Chemistry and Residence Time of Groundwater in Black Rock Forest Springs and Wells

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ABSTRACT

Samples of groundwater from springs and wells in the Black Rock Forest, New York, were collected over a five-month period (November 1996 - March 1997), analyzed and compared with precipitation data from Boston, Washington, and West Point. An additional preliminary sampling was performed in June 1996. The study was done in order to investigate and diagram the role groundwater plays in the hydrologic cycle in a fractured-rock environment. Analysis of the groundwater samples included in situ measurements of pH, conductivity, nitrate and dissolved oxygen, ion chromatography, and use of the tritium/^{3}helium dating technique.

In situ measurements for the groundwater showed apparent seasonal trends for pH and conductivity---peaking in the winter at 7.35 (Mineral Spring 2) and declining in the summer to 2.82 (Birch Spring). pH in West Point precipitation was relatively constant throughout the year, fluctuating slightly between 4 and 5. Conductivity, however, increased in the summer and decreased in the winter.

Only two sets of data for the ion chromatography measurements were obtained for spring groundwater samples (June and November 1996). Concentrations (in mg/l) for chloride, nitrate and sulfate in the groundwater were compared with the average monthly concentrations in West Point precipitation (1979-1996). Concentrations of chloride and sulfate were high and concentrations of nitrate low in springs compared with those in precipitation. This may be explained by dry deposition.

Tritium/^{3}He dating yielded ages ranging from 0.0 to 24.0 years for groundwater from springs and wells. The sum of tritium and ^{3}H concentrations were plotted to display a curve ascending with age. Two points off the ascending line (Gorwyn Well and Mineral Spring 2) were shown to contain additional (radiogenic) helium when neon versus ^{4}He concentrations were plotted. Water from these two locations may also have been mixed with older water (pre-1952) containing no tritium. Ages from groundwater data were consistent with precipitation input data from Boston and Washington D.C.

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INTRODUCTION

Groundwater is a basic component of the hydrologic cycle and the study of its chemistry and flow allows for identification, isolation and quantification of biogeochemical processes in a forested ecosystem (Likens, 1987). By comparing precipitation and groundwater in springs and wells, the input and output of the system, differences and similarities in seasonal and year-to-year variations diagram the fractured-rock environment and the role water plays in it. In addition, calculating the age of the water indicates time it has spent underground and may explain its chemistry.

Background

Hydrologic Cycle

The hydrologic cycle is defined as "the continuous circulation of water from the sea to the atmosphere to the land and back again to the sea" (Manning, 1987). Displayed in Figure 1, water in the form of precipitation falls onto the earth and follows three paths: it either flows down on the surface of the earth as runoff, or percolates into the ground to reach the water table as groundwater, or to provide moisture for plant growth and reproduction. Water returns to the atmosphere via evapotranspiration (evaporation from soil and surface water and transpiration from plants).

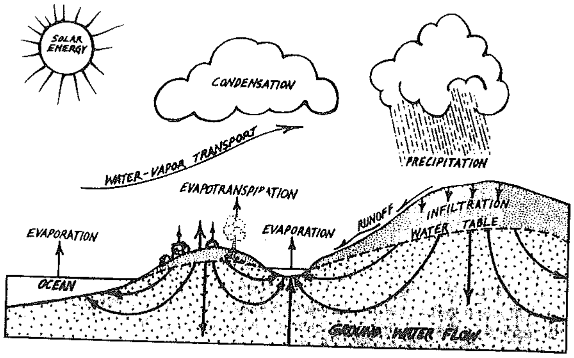


Figure 1. The hydrologic cycle. (Manning 1987)

Groundwater

Groundwater is defined as "all subsurface water (contained) in spaces within bedrock and regolith" (Murck, 1996). It includes less than one percent of the water in the Earth and more than 98 percent of all unfrozen freshwater in the hydrologic cycle. More than half of the Earth's groundwater occurs within 750 meters of the surface and is generally in constant motion (1996).

As previously shown, groundwater originates as rainfall and then soaks into the ground to become part of the groundwater reservoir. It moves slowly from the surface layer of moist soil, through the zone of aeration (vadose zone or unsaturated zone) where open spaces in bedrock and regolith are filled mainly with air, towards the saturated zone (phreatic zone) where all openings are filled with water (Murck, 1996). The upper surface of the water table (which divides the zone of aeration and the saturated zone) is the upper limit of readily usable groundwater. Water percolates through the saturated zone from areas of high pressure to areas of low pressure and eventually ends up in the ocean (1996).

The movement of groundwater is documented by its migration from areas of recharge to areas of discharge. Recharge is defined as the "replenishment of groundwater" (Murck, 1996) and discharge includes any region where groundwater leaves the saturated zone. Groundwater may either flow onto the ground surface as a spring, join surface bodies of water such as streams and lakes, etc., or be pumped out through a well (1996). Figure 2 diagrams paths of groundwater flow.

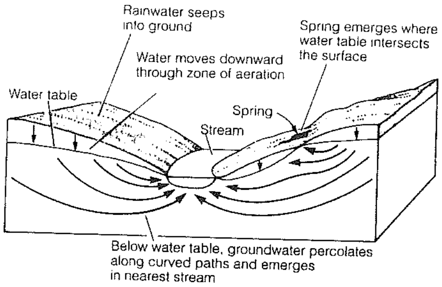


Figure 2. Paths of groundwater flow. (Murck 1996)

Springs and Wells

In this study, the groundwater from springs and wells is analyzed. Formation of springs is determined by geologic conditions; thus, they are classified on the basis of geology, type of opening, kind of water etc. (Manning, 148). Below (Figure 3) are examples of various common forms of springs.

The presence of a spring indicates that the underground reservoir is full to the point of spilling over, and water storage is at its maximum (148).

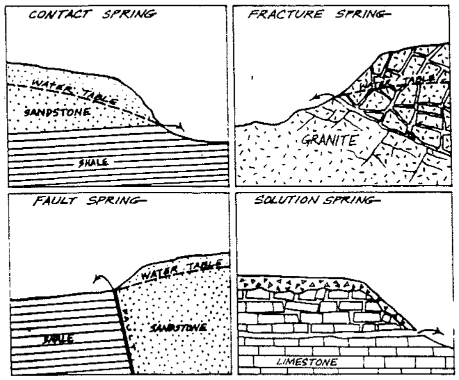


Figure 3. Common Types of Springs (Manning 1987)

Wells are holes dug into the earth until they intersect the water table. Water is pumped out of the saturated zone, creating a cone of depression of the water table surrounding the well. The slope of the water table is steepened and flow of water to the well increases (Murck, 1996). Shallow wells may be dry for part of the year, while deep wells reach well below the water table for continuous year-round water supply (1996).

Groundwater and Precipitation

The above diagrams show the relationship between precipitation and groundwater; precipitation is the input to the system and groundwater, the intermediary before output as surface water and evapotranspiration. Studying the chemistry of the two components of the hydrologic cycle highlights the biogeochemical processes that occur in the earth; for example, particular ions may be used by plants or added because of soil erosion and dissolution. This study examines the content of water in relation to these processes in a fractured-rock environment.

Groundwater and Residence Time

Dating groundwater using the tritium/^{3}helium technique is a relatively recent development. It essentially allows one to measure the time a water molecule reaches the water table to the time it departs the saturated zone at an area of discharge, such as a spring or well. Absolute dating can be achieved by comparing tritium concentrations in groundwater with those in precipitation as a result of nuclear bomb testing in the 1950s and 1960s. Residence time of groundwater may explain some of the trends found in the chemistry analysis.

Geography

Black Rock Forest

The springs and wells under investigation in this study are located in the Black Rock Forest, Cornwall, New York. The Forest is located on the western banks of the Hudson River in Orange County, New York (41.5 degrees N/ 74 degrees W) (Kantzos, 3). It is a natural ecosystem spanning 3750 acres (1500 ha) of forests, streams, ponds and natural wetlands in the Hudson Highlands (http:///www.httl.columbia.edu/groups/BRF, 4/1/97 and BRF, 1997).

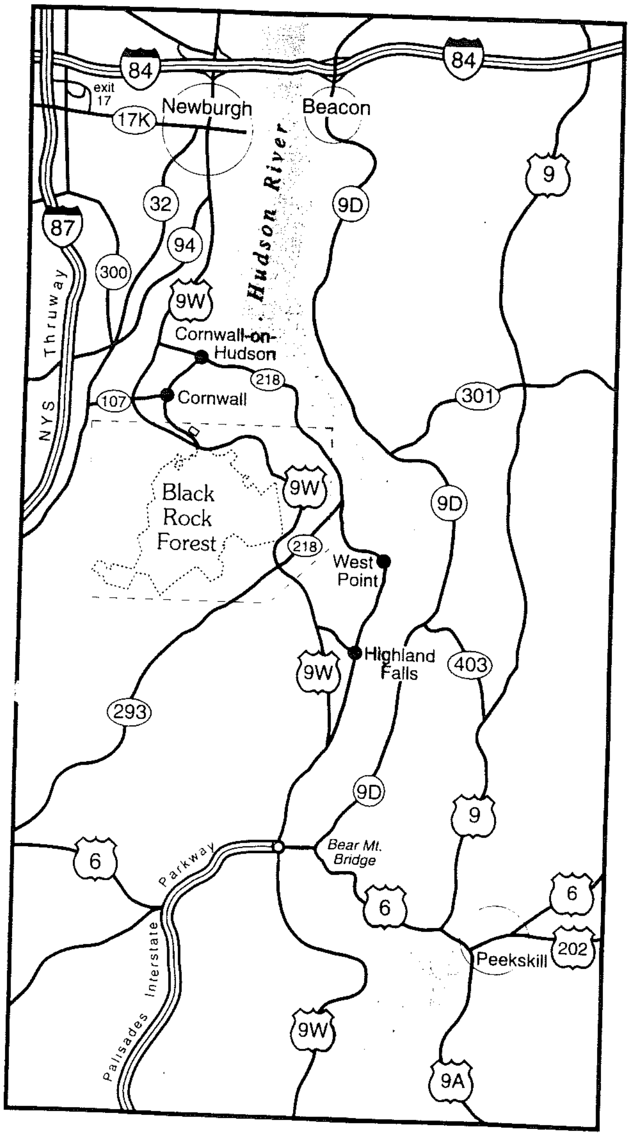
In 1928, the Black Rock Forest was established by Harvard University as a facility for forest management research. In 1989, it was acquired by the Black Rock Forest Preserve. Currently, it is in use as a field station for educational and research purposes by the Black Rock Forest Consortium (BRF, 1997). Please see Figures 4 and 5 on the following pages for maps of the region.

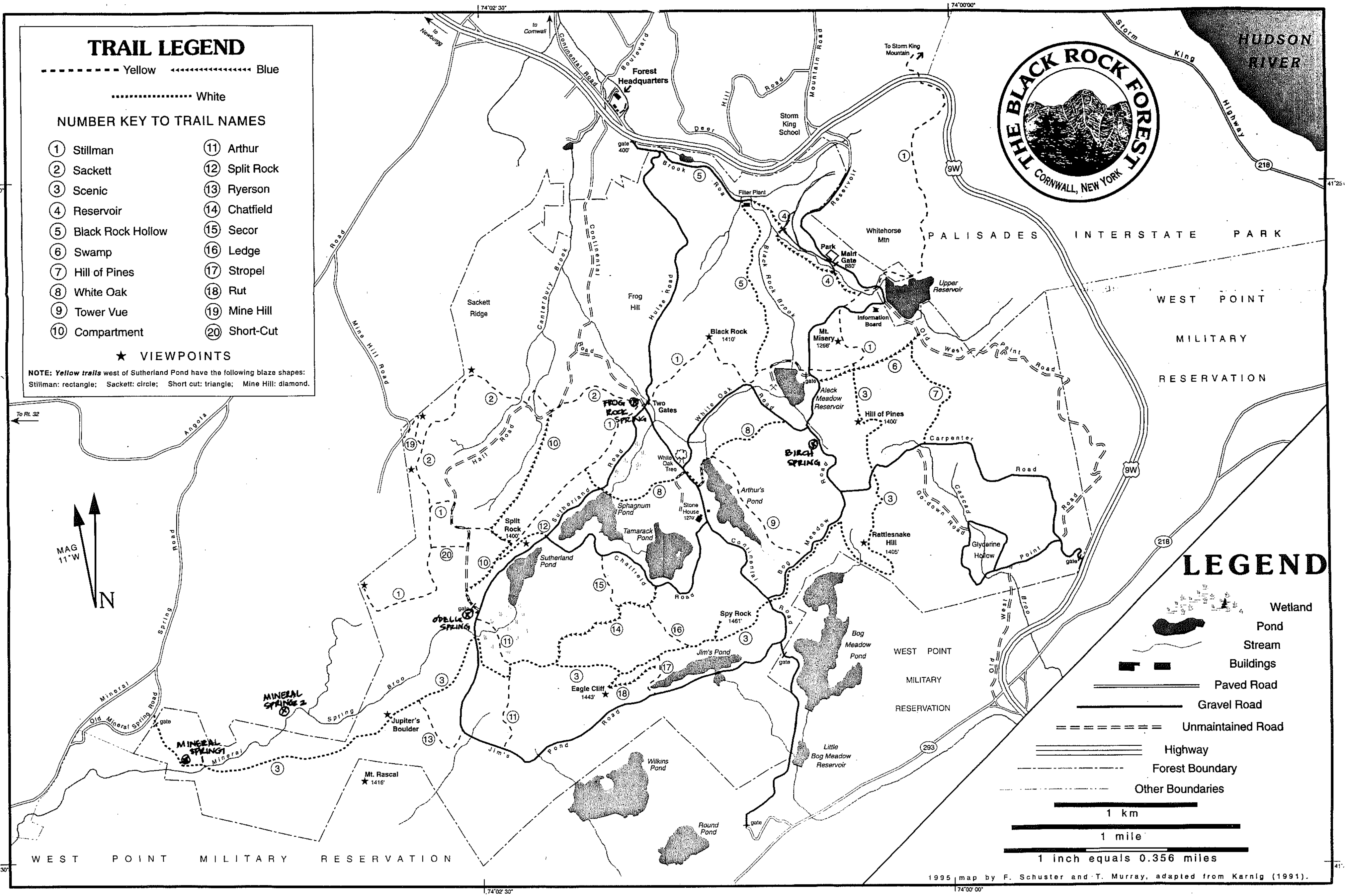
The Black Rock Forest is situated at the meeting point of the Hudson Highlands and the Hudson River Basin, contributing to a wide variety of habitats and species. Located on the central, highest section of the Highlands, the forest is underlain by granites and gneisses. These rocks, aged more than one billion years old, have undergone much movement; they have been "extensively folded, faulted, and metamorphosed" (http.../BRF). They are the basement bedrock for the entire Reading Prong Province, which spans from eastern Pennsylvania to the western Connecticut (http.../BRF). Thus, the region is considered a fractured-rock environment because of the nature of its geology, mainly bedrock with a thin surface layer of soil.

Springs and Wells

The Black Rock Forest contains several fractured-rock springs, five of which were chosen for this study: Mineral Springs 1, Mineral Springs 2, Birch Spring, Frog Rock Spring and O'Dells Spring.

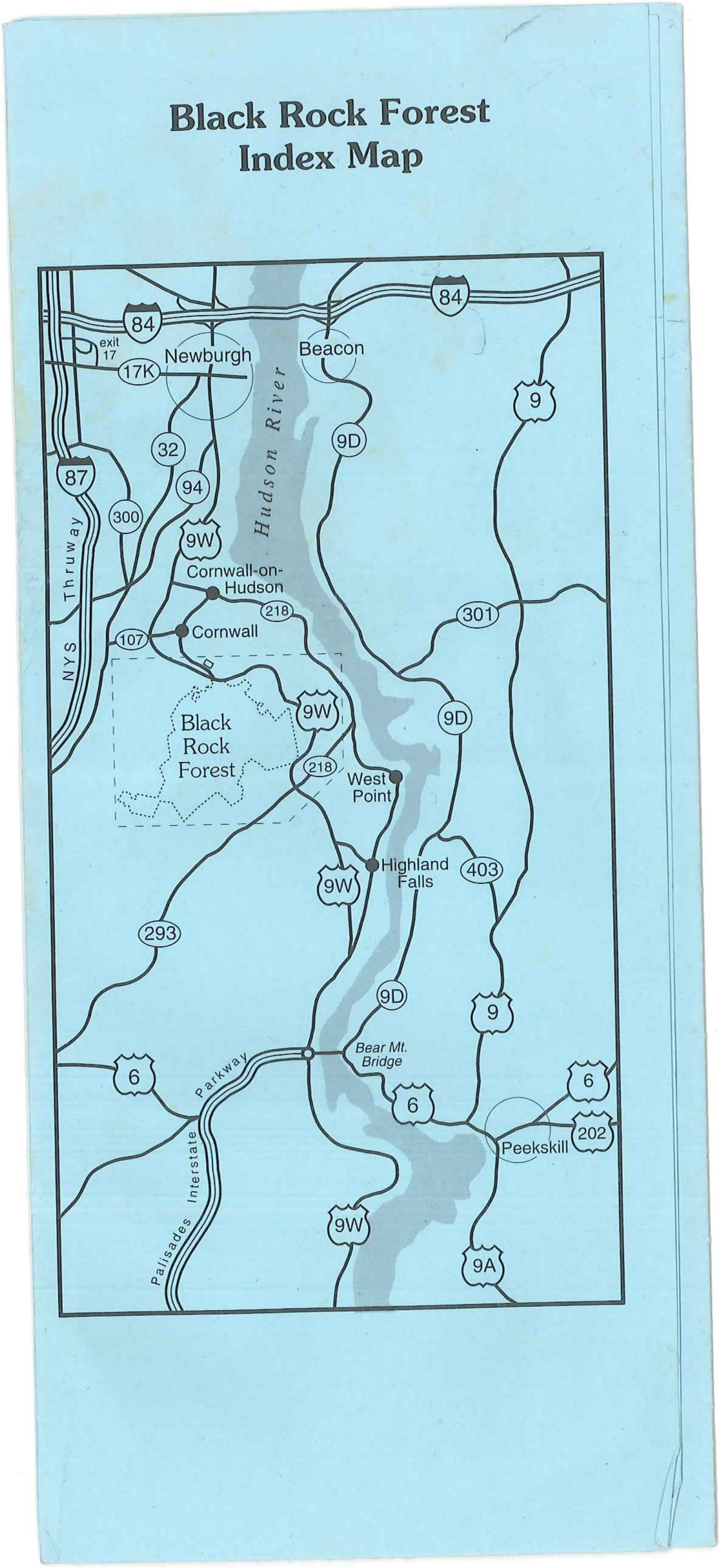
Figure 4. Black Rock Forest index map





1995 map by F. Schuster and T. Murray, adapted from Karnig (1991).

Figure 5. Black Rock Forest map.



Preliminary study included Continental Spring, but the study focuses mainly on the five mentioned. (Please see **Appendix I** for photographs of the sites.)

In order to prepare for groundwater analysis in the Black Rock Forest, preliminary studies were done in June 1996. A number of springs were located and samples taken. The springs were diagrammed in order to note location of groundwater outflow. Below is a brief introduction to the spring sites.

Mineral Spring 1 (Upper Mineral Spring) is located on the southwest corner of the Forest near Mineral Springs Road (41 22’ 48” N/ 74 03’ 50” W), just outside of the forest proper. It lies close to Minerals Springs Brook. Groundwater outflow originates in the mid-left portion of the fractured rock wall and forms a small stream leading down the slope (See Figure 6).

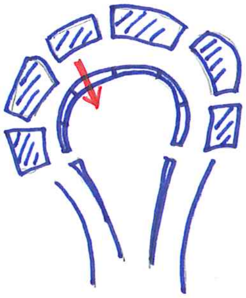


Figure 6. Mineral Springs 1

Mineral Spring 2 (Lower Mineral Spring) is located slightly east of Mineral Spring 1, between the latter and a waterfall to the east. Groundwater flow originates between two rocks and a root in the northwest (or left-middle) portion of the spring wall (Figure 7). The spring was distinct from the others because of the presence of excessive floculant of orange colour in the water, presumably oxidized iron.

