

University of Nevada

Reno

Use of Chlorofluorocarbons to Date Ground Water:
A Comparison to the Tritium Method

A thesis submitted in partial fulfillment of the
requirements for the degree of
Master of Science in Hydrology/Hydrogeology

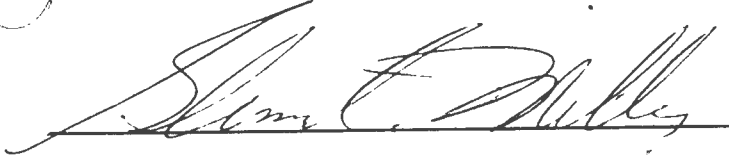
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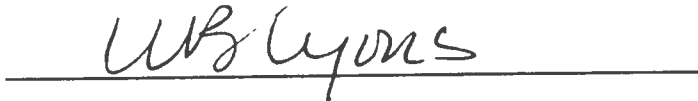
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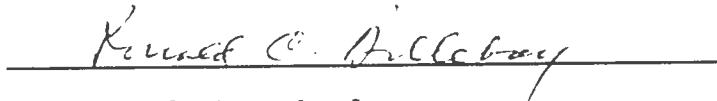
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PREFACE

This study on the use of chlorofluorocarbons to date ground water is associated with the U.S. Geological Survey National Water Quality Assessment (NAWQA) Program. NAWQA, which began in 1986, is a pilot program to assess the quality of the Nation's surface water and ground water reserves. One component of NAWQA is a study of regional ground water quality in the Carson River Basin of Western Nevada and Eastern California. Sites selected for CFC analysis were chosen from sites sampled for the NAWQA study.

ABSTRACT

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The presence of chlorofluorocarbons (CFCs) in ground water indicates the water has been recharged within the last 30-40 years. Therefore, CFCs may be an alternative to tritium for dating ground water.

Since atmospheric contamination of samples has been the main operational problem during testing of the CFC method, sampling and analytical techniques designed to reduce the potential for contamination were evaluated. Several problems were encountered with the methodology tested.

To evaluate the relationship between CFCs and tritium, ground water samples were collected throughout the Carson River Basin in Western Nevada and analyzed for dichlorodifluoromethane (F-12), trichlorofluoromethane (F-11), and tritium. Water with tritium ≤ 5 TU (assumed to be older than 40 years) had F-11 concentrations ≤ 1.2 pmol/l and F-12 concentrations < 0.7 pmol/l. Water with tritium > 10 TU (assumed to be less than 40 years) had F-11 concentrations > 2.1 pmol/l and F-12 concentrations > 1.0 pmol/l.

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INTRODUCTION

Knowledge of ground water age is an important component in the management of ground water resources. Ground water age can be used to identify recharge areas and determine recharge rates. This information is necessary for determining reasonable ground water withdrawal rates for water supply, and is useful for land use determinations such as siting industrial areas and landfills, and evaluating wellhead protection areas.

Tritium concentrations are currently used to determine the relative age of young ground water; however, an alternative method of dating is needed because the tritium method is becoming less useful with time. Due to the limited atmospheric input during above-ground nuclear testing in the 1950s and 1960s and the short half-life, tritium concentrations in ground water continue to decrease. Therefore, samples must now be enriched or concentrated in order to quantify the low levels.

Previous studies have indicated that chlorofluorocarbons (CFCs) can be used to determine whether ground water has been in contact with the atmosphere or recharged since the 1950s and is therefore less than 30-40 years old (Thompson, 1976; Busenberg and Plummer, 1992).

CFC concentrations in ground water range from less than one to about five picomoles per liter (Thompson, 1976;

Nevison 1987; Busenberg and Plummer, 1992). Because these values are two to three orders of magnitude less than CFC atmospheric concentrations, a primary concern with utilizing CFCs to date ground water is the potential for atmospheric contamination during sample collection, transport to the laboratory, storage prior to analysis and the analytical procedure.

The applicability of the CFC method on a large scale basis depends, in part, on the ability to store samples for some amount of time in order to allow for sample transport to the laboratory and for storage prior to analysis. In previous studies (Thompson, 1976; Nevison, 1987) samples were collected in glass syringes and analyzed in the field with a portable gas chromatograph or in a laboratory in close proximity to the sampling sites. Therefore, a major objective of this study was to test a sampling device which would isolate the sample from the atmosphere during collection and transport to the laboratory and allow for a reasonable sample holding time.

A second objective was to construct an analytical system for determining CFC concentrations in ground water which would minimize the potential for sample contamination during analysis. The sampling and analytical systems, which were implemented with varying degrees of success, are described in detail in this paper.

The third objective of this study was to evaluate the

general relationship between tritium and CFC concentrations in ground water. The basic premise for comparison is that, in general, tritium concentrations greater than 5 tritium units (TU) indicate the water is younger than 40 years old (Hendry, 1988). Therefore, water with tritium concentrations greater than 5 TU should also have detectable CFC concentrations. Conversely, water with tritium concentrations less than 5 TU is considered older than 40 years and should have very low or no CFC concentrations.

In order to compare CFC concentrations to tritium, it must be assumed the tritium concentrations represent ground water age and that CFC concentrations in ground water are equal to atmospheric equilibrium concentrations at the time of recharge. As shown by Busenberg and Plummer (1992) and discussed later in this paper, several factors can influence the CFC concentrations seen in ground water. Also, the tritium input functions as influenced by atmospheric concentrations and local precipitation must be determined for the study area. Since the CFC equilibrium concentrations and tritium input function for the Carson River Basin are unavailable and factors affecting CFC ground water concentrations were not evaluated, the results of this study are of a qualitative nature and only general comparisons between CFC and tritium concentrations are made.

TRITIUM VERSUS CHLOROFLUOROCARBONS FOR DATING GROUND WATER

Tritium concentrations are currently used to estimate the residence time of ground water. Above-ground thermonuclear testing, which began in 1952, released large amounts of tritium into the atmosphere. During the mid 1960s, tritium concentrations in precipitation over the northern hemisphere were 10,000 times greater than pre-atmospheric testing background concentrations (Hendry, 1988). Therefore, increased tritium levels in ground water indicate the water was exposed to the atmosphere or recharged within the last 30-40 years. Tritium concentrations near background levels indicate the water was recharged more than 40 years ago. A general estimate of ground water age based on tritium concentrations is shown in Table 1.

TABLE 1. Estimates of ground water age based on tritium concentrations (After Hendry, 1988).

Tritium Concentration TU (Tritium Units)	Age Estimates
Less than 0.2	Water is older than 50 years
Less than 2.0	Water is older than 30 years
2-10	Probably older than 20 years
10-100	Less than 35 years old

Due to the short half life of tritium (about 12.3 years), and the limited atmospheric input during the 1950s and early 1960s, the tritium method has become, and will continue to become, less useful with time. Tritium

concentrations in ground water continue to decrease as the tritium decays, so samples must now be concentrated or enriched during analysis. This increases analytical costs and time required for the procedure.

Potential advantages of using CFCs to determine ground water age are: 1) the method will provide for relatively inexpensive and rapid analysis of samples; 2) the method will be useful for many years into the future because CFC (atmospheric concentrations are expected to continue to increase; 3) ground water age may be defined within a small time period (Busenberg and Plummer, 1992); 4) low detection levels of the method allow more sensitive testing for small amounts of young water (post-1950) mixing with older water (Busenberg and Plummer, 1992); and 5) CFCs can be used as tracers of shallow ground water and sewage effluent in surface and shallow ground waters (Busenberg and Plummer, 1992).

The main operational problem with the CFC method will be the potential for sample contamination. CFC atmospheric concentrations are two to three orders of magnitude greater than concentrations found in ground water. Therefore, a high potential exists for sample contamination during collection, transport to the laboratory and analysis. During previous studies (Thompson, 1976; Nevison, 1987), samples were analyzed in the field or collected from sites in close proximity to the laboratory. The current inability to

maintain sample integrity over any length of time greatly restricts applicability of the method.

The interpretation of CFC analytical results may be complicated by several factors. Adsorption of CFCs to organic material and sediments (Brown, 1980; Stiles, 1982) and microbial degradation (Busenberg and Plummer, 1992) will decrease CFC concentrations in ground water. In this case, the defined age will be older than the actual age. Atmospheric diffusion through the unsaturated zone may cause elevated CFC concentrations in ground water (Russell, 1981; Weeks and others, 1982) and would result in a defined age younger than the actual age. Also, valid CFC-model recharge ages can be obtained only if the aquifer is not contaminated by local sources of CFCs which may include sewage-disposal ponds, sewage returns to rivers, septic tanks, and garbage-disposal sites (Busenberg and Plummer, 1992).

ATMOSPHERIC CHLOROFLUOROCARBONS

Chlorofluorocarbons (CFCs) are anthropogenic gases first developed in 1930 for use as nontoxic, nonflammable refrigerants (Rowland and Molina, 1975). The compounds of interest in this study are dichlorodifluoromethane (CCl_2F_2), commonly known as F-12, and trichlorofluoromethane (CCl_3F), also known as F-11.

These two compounds are highly volatile at room temperature, and only slightly soluble in water. Physical

Table 2. Physical properties of fluorocarbons F-11 and F-12
(After Stiles, 1982).

Property	F-11 (CCl ₃ F)	F-12 (CCl ₂ F ₂)
Molecular weight	137.37	120.92
Boiling point (1 atm, °C)	23.82	-29.79
Density, liquid (25 °C, g/cc)	1.475	1.311
Solubility (1 atm, 25 °C, wt%)	0.11	0.028
Distribution Coeff. (C _{gas} /C _{liquid})	3.6	12.9

properties are listed in Table 2.

During the late 1950s, worldwide production of chlorofluorocarbons increased rapidly as F-12 came into major use in refrigeration and air conditioning systems and both compounds were used as propellant gases in aerosol sprays and foam blowing agents. Production continued to rise to peak levels in 1974, followed by an overall decline in output until 1982 (Figure 1). Since 1982, world wide production has been increasing at a rate of about 5 percent per year (Gamlen and others, 1986; Layman, 1986).

The decline in F-11 and F-12 production after 1974 was influenced by the theory that free chlorine atoms in the stratosphere were involved in a reduction of the ozone layer, resulting in an increased amount of damaging ultraviolet radiation reaching the earth's surface (Molina and Rowland, 1974). Government and consumer pressure on the U.S. aerosol

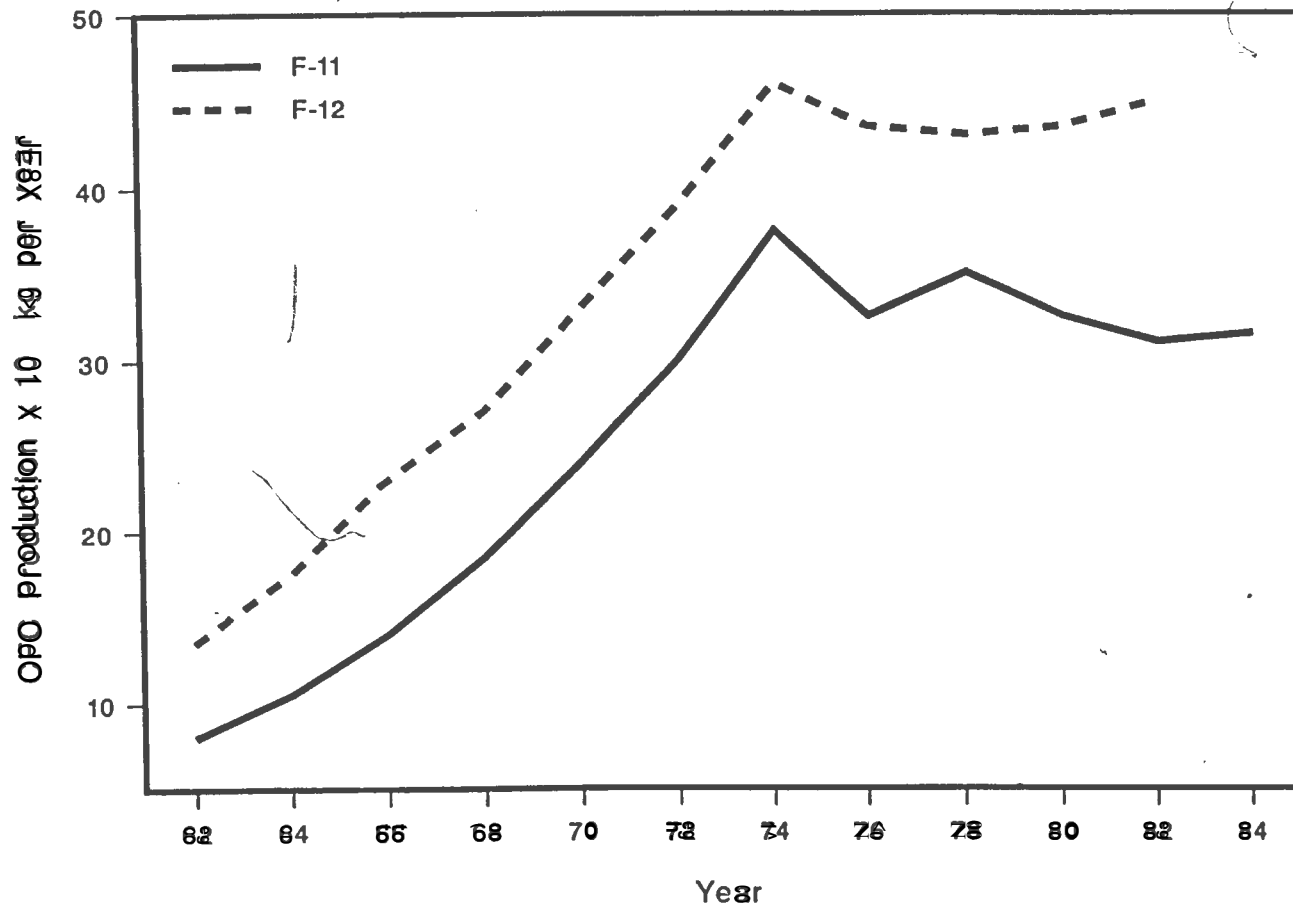


FIGURE 1. Annual worldwide production of F-11 and F-12, 1962-1984 (after Damon and others, 1986).

propellant industry resulted in decreased total production. However, manufactures in European and other industrial countries did not experience the same pressure, and did not reduce their output. The steady rise in production since 1982 has been due to increased use of CFCs for solvents and foam blowing agents (Laymen, 1986).

