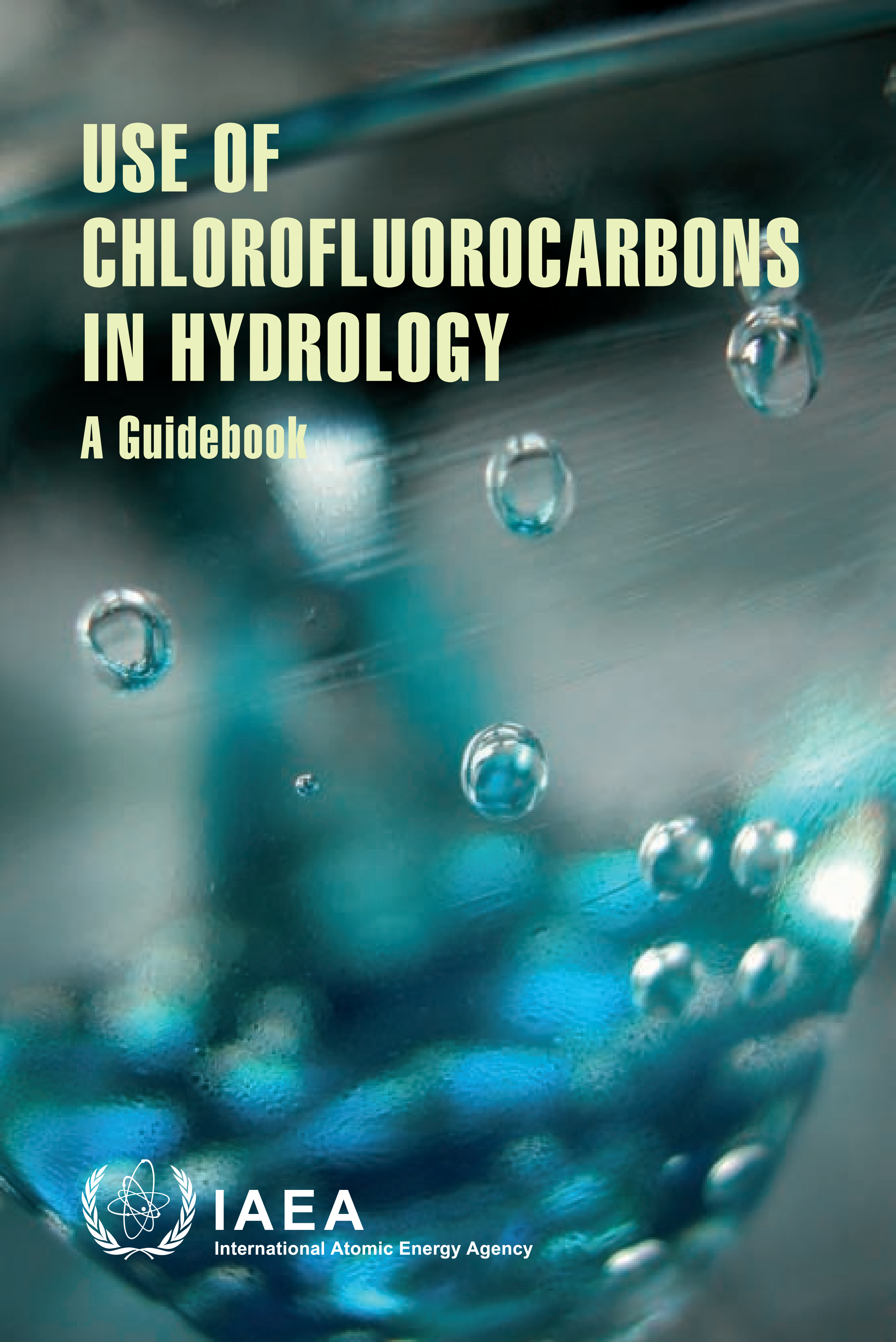
# USE OF CHLOROFLUOROCARBONS IN HYDROLOGY

## A Guidebook



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## A GUIDEBOOK

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# FOREWORD

Groundwater is used to meet nearly half of the global freshwater demand for domestic and agricultural use. Sustainable use of groundwater resources is, therefore, an important part of the overall efforts required for sustainable human development. Hydrological investigations to assess groundwater resources and to develop sustainable management strategies require a variety of scientific information, including the occurrence and rate of aquifer recharge. In arid and semi-arid areas, natural tracers, such as the environmentally stable isotopes of oxygen and hydrogen and the radioactive isotope tritium, are unique tools for recharge characterization. The atmospheric input of tritium from thermonuclear bomb tests of the 1950s and early 1960s provided an ideal tracer for determining the presence and rate of modern recharge in shallow aquifers. As the atmospheric concentration of tritium declined, its use for quantifying recharge by estimating the age of groundwater became less reliable. Alternative tools, such as concentrations of the daughter product of tritium ($^3$He) and chlorofluorocarbons (CFCs) were devised for quantifying modern groundwater recharge. Measurement of the concentrations of a number of CFCs, which are synthetic compounds used in the industry, provides a complementary tool for corroborating and/or validating recharge estimations based on isotope data.

The development of the CFC technique as a tool for dating groundwater has occurred over approximately the last 20 years and a number of research publications have documented its use in specific aquifers. This publication is intended to facilitate a comparative analysis of CFC and isotope techniques and a wider use of the CFC technique under appropriate conditions by providing a description of its scientific basis, sampling and measurement methods, interpretation and limitations of data, and a variety of case studies.

This publication is an addition to a number of other IAEA reports and guidebooks that have been published over the last forty years to facilitate the use of isotopes in hydrology. It is aimed at students, teachers and practitioners, and should serve as a reference document for more advanced researchers.

The IAEA officers responsible for this publication were M. Gröning, L.F. Han and P. Aggarwal of the Agency's Laboratories and the Division of Physical and Chemical Sciences.

# *EDITORIAL NOTE*

*Owing to their number, the references in this publication have been left, as an exception, in the 'author-date' style. They have not been converted into the IAEA's numbered reference style.*

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## Chapter 1

# CHLOROFLUOROCARBONS IN AQUATIC ENVIRONMENTS

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## 1.1. INTRODUCTION

Chlorofluorocarbons (CFCs) are volatile, synthetic compounds of carbon, chlorine and fluorine that were produced commercially at the beginning of the 1930s for uses in refrigeration. CFCs are non-flammable, non-corrosive, very low in toxicity, and well suited for a variety of industrial and refrigerant applications. CFC-12 (dichlorodifluoromethane, $CF_2Cl_2$), produced commercially from 1930, and CFC-11 (trichlorofluoromethane, $CFCl_3$) produced from 1936, found wide applications in air-conditioning and refrigeration, blowing agents in foams, insulation and packing materials, propellants in aerosol cans, and as solvents. Many other CFC compounds have since been produced, most notably CFC-113 (trichlorotrifluoroethane, $C_2F_3Cl_3$), produced commercially from 1944. CFC-113 has been used primarily by the electronics industry in the manufacture of semiconductor chips, in vapour degreasing and cold immersion cleaning of microelectronic components, and as a solvent in surface cleaning procedures (Jackson et al., 1992). Release of CFCs into the atmosphere and subsequent incorporation into the Earth's hydrological cycle has closely followed production (Gamlen et al., 1986; Midgley and Fisher, 1993). By the late 1980s, cumulative production of CFC-12, CFC-11 and CFC-113 totalled approximately 10.2, 7.7 and 2.4 million t, respectively (*http://www.afeas.org*), and in the northern hemisphere, atmospheric concentrations had risen to approximately 480, 260 and 70 parts per trillion by volume (pptv), respectively.

CFCs have been the subject of intensive research in the atmospheric sciences because of their atmospheric ozone depleting properties (Molina and Rowland, 1974; Rowland, 1996), contributions to global warming (Hansen et al., 1989; Kroeze and Reijnders, 1992; Sihra et al., 2001) and relatively long atmospheric lifetimes (Volk et al., 1997). By 2001, atmospheric CFC concentrations were nearly constant or falling, due to regulations imposed by the Montreal Protocol to Reduce Substances that Deplete the Ozone Layer (1987) and subsequent amendments. In 2001, the average northern hemisphere concentrations of CFC-12, CFC-11 and CFC-113 in air were about 547, 262 and 82 pptv, and water in solubility equilibrium with 2001 air at, for example, 10°C and 1 atmosphere (1013.25 hPa) total pressure contained about 358, 751 and 99 picogram per kg of water (pg/kg), respectively.

In analysing air and water samples for CFCs, the CFCs are pre-concentrated using purge and trap procedures, separated using gas chromatographic techniques and measured with an electron capture detector (GC-ECD) (Bullister, 1984; Bullister and Weiss, 1988; Busenberg and Plummer, 1992). CFCs are routinely detected at concentrations in water of 0.3–1 pg/kg. For water recharged at approximately 10°C and 1013.25 hPa total pressure, the detection of 1 pg/kg permits recognition of groundwater recharged in the years 1945, 1950 and 1957 based on CFC-12, CFC-11 and CFC-113. The presence of CFC-12 indicates post-1945 recharge or older water samples that contain a fraction of post-1945 water. Similarly, detection of CFC-11 and CFC-113 indicates post-1950 and post-1957 water, or their mixtures, respectively.

CFCs have provided useful tools for tracing and dating post-1945 water (Busenberg and Plummer, 1992; Plummer et al., 1998a; Plummer et al., 2000), estimating groundwater mixing properties (Plummer et al., 1998b; Plummer et al., 2000; Katz et al., 2001; Burton et al., 2002), calibrating groundwater flow models (Reilly et al., 1994; Szabo et al., 1996), and assessing susceptibility of drinking water sources to anthropogenic contamination (see Chapter 7, Section 7.5 and Chapter 9, Section 9.9). Groundwater dating with CFCs is possible because:

(1) The history of the atmospheric CFC concentrations is known or has been reconstructed from production/release data;
(2) The Henry's Law solubilities in water are known as a function of temperature, pressure and salinity;
(3) Instrumentation and analytical procedures are available to measure the concentrations of CFCs in air and water.

Early studies demonstrated the potential of CFCs as tracers of recent recharge and indicators of groundwater age (Thompson et al., 1974; Schultz et al., 1976; Randall and Schultz, 1976; Thompson, 1976; Hayes and Thompson, 1977; Randall et al., 1977; Thompson and Hayes, 1979; Schultz, 1979). Tracer tests with fluorescein dye and CFC-11 showed that CFC-11 was transported nearly conservatively in poorly sorted sands and gravel (Thompson et al., 1974). CFC-11 was also shown to be an excellent tracer of sewage effluent discharged to dry washes and riverbeds near Tucson, Arizona, United States of America (Schultz et al., 1976). Early attempts to date a water sample with CFCs were based on:

(1) Comparison of a measured CFC-11 concentration to an analysis of another water sample of known age;
(2) Estimation of sample age using Henry's Law and relating implied air concentrations to atmospheric values (Randall and Schultz, 1976).

Randall and Schultz (1976) recognized the need for reconstruction of atmospheric mixing ratios of CFCs to improve dating capability, the possibility of detecting both CFC-11 and CFC-12 in the same analysis (at that time, analytical procedures were capable of detecting only CFC-11), and potential for dating using ratios of CFCs. Thompson (1976), Hayes and Thompson (1977), and Thompson and Hayes (1979) refined field GC-ECD analytical procedures for CFC-11 and tested the feasibility of dating with CFC-11 in groundwater systems in parts of New Jersey, Arkansas and Texas, USA, where hydrological conditions were well established. In all three cases they found some agreement between CFC-11 concentrations in the groundwater and known hydrological conditions.

CFCs have been used extensively in oceanographic studies as tracers of oceanic circulation, ventilation and mixing processes (Bullister, 1989; Rhein, 1991; Smethie, 1993; Wallace et al., 1994; Warner et al., 1996; Bˆnisch et al., 1997, Shapiro et al., 1997; Sonnerup et al., 1999; Smethie et al., 2000; Nightingale et al., 2000; Sonnerup, 2001; Smethie and Fine, 2001; Donelan et al., 2002; Lee et al., 2002; McNeil et al., 2003; and references therein), as tools to study deep circulation in lakes (Killworth et al., 1996; Tyler et al., 1998; Kipfer et al., 2000; Peeters et al., 2000), and tools to study transport and gas exchange processes of volatile organic compounds (VOCs) in estuaries (Clark et al., 1992; Christof et al., 2002). The Henry's Law solubilities of CFC-11, CFC-12 and CFC-113 were measured to high precision as a function of temperature and salinity (Warner and Weiss, 1985; Bu and Warner, 1995), and purge and trap GC-ECD analytical procedures (Bullister and Weiss, 1988) were developed. A global network of air monitoring stations, established by the Climate Monitoring and Diagnostics Laboratory of the National Oceanic and Atmospheric Administration (NOAA), U.S. Department of Commerce and the ALE/GAGE/AGAGE network (Cunnold et al., 1997), has provided air composition data from the mid-1970s. CFC mixing ratios in air prior to 1976 have been reconstructed from production data (McCarthy et al., 1977; Wisegarver and Gammon, 1988; Tominaga, 1992; Fisher and Midgley, 1993; Fraser et al., 1996; Busenberg and Plummer 1993; unpublished data, 2001), and data from the NOAA. Much of this work developed by the oceanographic scientific community and atmospheric sciences was adopted for groundwater studies in the early 1990s (Epler, 1990; Busenberg and Plummer, 1991, 1992).

During the past decade, a series of studies investigated potential applications of CFCs in the hydrological sciences (see, for example, Busenberg and Plummer, 1991; 1992; Dunkle et al., 1993; Plummer et al., 1993; Ekwurzel et al., 1994; Reilly et al., 1994; Cook and Solomon, 1995; Böhlke and Denver, 1995; Katz et al., 1995; Cook et al., 1995; 1996; McMahon and Böhlke, 1996; Szabo et al., 1996; Oster et al., 1996; Böhlke et al., 1997; Cook and Solomon, 1997; Thorstenson et al., 1998; Johnston et al., 1998; Ho et al., 1998; Plummer et al., 1998a,b; Modica et al., 1998; Beyerle et al., 1999; Goode et al., 1999; Weaver and Talma, 1999; Plummer and Busenberg, 2000; Kipfer et al., 2000; Talma et al., 2000; Plummer et al., 2000; Plummer et al., 2001; Katz et al., 2001; Busenberg et al., 2001; Bauer et al., 2001; Burton et al., 2002; Böhlke et al., 2002; Lindsey et al., 2003; and references therein). Additional references and information on many aspects of applications of CFCs in hydrological studies can be found at: *http://water.usgs.gov/lab/cfc*.

This guidebook brings together the results of some of these studies, as they apply to the groundwater environment, and summarizes the principles of CFC dating, with special emphasis on applications and limitations of the methods. Methods of sample collection and analysis are also presented, along with new software to aid in the interpretation of measured groundwater concentrations of CFCs. Often the application of multiple environmental tracers to a particular hydrological system enhances the level of understanding that can be gained. Applications of CFCs in groundwater studies will complement and enhance uses of other atmospheric environmental tracers in the hydrological sciences, including uses of tritium and tritium/helium-3 (Solomon and Cook, 2000), krypton-85 (Loosli et al., 2000) and sulphur hexafluoride (Busenberg and Plummer, 2000). In the southern hemisphere and in low latitude/equatorial regions, the CFCs are particularly promising additional tools for groundwater dating because of very low tritium levels prevailing there and the associated problems for tritium dating. In addition, those regions were not affected so much by local industrial CFC emissions, as was the case for decades in western Europe and in the USA. However, the potential of applications for CFCs as groundwater tracers in low latitude regions has not yet been fully explored.

## 1.2. TERMINOLOGY

Some terms that are used throughout this guidebook are defined as follows:

— ‘Atmospheric concentration’ refers to the concentration of a trace gas in air. Atmospheric concentration is expressed as the dry air volume fraction of the gas in air, and given in parts per trillion by volume (pptv), which is equivalent to picomoles of the tracer per mole of dry air.

— The atmospheric concentration of trace gases, being expressed as a ratio of volumes or of moles is also referred to as a ‘mixing ratio’, given in pptv.

— Some waters are referred to as ‘contaminated’ with respect to CFCs or with respect to other trace gases. The term ‘contaminated’ indicates that the sample contains a concentration of the trace gas that is greater than is possible for a water sample in solubility equilibrium with air at the time the maximum CFC mixing ratio was attained in the atmosphere.

— ‘Modern’ refers to the time and locality of sampling.

— Sources of contamination are usually anthropogenic for CFCs (see Chapter 4, Section 4.1) or, in the cases of sulphur hexafluoride ($SF_6$) (see Chapter 10, Section 10.1) and helium-4 ($^4$He), can be ‘terrigenic’ in origin. $SF_6$ or $^4$He that is of terrigenic origin refers to quantities of these trace gases that are released from rocks.

— Several terms are used as general indicators of age, specifically, ‘modern’, ‘young’ and ‘old’:

— ‘Modern’ water contains a concentration of the trace gas that is, within the uncertainties of the measurements, that of water in solubility equilibrium with air at the time and locality of sampling.

— ‘Young’ water refers to samples that contain a detectible concentration of the atmospheric tracer.

— The ‘young fraction’ is the fraction of a water sample that contains a detectible concentration of the atmospheric tracer. Young water is defined as post-1940s recharge, or mixtures containing a fraction of post-1940s recharge, and can contain detectible $^3$H and CFCs, $^{14}$C activities greater than 100 pMc, and other substances that can be of anthropogenic origin such as $^{36}$Cl, $^{85}$Kr, $SF_6$, pesticides and VOCs.

— ‘Old water’ refers to pre-CFC water, that is, water recharged prior to the 1940s, and can include water that was recharged thousands or millions of years ago. Some characteristics of old water include $^3$H and CFC concentrations that are below detection limit, $^{14}$C activity of dissolved inorganic carbon that is less than 100 pMc, and dissolved He concentration in excess of air/water equilibrium. Ideally, the recognition of mixtures of young and old water would be based on a multi-tracer approach (Section 1.3).

— ‘Groundwater age’ is defined more specifically in Chapter 3, Section 3.5 and Chapter 6, but in general, refers to the number of years that have elapsed since the water sample was isolated from the atmosphere, i.e. time since recharge. Due to differences in atmospheric histories of trace gases and of the analytical detection limits, the age ranges of young and old water differ with each atmospheric tracer.

— As an initial approximation, and as a means of comparing results from multiple measurements, 'groundwater age' is often reported as an 'apparent age'. The apparent age is based on the assumption that the tracer concentration in the water sample has been unaffected by mixing processes in the aquifer or in the sampling process, such as in 'piston flow' from the point of recharge to the point of sample collection. In some cases, water reaching the open interval of a well or discharging at a shallow water table spring is nearly uniform in age and can be approximated adequately using a 'piston flow model', as if the water flowed through a pipe from the point of recharge to the point of discharge without mixing during transit. The apparent age is based on the assumption of piston flow. In general, interpretation of groundwater age requires consideration of the age–frequency distribution in the water sample (see Chapter 6).

The text assumes a general background in groundwater geochemistry and in other dating techniques for young groundwater, such as tritium/helium-3 dating ($^3$H/$^3$He). For additional background in groundwater geochemistry, the reader is referred to Lloyd and Heathcote (1985), Appelo and Postma (1993), Langmuir (1997) and Drever (1997). A general discussion of environmental isotopes in hydrogeology is given by Clark and Fritz (1997). Excellent summaries of theory and application of a wide range of environmental tracers in groundwater are given in Kendall and McDonnell (1998) and Cook and Herczeg (2000).

## 1.3. IMPORTANCE OF THE MULTI-TRACER APPROACH

Although the focus of this guidebook is on application of CFCs in hydrological investigations, a multi-tracer approach will generally yield more information and help to resolve conflicting results. As discussed in later sections of this Guidebook (see Chapter 3, Section 3.4 and Chapters 4 and 11), a number of physical and chemical processes can affect the concentrations of environmental tracers in groundwater to varying extents. Application of multiple age indicators, such as CFCs, $^3$H, $^3$H/$^3$He, $^{85}$Kr, $SF_6$, and others, combined with other supporting geochemical data, such as measurements of concentrations of dissolved noble gases, $N_2$, $O_2$, $H_2S$ and $CH_4$, can all help to resolve age estimates. In samples that are mixed by dispersion or other physical processes, the apparent ages based on multiple environmental tracers can differ because of differences in the shapes of atmospheric input functions (see Chapter 4, Section 4.7), and even for some unmixed samples, apparent ages can differ depending on when the ‘clock’ was set for each environmental tracer (see Chapter 3, Section 3.4). Although concordance in apparent age is often observed among various age indicators in some sandy aquifers (see, for example, Ekwurzel et al., 1994), transport processes in hydraulically complex aquifers may result in considerable disparity among age indicators (Weissmann et al., 2002). Concordance in apparent ages interpreted from differing age indicators is often offered as support of dating procedures, however, apparent ages interpreted from different age indicators may differ because of differences in recharge processes and transport of the tracer in the aquifer (see Chapter 3, Section 3.5). Application of transport simulations to multi-tracer data can often help to refine estimates of groundwater age and transit time (see Chapter 6 and Chapter 13, Section 13.3).

## 1.4. HOW TO USE THIS GUIDEBOOK

This guidebook is intended to provide the basic theoretical facts for an understanding of applications of CFCs as tracers for hydrological studies. For a general background on CFCs in the environment and introduction to potential applications in hydrology, the reader is referred to Chapters 1 and 2. Chapter 3 describes how apparent ages are determined based on measured CFC concentrations in water samples. The more important physical and chemical processes that can alter CFC concentrations during recharge and in groundwater systems are discussed in Chapter 4. Chapters 5 and 6 discuss mixing processes and their effects on age distributions in water samples. Some practical examples demonstrating how CFC data have been used to interpret hydrogeological processes are given in Chapter 7. Chapter 8 presents a series of water samples that have been interpreted as influenced by factors that may be affecting CFC concentrations in water samples. Case studies using CFCs in a wide range of hydrogeological environments are presented in Chapter 9. Chapter 10 discusses possibilities of using other atmospheric gases in dating and tracing young groundwater, and Chapter 11 compares CFC dating to dating with $^3$H, $^3$H/$^3$He, $SF_6$, $^{85}$Kr and other isotopic tracers. Chapter 12 provides information on sampling and analytical details, and information on preservation and storage of samples. The appendices provide information on physical properties of CFCs and contains a tabulation of atmospheric air curves for the northern and southern hemispheres. Appendix III, Section III.3 provides some background on software currently available for interpreting CFC concentration data. A list of abbreviations is provided after the appendices.