Figure 7. Mineral Springs 2

Birch Spring is located in the mid-eastern portion of the forest, off Bog Meadow Road. It is situated at the foot of a tree where the roots rise above ground and the water discharges from the rocks at the base of the trunk. There are two above surface flows (one to the left middle and one to the right middle). Samples were taken from the left-hand side flow (Figure 8).

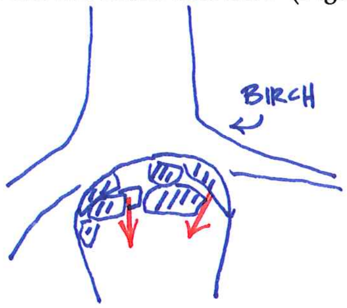


Figure 8. Birch Spring

Frog Rock Spring has no official name given by the Forest authorities, but was nicknamed 'Frog Rock' because of a huge rock that looks like a squatting frog near the road where it is located (see Appendix I). It is situated in the middle of the Forest, slightly west of the center. It flows directly beneath a large group of rocks and down the slope as a trickle. There is no pool of accumulated water like the other springs (Figure 9).

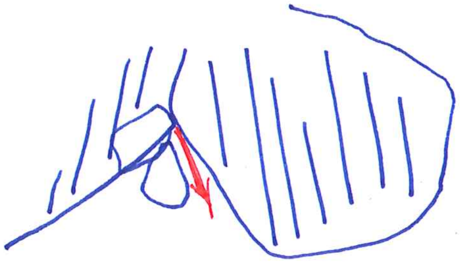


Figure 9. Frog Rock Spring

O'Dells Spring is located in the southwestern portion of the Forest, but not as far west as the Mineral Springs. It is near Sutherland Road and situated at the bottom of a hill. The spring is covered by a screen and looks like a little pool with rocks stacked around as walls. There are two flows from opposite corners (right and left) (Figure 10). The samples were taken from the flow at the left.

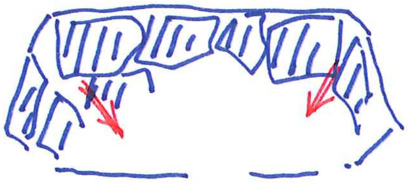


Figure 10. O'Dells Spring

Groundwater from five wells was also obtained. These wells were located mainly on residential property near and outside the Forest; they are identified by the surname of the property owner. Their approximate locations in relation to the Forest are as follows: Gorwyn (west), Osterby (west), Merrill (southwest), Kimple (southwest) and Jahaber (northeast).

METHODOLOGY

Fieldwork

A preliminary study identifying and locating the springs and wells to be investigated was done in the summer of 1996. Fieldwork for this study consisted of four trips to Black Rock Forest in November 1996, December 1996, February 1997 and March 1997. Initially, the aim was to look at the groundwater measurements over a period of four months, but because of schedule and time constraints, readings were done in February and March 1997.

Sampling Technique

In order to take the groundwater samples from the springs, two different methods were used. During the first two field trips, a peristaltic pump and plastic tubing were used to create pressure so that the water would flow through the tubing into the containers (rinsed twice before final sampling). 250 ml glass bottles were used for collection to take back for chemistry analysis, and 50 ml plastic bottles were filled for nitrate analysis. These plastic containers were used later for ion chromatography analysis. During the latter two trips, a 50 ml plastic syringe was used to draw in water from the source of flow. The second method did not require carrying a heavy battery to power the pump but took relatively longer to use.

A plastic filtration device and Advantec MFS 47 mm cellulose nitrate filters (pore size 0.45 u) were used to obtain clean water samples. Filtering was necessary because the water samples were to be run through sensitive instruments (such as the ion chromatrogam) and suspended matter would clog the injection tube. In addition, leaves and dirt might contaminate or alter the laboratory measurements.

During the second field trip, an instrument made of a copper tube connected by bolts on each end was used to collect water samples for the tritium/^{3}helium dating technique. This technique, which will be explained further, requires that the water has not been exposed to the atmosphere. Copper tubes are used because copper allows the least amount of leakage and contact with the media it lies between. The bolts at the end were tightened with a wrench in order to ensure that the sample was not in contact with the atmosphere.

The output end of the plastic tubing was attached to one end of the copper tube. Both bolts were loosened in order to allow the water from the springs to flow freely. After a certain amount of time, the bolts were sealed so that no air bubbles could be trapped inside (possible contamination of samples).

In Situ Measurements

A number of in situ measurements were made at the time of sample collection. These included temperature, pH, conductivity, and dissolved oxygen.

Temperature

Temperature was taken with an electronic temperature meter connected to a sensitive temperature probe placed close to the source of groundwater flow. Temperature was taken three times, at approximately five minute intervals.

pH

pH was measured using an electronic pH meter which registered both the temperature and pH with a combination probe. Prior to measurement, the pH meter was calibrated using a 4.0 and a 7.0 buffer standard solution. The pH probe was transported in a container of KCl solution.

Conductivity

Conductivity was measured with an electronic conductivity meter and probe. Temperature was also registered in the meter. The meter was also calibrated before measurement and the same procedure of three readings took place.

Dissolved Oxygen

Dissolved oxygen was measured with two chemkits. One kit measured dissolved oxygen concentrations for a range of 0 - 1 mg/l and the other kit measured a range of 1 - 10 mg/l. The procedure for both kits were identical. A conical plastic piece was attached to the end of the flow outlet tubing (without the filter), and a sealed glass tube with a pointed end containing an colour-sensitive solution was inserted into the conical piece while water was flowing. The tip of the glass tube submerged in the flowing water had to be carefully broken in order to allow the groundwater to react with the solution. The broken end of the glass tube was covered with a fingertip in order to avoid contamination from the atmosphere and turned upside down a few times to make sure the solution was completely mixed.

When the colour stabilized, the glass tube was placed next to a set of standard glass tubes depicting the range of shades and corresponding concentrations. The closest shade of blue or pink indicated the concentration of dissolved oxygen.

Laboratory Work

Ion Chromatography

Principle

Chromatography is very valuable in environmental analyses because it enables the separation and calculation of substance concentration in a complex mixture. In this study, ion-exchange chromatography was used to separate and identify major anions (chloride, nitrate and sulfate) and to quantify their concentrations (in mg/l) in the groundwater samples. This separation of ions relies on "principles of equilibration between a mobile (carrier) phase and adsorption onto a stationary phase packed within a separation column" (Nichols, 1997). It is achieved when analyte ions moving through the column exchange places with ions fixed at charged sites in the stationary phase (1).

Figure 11 diagrams the exchange processes within the separation column. Ions are in a continuous equilibration (known as the solute) between mobile and stationary phases. The mobile phase, or the eluent, is a liquid while the stationary phase (usuually a resin) consists of the "surface of fine particles used to pack the separation column" (Nichols, 1997). The eluent flowing through the separation column carries the ions in the sample; those ions with higher charge, decreased hydrated radius, and increased polarizability have a greater affinity for exchange with the particles in the stationary phase and thus, move more slowly through the column (1997).

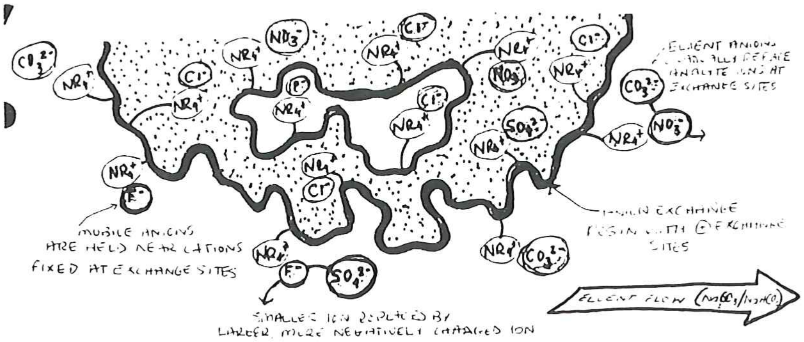


Figure 11. Exchange processes within the separation column.

The fixed bonding sites in the stationary phase (usually a resin) are the opposite charge of the analyte (or sample) ions. In anion analysis, a bonding site may be positively charged ammonium group ($-NR_4^+$) which attracts anions such as Cl^- or SO_4^{2-}. SO_4^{2-} are larger and more negatively charged than Cl^- ions so they hold more tightly to the resin surface and take longer to pass through the column. The eluent also contains anions (such as CO_3) which displace the analyte ions. It takes approximately 15 minutes for the ions to pass through the column. This varies according to eluent flow rate and composition and column packing material (Nichols, 1997).

After the ions have been separated in the column, they pass through an "ion supressor" which increases the difference in conductivity between the anaylte and eluent ions, thereby increasing ion detection sensitivity (Nichols, 1997). Na^+ in the eluent is exchanged "with H^+ in a "supressant" solution across a membrane permeable only to small cations" (1997). Strong acids such as HNO_3 and H_2SO_4 are formed by this exchange and they have a much higher conducitivity compared to the eluent acid (H_2CO_3).

Ions pass on finally to the detector which measures the conductivity of the analyte ions proportional to the concentration of the ion. This is recorded on a chromatogram (see Figure 12) as a function of elution time (Nichols, 1997). The y-axis of the chromatogram shows the area of the ion

Figure 12. Sample chromatogram.

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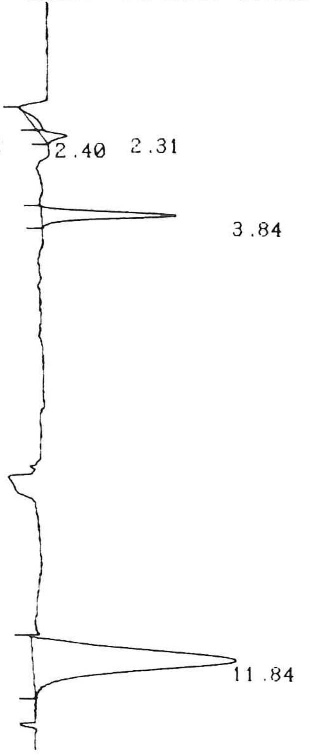
CHANNEL A      INJECT   04/05/97 11:58:33   STORED TO BIN #  21
```

RUN 7
SAMPLE 2
BRF # 2 6/6/96)



```
                        ER 0
DATA SAVED TO BIN #     21


ANION                              04/05/97 11:58:33      CH= "A"   PS=  1.

FILE  1.      METHOD  5.      RUN  21       INDEX  21               BIN  21

NAME                 CONC       RT       AREA BC        RF

  1                  0.        2.31     157288 02
FLUORIDE             0.        2.4      196850 03
CHLORIDE             0.        3.84    1102611 01
SULFATE              0.       11.84    5249347 01

TOTALS               0.                6706096

WARNING - MEMORY AT  8. K - UNPROTECTED CHROMATOGRAMS WILL BE REPLACED
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peak, or the concentration of the ion, and the x-axis represents the "retention time", or the time it takes for a particular ion to pass from the injection loop to the detector (1997).

To calculate the concentration of a particular ion, the following equation is used:

$$\text{Ion Concentration} = \text{Peak Area} / \text{Slope}$$

The peak area is determined by the detector and recorded at the bottom of the chromatogram. The slope is derived from a calibration curve using a range of standard solutions of different concentrations of the particular ion. The slope values (derived from standards described in **Appendix II**) used in this study are shown in Table 1.

Table 1. Slope values for ion concentration calculations.

ION	SLOPE (mg/l/peak area)
chloride (Cl^-)	7.3×10^5
nitrate (NO_3^-)	3.6×10^5
sulfate (SO_4^{2-})	4.3×10^5

Procedure

In order to use the ion chromatograph to measure concentrations of ions accurately, the instrument had to be calibrated using a number of standards with different concentrations. (The preparation procedure of the anion standard solutions for calibration can be found in **Appendix II.**) The standards used during the run of the samples to check calibration of the instrument were "D" and "E"; please find explanation in the appendix aforementioned. The specific procedure for running samples through the ion chromatograph can be found in **Appendix III**.

Tritium/^{3}He Dating Technique

Principle

The tritium/^{3}He dating technique is used to calculate the apparent and absolute age of water based upon its tritium (^3H) concentration and the ratio of $^3H/^3He$. Tritium is the heaviest radioactive isotope of hydrogen and has a half-life of 12.43 years (Schlosser et al., 1988). It is produced either naturally in the upper atmosphere as a result of reactions of protons and neutrons with nitrogen and oxygen ($^{14}N + n \rightarrow {}^{15}N \rightarrow {}^{12}C + {}^{3}H$) and oxidizes to HTO, or "artificially" as a product of hydrogen and nuclear bomb explosions (Mazor, 1991 and Schlosser et al, 1988).

In the 1950s and 1960s, the level of tritium in the atmosphere dramatically increased as a result of nuclear bomb testing. It peaked in 1963 at a concentration of 10,000 TU (or TR: tritium ratio equivalent to $^{3}H/H$ ratio of 10^{-18}) in a single monthly rain (International Atomic Energy Agency (IAEA)in Mazor, 1991 and Schlosser et al., 1988). After a ban on nuclear weapon testing was instituted in 1963, tritium levels began to decline (Figure 13) (1991).

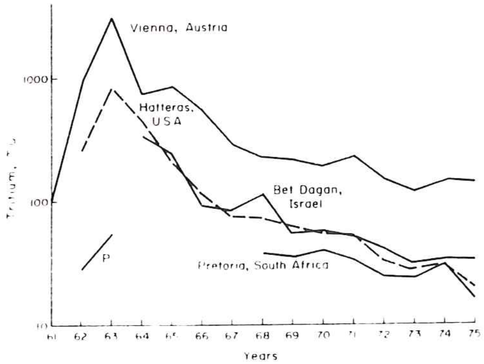


Figure 13. Annual weighted average tritium concentrations of representative weather stations (data from Environmental Isotope Data: World Survey of Isotope Concentrations in Precipitation, Vol.1 (1969) and Vol. 7 (1983) in Mazor, 1991).

Natural tritium concentrations in water (or water formed before 1952) are less than 0.5 TU (Mazor, 1991). Water with significant tritium concentration (bomb tritium) contains more than 10 TU, and water with little but measurable concentrations (0.5 - 10 TU) is probably a mixture of pre- and post-1952 water (1991). After the ban, tritium concentrations decreased to 25 TU in 1987 (Schlosser et al., 1988). Comparing tritium/^{3}He concentrations in groundwater with precipitation input allow for absolute dating of water.

During the last 40 years, the bomb tritium signal has been used to study water circulation in natural systems (oceans, lakes and groundwater) (Schlosser et al., 1988). The bomb tritium is used as a tracer which is followed in the exchange of water with the atmosphere and further movement through the system. Because of radioactive decay and dispersal, interpretation of bomb tritium studies has been complicated (1988).

Measuring the simultaneous concentrations of tritium and its decay product, ^{3}He, allows "determination of the elapsed time since a water parcel has been isolated from gas exchange with the atmosphere" (Schlosser et al., 1988). Once molecules of HTO in water have been exchanged across the water table into the saturated zone, they cannot escape until they reach areas of discharge where they come into contact with the atmosphere. During the time it remains in groundwater, tritium decays to produce ^{3}He according to equation (1):

$$^{3}H\ (t) = {}^{3}H\ (t_0)\ e^{\lambda - t} \tag{1}$$

where $^{3}H\ (t)$ is the tritium concentration at time t, $^{3}H\ (t_0)$ is the tritium concentration at the time of infiltration, and λ is ln $2/T_{1/2}$ ($T_{1/2}$ is the half life of tritium, 12.43 years) (1988). The increase in concentration of ^{3}He is measured by equation (2):

$$^{3}He(t) = {}^{3}H(t_0)(1 - e^{-\lambda t}) = {}^{3}H(t)(e^{\lambda t} - 1) \tag{2}$$

where $^{3}He(t)$ is the tritiogenic ^{3}He concentration at time t in TR (or TU) (1988).

The tritiogenic ^{3}He is added to the natural ^{3}He content of groundwater which consists of atmospheric ^{3}He (in solubility equilibrium), excess air ^{3}He, and nucleogenic ^{3}He (Stute in Schlosser et al, 1989). The concentration of tritiogenic ^{3}He is separated from the total helium content based on the "helium isotope measurement ($^{3}He/^{4}He$ ratio and ^{4}He concentration) and the knowledge of the ^{4}He concentration of the water in solubility equilibrium with the atmosphere" (Schlosser et al, 1989). The total ^{4}He content of groundwater includes the ^{4}He concentration in solubility equilibrium with teh atmosphere, excess air ^{4}He and radiogenic (1989). The separation of tritiogenic ^{3}He is complicated by the addition of radiogenic helium.

Radiogenic helium is the product of the radioactive decay of uranium and thorium:

$^{238}U \to {}^{206}Pb + 8\,{}^{4}He$

$^{235}U \to {}^{207}Pb + 7\,{}^{4}He$

$^{232}U \to {}^{208}Pb + 6\,{}^{4}He$ (Mazor, 1991).

Since common rocks contain uranium and thorium, radiogenic helium is constantly formed and partially released into water by dissolution (1991). It accumulates to relatively high concentrations in old groundwater (Schlosser et al, 1989).

Nucleogenic ^{3}He is also produced by a ^{6}Li(n,λ)^{3}H reaction in radiogenic helium (Schlosser et al, 1989). In order to separate tritiogenic ^{3}He from the atmospheric and the nucleogenic ^{3}He content, neon is measured "as an indicator of air in addition to the helium isotopes" (Schlosser et al, 1989). (See **Appendix IV** for details of procedure.)

$^3He_{trit}$ must be converted from cm^{3}STP/g to TR (tritium ratio) in order to calculate the tritium/^{3}He age. 1 TR means a tritium to hydrogen ratio of 10^{-18} (Benson and Krause, 1980 in Schlosser et al, 1989). $^3He_{trit}$ is multiplied by [4.021 & $10^{-14}/(1\text{-}S/1000)$] * TR/cm^{3}STP/g H_20), where S is the salinity of the water sample in ppt (Jenkins 1987 in Schlosser et al, 1989).

The tritium and tritiogenic ^{3}He concentrations together provide the tritium/^{3}He age. The calculation (3) for this is shown:

$$_{\mathrm{T}} = ((T_{1/2})/(\ln 2)) * \ln\,(1 + [^3\mathrm{He}]/[^3\mathrm{H}]) \qquad (3)$$

where $T_{1/2}$ is the half life of tritium, 12.43 years.

The tritium/^{3}He age is affected by mixing and ^{3}He loss due to incomplete confinement in the saturation zone (Schlosser, 1988). "Mixing of waters with different tritium/^{3}He values results in a non-linear behaviour of the tritium/^{3}He age (Jenkins and Clarke, 1987) while ^{3}He loss leads to a systematic deviation of the tritium/^{3}He ages to lower values (Schlosser, 1988)" (Schlosser, 1989). Thus, the age calculated is apparent age information within a certain precision of approximately +/- 30% (1989).

Tracing tritium/^{3}He concentrations and calculating the apparent age of groundwater from springs and wells allows determination of possible trends or correlation between age and depth or geography. Schlosser et al (1988, 1989) studied tritium/^{3}He concentrations to date shallow groundwater in multi-level wells in Liedern/Bocholt, West Germany, as a function of depth. A study of rock-water interrelation in the Mont Blanc tunnel by Fontes et al (1979) showed that sharp variation in tritium values indicated "recharge flow in separated fractures with varying flow velocities" (Mazor 1991). This analysis of a fractured-rock environment suggests that the Black Rock Forest values may also be varied.

Procedure

Water samples collected in bolted copper tubes from Black Rock Forest were stored for measurement of helium isotopes while water taken from the 250 ml glass bottle was retained for tritium analysis. ^{3}He analysis consists of degassing the water samples in a vacuum extraction system, separating other gases (including neon), sealing them in an ampule and using a dedicated helium isotope mass spectrometer to measure helium isotopes with an error of approximately 1% (Lynch and Kay, 1981 in Schlosser et al, 1988). "Tritium samples were measured by low level counting technique with a 1 error of +/- 5-10% and a detection of limit of about 1 TR" (Schlosser et al, 1988). They were set aside in a freezer for a few months in order to allow the tritium to decay to ^{3}He, which was measured then using the mass spectrometer with an error of 1 - 2 %. The tritium concentration used in calculations is decay corrected to the date of water sampling (1988).