CFCs contained in refrigeration systems, foam products, and aerosols volatilize and are gradually released to the atmosphere. In the troposphere, the lower 15 to 20 kilometers of the earth's atmosphere, these compounds are chemically and photochemically stable (Cicerone, 1987; Rowland and Molina, 1975). Dissolution in atmospheric moisture or the oceans is not considered an important sink because the compounds are relatively insoluble in water and have a high vapor pressure. Photodissociation in the troposphere is negligible because these molecules have no absorption beyond about 2200-2300 angstroms and radiation at these wavelengths is absorbed at higher altitudes in the stratosphere (Rowland and Molina, 1975). Estimated atmospheric lifetimes (the time it takes for 63 percent of the chemical to be washed out of the atmosphere) range from 70-79 years for F-11 and 120-139 years for F-12 (Cunnold and others, 1986; Cicerone, 1987; Shea, 1989).

Due to wide spread-use, high volatility from the end products, and long tropospheric residence times, F-11 and F-12 tropospheric concentrations have risen steadily over the

past few decades. These concentrations have been well documented since the mid 1970s. From 1975 to 1985, Northern Hemisphere F-11 atmospheric concentrations increased from approximately 120 parts per trillion (ppt) to 220 ppt, and F-12 concentrations rose from about 200 ppt to 400 ppt (Figure 2) (Rasmussen and Kahlil, 1986). Prior to 1975, atmospheric concentrations can be estimated from production data (available from the Chemical Manufactures Association), estimates of the amounts of CFCs released to the atmosphere, delay time between production and release from end use products, and average atmospheric lifetimes (McCarthy and others, 1977; Rowland and Molina, 1975).

Release of CFCs to the atmosphere is not uniform and is greatest around urban, industrialized areas. Although global tropospheric mixing is considered to be rapid and uniform, there is an observed F-11 and F-12 atmospheric concentration difference between the northern and southern hemispheres (Randall and Schultz, 1976; Rasmussen and Kahlil, 1986).

The main sink for these compounds is the stratosphere (Cicerone, 1987). On the average, it takes about 5 years for gases emitted at the earth's surface to be transported upward to the photochemically active altitudes in the stratosphere (about 25km and higher). In the stratosphere, ultraviolet radiation photolysis dissociates the compounds, producing free chlorine atoms. The chlorine atoms react with ozone (O_3) in a catalytic chain reaction resulting in a net loss of

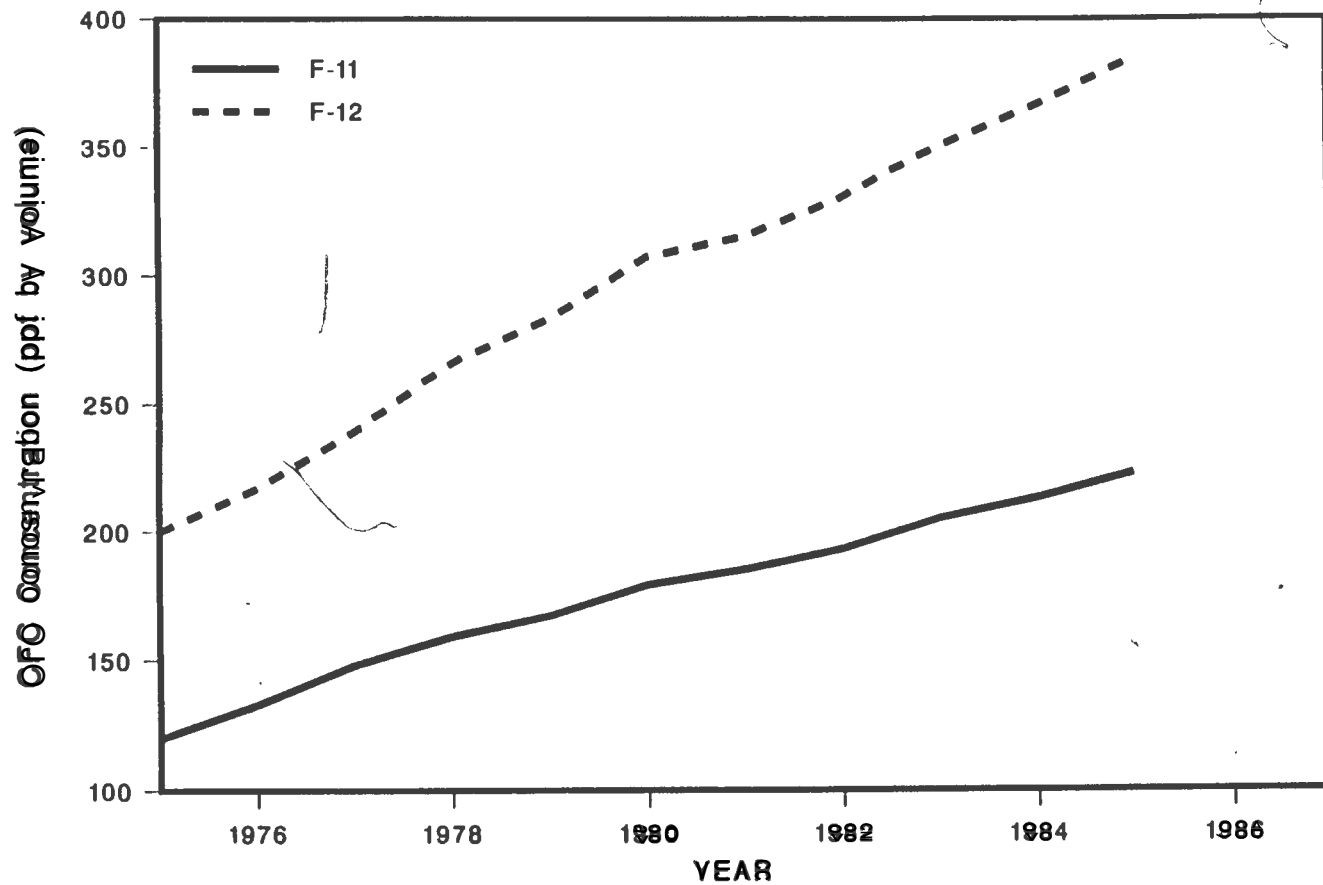


FIGURE 2. Atmospheric concentrations of F-11 and F-12 from 1975 to 1985, based on measurements taken each January in the Pacific Northwest (after Rasmussen and Kamill, 1988).

ozone (Molina and Rowland, 1974,). The reactions for F-11 are:



CHLOROFLUOROCARBONS IN THE HYDROLOGIC CYCLE

Chlorofluorocarbons enter the hydrologic cycle because they partition from the gas phase into atmospheric moisture and are incorporated into precipitation in the form of rain or snow (Figure 3). The dissolved CFCs are carried along as passive tracers as water enters the ground water system in recharge areas (Thompson, 1976).

The amount of CFCs that dissolves into precipitation is dependent upon temperature, solubility coefficients or Henry's Law constants for the compounds, and CFC atmospheric concentrations at the time the precipitation is formed (Nevison, 1987; Busenberg and Plummer, 1992). Therefore, as CFC atmospheric concentrations have increased over the last 30-40 years, the amount of CFCs dissolved in precipitation has also increased.

Using estimates of CFC atmospheric concentrations, temperature, solubility data, and precipitation records, Nevison (1987) modeled F-11 and F-12 concentrations in

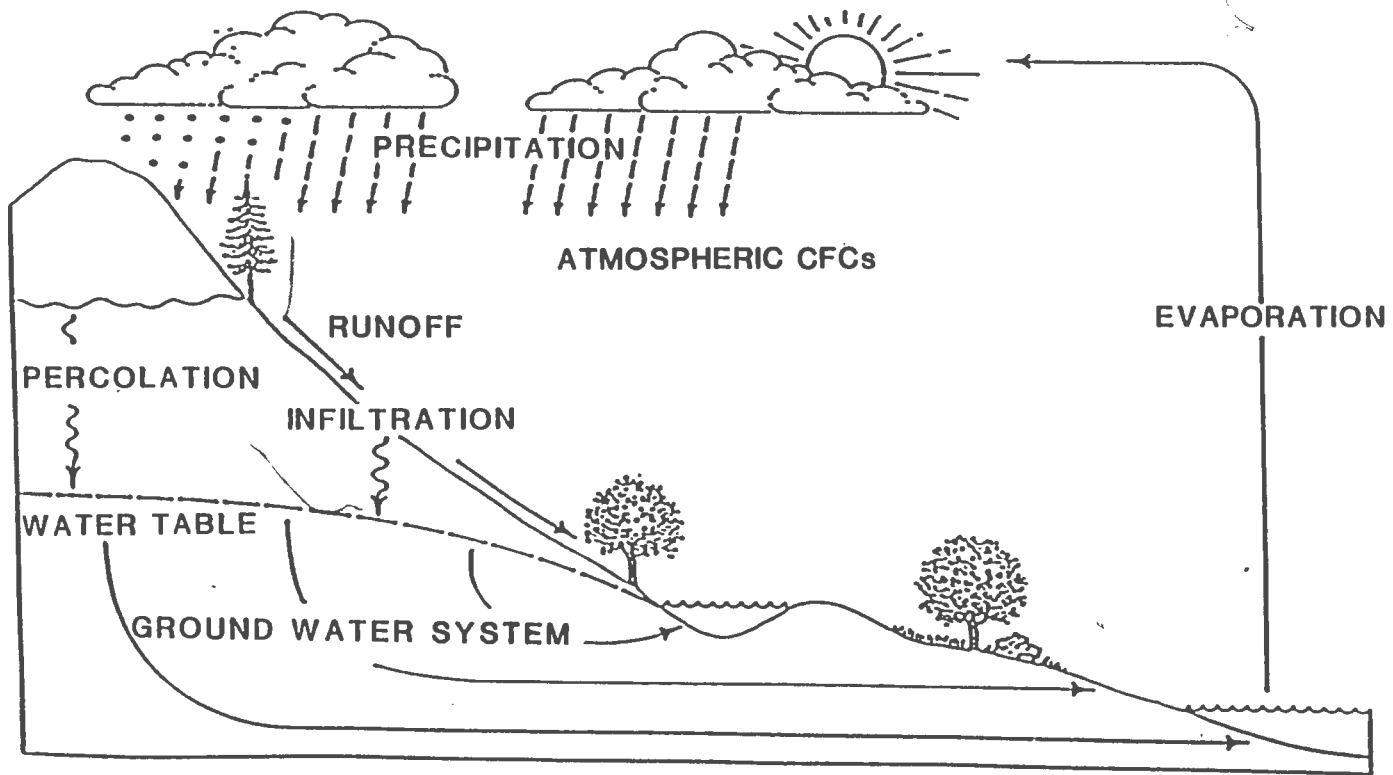


FIGURE 3. Hydrologic cycle (after Dreyer, 1982).

precipitation over Cape Cod (Figure 4). The model indicates a marked increase of F-11 and F-12 in precipitation since 1960.

Busenberg and Plummer (1992) determined concentrations of F-11 and F-12 in precipitation in equilibrium with air as a function of recharge temperature for the years 1945 through 1990 for Central Oklahoma. Their data showed decreasing CFC concentrations with increasing temperature, indicating the importance of temperature in evaluating the CFC input function.

CFC concentrations which enter the ground water system during recharge depend on several factors including:

- 1) recharge temperature at the base of the unsaturated zone;
- 2) depth of the unsaturated zone; 3) excess air entering the saturated zone; 4) unsaturated zone processes such as tortuosity, sorption and dissolution; 5) potential microbial degradation; and 6) point source contamination from sewage disposal sites, sewage returns to rivers, septic tanks, and garbage disposal sites (Busenberg and Plummer, 1992).