The number of laboratories that can perform such measurements is increasing at a rapid rate. For example, the IAEA has started two model projects to provide complete CFC analysis equipment to institutes in China and Pakistan to further enhance knowledge dissemination on the methodology and to strengthen their local analytical capabilities. It is anticipated that the addition of an analytical capability for CFCs will lead to improved water resources assessment with the final aim of improved water resources management.

# Chapter 2

# CHLOROFLUOROCARBONS IN THE ATMOSPHERE

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## 2.1. HISTORY OF ATMOSPHERIC CFC CONCENTRATIONS

CFCs were first synthesized in 1928 as replacements for the toxic ammonia, methyl chloride, and sulphur dioxide refrigerants that were in use since the late 1800s. Commercial production began in 1930 and CFCs gradually replaced older refrigerants in cooling devices. After the mid-1940s, CFCs became the preferred aerosol propellants, and were widely used as solvents and degreasers, and as blowing agents for plastic foam. By the 1950s and 1960s, CFCs were widely used in the air-conditioning of homes, commercial buildings and automobiles (Elkins, 1999). CFCs are eventually released into the atmosphere and hydrosphere. Current estimates of the atmospheric lifetimes of CFC-11, CFC-12 and CFC-113 are 45 ± 7, 87 ± 17, and 100 ± 32 years, respectively (Volk et al., 1997). Additional estimates of the atmospheric lifetimes of CFCs are summarized in Prinn (1999). Since CFCs are a prime contributor to stratospheric ozone depletion (Molina and Rowland, 1974), 37 nations agreed in 1987 to limit release of CFCs and to halve CFC emissions by the year 2000, following the signing of the Montreal Protocol on Substances that Deplete the Ozone Layer. Further strengthening of the Protocol occurred in 1992 with 90 countries agreeing to cut off production of CFCs by 1996. The Protocol requires the total phasing out in developing countries by the year 2015. As a result of this agreement, air mixing ratios of CFC-11, CFC-12 and CFC-113 peaked in the northern hemisphere in about 1994, 2001 and 1996, respectively (Montzka et al., 1999; Mangani et al., 2000; Elkins et al., 2001; see Appendix II, Table II.1). CFCs and their replacements, the HCFCs and HFCs, are strong infrared absorbers and contribute to global warming (Sihra et al., 2001).

Measurement of atmospheric concentrations of CFCs became possible after the invention of the ECD. Lovelock (1971) and Lovelock et al. (1974) made the first measurements of CFC-11 in the atmosphere. Variations of CFC-11 concentrations in air and sea water were measured in samples obtained between 40° N and 60° S latitude, and the results suggested that CFCs would be valuable tracers in atmospheric and ocean studies (Lovelock et al., 1973). Beginning in the mid-1970s, systematic atmospheric monitoring was initiated by global networks, such as the ALE/GAGE/AGAGE (Cunnold et al., 1986;

Prinn et al., 2001), and since 1976 by the Climate Monitoring and Diagnostic Laboratory of the NOAA, in the USA (Elkins et al., 1993).

Because there are no atmospheric measurements prior to 1970, atmospheric concentrations of CFCs have been reconstructed from:

- Records of the amounts of CFCs manufactured and estimates of release into the atmosphere (Chemical Manufacturers Association, 1990; Alternative Fluorocarbons Environmental Acceptability Study, AFEAS, 1999; McCarthy et al., 1977; Gamlen et al., 1986; McCulloch et al., 2001; Harnisch and Höhne, 2002);
- Measured concentrations of CFCs and other trace gases in dated polar-firn air (Schwander et al., 1988; Butler et al., 1999);
- Results from models incorporating the rates of photolysis, and removal by soils, the hydrosphere and the biosphere (Cunnold et al., 1986; Semprini et al., 1990, 1992; Khalil and Rasmussen, 1989; Russell and Thompson, 1983; Brown, 1980; Alyea et al., 1978; Lovelock et al., 1973).

Reconstructed curves are normalized to measured atmospheric concentrations at a particular location to obtain the pre-1975 atmospheric mixing ratios (McCarthy et al., 1977; Cunnold et al., 1986).

The pre-1975 atmospheric CFC mixing ratios used by the U.S. Geological Survey Chlorofluorocarbon Laboratory for North America were normalized to measured concentrations at Niwot Ridge Observatory (elevation 3013 m, latitude 40.04° N, longitude 105.54° W), near Boulder, Colorado, USA (Elkins, 1989), and are nearly identical to other published mixing ratios for North America (Bullister, 1984; Wisegarver and Gammon, 1988; Smethie et al., 1988; Walker et al., 2000). Pre-1975 mixing ratios for other locations can be similarly reconstructed by using the measured concentration of CFCs from stations located throughout the world. However, some differences in atmospheric mixing ratios of CFCs measured by various laboratories remain (Prinn et al., 1999), and caution should be excerised when combining measurements of air mixing ratios from various sources. For consistency, the CFC data in this report are on the Scripps Institution of Oceanography 1998 (SIO-98) scale (see Appendix II, Table II.1; see appendix in Walker et al., 2000). The mixing ratios for uncontaminated North American air on the SIO-98 scale are shown in Fig. 2.1(a). Mixing ratios of CFCs for five stations located between latitudes 71° N and 90° S (Table 2.1) are shown in Fig. 2.2. The data used to construct Figs 2.1 and 2.2 can be obtained with permission from:

*http://www.cmdl.noaa.gov/*
*http://cdiac.esd.ornl.gov/ndps/alegage.html*
*http://gaslab.ucsd.edu/pub/cfchist/*

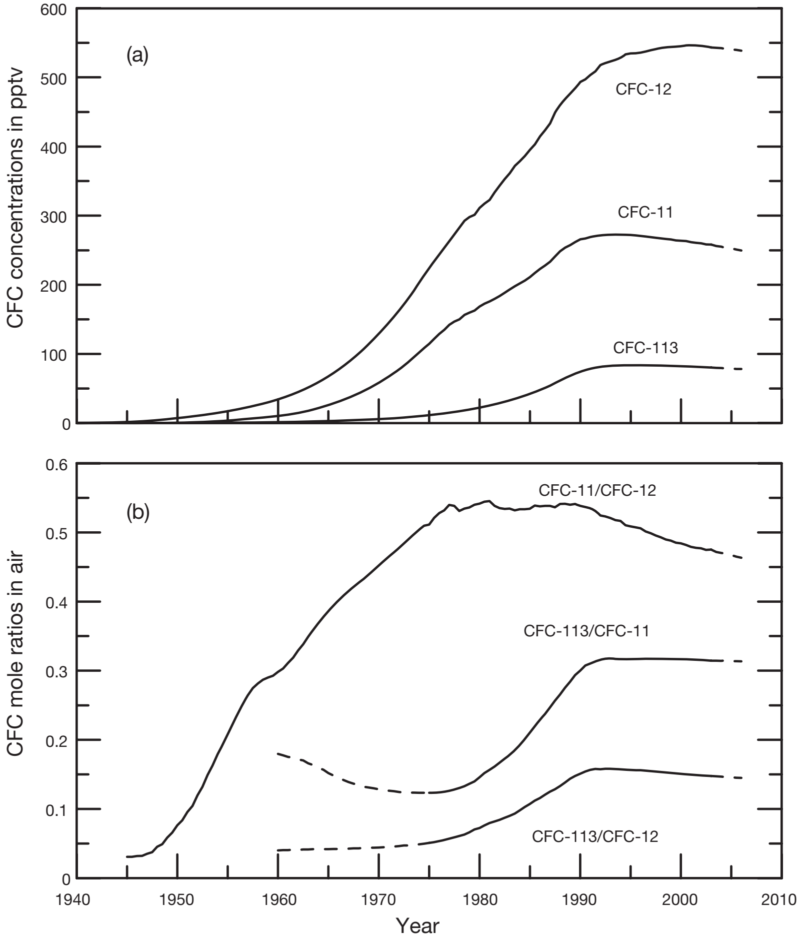

*FIG. 2.1. (a) Historical concentrations of CFCs in the North American atmosphere (see Appendix II, Table II.1); (b) historical ratios of CFCs in the North American atmosphere (calculated from data in Table II.1).*

## 2.2. CHARACTERISTICS OF THE DISTRIBUTION OF CFCs IN THE ATMOSPHERE

CFCs were predominantly consumed and released by industrialized nations between the latitudes of 30ºN and 70ºN (Hartley et al., 1996); therefore, the troposphere mixing ratios in the northern hemisphere historically have been higher than those of the southern hemisphere (Elkins et al., 1993).

TABLE 2.1. SELECTED AIR MONITORING STATIONS, THEIR GEOGRAPHICAL LOCATIONS AND ELEVATIONS

| Location | Latitude | Longitude | Elevation (m) |
|---|---|---|---|
| Point Barrow, AK, USA | 71.32° N | 136.60° W | 11 |
| Niwot Ridge, CO, USA | 40.04° N | 105.54° W | 3013 |
| Tuluila Island, American Samoa | 14.23° S | 170.56° W | 77 |
| Cape Grim, Tasmania, Australia | 40.41° S | 144.64° W | 94 |
| South Pole, Antarctica | 89.98° S | 102.00° E | 2841 |

However, with the phasing out of CFC production by the developed countries (Montreal Protocol on Substances that Deplete the Ozone Layer), the interhemispheric differences in the mixing ratios have appreciably decreased (Volk et al., 1996; Elkins et al., 2001; Prinn et al., 2000) (see Fig. 2.2).

Near urban areas, some CFC mixing ratios are often raised relative to background air composition. If these differences are neglected, then the calculated age of the water from these urban or densely populated sites will appear contaminated or younger than the actual recharge age of the groundwater. CFC-11 and CFC-113 mixing ratios of air collected from North Carolina, south-east USA (Hurst et al., 1997), from November 1994 through January 1996, closely tracked the Niwot Ridge, Colorado, values; however, the CFC-12 mixing ratios were 2% higher than the Niwot Ridge air. The CFC-12 anomalies were attributed to local and regional sources (Hurst et al., 1997). Similarly, mixing ratios of CFC-11 and CFC-113 closely tracked the Niwot Ridge mixing ratios, while the CFC-12 mixing ratios were approximately 2% higher in the weekly samples collected from September 1995 through September 2001 at Big Meadows Air Station, located 105 km west of Washington, D.C. (Plummer et al., 2000; 2001). CFC mixing ratios for CFC-11, CFC-12 and CFC-113 were 27%, 8% and 1% higher than North American air between June and August 2001 in Reston, Virginia, a suburb of Washington, D.C. (Busenberg and Plummer, unpublished data). At a site 25 km north of the city of New York, the mixing ratios of CFC-11 and CFC-12, analysed at approximately 10 min intervals, averaged 6% and 13% higher than the Niwot Ridge mixing ratios between July 1998 and October 1999 (Ho et al., 1998).

Oster et al. (1996) made 8000 CFC measurements in air at four sites in Germany between 1989 and 1992. In 1989, the CFC-11 and CFC-12 average mixing ratios were 125% and 62% greater than the northern hemisphere background in Heidelberg, respectively. At the rural Wachenheim site, the

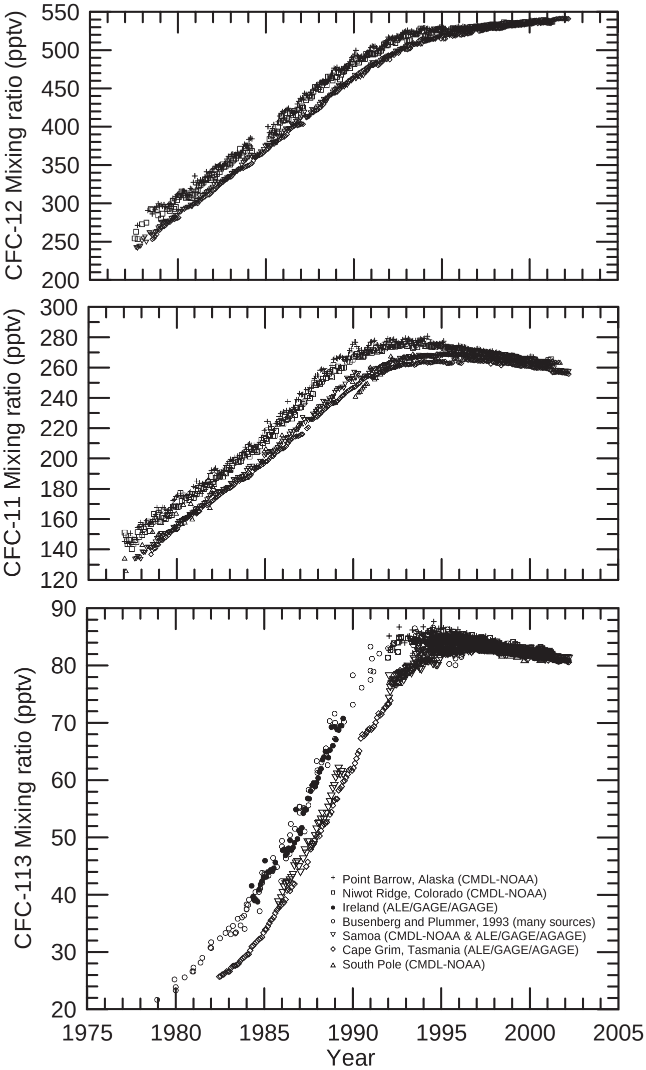

*FIG. 2.2. Atmospheric mixing ratios of CFC-11, CFC-12 and CFC-113 from air monitoring stations are depicted, showing latitudinal variations in CFC concentrations in the atmosphere. Data are from the CMDL/NOAA web site (Elkins, Butler, Thompson and Montzka, 2003; Montzka et al., 1996 and 1999), and from the CDIAC web site (Walker et al., 2000; Prinn et al., 2000; Cunnold et al., 1997). Data used to construct the northern hemisphere 1980–1990 atmospheric concentrations for CFC-113 were obtained from a number of sources (Busenberg and Plummer, 1993; Wisegarver and Gammon, 1988; Gilpin, 1991; Wang, 1993 and 1997; Tominaga, 1993). The pre-1980s mixing ratios were reconstructed from production and atmospheric release data (Fisher and Midgley, 1993; AFEAS, 2003).*

CFC-11 excess was 34%, while the CFC-12 excess was 24%. The measured excesses at a remote rural site were 11% and 23% for CFC-11 and CFC-12, respectively. Oster et al. (1996) also reported excesses of 10% for both CFC-11 and CFC-12 for a high alpine location. Frank et al. (1991) and Becker et al. (1978) obtained similar results for a number of locations in western Europe. The CFC-11 and CFC-113 mixing ratios were similar to background values, while an excess of 18% was observed in CFC-12 concentrations in 51 air samples collected randomly over a one hour period throughout the Taipei metropolitan area, Taiwan, China, in January 1997 (Wang et al., 1998).

Interhemispheric, longitudinal, geographical, topographical, vertical, seasonal, weekly, diurnal and episodic variations attributed to local emissions and changing of air masses have been documented in the literature (Elkins et al., 1993; Prinn et al., 2000; McCulloch et al., 1994; Prather et al., 1987; Frank et al., 1991; Tominaga, 1992; Oster et al., 1996; Ho et al., 1998; Hurst, et al., 1997; Walker et al., 2000).

It should be noted that the atmospheric measurement stations established for networks, such as the ALE/GAGE/AGAGE, and from which much of our information on atmospheric CFC concentrations is derived (see Section 2.1), were established to collect uncontaminated air samples which would be representative of the global atmosphere. They might not necessarily be appropriate for describing atmospheric concentrations in inland continental areas. There remains a shortage of long term data on atmospheric CFC concentrations near urban areas, and uncertainty in the input concentrations remains a potential cause of error, particularly in the more industrialized nations. In some cases, it may be possible to reconstruct local historical records of atmospheric CFC concentrations by, for example, measuring CFC concentrations in water samples that were dated by other means.

## 2.3. TIME DEPENDENT CFC CONCENTRATION RATIOS IN THE ATMOSPHERE

The ratios of any two CFCs can provide useful information on the date of recharge of groundwater because the three CFCs of interest were introduced at different times and have different atmospheric growth rates (Fig. 2.1(b)). In the North American atmosphere, the CFC-11/CFC-12 ratio increased from approximately 1947 through 1976, remained nearly constant from 1976 to 1992, and has decreased from 1992 to the present. The CFC-113/CFC-12 ratio increased from approximately 1975 through 1992 and decreased from 1992 to the present. The CFC-113/CFC-11 atmospheric ratio increased from about 1975 to 1990, and has been nearly constant from 1990 to the present (2004).

Because there can be significant geographical differences in the mixing ratios of CFCs, ratios of two CFCs should be calculated using the local atmospheric air concentrations. Ratios of two CFCs can date water into the early 1990s, however, the ratio method may become a useful dating tool in the future because of the significant differences in the atmospheric lifetimes of these three CFCs.

The ratios of two CFCs have been extensively used in oceanographical studies as a dating tool of water masses (Wisegarver and Gammon, 1988; Smethie at al., 1988; Wallace et al., 1994). From the measured concentrations, the ratio age of the mixture, and the historical atmospheric mixing ratios, the fraction of post-CFC water can be calculated. Ratio ages are valid only if the concentrations of the CFCs in the post-CFC water were not altered in any way before or after mixing.

# Chapter 3

# PRINCIPLES OF CHLOROFLUOROCARBON DATING

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## 3.1. BASIC ASSUMPTION

Groundwater dating with CFCs refers to the process of estimating the historical date at which a parcel of water was recharged to a groundwater system. Several assumptions are necessary in assigning an apparent age based on CFCs. It is first necessary to collect and analyse a water sample for CFCs that is representative of the aquifer at a given location (see Chapter 12, Section 12.2). It is then assumed that the water sample was in solubility equilibrium with the unsaturated zone air at the time of recharge. All gas solubilities are functions of temperature, pressure and dissolved solute content. Therefore, it is necessary to estimate the temperature and pressure during recharge. In some cases, recharge temperature can be estimated from shallow groundwater temperatures, but recharge temperatures are more precisely estimated from measurements of other dissolved gases, such as nitrogen and argon (Heaton, 1981; Heaton and Vogel, 1981; Heaton et al., 1986), or noble gases (Mazor, 1972; Andrews and Lee, 1979; Andrews, 1991; Stute and Sonntag, 1992; Stute et al., 1992; 1995; Andrews et al., 1994; Ballentine and Hall, 1999; Stute and Schlosser, 1999; Aeschbach-Hertig et al., 1999; 2000; Kipfer et al., 2002).

In groundwater dating with CFCs, it is further assumed that the local historical CFC composition of air is known and that the composition of unsaturated zone air closely follows that of the atmosphere. The recharge date is then determined by comparing the calculated partial pressures of CFCs in solubility equilibrium with the water sample with historical CFC concentrations in local air. One criterion for rejection of apparent CFC ages is that calculated CFC concentrations in air (in pptv) are greater than that possible for water in solubility equilibrium with air at the time of the peak in atmospheric concentration (designated as ‘contaminated’, ‘C’). For CFC concentrations near or below the detection limit for CFCs, only minimum ages can be assigned (designated as ‘less than’, ‘<’).

An important distinction can be made between dating based on CFCs and dating by parent–daughter nuclear dating techniques such as the $^3$H/$^3$He method. In the case of $^3$H/$^3$He dating, the initial tritium content of the water sample is reconstructed from measurement of both the parent isotope ($^3$H) and tritiogenic $^3$He, which is the daughter product (see Chapter 11, Section 11.3 for further details), while dating with CFCs — and, similarly, for dating with most other atmospheric environmental tracers such as $^{85}$Kr (Chapter 11, Section 11.4), $^3$H (Chapter 11, Section 11.2) and SF$_6$ (Chapter 10) — requires prior knowledge of the initial condition. In the case of CFC dating, knowledge of the history of the local atmospheric CFC concentrations is required.