RESULTS & DISCUSSION

In Situ Measurements

pH in Black Rock Forest springs

The apparent trend for pH in groundwater from springs in Black Rock Forest is to increase in the winter and to decrease in the summer (Figure 14). The range varies from a low of 2.82 to a high of 7.35 with a slightly acidic mean pH of 5.01 (Table 2). Most of the springs follow this trend except for Mineral Springs 2 (not enough data points - missing June 1996) and Birch Spring (which decreased earlier in the spring - see March 1997). The greatest range of values occurred in March 1997.

The pH at Mineral Springs 2 is unusually higher than the other springs. It seems to be the most basic of the springs. This may be because water-rock interaction tends to increase the pH because the acids in the water dissolve rocks.

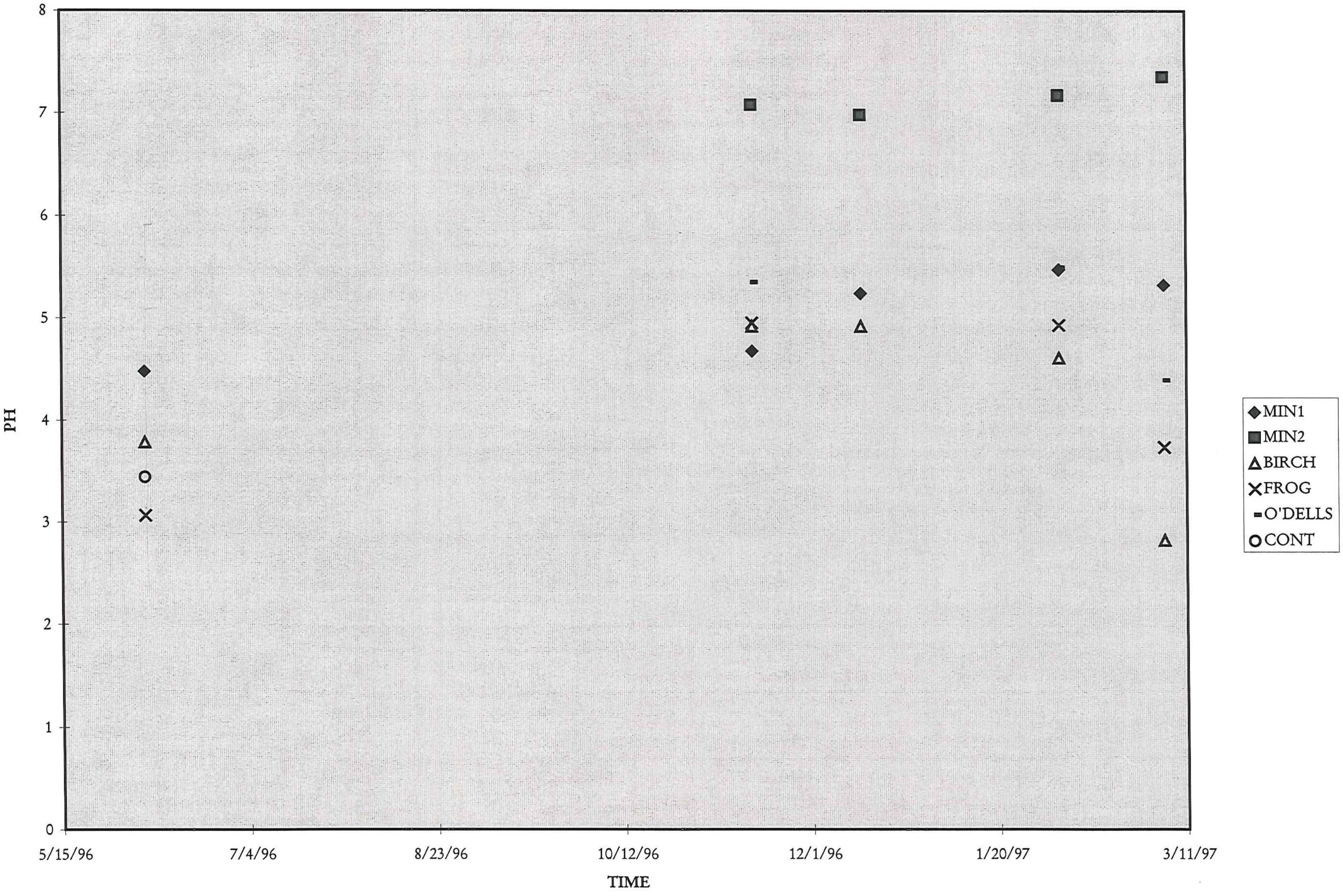
Table 2. pH in Black Rock Forest springs

DATE	MIN1	MIN2	BIRCH	FROG	O'DELLS	CONT
6/6/96	4.48		3.78	3.06		3.44
11/15/96	4.68	7.08	4.92	4.95	5.35	
12/14/96	5.24	6.98	4.92			
2/5/97	5.47	7.17	4.61	4.93	5.49	
3/5/97	5.32	7.35	2.82	3.73	4.39	
MEAN	5.04	7.15	4.21	4.17	5.08	3.44
STD DEV	0.43	0.16	0.91	0.93	0.60	-

RANGE:	**4.53 (2.82 - 7.35)**
MEAN:	**5.01**
STANDARD DEVIATION:	**1.21**

Compared with average pH values for groundwater ranging from 5.0 to 8.0, the data from Black Rock Forest springs is low (Walton, 1970). Although the overall mean is 5.01, the standard deviation of 1.21 indicates high fluctuation of values. The lower pH values may have been caused by dissolution of small amounts of mineral acids from sulfide sources or organic acids associated with soil or rocks the water percolated through (1970).

Figure 14. pH in Black Rock Forest springs.



Average monthly pH in Black Rock Forest springs and West Point precipitation

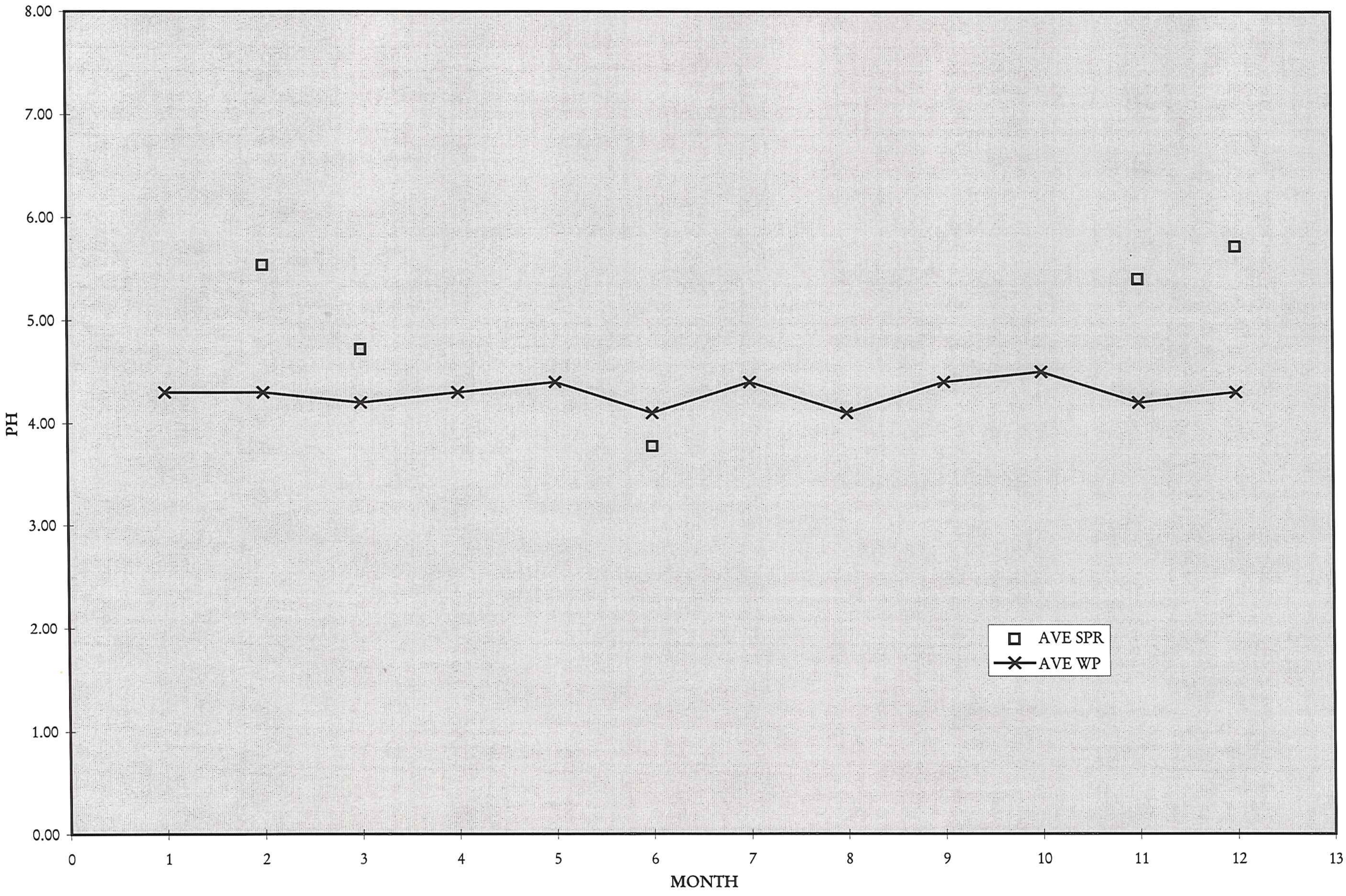
The average monthly pH for precipitation remains relatively constant, fluctuating throughout the year between 4 and 5 with a mean of 4.3 (Figure 15). This is consistent with average pH values calculated for north-eastern United States (Table 3).

Table 3. Average pH values for north-eastern United States (Likens et al 1995).

LOCATION	PH VALUE	REFERENCE
West Point, NY (1979 - 1996)	4.3	
Ithaca, NY (1973 - 1974	4.05	Cogbill and Likens 1974
Hubbard Brook,, NH (1963 - 1974)	4.1	Likens et al 1977
NE United States (1978 - 1979)	4.2	Pack 1980
NE United States (1965 - 1968)	4.4	Pearson and Fisher 1971

Figure 14 is a plot of precipitation data with average monthly spring pH. It seems as if pH in springs is generally higher than pH in precipitation and that it follows a seasonal trend while the latter doesn't. This graph, however, should not be misinterpreted. The average pH in springs is influenced considerably by the high values of the Mineral Springs 2 data. Also, there was no June 1996 reading for Minerals Springs 2 so the average in June is lower than the others. Since there is data missing for other months, it is erroneous to assume a seasonal pattern without a complete set of data. Also, the precipitation data is average monthly pH compiled from a 1979 - 1996. 1996 - 1997 may have been an unusually high year.

Figure 15. Average monthly pH in Black Rock Forest springs and West Point precipitation



Conductivity in Black Rock Forest springs

Conductivity of groundwater in the springs does not seem to have any recognizable seasonal trends (Figure 16). Data for each of the springs over the five readings are relatively constant over the year. Values of conductivity range from 36.2 to 178.7 us/cm with a mean of 59.8 us/cm.

Conductivity in Mineral Spring 2 is significantly higher than the others. This may be because of a higher concentration of ions in the groundwater. There is iron precipitate suspended in the water because of the influx of groundwater coming into contact with the atmosphere (See *Dissolved Oxygen* for further information). This may have affected the reading.

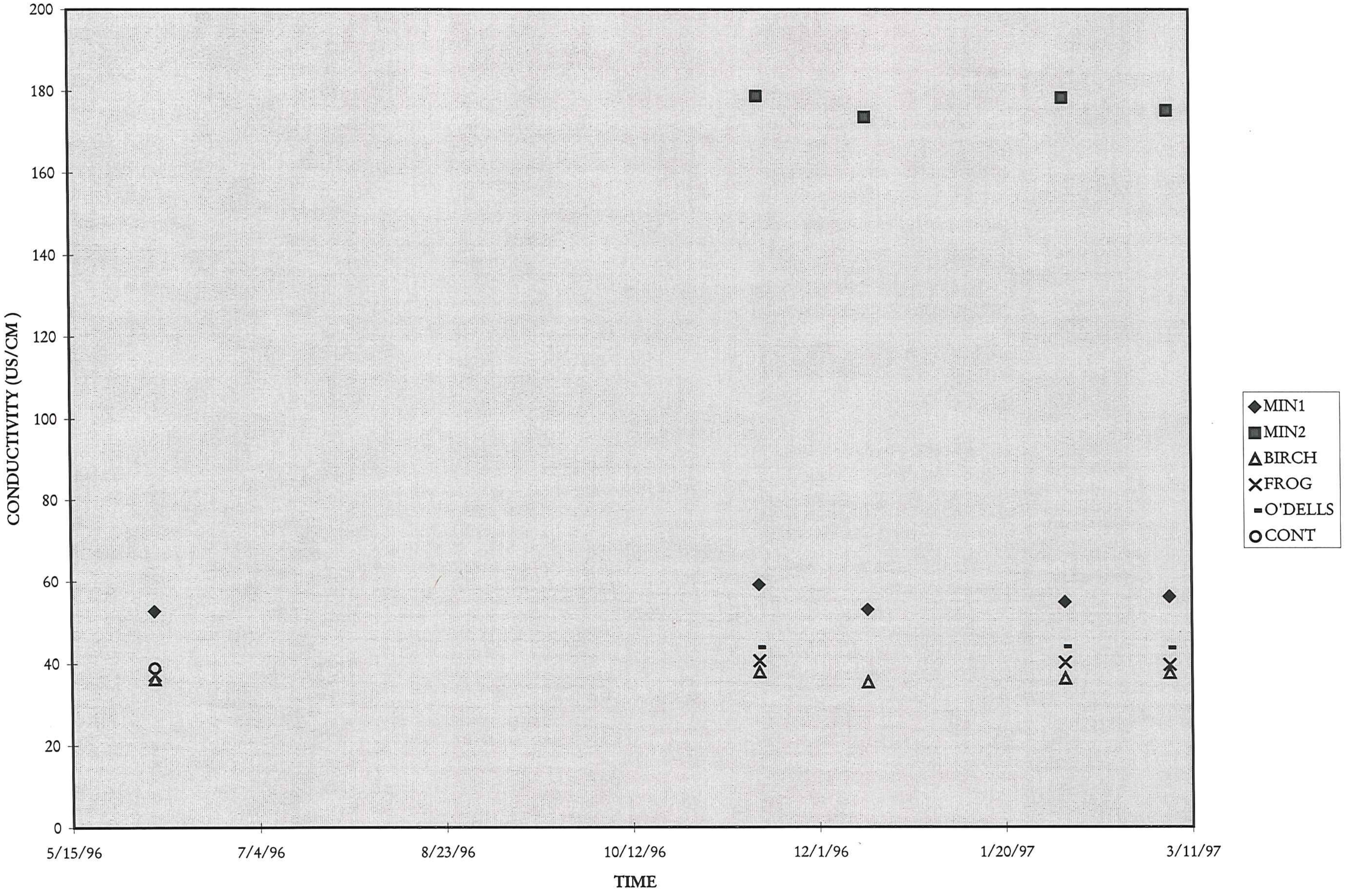
Table 4. Conductivity in Black Rock Forest springs.

DATE	MIN1	MIN2	BIRCH	FROG	O'DELLS	CONT
6/6/96	52.8		36.2	37.2		38.9
11/15/96	59.1	178.7	37.8	40.5	43.9	
12/14/96	53.0	173.6	35.4			
2/5/97	54.9	178.3	36.2	40.1	44.0	
3/5/97	56.1	175.2	37.5	39.5	43.7	
MEAN	55.18	176.45	36.62	39.33	43.87	38.90
STD DEV	2.6	2.5	1.0	1.5	0.2	-

RANGE: **142.5 (36.2 - 178.7)**
MEAN: **59.8 us/cm**
STANDARD DEVIATION: **52.9**

The conductivity values for springs in Black Rock Forest are within the normal range for groundwater: 30 - 2000 us/cm @ 35 C (Davis and DeWiest, 1966 in Walton, 1970).

Figure 16. Conductivity in Black Rock Forest springs.

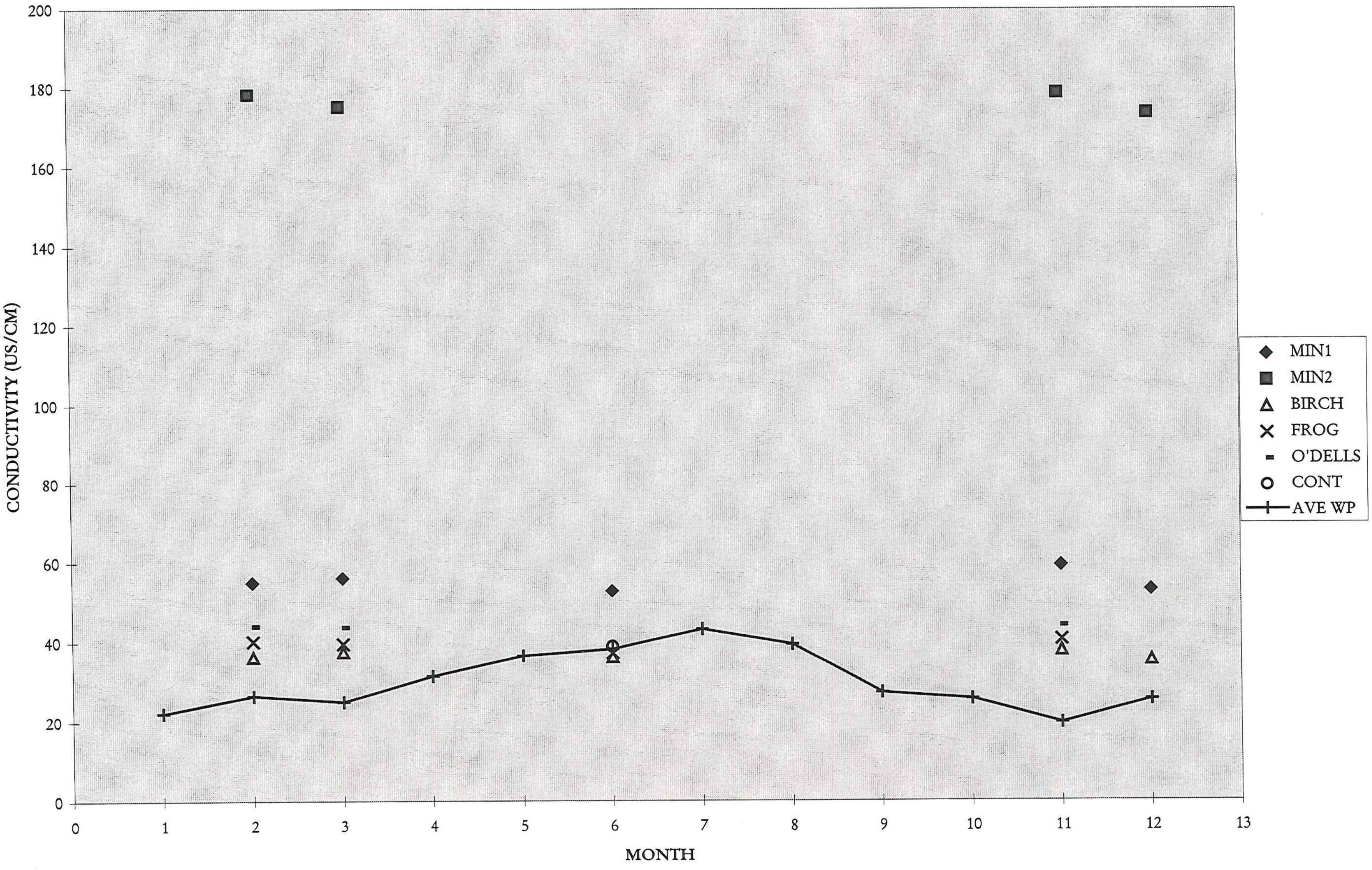


Conductivity in Black Rock Forest springs and average monthly conductivity in West Point precipitation

The average monthly conductivity of precipitation appears to show a seasonal trend of increasing in the summer and decreasing in the winter, between 20.0 and 40.0 us/cm (Figure 17). Values for conductivity in West Point precipitation are slightly higher than normal rainwater values which range from 5.0 - 30.0 us/cm (Davis and DeWiest, 1966 in Walton, 1970). This may be due to an increased concentration of dissolved ions from pollution or from proximity to the ocean.