Although these factors must be considered in determining CFC model recharge-ages, the presence or absence of CFCs generally indicates relative age of the water. Detectable CFC concentrations indicate the water has been in contact with the atmosphere or recharged within the last 30-40 years. The absence of CFCs in ground water indicates the water has been isolated from the atmosphere for at least that same

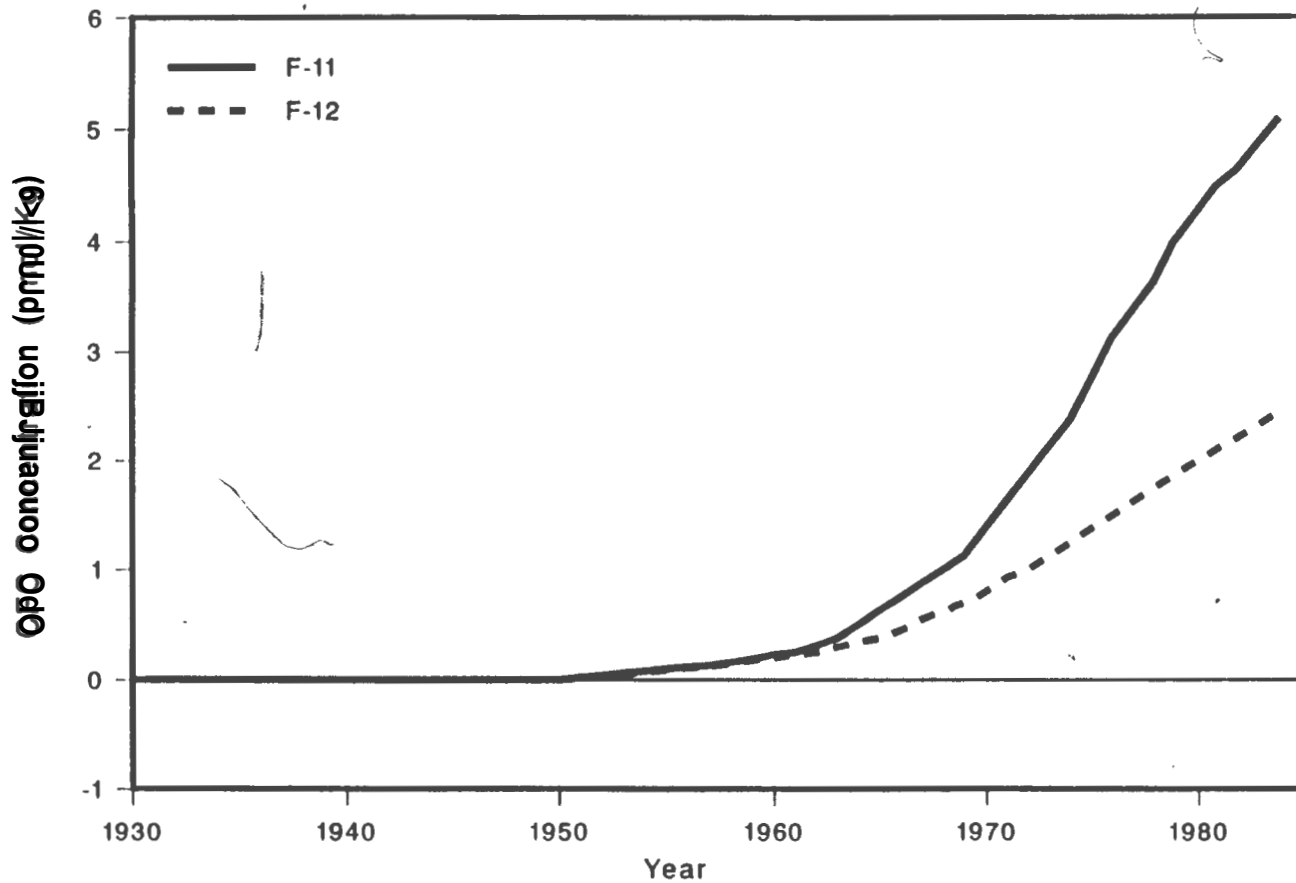


FIGURE 4. Modeled F-11 and F-12 concentrations in Cape Cod precipitation from 1930 to 1986 (from Neilson and Bullis, 1987).

length of time, or is older than 40 years.

PREVIOUS WORK IN THE USE OF CHLOROFLUOROCARBONS AS NATURAL TRACERS

Lovelock (1971) first detected minute quantities of atmospheric trichlorofluoromethane in the part per trillion range during analysis of atmospheric samples by gas chromatography with an electron capture detector. Since gaseous fluorine compounds are not found naturally in the atmosphere, Lovelock predicted the atmospheric distribution of F-11 and other carbon and sulfur fluorides could be useful indicators of air movements and wind directions.

Thompson and others (1974), Randall and Schultz (1976), Davis and others (1980), and Stiles (1982) have all reported that fluorocarbons may be useful as hydrologic tracers because they are virtually nonexistent in ambient concentrations, can be detected in minute quantities, are non-toxic, and are not degraded in the subsurface.

Limited studies have been performed to determine the feasibility of utilizing chlorofluorocarbons as hydrologic tracers or using these compounds to date ground water.

Leppo (1975) designed the first system to determine F-11 concentrations in ground water, utilizing a purge and trap concentration method with gas chromatography and electron capture detector.

Thompson (1976) was the first to evaluate the temporal

significance of trichlorofluoromethane in ground water. Preliminary investigations were conducted in three areas where the hydrology was well understood and where tritium concentrations were available. The areas were the Wharton Tract of southern New Jersey, Hot Springs National Park, Arkansas, and the Edwards Aquifer of south central Texas.

At the Wharton tract, good agreement was observed between F-11 data and the known hydraulic gradients. The highest F-11 concentrations were observed in surface waters and concentrations decreased rapidly with depth and decreasing gradient in the aquifer. Lower concentrations were found in areas where the observed hydraulic gradient indicated dilution by older ground water ascending from depth. Tritium and F-11 values were generally comparable in that high F-11 concentrations were associated with high tritium values and vice versa.

Tritium and F-11 concentrations from Hot Springs National Park were consistently absent, indicating older ground water.

In general, F-11 data paralleled that of tritium data in the Texas study. However, the data showed a series of anomalous F-11 concentrations greater than air/water equilibrium concentrations.

A subsequent study by Russell (1981), indicated the elevated F-11 concentrations seen in the Thompson study at known recharge areas may be due to sorption and desorption of

fluorocarbons from particle surfaces in response to changes in soil moisture content. Soil slurry experiments showed a significant increase in aqueous F-11 concentrations when introduced to dry soils, indicating soils may function as a reservoir for F-11. The F-11 concentrations increased as the clay and organic content of the soils increased.

Brown (1980) performed soil column studies designed to test the mobility of fluorocarbon compounds in a controlled saturated flow regime. The compounds were passed, in aqueous solutions, through columns filled with sand, sandy loam, and crushed coal. In all tests, the fluorocarbon tracers exhibited delayed breakthrough curves compared to salt tracer controls. Delays were least in the sand, significant in the sandy loam, and severe in the crushed coal. Calculated longitudinal dispersion coefficients averaged 3.9 times higher than salt tracer dispersion coefficients.

Stiles (1982) performed further field and soil column tests to study fluorocarbon sorption behavior. Field studies indicated sorption characteristics were highly variable, and fluorocarbons did not react as predictably as bromide. In the laboratory, consistent results in predicting peak breakthrough time were achieved under well-controlled conditions. Stiles theorized that hydrophobic interactions significantly influenced fluorocarbon retention in the column studies.

Schultz (1979), utilized a discrete-state model (DSM) to

predict F-11 concentrations in the Edwards Aquifer near San Antonio, Texas. The data indicated high F-11 values in recharge areas, intermediate values in the center of the aquifer and lower values at spring discharge points. Levels were below the detection limit in areas of low aquifer circulation.

Weeks and others (1982) determined that diffusion of atmospheric gases occurs through the unsaturated zone. Measurable F-11 and F-12 concentrations were found at depths as great as 43.9 meters. The analytical model solution for an estimated effective diffusion coefficient for F-11 in the unsaturated zone was 0.04 square meters per day. Numerical modeling indicated the combined retarding effect of tortuosity, sorption, and dissolution on the rate of fluorocarbon diffusion through the unsaturated zone is substantial and may be greater for F-11 than for F-12.

Bullister and Weiss (1988) developed an analytical system prototype and technique to effectively measure F-11 and F-12 concentrations in air and seawater. Using a similar system, Nevison (1987) determined F-11 and F-12 concentrations in ground water in the Cape Cod area. A comparison between tritium and fluorocarbon concentrations showed high CFC concentrations at sites with high tritium concentrations. The data were used to predict recharge rates and showed decreasing F-11 and F-12 concentrations with depth in a known recharge area.

Busenberg and Plummer (1992) conducted an extensive study in Central Oklahoma to investigate the use of CFCs as an age dating tool and ground water tracer. New sampling methodology using glass ampules fused in the field to completely isolate water samples was tested with good results. Analytical results showed CFCs can be used to date ground waters younger than 45 years. The study was very quantitative and under optimum conditions, ground water recharge ages were estimated within a two year period. The study showed CFCs can be used to detect mixing of old and young waters. CFCs were also used to trace sewage effluent in surface and shallow ground waters.

Chlorofluorocarbons have also been used as tracers of ocean mixing and circulation patterns (Lovelock and Maggs, 1973; Hammer and others, 1978; Gammon and others, 1982; Watson and Liddicoat, 1985; Bullister, 1984).

HYDROGEOLOGY OF STUDY AREA

In Nevada, the Carson River Basin lies within the Great Basin physiographic province and is comprised of five hydrographic areas: Carson Valley, Eagle Valley, Dayton Valley (includes the Carson Plains and Stagecoach Valley), Churchill Valley, and Carson Desert (Figure 5).

Climate in the Carson River Basin is influenced by the Sierra Nevada Mountain Range, which captures most

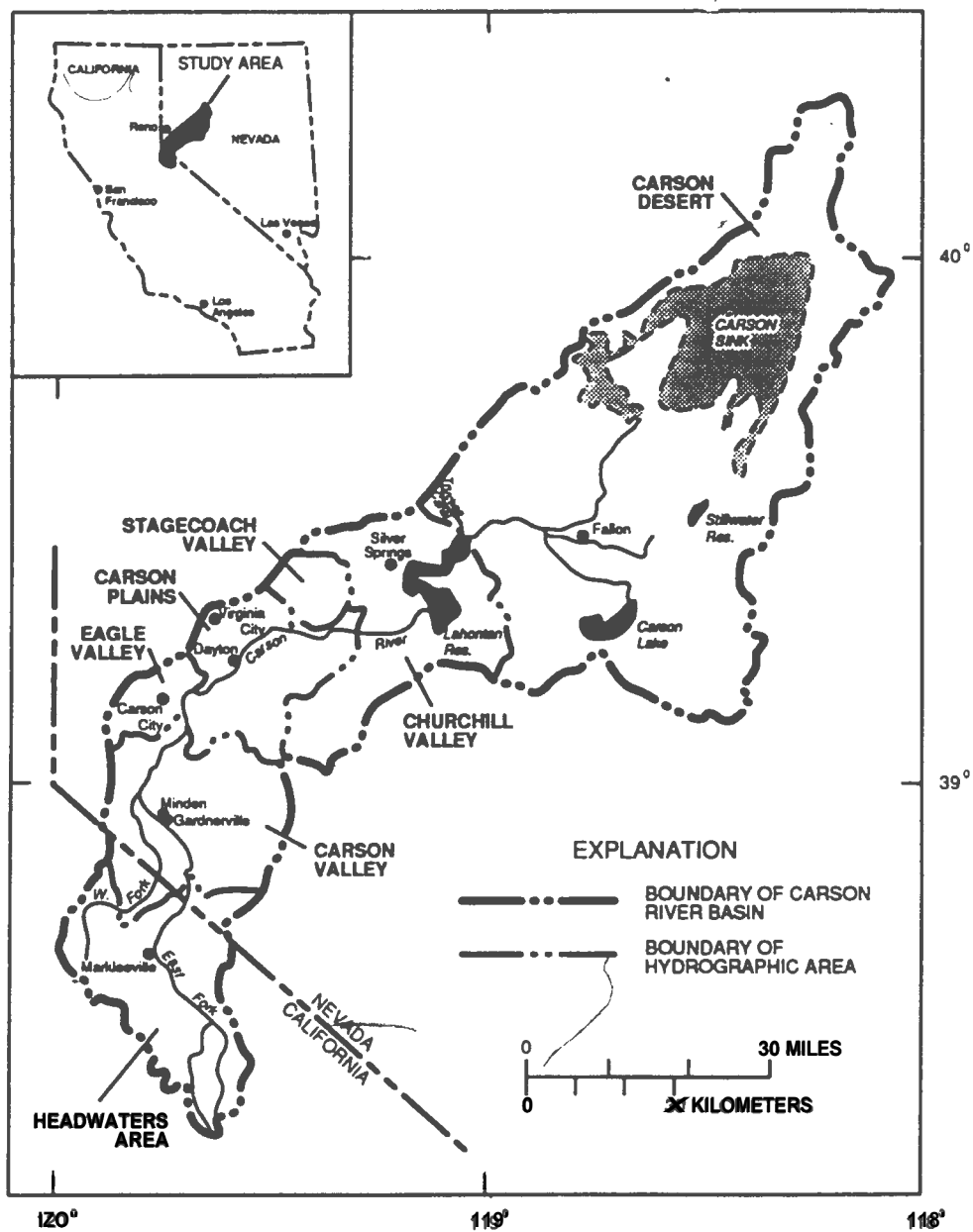


FIGURE 5. Study area—Carson River Basin (from Welch and others, 1989).

precipitation derived from the Pacific Ocean. In regions east of the Sierra, higher mountain elevations may receive up to 25 inches per year of precipitation, mostly in the form of snow during winter months. Lower elevations receive about 3 to 11 inches per year (Welch and others, 1989.)

Topography of the region is a product of Basin and Range extensional faulting which began about 17 million years ago, creating broad bedrock basins surrounded by high mountains. The consolidated rocks consist of five hydrogeologic units: 1) metasedimentary and metavolcanic rocks of Triassic and Jurassic age; 2) basic igneous rocks of Jurassic age consisting of diorite, gabbro, and marine volcanic rock; 3) granodiorite and quartz monzonite of Jurassic to Tertiary age; 4) silicic volcanic rocks of Tertiary and Quaternary age consisting of rhyolite, latite, and dacite; and 5) basic volcanic rocks of Tertiary and Quaternary age including basalt, andesite, and trachyte (Welch and others, 1989).

Subsequent erosion of the upland areas formed deep unconsolidated and semi-consolidated basin fill deposits of Tertiary to Quaternary age. These deposits, which are stratigraphically complex due to reworking by alluvial and lacustrine processes, form the major aquifers in the Basin (Glancy and Katzer, 1975; Mauer, 1986).

In Carson Valley, basin fill deposits range from hundreds to several thousands of feet in thickness and are underlain by consolidated rock of pre-Jurassic to Quaternary

age. The fill is characterized by unconsolidated deposits of interbedded clay, silt, sand and gravel. Water bearing strata are of varying thickness and depth, with depth to water ranging from a few feet on the valley floor to greater than 1000 feet along margins of the valley. Generally, two zones, a shallow and a deep aquifer system are recognized. While there is no continuous confining strata, partial confinement of saturated zones occurs locally due to overlapping clay lenses (Glancy and Katzer, 1975).