## 3.2. DATING WITH CFC CONCENTRATIONS

Groundwater dating with CFCs is based on Henry’s Law solubility. According to Henry’s Law, the concentration of a gas dissolved in water in equilibrium with air is proportional to the partial pressure, $p_i$, of the gas in air:

$$C_i = K_{H_i} p_i \tag{3.1}$$

where $C_i$ is the concentration of the $i$th CFC compound in water, and $K_{H_i}$ is the Henry’s Law constant for the $i$th CFC. The partial pressure of the $i$th CFC, $p_i$, is defined as:

$$p_i = x_i\,(P - p_{\mathrm{H_2O}}) \tag{3.2}$$

where $x_i$ is the dry air mole fraction of the $i$th CFC ($x_i$ <<1) in air, $P$ is the total atmospheric pressure and $p_{\mathrm{H_2O}}$ is the water vapour pressure (Warner and Weiss, 1985). For ideal gases, the dry air mole fraction is replaced with the dry air mixing ratio, volume per volume. The Henry’s Law constants, $K_H$, for CFC-11, CFC-12 and CFC-113 solubility in pure water and sea water have been determined at 1013.25 hPa total pressure over a range of salinities and temperatures (Warner and Weiss, 1985; Bu and Warner, 1995). Table 3.1 gives least squares fitting parameters to the temperature, and salinity, dependence of $K_H$ for CFC concentrations in mol·kg$^{-1}$(1013.25 hPa)$^{-1}$ and mol·L$^{-1}$ (1013.25 hPa)$^{-1}$, valid for temperatures of 273–313 kelvin (0–40°C), and salinities of 0–40‰ in the equation:

$$\ln K_H = a_1 + a_2\left(\frac{100}{T}\right) + a_3 \ln\left(\frac{T}{100}\right) + S\left[b_1 + b_2\left(\frac{T}{100}\right) + b_3\left(\frac{T}{100}\right)^2\right] \tag{3.3}$$

TABLE 3.1. CONSTANTS FOR CALCULATION OF $K_H$ FOR CFC-11 AND CFC-12 (WARNER AND WEISS, 1985), AND CFC-113 (BU AND WARNER, 1995), Eq. (3.3)

| CFC | $a_1$ | $a_2$ | $a_3$ | $b_1$ | $b_2$ | $b_3$ |
|---|---|---|---|---|---|---|
| $K_H$ in mol·kg$^{-1}$·(1013.25 hPa)$^{-1}$ | | | | | | |
| CFC-11 | –136.2685 | 206.1150 | 57.2805 | –0.148598 | 0.095114 | –0.0163396 |
| CFC-12 | –124.4395 | 185.4299 | 51.6383 | –0.149779 | 0.094668 | –0.0160043 |
| CFC-113 | –136.129 | 206.475 | 55.8957 | –0.02754 | 0.006033 | — |
| $K_H$ in mol·L$^{-1}$·(1013.25 hPa)$^{-1}$ | | | | | | |
| CFC-11 | –134.1536 | 203.2156 | 56.2320 | –0.144449 | 0.092952 | –0.0159977 |
| CFC-12 | –122.3246 | 182.5306 | 50.5898 | –0.145633 | 0.092509 | –0.0156627 |
| CFC-113 | –134.243 | 203.898 | 54.9583 | –0.02632 | 0.005874 | — |

where $T$ is the temperature in degrees kelvin and $S$ is the salinity in parts per thousand by weight (‰).

In assigning an apparent age to a CFC concentration measured in a water sample, the measured concentration is converted to units of mol·kg$^{-1}$ (or mol·L$^{-1}$) and then to a dry air atmospheric mixing ratio, $x_i$. In this process the Henry's Law constant must be calculated at the recharge temperature, that is, the temperature at the water table during recharge. The Henry's Law constant is also a function of salinity. Salinity corrections will be necessary for all studies of CFCs involving sea water, estuaries and saline lakes. The salinity corrections (Warner and Weiss, 1985; Bu and Warner, 1995) were determined explicitly for sea water compositions, and may not be directly applicable to some non-marine saline waters. But, as a general rule, most shallow groundwater of interest in dating with CFCs is too dilute to require corrections for salinity (Plummer and Busenberg, 2000).

The recharge elevation is also needed to estimate the total atmospheric pressure, $P$, during recharge. Barometric pressure decreases as elevation increases and, therefore, the gas concentrations decrease as the barometric pressure decreases. The average barometric pressure during recharge is not normally known, but can be estimated from the recharge elevation. For recharge elevations of less than 3000 m, the relationship:

$$\ln P = -H/8300 \qquad (3.4)$$

can be used, where $H$ is the recharge elevation in metres (List, 1949). If the recharge elevation is underestimated, the apparent CFC age will be biased old. Increasing the estimated elevation of recharge results in younger interpreted ages. In areas of low relief, the uncertainty in recharge elevation does not normally introduce significant errors in CFC dating. However, in mountainous terrain, the uncertainty in the recharge elevation can often be very large and can introduce a significant uncertainty in the interpreted age of the groundwater. An uncertainty in recharge elevation of 1000 m results in an age uncertainty of a few years or less for waters recharged prior to 1987 (Busenberg et al., 1993), however, the age uncertainty can be significant for groundwater recharged after 1990. It is important to realize that when the recharge elevation is not known, the estimated recharge temperature is also uncertain, because as the elevation increases, the air temperature decreases. For the standard atmosphere, the rate of cooling is assumed to be 0.0065°C for every metre of elevation (Committee on Extension to the Standard Atmosphere, 1976); however, local climatic factors can significantly affect the rate of change of air temperature with elevation (Meyer, 1992). The uncertainty in both elevation and recharge temperature must be considered in determining the age uncertainty.

Because recharge occurs in a moist unsaturated zone, relative humidity is near 100%. Therefore, to solve for the dry air mixing ratio of the particular CFC, the vapour pressure of water, $p_{H_2O}$, is subtracted from the total pressure. The vapour pressure of water is (Weiss and Price, 1980):

$$\ln p_{H_2O} = 24.4543 - 67.4509\left(\frac{100}{T}\right) - 4.8489\ln\left(\frac{T}{100}\right) - 0.000544S \qquad (3.5)$$

The dry air mixing ratio for the particular CFC, $x_i$, is then compared to the appropriate historical atmospheric mixing ratio to determine recharge date.

Figure 3.1 shows an example of CFC dating. In this example, a water sample analysed for CFC-11, CFC-12 and CFC-113 had concentrations of 486.5, 200.6 and 27.8 pg·kg$^{-1}$, respectively. (Concentration units of pg/kg are obtained by mutiplying concentration units of pmol/kg by the molecular weights of the respective CFCs given in Appendix I, Table I.1.) A recharge temperature of 10°C and recharge elevation of 0 m was assumed. It was further assumed that the soil air closely followed the composition of North American air, was saturated with water vapour at time of recharge, and that no salinity correction was necessary. Using Henry's Law, the calculated dry air CFC partial pressures are 170, 306 and 23 pptv for CFC-11, CFC-12 and CFC-113, respectively. In the example, all three measured CFC concentrations are consistent

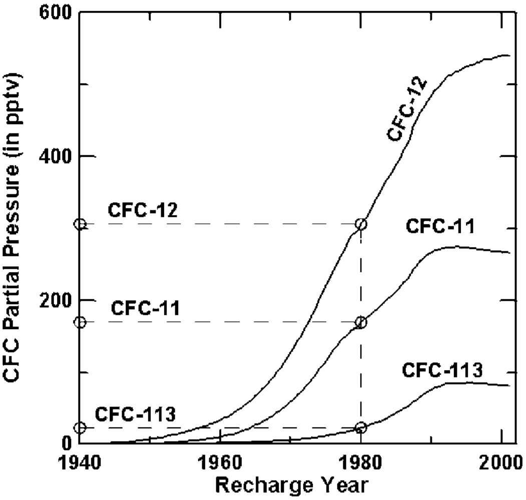

*FIG. 3.1. Example showing determination of an apparent recharge date of 1980 from independent analyses of CFC-12, CFC-11 and CFC-113. The curves show historical mixing ratios of CFCs in North American air.*

with a recharge date of 1980 (Fig. 3.1). Apparent age is simply the date of sampling minus the recharge date so, in the example, if the sample was collected in the year 2001, an apparent age of 21 years is implied by all three CFCs.

An example using the above equations to calculate the apparent recharge year for a water sample with a measured CFC-12 concentration is presented in Fig. 3.2.

Examples of the effects of varying recharge temperature, recharge elevation and salinity on the calculated model ages for CFC-11, CFC-12 and CFC-113 are shown in Table 3.2. The calculations of Table 3.2 assume two measured concentrations for CFC-11 (1 and 5 pmol/kg), CFC-12 (0.6 and 2 pmol/kg) and CFC-113 (0.06 and 0.3 pmol/kg). For each concentration, recharge temperature was varied between 5 and 25°C, recharge elevation was varied between 0 and 3000 m, and salinity was varied between 0 and 3 parts per thousand. Sensitivity analyses similar to that shown in Table 3.2 can be readily performed using software such as QCFC (see Appendix III, Section III.1).

Suppose that we measure a CFC-12 concentration of 200 pg/kg. Based on a molecular weight of 120.913 g/mol, this is equivalent to a molar concentration of CFC-12 of $C = 1.654$ pmol/kg = $1.654 \times 10^{-12}$ mol/kg.

Suppose also that:

Recharge temperature = 10°C = 283.15 K

Recharge elevation = 1000 m

Groundwater salinity = 1000 mg/L = 1 ppt

Using Eq. (3.5), we get

$p_{H_2O} = 0.0121$ atmosphere

Using Eq. (3.4), we get

$P = 0.886$ atmosphere

Using Eq. (3.3), we get

$K_H = 0.00543$ mol/kg/atm

Combining Eq. (3.1) and Eq. (3.2), we get

$$x = \frac{C}{K_H (P - p_{H_2O})}$$

Substituting for $C$, $K_H$, $P$ and $p_{H_2O}$ gives

$x = 3.48 \times 10^{-10} = 348$ pptv

This corresponds to a recharge year of approximately 1982.5, based on North American air (Appendix II, Table II.1).

*FIG. 3.2. An example calculation of apparent recharge year for a water sample containing 200 pg/kg of CFC-12 that was recharged at 10°C, 1000 m elevation and with a salinity of 1000 mg/L.*

TABLE 3.2. EFFECTS OF TEMPERATURE, ELEVATION AND SALINITY ON THE CALCULATED APPARENT AGE OF CFCs
(*based on North American air atmospheric mixing ratios provided in Appendix II*)

| CFC | | Recharge elev. = 0 m Salinity = 0 ‰ | | | Recharge temp. = 10°C Salinity = 0 ‰ | | | Recharge temp. = 10°C Recharge elev. = 0 m | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Conc. (pmol/kg) | Recharge temp. (°C) | Partial pressure (pptv) | Recharge year | Recharge elev. (m) | Partial pressure (pptv) | Recharge year | Salinity (‰) | Partial pressure (pptv) | Recharge year |
| CFC-11 | 1.0 | 5 | 35.8 | 1966.5 | 500 | 50.9 | 1969.0 | 0.0 | 47.9 | 1968.5 |
| CFC-11 | 1.0 | 10 | 47.9 | 1968.5 | 1000 | 54.1 | 1969.5 | 0.5 | 48.2 | 1968.5 |
| CFC-11 | 1.0 | 15 | 62.5 | 1970.5 | 1500 | 57.5 | 1970.0 | 1.0 | 48.4 | 1969.0 |
| CFC-11 | 1.0 | 20 | 79.5 | 1972.0 | 2000 | 61.2 | 1970.5 | 2.0 | 48.6 | 1969.0 |
| CFC-11 | 1.0 | 25 | 98.9 | 1973.5 | 3000 | 69.1 | 1971.0 | 3.0 | 48.9 | 1969.0 |
| CFC-11 | 5.0 | 5 | 178.9 | 1981.5 | 500 | 254.6 | 1988.5 | 0.0 | 239.5 | 1987.5 |
| CFC-11 | 5.0 | 10 | 239.5 | 1987.5 | 1000 | 270.6 | 1991.5[a] | 0.5 | 240.8 | 1987.5 |
| CFC-11 | 5.0 | 15 | 312.3 | C[b] | 1500 | 287.7 | C | 1.0 | 242.0 | 1987.5 |
| CFC-11 | 5.0 | 20 | 397.4 | C | 2000 | 305.8 | C | 2.0 | 244.5 | 1987.5 |
| CFC-11 | 5.0 | 25 | 494.5 | C | 3000 | 345.6 | C | 3.0 | 247.0 | 1988.0 |
| CFC-12 | 0.6 | 5 | 85.3 | 1967.0 | 500 | 117.7 | 1969.0 | 0.0 | 110.7 | 1968.5 |
| CFC-12 | 0.6 | 10 | 110.7 | 1968.5 | 1000 | 125.1 | 1969.5 | 0.5 | 111.3 | 1969.0 |
| CFC-12 | 0.6 | 15 | 140.4 | 1970.5 | 1500 | 133.0 | 1970.0 | 1.0 | 111.9 | 1969.0 |
| CFC-12 | 0.6 | 20 | 174.2 | 1972.5 | 2000 | 141.4 | 1970.5 | 2.0 | 113.0 | 1969.0 |

TABLE 3.2. EFFECTS OF TEMPERATURE, ELEVATION AND SALINITY ON THE CALCULATED APPARENT AGE OF CFCs (cont.)
(*based on North American air atmospheric mixing ratios provided in Appendix II*)

| CFC | | Recharge elev. = 0 m<br>Salinity = 0 ‰ | | | Recharge temp. = 10°C<br>Salinity = 0 ‰ | | | Recharge temp. = 10°C<br>Recharge elev. = 0 m | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Conc. (pmol/kg) | Recharge temp. (°C) | Partial pressure (pptv) | Recharge year | Recharge elev. (m) | Partial pressure (pptv) | Recharge year | Salinity (‰) | Partial pressure (pptv) | Recharge year |
| CFC-12 | 0.6 | 25 | 211.8 | 1974.5 | 3000 | 159.8 | 1972.0 | 3.0 | 114.1 | 1969.0 |
| CFC-12 | 2.0 | 5 | 284.4 | 1978.0 | 500 | 392.3 | 1985.0 | 0.0 | 369.1 | 1983.5 |
| CFC-12 | 2.0 | 10 | 369.1 | 1983.5 | 1000 | 417.0 | 1986.0 | 0.5 | 371.0 | 1983.5 |
| CFC-12 | 2.0 | 15 | 467.9 | 1988.5 | 1500 | 443.3 | 1987.5 | 1.0 | 372.8 | 1983.5 |
| CFC-12 | 2.0 | 20 | 580.5 | C | 2000 | 471.3 | 1988.5 | 2.0 | 376.6 | 1984.0 |
| CFC-12 | 2.0 | 25 | 706.2 | C | 3000 | 532.7 | 1994.5 | 3.0 | 380.4 | 1984.0 |
| CFC-113 | 0.06 | 5 | 6.8 | 1971.0 | 500 | 9.9 | 1974.0 | 0.0 | 9.3 | 1973.5 |
| CFC-113 | 0.06 | 10 | 9.3 | 1973.5 | 1000 | 10.5 | 1974.5 | 0.5 | 9.4 | 1973.5 |
| CFC-113 | 0.06 | 15 | 12.5 | 1975.5 | 1500 | 11.2 | 1975.0 | 1.0 | 9.4 | 1973.5 |
| CFC-113 | 0.06 | 20 | 16.3 | 1977.5 | 2000 | 11.9 | 1975.5 | 2.0 | 9.5 | 1973.5 |
| CFC-113 | 0.06 | 25 | 20.8 | 1979.5 | 3000 | 13.4 | 1976.0 | 3.0 | 9.6 | 1973.5 |
| CFC-113 | 0.30 | 5 | 33.8 | 1983.0 | 500 | 49.4 | 1986.5 | 0.0 | 46.5 | 1985.5 |
| CFC-113 | 0.30 | 10 | 46.5 | 1985.5 | 1000 | 52.6 | 1986.5 | 0.5 | 46.8 | 1986.0 |
| CFC-113 | 0.30 | 15 | 62.3 | 1988.0 | 1500 | 55.9 | 1987.0 | 1.0 | 47.0 | 1986.0 |

TABLE 3.2. EFFECTS OF TEMPERATURE, ELEVATION AND SALINITY ON THE CALCULATED APPARENT AGE OF CFCs (cont.)
(*based on North American air atmospheric mixing ratios provided in Appendix II*)

| CFC | | Recharge elev. = 0 m<br>Salinity = 0 ‰ | | | Recharge temp. = 10°C<br>Salinity = 0 ‰ | | | Recharge temp. = 10°C<br>Recharge elev. = 0 m | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Conc. (pmol/kg) | Recharge temp. (°C) | Partial pressure (pptv) | Recharge year | Recharge elev. (m) | Partial pressure (pptv) | Recharge year | Salinity (‰) | Partial pressure (pptv) | Recharge year |
| CFC-113 | 0.30 | 20 | 81.3 | 1992.0 [c] | 2000 | 59.4 | 1988.0 | 2.0 | 47.5 | 1986.0 |
| CFC-113 | 0.30 | 25 | 103.8 | C | 3000 | 67.1 | 1989.0 | 3.0 | 48.0 | 1986.0 |

[a] Because the CFC-11 atmospheric curve is now declining, the partial pressure of 270.6 pptv could be consistent with either recharge years of 1991.5 or 1996.0.

[b] C: contaminated.

[c] Because the CFC-113 atmospheric curve is now declining, the partial pressure of 81.3 pptv could be consistent with either recharge years of 1992.0 or 2001.5.

## 3.3. DATING WITH CFC CONCENTRATION RATIOS

As shown in Fig. 3.1 and in Chapter 2, Fig. 2.1, the atmospheric concentrations (mixing ratios) of CFCs have varied with time, and if the local historical concentrations in air can be reconstructed, they can be used through application of Henry's Law for groundwater dating. Similarly, the ratios of CFC concentrations in air are also functions of time and for some periods of time (Fig. 2.1), unique ages can be assigned. For example, Fig. 3.3 shows reconstructions of the historical CFC ratios (pptv/pptv), CFC-11/CFC-12, CFC-113/CFC-12 and CFC-113/CFC-11, in North American air. The CFC-11/CFC-12 ratio has a dating range of approximately 1947 through 1976. After 1976, the CFC-11/CFC-12 ratio in air was nearly constant and more recently has declined. In post-1992 waters, dual ages can be derived from the CFC-11/CFC-12 ratio. The rapid growth of CFC-113 concentration in air from the late 1970s to the early 1990s permits dating, using either the CFC-113/CFC-12 or CFC-113/CFC-11 ratio from approximately 1975 into the early 1990s. In homogeneous, unmixed samples, identical CFC ages can be determined either from the use of single CFC analyses (Fig. 3.1) or from their ratios (Fig. 3.3), provided no other chemical or physical processes have altered the CFC concentrations in the sample.

Consideration of age determined from multiple CFC ratios provides dating options when one of three CFC compounds has been contaminated, degraded or otherwise altered from its original concentration at or after recharge. More significantly, CFC ratios are preserved in simple binary mixtures of young water diluted with old, pre-CFC water. In samples that are simple binary mixtures of young and old, pre-CFC water, ratios of CFCs can define the age of the young fraction (see Chapter 5).

## 3.4. SETTING THE 'CLOCK'

Because the input signal of most environmental tracers (including CFCs) is determined by either atmospheric concentrations of a particular gas (e.g. $^{14}C$, CFCs) or tracer concentrations in rainfall (e.g. $^{3}H$), travel time information usually refers to time since exposure to the atmosphere, or since rainfall. The measured travel time thus includes residence times in both the saturated and unsaturated zones. The relative importance of the two components of the travel time will depend upon the environmental setting and on the characteristics of

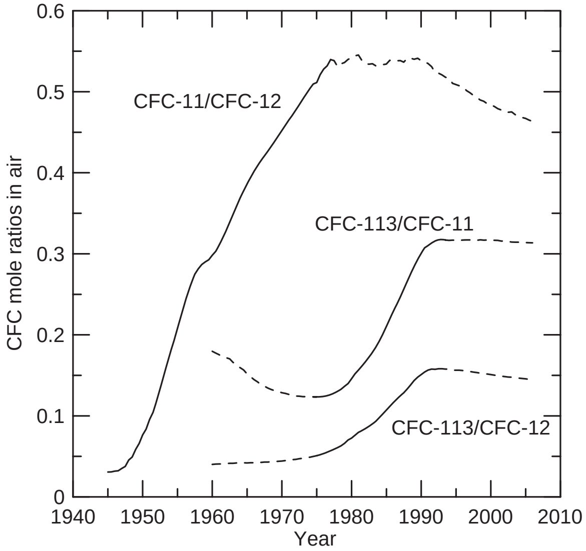

*FIG. 3.3. Historical atmospheric ratios of CFC-11/CFC-12, CFC-113/CFC-12 and CFC-113/CFC-11 in North American air. The solid lines show the useful dating range for each ratio.*

the tracer being considered. In particular, the transport of environmental tracers in the unsaturated zone will be strongly affected by the way that they partition between the liquid and gas phases.

Tracers such as $^{36}$Cl, $^{35}$S and $^{32}$Si are restricted to the liquid phase, and so their movement should reflect that of liquid water. For tracers that can move in both liquid and vapour phases, the travel time through the unsaturated zone is a composite of the travel time in the liquid and vapour phases. For gases with low solubilities in water, diffusion or advection within the gas phase will usually be more rapid than in the liquid phase. In some cases, this means that the concentrations of tracers, such as CFCs, $^{85}$Kr and the He isotopes are essentially constant throughout the unsaturated zone, and equal to the overlying atmospheric concentrations. In other cases, especially in thick unsaturated zones and for gases with higher solubilities, the concentrations of gas tracers may vary with depth. Differences between the transport processes of CFCs, $^{85}$Kr, $^{3}$He and $^{3}$H in the unsaturated zone arising from differences in the tracer partition coefficients can cause differences between apparent groundwater ages obtained with these tracers (Cook and Solomon, 1997).

The combined liquid and gas phase travel time through the unsaturated zone will often be small, so that the apparent CFC ages will simply reflect the saturated zone travel time (the groundwater age). It is this saturated zone travel time that is usually of interest. In Chapter 4, Section 4.2 discusses how the unsaturated zone travel time can be estimated. Where the unsaturated zone travel time is significant, it can be subtracted from the apparent CFC age, to estimate the apparent saturated zone travel time, or apparent groundwater age.

It should be noted that the CFC clock can become partially or completely reset if water is re-exposed to the atmosphere at any time along its flow path. Thus, following groundwater discharge to a stream, for example, CFC concentrations will increase due to gas exchange at the stream–atmosphere interface (i.e. the water surface). If the equilibration with the atmosphere is complete, and this river water subsequently recharges an aquifer, the clock will essentially be reset at the time of recharge (and this will be the zero age). If the equilibration is not complete, then the water will have an apparent age greater than zero at the time of stream recharge, and subsequent groundwater ages will be relative to this value.

## 3.5. GROUNDWATER AGE

Although reference is often made to dating of groundwater, it must be recognized that what is actually dated is the environmental tracer, rather than the water that carries the tracer. Whether the age information can be applied to the water in which the CFCs (or any other tracer) are dissolved depends on how perfectly the CFCs are transported with the water, and the extent to which mixing and other physical and chemical processes, such as degradation, sorption, dispersion and matrix diffusion during transit have affected the CFC concentrations in water.