The conductivity values of groundwater from Black Rock Forest springs is generally higher than those in West Point precipitation. This may be because chemical weathering resulted in the addition of dissolved ions and higher conductivity.

Figure 17. Conductivity in Black Rock Forest springs and average monthly conducitivity in West Point precipitation



Dissolved Oxygen in Black Rock Forest springs

Dissolved oxygen data taken from Black Rock Forest springs plotted on Figure 18 is variable. Mineral Springs 1 and 2 remain constant while Birch and Frog Rock Springs increase over time. O'Dells Spring data fluctuates with in both directions. No definitive conclusions can be drawn from this data with the exception of Mineral Spring 1.

The low dissolved oxygen content in Mineral Springs 1 may explain the presence of rusty orange-coloured precipitate found suspended in the water accumulated from the outflow. Below the water table, the groundwater is out of contact with the atmosphere, and as a result of continuing reactions, it may become anoxic (oxygen-free). When this occurs, Fe^{2+} and Mn^{2+} ions appear in solution because of a lack of dissolved oxygen, which would otherwise remove them by oxidation and precipitation. When groundwater is brought to the surface (as it is here), it undergoes rapid oxygen uptake from the atmosphere and consequently, ferric hydroxide and manganese hydroxide precipitate (Berner and Berner, 1987).

Table 5 displays the specific values of dissolved oxygen in groundwater. Most groundwater has dissolved oxygen content concentrations below 2.0 mg /l with a median value of 0.7 mg/l (Leenheer et al, 1974 in Drever, 1988). Water percolating through the soil loses dissolved oxygen content to several biological processes so by the time water reaches the water table, most of the dissolved oxygen is gone (Drever, 1988). There should be a seasonal trend since biological processes are more active in the summer.

Table 5. Dissolved oxygen content (mg/l) in Black Rock Forest springs. [Please note that maximum values are shown.]

DATE	MIN1	MIN2	BIRCH	FROG	O'DELLS
11/15/96		0.8		1.0	7.0
12/14/96	6.0	1.0	4.0		
2/5/97	6.0	1.0	4.0	8.0	3.0
3/5/97			5.0	7.0	5.0
MEAN	6.0	0.9	4.3	5.3	5.0
STD DEV	-	0.1	0.6	3.8	2

The data recorded here is for the winter, so it is consistent with minimal change. Any differences may be due to temperature since dissolved oxygen is temperature dependent, or possibly due to residence time in the ground.

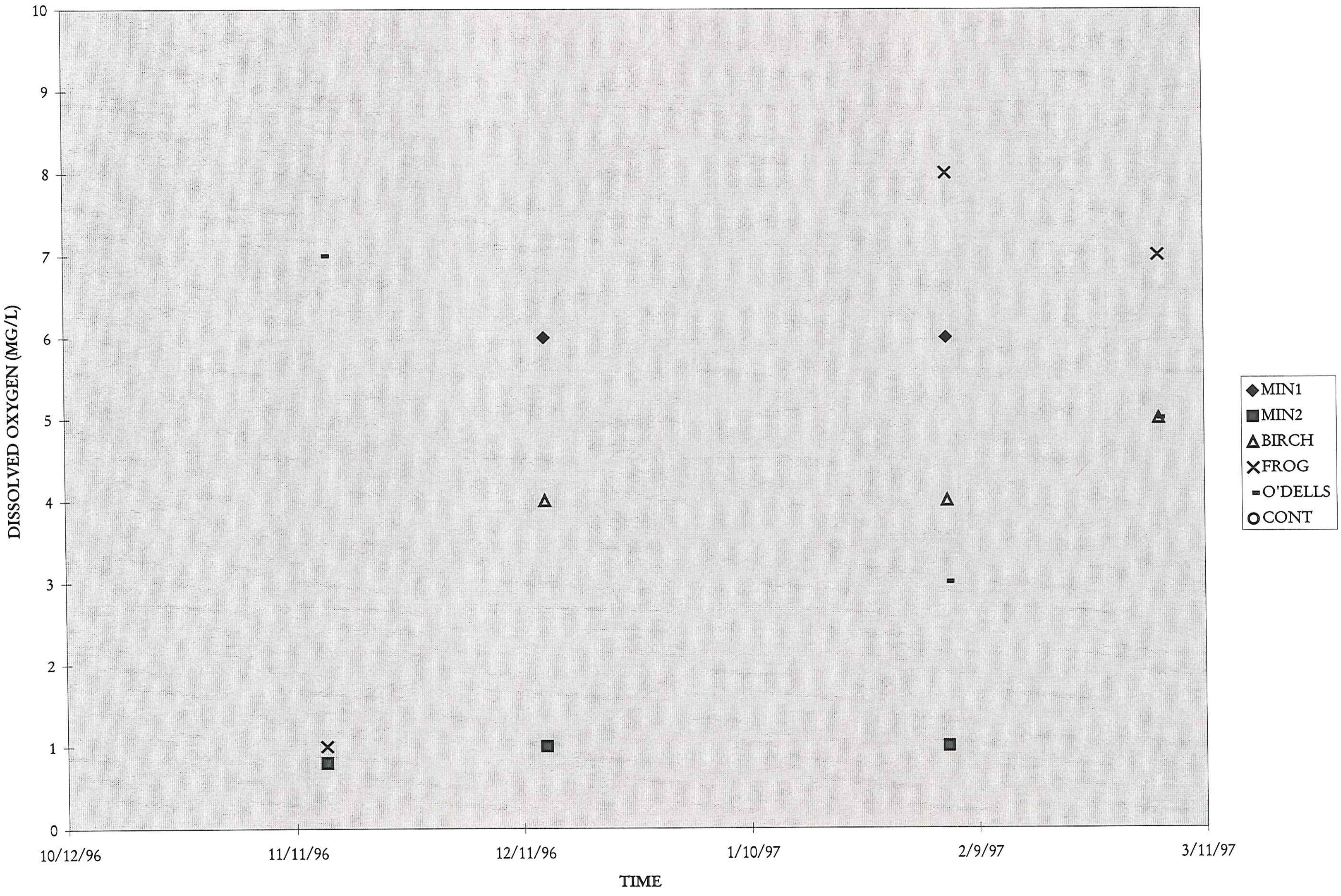
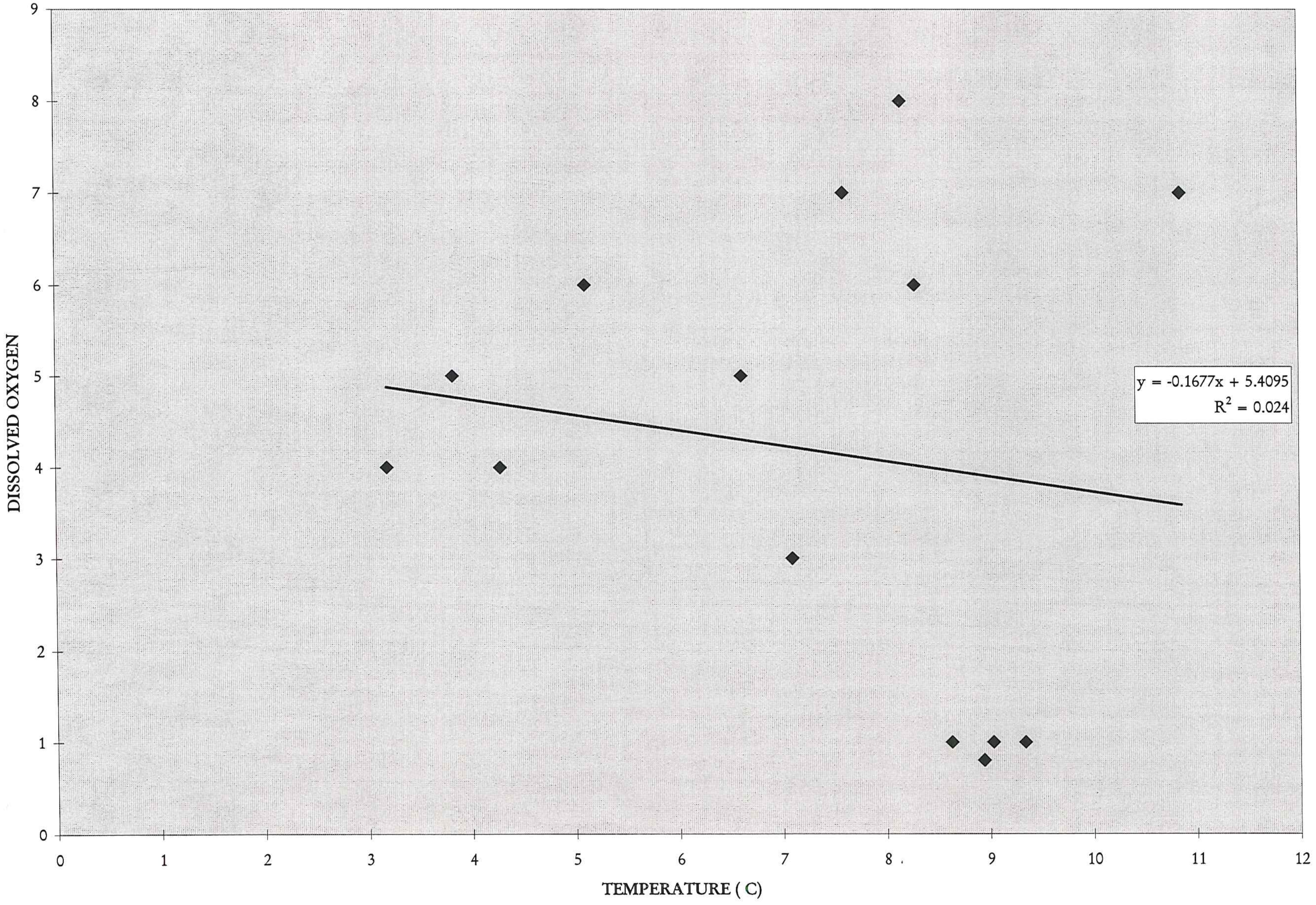


Figure 18. Dissolved oxygen in Black Rock Forest springs.

Dissolved oxygen and temperature in Black Rock Forest springs

Figure 19 shows a plot of dissolved oxygen versus temperature. Since dissolved oxygen concentration is temperature-sensitive, a correlation between the two factors was expected. Theoretically, the lower the temperature of water is, the greater concentration of dissolved oxygen there is. At higher temperatures, water tends to exchange molecules with the atmosphere at a faster rate. The trend towards lower dissolved oxygen at higher temperatures seems to be relatively weak in this plot.

Figure 19. Dissolved oxygen and temperature (Black Rock Forest springs).



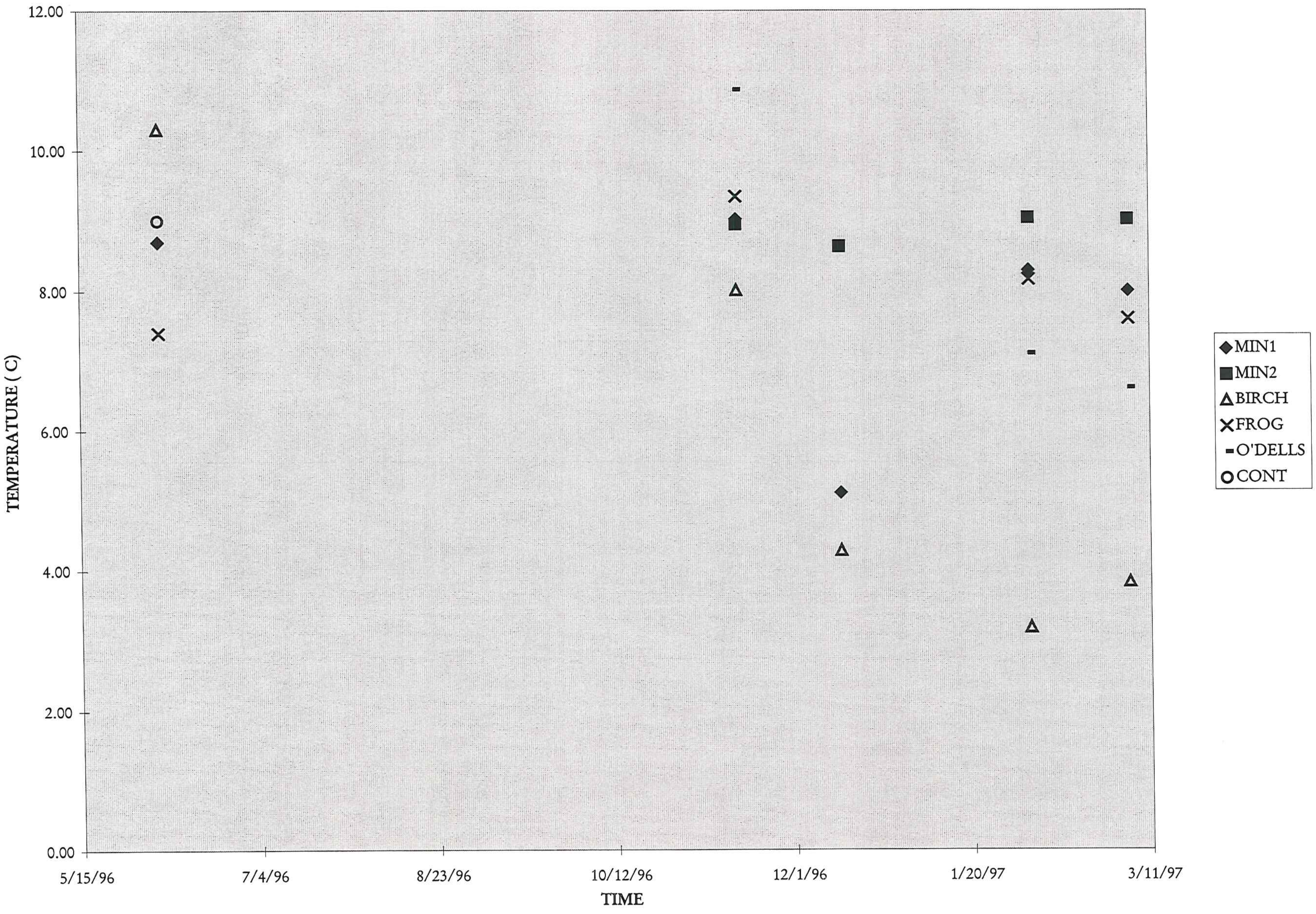
Time and temperature in Black Rock Forest springs

Figure 20 plots data listed in Table 6 below. Seasonality is not pronounced for all the spring measurements. Lower temperatures would have been expected in the winter and this is the case with the December 1996, February and March 1997 measurements, though not in the October 1996 measurement. While some values dip (Birch and O'Dells Springs), others fluctuate (Mineral Spring 2). Generalizations about seasonality cannot be made for all the springs. Most reflect colder temperatures in the winter and warmer temperatures in the summer. More data would be needed to make more definitive conclusions.

Table 6. Temperature in Black Rock Forest springs.

DATE	MIN1	MIN2	BIRCH	FROG	O'DELLS	CONT
6/6/96	8.70		10.30	7.40		9.00
11/15/96	9.02	8.94	8.01	9.34	10.86	
12/14/96	5.10	8.63	4.28			
2/5/97	8.29	9.03	3.18	8.16	7.10	
3/5/97	8.00	9.01	3.82	7.60	6.61	
MEAN	7.82	8.90	5.92	8.13	8.19	9.00
STD DEV	1.57	0.19	3.09	0.87	2.33	-

Figure 20. Time and temperature in Black Rock Forest springs



Laboratory Work

Ion Chromatography

Chloride in Black Rock Forest springs and West Point precipitation

Chloride concentrations in the springs range from 1.50 - 2.50 mg/l. Concentrations in samples taken from Mineral Spring 1, Birch Spring and Frog Rock Spring during the summer (June 1996) and winter (November 1996) are similar (Figure 21). The data is unusual, however, because the chloride concentrations are significantly higher than the average chloride concentration in precipitation from West Point (Table 7).

Table 7. Chloride in West Point precipitation and Black Rock Forest springs.

	1979 - 1996 (AVE)	6/6/96	11/15/96
WEST POINT	0.44		
MIN 1		2.4	2.5
MIN 2			1.6
BIRCH		1.7	1.9
FROG		1.5	1.4
O'DELLS			1.9
CONT		2.0	

MEAN	**1.73**
STANDARD DEVIATION	**0.58**

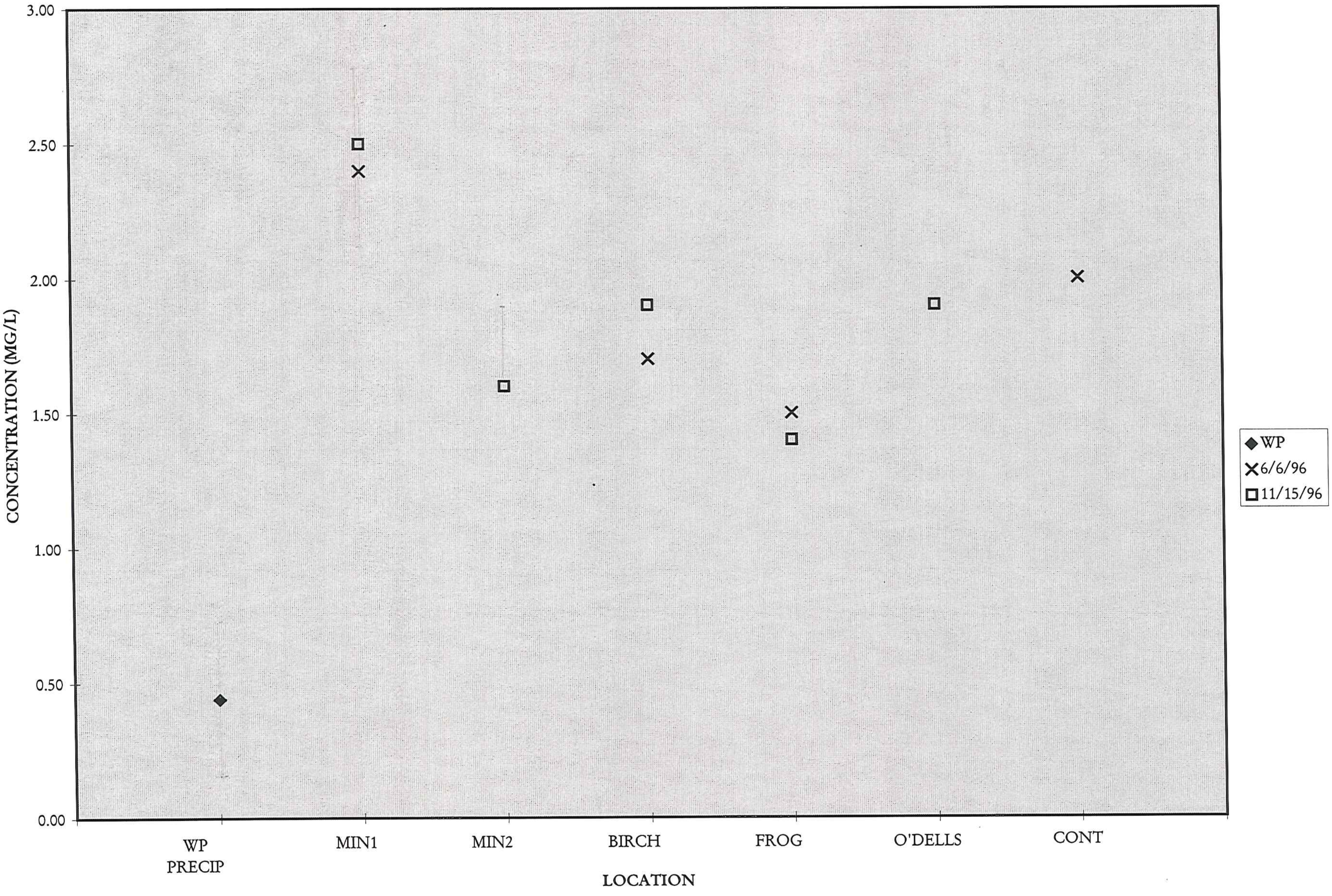
The data for West Point precipitation was consolidated from average annual monthly concentrations for the years 1979 - 1996. It is slightly higher than the mean (0.42 mg/l) of average chloride concentration data from other areas in the northeastern United States (Table 8), but well within the range. The values range from 0.29 mg/l to 0.51 mg/l.