In Eagle Valley, basin fill deposits are generally separated into two age categories. The younger alluvium, of Recent and Pleistocene age, ranges from 1 to 50 feet in thickness and is composed of interbedded clay, silt, sand and gravel. This shallow zone supplies some domestic wells. Older alluvium, of early to late Pleistocene age, ranges from 0 to 500 feet in thickness. Most domestic wells and all large capacity municipal wells penetrate the older alluvium (Worts and Malmberg, 1966).

The geology of Dayton and Churchill Valleys is similar to that of Carson and Eagle Valleys. Pre-jurassic to Quaternary age consolidated rocks are overlain by unconsolidated to semi-consolidated Tertiary to Quaternary age deposits of clay, silt, sand and gravel. This alluvium may be separated by bedrock to form independent or semi-independent valley fill reservoir systems (Glancy and Katzer, 1975).

In the Carson Desert, valley fill sediments of Tertiary and Quaternary age have been deposited by the Carson and Humboldt rivers and are also derived from material eroded from surrounding mountains.

Lake Lahontan covered this area during the Quaternary Period. Due to major climatic fluctuations which occurred during the Pleistocene Epoch, lake waters advanced and receded many times. Sediments were deposited and reworked, resulting in a complex geologic pattern of interbedded and inter-tonguing layers of gravel, sand, silt, and clay (Glancy and Katzer, 1975; Glancy, 1986).

The large interdependent aquifer system of the valley fill deposits is recognized as consisting of four subsystems: 1) a hydraulically complex, shallow, unconsolidated sedimentary aquifer with water of variable chemical character, extending from near land surface to a depth of 50 feet; 2) an intermediate-depth unconsolidated aquifer, underlying the shallow system and extending from 50 feet to 500-1000 feet, containing large quantities of good quality water; 3) a deep, generally unconsolidated aquifer, below depths of 500-1000 feet, containing mostly saline water; and 4) a highly permeable basalt aquifer of Quaternary age that stratigraphically transects all three sedimentary aquifers and may contain a blend of good quality and saline water (Glancy, 1986).

Valley fill reservoirs are the principal sources of

ground water, except in the Carson desert, where ground water for municipal use is pumped from the basalt aquifer about 500 feet below land surface (Glancy and Katzer, 1975).

Most recharge to the basin fill aquifers occurs from precipitation in the mountain areas. Water reaches the aquifers by seepage loss from streams on alluvial slopes and underflow from underlying consolidated rocks. Some recharge to the shallow aquifer system occurs as a result of infiltration of Carson River and irrigation return flows (Glancy and Katzer, 1975). Approximately 90 percent of municipal and domestic water use is supplied by ground water, and some ground water is pumped to meet irrigation needs (Welch and Plume, 1987).

METHODOLOGY

CFC WATER SAMPLE COLLECTION

The water samplers evaluated in this study were stainless steel samplers developed by Johnson and others (1987) at the Oregon Graduate Center. As the samplers were originally designed for use in collecting water samples for volatile organic compounds, the basic premise was complete isolation from the atmosphere.

The sampler consists of a length of 0.5 inch diameter stainless steel tubing equipped with copper crimping sections and swagelock fittings at each end (Figure 6). The sampler is inserted into the collection system via the swagelock

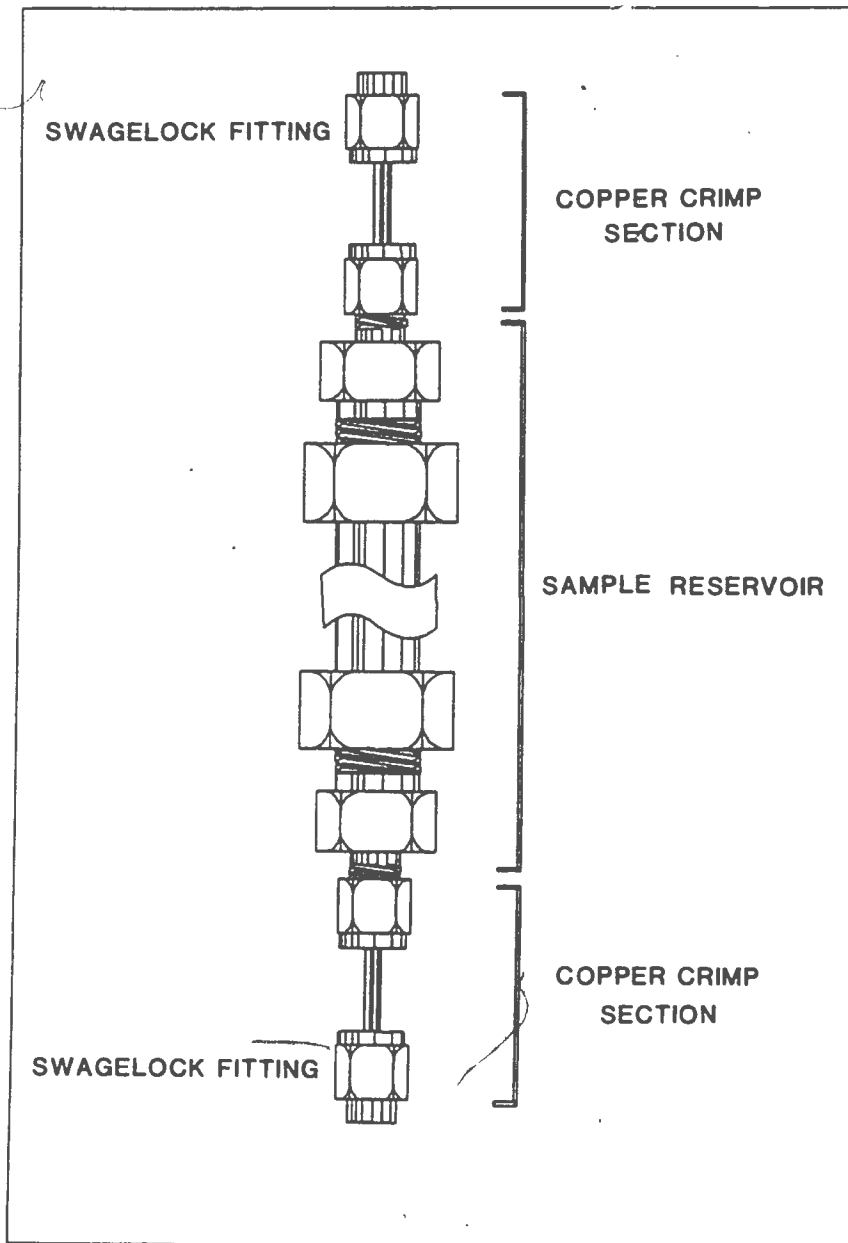


FIGURE 6. Ground water sample collection system (after Johnson and others, 1986).

fittings so that when properly tightened, an airtight seal exists and no outside air can enter the sampling system.

During sample collection, the sampler was inserted in line via a faucet connector and 1/8 inch diameter stainless steel tubing equipped with swagelock fittings. In order to ensure all gas was purged from the sampler, the sampler was held in a vertical position to allow flow to enter from the bottom. A one meter length of 1/8 inch diameter stainless tubing was attached to the top end of the sampler to prevent any potential backflow of air into the sampler. After a minimum of 3 sampler volumes had flowed through the sampler, the sample was collected by crimping the copper sections at the top and bottom of the sampler. The sampler was then removed from the system and the ends capped to prevent any atmospheric diffusion through the crimped ends.

Water samples were collected from municipal and domestic wells throughout the Carson River Basin. For domestic wells, samples were collected from the faucet nearest the wellhead after purging the system of at least three well volumes. For municipal wells which were continually pumping, the samples were obtained at the spigot nearest the wellhead. Duplicate or triplicate samples were collected at each site.

The samplers were transported to and from the field in coolers maintained between 10 and 17 degrees Centigrade. During sample analysis, the sampler was inserted directly

into the analytical system, and the copper sections uncrimped by placing vice grips at 90 degrees to the direction of the original crimp.

To reduce the potential for atmospheric contamination, prior to each sample collection run, samplers were purged in the laboratory, filled with clean carrier gas (a mixture of argon and methane) and capped.

CFC ANALYTICAL SYSTEM

CFC concentrations in ground water are determined by a purge and trap concentration method with gas chromatography and electron capture detection. This method is based on the premise that volatile organic compounds of relatively low solubility are readily purged from a water sample by a dispersed stream of inert gas. The volatile compounds partition to the gas phase and are cryogenically trapped and concentrated on an absorbent material. The trap is then heated to desorb the compounds, which are carried to the gas chromatograph for separation and quantification by an electron capture detector (Leppo, 1975; Thompson, 1976).

Due to their chemical structure, CFCs have a high electron capturing cross-section. Therefore, very low CFC concentrations, in the picomole per kilogram (pmol/kg) or picomole per liter (pmol/l) range, can be determined with the electron capture detector (ECD). Since the ECD response toward halocarbon compounds decreases in the order

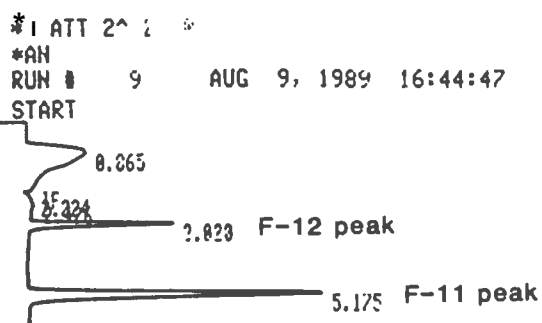
I>Br>Cl>>F, the detector is more sensitive to F-11 (CCl_3F) than to F-12 (CCl_2F_2) (Poole and Schuette, 1985). As shown in Figure 7, the injected concentration of F-12 in picomoles is about 30% greater than the F-11 concentration; however, the detector response, as indicated by the area of the peaks, is about 67% greater for F-11 than for F-12.

WATER SAMPLES

The analytical system used to determine F-11 and F-12 concentrations in water samples is modeled after a system developed by Bullister and Weiss (1988) to measure F-11 and F-12 concentrations in air and sea water.

A schematic of the system is shown in Figure 8. Argon-methane carrier gas is purified to remove any freons by passing through a molecular sieve trap. The gas stream is then directed through the water sample. The CFCs partition into the gas phase and, after passing through a MgClO_4 trap to remove moisture, are cryogenically trapped and concentrated. The cryogenic trap consists of 1/8 inch diameter stainless steel tubing packed with Porasil C and Poropak T absorbent material. The trap is cooled by submersion in propanol held at -30 degrees centigrade by a NESLAB model CC-60II CryoCool refrigeration unit. After purging is complete, the trap is isolated from the gas stream, removed from the propanol, and heated with water held at 100 degrees centigrade to desorb the compounds. Carrier

V_X.



TIMETABLE STOP

Closing signal file M:SIGNAL .BNA

RUN# 9 AUG 9, 1989 16:44:47

SAMPLE# 179

SIGNAL FILE: M:SIGNAL.BNA

ESTD

RT	AREA	TYPE	CAL#	AMOUNT
3.020	73002	TVB	1R	.075
5.175	221487	BB	2R	.052

TOTAL AREA= 497833
 MUL FACTORS: 1.000E+00

FIGURE 7. Typical chromatogram for injection of one large loop of standard gas containing 0.052 picomoles F-11 and 0.075 picomoles F-12.

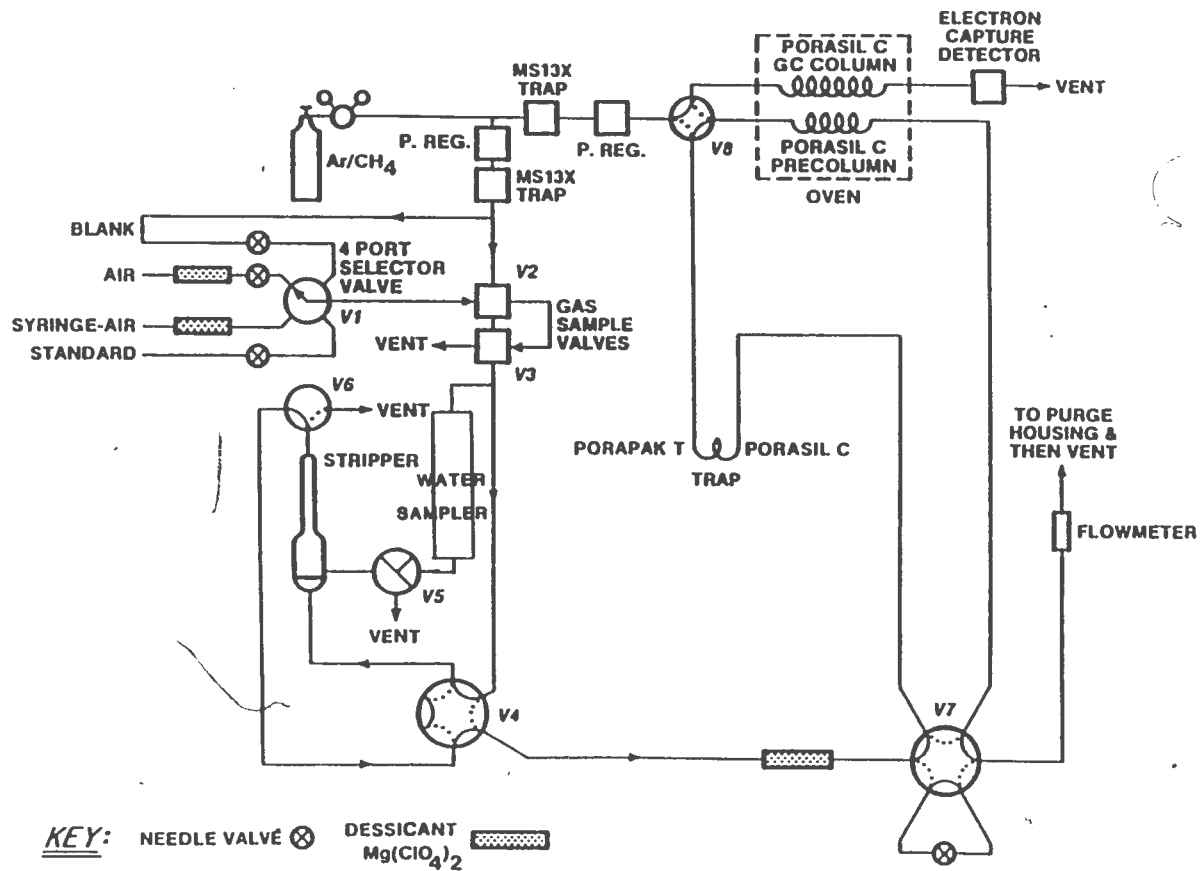


FIGURE 8. OFC analytical system (Water Bulletin of ONI, 1969). System was modified after June sampling period by removing the stripper and V5. The water sampler was then inserted between V4 and V6 for pumping directly into the sample.

gas is then sent through the trap and the desorbed compounds are carried to the chromatographic columns and electron capture detector for quantification. Typically, a 30 cc water sample is purged and trapped for 4 to 6 minutes. The entire analytical run required approximately 12 minutes.

