19-Jul-96	<0.005	0.005	0.014	0.016	0.275		y	y	-68.4
FS1-25	20-Jul-96	<0.005	0.009	0.016	0.011	0.005	y		y	-66.3
FS1-35	20-Jul-96	<0.005	0.011	0.002	0.121	0.018				-61.1
FS3C-19	14-Jul-95									-66.6
FS3C-19	18-Jul-96	<0.005	0.006	0.002	0.277	0.095				-62.4
FS3C-24	15-Jul-95									-67.02
FS3C-24	18-Jul-96	<0.005	0.003	0.002	0.303	0.178				-63.9
FS3C-24	12-Jun-97	<0.005	0.002	0.002	0.039	0.067				-69.83
FS3C-29	17-Jul-96	<0.005	0.004	0.004	0.841	0.14			y	-66.5
FS3C-29	11-Jun-97	<0.005	0.003	0.003	0.017	0.044				-70.58
FS4-WT	8-Jul-97	<0.005	0.016	0.004	0.018	0.040				-71.03
R1-36	10-Jul-95									-67.21
R1-55	11-Jul-95									-67.37
RR1-PZ	21-Aug-95									-59.88
S1 spring	6-Aug-97	<0.005	0.004	0.002	0.004	0.023				-64.67
S3 seep	7-Aug-97	<0.005	0.007	0.001	0.004	0.058				-68.16
S40	1-Jan-96									
S40	25-Jul-97	<0.005	0.006	0.002	0.010	0.021				-61.48
T1-8	12-Jul-95									-81.32
T1-8	26-Jun-97	<0.005	0.002	<0.001	0.007	0.176				-61.82
TR1-63	8-Jul-95									-67.26
TR1-63	25-Jun-97	<0.005	0.002	0.008	0.173	0.021				-65.41
W11	25-Jul-97	<0.005	0.004	<0.001	0.024	0.057				-65.67
W15	28-Jul-97	<0.005	0.006	0.002	0.003	1.70				-64.25
W16	28-Aug-96	<0.005	0.006	0.029	0.002	0.159				-64
W16	13-Jul-97	<0.005	0.007	0.027	0.002	0.189				-65.64
W16A	27-Aug-96	<0.005	0.003	0.013	0.006	0.028				-65.6
W16A	8-Jul-97									
W16A	12-Jul-97	<0.005	0.002	0.009	0.003	0.010				-63.55
W2	20-Jun-95									-49.51
W2	26-Aug-96									
W2	7-Jun-97	<0.005	0.004	0.008	0.004	0.046				-63.68
W25	21-Jun-95									-69.07
W25	13-Jul-97	<0.005	0.004	0.024	0.019	0.010				-66.89
W26	21-Jun-95									-65.01
W26	16-Aug-95									
W26	26-Aug-96									
W26	8-Jun-97	<0.005	0.004	0.012	0.004	0.041				-64.56
W26	26-Jul-97									
W27	16-Jul-95									-68.97
W27	19-Jun-97	<0.005	0.004	0.004	0.002	0.008				-66.75
W3	23-Jun-95									-63.31
W3	14-Jul-97	<0.005	0.001	0.008	0.124	0.009				-66.13
W3A	23-Jun-95									-65.83
W3A	14-Jul-97	<0.005	0.003	0.001	0.007	0.028				-69.15
W33	22-Aug-96	<0.005	0.003	0.01	0.007	0.023				-63.2
W33	7-Jul-97									
W34	22-Aug-96	<0.005	0.002	0.009	0.016	0.032	y			-66.4
W34	10-Jun-97	<0.005	0.001	0.006	0.004	0.046				-66.41
W34	14-Jul-97									
W34	14-Jul-97									
W35	27-Aug-96	<0.005	0.004	0.003	0.005	0.027				-64.4
W35	11-Jul-97									
W36	26-Aug-96	<0.005	0.004	0.002	0.005	0.016				
W36	27-Aug-96									
W36	17-Jun-97	<0.005	0.003	0.002	0.004	0.011				-66.00
W6	26-Jul-97	<0.005	0.004	0.024	0.003	0.366				-69.20

Table 4-4. Geochemical data from water samples (continued).

Well ID	Date	Oxygen-18 (per mil VSMOW)	Tritium TU	Tritium m 1 sig TU	C-13 (per mil VPDB)	CFC-11a	CFC-11b	CFC-11c	CFC-12a	CFC-12b
FS1-17	18-Jul-95	-10.14	13.1	0.4	-22.81	9025.8	5455.4	4206.8	392.8	366.9
FS1-17	19-Jul-96	-10.37	12	0.4	-21.9	6214	8481.4	6223.2	85.8	389.2
FS1-25	20-Jul-96	-10.11	13.2	0.4	-15.7	9403.3	88830.6	9083.3	427.1	393.6
FS1-35	20-Jul-96	-9.42	10.3	0.4	-24.5	ERR	ERR	ERR	1089.6	1355.5
FS3C-19	14-Jul-95	-10.08	12.5	0.4	-16.4	1110.7	1096.3	1060.5	408.7	417.3
FS3C-19	18-Jul-96	-9.71	9.9	0.3	-24.7	812.9	786.6	860.4	389.3	382.7
FS3C-24	15-Jul-95	-10.12	12.3	0.4	-24.05	1116.5	1135.2	1092.7	439.2	461.1
FS3C-24	18-Jul-96	-9.97	11.8	0.4	-20.1	939.8	953.1	976.1	396.5	402.7
FS3C-24	12-Jun-97	-10.58	8.80	0.4	-21.50					
FS3C-29	17-Jul-96	-9.84	10.3	0.4	-20.5	952.3	680	931.7	382.2	281.7
FS3C-29	11-Jun-97	-10.87	9.70	0.4	-17.57					
FS4-WT	8-Jul-97	-10.66	11.80	0.5	-17.16					
R1-36	10-Jul-95	-10.14	12.8	0.4	-22.57	922.1	922.9	892.5	422.1	421
R1-55	11-Jul-95	-9.95	11.1	0.4	-13.52	ERR	342.1	ERR	609.5	441.6
RR1-PZ	21-Aug-95	-9.01	13.7	0.4	-20.76	4133.8	4255.1	4421.6	411.5	376.4
S1 spring	6-Aug-97	-9.99	8.50	0.4	-19.19					
S3 seep	7-Aug-97	-10.37	10.10	0.4	-28.14					
S40	1-Jan-96		12.1	0.4						
S40	25-Jul-97	-9.36	12.60	0.5	-27.10					
T1-8	12-Jul-95	-12.02	9.4	0.3	-16.35	781.8	727.8	736.1	407.2	374.3
T1-8	26-Jun-97	-9.31	8.70	0.4						
TR1-63	8-Jul-95	-10.06	12.2	0.4	-23.42	5770.7	5561	5181.4	347.9	361.4
TR1-63	25-Jun-97	-9.92	11.20	0.5						
W11	25-Jul-97	-9.73	10.30	0.5	-22.31					
W15	28-Jul-97	-9.76	11.00	0.5	-21.51					
W16	28-Aug-96	-9.91	3.4	0.18	-10.6	59.8	89.4	94.3	31.7	42.8
W16	13-Jul-97	-9.88	3.40	0.3	-10.21					
W16A	27-Aug-96	-9.91	11.8	0.4	-18.1	569.3	600	664	303.8	430.4
W16A	8-Jul-97									
W16A	12-Jul-97	-9.85	9.90	0.5	-16.94					
W2	20-Jun-95	-5.62	16.6	0.5	-21.48	8.9	11.2		240	250
W2	26-Aug-96									
W2	7-Jun-97	-9.71	14.80	0.6	-20.96					
W25	21-Jun-95	-10.4			-20.54	137.2	165.7	161.3	166.8	178
W25	13-Jul-97	-10.25	24.40	0.8	-20.25					
W26	21-Jun-95	-9.97	22.4	0.7		6.4	3.9	4.6	172.7	193.3
W26	16-Aug-95									
W26	26-Aug-96									
W26	8-Jun-97	-9.87	17.80	0.6	-20.66					
W26	26-Jul-97									
W27	16-Jul-95	-10.66	12.1	0.4	-23.65	784.5		783.8	390.6	
W27	19-Jun-97	-9.96	9.20	0.4						
W3	23-Jun-95	-9.79	14.4	0.4		503.6	507.5	507.9	333.6	342.4
W3	14-Jul-97	-9.85	12.00	0.5	-22.54					
W3A	23-Jun-95	-10.07	12.5	0.4	-12.67	932.4	947.8	921	423.4	430.7
W3A	14-Jul-97	-10.60	9.60	0.4	-19.24					
W33	22-Aug-96	-9.74	12.8	0.4	-20.6	389	58.9	514.1	254.8	247.9
W33	7-Jul-97	-9.76	14.20	0.6	-20.83					
W34	22-Aug-96	-9.98	12	0.4						
W34	10-Jun-97	-10.22	10.90	0.5	-24.78					
W34	14-Jul-97									
W34	14-Jul-97									
W35	27-Aug-96	-9.79	10.6	0.4	-20.7					
W35	11-Jul-97	-10.15	10.10	0.5						
W36	26-Aug-96		10.1	0.3	-23.3	753.8	737.8	734.4	385.6	387.9
W36	27-Aug-96									
W36	17-Jun-97	-9.98	9.50	0.4	-18.92					
W6	26-Jul-97	-10.45	10.70	0.5	-21.20					

Table 4-4. Geochemical data from water samples (continued).

Well ID	Date	CFC-12c	CFC-113a	CFC-113b	CFC-113c	CFC-11 avg	CFC-12 avg	CFC-113 avg	oldage CFC-11	oldage CFC-12
FS1-17	18-Jul-95	359.3	ERR	63.6	75.7				contam.	6
FS1-17	19-Jul-96	386	48.8	149.4	106.2				contam.	28
FS1-25	20-Jul-96	372.3	224.1	162	119.9				contam.	7.5
FS1-35	20-Jul-96	1128.7	ERR	ERR	ERR				ERR	contam.
FS3C-19	14-Jul-95	419.9	118	131.3	129.5	1089.17	415.3	126.267	contam.	0
FS3C-19	18-Jul-96	377.8	163.6	148.4	153.2				11	7
FS3C-24	15-Jul-95	432.9	242.9	214.5	205	1114.8	444.4		contam.	0
FS3C-24	18-Jul-96	386.2	154.2	161.1	145.8				7	6.5
FS3C-24	12-Jun-97									
FS3C-29	17-Jul-96	381.8	182.8	130.1	169.1				14	13.5
FS3C-29	11-Jun-97									
FS4-WT	8-Jul-97									
R1-36	10-Jul-95	421.1	175.5	173.4	181.7	912.5	421.4		6	0
R1-55	11-Jul-95	234.6	ERR	ERR	ERR				22	15
RR1-PZ	21-Aug-95	415.6	163.4	191	159				contam.	4
S1 spring	6-Aug-97									
S3 seep	7-Aug-97									
S40	1-Jan-96									
S40	25-Jul-97									
T1-8	12-Jul-95	377.5	102.3	105.6	110.3				10.5	4.5
T1-8	26-Jun-97									
TR1-63	8-Jul-95	351.6	80.9	87.5	82.3				contam.	7
TR1-63	25-Jun-97									
W11	25-Jul-97									
W15	28-Jul-97									
W16	28-Aug-96	40.9	57.5	26.7	29.6				34	35.5
W16	13-Jul-97									
W16A	27-Aug-96	313.1	102.9	107.3	98				18	12
W16A	8-Jul-97									
W16A	12-Jul-97									
W2	20-Jun-95		0	0		10.05	245	0	41.5	14.5
W2	26-Aug-96									
W2	7-Jun-97									
W25	21-Jun-95	171	11.3	15.3	15.1	154.733	172	13.9	28	20.5
W25	13-Jul-97									
W26	21-Jun-95	180.1	0	0	0	4.96667	182	0	44	20.5
W26	16-Aug-95									
W26	26-Aug-96									
W26	8-Jun-97									
W26	26-Jul-97									
W27	16-Jul-95	398.8	102.5		97.7	784.15	395	100.1	9	2.5
W27	19-Jun-97									
W3	23-Jun-95	340.2	59	62.3	62.7	506.333	338.667	61.3333	18	8
W3	14-Jul-97									
W3A	23-Jun-95	424.1	104.4	105.4	92.6	933.733	426	100.533	1.5	0
W3A	14-Jul-97									
W33	22-Aug-96	234.9	15.7	5.4	13.9				34	17
W33	7-Jul-97									
W34	22-Aug-96									
W34	10-Jun-97									
W34	14-Jul-97									
W34	14-Jul-97									
W35	27-Aug-96									
W35	11-Jul-97									
W36	26-Aug-96	430.6	115.3	190.7	230.1				12	6.5
W36	27-Aug-96									
W36	17-Jun-97									
W6	26-Jul-97									

Table 4-4. Geochemical data from water samples (continued).