Table 8. Chloride in precipitation in the northeastern United States.

LOCATION	AVERAGE [CHLORIDE] (mg/l)	REFERENCE
West Point, NY (1979 - 1996)	0.44	
Ithaca, NY (1972 - 1973)	0.47	Cogbill and Likens 1974
Hubbard Brook, NH (1963 - 1974)	0.51	Likens et al 1977
NE United States (1978 - 1979): All	0.40	Pack 1980
NE United States (1978 - 1979): Non-Coastal	0.29	Pack 1980
NE United States (1965 - 1968)	0.45	Pearson and Fisher 1971

Since chloride concentrations in precipitation seem to within the normal range and precipitation is the main source of chloride in groundwater, there must be another source of chloride other than precipitation. Possibilities include chemical weathering, dissolution of NaCl, and dry deposition (Berner and Berner, 1987).

Figure 21. Chloride in Black Rock Forest springs and West Point precipitation



Nitrate in Black Rock Forest springs and West Point precipitation

Nitrate concentrations in Black Rock Forest springs are very low, almost to the point of zero concentration (Figure 22). This is consistent for all the springs measured. For many of the samples, the concentrations were so low the ion chromatograph did not even record them.

Table 9. Nitrate in West Point precipitation and Black Rock Forest springs.

	1979 - 1996 (AVE)	6/6/96	11/15/96
WEST POINT	1.81		
MIN 1		0.1	
MIN 2			
BIRCH			0.1
FROG		0.1	
O'DELLS			
CONT		0.1	

MEAN	0.44
STANDARD DEVIATION	0.76

The average nitrate concentration (1.81 mg/l) in West Point precipitation is considerably higher than the spring concentrations. It is, however, within the range of average nitrate concentrations taken from the area (Table 10).

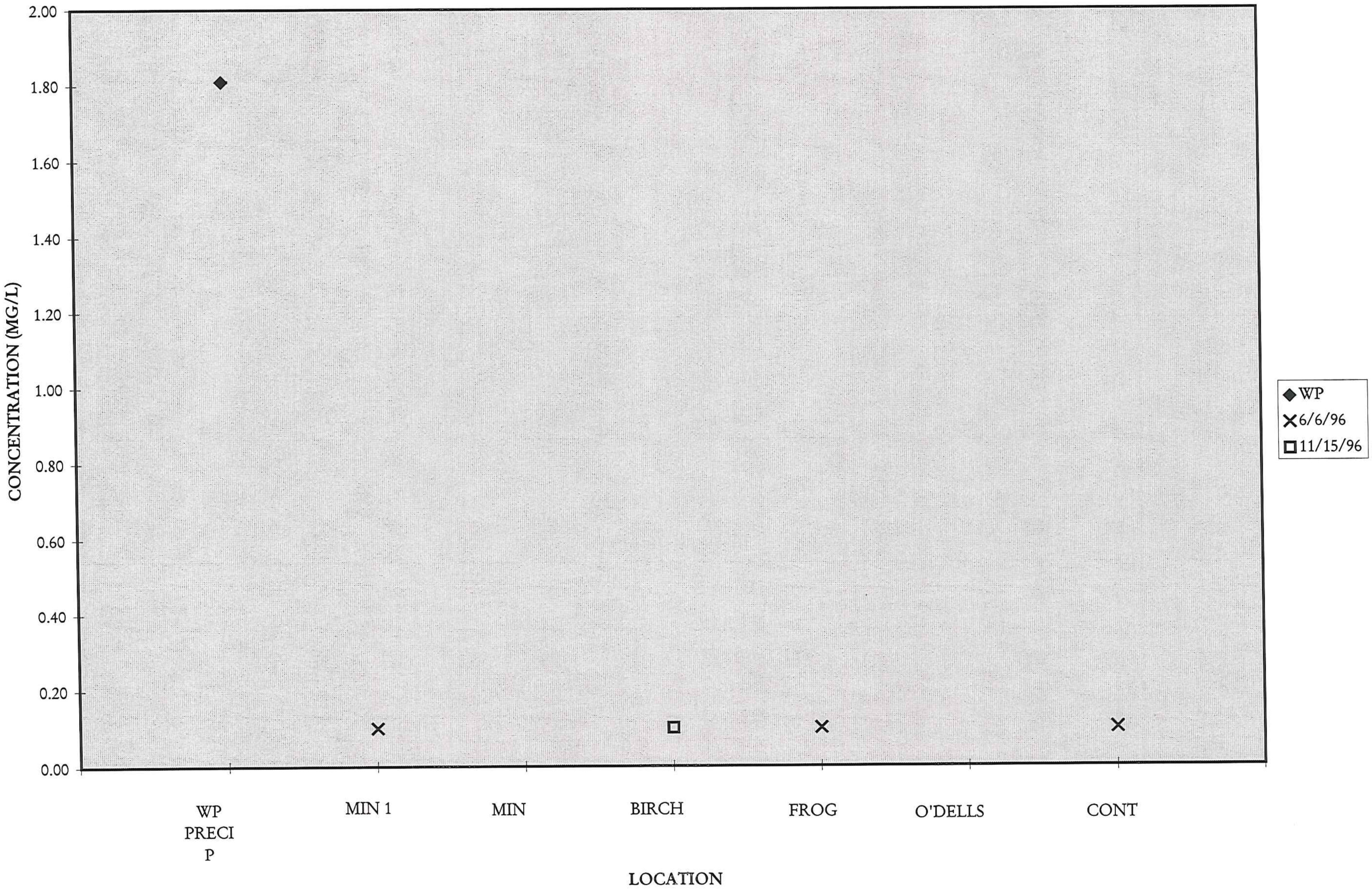
Table 10. Nitrate in precipitation in the northeastern United States.

LOCATION	AVERAGE [NITRATE] (mg/l)	REFERENCE
West Point, NY (1979 - 1996)	1.81	
Ithaca, NY (1972 - 1973)	2.88	Cogbill and Likens 1974
Hubbard Brook, NH (1963 - 1974)	1.47	Likens et al 1977
NE United States (1978 - 1979): All	1.58	Pack 1980
NE United States (1965 - 1968)	0.34	Pearson and Fisher 1971

Higher nitrate concentration in precipitation than in groundwater is expected. Nitrate is used as an important component of biogeochemical processes in the earth. It is an essential nutrient for plant and animals. Once it reaches the earth, it is taken up by plants for growth and reproduction and various other biological processes. Thus, it makes sense for there to be very little nitrate in groundwater.

Note: In Figure 21, maximum values of nitrate are shown.

Figure 22. Nitrate in Black Rock Forest springs and West Point precipitation



Sulfate in Black Rock Forest springs and West Point precipitation

Like chloride, sulfate concentrations in Black Rock Forest springs are unusually high (Figure 23). The measurements are also relatively close whether taken in the summer or in the winter. Sulfate concentrations range from 9.8 mg/l to 14.6 mg/l with mean of 10.99 mg/l (Table 11).

Table 11. Sulfate in West Point precipitation and Black Rock Forest springs.

	1979 - 1996 (AVE)	6/6/96	11/15/96
WEST POINT	2.50		
MIN 1		14.7	15.1
MIN 2			10.3
BIRCH		11	9.8
FROG		12.2	11.1
O'DELLS			13.3
CONT		9.9	

MEAN	**10.99**
STANDARD DEVIATION	**3.54**

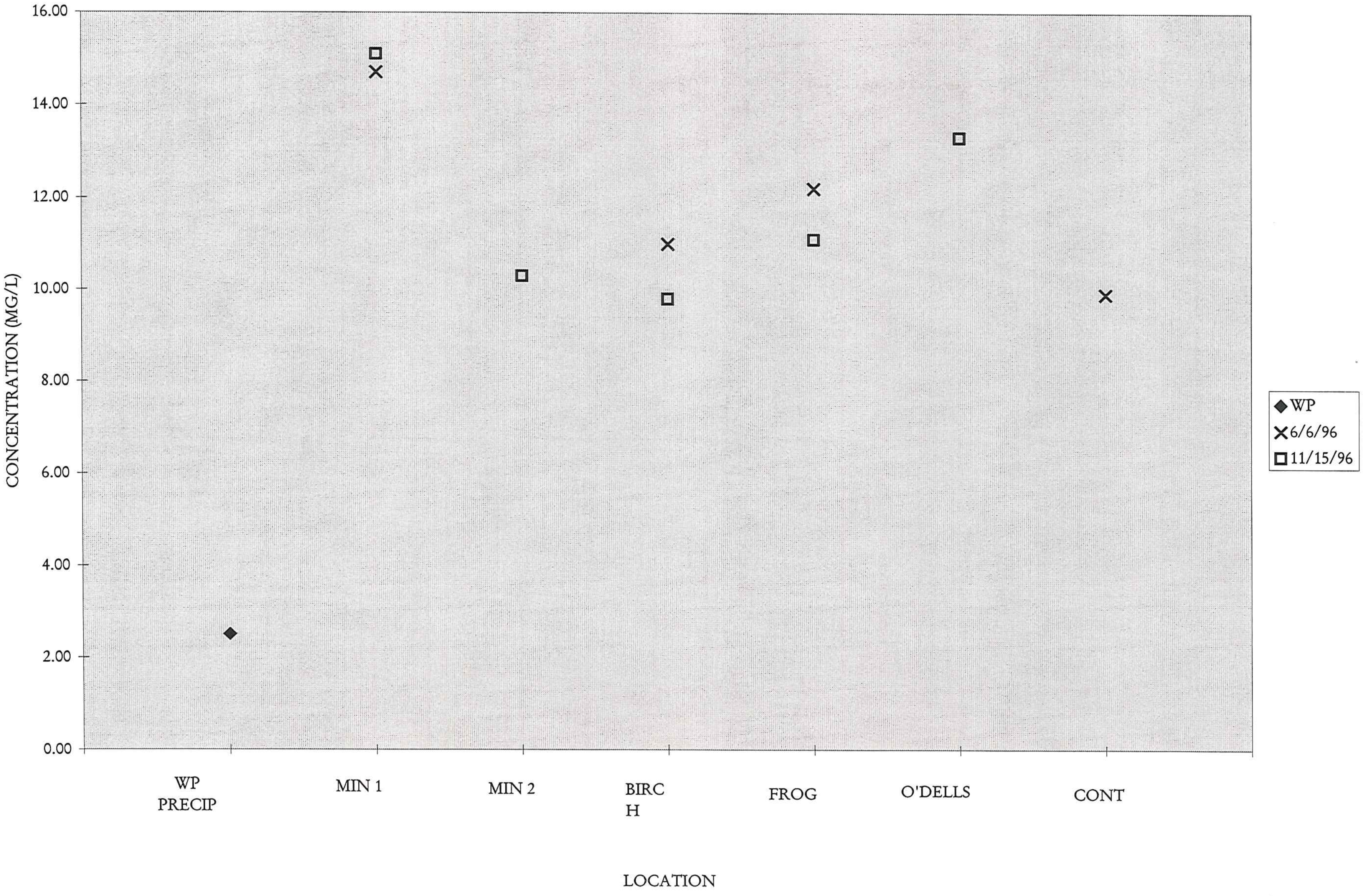
These values are very high in comparison to the average sulfate concentration in West Point precipitation, 2.5 mg/l. The precipitation data is within range of average sulfate concentrations in the surrounding area (Table 12).

Table 12. Sulfate in precipitation in the north-eastern United States.

LOCATION	AVERAGE [SULFATE] (mg/l)	REFERENCE
West Point, NY (1979 - 1996)	2.50	
Ithaca, NY (1972 - 1973)	4.96	Cogbill and Likens 1974
Hubbard Brook, NH (1963 - 1974)	2.87	Likens et al 1977
NE United States (1978 - 1979): All	2.81	Pack 1980
NE United States (1978 - 1979): Non-Coastal	2.70	Pack 1980
NE United States (1965 - 1968)	4.3	Pearson and Fisher 1971

Sulfate addition may also be due to dry deposition. SO_2 gas can be directly dissolved or absorbed by vegetation, soil or other surfaces (Berner and Berner, 1987). Also, "sulfate particles may settle out of the air or be trapped by vegetation" (1987).

Figure 23. Sulfate in Black Rock Forest springs and West Point precipitation

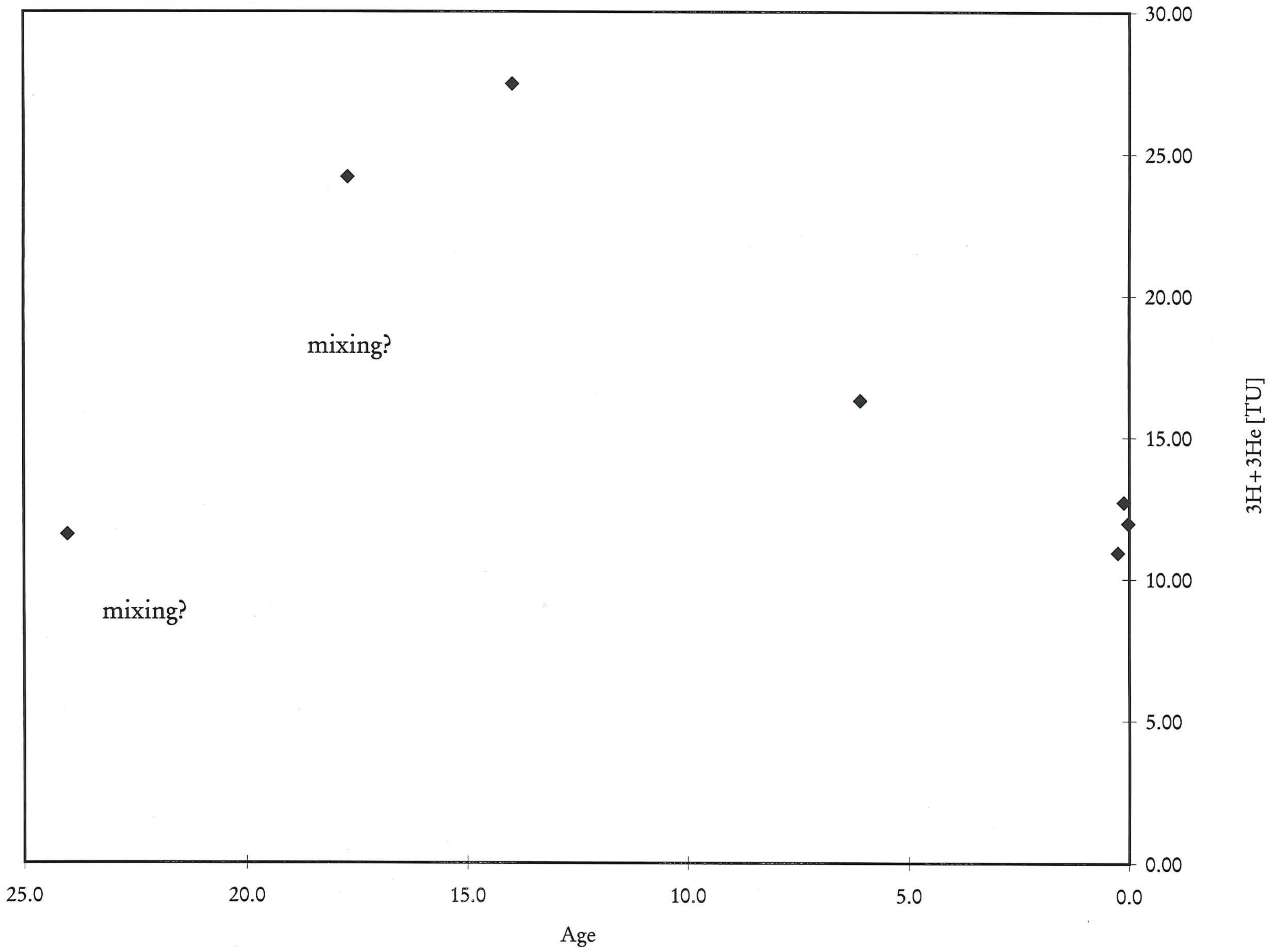


Age and sum of Tritium and ^{3}He concentrations in Black Rock Forest springs and wells

The apparent age (or years before extracted) of the groundwater in the springs plotted against the sum of the tritium and ^{3}He shows a peaked curve (Figure 25). Theoretically, the age and tritium/^{3}He concentration should have a linear relationship, ascending at least up to 30 years of age. Most of the tritium in the world today is a result of bomb-testing in the 1950s and 1960s. A nuclear weapon testing ban in 1963 brought the production of tritium to a halt. From 1963 on, tritium should be in decay. Therefore if water was old enough, data would show a peak in 1963 and decline from then on.

The data is consistent with this theory with the exception of two points: ages of 17.7 and 24.0 years which correspond to water taken from the Gorwyn Well and Mineral Spring 2, respectively. The lower concentration of tritium/^{3}He in older water indicates mixing of post-1952 water with pre-1952 water (as discussed in the methodology section).

Figure 25. Age and sum of tritium/^{3}He concentrations in Black Rock Forest springs and wells

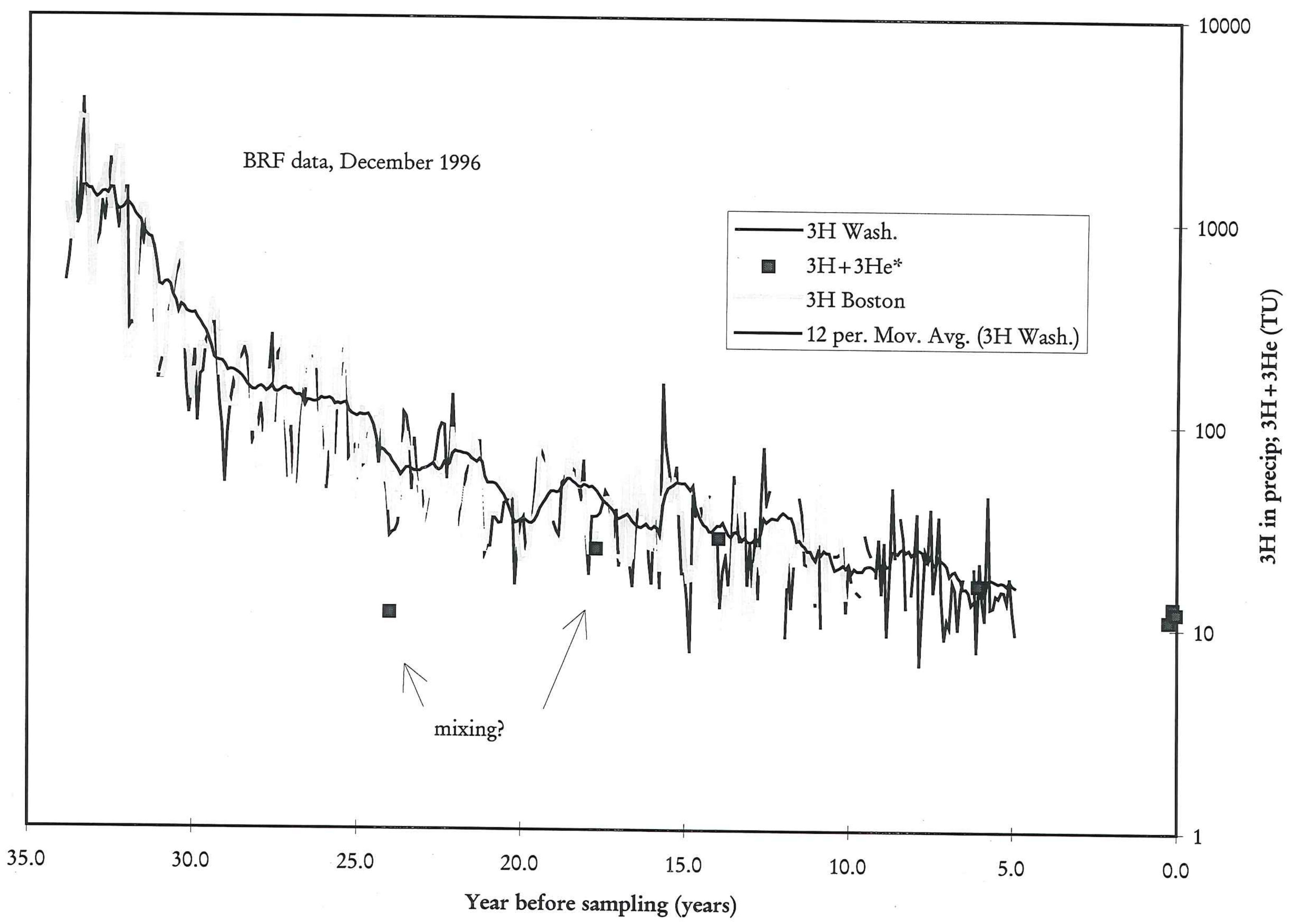


Age and tritium input/ sum of Tritium/3 He concentrations in Black Rock Forest springs and wells and precipitation from Boston and Washington

The sum of the tritium and ^{3}He concentrations should equal the input of tritium from precipitation. In Figure 26, these concentrations are compared with age of water. Precipitation data was taken from Boston and Washington (see **Appendices VII** and **VIII**). Data from springs and wells corresponds to the ascending curve with the exception of the two points previously mentioned.