The age determined from CFCs is an apparent age or model age because it is based on certain simplifying assumptions. The term ‘age’ is used throughout for brevity but, in principle, all ages are apparent or model ages. Reference is also made to recharge date. This is the date of recharge implied by the measured concentration of the CFC compound in the water, assuming a piston flow model with minimal unsaturated zone travel time, and also assuming that the concentration of CFC was not altered by transport processes between the point of recharge and the measurement point in the aquifer. It is important to use recharge date, especially when interpreting temporal significance from the concentrations of other solutes in groundwater (e.g. nitrates) that may have transient input behaviour.

## 3.6. FUTURE APPLICATIONS OF CFCs

As a result of the Montreal Protocol on Substances that Deplete the Ozone Layer, air mixing ratios of CFC-11, CFC-12 and CFC-113 peaked in the northern hemisphere in about 1994, 2001 and 1996, respectively (Fig. 2.1(a)). Because of nearly level atmospheric input functions of CFC mixing ratios in the 1990s and early 2000s, it is not possible to resolve modern CFC ages as precisely as can be done with waters recharged earlier, when atmospheric mixing ratios were increasing rapidly. Yet there are still important future uses of CFCs in dating groundwater.

Although the apparent ages of modern waters have relatively large uncertainties, the CFC record of recharge over the past 60 years remains in aquifers and most of this record can be sampled and age can be interpreted, often with lower uncertainty than for modern samples. The pre-1990s groundwater CFC record remains useful in establishing chronologies for parcels of water recharged to aquifers spanning some 50 years (from the 1940s to the 1990s).

As atmospheric mixing ratios of CFCs fall, it will once again be possible to use CFCs to date modern waters, though an additional caution is that dual ages will be possible. For example, North American air contained about 262 pptv CFC-11 in 1989.5 and in 2001 (Appendix II, Table II.1). In using CFC-11 to date nearly modern water today, other criteria, such as depth below the water table or determination of the concentrations of other environmental tracers, would be needed to determine if a sample with a calculated CFC-11 concentration of 262 pptv was recharged in 1989.5 or 2001. The CFC-113 atmospheric mixing ratio has fallen more than 4 pptv since the peak in 1996 and will, within several years, also be useful in dating modern waters. CFC-12 atmospheric mixing ratios are expected to decline more slowly than those of CFC-11 and CFC-113. Consequently, relatively large uncertainties will apply to modern ages based on CFC-12 data. As the various CFCs are expected to decline at differing rates, it is anticipated that CFC ratios will once again be useful in dating, particularly in resolving cases of dual apparent ages.

Because of the relatively smooth changes in CFC atmospheric mixing ratios, the possibility of determining multiple ages is not nearly so severe as results from attempts to deduce apparent ages for tritium data alone (Chapter 11, Fig. 11.1). It is also anticipated that the effects of hydrodynamic dispersion will be relatively small for CFCs due to the relatively smooth changes in atmospheric mixing ratios. Hydrodynamic dispersion will cause greatest uncertainty for waters with CFC ages corresponding to concentrations close to the peak values.

## Chapter 4

# EFFECTS AND PROCESSES THAT CAN MODIFY APPARENT CFC AGE

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### 4.1. CONTAMINATION

CFC contamination refers to concentrations of one or more CFCs that are in excess of concentrations expected from atmospheric sources. The concentrations of CFCs in 'contaminated' samples are typically quite small, but from a dating standpoint, the concentrations exceed modern air–water equilibrium values and no age information can be assigned. Some commonly recognized sources of CFC contamination include seepage from septic tanks, landfills (Kjeldsen and Christophersen, 2001), release from polyurethane foam waste (Kjeldsen and Jensen, 2001), leaky sewer lines, leakage from underground storage tanks, infiltration or disposal of industrial wastes, and recharge from rivers contaminated with CFCs, such as from rivers that historically carried effluent from sewage treatment plants. Thompson and Hayes (1979) described a plume of CFC-11 contamination that extended 74 km along a fault zone. The narrow shape of the plume suggested a point source of contamination that was traced back to a residential area near San Antonio, Texas, USA. The source could not be identified, but represented an estimated total release of approximately 21 kg of CFC-11 spread through approximately 14 km$^3$ of aquifer.

Busenberg et al. (1993) used CFCs to map a waste plume at the Idaho National Engineering and Environmental Laboratory in south-east Idaho, USA.

As rivers commonly contain discharge from sewage treatment plants, many rivers in the 1960s until the early 1980s, prior to regulation of CFCs in industrialized countries, often contained large excesses of CFCs. Shallow groundwater near rivers was often contaminated with CFCs wherever there was net seepage from the river to the groundwater (Schultz et al., 1976; Busenberg and Plummer, 1992). Because CFCs were not regulated, CFC contamination of rivers from sewage effluent and other discharge of wastes may have been greater in the past than today. Böhlke et al. (1997) used $^3$H/$^3$He dating (Stute et al., 1997) to retrieve a record of the history of halocarbon contamination in the Danube River in north-west Hungary from shallow groundwater recharged from the river in the 1960s to the 1990s. CFC concentrations in rivers have decreased since the 1960s and 1970s because of increased levels of treatment (including aeration), and controls on production of CFCs imposed by the Montreal Protocol. However, Clark et al. (1995) found that surface water in the Hudson River in the New York City area was contaminated with respect to CFC-11 and CFC-12 with factors of 3 to 5 and 10 to 20, respectively, over a five month period in 1992. Beyerle et al. (1999) found that CFC-11 and CFC-12 in groundwater recharged by river infiltration at Linsental, north-eastern Switzerland, was contaminated with both CFCs. In the excess CFCs, the ratio of CFC-11 to CFC-12 was 10 in all the samples and the excess CFCs increased linearly with increasing $^3$H/$^3$He age of the groundwater. This suggested that the samples were mixtures of uncontaminated river water with older contaminated water. The older contaminated water had apparently a CFC-11/CFC-12 ratio of 10, however, the source of this contamination was not apparent.

In an agricultural area in south-central Idaho, unsaturated zone air samples collected from the annulus of blowing wells (wells that exhaust unsaturated zone air during periods of low barometric pressure at the land surface, and inhale air when barometric pressure rises at the land surface) were enriched in CFC-11 as much as fivefold compared with North American air (Plummer et al., 2000). Such enrichments in air CFC compositions are uncommon in rural areas, but have been noted in some urban and industrialized areas (Oster et al., 1996; Ho et al., 1998). The source of excess CFCs in Idaho could not be confirmed. However, it was noted that the U.S. Environmental Protection Agency regulations (USEPA, 1998) currently allow CFC-11, CFC-12 and CFC-113 as inert ingredients in pesticide formulations (Plummer et al., 2000). It was suggested that agricultural application of pesticides introduced CFCs, particularly CFC-11, to unsaturated zone air, which has subsequently mixed and dispersed through the unsaturated zone by barometric pumping (Plummer et al., 2000). CFC-12 and CFC-113 concentrations in unsaturated zone air in south-central Idaho were near or below North American air mixing ratios. Unsaturated zone air from rangeland wells more than 50 km from irrigated areas in south-central Idaho contained low concentrations of CFC-12 and CFC-113 (only 19.6% and 6.9% of modern North American air, respectively), but was contaminated with CFC-11, with concentrations nearly three times that of North American air (Plummer et al., 2000). Most of the surface water samples were from canals that carry water from the Snake River, in south-central Idaho, which is diverted for crop irrigation, and these waters were near solubility equilibrium with CFC-12 and CFC-113. However, CFC-11 concentrations were up to twelvefold saturation in some of the surface waters, therefore, local recharge of contaminated river water used for crop irrigation is also a likely source of CFC-11 contamination in south-central Idaho. However, as the Snake River contains runoff from agricultural lands, it is possible that pesticides may be the ultimate source of CFC contamination in south-central Idaho (see Chapter 9, Section 9.5 for further details).

One advantage of measuring the concentrations of multiple CFCs in a single water sample is that if the sample is contaminated with one CFC compound, it may not necessarily be contaminated with other CFCs. More than half the groundwater samples in south-central Idaho (Plummer et al., 2000) had CFC-11 or CFC-12 concentrations that were less than modern and potentially could be dated using CFC-11 or CFC-12. Ages based on CFC-113 could be assigned to water from 46 of the 48 sampled wells. However, the CFC data do not permit separation of uncontaminated water samples from those that could have low levels of contamination, that is, the sample may contain excesses of one or more CFCs, but the concentrations remain within the dating range, or could be mixed with waters containing some ranges of low level contamination. Since it is very difficult to recognize low level contamination of one or more CFCs, it is best to resort to additional tracer data to help confirm and eliminate possible contaminated samples. Approaches using ratios of CFCs and comparison of CFC based ages with reconstructed and expected tritium concentrations have been used in south-central Idaho (Plummer et al., 2000) and southern Georgia, USA (Plummer et al., 1998b). In cases where low level contamination may be occurring, the CFC ages obtained may be minimum estimates of the actual age.

Urban air can be another source of excess CFCs in groundwater. However, Oster et al. (1996) showed that CFC anomalies in western European air were damped by diffusive mixing processes in the unsaturated zone. This raises the possibility of reconstructing the local history of air enrichment in CFCs that could be applied in dating other samples in the area. In some areas, groundwater may provide an archive of local CFC mixing ratios that may be dated by other techniques and used for other local dating studies. Ho et al.

(1998) considered the implications of failure to include local enrichment in CFCs in urban air in groundwater dating. For example, water recharged in urban areas prior to 1987 in equilibrium with air having CFC-11 and CFC-12 excesses that are 10% higher than North American air will be biased young by two years or less. However, the errors resulting from urban air became very large in the 1990s, due to the levelling off of the CFC atmospheric mixing ratios.

Johnston et al. (1998) have shown that groundwater samples that recharged in the 1960s through the 1970s were contaminated with CFC-12. The CFC-11 derived ages were consistently greater than the $^3H/^3He$ ages by about eight years; a difference attributed to the CFC-11 lag time in the unsaturated zone. The authors suggest atmospheric concentrations of CFC-12 may have been much higher than the northern hemisphere mixing ratios as a result of local atmospheric sources. The source of the CFC-12 may have originated within the cities of Kitchener and Waterloo, Ontario, Canada, which are located a few kilometres west of the site.

Air samples from the Blue Ridge Mountains of Virginia, USA (1995–2000) had CFC-11 and CFC-113 mixing ratios that closely followed the NOAA Niwot Ridge, Colorado, values used here for North American air (Elkins et al., 1993), whereas the CFC-12 and $SF_6$ mixing ratios were slightly higher, by approximately 2% and 5%, respectively, than those at Niwot Ridge (Plummer et al., 2001). Although included in the age analysis, by accounting for the small excesses, the adjusted ages were typically less than one year older than those based on average North American air and were within the uncertainties of the dating methods.

Other ways in which excesses of CFCs can be introduced into water samples include contamination from materials in pumps and sampling equipment (Reynolds et al., 1990), contact with air during sampling, introduction of young (and/or contaminated) water induced by pumping, and introduction of CFCs during well construction.

In some cases, the sample tubing is a source of CFC contamination. A series of tests were conducted in the early 1990s to determine the contamination potential of various tubing materials. In these tests, blank $N_2$ was passed through lengths of about 2 m (unless otherwise indicated) of new tubing at a rate of about 30 $cm^3$/min. The $N_2$ was then analysed for CFC contamination by the tubing. The results are shown in Table 4.1. The contamination potential of any specific type of tubing varied greatly even for the same type of polymeric material.

Refrigeration grade copper or aluminium tubing does not contaminate groundwater samples with CFCs. If copper or any other tubing is contaminated with a thin coating of oil, then it should be discarded because the oil will contaminate the sample. High quality nylon tubing is acceptable and has been used extensively for sampling by the U.S. Geological Survey. Of all the other

TABLE 4.1. RELEASE OF CFCs BY NEW TUBING TO A STREAM OF CFC-FREE NITROGEN

*(Concentrations greater then 'trace' indicate tubing that is not suitable for sampling for CFCs. These tests were conducted at the U.S. Geological Survey)*

| Material | CFC-12 | CFC-11 | CFC-113 |
|---|---|---|---|
| Silicone rubber (sample 1) | High | Very high | Very high |
| Silicone rubber (sample 2) | Low | Medium | —[a] |
| Natural rubber | Low | Medium | —[a] |
| Viton (sample 1) 16 m | None | Trace | Trace |
| Viton (sample 2) 16 m | None | None | None |
| Fisher brand tubing | Low | Medium | High |
| Tygon brand tubing (sample 1) | Trace | Medium | Very high |
| Tygon brand tubing (sample 2) | None | Trace | —[a] |
| Polyethelene | Trace | Low | Low |
| Polypropylene | Trace | Very high | —[a] |
| Nylon (sample 1) 30 m | None | None | None |
| Nylon (sample 2) 30 m | None | None | None |
| Teflon (sample 1) | Trace | Low | Medium |
| Teflon (sample 2) | Trace | Medium | —[a] |
| Refrigerator grade copper tubing (many samples) 17 m | None | None | None |
| Refrigerator grade aluminium tubing 17 m | None | None | None |

[a] No data: chromatography was terminated prior to elution of CFC-113.

polymeric tubing, the Viton synthetic rubber tubing is the most reliable. Small lengths of Viton tubing (20 cm) can be used in the head of peristaltic pumps for sampling. The Viton tubing is connected to copper or nylon tubing. All polymeric materials can become a source of contamination after they have been exposed to very high concentrations of CFCs present in groundwaters or in the air of storage rooms (Dunkle et al., 1993). The CFCs diffuse into the polymers and then are slowly released from the tubing, making the tube a significant source of groundwater contamination (Reynolds et al., 1990).

Water samples can also be contaminated from permanently installed submersible pumps in wells. Newly installed submersible pumps can contaminate samples with CFCs and other VOCs. The sample should be collected before the pressure tank and before the location where disinfectant or other chemicals are added to the groundwater. Many large municipal wells are lubricated with vegetable oil, however, usually this does not present a problem. Other turbine pumps are water lubricated and unsatisfactory results will be obtained if the lubrication water has been treated or aerated. Piezometers have been successfully sampled with all-metal pumps. The gas driven Bennett pumps and the electric Grundfos pumps with stainless steel impellers are excellent. Pumps that have rubber parts should be avoided because they can contaminate groundwater samples (Dunkle et al., 1993). Many of the older (pre-1960) water samples reported by Dunkle et al. (1993) from shallow sands in the Atlantic coastal plain of Maryland and Virginia in the USA contain small excesses of CFC-11 relative to CFC-12. Subsequent tests showed that up to 200 pg/kg of excess CFC-11 was released from a rubber rotor inside the pump used to collect the samples (Plummer and Busenberg, 2000). This contamination resulted in a young bias of as much as 20 years in the CFC-11 ages relative to those based on CFC-12 in samples with CFC-12 ages near the CFC-12 detection limit (1940s to early 1950s). Pumps with rubber parts may yield initially satisfactory results, but once they become contaminated, they can never again be cleaned or used.

Another source of contamination is air that can sometimes be introduced into water samples when the water level in the well is lowered to the level of the pump intake during sampling. This is not always evident in discharge from wells because the water pressure in the discharge line can be sufficient to dissolve the excess air before reaching the sampling point. Excesses of dissolved atmospheric gases (including $O_2$, $N_2$, Ar and Ne) are good indicators of air contamination. Water pumped from monitoring wells with screens that cross the water table can also contact air in the sampling process.

Other contamination can result from the drilling process. If, for example, a monitoring well has been inadequately completed, groundwater in the vicinity of the well may still contain traces of drilling fluid that contained CFCs, or the water near the well may have been contaminated with CFCs from the drilling equipment. This has probably occurred with a few monitoring wells drilled in the sands and gravels of the Santa Fe aquifer system near Albuquerque in central New Mexico, USA. Here, one monitoring well has an open interval of only 2 m at a depth of 245 m below the water table. This sample contained 18 pg/kg of CFC-12 and had a $^{14}$C activity of only 15.3 pmc with a conventional radiocarbon age of about 15 ka (Plummer, unpublished data, 1998). Use of compressed air in rotary drilling and well development can also introduce large quantities of CFCs and other dissolved gases. In low permeability environments, the inability effectively to purge wells can mean that the removal of this contamination may take many years. (See Chapter 8, Section 8 for examples of wells contaminated by the drilling process.)

## 4.2. UNSATURATED ZONE TRANSPORT OF CFCs

### 4.2.1. Introduction

Where a thick unsaturated zone separates the atmosphere from the water table, then the concentrations of CFCs in the soil air immediately above the water table may not be the same as their atmospheric concentrations at that time. The CFC concentration in the soil air will depend on the rate of transport of CFCs through the unsaturated zone, and will be less than the atmospheric concentrations. If this effect is not considered, groundwater ages obtained with CFCs may overestimate true groundwater ages.

The transport of gases through unsaturated soil can occur by diffusion and advection in the gas and liquid phases. Advection of soil air may occur in response to pressure variations in the soil resulting from wind eddies, changes in atmospheric pressure and changes in soil temperature. Air movement may also result from changes in soil water content that occur during infiltration, or from variations in the position of the water table. However, while transport of soil gas through advection appears important in the upper few metres of the soil profile, at greater depths diffusive processes are likely to dominate (e.g. Kimball and Lemon, 1972; Farrell et al., 1966). This conclusion is supported by measured profiles of CFCs obtained from deep (> 50 m) unsaturated zones, which appear to be diffusion controlled (Weeks et al., 1982; Severinghaus et al., 1997). An exception to this may be in low permeability fractured rock systems, where fluctuations in barometric pressure may induce significant movement of air to great depths (e.g. Thorstenson et al., 1989).

### 4.2.2. Calculation of time lags

Cook and Solomon (1995) used a one-dimensional model to describe gas transport processes in the unsaturated zone. The model allowed for advective and diffusive transport of gases through unsaturated soil in both the liquid and gas phases, with retardation through sorption onto the solid phase, and degradation. The concentration of atmospheric trace gases in the soil gas phase near the soil surface should be the same as the atmospheric concentration at that time. Concentrations at greater depth will depend on past atmospheric concentrations, the vertical water velocity, soil water content, liquid and gas phase diffusion coefficients, and partitioning between the three phases.

Figure 4.1 depicts soil gas profiles of CFC-11, CFC-12 and CFC-113 in 1992 for a uniform soil with volumetric water content of 0.15 and gas filled porosity of 0.2 (total porosity 0.35), above a 30 m deep water table. (This figure has been revised from that presented by Cook and Solomon (1995) using the

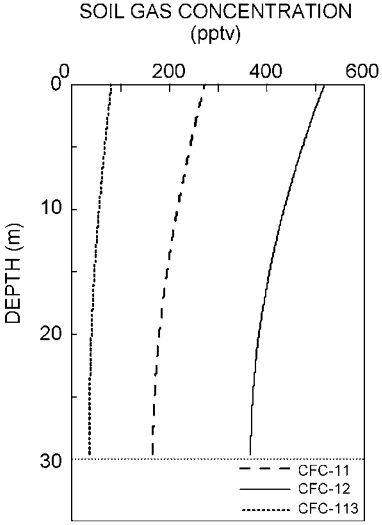

*FIG. 4.1. Modelled soil gas concentrations in 1992 above a water table at 30 m depth. Revised from Cook and Solomon (1995) using atmospheric CFC data for the northern hemisphere as reproduced in Appendix II, Table II.1.*

atmospheric CFC data for the northern hemisphere given in Appendix II, Table II.1.) Gas diffusion coefficients were assumed to be 260, 285 and 230 $m^2/a$ for CFC-11, CFC-12 and CFC-113, respectively (diffusion into $N_2$ at 283 K, 1013.25 hPa.). Air–water partition coefficients have been taken to be 0.51, 0.13 and 0.15 for CFC-11, CFC-12 and CFC-113, respectively, reflecting solubilities at 283 K. Other model parameters are given by Cook and Solomon (1995). In these simulations, both gas and liquid phases were considered to be immobile, to simulate conditions of low recharge (transport by diffusion only), and sorption to the solid phase was considered negligible. For CFC-11, the concentration in the soil gas phase at the top of the water table is estimated to be 166 pptv, compared with a concentration of 272 pptv in the atmosphere (in 1992). The soil gas concentration of 166 pptv is equivalent to the atmospheric concentration measured in 1980. Hence, a water sample collected at the water table would appear 12 years old, if dated by CFC-11. We say that the ‘apparent time lag’ for transport of CFC-11 through the unsaturated zone is 12 years. Apparent time lags in 1992 for water table depths between 5 and 40 m using these same soil parameters are given in Table 4.2.

As described by Cook and Solomon (1995), the apparent time lag increases with increasing thickness of the unsaturated zone, and generally becomes significant for water table depths greater than about 10 m. However, its magnitude is dependent on soil parameters, particularly the soil water content. Increases in soil water content (and thus decreases in gas filled porosity) will usually result in retardation of tracer movement, as the cross-sectional area available for gas diffusion is reduced and the tortuosity of the flow path is increased, and there is increased partitioning of the tracer into the less mobile liquid phase. The simulation results shown in Table 4.2 are for a water content of $\theta = 0.15$ (gas filled porosity = 0.20). For soil water contents of $\theta = 0.10$ (gas filled porosity = 0.25) and $\theta = 0.20$ (gas filled porosity = 0.15), the time lag in 1992 for CFC-11 and a 30 m water table becomes 6.3 years and 19 years, respectively. For a 10 m water table, the time lags in 1992 for CFC-11 become 1 year and 3 years, respectively.

While unsaturated zone water contents in sand and loam textured soils will usually be less than 0.20 (away from the influence of the water table), higher water contents may be encountered in clay soils. At water contents of $\theta = 0.25$ (gas filled porosity = 0.10), and $\theta = 0.30$ (gas filled porosity = 0.05), the time lag in 1992 for CFC-11 to a 10 m water table increases to 11 years and 32 years, respectively. For a 5 m water table, the time lags become 3 years and 19 years, respectively. Thus, where the soil water content is very high, significant time lags can occur for even very shallow water tables.