Well ID	Date	oldage CFC-113	CH4 (mg/L)	CH4 b	CO2 (mg/L)	CO2 b	N2 (mg/L)	N2 b	O2 (mg/L)	O2 b
FS1-17	18-Jul-95	10.5								
FS1-17	19-Jul-96	14								
FS1-25	20-Jul-96	6								
FS1-35	20-Jul-96	ERR								
FS3C-19	14-Jul-95	3.5								
FS3C-19	18-Jul-96	contam.								
FS3C-24	15-Jul-95	contam.								
FS3C-24	18-Jul-96	contam.								
FS3C-24	12-Jun-97		0.0000		18.735		17.270		8.655	
FS3C-29	17-Jul-96	4.5								
FS3C-29	11-Jun-97									
FS4-WT	8-Jul-97		0.0003	0.0003	60.638	75.126	17.776	20.749	5.447	5.352
R1-36	10-Jul-95	contam.	0		6.8		28.04		11.7	
R1-55	11-Jul-95	ERR	0.486		0.1		21.86		0.2	
RR1-PZ	21-Aug-95	contam.								
S1 spring	6-Aug-97									
S3 seep	7-Aug-97									
S40	1-Jan-96									
S40	25-Jul-97		0.0174	0.0350	37.805	37.957	16.420	18.105	0.662	0.740
T1-8	12-Jul-95	6	0.013		14.6		19.71		4.7	
T1-8	26-Jun-97		0.0574	0.0488	16.640	17.325	18.701	18.709	4.100	4.229
TR1-63	8-Jul-95	8.5	0		11.6		20.55		8.6	
TR1-63	25-Jun-97		0.0000		10.322		21.804		10.576	
W11	25-Jul-97		0.0000	0.0000	36.689	36.163	21.534	19.509	8.186	7.426
W15	28-Jul-97		0.0139	0.0130	25.765	25.443	18.507	18.434	0.678	0.700
W16	28-Aug-96	18.5	0.5624	0.5663	3.648	2.775	21.55	20.963	0.248	0.115
W16	13-Jul-97		0.1891	0.2847	12.883	12.274	21.248	21.214	0.020	0.080
W16A	27-Aug-96	8.5								
W16A	8-Jul-97		0.0005	0.0005	16.731	16.974	19.708	19.416	5.511	5.432
W16A	12-Jul-97		0.0000	0.0009	15.093	15.050	18.768	18.670	6.833	6.839
W2	20-Jun-95	>30.5								
W2	26-Aug-96		0.0011		19.911		19.507		0.405	
W2	7-Jun-97		0.0000		9.298		16.818		0.048	
W25	21-Jun-95	25.5								
W25	13-Jul-97		0.0000	0.0000	7.425	7.450	21.482	21.485	0.061	0.033
W26	21-Jun-95	>30.5								
W26	16-Aug-95									
W26	26-Aug-96		0		7.083		20.759		0.018	
W26	8-Jun-97		0.0000		13.576		18.865		0.402	
W26	26-Jul-97									
W27	16-Jul-95	6.5								
W27	19-Jun-97		0.0024		19.698		18.503		3.831	
W3	23-Jun-95	11								
W3	14-Jul-97		0.0006	0.0007	17.304	17.317	21.014	20.751	2.682	2.762
W3A	23-Jun-95	6								
W3A	14-Jul-97		0.0000	0.0000	36.813	37.075	20.366	21.253	3.660	3.961
W33	22-Aug-96	30.5	0		6.81		20.32		0.376	
W33	7-Jul-97		0.0004	0.0005	7.968	7.735	20.100	20.291	0.027	0.065
W34	22-Aug-96		0.0014		7.14		20.15		3.618	
W34	10-Jun-97		0.0000		6.285		17.481		8.253	
W34	14-Jul-97		0.0000	0.0001	8.498	8.795	19.384	19.368	7.757	7.239
W34	14-Jul-97		0.0000		8.773		19.526		7.499	
W35	27-Aug-96		0.0051		14.571		34.163		5.947	
W35	11-Jul-97		0.0052	0.0060	21.778	21.049	21.397	21.502	5.693	6.086
W36	26-Aug-96	6.5	0.0025		19.308		19.106		4.005	
W36	27-Aug-96		0.0029		18.707		20.775		4.298	
W36	17-Jun-97		0.0000		19.284		17.639		9.285	
W6	26-Jul-97		0.7135	0.9744	12.952	10.973	19.729	19.838	0.000	0.015

Table 4-4. Geochemical data from water samples (continued).

Well ID	Date	Ar (mg/L)	Ar b	Lab notes
FS1-17	18-Jul-95			
FS1-17	19-Jul-96			FE dropping out in FU
FS1-25	20-Jul-96			
FS1-35	20-Jul-96			
FS3C-19	14-Jul-95			
FS3C-19	18-Jul-96			
FS3C-24	15-Jul-95			
FS3C-24	18-Jul-96			
FS3C-24	12-Jun-97	0.7073		
FS3C-29	17-Jul-96			
FS3C-29	11-Jun-97			
FS4-WT	8-Jul-97	0.6725	0.7257	downhole °C
R1-36	10-Jul-95	0.8659		
R1-55	11-Jul-95	0.7812		
RR1-PZ	21-Aug-95			
S1 spring	6-Aug-97			spring °C
S3 seep	7-Aug-97			downhole °C
S40	1-Jan-96			
S40	25-Jul-97	0.6096	0.6330	
T1-8	12-Jul-95	0.7279		
T1-8	26-Jun-97	0.7030	0.7036	
TR1-63	8-Jul-95	0.7328		
TR1-63	25-Jun-97	0.7849		
W11	25-Jul-97	0.7629	0.7427	
W15	28-Jul-97	0.6767	0.6618	
W16	28-Aug-96	0.7721	0.7543	Fe dropping out in FU
W16	13-Jul-97	0.7715	0.7708	
W16A	27-Aug-96			
W16A	8-Jul-97	0.7393	0.7356	
W16A	12-Jul-97	0.7077	0.7089	
W2	20-Jun-95			
W2	26-Aug-96	0.7361		
W2	7-Jun-97	0.6620		
W25	21-Jun-95			
W25	13-Jul-97	0.7800	0.7760	
W26	21-Jun-95			
W26	16-Aug-95			
W26	26-Aug-96	0.7496		
W26	8-Jun-97	0.7125		
W26	26-Jul-97			
W27	16-Jul-95			
W27	19-Jun-97	0.7054		
W3	23-Jun-95			
W3	14-Jul-97	0.7661	0.7632	
W3A	23-Jun-95			
W3A	14-Jul-97	0.7507	0.7738	
W33	22-Aug-96	0.7262		Fe dropping out in FU
W33	7-Jul-97	0.7570	0.7618	
W34	22-Aug-96	0.7368		
W34	10-Jun-97	0.6774		
W34	14-Jul-97	0.7219	0.7236	
W34	14-Jul-97	0.7175		
W35	27-Aug-96	0.9135		diss.gas leaked?
W35	11-Jul-97	0.7708	0.7636	downhole °C
W36	26-Aug-96	0.7124		4 CFC analyses
W36	27-Aug-96	0.7475		
W36	17-Jun-97	0.7012		
W6	26-Jul-97	0.6980	0.7064	

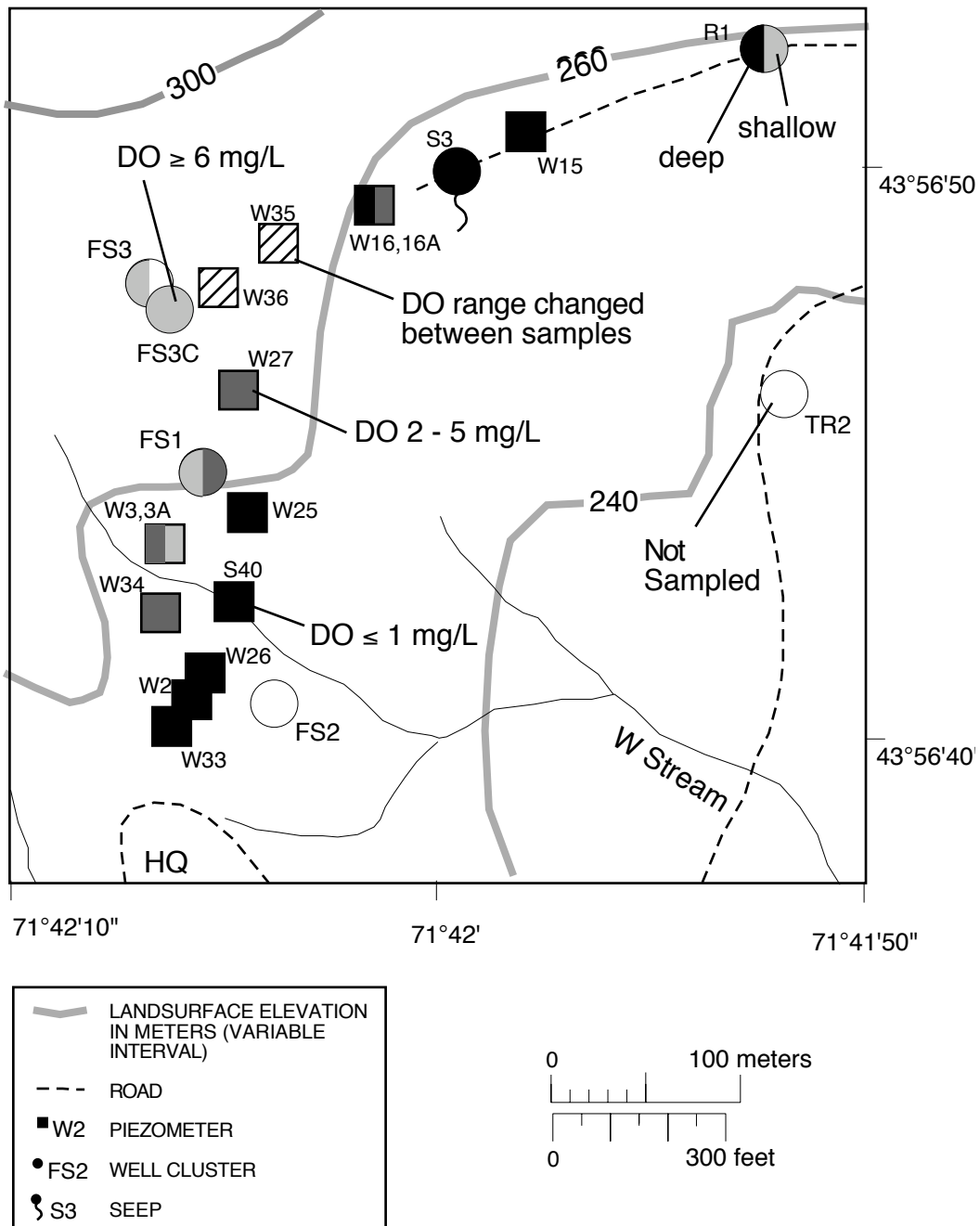


Figure 4-13 Spatial distribution of dissolved oxygen concentrations in water samples from piezometers at the Mirror Lake site, Grafton County, New Hampshire.