It is apparent that the sum of tritium/^{3}He concentrations in Gorwyn Well and Mineral Spring 2 water do not fall within the range of tritium concentrations in precipitation input. Based upon evidence presented before, the water may have been mixed with older water. Mixed water does not show a linear relationship with age. Gorwyn Well appears closer to precipitation input concentrations but since this graph has been plotted on a logarithmic scale, it is actually much further from the average input than appears. Figure 24 is plotted linearly so this information is more clear.

Figure 26. Age and tritium input/ sum of tritium /^{3}He concentrations in Black Rock Forest springs and precipitation from Boston and Washington D. C.



CONCLUSIONS

Trends and Implications

The results obtained show that the nature of groundwater from Black Rock Forest springs and wells agrees with that of a fractured-rock environment. Based upon the first set of analyses (pH, conductivity and dissolved oxygen content), one may conclude that groundwater from springs in Black Rock Forest is slightly acidic in comparison to West Point precipitation because of addition of dissolved ions, presumably from chemical weathering. However, generalizing data from all the springs cannot be justified since data shows that groundwater from the springs undergoes different flow rates and may originate from different sources (snow melt, precipitation etc.), causing a variation in values of pH, conductivity and dissolved oxygen content. For example, Mineral Spring 2 and Mineral Spring 1 are geographically located relatively near each other, but the values for pH, conductivity and dissolved oxygen content are significantly different. Conditions at each of the wells are varied and further research should take this into consideration.

Concentrations of chloride and sulfate in the groundwater from springs were significantly higher than concentrations in West Point precipitation. This is unusual since the source of chloride and sulfate in groundwater is usually precipitation. This indicates there are other sources of these anions. Dry deposition was suggested as a source. This phenomena is currently under study at the Forest.

The residence time of groundwater in springs and wells varied. Ages of water taken from wells ranged from 0.1 to 17.7 years, while ages of water from springs ranged from 0.0 to 24.0 years. This does not indicate any correlation between age and depth (wells=deep, springs=shallow) nor does geography have any relationship with age. This data is consistent with a non-uniform, fractured-rock environment where variability is the status quo.

Problems/ Limitations with Data and Analysis

The primary limitation in this study was lack of complete sample data sets. Results for in situ measurements could only be analyzed to a certain extent because there was missing information during the summer and fall. Had there been data for a full year, analyses may have been much more interesting and comprehensive.

RECOMMENDATIONS

Though this study succeeded in following the input and output of water in a fractured-rock environment, much more could have been done to fill in missing blanks of data. I would recommend further research in the following areas:

(1) **In situ measurements**: Sampling groundwater and taking in situ measurements of pH and conductivity would provide a more complete picture of seasonal or non-seasonal trends. Also, comparison with the West Point precipitation would be more consistent if data included measurements taken on coinciding dates (for example, if precipitation measurements from 1996 - 1997 had been used for comparison).

(2) **Ion chromatography (1)**: It would be interesting to sample groundwater for a full year and run it through the ion chromatograph to study temporal changes in ion concentration. In addition, cation concentrations should be obtained.

The unusually high data for chloride and sulfate concentrations compared to precipitation should be investigated further. Dry deposition as a source of the additional ions specifically should be looked into.

(3) **Tritium/3Helium Dating Technique**: The data obtained from this technique yielded encouraging results when compared to precipitation input from Boston and Washington. Study of other sites in the forest should be done. Also, the relationship between depth and residence time might be interesting to look at. Results from this fractured-rock environment did not show any correlation between geography and age, but perhaps taking more data points would reveal otherwise.

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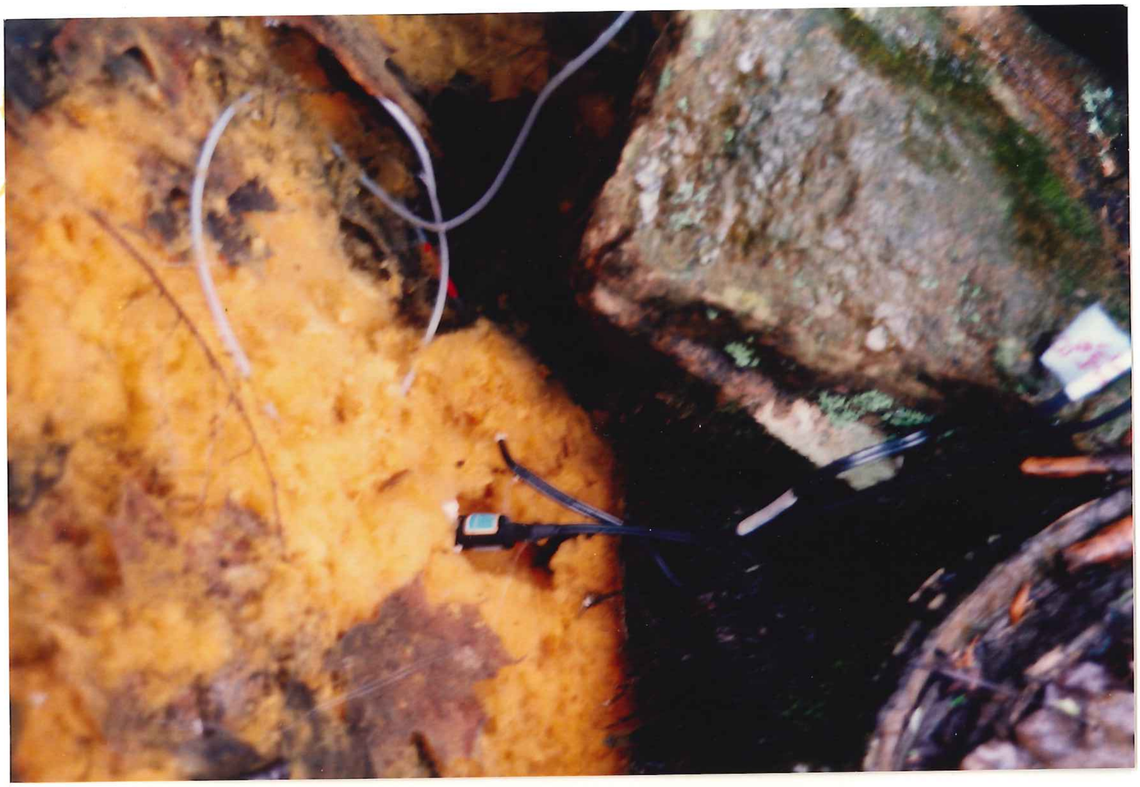
APPENDIX I : Photographs of spring sites.

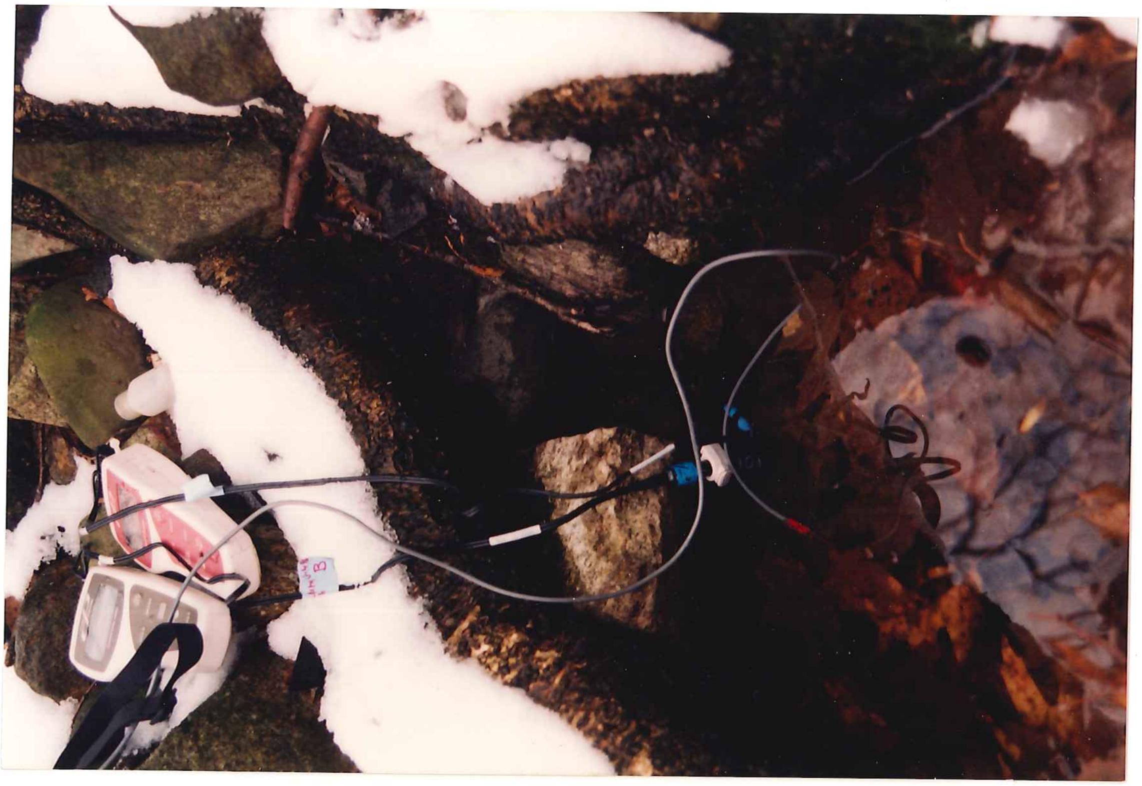
Note: These photographs were taken on March 3, 1995.

Mineral Spring 1 (Upper Mineral Spring)

Mineral Springs 2 (Lower Mineral Springs)



Birch Spring



O'Dells Spring

Frog Rock Spring

Measuring dissolved oxygen content (DOC)

Sampling water from Frog Rock Spring with syringe, filter and bottle

APPENDIX II: Preparation of anion standard solutions.

Please note: This information was taken from Julie Nichol's laboratory notebook records for work with the ion chromatograph in Milbank Hall, Barnard College.

2/18/97

Reagants used for standard solutions included Na_2SO_4 (anhydrous sodium sulfate), NaF (sodium fluoride), $NaNO_3$ (sodium nitrate), NaCl (sodium chloride), and KH_2PO_4 (potassium dihydrogen phosphate). Relative amounts of anions were equal to the amounts given in the Dionex 5 anion standard lot #960424 part #37157 and double the concentration.

ANION	MOL. WT.	CONCENTR.	SALT FW	AMT. TO ADD	X 5	X 2
Fl^-	19.00 g/mol	40 mg/l	41.99 g/mol	88.40 mg	0.442 g	0.884 g
Cl^-	35.45	60	58.44	98.91	0.4946	0.9892
NO_3^-	62.00	200	84.99	274.16	1.3708	2.7416
$PO4_2^-$	94.97	300	136.09	429.89	2.1495	4.299
$SO4_2^-$	119.05	300	142.04	357.93	1.7897	3.5794

The above amounts were concentrated by five times to make a stock anion solution (then an additional two times because the volume = two liters).

ANION	ACTUAL AMT. ADDED	EXACT CONCENTRATION
Fl^-	0.886 +/- 0.002 g	200.5 mg/l
Cl^-	0.990	300.3
NO_3^-	2.779	1013.6
$PO4_2^-$	4.315	1505.6
$SO4_2^-$	3.622	1517.9

(Exact Concentration = grams of salt/volume of solution * molecular weight of ion/f weight of salt * 1000)

Distilled, ultra-purified water was added to salts in a a 2000 ml volumetric flask. The stock solution was then diluted to create five standard solutions with the following concentrations:

SOLUTION	A (ORIGINAL)	B (A:5)	C (B:5)	D (C:5)	E (D:5)	F (E:5)
Fl^-	200.5 mg/l	40.10 mg/l	8.020 mg/l	1.604 mg/l	0.3208 mg/l	0.06416 mg/l
Cl^-	300.3	60.06	12.01	2.402	0.4804	0.09608

NO_3^-	1013.6	202.72	40.544	8.1088	1.6218	0.32436
$PO4_2^-$	1505.6	301.12	60.224	12.045	2.4090	0.48180
$SO4_2^-$	1517.9	303.58	60.716	12.143	2.4286	0.48572

Successive dilutions were made by taking five ml of the more concentrated solution and filling to the mark in a 25 ml volumetric flask. Five ml of that solution was then removed and diluted to 2.5 ml to create the next solution, etc...

2/19/97

Eluent solution used: $NaHCO_3$ (1.2 ml) / Na_2CO_3 (10.8 ml)

3/6/97

Ion chromatograph was switched from recycling mode to external water mode (suppressor mode to see if sensitivity improves).

3/10/97

New solutions were made up for standards using the same procedure as above. The data for measurements was as follows:

SALT	APPROX. AMOUNT	ACTUAL AMOUNT	SOLUTION A [ ]
NaF	0.884 g	0.893 g	202.04 mg/l
NaCl	0.9892	1.002	303.91
$NaNO_3$	2.7416	2.737	998.32
KH_2PO_4	4.299	4.330	1510.84
Na_2SO_4	3.5794	3.580	1500.28

SOLUTION	A (ORIGINAL)	B (A:5)	C (B:5)	D (C:5)	E (D:5)
Fl^-	202.04 mg/l	40.41 mg/l	8.0816 mg/l	1.616 mg/l	0.3233 mg/l
Cl^-	303.91	60.78	12.156	2.431	0.4862
NO_3^-	998.32	199.66	39.93	7.986	1.597
$PO4_2^-$	1510.84	302.17	60.43	12.09	2.417
$SO4_2^-$	1500.28	300.06	60.01	12.00	2.400

APPENDIX III: Procedure for ion chromatography laboratory work.

Running samples through the instrument.

1. First check that proton (H+) (distilled water) supply and eluent ($NaHCO_3/Na_2CO_3$) solution are sufficient for running samples and if not, to refill.
2. Turn on gas tanks of N_2 to create pressure.
3. Turn on ion chromatograph. The high limit for pressure should be set at 2000 (psi), the range at 30 (us/cm).
4. Turn the pump on.
5. As the instrument warms up, the pressure will rise so it is necessary to monitor the pressure increase to make sure it does not exceed 2000 psi.
6. Leave the instrument to warm up for approximately 20 - 30 minutes.
7. Turn on the integrator and run in order to check that the baseline for print-out of conductivity peaks is relatively stable.
8. While the instrument warms up, prepare the syringe for injection (see below).
9. When the instrument is warmed up and the syringe in place, inject the sample manually into the nozzle.
10. Press the "load" button to begin the flow of eluent and solute.
11. The Dionex 4400 Integrator will immediately begin reading and printing the results.

Preparation of syringe.

1. Uncover the cap of sample bottle and fill it with sample water.
2. Flush the syringe a few times with the sample water.
3. Repeat again and attach a plastic filter on the syringe when ejecting the liquid.
4. Withdraw sample water directly from the bottle.

5. Tap the syringe carefully to check for air bubbles. (Air bubbles can affect readings because they may dilute the concentrations of ions cause an embolism in the instrument.)
6. Replace the filter on the syringe and tap again to check for air bubbles. Small amounts of liquid may be ejected to remove air bubbles.
7. Place the syringe firmly but gently into injection nozzle of the ion chromatograph.

APPENDIX IV: Procedure for measurement of neon and helium isotope components in groundwater.

Note: This is taken verbatim from Schlosser et al, 1989.

If it is assumed that neon has no sources other than the atmosphere, and that the ratio $(Ne/He)_{exc} = (Ne/He)_{atm}$ the radiogenic ^4He component can be calculated to be:

$$^4He_{rad} = {}^4He_{tot} - (Ne_{tot} - Ne_{eq}) * {}^4He_{atm}/Ne_{atm} - {}^4He_{eq}$$

where Ne_{tot} = measured Ne concentrations, Ne_{eq} = Ne concentration in solubility equiilibrium with the atmosphere, $^4He_{atm}/Ne_{atm}$ = atmospheric $^4He/Ne$ ratio (0.288, Osima and Podosek, 1983), and $(Ne_{tot} - Ne_{eq}) = Ne_{exc}$ = Ne concentration originating from excess air.

Using a mean helium isotope ratio R_{rad} of $2 * 10^{-8}$ for radiogenic helium (Mamyrin and Tolstikhin, 198^{4}), $^3He_{nuc}$ can be calculated to:

$$^3He_{nuc} = {}^4He_{rad} \,\&\, R_{rad}$$

The atmospheric ^3He component $({}^3He_{atm} = {}^3He_{eq} + {}^3He_{exc})$ can be written as:

$$^3He_{atm} = ({}^4He_{tot} - {}^4He_{rad}) * R_{atm} - {}^4He_{eq} * R_{atm} * (1 - \lambda)$$

where R_{atm} = atmospheric $^3He/^4He$ ratio ($1.38 * 10^{-6}$, Clarke et al, 1976), and λ= solubility isotope effect (0.983, Benson and Krause, 1980).

The tritiogenic ^3He component is obtained by:

$$^3He_{trit} = {}^4He_{tot} * R_{tot} - ({}^4He_{tot} - {}^4He_{rad}) * R_{atm} + {}^4He_{eq} * R_{atm} * (1 - \lambda) - {}^4He_{rad} * R_{rad}$$

where R_{tot} = measured $^3He/^4He$ ratio of the water sample.