Variations in aquifer recharge rate can also affect CFC concentrations within the unsaturated zone. Because CFCs are soluble in the liquid phase, higher recharge fluxes will result in deeper penetration of the tracer into the soil. For a recharge flux of 300 mm/a, the concentration of CFC-11 in the gas phase immediately above a 30 m water table increases from 166 pptv to

TABLE 4.2. APPARENT TIME LAGS (IN YEARS) FOR TRANSPORT OF CFCs THROUGH THE UNSATURATED ZONE, BASED ON ATMOSPHERIC CONCENTRATIONS IN 1992 (COOK AND SOLOMON, 1995) AND 2002

| Water table depth (m) | Time lag in 1992 | | | Time lag in 2002 | | |
|---|---|---|---|---|---|---|
| | CFC-11 | CFC-12 | CFC-113 | CFC-11 | CFC-12 | CFC-113 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 | 0.5 | 0 | 0 | 0 | 0 | 0 |
| 10 | 2 | 1 | 1.5 | 1 | 2 | 1 |
| 20 | 5 | 4 | 4.5 | 12 | 6 | 11 |
| 30 | 12 | 9 | 8 | 15 | 12 | 13 |
| 40 | 17 | 15 | 13 | 21 | 16 | 16 |

182 pptv, and consequently the time lag decreases from 12 to 10 years. As solubility decreases, the effect of variations in recharge rate becomes less pronounced. For CFC-12, the apparent time lag to a 30 m water table decreases from 8.5 to 8.0 years, as the recharge rate increases from 0 to 300 mm/a.

If the water content is very high, however, then the flux of dissolved gas in the liquid phase may be much greater than the diffusive flux in the gas phase. In particular, for a soil water content of $\theta = 0.30$, the time lag for CFC-11 and a 30 m water table decreases from more than 60 years (no atmospheric CFC-11 in the groundwater) at 0 recharge to $t_L = 34$ years at a recharge flux of 300 mm/a. The latter is very close to the residence time of water in the unsaturated zone (30 years).

Increased sorption onto the immobile solid phase results in retardation of tracer movement. However, in unsaturated zone gas transport the effect is usually minor, as the gases must first partition into the water phase (which is usually assumed to completely surround the solid phase particles). For CFC-113, the strongest sorbing of the CFCs, a partition coefficient of $K_d = 0.1$ increases the apparent time lag for a 30 m water table from 8 to 9 years.

The apparent time lag would be relatively constant in time if the atmospheric concentration of the tracers followed an exponentially increasing trend (Cook and Solomon, 1995). Because the rate of increase has declined in recent years, the magnitude of the time lag has increased.

Figure 4.2 depicts concentrations of CFC-11 in the atmosphere (solid line) and in soil air immediately above a water table at 30 m depth (broken line). The apparent time lag has increased over time, from approximately 8–9 years before 1980, to 10–12 years between 1980 and 1995. The time lag has increased more rapidly in recent years, as the atmospheric growth rate has declined, to be 15 years in 2002. Table 4.2 compares the time lags in 1992 and 2002 for CFC-11, CFC-12 and CFC-113 for water table depths between 5 and 40 m.

### 4.2.3. Accounting for the time lag in calculation of groundwater ages

Where the unsaturated zone is thick, the time lag for CFC diffusion through the unsaturated zone will result in calculated CFC ages being greater than hydraulic groundwater ages. Apparent groundwater ages should be calculated using the CFC concentration in soil air immediately above the water table as the input, rather than the atmospheric concentration. The CFC concentration in soil air can be calculated using the model presented by Cook and Solomon (1985). The model can be validated from measurements of CFC concentrations in the unsaturated zone, or by comparing CFC ages with those obtained using other tracers (e.g. $^3H/^3He$).

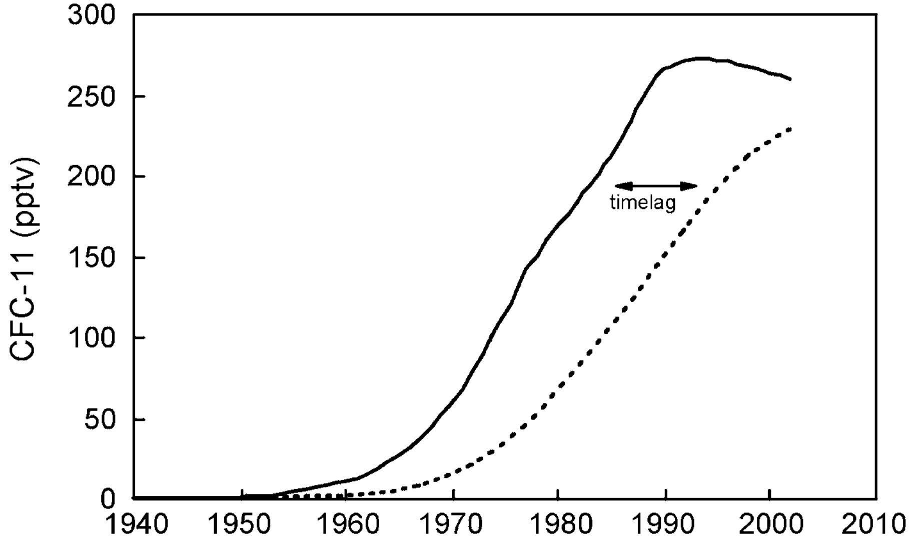

*FIG. 4.2. Concentrations of CFC-11 in the atmosphere (solid line), and in the soil atmosphere immediately above a water table at 30 m depth (broken line). The horizontal distance between the two lines indicates the time lag, which was 8–9 years before 1980, and increased to 15 years in 2002.*

Weeks et al. (1982) found CFC-12 concentrations were only about 80% of modern air at 10 m depth within the unsaturated zone of the Southern High Plains of Texas, USA, and fell with depth to about 10% of air mixing ratios at 43.9 m depth. The vertical CFC profiles could be modelled using a soil diffusion model equivalent to that presented by Cook and Solomon (1985). Busenberg et al. (1993) measured CFC profiles in unsaturated zone playa sediments and in the underlying Snake River Plain basalts to depths of nearly 60 m in southern Idaho. In 1991, CFC-11 and CFC-12 concentrations at 57.5 m were 7% and 27% of the respective soil air concentrations measured at 3 m. Although both CFC mixing ratios fell dramatically along the vertical profile, CFC-11 was depleted relative to CFC-12, as predicted by the soil–gas diffusion model. Severinghaus et al. (1997) measured profiles of CFC-11, CFC-12 and CFC-113 to depths of 60 m in two test holes in the Algodones Dunes, Imperial Valley, California, USA, and also found the profiles matched results of the diffusion model closely. In southern Ontario, Canada, Johnston et al. (1998) found groundwater ages beneath a 25 m thick unsaturated zone in southern Ontario determined using CFC-11 to be consistently greater than $^{3}H/^{3}He$ ages by approximately 8 years, which they attributed to slow diffusion of CFCs through the unsaturated zone.

In fractured rock, however, barometric pumping can transport gas through hundreds of metres on timescales of months, rather than the few metres and decades required for diffusive transport (Nilson et al., 1991). Studies of gas flow in boreholes in Yucca Mountain, Nevada, USA, indicate a combination of thermal-topographic, barometric and wind effects controlling unsaturated zone CFC advection on timescales of ≤5 years (Thorstenson et al., 1998). In these systems, the diffusion model may not be correct, and direct measurements of CFCs in the unsaturated zone may be necessary.

### 4.3. RECHARGE TEMPERATURE

The recharge temperature is the air–water equilibrium temperature at the time the groundwater sample was isolated from the atmosphere. Groundwater temperature may not be a reliable indicator of the recharge temperature. In principle, the recharge temperature can be calculated from the concentration of noble gases or $N_2$ and Ar from Henry's Law and the assumption that these gases were equilibrated with the atmosphere at recharge. Concentrations of dissolved $N_2$, Ne, Ar, Kr and Xe are useful in determining recharge temperatures because the solubilities of these gases vary differently as a function of temperature (Weiss, 1970). Noble gas compositions in groundwaters can be used to determine recharge temperatures with high precision, but also the temperature and recharge elevation at a lower precision (Aeschbach-Hertig et al., 1999; Kipfer et al., 2002). However, nearly all groundwater samples have concentrations of noble gases in excess of Henry's Law solubility at the recharge temperature. The source of this excess has been attributed to 'excess air', and is discussed in Section 4.4.

Where the unsaturated zone is more than a few metres thick, the recharge temperature is usually within about 1°C of the mean annual surface-soil temperature (Mazor, 1972; Andrews and Lee, 1979; Herzberg and Mazor, 1979; Heaton and Vogel, 1981; Stute and Schlosser, 1999). In the contiguous USA, the mean annual surface-soil temperature is within 1 ± 1°C of the mean annual air temperature (Smith et al., 1964; Toy et al., 1978); however, larger temperature differences have been reported in deserts and snow covered areas (Stute and Schlosser, 1999). Where the unsaturated zone is less than 1–2 m thick, the unsaturated zone temperature responds to seasonal variations in soil temperature (Matthess, 1982). In such instances, episodic recharge to the groundwater may reflect the temperature of the unsaturated zone at the water table at specific times rather than the mean annual surface-soil temperature

(Sugisaki, 1961; Stute and Schlosser, 1999). Gas concentrations in water recharging aquifers through sinkholes or from losing streams often reflect the water temperature during recharge rather than the mean annual surface-soil temperature (Plummer et al., 1998b; Sugisaki, 1961). Many other factors, including vegetation cover, can significantly affect the recharge temperatures calculated from gas concentrations (Stute and Sonntag, 1992; Kipfer et al., 2002).

Figure 4.3 shows concentrations of CFC-11, CFC-12 and CFC-113 in groundwater recharged between 1940 and 2000, at sea level, and in equilibrium

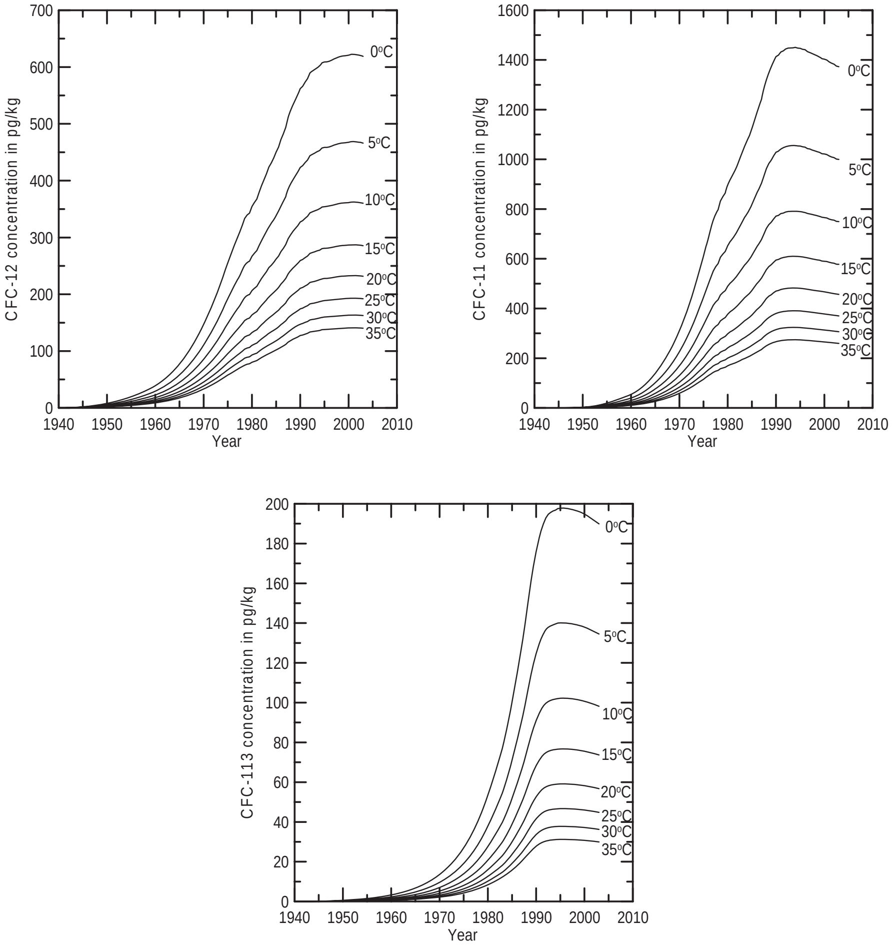

*FIG. 4.3. The concentration of CFCs in water as a function of temperature in equilibrium with North American air at sea level are shown.*

with the North American atmosphere at 5–30°C. CFC-11 concentrations in water recharged in the year 2000 at 5°C are about three times the CFC-11 concentrations of water recharged at 30°C. An uncertainty of ±2°C in recharge temperature is reasonable to expect for samples where the gas recharge temperatures were not determined. The expected age uncertainty for these samples is three years or less for water recharged between the mid-1970s and about 1990. Uncertainty in recharge temperature of ±2°C leads to uncertainty in apparent CFC ages of one year or less for water recharged prior to the mid-1970s (Busenberg et al., 1993). However, in groundwater recharged after 1990, the ±2°C uncertainty can result in very significant error in the calculated apparent age of the groundwater. Overestimation of recharge temperature results in apparent ages that are too young, and underestimation gives ages that are biased old (Chapter 3, Table 3.2).

When ratios are used to calculate groundwater age (Chapter 2, Fig. 2.1(b)), the ratio of the partial pressures ($R_{xy}$) is calculated from the concentrations of the two CFCs in the groundwater using the equation:

$$R_{xy} = \frac{p_x}{p_y} = \frac{C_x K_y}{C_y K_x} \tag{4.1}$$

where $x$ and $y$ represent different tracers. The uncertainty in temperature introduces an uncertainty in the Henry's Law constants in the above equation that are used to calculate the partial pressures of the two tracers. The CFC concentrations in the water are measured values and are independent of temperature. The per cent error introduced by a 1°C uncertainty in the recharge temperature for water recharged at 10°C in the CFC-11/CFC-12, CFC-113/CFC-12 and CFC-113/CFC-11 ratios are 0.534%, 1.12% and 0.584%, respectively. The change in $R_{xy}$ per degree uncertainty in temperature is dependent on the rate of change of the ratio of the Henry's Law constants with temperature. The per cent error in the ratio of two CFC partial pressures for waters recharged between 0 and 25°C are given in Fig. 4.4. Figure 4.5 shows the uncertainty in the ages introduced by ±2°C and ±5°C error in the temperature used to calculate the CFC partial pressures for the water that recharged at 10°C. For recharge temperatures between 0 and 30°C, a recharge temperature uncertainty of ±2°C introduces a maximum dating error of ±1–2 years at the upper dating range of the ratio method, and this dating error decreases to less than ±1 year for older waters.

The solubilities of CFC-11, CFC-12 and CFC-113 in water depend strongly on the temperature during groundwater recharge and decrease with

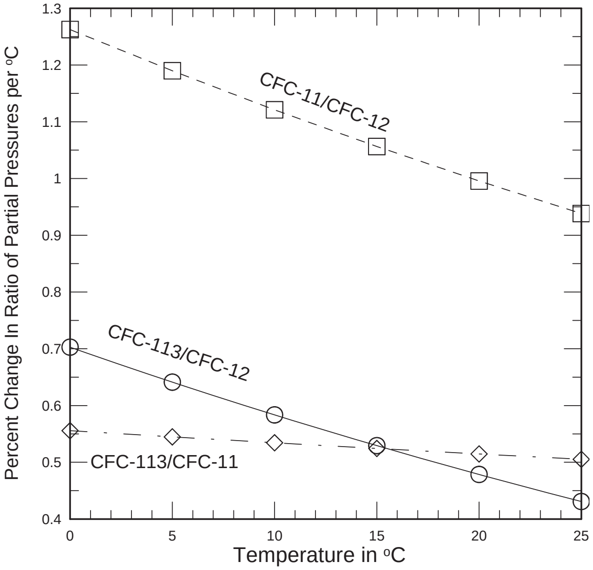

*FIG. 4.4. Per cent error in the ratio of two CFC partial pressures for waters recharged between 0 and 25°C for an uncertainty of 1°C in the recharge temperature.*

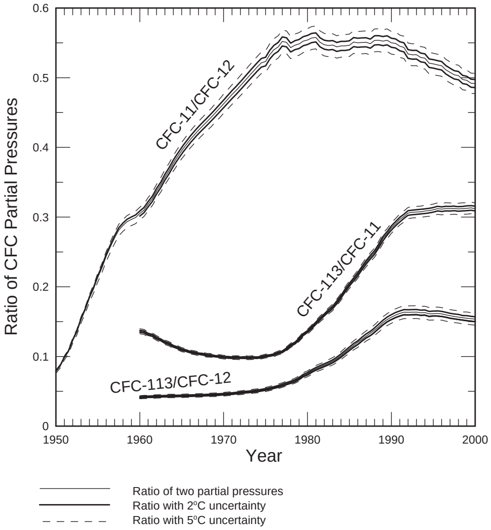

*FIG. 4.5. Uncertainty in the ages of groundwater dated by the ratio method introduced by ±2 and ±5°C error in the temperature used to calculate the CFC partial pressures. The water in this example recharged at 10°C.*

increasing temperature (see Chapter 3, Section 3.2). The solubilities as a function of temperature have been determined accurately for CFC-11, CFC-12 (Warner and Weiss, 1985) and for CFC-113 (Bu and Warner, 1995). Those data and the ratios of solubilities for the three CFCs are presented in Table 4.3 for 0 to 30°C in five degree intervals. The solubility ratios for any two of the CFCs are much less temperature dependent compared with the solubilities.

As seen in Figs 4.4 and 4.5, the uncertainties in recharge temperature estimation result in uncertainties in the CFC model ages derived from CFC concentrations. The younger the water, the more sensitive is the CFC model age to uncertainties in recharge temperature. In general, an error of several degrees in estimation of the recharge temperature would result in a corresponding error in the calculated atmospheric CFC concentration that could cause an offset of several years as CFC model age for water recharged after 1975. As seen in Fig. 4.6, even for recent recharge, the uncertainties in estimation of recharge temperature have only a minor effect on the CFC model ages derived from CFC concentration ratios. Figure 4.6 shows the effects of ±5ºC error in estimation of recharge temperature on the CFC model ages for waters recharged in different years derived from CFC concentrations (a), (b) and (c), and concentration ratios (d).

Consequently, in circumstances where the recharge temperature is uncertain or even unknown, the age of the groundwater can still be estimated reliably using CFC concentration ratios, provided that the estimates are not too far away from the actual temperature. Additionally, in cases of well understood

TABLE 4.3. TEMPERATURE DEPENDENT SOLUBILITIES AND RATIOS OF CFC SOLUBILITIES

| t (ºC) | Solubilities ($10^{-3}$·mol·kg$^{-1}$·(1013.25 hPa)$^{-1}$) | | | Ratio of solubilities | | |
|---|---|---|---|---|---|---|
| | CFC-11 | CFC-12 | CFC-113 | CFC-11/ CFC-12 | CFC-113/ CFC-11 | CFC-113/ CFC-12 |
| 0 | 38.71 | 9.42 | 12.63 | 4.11 | 0.326 | 1.341 |
| 5 | 28.18 | 7.09 | 8.95 | 3.97 | 0.317 | 1.261 |
| 10 | 21.13 | 5.49 | 6.53 | 3.85 | 0.309 | 1.190 |
| 15 | 16.29 | 4.35 | 4.90 | 3.75 | 0.301 | 1.127 |
| 20 | 12.88 | 3.53 | 3.78 | 3.65 | 0.293 | 1.071 |
| 25 | 10.44 | 2.92 | 2.98 | 3.57 | 0.286 | 0.981 |
| 30 | 8.65 | 2.47 | 2.41 | 3.50 | 0.279 | 0.975 |

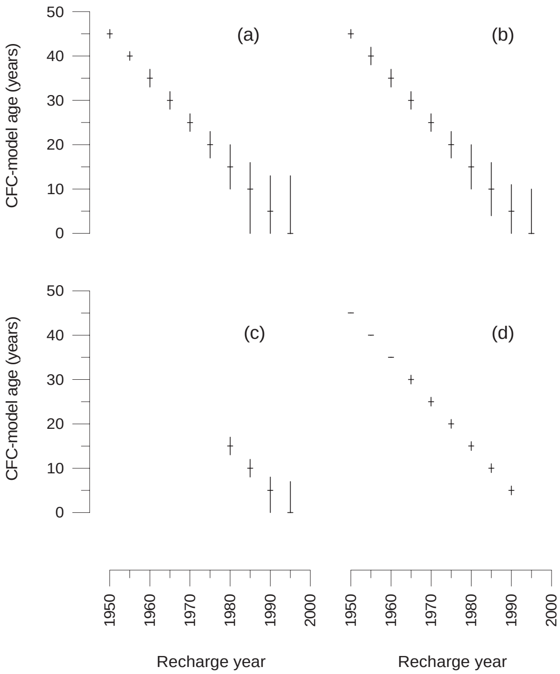

*FIG. 4.6. The effects of ±5°C error in estimation of recharge temperature on the CFC model ages derived from CFC concentrations and concentration ratios (upper and lower end of vertical bars) are shown: (a) CFC-11; (b) CFC-12; (c) CFC-113; (d) CFC-11/CFC-12 (before 1980) and CFC-113/CFC-12 (after 1980). The calculations are based on waters recharged in different years at 9°C. The CFC model ages calculated from the recharge temperature of 9°C are represented with horizontal bars.*

flow systems, in an inverse approach the known water age could be used to constrain unknown recharge temperatures. That case could be especially interesting in mountainous regions to derive recharge altitudes via the temperature dependency.

## 4.4. EXCESS AIR

Numerous observations of dissolved gas concentrations in groundwater have shown that groundwater frequently contains more gas than can be explained by equilibrium solubility with the atmosphere (e.g. Herzberg and Mazor, 1979; Heaton and Vogel, 1981). The excess concentrations of various gases are often in accordance with air composition and this effect is, therefore, called excess air (Heaton and Vogel, 1981). This is probably a result of a transient rise in the water table that does not fully displace the gas phase, or can be artificially introduced during well construction, development or purging. The resulting trapped gas then partitions into groundwater at a pressure that is greater than the local atmospheric pressure. Typically, the amount of excess air is determined by analysis of the concentrations of different noble gases or from the nitrogen/argon ratio in the sample. When such measurements are available, it is possible to correct CFC ages for the presence of excess air.