Major ion concentrations characterize the overall water quality of the shallow ground-water in the Mirror Lake watershed (Table 4-4). The general water type is calcium-bicarbonate-sulfate in piezometers (fig. 4-14). Outliers include: RR1-PZ located below the Mirror Lake watershed between Route 3 and the Pemigewasset River in an agricultural area; W6 located adjacent to Mirror Lake Road, also contains nitrate; W11 behind an experimental sand plot that has been fertilized, also contains nitrate; FS1-25

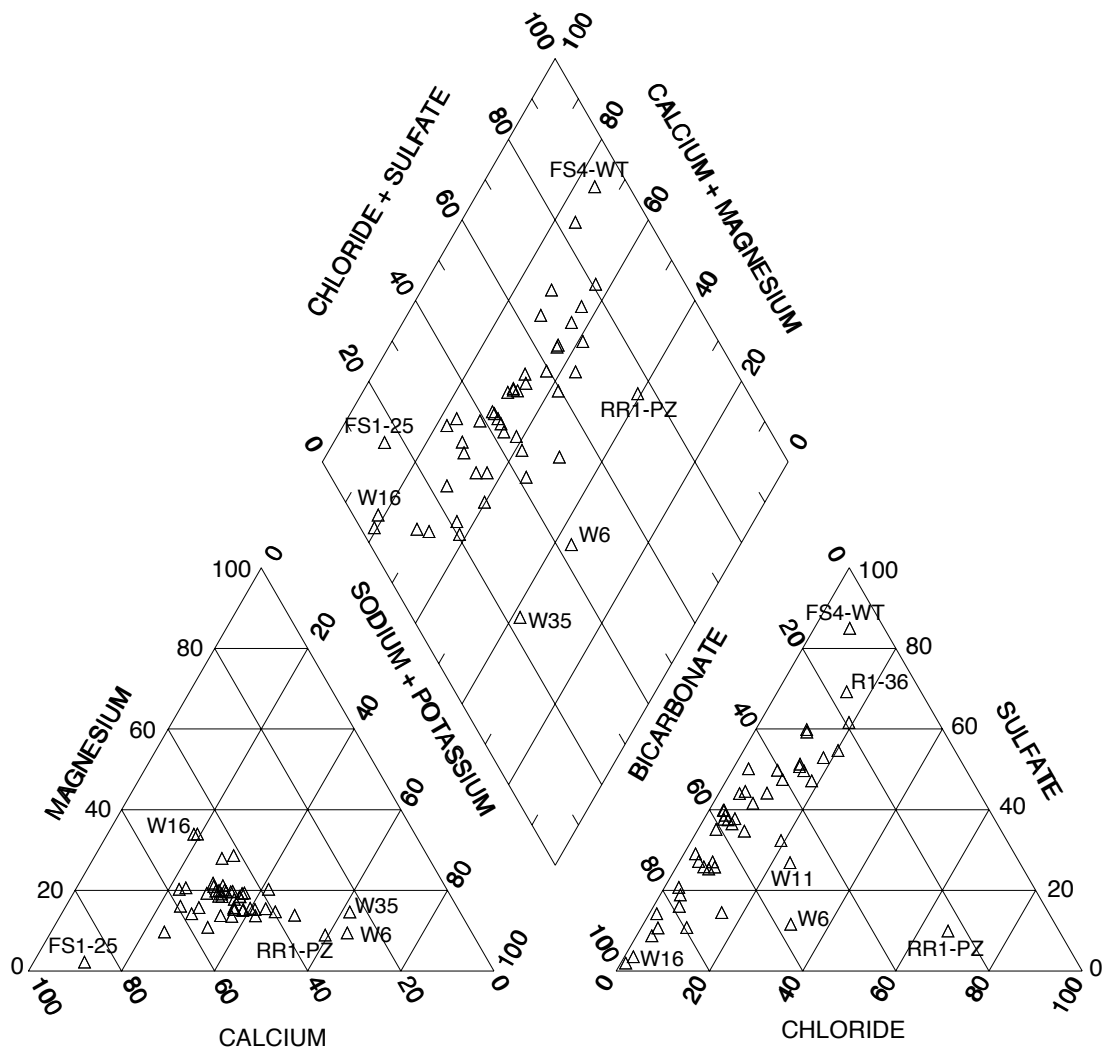


Figure 4-14 Piper plot of major ions in samples from piezometers.

apparently contaminated from well construction materials; W16, a steel well screened several meters below the water table; and R1-36, a high-yielding well with low alkalinity and high sulfate. New piezometers for this study include FS4-WT, installed high in the watershed near the basin divide, that has low alkalinity and high sulfate, and that also contains high CO₂; and W35 that contains high potassium.

Nitrogen and argon dissolved gas concentrations (Table 4-4) indicate that little excess air is present near the water table, and that the recharge temperature is between 5 and 10°C (fig. 4-15). Concentrations of dissolved nitrogen gas and argon in ground water are used to infer the recharge temperature and excess air amounts (Heaton and Vogel, 1981). These quantities are used in turn to determine equilibrium air concentrations from measured water concentrations to date ground water by the CFC method (Busenberg and Plummer, 1992). In contrast to samples from bedrock wells at Mirror Lake (Busenberg and Plummer, 1996), nitrogen and argon concentrations fall approximately along the line corresponding to equilibration with the atmosphere. This suggests that the elevated argon and nitrogen in bedrock waters is not due to entrapped or excess air, but is caused by some other in situ production.

Methane is observed in several samples from water-table piezometers. Measurable methane and lack of DO are consistent with methanogenic biodegradation conditions near the water table.

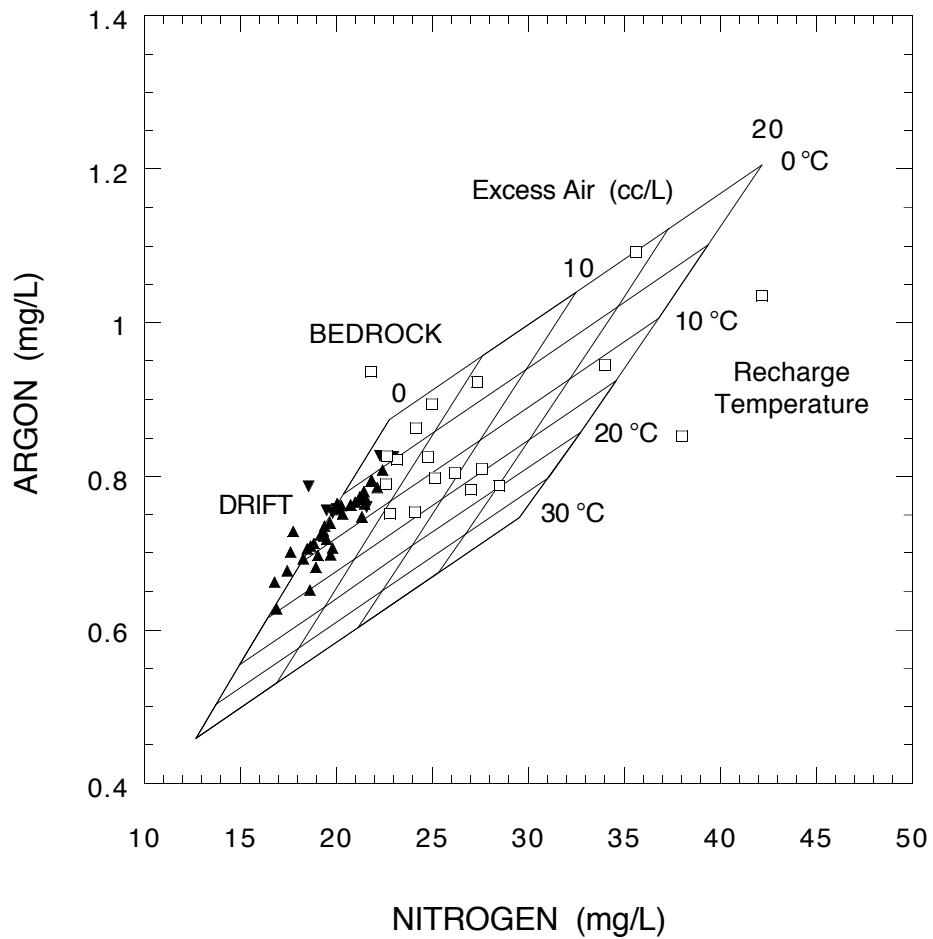


Figure 4-15 Concentrations of dissolved argon and nitrogen in water samples from piezometers (solid symbols) and packer-isolated zones of bedrock wells (open symbols) at the Mirror Lake site, Grafton County, New Hampshire. The superposed grid indicates the concentrations of argon and nitrogen in water that is in equilibrium with the atmosphere as a function of temperature, and that contains varying volumes of entrapped dissolved air.

4.3.4 Chlorofluorocarbon Concentrations

CFC concentrations in water samples from shallow piezometers range from zero to levels greater than those in equilibrium with the modern (1995-1997) atmosphere (Table 4-4). Many samples do contain CFC concentrations near modern atmospheric-equilibrium levels, which are about 950, 450, and 150 pg/kg for CFC-11, -12, and -113, respectively (at 7 °C). This observation supports use of CFC concentrations to date saturated-zone ground water.

Many samples contain CFC concentrations higher than those in equilibrium with the atmosphere (fig. 4-16). Following Busenberg and Plummer (1992), these samples are designated “contaminated.” In some cases, contamination of samples was so high that the analytical procedures used to concentrate the normal low levels resulted in analytical responses beyond the instrumentation limits (“ERR” results in Table 4-4).

However, many samples contain CFC concentrations significantly less than those in equilibrium with the modern atmosphere. A preliminary review of the data indicated that CFC concentrations were highly correlated with dissolved oxygen (DO) concentrations. For this reason, the CFC data are plotted here against DO (fig. 4-17).

CFC-12 concentrations range from about 170 pg/kg to about 2,300 pg/kg (Table 4-4). For uncontaminated samples, CFC-12 concentrations are correlated with DO (fig. 4-17). Samples containing zero or very small amounts of oxygen, have CFC-12 concentrations about 1/3 of the concentration of water in equilibrium with modern air. High oxygen concentrations correspond to CFC-12 concentrations near modern levels.