Water samples were initially transferred to the analytical system by inserting the sampler into the system via swagelock fittings. To reduce the potential for contamination, after the end caps were removed from the sampler, the portion of copper tubing above the crimped area was flushed with carrier gas. Flushing continued as the swagelock fittings were tightened.

After the copper sections were uncrimped, the water sample was transferred to the purge vessel (stripper) through a Hamilton valve (V5) for volume control. The purge vessel was a Supelco 10 cc glass model containing a porous frit at the lower end for dispersing the gas stream. The vessel was modified by fusing a portion of a glass buret to the top end to accommodate a larger sample and to allow for precise determination of sample volume.

Since the potential for sample contamination during the transfer step was high, the system was redesigned slightly by removing the Hamilton valve and purge vessel. The sampler was then inserted directly into the system to allow purging of the water sample within the sampler.

GAS SAMPLES

The analytical system also allows for analysis of blank and standard gas samples. Through a series of valves, standard or purified carrier gas is directed through a small (0.5 cc) and large (3.0 cc) gas sample loop (Figure 8). By switching valves, gas in one or both loops is isolated and allowed to reach equilibrium with atmospheric pressure. Carrier gas is then sent through the loop(s) and carries the known volume of blank or standard gas through the system. Gas samples are cryogenically trapped and concentrated, then desorbed and quantified by the same procedures followed for water samples. To obtain various gas sample volumes other than 0.5 or 3.0 cc, successive volumes of gas are isolated in the loop(s) and then injected through the system. The successive volumes are cryogenically trapped and the total volume quantified during one analytical run.

Figure 7 illustrates a typical chromatogram from the injection of one large loop of standard gas or 0.075 picomoles F-12 and 0.052 picomoles F-11. The initial large peak is due to valve switching at the beginning of the run. The F-12 peak appears at approximately 3 minutes; the F-11 peak appears at about 5.2 minutes.

To ensure the system was free of contamination, blank runs with purified carrier gas were usually conducted with one large gas sample loop. Typically, no F-11 or F-12 were detected during the blank runs. The molecular sieve traps

absorbed F-11 or F-12 in the carrier gas for about 2 weeks. Appearance of a small F-12 peak during blank runs indicated the need to bake the molecular sieve traps at approximately 200 degrees Centigrade for 4 hours for reconditioning.

Compressed air obtained from a local dive shop was utilized as standard gas. The gas was contained in two aluminum tanks with a specially prepared inside coating of inert material. F-11 and F-12 concentrations in one tank were determined at Scripps Oceanographic Institute to be 371.9 ppt and 729.8 ppt, respectively. Using this gas as the primary standard, fluorocarbon concentrations in the second tank were determined for use as the working standard. F-11 and F-12 concentrations of the working standard were determined to be 499.7 ppt and 726.0 ppt, respectively.

Calibration curves were generated by injecting known volumes of standard gas through the gas samples loops. During sample analysis, five point calibration curves were established on a daily basis. As shown in Figures 9a and 9b, the curves were constructed using 1 Small Loop (SL), 3 SL, 1 Large Loop (LL), 2 LL, and 4 LL of standard gas.

To determine F-11 and F-12 concentrations in picomoles, the total number of moles (n) of standard gas injected through the gas sample loop(s) was calculated using the ideal gas law,

$$n = RT/PV$$

where P is atmospheric pressure, V is volume of gas, R is the

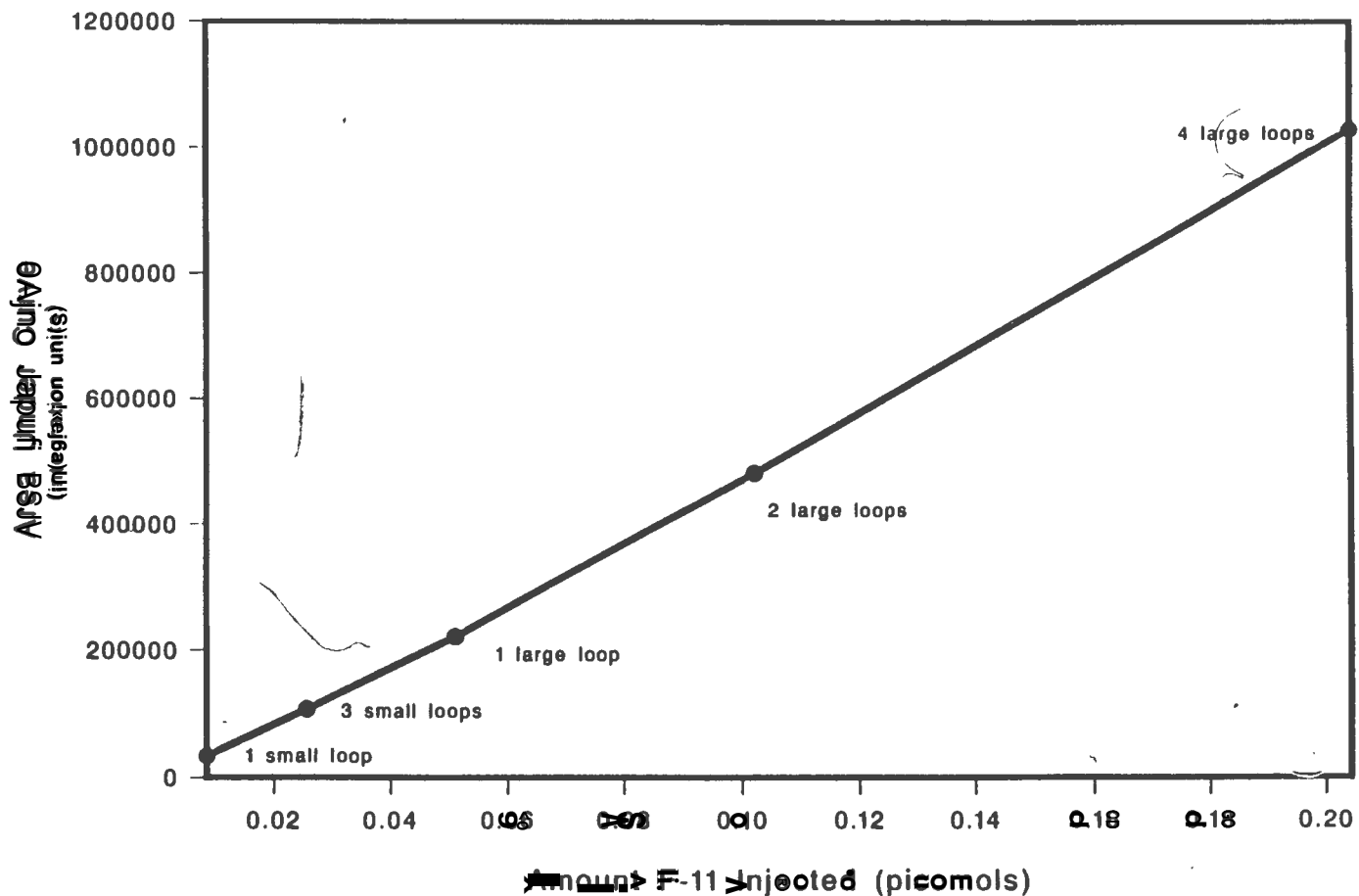


FIGURE 9a. F-11 calibration curve, 9/16/69.

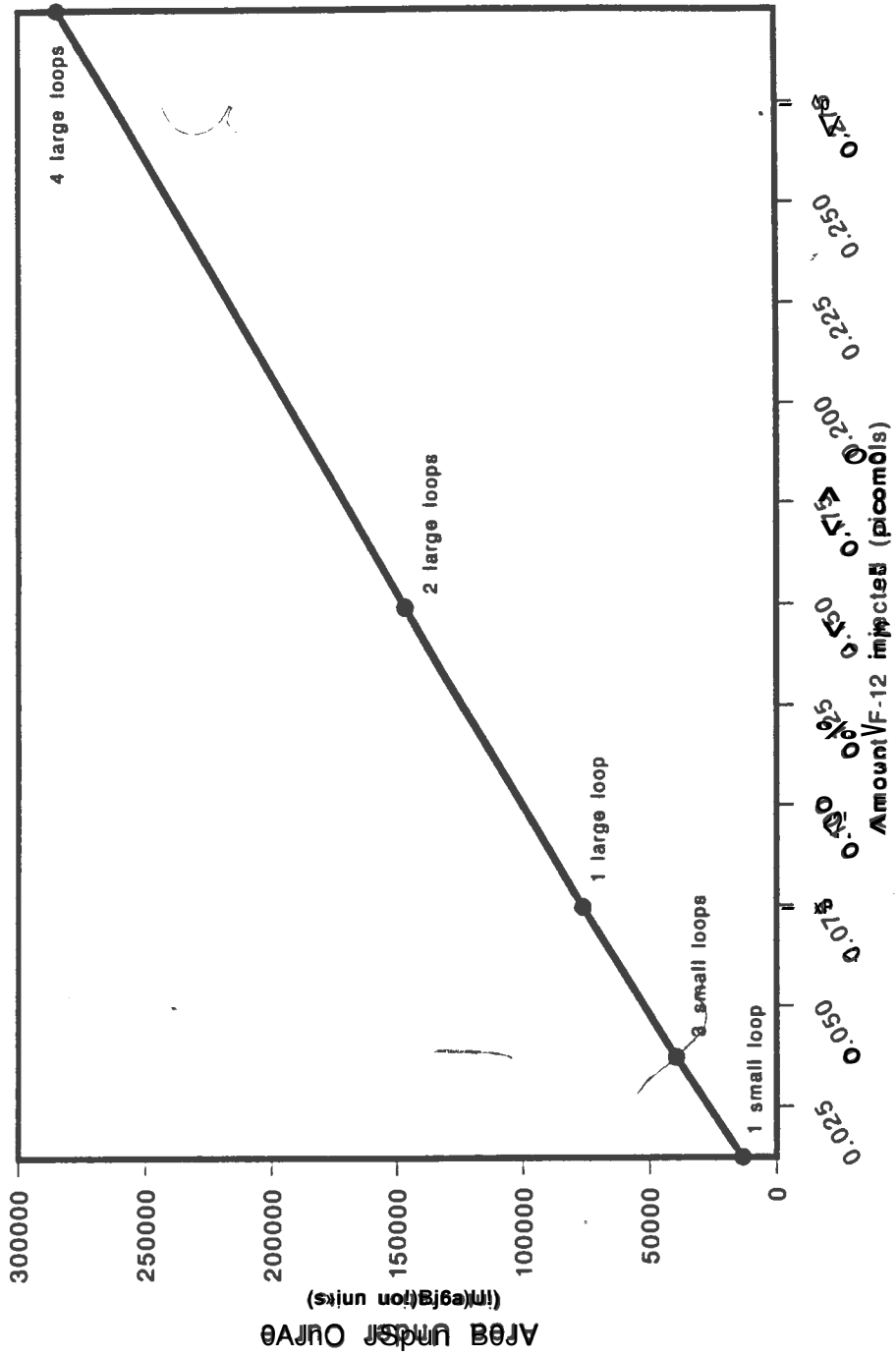


Figure 9B. F-12 calibration curve, 9/6/89.

universal gas constant, and T is temperature in degrees Kelvin. F-11 and F-12 concentrations in picomoles were calculated by multiplying (n) by the F-11 and F-12 concentrations, in part per trillion (ppt) contained in the standard gas. Atmospheric pressure and gas sample loop temperature were recorded during each analytical run.

Analyses of 1 large loop of standard gas were usually performed after every second or third water analysis to monitor short term variation in detector sensitivity due to changes in temperature and pressure. Typically, the variability for analyses of 1 large gas sample loop during the daily analytical runs was less than one percent.

WATER BLANKS

Initial attempts to obtain blank water for this study were made using a 750 milliliter glass sparging apparatus. Reagent grade distilled water was purged with purified nitrogen for varying time increments ranging from 30 minutes to 1.5 hours. A stainless steel sampler attached in a vertical position to a glass side arm near the bottom of the sparging vessel was then ~~bottom~~-filled with the water. After three sample volumes passed through the sampler, the copper ends were crimped and capped. A one meter length of 1/8 inch diameter stainless steel tubing was attached to the top of the sampler to prevent any back diffusion of atmosphere into the sampler.

Because the glass sparging apparatus proved to be quite fragile, numerous episodes of breakage of the glass side arm occurred during sampler attachment. Therefore, during the remainder of the study, blank water was obtained by filling the samplers with distilled water and purging directly into the samplers for varying time periods.