Several conceptual models exist for accounting for excess air. In the simplest model, the excess air is assumed to be unfractionated, having the same composition as the atmosphere. Stute (1995) observed that in some cases the composition of excess air appears to be fractionated, and to contain a disproportionate amount of the heavy noble gases. He proposed a two-step process in which trapped air bubbles completely dissolve in groundwater (to produce unfractionated excess air) but then the excess air starts to diffusionally re-equilibrate with the soil atmosphere. Because the lighter gases have higher diffusion coefficients, the composition of excess air becomes fractionated. The concept of complete dissolution of trapped air is difficult for some systems, as large hydrostatic pressures are required to dissolve the amount of air needed that can then be fractionated to produce observed concentrations in groundwater. Aeschbach-Hertig et al. (2000) introduced a model in which trapped air bubbles partially dissolve into groundwater under closed system conditions. Because the heavier gases are more soluble than light gases, the water becomes enriched in heavy gases.

Regardless of the formation mechanism, trapped air will contain CFCs and the resulting groundwater will be enriched in CFCs above the level predicted using Henry's Law. Thus, if any CFC model ages are calculated from measured concentrations and from the recharge temperature, ignoring the presence of excess air, the calculated CFC ages will generally be too low (due to the higher concentration). In general, the effects of excess air on calculated CFC ages are larger:

(1) At higher recharge temperatures;
(2) For CFC-12 rather than for CFC-11 and CFC-113;
(3) For younger waters rather than for older waters (Busenberg and Plummer, 1992).

The sensitivity of CFC ages to excess air is less than 1 year per $cm^3/kg$ of excess air for CFC-12 and CFC-113 and is less than 0.05 year per $cm^3/kg$ for CFC-11 for modern water at 30°C. When excess air results during well construction or purging, the effect on apparent ages depends on the

TABLE 4.4. DIFFERENCES BETWEEN THE ACTUAL GROUNDWATER AGES AND THE APPARENT CFC MODEL AGES BASED ON CALCULATIONS THAT IGNORE THE PRESENCE OF 30 CM$^3$/KG OF EXCESS AIR IN A WATER SAMPLE FORMED AT 30°C

| Recharge year | Age offsets from recharge year calculated from CFC concentrations and ratios (a) | | | | | |
|---|---|---|---|---|---|---|
| | CFC-11 | CFC-12 | CFC-113 | CFC-11/ CFC-12 | CFC-113/ CFC-11 | CFC-113/ CFC-12 |
| 1950 | 0 | 2 | N/A[a] | –1 | N/A[a] | N/A[a] |
| 1955 | 0 | 3 | N/A[a] | –1 | N/A[a] | N/A[a] |
| 1960 | 0 | 3 | N/A[a] | –4 | N/A[a] | N/A[a] |
| 1965 | 0 | 3 | N/A[a] | –5 | N/A[a] | N/A[a] |
| 1970 | 1 | 4 | N/A[a] | –7 | N/A[a] | N/A[a] |
| 1975 | 1 | 5 | 1 | N/A[a] | 0 | 0 |
| 1980 | 3 | 8 | 3 | N/A[a] | 2 | 0 |
| 1985 | 4 | 11 | 3 | N/A[a] | 2 | 0 |
| 1990 | C[b] | C[b] | C[b] | N/A[a] | C[b] | 0 |
| 1995 | C[b] | C[b] | C[b] | N/A[a] | C[b] | 0 |

[a] N/A indicates not applicable (below one year offset).

[b] C: CFC concentrations or ratios higher than the surface water which is at equilibrium with the modern atmosphere, indicating contamination effects.

groundwater age. Injecting modern air into old groundwater can result in apparent CFC ages that are more than 100% in error.

Wilson and McNeill (1997) reported quantities of excess air in groundwater ranging from 0 to about 50 cm$^3$/kg; however, the majority of values were less than 10 cm$^3$/kg. Furthermore, the maximum amount of excess air that can result from a rising water table is about 1 cm$^3$/kg per m rise in the water table. Since transient water table changes that are greater than 10 m are not common, ‘natural’ excess air values greater than 10 cm$^3$/kg are not likely to be common.

The effects of 30 cm$^3$/kg of excess air on apparent CFC ages is illustrated in Table 4.4. These values were computed assuming complete dissolution (unfractionated) of trapped air. A value of 30 cm$^3$/kg for excess air is not typical of most groundwaters, but could occur under extreme conditions. Hydrogeological environments in which large amounts of excess air might occur in groundwater include fractured rock systems in mountainous terrains, ephemeral streams in arid regions and infiltration basins.

The program QCFC allows the effects of excess air (as well as other relevant parameters) on apparent CFC ages to be evaluated (see Appendix III).

## 4.5. SORPTION

A few studies have suggested that groundwater dating with CFCs may be difficult in aquifers with high organic carbon content because of sorption of CFCs to the aquifer solid phase.

Under the assumption of linear, reversible, instantaneous adsorption, the velocity of a sorbed tracer, $V_t$, is related to the groundwater velocity, $V_w$, by:

$$R = \frac{V_w}{V_t} = 1 + \rho_s \left( \frac{1-\theta}{\theta} \right) K_d \tag{4.2}$$

where $R$ is termed the retardation factor, $\rho_s$ is the density of the solid phase, $\theta$ is the water content, and $K_d$ is the ratio of the mass of solute on the solid phase per unit mass of solid phase, to the concentration of solute in solution.

The sorption of CFCs on the solid phase of soils has been studied in column experiments by Ciccioli et al. (1980), Brown (1980) and Jackson et al. (1992). Ciccioli et al. (1980) found negligible retardation for CFC-11, CFC-12 or CFC-113 during passage through a column of ground Ottawa sand. For transport through ground limestone, retardation factors were measured to be 1.0, 1.1 and 1.5 for CFC-12, CFC-11 and CFC-113, respectively. From these data, partition coefficients are estimated to be $K_d = 0.00$, 0.01 and 0.07, respectively. Brown (1980) measured the retardation of CFC-11 to be 1.4 ($K_d = 0.05$) and 2.2 ($K_d = 0.16$) during passage through columns of (unground) Ottawa sand and Yolo sandy loam, respectively, and Jackson et al. (1992) measured a retardation factor of 12 ($K_d = 1.45$) for CFC-113 during passage through a column of Gloucester aquifer sediments (fine sand, $f_{\mathrm{oc}} = 0.06\%$; velocity 0.03 cm/min).

Difference in sorption characteristics for Ottawa sand in the two studies may be due in part to a difference in flow velocity. In the study of Brown (1980), the water velocity was 2.9 cm/min, while in the study of Ciccioli et al. (1980) it was 21 cm/min, suggesting that in the latter case, equilibrium partitioning between the liquid and solid phases may not have occurred.

Field measurements of partition coefficients under natural groundwater flow rates have been obtained by Cook et al. (1995) and Bauer et al. (2001). Cook et al. (1995) measured CFC-11, CFC-12 and CFC-113 concentrations in a piezometer nest near a groundwater flow divide (vertical flow predominating) in a silty sand aquifer at Sturgeon Falls, Ontario, Canada. Thirteen piezometers were sampled between the surface and 20 m depth. Tritium concentrations on the same piezometer nest had been measured previously (Solomon et al., 1993). Simulation of tracer concentrations using a groundwater flow and transport model indicated a partition coefficient of $K_d = 0.14$ (R = 1.70) for CFC-113 relative to $^3$H. A partition coefficient of $K_d = 0.03$ (R = 1.15) for CFC-12 was estimated, although this may not have been significantly different from zero. A partition coefficient could not be determined for CFC-11, because this tracer was removed by microbial degradation. Bauer et al. (2001) estimated a retardation factor of 1.5 for CFC-113 (with respect to $SF_6$, $^3$H and $^{85}$Kr) in a fractured basalt aquifer, by simulating tracer concentrations using a two-dimensional solute transport model. In contrast, Busenberg and Plummer (1993) found good agreement between CFC-12 and CFC-113 ages in a shallow, coarse sand aquifer on the Delmarva Peninsula (Delaware, Maryland, and Virginia, USA), indicating minimal sorption of CFC-113.

## 4.6. MICROBIAL DEGRADATION

Although CFC-11, CFC-12 and CFC-113 may be considered essentially stable under aerobic conditions (Rowland and Molina, 1975; Lovley and Woodward, 1992), they are subject to degradation processes under anaerobic conditions (Khalil and Rasmussen, 1989; Semprini et al., 1992; Lovley and Woodward, 1992). CFCs are degraded primarily by dechlorination reactions that produce hydrochlorofluorocarbons (HCFCs). For example, Sonier et al. (1994) demonstrated that reductive dechlorination of CFC-11 was nearly stoichiometric in the production of fluorodichloromethane (HCFC-21) under sulphate reducing conditions. In a sulphate-reducing contaminant plume associated with an organic waste disposal site near Ottawa, Canada, Lesage et al. (1990) found two dechlorination products (1,2-dichloro-1,2,2-trifluoroethane (CFC-123a), and chlorotrifluoroethene (CFC-1113)), and one defluorination product (1,1,2-trichloro-1,2-difluoroethane (CFC-122a)) of CFC-113.

Field and laboratory studies have usually found CFC-11 to be the most rapidly degraded of the three compounds. In one of the earlier studies, Khalil and Rasmussen (1989) studied the degradation of CFCs in termite mound soils. CFC-11 was found to be 12% depleted at 25 cm below the surface, CFC-12 was 4% depleted and CFC-113 was only 2% depleted (the latter within experimental error). In comparison, carbon tetrachloride was found to be 52% depleted over the same distance. After biostimulation of indigenous bacteria through the addition of acetate, Semprini et al. (1992) found carbon tetrachloride to be 95% depleted, CFC-11 to be 68% depleted and CFC-113 to be 20% depleted within 2 m travel in anaerobic groundwater at Moffett Naval Air Station, California, USA. Deipser and Stegmann (1997) investigated the microbial degradation of CFCs in simulated landfill conditions. Under 'acid phase' conditions, created by the addition of compost, CFC-11 was degraded to HCFC-21, but CFC-12 and CFC-113 were hardly degraded. Under 'methanephase' conditions, CFC-11 was again degraded to HCFC-21 with an average rate nearly 37-fold that observed under acid phase conditions. CFC-12 and CFC-113 also decomposed under 'methane phase' conditions, but at an average rate nearly 16-fold more slowly than that of CFC-11.

Cook et al. (1995) demonstrated nearly complete degradation of CFC-11 and stability of CFC-12 in a sulphate reducing sand aquifer near Sturgeon Falls, Ontario, Canada. There the groundwater ages based on CFC-12 agreed well with the observed depth of the mid-1960s $^3$H bomb peak (see Chapter 9, Section 9.2). Oster (1996) reported degradation of CFC-11 and CFC-12 in various (likely methanogenic, but generally unspecified) anoxic environments, with the rate of CFC-11 degradation approximately 10-fold that of CFC-12. Under marine, sulphate-reducing conditions in a Norwegian fjord, Shapiro et al. (1997) found rapid degradation of CFC-11 and, within the uncertainties of the measurements, CFC-12 degradation could not have been more than 1/600 that of CFC-11. The half-life for CFC-11 degradation in sulphate-reducing, organic rich sea water was 0.1 ± 0.02 years and considerably smaller than that found by Cook et al. (1995) of 0.9–1.7 years. In northern Florida, USA, Katz et al. (1995) found CFC-11 apparent ages that were 6–12 years older than those based on CFC-12 in groundwater undergoing sulphate reduction and methanogenesis, also indicating preferential degradation of CFC-11. Happell et al. (2003) concluded that CFCs were removed from recharging groundwater during methanogenesis near the sediment-water interfaces in the Everglades, Florida, USA. Similarly, Böhlke and Krantz (2003) concluded that CFC-11 and CFC-113 were completely degraded, while CFC-12 was partially degraded, in anoxic saline groundwater that recharged beneath an estuary near the coast of Delaware, USA, with slightly elevated methane concentrations.

Under aerobic conditions, many groundwater studies have demonstrated agreement in apparent ages based on CFC-11, CFC-12 and CFC-113 (Dunkle et al., 1993; Katz et al., 1995; Szabo et al., 1996; Plummer et al., 1998b), and agreement between apparent CFC ages and ages obtained with other environmental tracers, both of which indicate lack of degradation of CFCs under such conditions.

## 4.7. MATRIX DIFFUSION

Solute transport through fractured rocks can usually be characterized by advection through the fractures, with diffusion into the immobile water in the matrix. Diffusion of solute from the fractures to the matrix (matrix diffusion) causes an apparent retardation of the solute tracer relative to the water. The matrix diffusion process will mean that apparent groundwater ages obtained for water from fractures will be much greater than the true hydraulic age of the water. Furthermore, water ages will be different for different tracers, depending on their aqueous diffusion coefficients, and on the rate of change of the input concentrations over time (Cook and Simmons, 2000). Matrix diffusion thus results in apparent solute velocities, $V_a$, which are less than water velocities in fractures ($V_a < V_w$) and apparent solute residence times, $t_a$, which are greater than water residence times, $t_w$ ($t_a > t_w$).

Quantitative interpretation of apparent groundwater ages in fractured rock systems is difficult, and estimation of groundwater flow rates from such data requires information on fracture and matrix properties. Chapter 9, Section 9.11 presents an example of the interpretation of groundwater ages from a fractured rock environment. In most systems, however, the data required to interpret apparent groundwater ages correctly will not be available.

Where fractures are spaced very closely together, however, matrix diffusion can result in complete equilibration of tracer concentrations within the fractures and within the matrix. Where this occurs, then the apparent age of the tracer within the fractures, $t_a$, will be related to the age of the water in the fractures, $t_w$, by the ratio of the total porosity, $\theta_t$, to the fracture porosity, $\theta_f$:

$$t_a = t_w \frac{\theta_t}{\theta_f} \tag{4.3}$$

The fracture porosity is equal to the fracture aperture divided by the fracture spacing. The total porosity is equal to the fracture porosity plus the matrix porosity: $\theta_t = \theta_f + \theta_m$. (In practice, $\theta_m >> \theta_f$, and so $\theta_t$ and $\theta_m$ are often used interchangeably.) The tracer velocity will be equal to the Darcy velocity divided by the total porosity:

$$V_a = V_w \frac{\theta_f}{\theta_t} = \frac{V_D}{\theta_t} \tag{4.4}$$

This condition is sometimes referred to as equivalent porous media (EPM) for solute transport. It arises only where the fracture spacing is very small, the residence time is very long, and the diffusion coefficient is high. Cook et al. (1996) argued that EPM conditions did apply to CFC concentrations measured in fractured shale aquifers at Oak Ridge, Tennessee, USA, and used this simplification to interpret the apparent ages in terms of aquifer recharge rates.

## 4.8. HYDRODYNAMIC DISPERSION

Hydrodynamic dispersion is a process whereby CFC molecules that enter an aquifer at different times or different locations can be mixed. If it were possible to describe groundwater velocity vectors at a microscopic (e.g. sub-pore) scale, then dispersion (or mixing) of tracer molecules would result solely from complex patterns of fluid flow accompanied by molecular diffusion of molecules across flow lines. However, when a macroscopic description of the flow field is used (i.e. the flow field is described using Darcy's Law), microscopic mixing is commonly modelled using a hydrodynamic dispersion coefficient. In one dimension, the hydrodynamic dispersion coefficient ($D_h$) is related to the dispersivity ($\alpha$) of the porous media by:

$$D_h = \alpha V + D_d \tag{4.5}$$

where $V$ is the average linear velocity, and $D_d$ is the effective diffusion coefficient.

Of importance when using CFCs as an age tracer is the fact that the net effect of hydrodynamic dispersion depends on the magnitude of concentration gradients. When a spike of tracer moves through the subsurface, the peak concentration will diminish and the width of the spike will increase as a result of dispersion. In contrast, when a tracer is introduced as a broad pulse, the net effects of dispersion are greatly diminished.

Because the relationship between atmospheric CFC concentrations is not very spike-like, the effects of dispersion on CFC ages may be rather small. Figure 4.7 shows apparent CFC-12 ages as a function of distance in a one-dimensional (e.g. vertical) flow system. This diagram was prepared by solving the one-dimensional advection dispersion equation using a velocity (V) of 1 m/a, an effective diffusion coefficient ($D_d$) of $1.0 \times 10^{-10}$ m$^2$/a, and values of

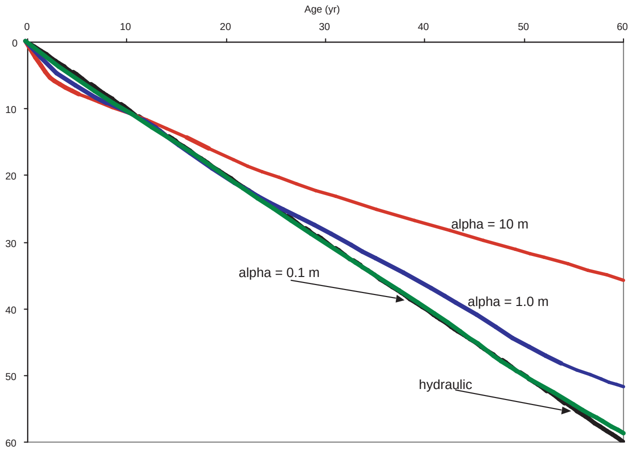

*FIG. 4.7. The results of 1-D transport of CFC-12 using various values for longitudinal dispersivity (alpha) are shown. The curves respresent solutions to the advection–dispersion equation using the CFC-12 time history in the atmosphere as an input function. In many (if not most) shallow aquifers, the dispersivity acting in the vertical direction will be less than 1.0, resulting in only minimal effects of dispersion on CFC ages.*

dispersivity ($\alpha$) that range from 0.1 to 10 m. As shown in Fig. 4.7, the apparent age is very close to the hydraulic age (which is simply distance/velocity) for a dispersivity of 0.1 m, and has a maximum difference of only about 5 years for a dispersivity of 1.0 m. When the dispersivity is larger than 10 m, the effects of dispersion become large. However, in a two or three dimensional flow system, where recharge is areally distributed, variations in CFC concentration occur mostly in the vertical direction and, hence, it is the dispersivity in the vertical direction that will cause the largest difference between hydraulic and apparent ages (Solomon and Sudicky, 1991.) When flow is predominately vertical (e.g. in a primary recharge area), it is the longitudinal dispersivity that leads to dispersion in the vertical direction. This is the situation modelled in Fig. 4.7. When flow is predominately horizontal, it is the transverse dispersivity that leads to vertical dispersion. While this situation is not explicitly considered in the results shown in Fig. 4.7, numerous high resolution field studies have shown that transverse dispersion is typically orders of magnitude less significant than longitudinal dispersion (Sudicky, 1986; Garabedian et al., 1991, van der Kamp et al., 1994.) Thus, the results shown in Fig. 4.7 represent a worst-case scenario. Gelhar et al. (1992) showed that typical longitudinal dispersivities are on the order of 1 for transport over distance of 10–100 m. The conclusion is that dispersion is not likely to be a significant factor in CFC dating, especially when samples are collected from shallow aquifers. However, recent simulations performed by Weissmann et al. (2002) indicated groundwater ages that spanned over 50 years even when sampled over short (< 1.5 m) screened intervals. Whether or not this is a numerical artefact or characteristic of heterogeneous aquifers remains unclear.

## 4.9. SUMMARY

As shown in the preceding sections, there are numerous processes that can occur in the groundwater environment that, if not recognized or properly accounted for, can appreciably affect the interpretation of the CFC age of a water sample. These processes are summarized in Table 4.5, where reference to chapter and section in this Guidebook is given for further information. Table 4.5 summarizes for each process the hydrological environments most affected by uncertainty in the process, a description of the process, and qualitative effect on apparent age. Depending on whether the recharge temperature, excess air and recharge elevation is underestimated or overestimated, the resulting apparent age can be biased either young or old (Table 4.5). The addition of anthropogenic sources of CFCs, concentrations greater than that expected for equilibrium with regional air composition, leads to a young bias in apparent age. Processes that remove CFCs or lower their concentration in groundwater, such as microbial degradation, sorption, mixing with old water, matrix diffusion and some cases of hydrodynamic dispersion, can lead to an old bias in the apparent age.

Although the processes that can affect the interpretation of CFC age have been investigated and quantified to some extent, it is not always possible to know whether a particular process that can affect the interpretation of CFC age is actually occurring in the environment under study. The reliable interpretation of age information from analyses of CFCs in groundwater depends on having available additional supporting information that can help characterize the geochemical and hydrological environment, and lead to more reliable age interpretation. Examples of water samples affected by the various processes discussed in this chapter are presented in Chapter 8, and Section 8.10 provides some guidelines on additional data that, if available, can aid in age interpretation.