Concentrations of CFC-11 range from zero to 88,000 pg/kg (Table 4-4). Some samples were so highly contaminated with CFC-11 that quantification of the concentrations was not analytically possible (Table 4-4). For uncontaminated samples, CFC-11 concentrations are strongly correlated with DO (fig. 4-18). Samples containing

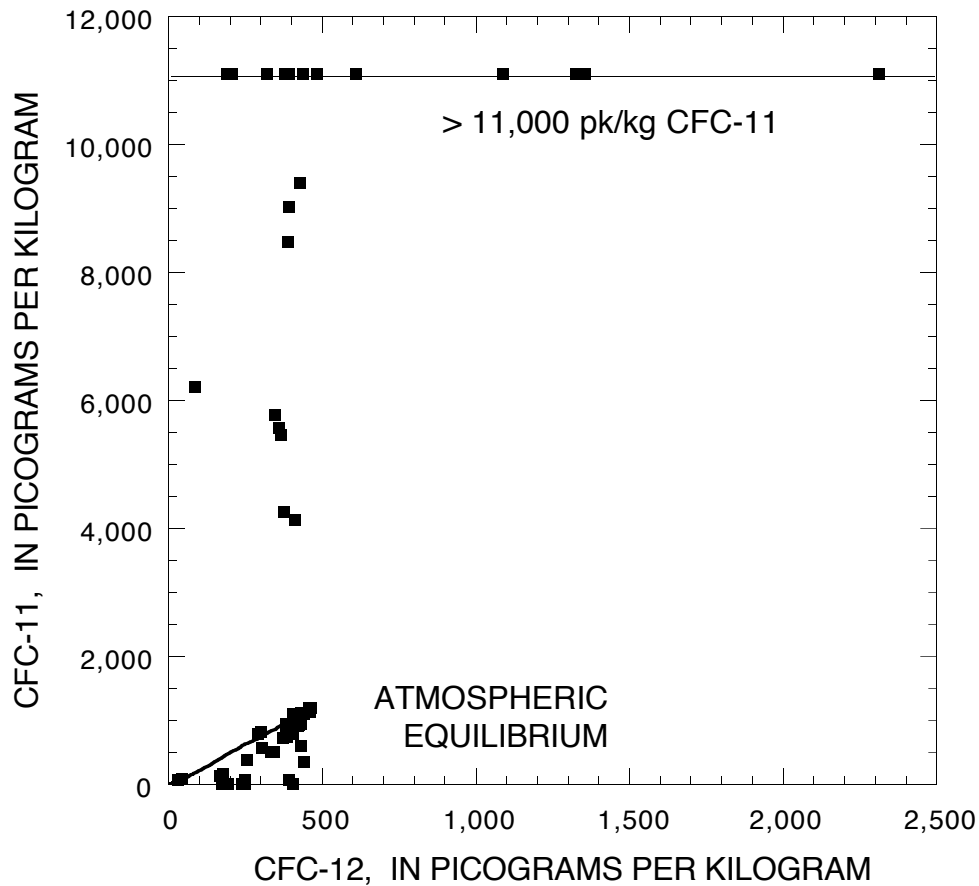


Figure 4-16 Concentrations of CFC-11 and CFC-12 in water samples from water-table piezometers at the Mirror Lake site, Grafton County, New Hampshire. The dashed line is the concentrations in water in equilibrium with the atmosphere during the last 50 years (at 7 °C). The horizontal line indicates CFC-11 concentrations greater than 11,000 pg/kg.

zero or very small amounts of oxygen, also contain zero or very small amounts for CFC-11. High oxygen concentrations corresponds to CFC-11 concentrations near modern levels. Taken at face value, these CFC-11 concentrations corresponds to ages of 0 years, for the high concentrations, to ages of more than 45 years, for the zero-CFC-11 waters.

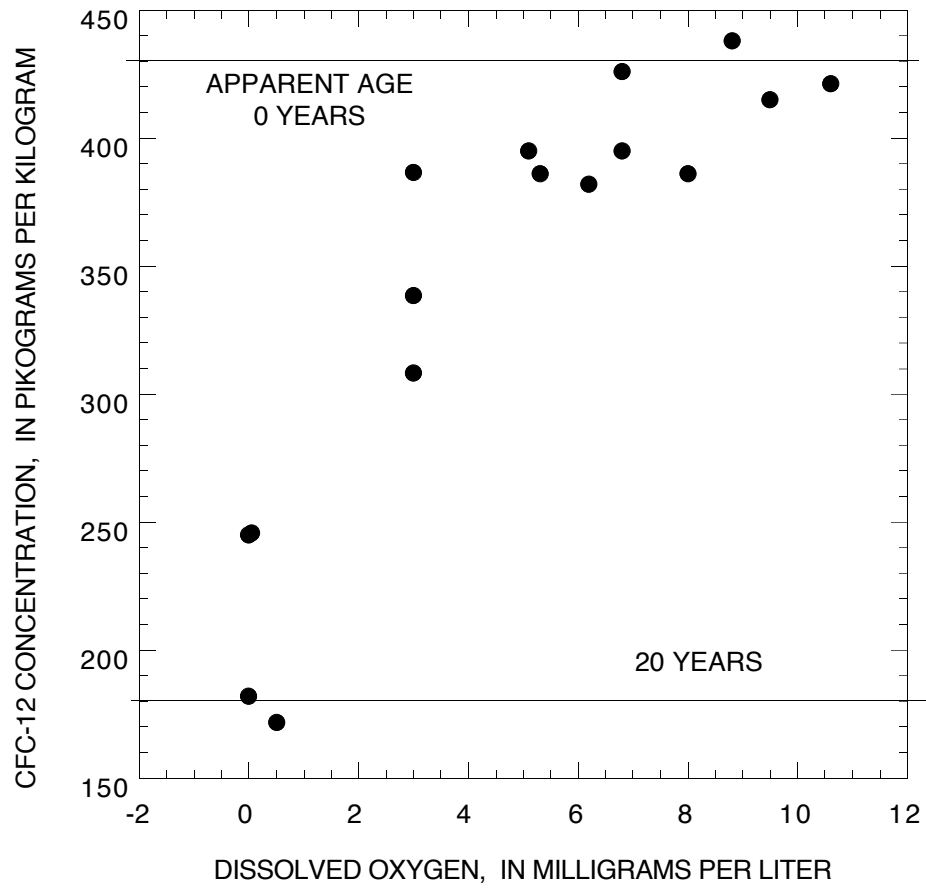


Figure 4-17 Concentrations of CFC-12 and dissolved oxygen in water samples from piezometers at the Mirror Lake site, Grafton County, New Hampshire. The horizontal lines correspond to CFC-12 concentrations in water equilibrated with the atmosphere at the time of sampling (0 years) and 20 years before sampling.

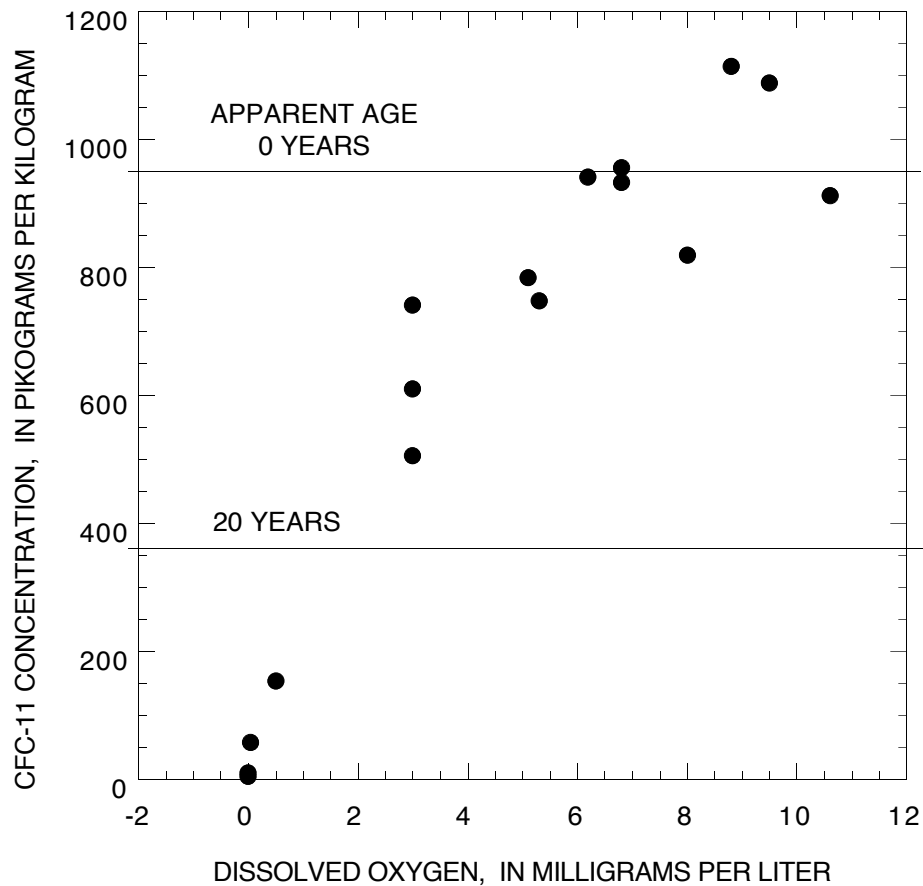


Figure 4-18 Concentrations of CFC-11 and dissolved oxygen in water samples from piezometers at the Mirror Lake site, Grafton County, New Hampshire. The horizontal lines correspond to CFC-11 concentrations in water equilibrated with the atmosphere at the time of sampling (0 years) and 20 years before sampling.

Concentrations of CFC-113 range from zero to 240 pg/kg (Table 4-4). Some samples were so highly contaminated with CFC-113 that quantification of the concentrations was not analytically possible (Table 4-4). For uncontaminated samples, CFC-113 concentrations are strongly correlated with DO (fig. 4-19). Samples containing

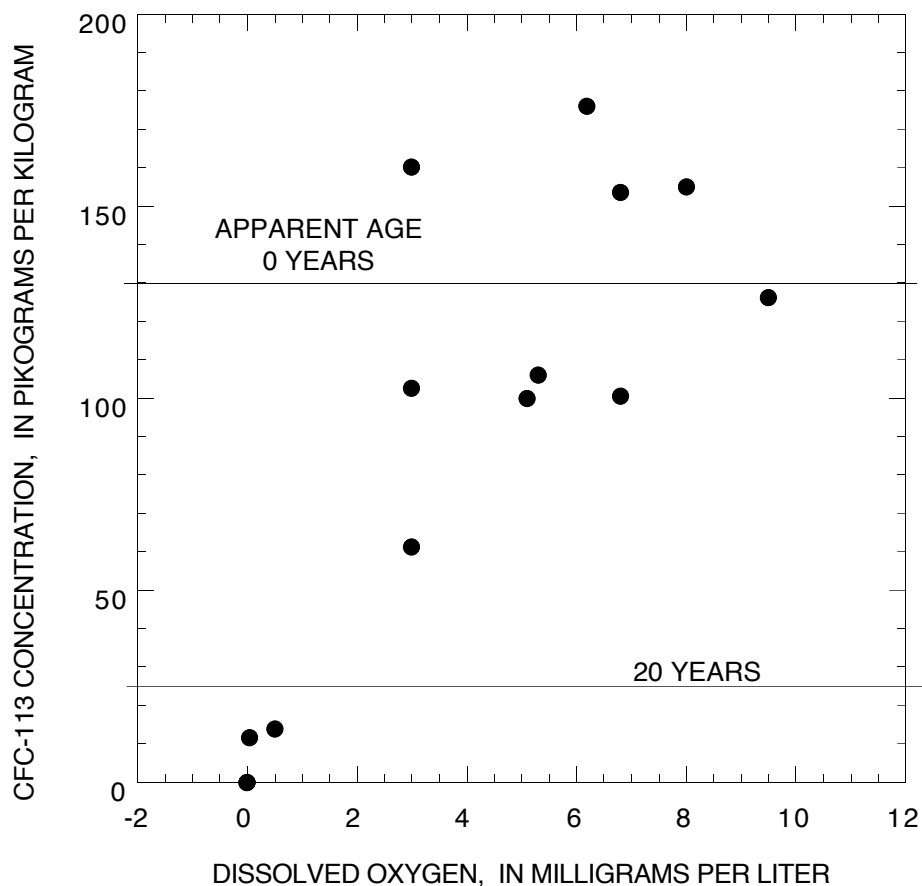


Figure 4-19 Concentrations of CFC-113 and dissolved oxygen in water samples from piezometers at the Mirror Lake site, Grafton County, New Hampshire. The horizontal lines correspond to CFC-113 concentrations in water equilibrated with the atmosphere at the time of sampling (0 years) and 20 years before sampling.

zero or very small amounts of oxygen, also contain zero or very small amounts for CFC-113. High oxygen concentrations corresponds to CFC-113 concentrations near modern levels. The scatter in CFC-113 concentrations in high-DO samples is larger than the scatter for either CFC-12 or CFC-11.