TRITIUM SAMPLE COLLECTION AND ANALYSIS

Samples for tritium analysis were collected in one liter glass bottles by U.S. Geological Survey workers. Analyses were performed either at the Desert Research Institute Laboratory, Reno, Nevada, or through the U.S. Geological Survey at the University of Miami, Miami, Florida.

RESULTS AND DISCUSSION

The Results and Discussion section is divided into three components: I) problems encountered with the analytical system and modifications to the system; II) experiments conducted to evaluate the samplers and determine an appropriate holding time for samples; and III) CFC and tritium analytical results for ground water samples collected throughout the Carson River Basin and comparison of CFC concentrations to tritium.

I: ANALYTICAL SYSTEM

Several problems were encountered with the analytical system and procedures. During the initial phase of this study in June 1989, water samples were transferred from the sampler to a purge vessel for analysis. As shown in Table 6, large variability for replicate samples was seen when using this method. For F-11, variability ranged from 0 to 99 percent, with most values greater than 30 percent. For F-12, variability ranged from 0 to 173 percent with most values greater than 50 percent.

There are two possible procedural explanations for this high variability. With this method, it was necessary to apply a small amount of back pressure to the sampler to force the water to drain through the valve into the purge vessel. Also, it was necessary to open the valve above the purge

vessel for pressure relief within the vessel during filling. Due to the high volatility of CFCs, some F-11 and F-12 may have been purged from the sample during filling and lost from the system. Also, the Hamilton valve was constructed with a teflon seat. Since teflon contains fluorocarbons and has also been shown to absorb fluorocarbons, F-11 and F-12 could have been removed from or introduced to the sample.

The other possible explanation for the large variability may be that CFC concentrations in pumped wells follow similar trends to VOC concentrations. Gibs and Imbrigiotta (1990) showed that VOC concentrations in pumped wells did not stabilize even though other monitored chemical and physical parameters such as EC, pH, and dissolved oxygen had stabilized. Therefore, the variation may be naturally occurring. High variation in samples from pumped wells was also seen by Busenberg and Plummer (1992).

Because sample contamination could not be ruled out as the source of variability, the transfer step was eliminated by purging the water sample directly in the sampler.

Although reproducibility of results increased significantly by purging directly into the sampler, there were some problems associated with this method. The porous frit contained in the lower end of the purge vessel dispersed the gas stream as it entered the water sample. Water samples in the purge vessel were completely purged of F-11 and F-12 after 4 minutes of purging. To disperse the gas stream in

the modified system, a plug of glass wool was placed in the tubing below the connection point of the sampler; however, the glass wool did not disperse the gas stream as finely as the frit. Therefore, even after increasing the purge time to 6 minutes, it was often necessary to restrip samples with this procedure.

Also increased pressure within the sampler during purging sometimes caused the water sample to rise into the magnesium perchlorate trap. When this happened, the sample was lost because purging had to be discontinued to prevent water from entering the cryogenic trap.

Additionally, when the water sample was transferred to the modified purge vessel, the exact amount of sample purged was read from the buret. When purging directly into the sampler, sample volume could only be obtained by calibrating each sampler with distilled water, which may have lead to some small error in determining sample volume.

The other main problem with the analytical system was quantification at very low concentrations. As shown in Figures 9a and 9b, the F-11 calibration curve appears to be non-linear at very low concentrations, and the curves for both F-11 and F-12 do not pass through zero. A consequence of this is that for small peak areas, the picomole value assigned from the calibration curve was larger than would be expected if the curve was linear for very small concentrations. This may have contributed to the difficulty

in obtaining blank water.

Also, for very small peak areas, the peak was not integrated or a negative picomole value was provided from the calibration curve. These results have been reported as 0.01 pmol/l.

II: SAMPLER EVALUATION EXPERIMENTS

One of the main study objectives was to evaluate the stainless steel sampler described in the methods section to determine if the sampler would minimize contamination during sampling and allow for storage prior to analysis.

In order to reduce sampling costs, the original proposal was to re-use the copper crimp sections for several sampling runs. However, after several laboratory experiments with re-used crimp sections and use during some actual sampling runs, it was determined that copper sections could only be used once. Although the copper tubing was malleable enough to be closed off with vice grips and then reopened once, subsequent use created openings which were a fraction of the original inside diameter. The reduced inside diameter allowed for very slow filling of the sampler during the next sampling run. Also, during sample analysis, when the re-used tubing was uncrimped, the opening was even more reduced, resulting in very slow filling of the purge vessel. Slow filling of the purge vessel during the transfer step probably allowed for some volatilization of CFCs, contributing to poor

reproducibility of analytical results for this method.

Since an average of 18 crimp sections was needed to collect samples from three sites per day, and the process of making the sections was fairly labor and time intensive, experiments were performed to test the feasibility of using Valco mini valves to replace the copper sections.

Blank water experiments were conducted to compare the valves and copper crimp sections and evaluate sample holding time. The experiments were conducted by filling samplers equipped with either valves or crimp sections with distilled water and purging with CFC free nitrogen to obtain CFC free water. Samplers were purged for varying time increments, from 15 minutes to 1 hour. The purged samples were either analyzed immediately or held for varying time periods from 30 minutes to 24 hours.

The criteria for determining blank water was based on blank values seen in previous studies. Bullister (1984) sampled deep ocean water stations expected to contain negligible levels of CFCs based on tritium and radiocarbon data. The samples showed very low concentrations, 0.005-0.010 pmol/kg, of both F-11 and F-12. Nevison (1987) found average residual values of 0.079 pmol/kg for both F-11 and F-12 in ground water samples collected from wells. These values were considered to be background concentrations for that study and were subtracted from analytical results. For the experimental blank water determinations in this study, a

CFC concentration of less than 0.05 pmol/l was used.

Results of the experiments to compare valves and crimp sections and evaluate sample holding times are discussed below.

RESULTS OF LABORATORY EXPERIMENTS CONDUCTED TO COMPARE CRIMP SECTIONS AND VALVES AND EVALUATE SAMPLE HOLDING TIMES

Results of the laboratory experiments are shown in Table 3. F-12 was not detected in experiments until August, 1989. The initial laboratory experiments with purged water conducted through May 1989 to compare valves and crimp sections showed that samplers with copper crimp sections consistently showed F-11 concentrations less than 0.05 pmol/l immediately after purging and after holding times up to 24 hours (Table 3). F-11 concentrations greater than 0.1 pmol/l were consistently seen in samplers with valves after holding the sample for a period of time before analysis. This indicated the valves which contained a teflon seat may be preferentially adsorbing or desorbing F-11 or that valves allowed for some atmospheric diffusion into the sampler.

On June 17, 1989, crimp section experiments showed high F-11 concentrations after holding the purged water for twelve or more hours; however, it is not known if these values are a result of the purging/holding procedure, sample contamination, or malfunctioning of the analytical system. On June 19, 1989, chromatographic instrument problems occurred and the system was down until July 3, 1989.

Table 3. Results of laboratory experiments comparing samplers equipped with valves or crimp sections.

DATE	METHOD	PURGE TIME Hours	HOLD TIME Hours	F-11 pmol/l ¹	F-12 pmol/l
5/9/89	valves	0.75	0 ²	0.01 ³	ND ⁴
	valves	1.0	0	0.01 ³	ND
	valves	0.5	0	0.01 ³	ND
	valves	0.25	0	0.01 ³	ND
	valves	0.50	0	0.01 ³	ND
	valves	0.50	0	0.00	ND
	valves	0.50	0	0.01 ³	ND
	valves	0.50	0	1.5	ND
5/10/89	valves	0.50	17	0.07	ND
	valves	0.50	17	0.2	ND
	valves	0.50	17	0.17	ND
	valves	0.50	6	0.13	ND
	valves	0.50	4	5.0	ND
5/11/89	valves	0.50	0	0.03	ND
	valves	0.50	0	0.13	ND
5/12/89	valves	0.50	0	0.03	ND
	valves	0.50	0	0.13	ND
	valves	1.0	0	0.13	ND
5/21/89	valves	0.75	0	0.03	ND
	valves	0.50	2	0.27	ND
	crimps	0.75	0	0.03	ND
	crimps	0.50	2	0.01 ³	ND
5/25/89	valves	0.50	1	0.07	ND
	valves	1.0	0	0.01 ³	ND
	valves	0.50	0	0.03	ND
	crimp	1.0	0	ND	ND
	crimp	1.0	0	0.01 ³	ND
5/26/89	crimp	1.0	0	ND	ND
	crimp	1.0	6	ND	ND
	crimp	1.0	5.5	0.03	ND
5/29/89	valves	1.0	14	0.03	ND
	crimps	1.0	14	0.01 ³	ND
	crimps	1.0	15	0.03	ND
	crimps	1.0	15	0.01 ³	ND
	crimps	1.0	15	0.01 ³	ND
	crimps	1.0	18	0.01 ³	ND
	crimps	1.0	18	ND	ND
	crimps	1.0	18	ND	ND

%

Table 3.-continued-

DATE	METHOD	PURGE TIME Hours	HOLD TIME Hours	F-11 pmol/l	F-12 pmol/l
5/30/89	valves	1.0	18	ND	ND
	valves	1.0	19	0.03	ND
	valves	1.0	20	0.10	ND
	valves	1.0	20	0.07	ND
5/31/89	valves	1.0	9.5	0.07	ND
	valves	1.0	10	0.10	ND
	valves	1.0	9.5	0.03	ND
	valves	1.0	9.5	0.07	ND
	valves	1.0	10	0.13	ND
	valves	1.0	10	0.23	ND
6/7/89	valves	1.0	11.5	0.5	ND
	valves	1.0	12	0.8	ND
	valves	1.0	13	0.4	ND
	valves	1.0	12	1.13	ND
	valves	1.0	12	0.5	ND
	valves	1.0	13	0.3	ND
6/17/89	crimps	1.0	13	ND	ND
	crimps	1.0	13	0.27	ND
	crimps	1.0	13	1.33	ND
	crimps	1.0	13	1.8	ND
	crimps	1.0	12	8.1	ND
	crimps	1.0	12	3.4	ND
8/1/89	valves	1.0	0	0.10	0.13
	restrip			0.07	0.07
	valves	1.0	0	0.21	0.12
	restrip			0.09	ND
	valves	1.0	0	0.07	ND
	restrip			0.03	ND
	valves	1.0	0	0.13	0.21
	restrip			0.03	ND
	crimps	1.0	0	0.03	ND
restrip			ND	ND	
8/2/89	crimps	1.0	24	0.13	ND
	crimps	1.0	24	0.03	ND
	restrip			ND	ND
	crimps	1.0	24	0.09	0.07
	valves	1.0	24	0.37	2.97
	valves	1.0	24	0.25	0.10
	valves	1.0	24	0.41	0.16
	valves	1.0	24	0.66	0.21

1. picomoles per liter
2. analyzed immediately after purging
3. Due to shape of calibration curve, the integrator assigned a value of 0.000 pmol/L or a negative pmol/L value for very low CFC concentrations which produced small peaks. For this study, such values were assigned a value of 0.01 pmol/L for this study.
4. No detection; no peak was produced on the chromatogram.

Water with low levels of F-11 and F-12 could not be obtained consistently during June through September, 1989. Experiments conducted in August, 1989, consistently showed F-11 and F-12 concentrations greater than 0.1 pmol/l in purged samples for both the valve and crimp methods. This may have been due to incomplete purging of the water sample, contamination, or relatively high picomole values assessed to small peak areas.

RESULTS OF GROUND WATER SAMPLES COLLECTED IN SAMPLERS WITH VALVES OR COPPER CRIMP SECTIONS

To compare results of ground water samples collected in samplers with valves or copper crimp sections, samples using both methods were collected at sites CDP-7 and CDP-16 in the Carson Desert (Figure 10).

As shown in Table 4, at CDP-7 there was no difference in F-11 concentrations between samples collected in samplers with valves versus samplers with crimp sections. Variability within each method was fairly small (9% for crimp method and 16% for valve method).

F-12 analytical results for this site show a slight difference between methods. The average ~~F-12~~ concentration with the crimp method was near the detection limit (0.01 pmol/), while the F-12 concentration with the valve method was 0.11 pmol/l. Variability for triplicate samples with each method was greater than 100 percent.