TABLE 4.5. SUMMARY OF PROCESSES THAT, IF NOT ACCOUNTED FOR, CAN APPRECIABLY AFFECT THE APPARENT CFC AGE (AFTER PLUMMER AND BUSENBERG, 2000)

| Property (section in text) | Environment most affected | Description of process | Effect on apparent age |
|---|---|---|---|
| Recharge temperature (4.3) | Shallow water table | Temperature at the water table during recharge | |
| | | Overestimated | Too young |
| | | Underestimated | Too old |
| | | ±2°C, ≤1970 ± 1 year or less | |
| | | ±2°C, 1970–1990 ± 1–3 years | |
| | | ±2°C, >1990 > 3 years | |
| Excess air (4.4) | Rapid, focused recharge; fractured rock | Addition of air trapped and dissolved during recharge. Significant for post-1990 recharge | Too young |
| Recharge elevation (3.2) | Mountain recharge | Water recharged at high altitude dissolves less CFCs because of lower barometric pressure | |
| | | Elevation overestimated | Too young |
| | | Elevation underestimated | Too old |
| | | ±100 m not important | |
| | | ±1000 m < 1987 ± few years | |
| | | Significant for post-1990 recharge | |
| Thickness of unsaturated zone (4.2) | Unsaturated zone >10 m | Air in deep unsaturated zone is older than that of the modern troposphere | Too old |
| | | 0–10 m, error < 2 years | |
| | | 30 m, error 8–12 years | |
| Urban air (4.1) | Eastern USA, western Europe, urban areas | CFC mixing ratios in urban and industrialized areas can exceed regional values | Too young |
| CFC contamination (4.1) | Urban and industrial areas, sewage effluent, recharge from contaminated sources | CFCs added to water from local anthropogenic sources, in addition to that of air–water equilibrium | Too young (impossibly young) |

TABLE 4.5. SUMMARY OF PROCESSES THAT, IF NOT ACCOUNTED FOR, CAN APPRECIABLY AFFECT THE APPARENT CFC AGE (AFTER PLUMMER AND BUSENBERG, 2000) (cont.)

| Property (section in text) | Environment most affected | Description of process | Effect on apparent age |
|---|---|---|---|
| Microbial degradation (4.6) | Anaerobic environments, sulphate-reducing, methanogenic | No degradation in aerobic environments | No effect |
| | | Sulphate reducing, and fermentation: CFC-11, CFC-113 degraded, CFC-12 quasi-stable | CFC-11, CFC-113 Too old |
| | Fluvial and glacial drift sediment, coal | Methanogenic:<br>CFC-11≥ CFC-113>>CFC-12 | Too old |
| Sorption (4.5) | Organic-rich sediment, peat, coal | Sorption of CFCs onto particulate organic carbon and mineral surfaces CFC-113>>CFC-11≥CFC-12 | Too old |
| Groundwater mixtures (5, 6) | Production wells, fractured rock, mixing in aquifers, spring discharge, etc. | Mixing of young and older water in aquifers, in discharge areas, in water pumped from open intervals in wells.<br>Apparent age of young fraction in mixture | Too old |
| | | Apparent age of old fraction in mixture | Too young |
| Matrix diffusion (4.7) | Fractured rocks, dual-porosity systems | CFCs and other recent environmental tracers diffuse into dead-end pore spaces, and are removed from the active flow system | Too old |
| Hydrodynamic dispersion (4.8) | All groundwater environments | Generally small effect for CFCs<br>1975–1993 | Too old |
| | | <1975 | Too young |

## Chapter 5

# CFCs IN BINARY MIXTURES OF YOUNG AND OLD GROUNDWATER

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## 5.1. GROUNDWATER MIXTURES

Water that is pumped from a well or discharges from a spring is a mixture of the waters from all the flow lines reaching the discharge point. If the age distribution of waters reaching the point of discharge is narrow, the apparent CFC age can be reasonably representative of the travel time from the point of recharge through the aquifer. Thus, water samples from wells open to relatively narrow intervals of an aquifer, or water discharging from a spring in a predominantly conduit flow system will tend to have apparent ages that are less affected by mixing than those samples from wells with large open intervals, or springs discharging from diffuse flow systems.

Mixtures of groundwater can also be produced by the sampling process, such as in water pumped from fractured rock aquifers (Talma et al., 2000; Burton et al., 2002; Shapiro, 2002). In the general case, if N waters, each with a unique and definable age, mix in a well bore, the mixing fractions and ages of end-member waters could be calculated if the concentrations of 2N-1 tracers in the mixture are measured (Plummer and Busenberg, 2000). If the sample is unmixed (N = 1), the age of the 'mixture' is equal to the apparent age determined from the concentration of a single tracer. If two waters mix, the mixing problem could be solved with measurement of CFC-11, CFC-12 and CFC-113, provided the CFC concentrations are representative of air–water equilibrium at recharge and have not been altered by any other physical or chemical process following recharge. In application, the problem becomes rapidly unsolvable when more than two waters of definable age mix, simply because there are not enough well established tracers that can be used for dating. Interpretation of mixing problems, even for binary mixtures of young waters, is at best uncertain because, if the two end-member waters could be isolated, the tracer concentrations measured would probably have some uncertainty in defining end-member age. Nevertheless, error simulation techniques could be used to place limits on mixing fractions and ages (Thorstenson et al., 1998; Plummer et al., 1998a,b).

The possibilities of mixing in discharge from groundwater systems are unlimited, and can be considerably more complex than that of simple binary mixtures. One approach that is often taken in interpreting mean age is to apply 'lumped-parameter' or 'reservoir' models to trace concentration in groundwater discharge. Reservoir models (Eriksson, 1958; Vogel, 1967; Maloszewski and Zuber, 1982; Maloszewski et al., 1983; Zuber, 1986; Burgman et al., 1987; Cook and Böhlke, 2000) compare input and output signals of the concentrations of environmental tracers in groundwater systems assuming various age distribution models to estimate the average age (residence time) of water in the system. Chapter 6 presents some of the more useful reservoir models. Appendix III provides some background information on some of the available software that can be used to interpret residence time in aquifers from environmental tracer data.

## 5.2. BINARY MIXTURES

In many cases, the identification of water mixing processes can give useful information in hydrological investigations. In such cases, the assumption of mixing of two different water masses is often taken as a simple working approach. This approach, here called binary groundwater mixing, is widely used for the interpretation of variations of physical and chemical parameters (e.g. conductivity, water chemistry, stable isotopes) in a set of samples of a given hydrological system.

Here, the simplest mixing model is assumed, which is a mixture of water with distinct CFC concentrations and CFC-free water. This simplifying approach often is a good working hypothesis for many real case studies. It can be easily extended to the general case of mixing of two water fractions with different CFC concentrations.

Similar to the method comparing $^{14}C$ and $^{3}H$ ages for a given sample, a contradictory combination of apparent CFC ages is occasionally observed for groundwater samples. For example, a low CFC-12 concentration in a water sample may indicate that the water was recharged before 1957, but its detectable CFC-113 concentration indicates recharge after 1957 (see atmospheric CFC input functions). The contradicting combination of apparent ages may indicate possible mixing (Fig. 5.1).

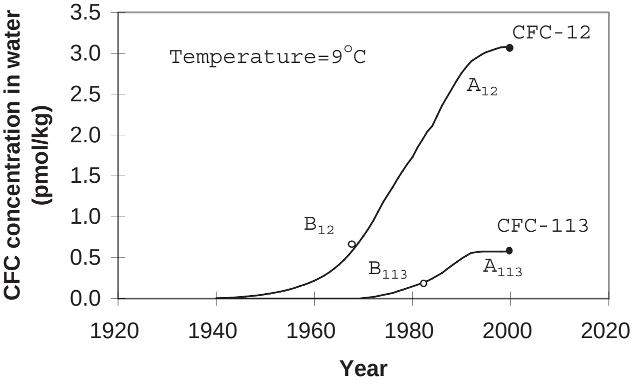

*FIG. 5.1. Effect of dilution of CFC containing water by CFC-free water. The curves represent CFC concentrations in water in equilibrium with atmospheric air as a function of time for a water temperature of 9°C. Solid circles mark the CFC containing water sample (year 2000). Open circles represent the measured CFC concentrations of the dilution of 25% of that water by 75% of CFC-free water.*

In Fig. 5.1, CFC-12 and CFC-113 concentrations of water recharged in the year 2000 are indicated by the filled circles (points $A_{12}$ and $A_{113}$). A mixture of 25% of this water with 75% of CFC-free water is indicated by the open circles, resulting in apparent recharge years of 1969 for CFC-12 and 1982 for CFC-113 (points $B_{12}$ and $B_{113}$); the CFC-113 age being always smaller than the corresponding CFC-12 age in such mixing scenarios. Likewise, a similar separation can be observed between CFC-113 and CFC-11 apparent ages.

The characteristic pattern of younger CFC-113 ages and older CFC-12 (CFC-11) ages may, therefore, qualitatively indicate mixing processes. However, it does not provide any information on the actual ages of the different water fractions.

In Fig. 5.2, the effect of mixing CFC-free water with recent water (year 1993) is shown for simple binary mixtures. The curves show the apparent recharge year in mixtures of water in equilibrium with 1993 air and old (CFC-free) water as a function of the fraction of 1993 water in the mixture. The curves intersect the right side of the figure at the year 1993 (recharge year of the pure recent component) and the left side at the recharge year of the pure CFC-free component (1940 or earlier). In this system, depending on the degree of mixing, the recharge years derived directly from the CFC concentrations could potentially vary between pre-1940 and the present. Unlike CFC concentrations, however, the CFC ratios usually represent very well the age of the CFC-containing component in such a mixed system (see dashed line in Fig. 5.2). The recharge year derived from such a plot is nearly independent of the mixing

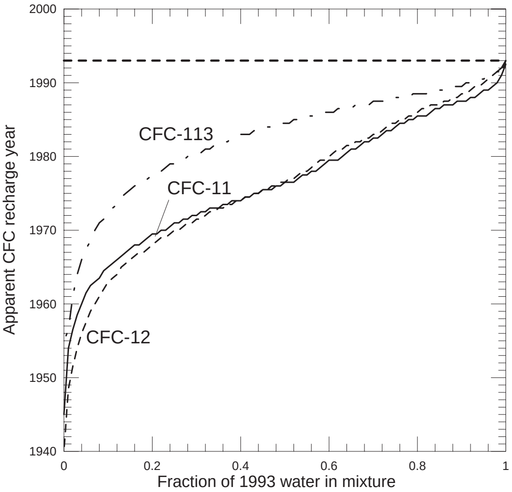

*FIG. 5.2. Effects of mixing of recent water (recharged in the year 1993) with CFC-free water on the apparent recharge year of the mixture, as a function of the fraction of recent water in the mixture. The curves are analogue to the CFC air mixing ratios, and show apparent recharge years. The dashed line shows apparent recharge years derived from the CFC ratios which, in the case of mixing with a CFC-free component, is independent of the mixing fraction.*

ratio of the two water components, provided that the older water is either CFC-free or has relatively low CFC concentrations (see Chapter 3, Fig. 3.3).

Thus, for a water sample with the apparent ages deduced from the CFC concentrations (based on CFC input functions) being older than those deduced from the concentration ratios, mixing of water of different ages is possible. This method provides not only information about the mixing of waters but also information about the fraction of young water in the mixture and the age of the young fraction (see Chapter 3, Section 3.3).

The case of binary mixing of young and old water can be solved mathematically using CFC-12 and CFC-113 data as shown in the following.

If a fraction $x$ of CFC-free water is mixed with a fraction $(1 - x)$ of CFC containing water, the concentrations of CFCs in the mixture are:

$$[CFC-113]_{mix} = (1-x)[CFC-113]_{y} \tag{5.1}$$

$$[CFC-12]_{mix} = (1-x)[CFC-12]_{y} \tag{5.2}$$

where $[\text{CFC-113}]_{\text{mix}}$ and $[\text{CFC-12}]_{\text{mix}}$ are the CFC concentrations in the mixture, x is the CFC-free fraction, and $[\text{CFC-113}]_{y}$ and $[\text{CFC-12}]_{y}$ are the concentrations in the CFC containing fraction.

Equation (5.1) divided by Eq. (5.2) gives:

$$\frac{[CFC-113]_{mix}}{[CFC-12]_{mix}}=\frac{[CFC-113]_{y}}{[CFC-12]_{y}} \tag{5.3}$$

From Eq. (5.3), where $[\text{CFC-113}]_{\text{mix}}$ and $[\text{CFC-12}]_{\text{mix}}$ are values determined from the sample, the apparent CFC age of the young CFC containing fraction can be obtained from the measured concentrations of two CFCs (based on time dependent atmospheric CFC concentration ratios, Chapter 3, Section 3.3, Fig. 3.3).

Equation (5.3) can be written as:

$$\frac{[CFC-113]_{mix}}{[CFC-113]_{y}}=\frac{[CFC-12]_{mix}}{[CFC-12]_{y}} \tag{5.4}$$

After the apparent age of the CFC-containing fraction has been determined from Chapter 3, Fig. 3.3, the mixing ratio can then be calculated from the measured CFC concentration and CFC concentration in the young fraction, as defined by the determined recharge date, using Eq. (5.4).

## 5.3. GENERAL CASE OF BINARY MIXING

In the general case of binary mixtures of young and old water, the young water fraction will contain CFCs and the old water fraction will have CFC concentrations lower than those in the young water fraction, and may be CFC-free water. Thus, the apparent age is intermediate to the ages of the end members. The resulting deviation of the apparent age from the ages of the end members is a function of many variables, including ages of the end members, mixing fractions, recharge temperatures and recharge elevations.

Figure 5.3 compares calculations of the apparent age based on CFC-11, CFC-12 and CFC-113 resulting from simple binary mixing of 1993 water with four representative old waters that range from CFC-free (a) to water recharged in the year 1985 (d). The recharge year 1993 was selected for the young end member in the mixing calculations because water of that year is generally representative of waters from the mid- and late-1990s as CFC concentrations in air have levelled off, and is considered representative of modern water in CFC composition.

Some generalizations that can be drawn from the mixing calculations of Fig. 5.3 are:

- The apparent age of a binary mixture is intermediate to the ages of the end members.
- The apparent ages in binary mixtures that are based on CFC-11 and CFC-12 tend to be similar and biased older than the apparent age based on CFC-113.

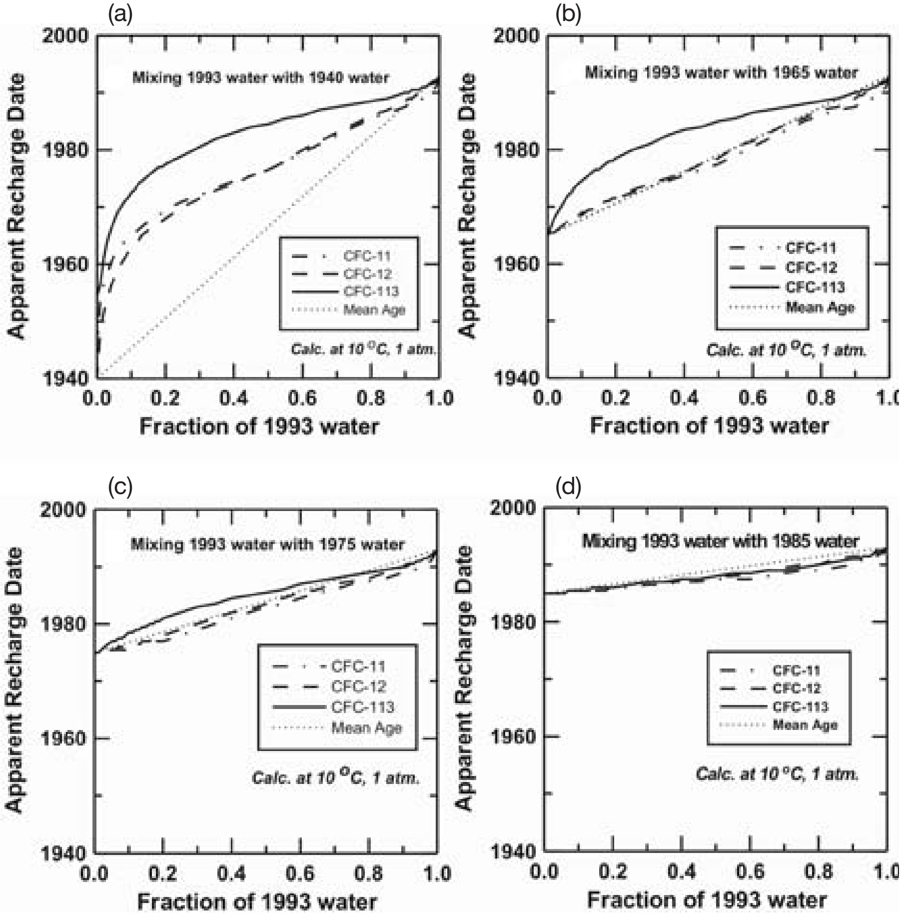

*FIG. 5.3. Calculations showing the effect on the apparent age of mixing 1993 water with older water: (a) mixing with old, CFC-free water; (b) mixing with water recharged in 1965; (c) mixing with water recharged in 1975; (d) mixing with water recharged in 1985. The plots were constructed assuming recharge at 10°C and 1013.25 hPa total pressure.*

- The difference in apparent age based on CFC-113 and that from CFC-11 and CFC-12 is a maximum when young water mixes with old, CFC-free water.
- In mixtures of modern and old, pre-CFC water, all three apparent ages determined from CFCs will be younger than the mean age, shown as the dotted line in Fig. 5.3.
- The separation between apparent ages based on CFC-113 and those based on CFC-11 and CFC-12 decreases as the age of the old fraction approaches that of the young fraction, particularly when the recharge date of the old fraction is more recent than 1975.
- In binary mixtures of post-1985 and modern water, the apparent recharge dates determined from all three CFCs are in close agreement, yet the ages of the two end members still differ by eight years or more. In this case, additional tracers would be necessary to determine the mixing ratios.

The calculations shown in Fig. 5.3 were constructed using North American air and a recharge temperature of 10ºC and 1013.25 hPa total pressure. Similar diagrams can be constructed for other conditions.

Errors can result when applying the model for binary mixing of old, CFC-free water with young water to samples in which the old fraction is not entirely free of CFCs. Figure 5.4 shows the CFC-11/CFC-12 and CFC-113/CFC-12 ratios for mixing of 1993 (modern) water with various fractions of old water, in which the old water ranges from pre-CFC water to 1985 water. For example, consider the effect on the CFC-113/CFC-12 ratio of mixing 50% 1993 water with 50% older water. If the older fraction was from 1975, the CFC-113/CFC-12 ratio would be approximately 0.13. However, if the age ratio was interpreted by assuming the old water contained no CFCs, then the ratio of 0.13 would imply an age of the young fraction from the mid-1980s (Chapter 3, Fig. 3.3), instead of 1993. The ratios are constant only in mixtures with CFC-free water. In most cases, the CFC ratios decrease as the fraction of older, CFC-bearing water is increased, resulting in an old bias in the calculated age of the young fraction in the mixture. Therefore, great caution is needed in interpreting fractions of young water in binary mixing using the CFC ratio method, if there is a possibility that the old fraction contains CFCs.

## 5.4. TRACER PLOTS

Because the various environmental tracers considered here have differing temporal patterns to their input functions, plots of one tracer against another can be useful in distinguishing hypothetical mixing processes that may affect

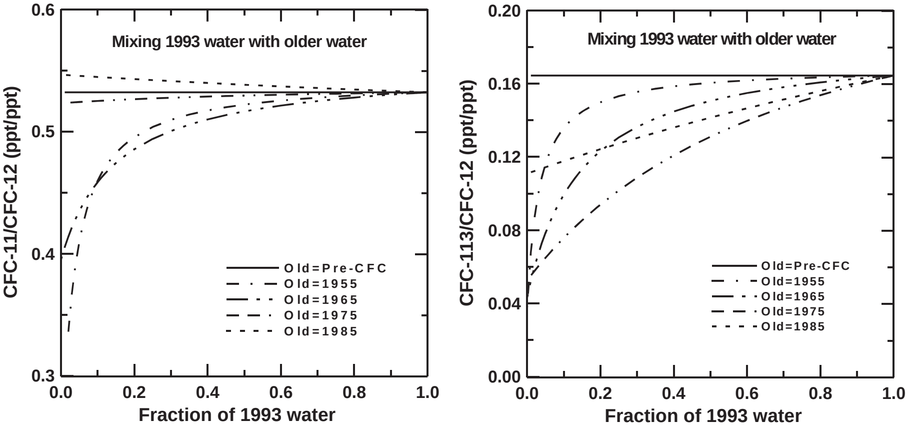

*FIG. 5.4. Calculations showing variations in the CFC-11/CFC-12 and CFC-113/CFC-12 ratio in binary mixtures of modern 1993 water with various fractions of water recharged in the years 1955, 1965, 1975 and 1985. The CFC ratios are constant only in binary mixtures of young water with old, CFC-free water. These calculations were made using North American air at 10°C and 1013.25 hPa total pressure.*

the samples, in addition to recognizing samples affected by microbial degradation (Chapter 4, Section 4.6) and/or anthropogenic contamination (Chapter 4, Section 4.1). Some particularly useful relations emerge when concentrations of one CFC are compared with another.

Figure 5.5 compares the concentrations of CFC-113 and CFC-12 that can be found in water samples recharged at air–water equilibrium and/or diluted by mixing with old, CFC-free water. In constructing the tracer plot of Fig. 5.5, the concentrations of dissolved CFC-113 and CFC-12 were expressed as the atmospheric gas mixing ratios (in parts per trillion by volume, or pptv) that would be in equilibrium with the measured concentrations in the water calculated at the recharge temperature and recharge elevation of each sample. The normalized gas mixing ratios are preferred over the aqueous concentrations because the normalization removes effects of local variations in recharge temperature and elevation, and permits direct comparison of the data with regional records of atmospheric mixing ratios. The solid line on Fig. 5.5 represents the historical atmospheric concentrations (mixing ratios) in pptv and represent piston flow, apparent recharge dates based on North American air.

Selected apparent recharge dates of 1960 to 2002 are noted at '+' (Fig. 5.5). Simple binary mixtures of water recharged in the years 2002, 1995, 1990, 1985, 1980 and 1975 with old, CFC-free, water are shown as dashed lines.