The observed CFC-12 and CFC-11 concentrations indicate that some process is, or several processes are, modifying the concentrations from atmospheric equilibrium (fig. 4-20). Water isolated from the atmosphere during the last 50 years should have CFC-12 and CFC-11 concentrations that lie on the atmospheric equilibrium line shown in Figure 4-21 if the only process affecting concentrations is advection with moving saturated-zone ground water. The fact that most samples fall below this line indicate that more CFC-11 has been removed relative to CFC-12.

The similarity between the correlations of CFC-11 and CFC-12 to DO is shown in Figure 4-21. The only major difference is that the lowest CFC-12 concentrations correspond to about 1/3 of modern levels, whereas the lowest CFC-11 concentrations are zero. The correlation between CFC-113 and DO is essentially the same as the CFC-11 pattern, but with more scatter at the upper concentration levels.

The hypothetical mixing line of Figures 4-20 and 4-21 corresponds to concentrations of CFC-11 and -12, and dissolved oxygen, in a volumetric mixture of two end-members waters: (a) anaerobic water containing no CFC-11 and 150 pg/kg CFC-12, and (b) water containing 7 mg/L DO, 950 pg/kg CFC-11, and 430 pg/kg CFC-12. Without this mixing, the apparent degradation of CFC's in the presence of 1 to 4 mg/L of dissolved oxygen is difficult to explain because it is assumed that degradation is limited to anaerobic conditions.

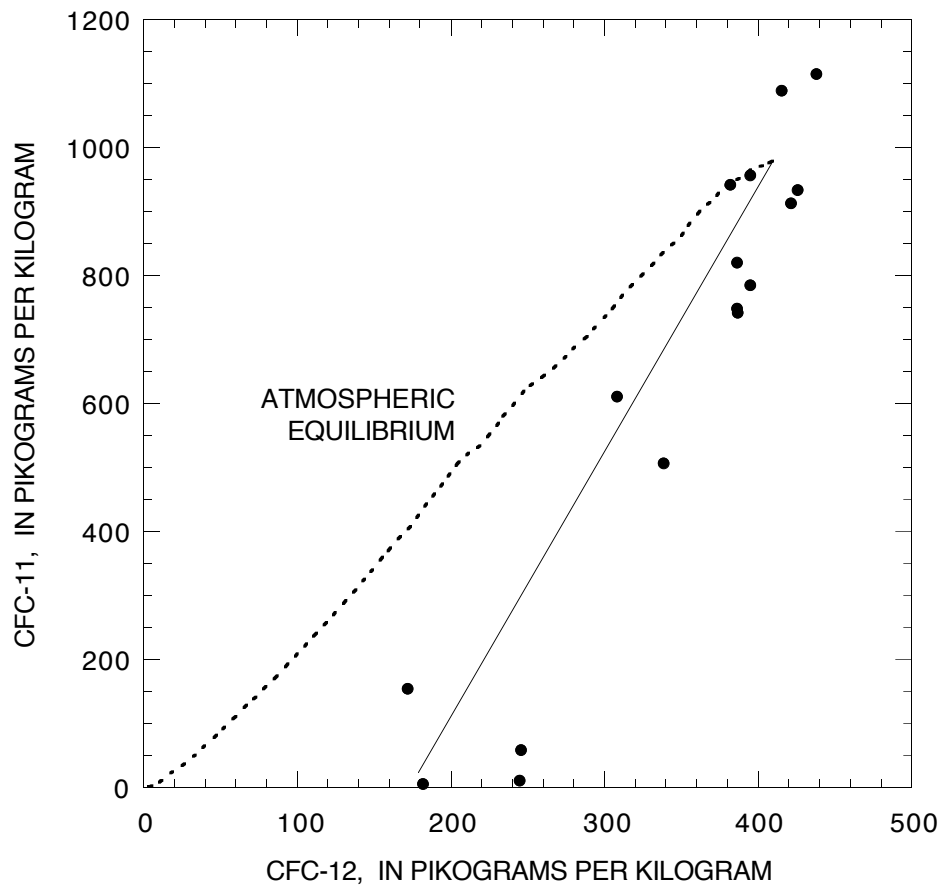


Figure 4-20 Concentrations of CFC-11 and CFC-12 in water samples from water-table piezometers at the Mirror Lake site, Grafton County, New Hampshire. The dashed line is the concentrations in water in equilibrium with the atmosphere during the last 50 years (at 7 °C). The solid line is a suggested mixing line.

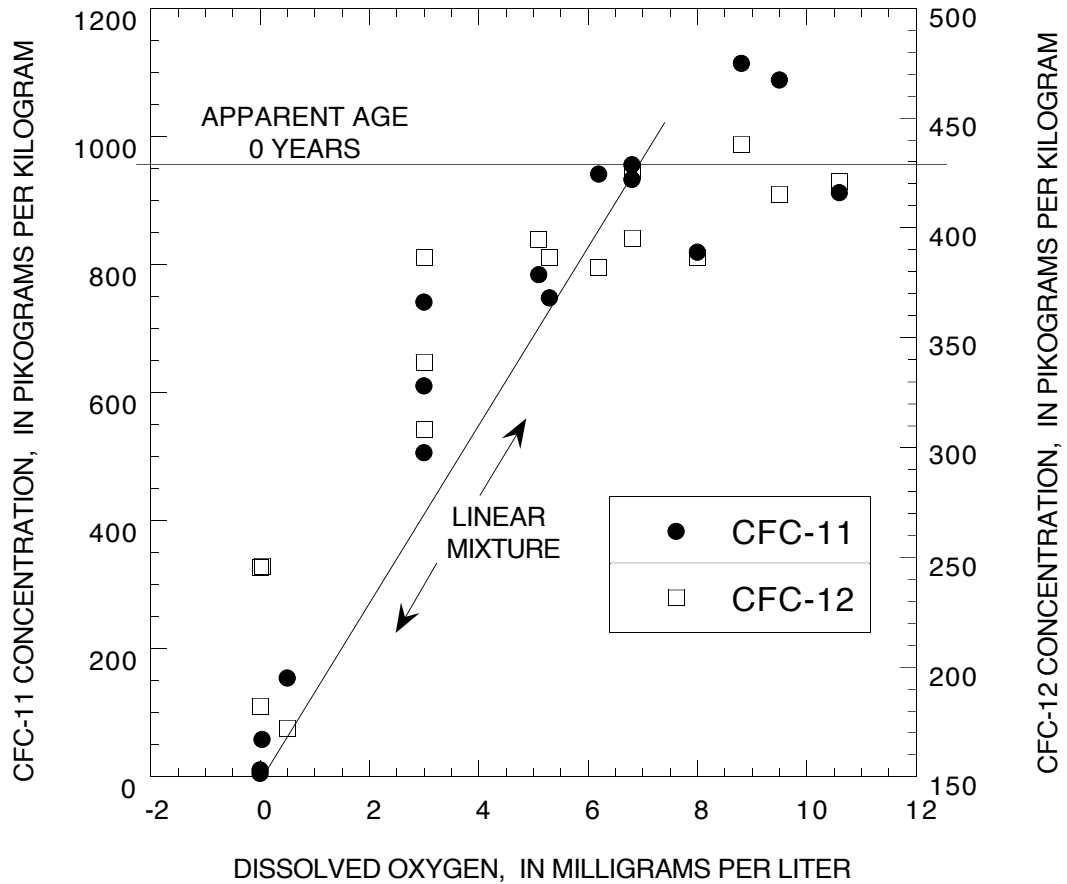


Figure 4-21 Concentrations of CFC-11, CFC-12, and dissolved oxygen in water samples from water-table piezometers at the Mirror Lake site, Grafton County, New Hampshire. The horizontal line corresponds to CFC-11 and CFC-12 concentrations in water equilibrated with the atmosphere at the time of sampling. The solid line is a suggested mixing line.

The relation between CFC-11 and tritium in samples from water-table piezometer is shown in Figure 4-22. Assuming an equilibration temperature of 7 °C, the CFC-11 concentration in water recharged in 1963 would be about 62 pg/kg. The concentration of tritium in waters recharged in 1963, accounting for subsequent radioactive decay until

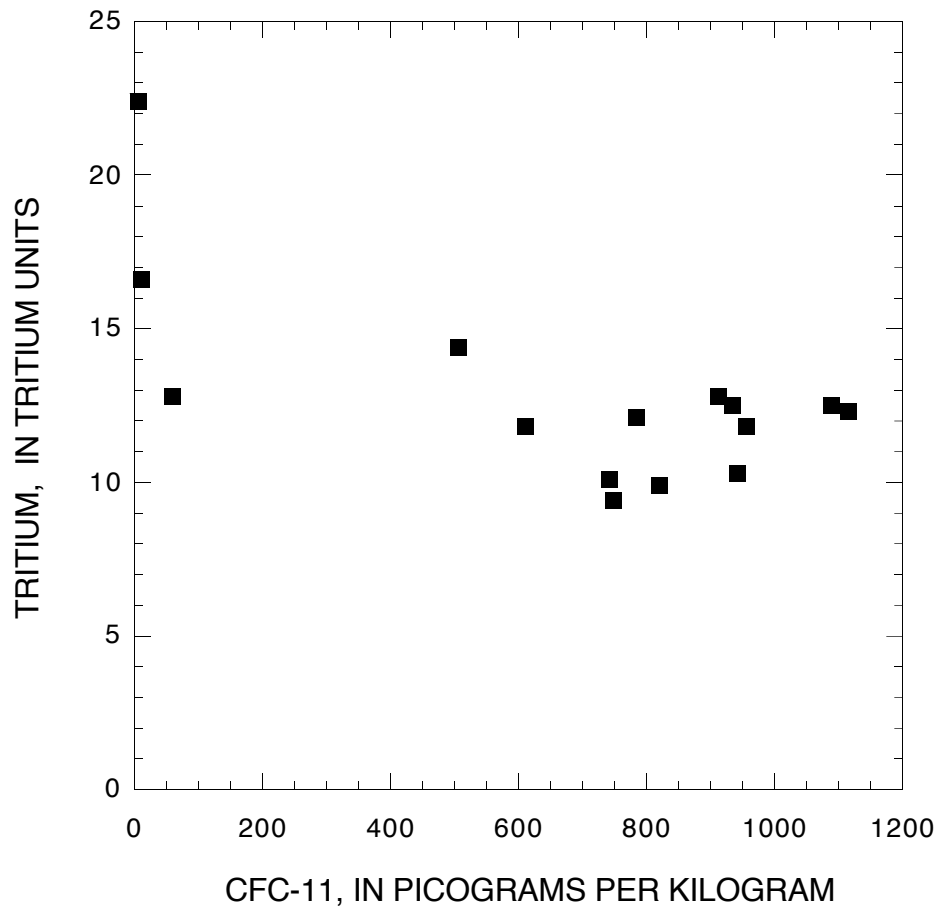


Figure 4-22 Concentrations of CFC-11 and tritium in water samples from piezometers at the Mirror Lake site, Grafton County, New Hampshire.

1995, would be more than 150 tritium units (TU). Thus, under ideal conditions, water samples containing about 63 pg/kg CFC-11 should also contain more than 150 TU tritium. Almost all measured tritium concentrations are about 10-15 TU. The highest observed tritium is 23 TU in a water sample containing no CFC-11. Based on the age-dating assumptions, a sample containing zero CFC-11 was recharged prior to 1945. Tritium in recharge in 1945, decayed to 1995, would amount to less than 5 TU, and older

waters would contain even less tritium. All of these tritium concentrations are significantly below bomb-peak levels dating from the late 50's and early 60's. Busenberg and Plummer (1996) estimate that peak tritium levels in precipitation in New Hampshire from the early 1960's decayed to 1992 would amount to about 300 TU, over an order of magnitude higher than the values observed here. The observed tritium and CFC concentrations suggest that these water samples represent modern recharge, but that CFC concentrations have been reduced by degradation.