APPENDIX V: West Point precipitation data (1979 - 1996)

Note: Taken from the National Atmospheric Deposition Program/National Trend Network Precipitation - Weighted Averages (Reported in milligrams/liter)

CAL CODE	SUMMARY PERIOD	YEAR	NO_3 MG/L	Cl MG/L	SO_4 MG/L	pH	COND. US/CM
NY51	JUN	1979	3.2	0.75	3.9	3.99	47.7
NY51	JUL	1979	3.65	0.18	6.32	3.87	67.3
NY51	AUG	1979	2.23	0.14	3.52	4.14	37.4
NY51	SEP	1979	0.63	1.27	1.68	4.74	15.3
NY51	OCT	1979	1.49	0.28	2.8	4.25	31.3
NY51	NOV	1979	0.83	0.82	2.38	4.46	22.2
NY51	DEC	1979	1.27	0.31	1.61	4.45	18.4
NY51	JAN	1980	--	--	--	--	--
NY51	FEB	1980	3.24	0.32	2.02	4.15	32
NY51	MAR	1980	0.87	0.43	1.71	4.45	17.4
NY51	APR	1980	0.9	0.55	1.67	4.48	16.5
NY51	MAY	1980	2.78	0.28	5.17	4.1	41.4
NY51	JUN	1980	3.02	0.34	4.86	3.93	45.9
NY51	JUL	1980	2.39	0.21	4.28	3.95	44.8
NY51	AUG	1980	3.61	0.22	6.49	3.79	70.7
NY51	SEP	1980	2.18	0.34	3.78	4.1	38.1
NY51	OCT	1980	1.45	0.46	2.26	4.34	25.6
NY51	NOV	1980	0.89	0.25	1.65	4.49	15.4
NY51	DEC	1980	3.37	0.41	2.82	4.15	37.4
NY51	JAN	1981	1.48	1.82	1.72	4.34	30.7
NY51	FEB	1981	1.05	2.47	1.86	4.4	30.5
NY51	MAR	1981	2.59	1.1	4.3	4.22	42
NY51	APR	1981	2.61	0.3	3.81	4.04	45.3
NY51	MAY	1981	1.6	0.48	2.52	4.25	31.5
NY51	JUN	1981	3.84	0.22	7.63	3.77	78.6
NY51	JUL	1981	1.19	0.41	2.24	4.33	26.2
NY51	AUG	1981	3.06	0.3	5.22	3.98	55.5
NY51	SEP	1981	1.66	0.19	2.99	4.23	34.2
NY51	OCT	1981	1.71	0.16	2.73	4.26	29.4
NY51	NOV	1981	2.42	0.45	3.66	4.21	39.6
NY51	DEC	1981	1.01	0.14	1.88	4.43	19.9
NY51	JAN	1982	0.85	0.38	1.49	4.51	16.8
NY51	FEB	1982	0.94	0.43	1.27	4.49	18.1
NY51	MAR	1982	2.29	0.28	3.4	4.16	35.6
NY51	APR	1982	1.43	0.41	2.42	4.42	23.1
NY51	MAY	1982	1.48	0.11	2.47	4.3	26.9
NY51	JUN	1982	1.2	0.06	1.46	4.4	21.5
NY51	JUL	1982	1.77	0.11	4.13	4.06	48.3
NY51	AUG	1982	1.25	0.04	2.7	4.28	29.3
NY51	SEP	1982	2.67	0.3	2.72	4.16	36.6
NY51	OCT	1982	2.62	0.43	2.87	4.22	35.5
NY51	NOV	1982	0.62	0.24	0.88	4.74	11.6

CAL CODE	SUMMARY PERIOD	YEAR	NO_3 MG/L	Cl MG/L	SO_4 MG/L	pH	COND. US/CM
NY51	DEC	1982	1.75	1.29	1.56	4.39	26.9
NY51	JAN	1983	0.72	0.29	1.06	4.67	13.4
NY51	FEB	1983	0.98	1.07	1.6	4.53	20.1
NY51	MAR	1983	0.71	0.37	1.24	4.59	15.1
NY51	APR	1983	0.89	0.21	1.76	4.37	22.3
NY51	MAY	1983	2.2	0.25	3.27	4.17	35.9
NY51	JUN	1983	2.37	0.16	2.91	4.14	36.4
NY51	JUL	1983	2.05	0.08	4.02	4.06	41.9
NY51	AUG	1983	2.35	0.28	3.35	4.04	40.2
NY51	SEP	1983	0.92	0.38	1.39	4.54	16.8
NY51	OCT	1983	1.04	0.36	1.1	4.56	16
NY51	NOV	1983	1.26	0.42	1.74	4.46	20.6
NY51	DEC	1983	0.77	1.18	1.37	4.56	18.8
NY51	JAN	1984	2.68	0.61	1.69	4.31	29
NY51	FEB	1984	0.89	1.57	1.71	4.48	22.2
NY51	MAR	1984	1.05	0.12	1.25	4.54	15.3
NY51	APR	1984	0.65	0.28	1.53	4.51	16.5
NY51	MAY	1984	1.65	0.25	2.31	4.32	26.3
NY51	JUN	1984	1.25	0.12	1.71	4.37	21.9
NY51	JUL	1984	1.85	0.16	2.44	4.22	31.5
NY51	AUG	1984	2.35	0.16	3.19	4.08	39.7
NY51	SEP	1984	1.55	0.19	2.39	4.31	24.7
NY99	SEP	1983	0.75	0.31	1.17	4.64	13.5
NY99	OCT	1983	1	0.36	1.04	4.52	15.9
NY99	NOV	1983	1.25	0.45	1.56	4.45	21.2
NY99	DEC	1983	0.76	1.13	1.24	4.58	18.1
NY99	JAN	1984	3.81	0.89	2.22	4.17	40.6
NY99	FEB	1984	1.17	1.64	1.95	4.4	26.6
NY99	MAR	1984	1	0.21	1.32	4.52	17.8
NY99	APR	1984	0.77	0.38	1.74	4.44	19
NY99	MAY	1984	1.84	0.26	2.51	4.29	28.1
NY99	JUN	1984	1.28	0.19	1.86	4.43	21.1
NY99	JUL	1984	2.01	0.16	2.71	4.17	34.8
NY99	AUG	1984	2.11	0.13	2.91	4.13	35.4
NY99	SEP	1984	1.32	0.15	2.34	4.47	19.6
NY99	OCT	1984	3.04	0.28	3.12	4.11	41.2
NY99	NOV	1984	0.64	1.03	1.4	4.52	18.4
NY99	DEC	1984	2.05	0.34	2.42	4.21	32.6
NY99	JAN	1985	2.12	0.36	2.35	4.36	26.6
NY99	FEB	1985	1.29	0.61	1.12	4.57	16.9
NY99	MAR	1985	2.54	0.41	2.89	4.16	39.4
NY99	APR	1985	4.27	0.52	3.92	4	52.9
NY99	MAY	1985	1.36	0.17	2.22	4.33	24.4
NY99	JUN	1985	1.79	0.15	2.68	4.19	31.5
NY99	JUL	1985	1.76	0.13	3.49	4.13	37.5
NY99	AUG	1985	2.66	0.26	3.78	4.03	44.8

CAL CODE	SUMMARY PERIOD	YEAR	NO_3 MG/L	Cl MG/L	SO_4 MG/L	pH	COND. US/CM
NY99	SEP	1985	1.1	0.61	2.18	4.39	24.2
NY99	OCT	1985	2.63	0.5	3.36	4.04	45
NY99	NOV	1985	1.53	0.19	1.86	4.28	25.6
NY99	DEC	1985	4.16	0.7	3.16	3.99	49.9
NY99	JAN	1986	1.02	0.54	1.61	4.36	22.3
NY99	FEB	1986	1.71	0.22	1.96	4.21	27.6
NY99	MAR	1986	1.61	0.46	2.56	4.31	27.6
NY99	APR	1986	2.39	0.38	4.06	4.05	42.7
NY99	MAY	1986	5	0.33	6.71	3.89	69.4
NY99	JUN	1986	2.62	0.16	3.69	4.14	42.8
NY99	JUL	1986	3.88	0.43	3.76	4.26	26.4
NY99	AUG	1986	2.86	0.18	4.41	3.98	53
NY99	SEP	1986	5.39	0.34	6.37	3.8	78.1
NY99	OCT	1986	2.41	0.19	2.73	4.16	36.1
NY99	NOV	1986	0.98	0.31	1.23	4.51	17.4
NY99	DEC	1986	0.76	0.66	1.16	4.53	16.9
NY99	JAN	1987	1.38	0.38	1.38	4.35	20.8
NY99	FEB	1987	2.27	0.49	1.43	4.29	25.5
NY99	MAR	1987	0.95	0.64	1.57	4.49	18.5
NY99	APR	1987	0.79	0.5	1.53	4.47	18.7
NY99	MAY	1987	2.17	0.13	4.28	4.08	40.4
NY99	JUN	1987	3.49	0.23	5.4	3.91	60.6
NY99	JUL	1987	3.34	0.24	4.95	3.93	58.4
NY99	AUG	1987	2.63	0.18	4.36	3.99	50.2
NY99	SEP	1987	0.98	0.28	1.65	4.42	19.4
NY99	OCT	1987	0.94	0.2	1.42	4.49	16.7
NY99	NOV	1987	0.98	0.98	1.6	4.44	21
NY99	DEC	1987	2.46	0.35	2.77	4.13	35
NY99	JAN	1988	0.86	0.28	1.23	4.45	17.4
NY99	FEB	1988	1.4	0.45	1.72	4.36	22.8
NY99	MAR	1988	2.59	0.21	2.76	4.18	33.4
NY99	APR	1988	3.28	0.33	3.41	4.1	40.6
NY99	MAY	1988	2.15	0.19	3.38	4.11	37.3
NY99	JUN	1988	2.8	0.32	4.02	4.24	35.2
NY99	JUL	1988	2.53	0.14	4.34	3.97	47.8
NY99	AUG	1988	1.33	0.49	2.4	4.42	21.6
NY99	SEP	1988	0.77	0.23	1.53	4.42	17.7
NY99	OCT	1988	1.09	0.53	1.46	4.47	17.6
NY99	NOV	1988	0.43	0.42	1.07	4.63	12.1
NY99	DEC	1988	1.41	0.91	2.93	4.18	32.6
NY99	JAN	1989	2.67	0.88	2.85	4.12	37.9
NY99	FEB	1989	1.76	0.51	3.12	4.18	33
NY99	MAR	1989	1.69	0.32	2.37	4.26	27.5
NY99	APR	1989	2.39	0.28	2.72	4.15	34.1
NY99	MAY	1989	1.23	0.25	2.13	4.38	23
NY99	JUN	1989	3.08	0.31	3.33	4.07	44

CAL CODE	SUMMARY PERIOD	YEAR	NO_3 MG/L	Cl MG/L	SO_4 MG/L	pH	COND. US/CM
NY99	JUL	1989	1.83	0.39	3.13	4.16	36.7
NY99	AUG	1989	0.93	0.22	1.3	4.5	16
NY99	SEP	1989	0.87	0.99	1.72	4.39	23.4
NY99	OCT	1989	0.77	0.29	1.28	4.5	16.4
NY99	NOV	1989	1.2	0.47	1.49	4.42	20.3
NY99	DEC	1989	3.74	0.49	1.59	4.14	36.4
NY99	JAN	1990	1.48	0.41	1.48	4.34	22.5
NY99	FEB	1990	2.26	0.38	2.54	4.18	34
NY99	MAR	1990	1.66	0.3	2.35	4.24	28.3
NY99	APR	1990	1.9	0.32	2.46	4.27	28.6
NY99	MAY	1990	1.52	0.3	2.23	4.29	26.1
NY99	JUN	1990	2	0.15	4	4.09	41.7
NY99	JUL	1990	1.92	0.21	2.82	4.18	34.2
NY99	AUG	1990	1.4	0.17	2.56	4.23	29.7
NY99	SEP	1990	1.82	0.29	2.6	4.25	30.1
NY99	OCT	1990	0.66	0.87	1.24	4.57	16.4
NY99	NOV	1990	0.95	1.32	1.58	4.45	22.4
NY99	DEC	1990	1.09	0.68	1.55	4.37	21.9
NY99	JAN	1991	0.91	0.4	0.71	4.73	10.9
NY99	FEB	1991	3.33	0.47	3.2	4.03	46.8
NY99	MAR	1991	1.3	0.57	1.52	4.39	21.5
NY99	APR	1991	1.21	0.33	1.91	4.42	20.9
NY99	MAY	1991	1.87	0.19	3.68	4.14	37.8
NY99	JUN	1991	0.97	0.16	1.77	4.6	15.8
NY99	JUL	1991	2.73	0.23	4.57	3.96	55.9
NY99	AUG	1991	1.53	0.22	2.26	4.27	26.6
NY99	SEP	1991	1.02	0.12	2.22	4.41	20.6
NY99	OCT	1991	1.8	0.65	2.79	4.19	35.4
NY99	NOV	1991	0.86	0.25	1.44	4.43	17.9
NY99	DEC	1991	1.28	0.26	1.63	4.34	22
NY99	JAN	1992	0.98	0.66	1.44	4.44	20
NY99	FEB	1992	2.14	0.4	2.55	4.18	33.8
NY99	MAR	1992	1.41	0.88	1.76	4.34	25.7
NY99	APR	1992	3.86	0.51	4.43	3.95	56.7
NY99	MAY	1992	1.32	0.6	2.32	4.31	26.6
NY99	JUN	1992	1.45	0.14	2.36	4.32	26.2
NY99	JUL	1992	2.56	0.24	4.19	4.01	48.3
NY99	AUG	1992	1.34	0.16	1.85	4.35	22.6
NY99	SEP	1992	1.62	0.47	2.25	4.37	24.9
NY99	OCT	1992	1.49	0.56	1.88	4.36	23
NY99	NOV	1992	0.74	0.56	0.94	4.55	15.5
NY99	DEC	1992	1.02	0.58	1.32	4.43	19.1
NY99	JAN	1993	0.96	0.37	1.29	4.4	19.7
NY99	FEB	1993	0.92	0.2	1	4.51	15
NY99	MAR	1993	1.08	0.66	1.3	4.57	17.3
NY99	APR	1993	1.29	1.21	1.88	4.38	25.3

CAL CODE	SUMMARY PERIOD	YEAR	NO_3 MG/L	Cl MG/L	SO_4 MG/L	pH	COND. US/CM
NY99	MAY	1993	4.75	0.21	5.75	3.86	69.1
NY99	JUN	1993	2.69	0.23	4.28	4.07	44.7
NY99	JUL	1993	4.26	0.61	5.96	4.15	49.3
NY99	AUG	1993	3.92	0.5	6.44	3.84	72.2
NY99	SEP	1993	1.72	0.23	3.17	4.13	36.6
NY99	OCT	1993	0.77	0.24	1.76	4.53	19.5
NY99	NOV	1993	2.26	0.47	2.42	4.3	27.9
NY99	DEC	1993	1.23	0.37	1.18	4.42	18.7
NY99	JAN	1994	1.14	0.42	1.05	4.42	18
NY99	FEB	1994	1.11	0.14	0.74	4.56	12.9
NY99	MAR	1994	1.44	0.37	1.63	4.32	25.3
NY99	APR	1994	2.01	0.52	2.81	4.22	33.7
NY99	MAY	1994	1.64	0.21	2.53	4.29	28.2
NY99	JUN	1994	3.2	0.4	5.12	4.02	55.4
NY99	JUL	1994	2.91	0.21	3.33	4.07	44.4
NY99	AUG	1994	1.23	0.19	2.22	4.44	21.7
NY99	SEP	1994	1.33	0.39	1.72	4.36	22.9
NY99	OCT	1994	1.93	0.53	2.2	4.18	33.6
NY99	NOV	1994	0.65	0.68	0.81	4.64	13.5
NY99	DEC	1994	1.04	0.28	1.14	4.45	17.7
NY99	JAN	1995	0.84	1.09	0.9	4.6	15.9
NY99	FEB	1995	1.36	0.15	0.96	4.45	18.7
NY99	MAR	1995	1.07	0.33	1.4	4.5	17.4
NY99	APR	1995	2.99	0.28	2.92	4.19	36.2
NY99	MAY	1995	3.46	0.64	3.67	4.08	48.3
NY99	JUN	1995	1.72	0.17	1.78	4.68	17.4
NY99	JUL	1995	2.45	0.12	3.44	4.09	42.4
NY99	AUG	1995	2.75	0.24	3.12	4.06	43
NY99	SEP	1995	1.52	0.53	1.87	4.46	22.4
NY99	OCT	1995	0.35	0.66	0.49	5	8.6
NY99	NOV	1995	0.44	1.14	0.68	4.75	12.8
NY99	DEC	1995	1.53	0.28	0.81	4.49	17.4
NY99	JAN	1996	0.57	1.4	0.89	4.7	15.3
NY99	FEB	1996	2.48	2.13	1.94	4.16	40.3

APPENDIX VI: Tritium/^{3}He calculations.

*Note: The term * (or "exc" in formula's) after [3He] refers to tritiogenic 3He calculated w/out a correction for radiogenic helium. The term "tri" after [3He] refers to tritiogenic helium calculated with a correction for radiogenic helium*

	LDGO #	NAME	SAMPLING DATE mm/dd/yy	EXTRACTION DATE mm/dd/yy	MEASUREMENT DATE mm/dd/yy	BEGIN WEIGHT g
Ratm 1.38E-06 **4He/Ne)atm** 0.288 **Rrad** 2.00E-08 **-Rrad Error** 1.00E-08 **T1/2** 12.43 **a** 0.983 **Ne_conc in air** 1.818E-05 **He A1 (ml/kg)** -167.2178 **He A2 (ml/kg)** 216.3442 **He A3 (ml/kg)** 139.2032	3137	example	4/26/89	6/10/89	9/6/89	1352.94
		L9470,BNL_053-01,1.3,10/28/96	10/27/92	12/16/92	3/3/93	
		L9473,BNL_053-02,2.1	10/27/92	12/17/92	3/3/93	
		L9469,BRF,20.1	12/13/92	12/16/92	3/3/93	
		L9476,BRF,21.1	12/13/92	12/16/92	3/3/93	
		L9472,BRF,23.1	12/13/92	12/16/92	3/3/93	
		L9474,BRF,24.1	12/13/92	12/16/92	3/3/93	
		L9475,BRF,25.1	12/13/92	12/16/92	3/3/93	
		L9495,BRF,26.1	12/13/92	12/18/92	3/3/93	
		L9493,BRF,27.1	12/13/92	12/18/92	3/3/93	
		L9494,BRF,28.1	12/13/92	12/18/92	3/3/93	

He A4 (ml/kg)		NAME	END WEIGHT g	SAMPLE WEIGHT g	Water Temp During Sampling °C	RECHARGE TEMPERATURE °C
-22.6202		example	1311.63	41.31	14	8.00
He B1 (ml/kg)						
-0.044781		L9470,BNL_053-01,1.3,10/28/96		39.43	11	11
He B2 (ml/kg)		L9473,BNL_053-02,2.1		39.43	11	11
0.023541		L9469,BRF,20.1		39.55	9	8
He B3 (ml/kg)		L9476,BRF,21.1		39.53	9	8
-0.0034266		L9472,BRF,23.1		39.58	9	8
Ne A1 (ml/kg)		L9474,BRF,24.1		39.55	9	8
-170.6018		L9475,BRF,25.1		39.53	9	8
Ne A2 (ml/kg)		L9495,BRF,26.1		39.42	9	8
225.1946		L9493,BRF,27.1		39.46	9	8
Ne A3 (ml/kg)		L9494,BRF,28.1		39.55	9	8
140.8863						
Ne A4 (ml/kg)						
-22.629						
Ne B1 (ml/kg)						
-0.127113						
Ne B2 (ml/kg)						
0.079277						
Ne B3 (ml/kg)						
-0.0129095						
ccSTP/gH20->TU						
4.021E+14						

TU->ccSTP/gH20		NAME	RECHARGE TEMPERATURE ERROR ±°C	SALINITY ‰	ELEVATION [m]	TRITIUM [3H] TU
2.48694E-15		example	1	0	120	63.6
		L9470,BNL_053-01,1.3,10/28/96	1	0	50	16.42
		L9473,BNL_053-02,2.1	1	0	50	
		L9469,BRF,20.1	1	0	200	9.00
		L9476,BRF,21.1	1	0	200	12.63
		L9472,BRF,23.1	1	0	200	11.59
		L9474,BRF,24.1	1	0	200	12.58
		L9475,BRF,25.1	1	0	200	10.78
		L9495,BRF,26.1	1	0	200	
		L9493,BRF,27.1	1	0	200	3.03
		L9494,BRF,28.1	1	0	200	11.96

NAME	[3H] E¬¬O¬ 1 s	R meas [3He]/[4He] meas	R meas ERROR relative %	¯R meas ERROR	[4He] meas ccSTP	[4He] meas ERROR relative %
example	1.64	8.31E-06	1	8.3E-08	3.09E-06	1
L9470,BNL_053-01,1.3,10/28/96	0.13	1.585E-06	0.29	4.6E-09	2.38E-06	0.18
L9473,BNL_053-02,2.1		1.745E-06	0.3	5.2E-09	2.03E-06	0.17
L9469,BRF,20.1	0.09	1.793E-06	0.39	7E-09	2.71E-06	0.34
L9476,BRF,21.1	0.11	1.366E-06	0.3	4.1E-09	1.89E-06	0.18
L9472,BRF,23.1	0.11	1.574E-06	0.3	4.7E-09	2.21E-06	0.17
L9474,BRF,24.1	0.11	1.93E-06	0.29	5.6E-09	2.60E-06	0.18
L9475,BRF,25.1	0.11	1.373E-06	0.3	4.1E-09	2.36E-06	0.17
L9495,BRF,26.1		1.365E-06	0.25	3.4E-09	1.87E-06	0.22
L9493,BRF,27.1	0.06	1.051E-06	0.24	2.5E-09	4.02E-06	0.22
L9494,BRF,28.1	0.11	1.363E-06	0.25	3.4E-09	1.94E-06	0.22