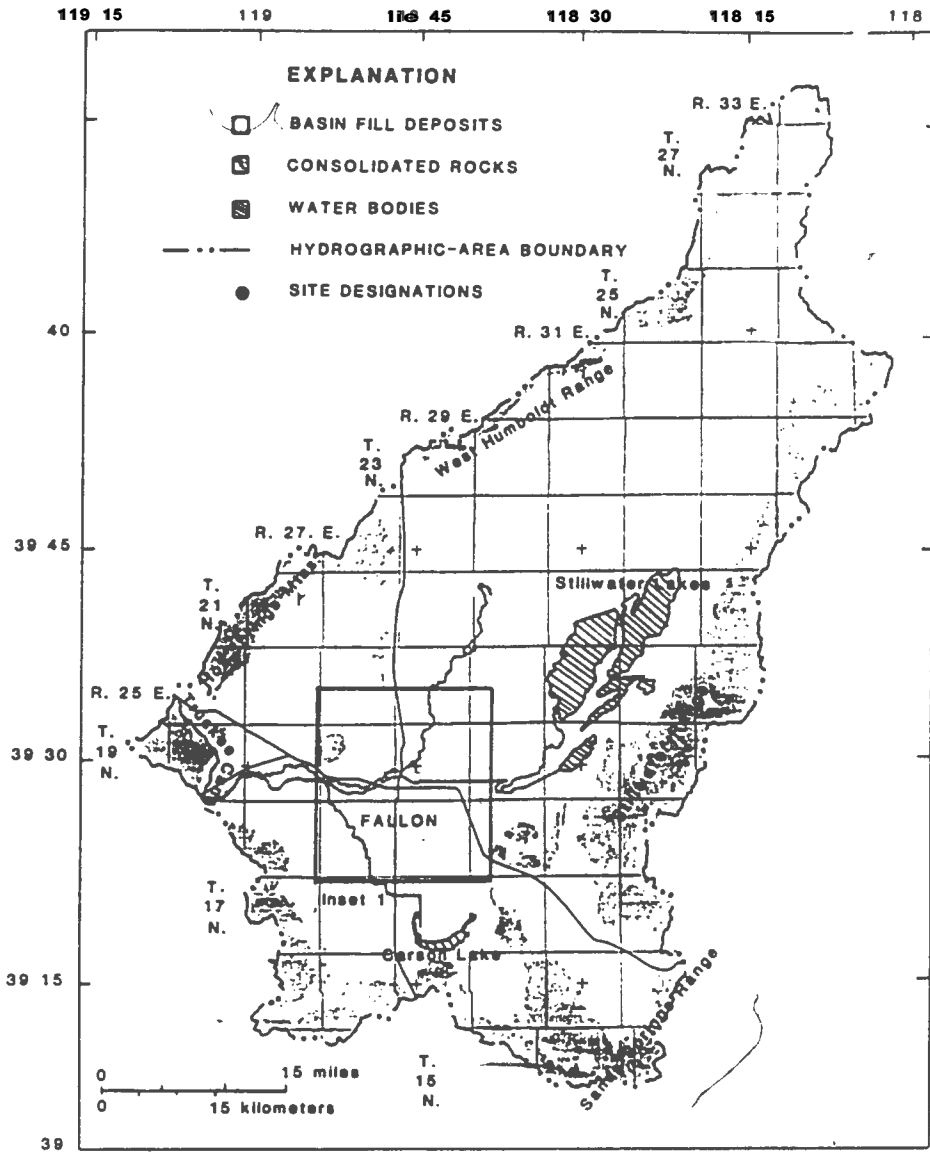


FIGURE 10. Location of ground water sampling sites in the Carson Desert (after Welch and others, 1969). Site designations correspond to CDP-number in Tables 6 and 7. Details of Inset 1 are shown on the following page.

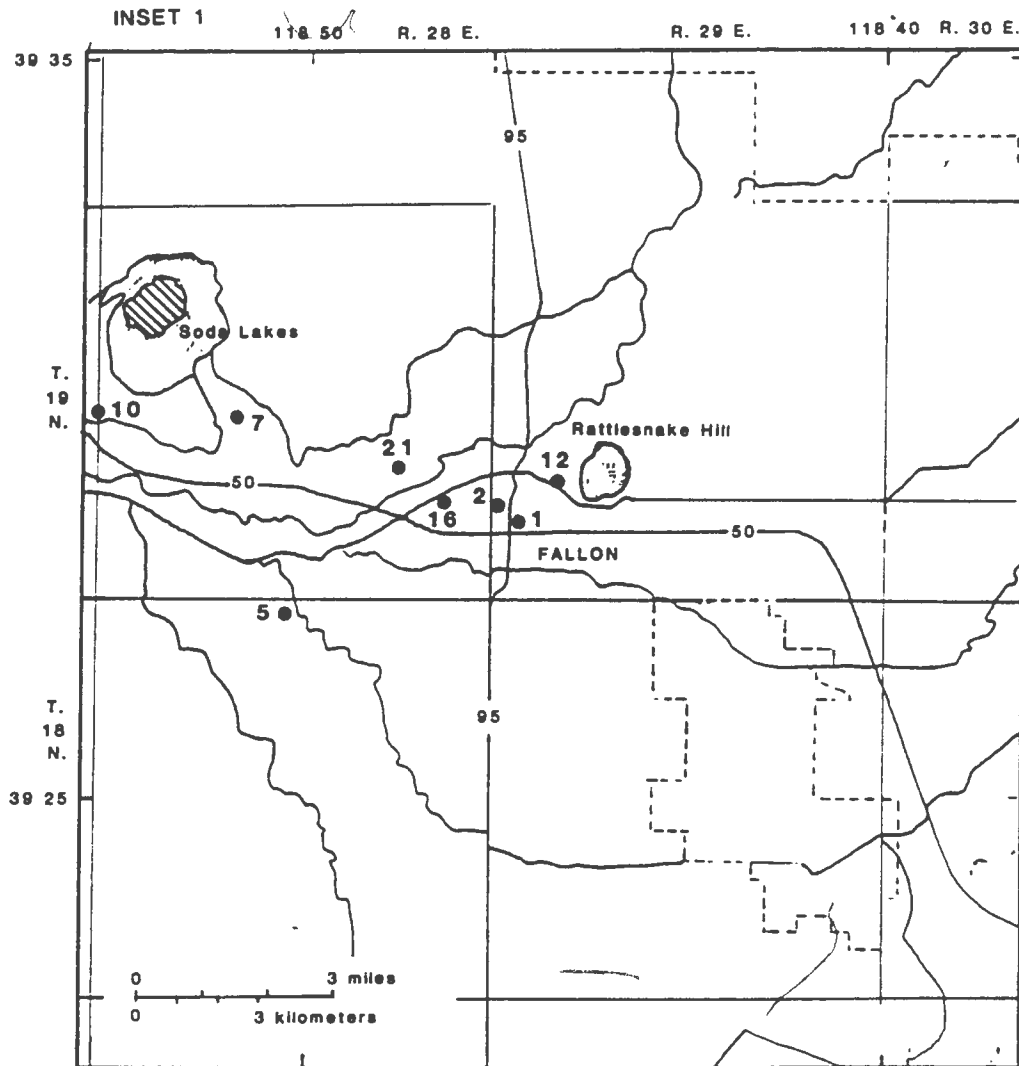


FIGURE 10.-Continued. Details of Inset 1.

Table 4. Results of field samples collected to compare samplers equipped with valves or crimp sections.

DATE	SITE	COMMENTS	F-11 pmol/l ¹	F-12 pmol/l
6/1/89	CDP-7 31 TU ²	field blank	0.3	ND ³
		crimped	0.6	0.03
		crimped	0.7	0.0
		crimped	0.7	0.0
			X ⁴ =0.7	X= 0.01
			% ⁵ =8.6	%= 173
		valves	0.8	0.0
		valves	0.8	0.07
		valves	0.6	0.27
			X= 0.7	X= 0.11
	%= 15.8	%= 123		
6/2/89	CDP-16 <5 TU	lab blank	0.2	ND
		field blank	0.2	ND
		crimped	0.5	ND
		crimped	2.0	0.2
		crimped	0.3	ND
			X= 0.9	X= 0.07
			%= 99	%= 173
		valves	0.3	ND
		valves	0.5	0.3
		valves	0.3	0.3
	X= 0.4	X= 0.2		
	%= 31	%= 86		

1. picomoles per liter
2. tritium units
3. no detection
4. mean of replicate sample results
5. % variability of replicate sample results

At CDP-16, the average F-11 concentration using the valve method was 0.4 pmol/l with 31% variability. The average F-11 concentration using the crimp method was 0.9 pmol/l with 99 percent variability; however, one sample had an F-11 concentration of 2.0 pmol/l, which is a much higher concentration than all other samples collected at this site and may represent sample contamination. If this value is disregarded, the average F-11 concentration for the crimp method is 0.4 pmol/l.

F-12 results for CDP-16 showed large variability within each method, with concentrations ranging from no detection to 0.2 pmol/l for the crimp method and no detection to 0.3 pmol/l for the valve method.

Generally, the field sampling analytical results show no significant difference between field samples collected in samplers with valves or copper crimp sections. The large variability in F-12 results for triplicate samples collected at a site for both methods may be due to natural variation of F-12 concentrations in pumped wells (Busenberg and Plummer, 1992) or result from contamination during sampling and analysis.

FIELD BLANKS

As shown in Tables 4 and 5, results of purged samples used as lab and field blanks during sampling periods were not consistent. Results, especially for F-11, were often much

Table 5. Results of laboratory and field blank water samples; values in picomoles/liter.

DATE	F-11		F-12	
	LAB	FIELD	LAB	FIELD
6/1/89	0.3	0	0	0
6/2/89	0.2	0.2	0	0
6/8/89	0.2	0	0	0
6/13/89	0.2	0.2	0	0
8/21/89	0.09	0.09	0	0
8/22/89	0.09	0.09	0.7	0.5
9/12/89		2.2		0.1
9/14/89		0.45		0.01
9/15/89		0.3		0.01
9/18/89		0.9		0.01
9/19/89		2.8		0.01

greater than accepted blank values and sometimes greater than concentrations seen in ground water samples for that day. Blank values for F-12 obtained on August 22, 1989, and for F-11 on September 19, 1989, were greater than sample concentrations.

Elevated field blank water results on September 12 and 19, 1989, most likely indicate atmospheric contamination of the sample. Other elevated results may be due to the relatively high picomole values assessed to small peak areas.

GENERAL CONCLUSIONS OF SAMPLE EVALUATION EXPERIMENTS

- The results indicate that blank water with CFC concentrations less than 0.05 pmol/l could not be consistently obtained. As indicated previously, one problem may have been the high picomole values produced from the calibration curve for very small peak areas. Another problem may have been incomplete purging of CFCs from the distilled water used for the experiments. Due to the inconsistent values obtained for blank water, it was not possible to evaluate sample holding times. Therefore, all ground water samples collected for the CFC/tritium comparison were analyzed the same day as collected.
- Laboratory experiments conducted to compare valves and crimp sections initially showed that blank water with no detectable F-12 concentrations and F-11 concentrations of about 0.03 pmol/l were obtained using samplers with copper crimp sections. Holding times up to 24 hours were possible. However, water with low levels of F-11 and F-12 could not be obtained consistently during June through September, 1989. Again, this may have resulted from incomplete purging of blank samples or problems with quantifying small peak areas.
- Field sampling results showed little difference between the valves and crimp sections for F-11; however, F-12 results showed large variabilities.

- Based on the laboratory experiment results, a decision was made to conduct all further site sampling using samplers with copper crimp sections.
- CFC concentrations in some field and lab blanks were greater than CFC concentrations for the water samples collected the same day. Therefore, no blank values were subtracted from final analytical results.

III: RESULTS OF SAMPLES COLLECTED TO TEST THE RELATIONSHIP BETWEEN CFC AND TRITIUM CONCENTRATIONS

GENERAL COMMENTS

To evaluate the general relationship between CFC and tritium concentrations, eighteen domestic and fifteen municipal wells throughout the Carson River Basin were sampled and analyzed for dichlorodifluoromethane (F-12), trichlorofluoromethane (F-11), and tritium. Samples were collected during two periods, June 1989 and August/September 1989. During the June period, samples were only collected in the Carson Desert (Figure 10). Additional sampling sites during August and September are shown in Figures 11-14. A complete data table including well locations is presented in Appendix I.

Results of the June sampling period are discussed separately from the August/September results for two reasons. The electron capture detector was replaced in July, 1989. The

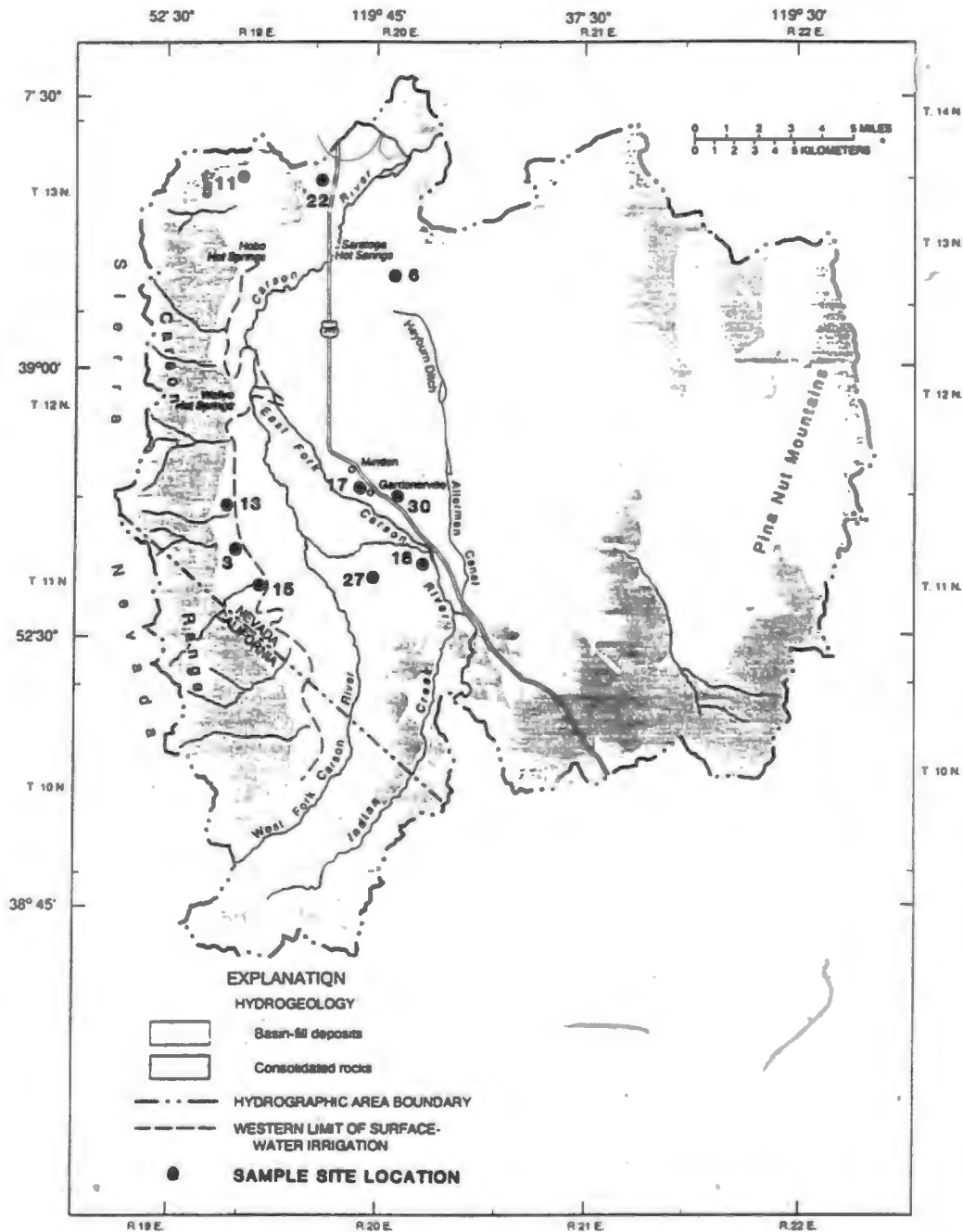


FIGURE 11. Location of ground water sampling sites in Carson Valley (after Welch and others, 1989). Site designations correspond to CVP-number in Table 7.