Concentrations of CFC's in soil gas exhibit much less variability than liquid concentrations (Table 4-5). All CFC-12 soil gas concentrations are close to 100 percent of modern atmospheric levels (fig. 4-23). The average CFC-12 soil gas concentration at each sampling location ranges from 0.97 to 1.06 times modern air concentrations. CFC-12 concentrations in local air are close to the global average, with individual measurements ranging from 0.97 to 1.01 times the global average.

CFC-11 concentrations vary somewhat more than CFC-12 concentrations and are reduced compared to modern air. The average CFC-11 soil gas concentration at each sampling location range from 0.82 to 1.01 times modern air concentrations. CFC-11 soil gas concentrations are low near well W33 (fig. 4-24), where zero CFC-11 is measured in shallow water-table piezometers, and where the water table is anaerobic (fig. 4-13).

CFC-113 concentrations vary somewhat more than either CFC-12 or CFC-11 concentrations, and several locations exhibit reduced concentrations compared to modern air. The average CFC-113 soil gas concentration at each sampling location ranged from 0.83 to 1.08 times modern air concentrations. CFC-113 soil gas concentrations are low near well W33, where zero CFC-113 is measured in shallow water-table piezometers, and where the water table is anaerobic (fig. 4-13).

CFC concentrations in soil gas show essentially no correlation with depth. However, in a few cases, a systematic pattern in time occurs. In these cases, the winter soil gas CFC-11 and CFC-113 concentrations are a lower fraction of modern air than the

summer concentrations. This may be caused by increasing partitioning into the liquid phase as unsaturated zone temperatures decrease. This temporal pattern is not significant for CFC-12 concentrations.

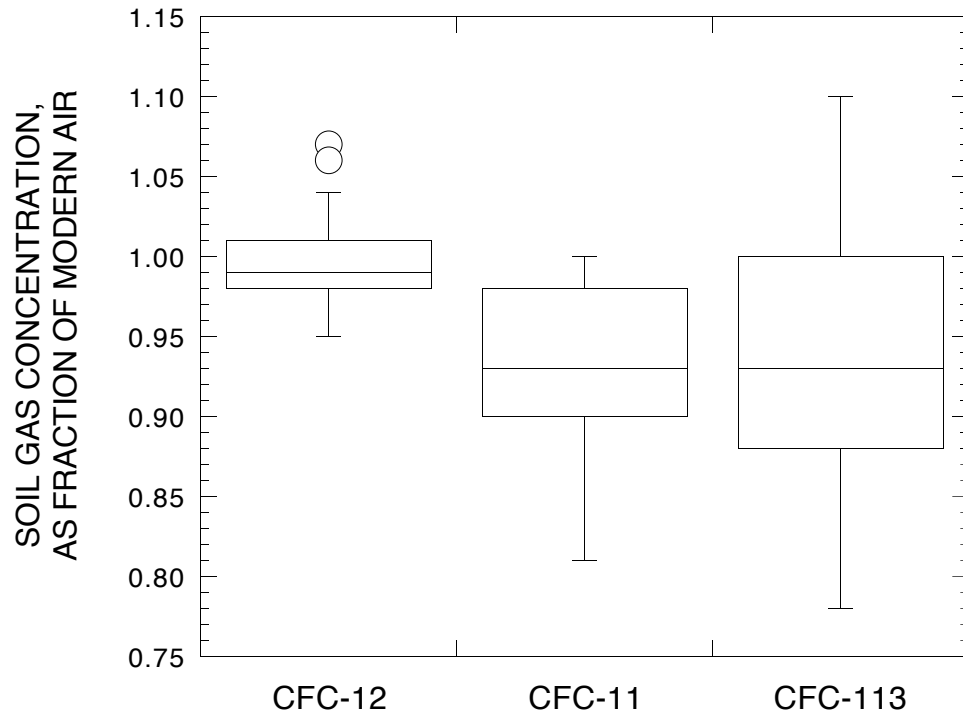


Figure 4-23 Box plot of CFC concentrations in soil gas at the Mirror Lake site, Grafton County, New Hampshire.

Table 4-5. Concentrations of CFC's in soil gas.

ID	Screen depth (cm)	Sample date	Sample time	Sequence		Concentration in gas (pptv)			Fraction of Air Concentration			Notes
				Lab	Field	CFC-12	CFC-11	CFC-113	CFC-12	CFC-11	CFC-113	
W33-red	140	30-Jan-97	1536	1		525.4	226.5	70.0	0.98	0.83	0.83	
		30-Jan-97	1546	2		523.3	224.9	69.2	0.97	0.82	0.82	lab time 1548
		avg							0.97	0.82	0.83	
W33-white	200	30-Jan-97	1512	1		525.2	232.3	71.6	0.98	0.85	0.85	
		30-Jan-97	1518	2		535.0	223.1	69.5	0.99	0.81	0.83	
		30-Jan-97	1525	3		521.9	233.5	71.0	0.97	0.85	0.84	
		avg							0.98	0.84	0.84	
W33-blue	240	30-Jan-97	1440	1		529.2	237.1	73.0	0.98	0.87	0.87	
		30-Jan-97	1455	3		526.0	233.9	71.8	0.98	0.85	0.85	
		avg							0.98	0.86	0.86	
W2-blue FS2-R25	100 0	29-Jan-97	1600	R-25		530.1	276.6	91.1	0.99	1.01	1.08	
		29-Jan-97	1600	R-25		534.4	275.1	91.1	0.99	1.00	1.08	
		avg							0.99	1.01	1.08	
FS2-air	0	17-Jul-96	910	3		530.9	255.4	79.8	0.99	0.93	0.95	lab date 7/7/96
		17-Jul-96	913	3		526.1	252.8	78.2	0.98	0.92	0.93	
		avg							0.98	0.93	0.94	
FS2-red	65	17-Jul-96	849	1		535.9	258.2	82.3	1.00	0.94	0.98	low flow rate
		17-Jul-96	853	2		530.4	267.5	83.8	0.99	0.98	1.00	
		17-Jul-96	856	3		537.8	273.1	87.5	1.00	1.00	1.05	
		29-Jan-97	1205		1	545.0	253.9	80.1	1.01	0.93	0.95	
		avg							1.00	0.96	1.00	
FS2-blue	180	17-Jul-96	749	1	1	536.5	261.8	82.0	1.00	0.96	0.98	purged 1 min, 50 sec ea. sample
		17-Jul-96	753	2	2	528.9	269.9	91.8	0.98	0.99	1.10	
		17-Jul-96	756	3	3	510.5	257.8	83.1	0.95	0.94	0.99	lab time was 1651?
		29-Jan-97	1237	1	1	537.4	252.7	80.3	1.00	0.92	0.95	
		29-Jan-97	1242	2	2	542.7	246.5	75.5	1.01	0.90	0.90	
		29-Jan-97	1247	3	3	535.7	250.8	77.5	1.00	0.92	0.92	
		avg							0.99	0.94	0.97	

Table 4-5. Concentrations of CFC's in soil gas (continued).

ID	Screen depth (cm)	Sample date	Sample time	Sequence		Concentration in gas (pptv)			Fraction of Air Concentration			Notes
				Lab	Field	CFC-12	CFC-11	CFC-113	CFC-12	CFC-11	CFC-113	
W34	180											
W25-red	95											
W25-white	190											
W25-blue	300											
FS1-red	90	29-Aug-96	1715			522.5	271.7	86.6	0.97	0.99	1.04	
		29-Aug-96	1722			529.6	270.9	88.5	0.99	0.99	1.06	
		avg							0.98	0.99	1.05	
FS1-blue	180											
FS3-air	0	31-Jan-97	1034			528.5	260.9	86.0	0.98	0.95	1.02	
FS3	200	31-Jan-97	1012	1	1	538.1	249.4	74.6	1.00	0.91	0.89	
		31-Jan-97	1019	2	2	536.3	242.0	65.9	1.00	0.88	0.78	
		31-Jan-97	1024	3	3	527.8	247.0	73.8	0.98	0.90	0.88	
		avg							0.99	0.90	0.85	
FS3-red	130											
FS3-blue	215	30-Jan-97	1603	1	1	577.8	268.5	75.4	1.07	0.98	0.90	lab fs3c
		30-Jan-97	1608	2	2	568.1	267.2	77.0	1.06	0.98	0.91	
		30-Jan-97	1613	3	3	561.6	273.9	78.6	1.04	1.00	0.93	
		avg							1.06	0.99	0.91	
FS3T-red	60	16-Jul-96	1630	2	1	541.6	266.6	83.0	1.01	0.97	0.99	lab fs3
		16-Jul-96	1635	1	3	532.9	265.0	79.8	0.99	0.97	0.95	
		30-Jan-97	1637	1	1	531.6	252.8	77.2	0.99	0.92	0.92	labeled fs3c-a
		30-Jan-97	1645	2	2	534.7	243.9	73.4	0.99	0.89	0.87	
		30-Jan-97	1651	3	3	532.2	253.2	77.9	0.99	0.92	0.92	
		avg							0.99	0.94	0.93	
FS3T-white	120	16-Jul-96	1559	1	1	535.1	271.8	86.8	1.00	0.99	1.04	
		16-Jul-96	1610		3	536.5	269.7	84.2	1.00	0.98	1.01	
		31-Jan-97	917	1	1	523.3	246.4	77.0	0.97	0.90	0.91	
		31-Jan-97	922	2	2	544.1	241.6	73.1	1.01	0.88	0.87	
		31-Jan-97	927	3	3	524.9	247.4	79.7	0.98	0.90	0.95	
		avg							0.99	0.93	0.95	

Table 4-5. Concentrations of CFC's in soil gas (continued).

ID	Screen depth (cm)	Sample date	Sample time	Sequence		Concentration in gas (pptv)			Fraction of Air Concentration			Notes
				Lab	Field	CFC-12	CFC-11	CFC-113	CFC-12	CFC-11	CFC-113	
FS3T-blue	180	16-Jul-96	1548		3	534.5	266.4	89.2	0.99	0.97	1.07	
		16-Jul-96	1534	1	1	530.7	270.2	88.7	0.99	0.99	1.06	lab time 1630?
		31-Jan-97	936	1	1	539.4	262.0	77.2	1.00	0.96	0.92	
		31-Jan-97	941	2	2	547.6	253.7	74.8	1.02	0.93	0.89	
		31-Jan-97	946	3	3	554.0	257.0	76.0	1.03	0.94	0.90	lab fs3c
		avg								1.01	0.96	0.97
W36-R6	0	31-Jan-97	1400	R-6		529.8	265.6	82.3	0.99	0.97	0.98	
		31-Jan-97	1400	R-6		530.6	264.4	82.3	0.99	0.97	0.98	
		avg							0.99	0.97	0.98	
W36-air	0	29-Aug-96	1453			519.6	254.4	79.8	0.97	0.93	0.95	
W36-red	60	29-Aug-96	1504	1	1	516.3	251.5	77.8	0.96	0.92	0.93	
		29-Aug-96	1511	3	3	520.9	250.6	79.0	0.97	0.91	0.94	lab time 1610?
		31-Jan-97	1538	1	1	525.8	242.6	73.7	0.98	0.89	0.88	
		avg							0.97	0.91	0.92	
W36-white	150	29-Aug-96	1539	1	1	520.8	260.6	83.2	0.97	0.95	0.99	
		29-Aug-96	1546	3	3	534.2	259.7	80.5	0.99	0.95	0.96	
		31-Jan-97	1559	1	1	546.4	253.7	74.4	1.02	0.93	0.88	
		31-Jan-97	1605	2	2	549.7	249.7	71.7	1.02	0.91	0.85	
		31-Jan-97	1610	3	3	542.5	251.6	71.9	1.01	0.92	0.85	
		avg							1.00	0.93	0.91	
W36-blue	260	29-Aug-96	1600	3	2	551.8	270.1	83.8	1.03	0.99	1.00	
		29-Aug-96	1604	1	3	531.6	271.7	88.5	0.99	0.99	1.06	
		31-Jan-97	1623	1	1	546.7	268.5	86.4	1.02	0.98	1.03	
		31-Jan-97	1634	3	3	547.4	270.4	85.8	1.02	0.99	1.02	
		avg							1.01	0.99	1.03	
FS4-R12	0	30-Jan-97	945	R-12		541.9	278.7	95.1	1.01	1.02	1.13	
		30-Jan-97	945	R-12		530.4	280.8	96.8	0.99	1.03	1.15	
		avg							1.00	1.02	1.14	

Table 4-5. Concentrations of CFC's in soil gas (continued).