NAME	¯[4He] meas ERROR ±ccSTP	TIME ELAPSED (extration date - sampling date) days	C4 [4He] ccSTP/gH20	[3H] convert TU --> ccSTP/gH20	[3He] produced in Cu Tube TU	[3He] produced in Cu Tube convert TU --> ccSTP/gH20
example	3.088E-08	45	7.48E-08	1.582E-13	0.44	1.084E-15
L9470,BNL_053-01,1.3,10/28/96	4.2875E-09	50	6.04E-08	4.085E-14	0.00	0
L9473,BNL_053-02,2.1	3.4494E-09	51	5.15E-08		0.00	0
L9469,BRF,20.1	9.2206E-09	3	6.86E-08	2.237E-14	0.00	0
L9476,BRF,21.1	3.3933E-09	3	4.77E-08	3.142E-14	0.00	0
L9472,BRF,23.1	3.7485E-09	3	5.57E-08	2.883E-14	0.00	0
L9474,BRF,24.1	4.6815E-09	3	6.58E-08	3.128E-14	0.00	0
L9475,BRF,25.1	4.0085E-09	3	5.97E-08	2.682E-14	0.00	0
L9495,BRF,26.1	4.1185E-09	5	4.75E-08		0.00	0
L9493,BRF,27.1	8.8461E-09	5	1.02E-07	7.534E-15	0.00	0
L9494,BRF,28.1	4.2757E-09	5	4.91E-08	2.975E-14	0.00	0

NAME	¯[3He]* error ±TU	[3He] meas ccSTP/gH20	[3He] CORRECTED ccSTP/gH20	Rcorr [3He]/[4He] CORRECTED	d 3He	Ceq [4He] equilib ccSTP/gH20
example	3.25	6.21E-13	6.2E-13	8.292E-06	499.15	4.621E-08
L9470,BNL_053-01,1.3,10/28/96	0.11	9.58E-14	9.58E-14	1.585E-06	14.53	4.598E-08
L9473,BNL_053-02,2.1		8.98E-14	8.98E-14	1.745E-06	26.08	4.598E-08
L9469,BRF,20.1	0.20	1.23E-13	1.23E-13	1.793E-06	29.55	4.577E-08
L9476,BRF,21.1	0.08	6.51E-14	6.51E-14	1.366E-06	-1.30	4.577E-08
L9472,BRF,23.1	0.11	8.77E-14	8.77E-14	1.574E-06	13.73	4.577E-08
L9474,BRF,24.1	0.15	1.27E-13	1.27E-13	1.93E-06	39.46	4.577E-08
L9475,BRF,25.1	0.10	8.19E-14	8.19E-14	1.373E-06	-0.83	4.577E-08
L9495,BRF,26.1		6.48E-14	6.48E-14	1.365E-06	-1.34	4.577E-08
L9493,BRF,27.1	0.11	1.07E-13	1.07E-13	1.051E-06	-24.06	4.577E-08
L9494,BRF,28.1	0.07	6.7E-14	6.7E-14	1.363E-06	-1.52	4.577E-08

NAME	[3He]* TU	[3He]* ccSTP/gH20	[3H]/[3He]* AGE (No crustal) yrs	[3H]/[3He]* AGE ERROR (No crustal) ± yrs	- 4He	[3H]+[3He]* TU
example	208.08	5.17E-13	26.04	0.41	61.75	271.68
L9470,BNL_053-01,1.3,10/28/96	5.32	1.32E-14	5.03	0.10	31.40	21.74
L9473,BNL_053-02,2.1	7.90	1.97E-14			11.93	7.90
L9469,BRF,20.1	11.71	2.91E-14	14.95	0.20	49.81	20.71
L9476,BRF,21.1	0.09	2.19E-16	0.12	0.11	4.19	12.72
L9472,BRF,23.1	4.69	1.17E-14	6.09	0.13	21.71	16.28
L9474,BRF,24.1	14.87	3.70E-14	14.00	0.13	43.67	27.45
L9475,BRF,25.1	0.16	3.92E-16	0.26	0.16	30.32	10.94
L9495,BRF,26.1	0.08	1.96E-16			3.75	0.08
L9493,BRF,27.1	-13.21	-3.29E-14			122.62	-10.18
L9494,BRF,28.1	0.02	4.32E-17	0.03	0.10	7.36	11.98

NAME	[3H]+[3He]* ERROR ± TU	[Ne-20] meas ccSTP	[Ne] ERROR relative %	[Ne] meas ccSTP/gH20	[Ne] meas ERROR ccSTP/gH20	[Ne] equilib ccSTP/gH20
example	4.89	1.13E-05	1	3.01E-07	3.01E-09	2.028E-07
L9470,BNL_053-01,1.3,10/28/96	0.24		1	2.57E-07	7.72E-10	1.986E-07
L9473,BNL_053-02,2.1	0.00		1	2.21E-07	6.62E-10	1.986E-07
L9469,BRF,20.1	0.29		1	2.67E-07	8.80E-10	2.009E-07
L9476,BRF,21.1	0.19		1	2.08E-07	6.23E-10	2.009E-07
L9472,BRF,23.1	0.21		1	2.4E-07	7.20E-10	2.009E-07
L9474,BRF,24.1	0.26		1	2.84E-07	8.51E-10	2.009E-07
L9475,BRF,25.1	0.21		1	2.57E-07	7.72E-10	2.009E-07
L9495,BRF,26.1	0.00		1	2.09E-07	5.42E-10	2.009E-07
L9493,BRF,27.1	0.17		1	2.67E-07	6.94E-10	2.009E-07
L9494,BRF,28.1	0.18		1	2.21E-07	5.75E-10	2.009E-07

NAME	[4He] rad ccSTP/gH20	[3He] tri ccSTP/gH20	¯[3He] tri ERROR ccSTP/gH20	[3He] tri TU	¯[3He] tri ERROR TU	[3H]/[3He]tri AGE (With crustal) yrs
example	2.85E-10	5.179E-13	8.85E-15	208.24	3.56	26.05
L9470,BNL_053-01,1.3,10/28/96	-2.30E-10	1.29E-14	4.45E-16	5.19	0.18	4.93
L9473,BNL_053-02,2.1						
L9469,BRF,20.1	6.34E-09	3.78E-14	7.24E-16	15.19	0.29	**17.73**
L9476,BRF,21.1	2.38E-10	5.44E-16	3.34E-16	0.22	0.13	0.31
L9472,BRF,23.1	1.83E-10	1.19E-14	4.13E-16	4.79	0.17	6.20
L9474,BRF,24.1	-6.92E-10	3.60E-14	5.46E-16	14.49	0.22	13.75
L9475,BRF,25.1	-2.02E-10	1.16E-16	4.14E-16	0.05	0.17	0.08
L9495,BRF,26.1						
L9493,BRF,27.1	3.96E-08	2.12E-14	5.92E-16	8.53	0.24	**24.02**
L9494,BRF,28.1	-1.69E-09	-2.26E-15	3.17E-16	-0.91	0.13	-1.42

NAME	[3H]/[3He]tri AGE ERROR (With crustal) yrs	[3H]+[3He] tri TU	DIFFERENCE CRUSTAL AND NON CRUSTAL AGES yrs
example	0.42	271.84	0.01
L9470,BNL_053-01,1.3,10/28/96	0.15	21.62	-0.10
L9473,BNL_053-02,2.1			
L9469,BRF,20.1	**0.25**	24.19	2.79
L9476,BRF,21.1	0.19	12.85	0.18
L9472,BRF,23.1	0.19	16.38	0.11
L9474,BRF,24.1	0.17	27.07	-0.25
L9475,BRF,25.1	0.28	10.83	-0.18
L9495,BRF,26.1			
L9493,BRF,27.1	**0.46**	11.56	24.02
L9494,BRF,28.1	0.21	11.05	-1.44

APPENDIX VII: Boston precipitation data (1963 - 1986).

YEAR	MONTH	[^{3}H] INPUT
1963	1	1150.0
63	2	970.0
63	3	790.0
63	4	1890.0
63	5	2390.0
63	6	3170.0
63	7	3110.0
63	8	3110.0
63	9	1080.0
63	10	470.0
63	11	470.0
63	12	1280.0
64	1	1440.0
64	2	1490.0
64	3	1800.0
64	4	1260.0
64	5	1120.0
64	6	1750.0
64	7	2210.0
64	8	2210.0
64	9	2210.0
64	10	340.0
64	11	205.0
64	12	205.0
65	1	260.0
65	2	260.0
65	3	880.0
65	4	1150.0
65	5	1150.0
65	6	1150.0
65	7	730.0
65	8	730.0
65	9	730.0
65	10	165.0
65	11	165.0
65	12	165.0
66	1	180.0
66	2	335.0
66	3	335.0
66	4	500.0
66	5	605.0
66	6	690.0
66	7	740.0
66	8	230.0
66	9	230.0
1966	10	205.0
66	11	130.0
66	12	180.0
67	1	180.0
67	2	240.0
67	3	240.0
67	4	230.0
67	5	230.0
67	6	395.0
67	7	350.0
67	8	350.0
67	9	170.0
67	10	170.0
67	11	125.0
67	12	125.0
68	1	120.0
68	2	120.0
68	3	120.0
68	4	240.0
68	5	240.0
68	6	240.0
68	7	240.0
68	8	240.0
68	9	90.0
68	10	105.0
68	11	57.0
68	12	85.0
69	1	56.5
69	2	109.0
69	3	175.0
69	4	88.4
69	5	140.0
69	6	194.0
69	7	193.0
69	8	256.0
69	9	108.0
69	10	81.1
69	11	43.8
69	12	41.2
70	1	90.6
70	2	123.0
70	3	196.0
70	4	148.0
70	5	161.0
70	6	244.0
1970	7	240.0
70	8	185.0
70	9	255.0
70	10	72.9
70	11	49.5
70	12	80.6
71	1	115.0
71	2	54.7
71	3	178.0
71	4	116.0
71	5	212.0
71	6	198.0
71	7	265.0
71	8	138.0
71	9	80.9
71	10	42.6
71	11	71.3
71	12	53.7
72	1	116.0
72	2	63.0
72	3	79.5
72	4	91.5
72	5	75.6
72	6	104.0
72	7	94.4
72	8	116.0
72	9	51.6
72	10	51.6
72	11	37.4
72	12	55.6
73	1	44.7
73	2	34.5
73	3	50.2
73	4	76.8
73	5	87.4
73	6	73.9
73	7	73.9
73	8	56.8
73	9	49.8
73	10	49.8
73	11	28.8
73	12	36.6
74	1	43.1
74	2	48.6
74	3	62.6

YEAR	MONTH	[^{3}H] INPUT	YEAR	MONTH	[^{3}H] INPUT	YEAR	MONTH	[^{3}H] INPUT
1974	4	62.6	1978	2	27.0	1981	12	16.8
74	5	54.8	78	3	38.6	82	1	17.2
74	6	54.0	78	4	65.3	82	2	19.9
74	7	46.7	78	5	55.2	82	3	19.9
74	8	45.9	78	6	71.8	82	4	24.6
74	9	45.9	78	7	84.2	82	5	27.3
74	10	92.1	78	8	48.9	82	6	33.6
74	11	70.3	78	9	48.9	82	7	44.0
74	12	16.9	78	10	50.3	82	8	37.6
75	1	29.0	78	11	31.5	82	9	32.6
75	2	35.8	78	12	23.3	82	10	13.6
75	3	47.1	79	1	22.8	82	11	13.6
75	4	50.1	79	2	26.0	82	12	
75	5	61.6	79	3	28.8	83	1	9.9
75	6	88.5	79	4		83	2	14.1
75	7	79.6	79	5		83	3	12.6
75	8	62.0	79	6	42.9	83	4	12.6
75	9	30.1	79	7	42.9	83	5	26.4
75	10	23.7	79	8	40.8	83	6	49.4
75	11	29.7	79	9	22.0	83	7	50.9
75	12	35.6	79	10	22.3	83	8	38.6
76	1	35.6	79	11	22.2	83	9	11.9
76	2	35.6	79	12	21.4	83	10	13.1
76	3		80	1	55.3	83	11	11.1
76	4	52.9	80	2	55.2	83	12	12.2
76	5	52.9	80	3	20.3	84	1	20.5
76	6	45.5	80	4	22.2	84	2	24.6
76	7	43.3	80	5	51.7	84	3	18.7
76	8	48.5	80	6	60.5	84	4	19.0
76	9	51.3	80	7	36.0	84	5	19.8
76	10	25.3	80	8	44.5	84	6	26.2
76	11	21.4	80	9	38.2	84	7	33.3
76	12	21.4	80	10	24.7	84	8	31.1
77	1	21.4	80	11	24.1	84	9	29.9
77	2	25.0	80	12	34.7	84	10	22.8
77	3	31.4	81	1	65.2	84	11	30.2
77	4	34.9	81	2	19.2	84	12	16.2
77	5	44.7	81	3	43.5	85	1	23.6
77	6	81.5	81	4	51.1	85	2	
77	7	81.5	81	5	53.1	85	3	23.0
77	8	75.7	81	6	42.3	85	4	26.2
77	9	58.4	81	7	53.7	85	5	32.6
77	10	28.5	81	8	50.5	85	6	25.8
77	11	28.0	81	9	36.8	85	7	24.7
77	12	20.6	81	10	36.5	85	8	30.5
78	1	23.6	81	11	22.1	85	9	16.7

YEAR	MONTH	$[^3H]$ INPUT
1985	10	23.6
85	11	13.6
85	12	50.0
86	1	26.5
86	2	39.0
86	3	15.7
86	4	
86	5	
86	6	
86	7	
86	8	28.0
86	9	18.8
86	10	14.0
86	11	
86	12	

APPENDIX VIII: Washington D. C. Precipitation data (1963 -1991).

YEAR	MONTH	[^{3}H] INPUT	YEAR	MONTH	[^{3}H] INPUT	YEAR	MONTH	[^{3}H] INPUT
63	1	500.0	66	9	150.0	70	5	186.0
63	2	625.0	66	10	110.0	70	6	207.0
63	3	890.0	66	11	150.0	70	7	208.0
63	4	1710.0	66	12	225.0	70	8	196.0
63	5	975.0	67	1	100.0	70	9	114.0
63	6	1470.0	67	2	170.0	70	10	99.0
63	7	3890.0	67	3	175.0	70	11	70.5
63	8	1500.0	67	4	250.0	70	12	46.5
63	9	1000.0	67	5	270.0	71	1	70.0
63	10		67	6	305.0	71	2	70.0
63	11	600.0	67	7	305.0	71	3	69.5
63	12	750.0	67	8	205.0	71	4	146.0
64	1	825.0	67	9	125.0	71	5	167.0
64	2	1190.0	67	10	95.0	71	6	226.0
64	3	1000.0	67	11	50.0	71	7	223.0
64	4	1340.0	67	12	90.0	71	8	66.5
64	5	1980.0	68	1	125.0	71	9	70.0
64	6	1380.0	68	2	155.0	71	10	74.5
64	7	1155.0	68	3	140.0	71	11	51.8
64	8	910.0	68	4	200.0	71	12	76.6
64	9	1140.0	68	5	210.0	72	1	60.6
64	10	1415.0	68	6	230.0	72	2	62.8
64	11	1415.0	68	7	200.0	72	3	85.5
64	12	290.0	68	8	145.0	72	4	83.6
65	1	305	68	9	80.0	72	5	79.2
65	2	295	68	10	90.0	72	6	82.3
65	3	525	68	11	95.0	72	7	62.6
65	4	895	68	12	120.0	72	8	94.2
65	5	770.0	69	1	87.1	72	9	53.7
65	6	990.0	69	2	94.3	72	10	44.9
65	7		69	3	179.0	72	11	27.8
65	8		69	4	271.0	72	12	28.8
65	9	345.0	69	5	98.1	73	1	29.4
65	10	175.0	69	6	217.0	73	2	31.6
65	11	175.0	69	7	226.0	73	3	42.9
65	12	200.0	69	8	197.0	73	4	112.0
66	1		69	9	89.9	73	5	107.0
66	2	320.0	69	10	52.7	73	6	85.4
66	3	380.0	69	11	94.1	73	7	46.5
66	4	420.0	69	12	43.3	73	8	83.7
66	5	530.0	70	1	52.3	73	9	53.3
66	6	585.0	70	2	103.0	73	10	42.8
66	7	635.0	70	3	142.0	73	11	44.7
66	8	270.0	70	4	131.0	73	12	33.1

YEAR	MONTH	[^{3}H] INPUT	YEAR	MONTH	[^{3}H] INPUT	YEAR	MONTH	[^{3}H] INPUT
74	1	39.4	77	12	29.5	81	10	18.4
74	2	49.8	78	1	28.1	81	11	18.4
74	3	58.3	78	2	51.2	81	12	13.4
74	4	72.1	78	3	53.0	82	1	7.5
74	5	91.0	78	4	64.8	82	2	45.1
74	6	98.8	78	5	64.8	82	3	35.4
74	7	97.3	78	6	59.4	82	4	
74	8	52.8	78	7	57.8	82	5	38.6
74	9	69.8	78	8	49.7	82	6	33.6
74	10	138.0	78	9	43.0	82	7	41.5
74	11	69.0	78	10	66.1	82	8	44.2
74	12	23.4	78	11	27.6	82	9	
75	1	36.0	78	12	18.0	82	10	29.2
75	2	39.8	79	1	34.9	82	11	29.2
75	3	55.4	79	2	34.9	82	12	12.4
75	4	60.8	79	3	35.1	83	1	18.8
75	5	61.8	79	4	36.3	83	2	22.4
75	6	80.9	79	5	40.3	83	3	16.3
75	7	80.9	79	6	46.5	83	4	20.7
75	8	80.9	79	7	44.0	83	5	56.0
75	9	40.0	79	8	34.8	83	6	36.5
75	10	22.6	79	9	27.4	83	7	26.7
75	11	24.8	79	10	37.9	83	8	
75	12	24.8	79	11	19.9	83	9	36.8
76	1	35.0	79	12	25.0	83	10	16.1
76	2	33.7	80	1	41.6	83	11	26.0
76	3	32.2	80	2	42.6	83	12	15.9
76	4	32.4	80	3	20.0	84	1	31.1
76	5	40.4	80	4	15.8	84	2	13.8
76	6	41.3	80	5	28.8	84	3	43.1
76	7	43.6	80	6	37.6	84	4	77.0
76	8	42.2	80	7	39.4	84	5	40.7
76	9	16.0	80	8	42.5	84	6	46.9
76	10	26.7	80	9	36.1	84	7	
76	11	32.2	80	10	21.1	84	8	31.8
76	12	34.4	80	11	16.3	84	9	
77	1	24.0	80	12	36.1	84	10	31.6
77	2	24.0	81	1	32.4	84	11	
77	3	30.7	81	2	15.5	84	12	9.0
77	4	41.9	81	3	158.0	85	1	21.9
77	5	65.8	81	4	78.7	85	2	12.4
77	6	76.0	81	5	64.0	85	3	19.8
77	7	69.3	81	6	50.6	85	4	
77	8	65.0	81	7	49.0	85	5	43.3
77	9		81	8	61.8	85	6	36.3
77	10		81	8	61.8	85	7	20.7
77	11	32.5	81	9	31.2	85	8	20.4

YEAR	MONTH	[^{3}H] INPUT
85	9	
85	10	18.4
85	11	12.8
85	12	34.8
86	1	10.1
86	2	
86	3	14.7
86	4	
86	5	
86	6	22.7
86	7	22.7
86	8	23.4
86	9	24.4
86	10	11.9
86	11	20.3
86	12	17.1
87	1	
87	2	15.0
87	3	14.5
87	4	
87	5	28.4
87	6	24.7
87	7	22.9
87	8	
87	9	18.0
87	10	27.5
87	11	14.7
87	12	26.4
88	1	9.1
88	2	18.3
88	3	49.2
88	4	22.5
88	5	
88	6	34.8
88	7	27.6
88	8	12.6
88	9	
88	10	14.7
88	11	20.9
88	12	36.8
89	1	6.5
89	2	13.0
89	3	24.0
89	4	22.0
89	5	38.7
89	6	15.0
89	7	19.6
89	8	35.5
89	9	13.9
89	10	8.8
89	11	10.9
89	12	10.1
90	1	16.9
90	2	15.6
90	3	9.8
90	4	15.0
90	5	17.5
90	6	
90	7	12.8
90	8	
90	9	19.6
90	10	7.6
90	11	21.1
90	12	13.7
91	1	10.9
91	2	45.0
91	3	12.5
91	4	12.7
91	5	14.6
91	6	14.2
91	7	15.3
91	8	15.2
91	9	13.5
91	10	17.8
91	11	12.3
91	12	9.4