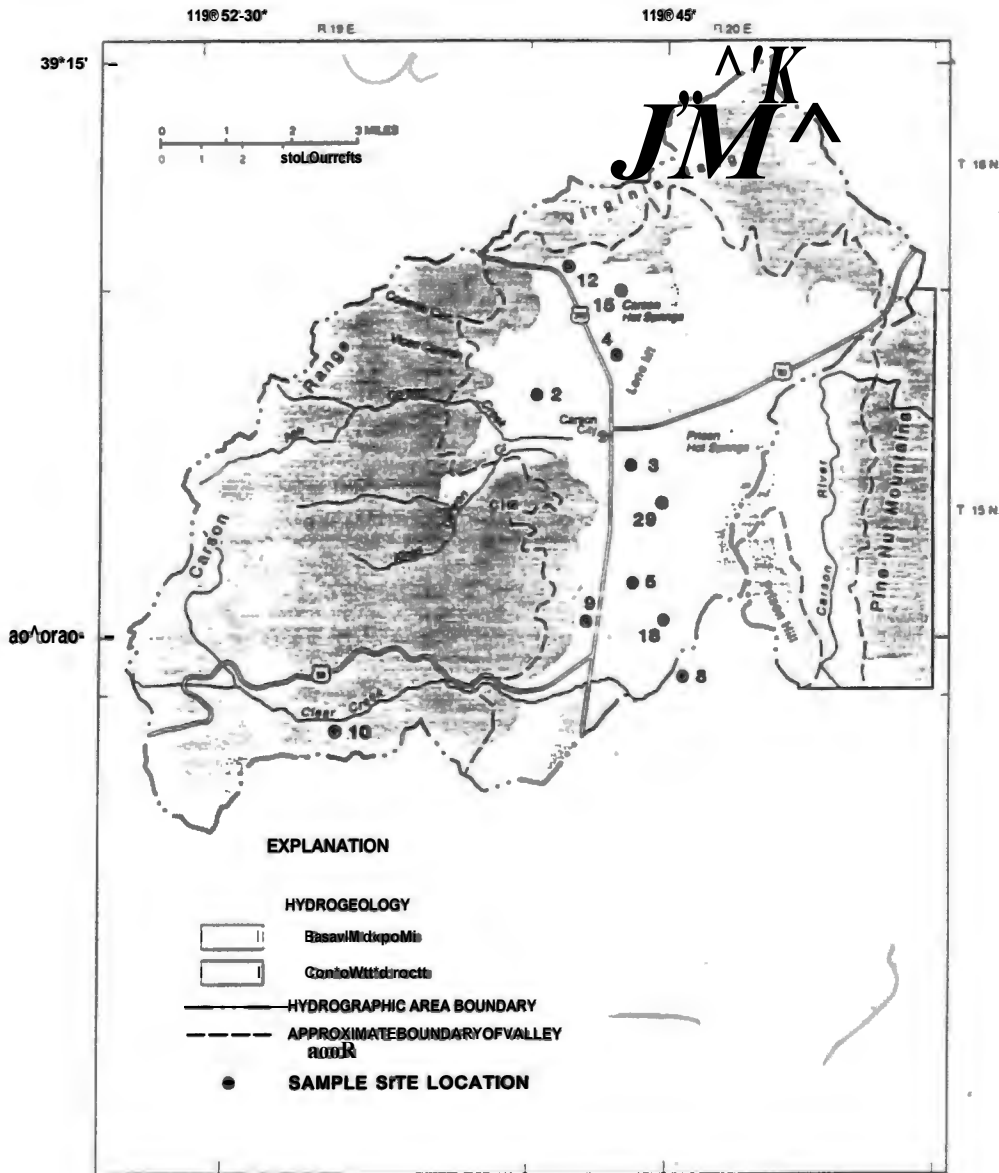


FIGURE 12. Location of sampling sites in Eagle Valley (after Welch and others, 1989). Site designations correspond to EVP-number in Table 7.

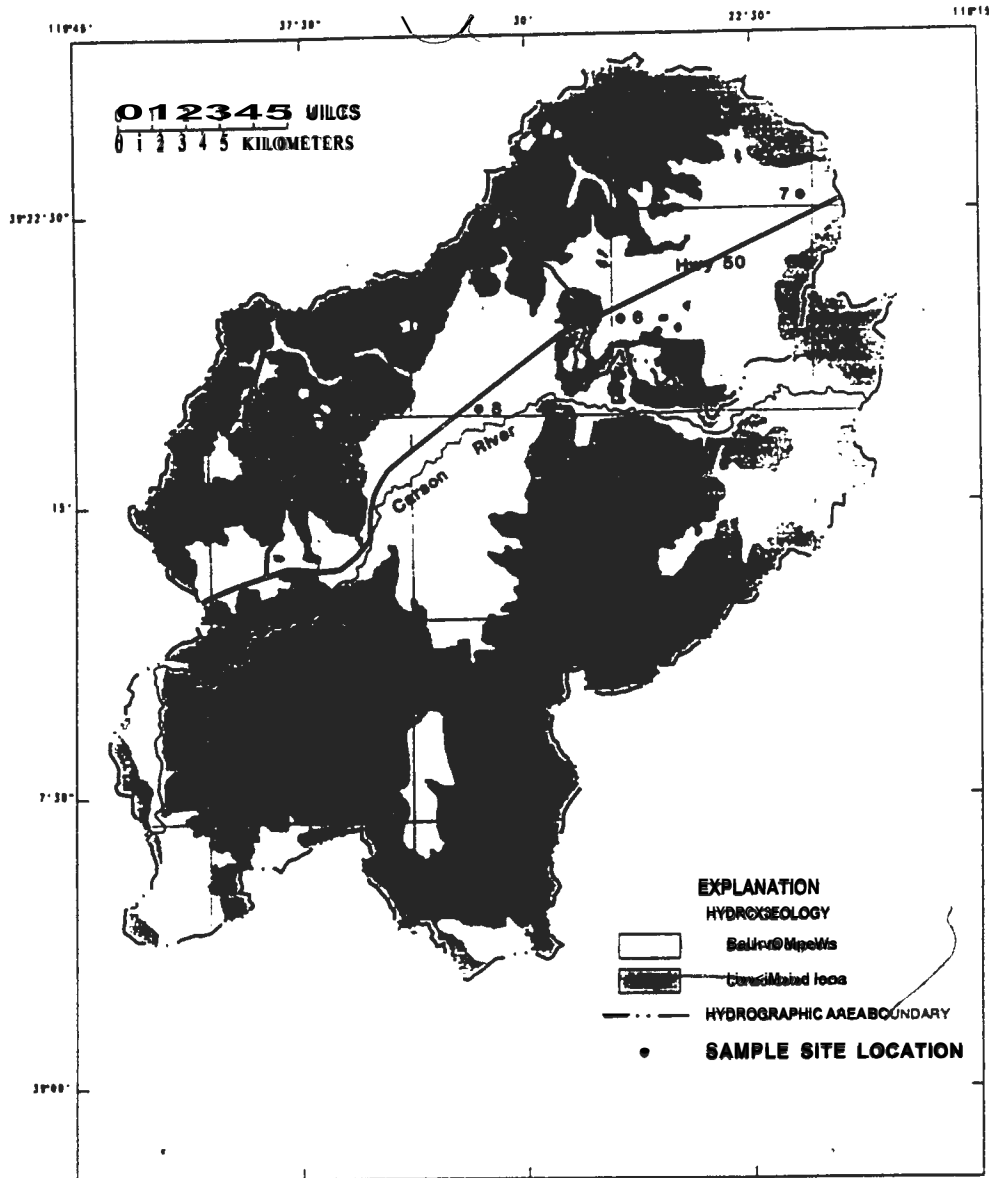


FIGURE 13. Location of ground water sampling sites in Dayton Valley (after Welch and others, 1989). Site designations correspond to DVP-number in Table 7.

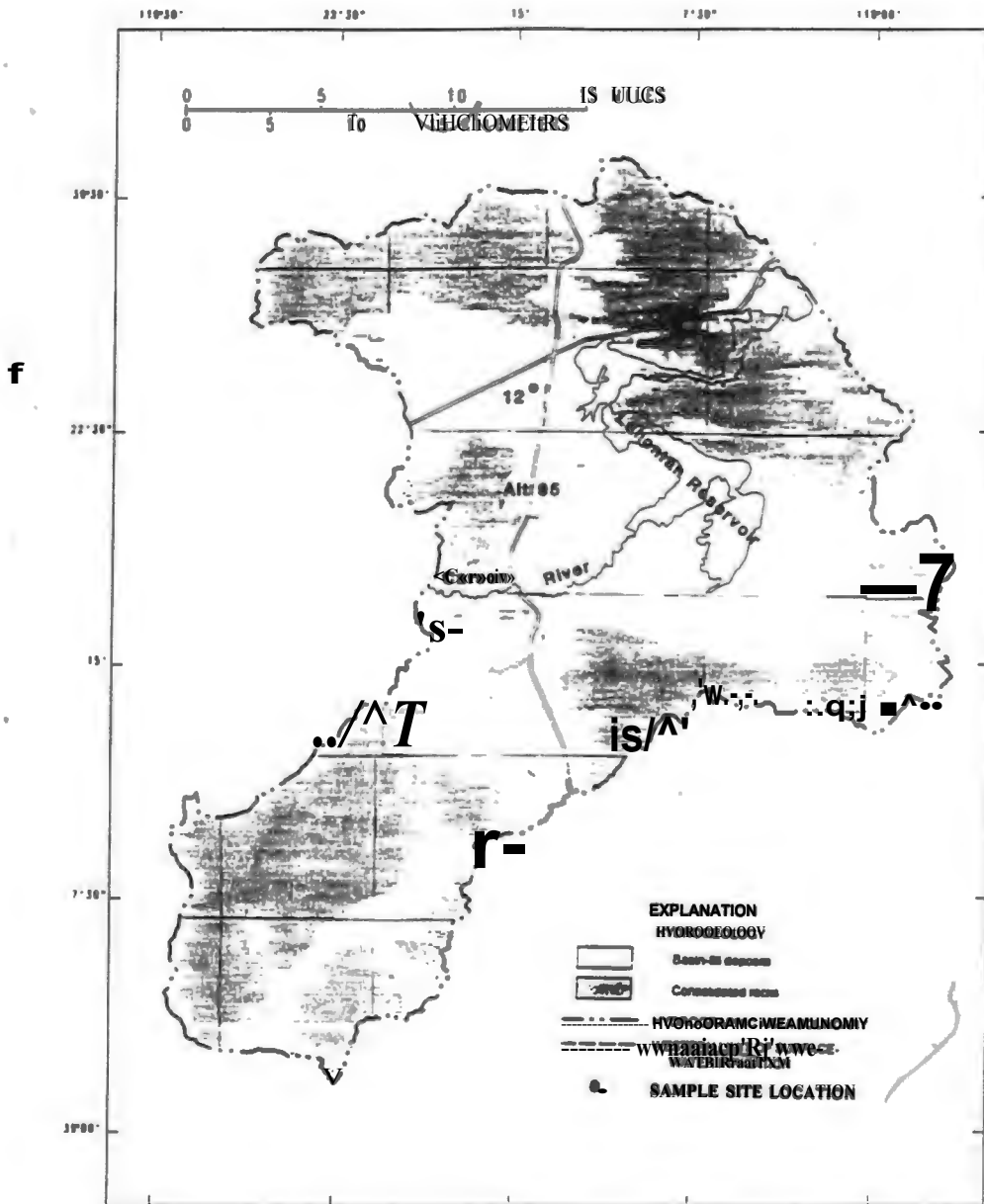


FIGURE 14. Location of ground water sampling site in Churchill Valley (after Welch and others, 1989). Site designation corresponds to DVP-number in Table 7

new detector provided for increased sensitivity of the analytical system which potentially affected results, especially at very low concentrations. Also, for sample analysis during August and September, samples were purged directly in the sampler without transferring the sample to the purge vessel.

Comparison of CFC concentrations to tritium in order to determine relative ground water age assumes the tritium values represent the relative age of the water. Estimates of ground water age based on tritium concentrations are presented in Table 1. A general interpretation of the age relationship is that tritium values less than 5 tritium units (TU) indicate the water is greater than forty years old, and tritium values greater than 5 TU indicate the water is less than forty years old.

Anomalous CFC concentrations considered to be contaminated are based on CFC air/water equilibrium concentrations observed in other studies. Bullister (1984) determined F-11 concentrations of 5.5 pmol/kg and F-12 concentrations of 2.3 pmol/kg in surface seawater in equilibrium with the atmosphere. ~~BUSENBERG~~ and ~~PLUMMER~~ (1992) determined concentrations of CFCs at or near equilibrium with 1989 air at sites located in rural areas away from major sewage-treatment plants. F-11 concentrations ranged from about 5.7 to 7.4 pmol/kg. F-12 concentrations ranged from about 3.2 to 4.7 pmol/kg. For this study,