ID	Screen depth (cm)	Sample date	Sample time	Sequence		Concentration in gas (pptv)			Fraction of Air Concentration			Notes
				Lab	Field	CFC-12	CFC-11	CFC-113	CFC-12	CFC-11	CFC-113	
FS4-red	45											
FS4-blue	75	30-Jan-97	1012	1	1	541.3	259.6	82.3	1.01	0.95	0.98	
		30-Jan-97	1017	2	2	537.8	249.6	75.9	1.00	0.91	0.90	
		30-Jan-97	1028	3	3	526.3	254.8	84.8	0.98	0.93	1.01	
		avg							1.00	0.93	0.96	
FS4B-red	30											
FS4B-blue	80											
FS5-red	50											
FS5-blue	115											
Global average air		30-Jun-96				537.8	273.9	84.2	1.00	1.00	1.00	
		1-Jan-97				537.6	273.9	83.7	1.00	1.00	1.00	

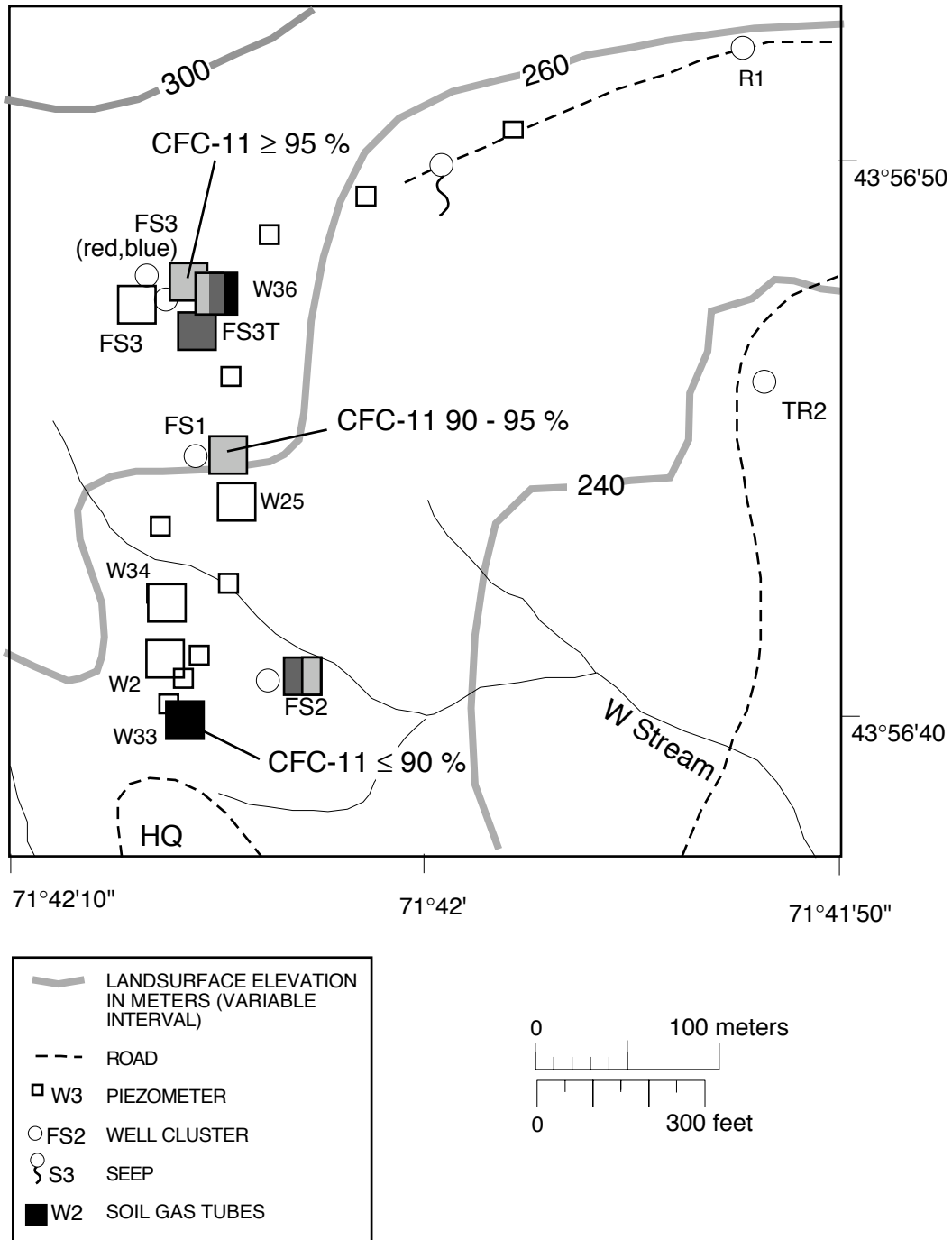


Figure 4-24 Spatial distribution of CFC-11 concentrations in soil gas samples from sampling tubes at the Mirror Lake site, Grafton County, New Hampshire.

4.4 Discussion

The goals of this field study involve characterization of the concentrations of CFC's in water recharging the saturated zone. Where dissolved oxygen concentrations are relatively high (greater than 5 mg/L), CFC concentrations at the water table appear to be approximately in equilibrium with the modern atmosphere. However, even in these well-oxygenated samples, there is significant variability in CFC concentrations. The observed range of concentrations in aerobic water-table samples corresponds to uncertainty in ground-water ages determined from CFC-12, CFC-11, and CFC-113 concentrations on the order of ± 4 , 7, and 8 years, respectively. This variability in concentrations at the water table presumably impacts the uncertainty in ages associated with water samples from deeper in the saturated zone at the Mirror Lake site. This uncertainty is significantly larger than the analytical uncertainty in the laboratory (± 1 yr).

The hydraulic data collected during this study suggests that recharge is highest in the early spring and fall, but recharge occurs throughout the year depending on the intensity of precipitation. Significant recharge also occurs slowly throughout the winter, and more rapidly in the winter during mid-winter snowmelt, when it occurs.

Soil temperatures are consistent with measured noble gas concentrations and suggest that recharge temperatures at the water table range between 5 and 10 °C. The average recharge temperature of 7 °C is probably a reasonable approximation for estimating past atmospheric gas concentrations from water samples.

Samples from wells screened near the water table that contain low dissolved oxygen also contain low CFC's, relative to atmospheric equilibrium. In the case of CFC-11 and CFC-113, these compounds are completely absent from some anaerobic samples. CFC-12 is not reduced as much, with concentrations in anaerobic samples as low as 1/3 of modern levels. Ground water in the saturated zone that was anaerobic shortly after recharge near the water table is likely to have low CFC concentrations. These low CFC

concentrations would yield apparent ages for deeper saturated-zone samples much larger than the actual time since recharge.

CFC concentrations are also significantly reduced in samples that have dissolved oxygen concentrations ranging from 1-4 mg/L. This pattern is not consistent with degradation of CFC's only under anaerobic conditions because these DO levels are not low enough to be considered anaerobic. However, this pattern of intermediate CFC concentrations in samples having intermediate DO is consistent with a linear mixing model.

The general pattern of the correlation between CFC's and DO suggests a linear mixing model, although there is scatter in the measurements. This mixing model assumes that samples are linear mixtures of two end-members: (a) aerobic water having about 6 mg/L DO and CFC concentrations in equilibrium with the modern atmosphere; and (b) anaerobic water having no oxygen, no CFC-11 or CFC-113, and CFC-12 concentrations about 1/3 of modern atmospheric-equilibrium levels. That a water sample pumped from a well with a 0.6 to 0.9 m long screen represents a mixture is not surprising. Numerous investigators have reported small-scale water-quality variation in ground water (e.g. Cozarelli et al., 1996). Such small-scale variability is supported by limited diffusion in saturated ground water, and by large variations in permeability. Other evidence of mixing of samples is the presence of iron (II) and methane in oxygenated samples. With this mixing model, the lower concentrations in low-DO waters are explained not as degradation under low-DO conditions, but as degradation under anaerobic conditions, occurring in only a fraction of the total sample volume.

Anaerobic degradation of CFC-11 and CFC-113 has been observed in the laboratory (Lovely and Woodward, 1992) and the field (Cook et al., 1995; Plummer et al., in press), although CFC-12 degradation has only recently been reported for ground waters (Oster et al., 1996). These field results are consistent with the observations reported herein in that CFC-12 is less degraded, but concentrations of CFC-12 are

apparently reduced to about 1/3 of modern levels; not complete degradation, but a significant loss that would cause significant differences between apparent and actual ground-water ages.

Independent evidence of anaerobic biodegradation is presented by hydrogen gas, methane, and carbon dioxide concentrations measured in several piezometers (Table 4-3). Hydrogen gas concentrations can identify the controlling redox processes in anaerobic systems (Lovely and Goodwin, 1988). CFC-11 degradation has been observed in the laboratory for sulfate-reduction and methanogenesis redox conditions (Lovely and Woodward, 1992), both of which are indicated in sampled piezometers. Sulfate and iron (II) are present in shallow ground water at Mirror Lake (fig. 4-25) to support sulfate-reduction and iron-reduction reactions. There is limited laboratory evidence that iron (II) may play a role in abiotic degradation of CFC-11 under anaerobic conditions (Lovely and Woodward, 1992).

Overall, CFC-12 concentrations appear to be least affected by anaerobic degradation or contamination. The use of CFC-12 for age-dating ground water is likely to be more robust in the field, particularly for systems where anaerobic degradation conditions may exist.

Given the variability in geochemical conditions observed in different water-table piezometers, it is not possible to characterize the distribution of CFC's in recharge in the Mirror Lake drainage basin on the basis of these 31 wells. These results suggest that in areas where the shallow water table is anaerobic, CFC's in recharge will be significantly reduced from modern equilibrium levels. Furthermore, concentrations may also be reduced due to anaerobic degradation in micro-environments, even though the apparent redox conditions in pumped samples are not anaerobic. However, it is likely that these micro-environments will have relatively low permeability, and thus may play a less important role in controlling recharge chemistry, which will be weighted toward the conditions occurring in higher permeability zones.

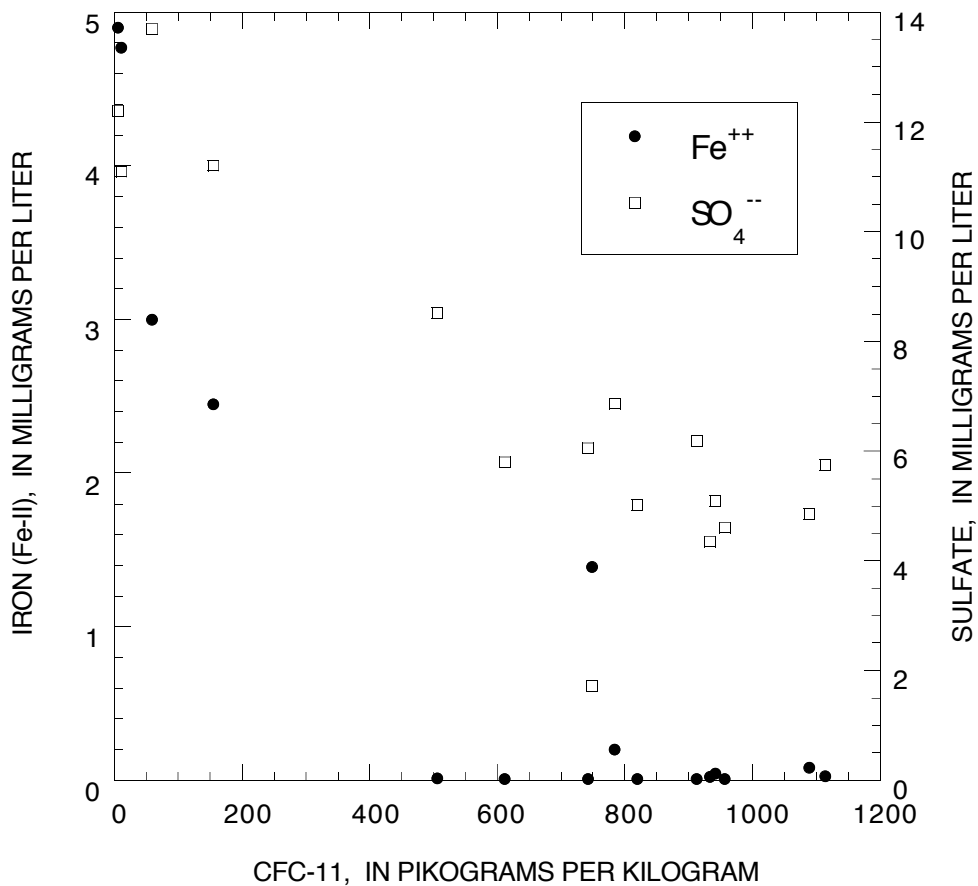


Figure 4-25 Iron (II) and sulfate as a function of CFC-11 concentrations.

A local flow system associated with streamloss and flow across a sandy terrace exhibits strong anaerobic conditions. Shattuck (1991) identified an area in the Mirror Lake drainage basin where the water table gradient is across the W stream (fig. 4-26). It appears that in this area stream water may enter the subsurface and flow across the sandy terrace to another branch of the W stream. Dissolved oxygen (DO) and total organic carbon (TOC) concentrations in water-table piezometers along the apparent flow direction (approximately) suggest that the provision of organic carbon to the aquifer by

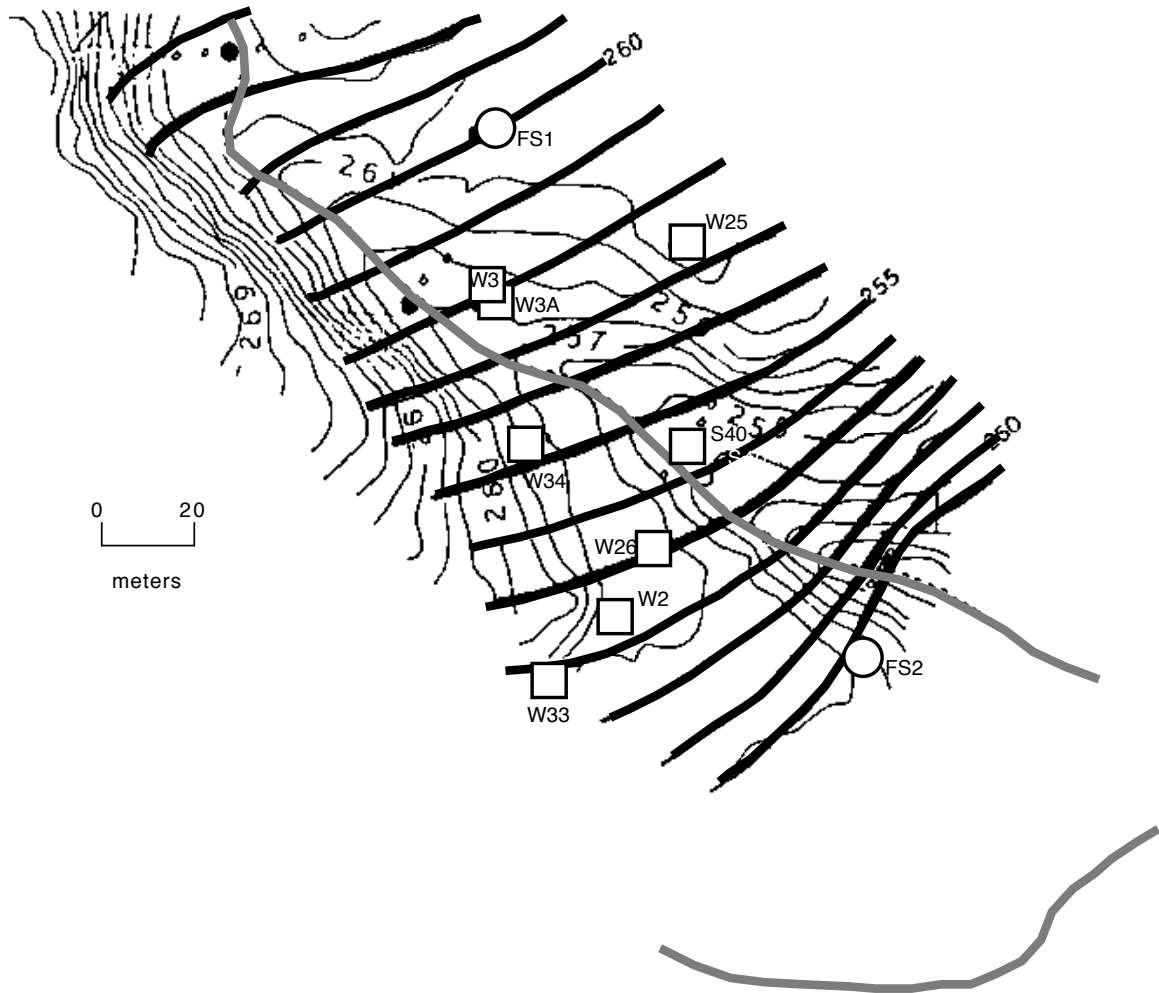


Figure 4-26 Water table elevations in the lower part of the W stream drainage basin (Shattuck, 1991).

the stream may contribute to the anaerobic redox conditions (fig. 4-27). Organic carbon may be carried into the aquifer from the bottom of the stream. Dissolved oxygen is consumed by the biologic activity and is only slowly replenished by diffusion downward through the unsaturated zone. This streamloss is not the only factor contributing to anaerobic conditions because such low-DO environments are also present upgradient of streams (for example, W25 in fig. 4-27).

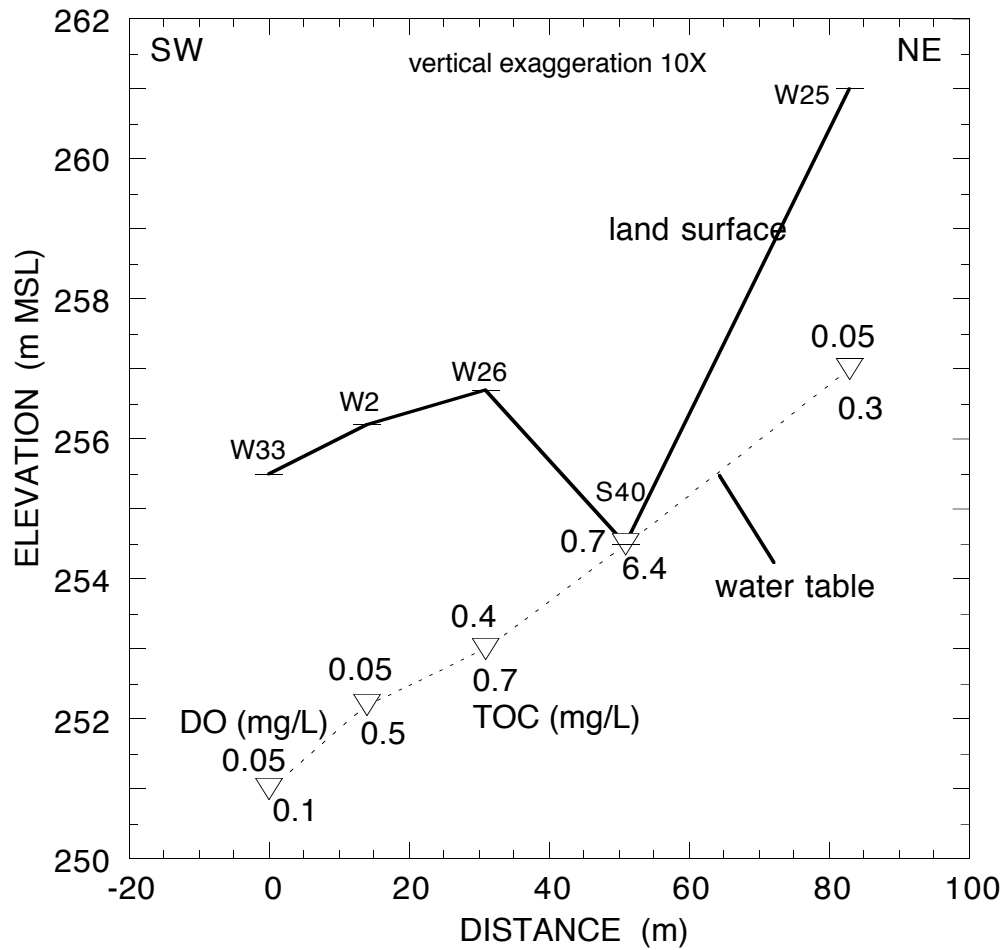


Figure 4-27 Cross-section in the lower part of the W stream drainage basin showing the land surface elevation, water table elevation, and concentrations of dissolved oxygen (DO) and total organic carbon (TOC) in samples from water-table piezometers.

4.5 Summary

The use of chlorofluorocarbons (CFC's) as age-dating tracers for ground water at the Mirror Lake fractured-rock research site may be limited because concentrations of CFC's in at least some areas are significantly reduced by anaerobic degradation. CFC concentrations in water samples from high-conductivity fractures in schist and granite bedrock indicate ages ranging from greater than 45 years to about 7 years, but the spatial pattern of ages is complex and the youngest measured ages occur near the lake at the bottom of the forested watershed. Equilibrium between CFC in the atmosphere and at the water table is needed to date saturated-zone waters. However, samples from piezometers screened just below the water table in the glacial drift indicate that CFC-11, CFC-12, and CFC-113 are substantially degraded where dissolved oxygen (DO) concentrations are low. Anaerobic ($DO < 0.1$ mg/L) conditions existing in a sandy terrace deposit may be caused by biodegradation of organic carbon in infiltrating stream water. Samples from this and other shallow anaerobic zones lack CFC-11 and CFC-113 and have CFC-12 concentrations that are as low as 1/3 of modern equilibrium concentrations. Furthermore, several hypoxic ($0.1 < DO < 3$ mg/L) samples have significantly reduced CFC's. As expected, samples with high DO collected at the water table generally contain CFC's near atmospheric-equilibrium concentrations. Many samples plot on a mixing line for CFC's and DO, suggesting that the water sampled can be a mixture of two end members: (1) waters saturated with oxygen and containing CFC's in equilibrium with the modern atmosphere, and (2) zero-DO waters containing no CFC-11 or CFC-113 and containing about 1/3 of modern CFC-12. Several samples contain CFC-11 and CFC-113 concentrations higher than those from equilibration with peak atmospheric levels, suggesting a non-atmospheric source. Possible sources of this contamination include sampling equipment (Busenberg and Plummer, 1996) and well-construction materials, including sand installed at well screens, grout used to seal the borehole annulus and PVC

adhesives. Evidence of active anaerobic biodegradation, which can degrade CFC's, includes high methane and ample iron (Fe-II) and sulfate and generally low DO. Hydrogen gas concentrations in anaerobic samples from water-table piezometers are consistent with methanogenesis or sulfate-reduction as the terminal electron-accepting process.

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