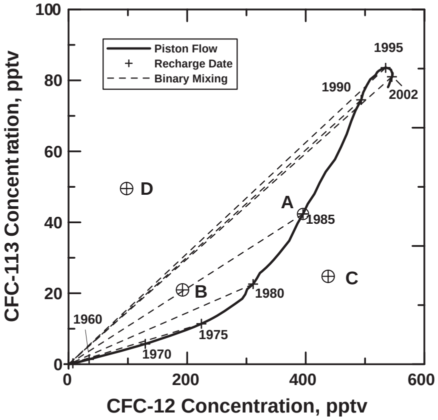

*FIG. 5.5. Plots comparing CFC-113 and CFC-12 concentrations in water in pptv (solid line) if unaffected by mixing (piston flow), and in binary mixtures of young water (recharged in 2002, 1995, 1990, 1985, 1980 and 1975) with old, CFC-free water (dashed lines). The '+' denotes selected apparent ages. An unmixed sample recharged in 1985 would plot at point A. A 50:50 mixture of 1985 water and old, CFC-free water would plot at point B. Samples plotting outside the region bounded by piston flow and binary mixing (see, for example, points C and D) have been affected by other processes, such as contamination or degradation that have altered the CFC concentrations from air–water equilibrium values.*

The region bounded by the CFC input function (solid line) and upper-most mixing line (1995-pre-CFC line) represents the range of CFC-113 and CFC-12 concentrations that can be expected in waters if air–water equilibrium and mixing with old, CFC-free water account for the observed variations in CFC concentrations. A few other samples could plot slightly outside this region if, for example, water recharged in 2002 mixed with water recharged in 1985 (Fig. 5.5).

Selected examples are shown on Fig. 5.5. Point A shows the location of an unmixed sample recharged in the year 1985. Point B shows the location of a 50:50 mixture of water recharged in 1985 with old, CFC-free water. The percentage of end-member waters in simple binary mixtures of young and old can be interpreted graphically using the lever rule on Fig. 5.5. For example, the fraction of young water in the mixture is the length of the line between the sample and the old end member divided by the length of the line between the young and old end members. Alternatively, the age and fraction of young water can be calculated using the ratio method discussed in Chapter 3, Section 3.3. Samples that plot outside the region bounded by piston flow and binary mixing have probably been affected by other processes besides those of air–water equilibrium and dilution. For example, a sample plotting at point C (Fig. 5.5) could be contaminated with CFC-12 relative to CFC-113, or degraded in CFC-113 relative to CFC-12; and a sample plotting at point D could contain an excess of CFC-113 relative to CFC-12, or (less likely) degraded in CFC-12 relative to CFC-113.

## 5.5. MULTI-TRACER PLOTS

Plots similar to Fig. 5.5 can be constructed for many other environmental tracers and used to recognize samples containing mixtures or exhibiting contamination or degradation. Multi-tracer concentration plots have some advantages over plots comparing apparent ages and tracer ratios because they reflect more directly the measured quantities and potential mixtures. Various combinations of multi-tracer concentration plots have been used in a number of groundwater studies (see, for example, Böhlke and Denver, 1995; Loosli et al., 2000; Talma et al., 2000; Katz et al., 2003; Plummer et al., 2003; Böhlke and Krantz, 2003). Theoretical variations in the concentrations of CFCs and $SF_6$ (Fig. 5.6), and $^3H$, CFCs and $SF_6$ (Fig. 5.7) were constructed using North American air and a record of tritium in precipitation from Washington, D.C., for cases of piston flow and binary mixing. Excess air was assumed to be zero in all plots of Figs 5.6 and 5.7. In general, the areas in the diagrams that are bounded by the curves representing the different modelled tracer concentrations should include the measured values for water samples if no other processes have affected them. Samples with tracer concentrations that plot far outside the bounded areas may be contaminated, or may have been affected by tracer degradation. For example, it is relatively common for anaerobic groundwater to plot below the curves in Fig. 5.6(a), with relatively low CFC-11/CFC-12 ratios indicating degradation of CFC-11. Contamination of CFCs and/or $SF_6$ will cause samples to plot outside the curves shown in Fig. 5.6. The model calculations for CFCs are nearly insensitive to expected variations in amount of excess air, but similar calculations involving $SF_6$ are sensitive to variations in excess air (Busenberg and Plummer, 2000; Plummer et al., 2001). The sensitivity of $SF_6$ to excess air relative to CFCs is a consequence of the low Henry's Law solubility of $SF_6$ relative to solubilities of CFCs.

If all tracers were reliable (no contamination, no degradation), it should be possible to derive information about both the age frequency distribution and the magnitude of the mean age in a sample. For example, a sample of water that is not a mixture should plot somewhere along the solid piston flow curves

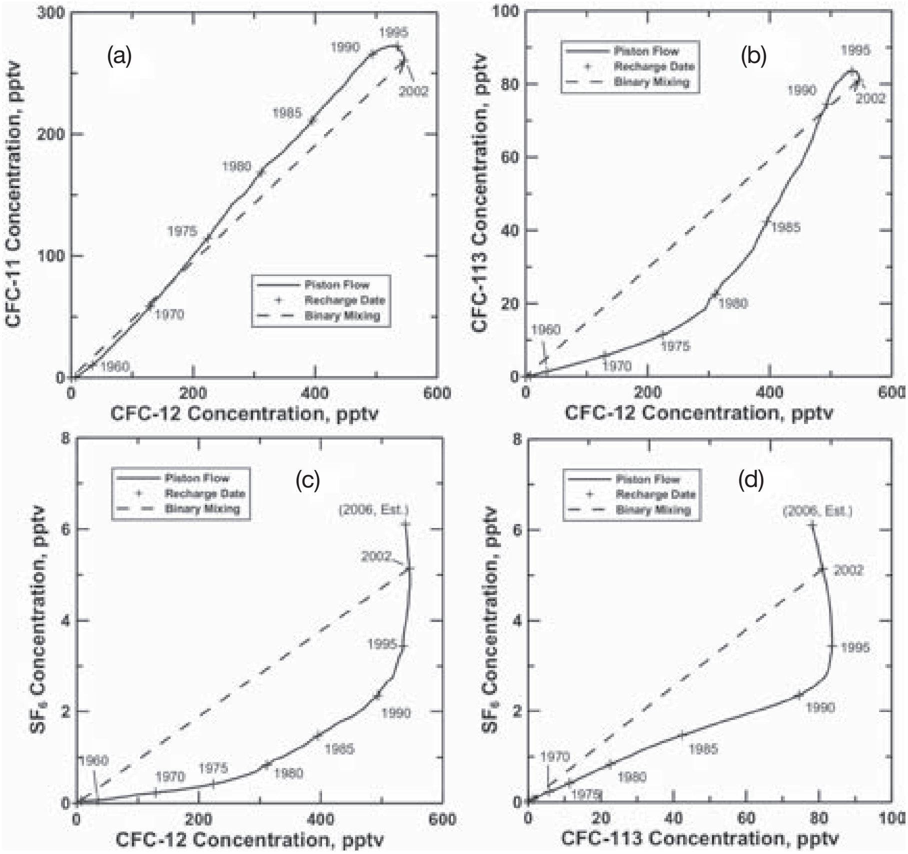

*FIG. 5.6. Tracer plots comparing CFC-11, CFC-12, CFC-113 and SF$_6$ concentrations in pptv for North American air. The solid lines represent unmixed (piston flow) with selected apparent ages ('+'). The dashed line shows one example of binary mixing for the case of water recharged in 2002 diluted with old, CFC-free water.*

for all the tracers at points corresponding to the single age of the water. Samples that do not plot on the piston flow curves are more likely to represent mixtures. An exponential mixture (see Chapter 6) should plot somewhere along the exponential mixing curves at points corresponding to a single mean age. Binary mixtures could plot almost anywhere within the bounded area depending on the ages of the end members.

It is evident from Figs 5.6 and 5.7 that the uncertainties in calculated ages of mixing fractions will depend on the tracer used and on the value of the age of the young fraction. For example, it would be difficult to distinguish from the CFC-113/CFC-12 ratio of a binary mixture whether the young fraction had an

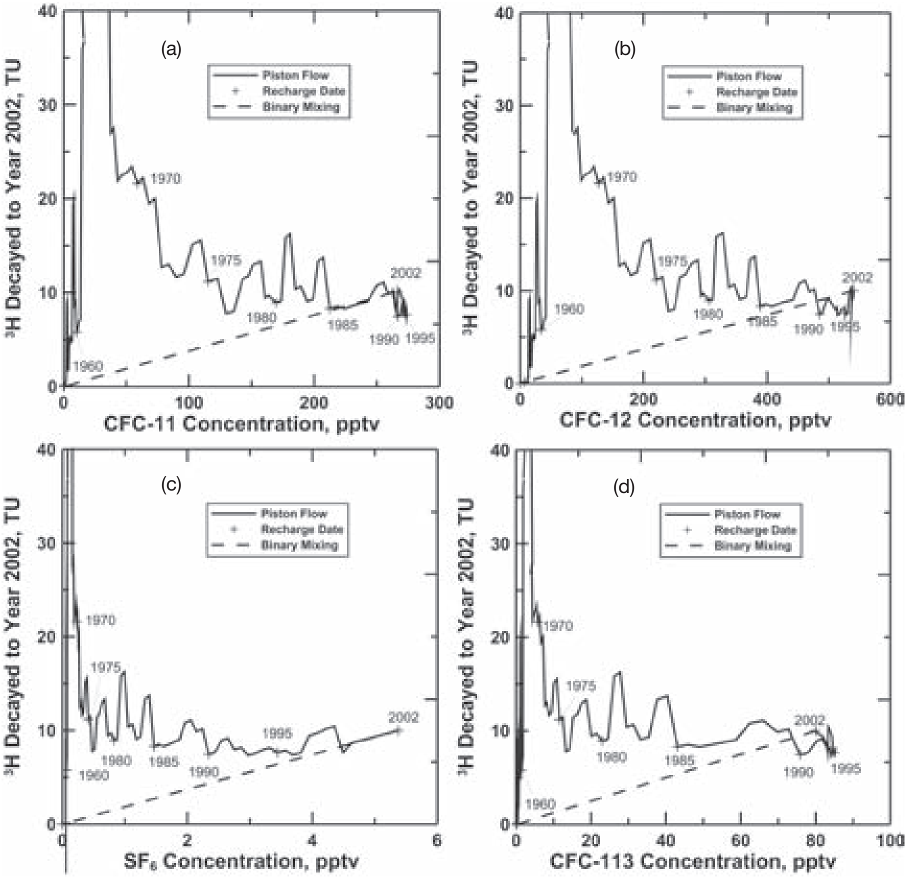

*FIG. 5.7. Tracer plots comparing $^3H$ in precipitation from Washington, D.C., decayed to the year 2002 with CFC-11, CFC-12, CFC-113 and $SF_6$ concentrations in pptv for North American air. The solid lines represent unmixed (piston) flow with selected apparent ages ('+'). The dark dashed lines show one example of binary mixing, for the case of water recharged in 2002 diluted with old, CFC-free water.*

age of 0 or 12 years (see Fig. 5.6(b)). Also, because of the way the different tracer concentrations in the atmosphere have changed over time, it may not be possible to distinguish between mixing models for some combinations. For example, because CFC-11 and CFC-12 have similar historical records, the piston flow, exponential mixing and binary mixing models all yield similar curves (see Chapter 6), despite the fact that they could imply very different age distributions and magnitudes.

Some of the most useful indicators of binary mixtures of old and young water are combinations of $^3H$ and gas tracer data. Because atmospheric $^3H$ concentrations have been elevated for a long time, old water components can be identified by anomalously low $^3H$ values in comparison with CFCs or $SF_6$ (Fig. 5.7). Because of ambiguities in distinguishing age distribution models, and the possibility of degradation or contamination of various constituents, it is important to consider simultaneously as many different tracer measurements as possible in a single sample to determine its history (see Chapter 1, Section 1.3 and Chapters 10 and 11).

## 5.6. SUMMARY OF BINARY MIXING

To summarize the discussions above, a mixed water system can be identified by:

- Detectable concentrations of CFC-113 while the CFC-12 and/or CFC-11 apparent ages indicate that the water was recharged before 1955;
- The apparent age deduced from CFC-113 being distinctly younger than that from CFC-12 and CFC-11;
- The apparent ages deduced from CFC concentration ratios being younger than those deduced from CFC concentrations;
- A sample point in Fig. 5.5 that does not lie on the CFC input curve but on a mixing line.

Using CFCs, a quantitative calculation of the mixing fraction can be performed easily in the case of binary mixing with one end member being basically CFC-free. Because the CFC concentrations in water can be determined to a detection limit of about 0.3 pg/kg of water, in principle, a modern (recharge year 2000) water fraction of less than 1% in a mixture with CFC-free water can be detected.

For binary mixtures in which both of the end members contain CFCs, the estimation of water ages and calculation of mixing fractions are more complicated, though mathematically possible. In such cases, no unique solutions for water mixtures can be expected. In any case, the approximation of binary mixing of CFC-free and CFC-containing waters may be justified in some groundwater systems; therefore, the methods described above may be useful tools for interpretation of CFC data towards solving a number of practical hydrological problems.

The methods to calculate mixing ratios are restricted to cases where the CFC concentrations are not influenced by non-atmospheric CFCs (see

Chapter 4, Section 4.1) and not modified by other processes, such as degradation (Section 4.6) or sorption (Section 4.5). These effects, however, can be relatively easily detected due to the quite strict correlation of the different CFC compounds, as shown in Fig. 5.5. All data points in such a plot that are outside the very limited area as enclosed by the input curve and the mixing line are most probably affected by contamination or degradation effects.

The methods described can be applied most effectively as an integral part of a multidisciplinary approach to a groundwater dating and/or mixing problem. For example, the $^3H/^3He$ method (Chapter 11, Section 11.3) can be used to determine the age of the young fraction, and check the result with that obtained from the CFC data.

## Chapter 6

# MODELS OF GROUNDWATER AGES AND RESIDENCE TIMES

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## 6.1. INTRODUCTION

CFC ages are generally based on absolute concentrations. As a result, when waters of different ages mix, the CFC concentration changes and so does the apparent age. Because CFC concentrations in the atmosphere are not a linear function of time, the apparent age is not necessarily proportional to the fraction of each component of water in the mixture. The previous chapter considered simply binary mixing models, with water of two discrete ages. In this chapter, more general models of groundwater age distributions in simple aquifer types are reviewed, as well as how the age distribution relates to aquifer properties.

Much research over the past 20 years has examined the manner in which groundwater mixes (or disperses) in the subsurface. Over small scales (e.g. < 1 km) applied tracer tests in granular aquifers have shown that mixing is a rather weak process (Sudicky, 1986; LeBlanc, 1991). This is especially true in a direction that is transverse to the direction of flow. At larger scales and in more geologically complex aquifers, the extent of mixing is likely to be greater (and is certainly more uncertain), but may still be moderately small. In any event, when groundwater discharges at springs or into streams or lakes, flow lines converge. As a result, water of vastly different ages can come into close contact where only a weak dispersion mechanism is required to mix water before sampling occurs. This situation may also apply when boreholes that are screened over the entire thickness of the aquifer are sampled; however, the extent to which an open borehole effectively samples all flow paths depends on many variables, including where the pump is located, the pumping rate and the intrinsic heterogeneities that exist in the aquifer. Nevertheless, to the extent that a sampling method effectively samples all flow paths, the resulting CFC concentration needs to be interpreted in the context of an integrated signal for the entire aquifer.

Lumped parameter or reservoir models have been developed since the late 1950s for both chemical engineering and hydrological applications (Eriksson, 1958; Vogel, 1967; Maloszewski and Zuber, 1982; Maloszewski et al., 1983; Zuber, 1986; Burgman et al., 1987; Cook and Böhlke, 2000). In general, these models transform input using a convolution integral to represent a mixing process.

Cook and Böhlke (2000) divided subsurface transport models for environmental tracers into two general categories:

(1) Models that predict variations in ages within the aquifer; since ages increase with depth in most aquifers, these are referred to as 'groundwater stratigraphy' models;
(2) Models that predict the integrated age of water discharging from the system.

The choice between these two categories depends on the type of data available, and the objectives of the study. For example, if one desires to obtain a detailed understanding of the spatial distribution of recharge, then samples collected from multilevel monitoring wells (i.e. from discrete points in the aquifer) can be evaluated in the context of a groundwater stratigraphic model. Alternatively, if samples are collected from major springs that are thought effectively to integrate subsurface flow paths, then one might evaluate the mean residence time of fluid in the system by employing a groundwater discharge model. In either case, it is critical that the type of available data be matched with the appropriate model. Applying a groundwater discharge model to samples collected from specific points in the aquifer is not likely to produce a meaningful understanding of the system.

The models that follow in this chapter assume relatively simple aquifer geometries and relatively uniform material properties. They also assume that within a given flow tube, transport is purely piston flow as they do not include hydrodynamic dispersion; however, discharge models that do include hydrodynamic dispersion have been developed (Lenda and Zuber, 1970). The conditions assumed in these simple models are most closely met in shallow aquifers consisting of granular materials. More complex models that consider effects, such as stagnant water (e.g. matrix pore water between permeable fractures), are beyond the scope of this Guidebook. (See IAEA-TECDOC-77 and IAEA-TECDOC-910, and references therein, for the treatment of more complex systems. Also, see Zuber (1986) for a more complete treatment of the models discussed in this chapter.)

Four idealized models of groundwater flow are considered in this chapter, including:

1. An unconfined aquifer of constant thickness with uniform recharge;
2. An unconfined aquifer with thickness increasing linearly with distance and with uniform recharge;
3. A confined aquifer of constant thickness that receives flow from an adjacent unconfined aquifer that is also of constant thickness;
4. A confined aquifer of constant thickness that receives flow from an adjacent unconfined aquifer with thickness increasing linearly with distance.

While the geometries of these models are highly idealized, they provide insight into the general patterns of ages in aquifers and how flow integrated samples of discharge can be used to quantify bulk aquifer properties. This discussion follows closely that of Cook and Böhlke (2000), but has been organized by the model geometry (i.e. unconfined constant thickness versus confined constant thickness, etc.) rather than by category (i.e. groundwater stratigraphy versus groundwater discharge).

## 6.2. UNCONFINED AQUIFER WITH CONSTANT THICKNESS

Consider a simple unconfined aquifer in which recharge (R) is spatially uniform, the aquifer has a constant thickness (L), and the porosity ($\theta$) is spatially uniform. A flow net for this system is shown in Fig. 6.1. The distribution of travel times (i.e. age) in this system was shown by Vogel (1967) to be:

$$t = \frac{L\theta}{R} \ln\left(\frac{L}{L-z}\right) \tag{6.1a}$$

It is interesting to note that the travel time given by Eq. (6.1a) is independent of the horizontal location in the aquifer. Thus, contours of travel time are horizontal lines as shown in Fig. 6.1. An important consequence of the

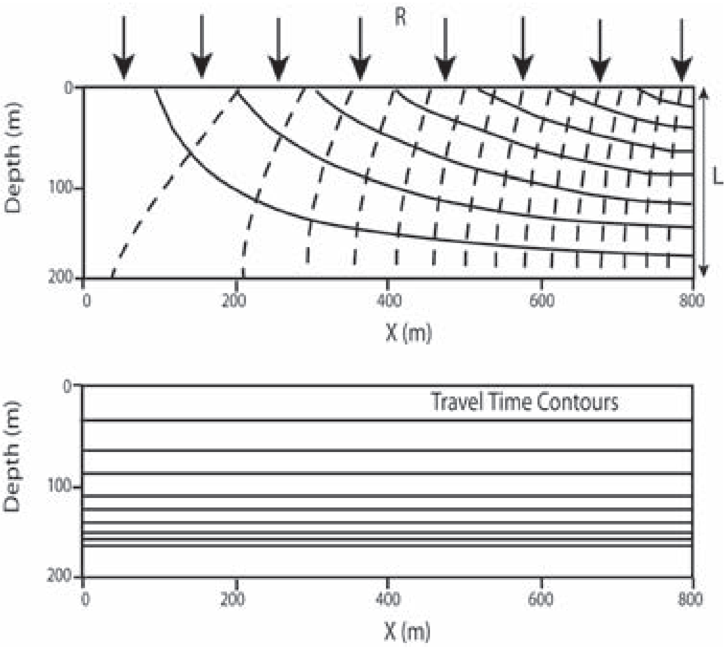

*FIG. 6.1. Unconfined aquifer of constant thickness (L) and uniform recharge (R). The upper diagram is a flow net for this system; the solid lines represent flow paths and the broken lines represent equipotential lines. The lower diagram shows contours of travel time, with age increasing exponentially with depth. The contour interval for travel times is arbitrary, as it depends on the values for recharge and porosity.*

age distribution in this system is that large differences in age can occur over relatively short vertical distances when the recharge rate is small. For example, if the aquifer thickness, porosity and recharge rate are 30 m, 0.3 m and 0.02 m/a, respectively, then the difference in age from the water table to a depth of 1 m is more than 15 years. It is also worth noting that for cases in which $z << L$ (i.e. sampling a thick aquifer near the water table), then the travel time is approximately given by:

$$t \approx \frac{z\theta}{R} \tag{6.1b}$$

In this case, the travel time distribution is a linear function of depth.

The horizontal groundwater velocity in this system can be derived by considering a fluid mass balance and is given by:

$$v_x = \frac{Rx}{L\theta} \tag{6.2}$$

The horizontal velocity in this model increases with increasing distance in the direction of flow ($x$) because the total input of water from recharge increases continuously in the direction of flow.

The vertical velocity for this system can be obtained by differentiating Eq. (6.1a) with respect to $z$ and is given by:

$$v_z = \frac{R(L - z)}{L\theta} \tag{6.3}$$

Like the travel time, the vertical velocity in this model is not a function of the horizontal location. Also note that at $z = 0$, Eq. (6.3) reduces to simply $R/\theta$.

If it is possible to obtain an integrated sample from all flow tubes, then this unconfined aquifer can be evaluated using a groundwater discharge model. For example, if all of the flow tubes discharge into a spring or river where they are effectively mixed (i.e. where water of different ages is mixed together), then the mean age (also known as the mean transit time or the residence time) of this mixed sample is given by:

$$\tau = \frac{L\theta}{R} \tag{6.4}$$

It is interesting to note that Eq. (6.4) is not a function of horizontal location. In other words, if at a given horizontal location in the system *all* flow paths are effectively integrated, then the residence time will be the same if one examines the flow system at some other location provided again that *all* flow paths are integrated (or mixed together). This concept can be seen more clearly by examining two horizontal locations in the flow system as illustrated by Fig. 6.2. There are three flow tubes that cross the line A-A'. The travel time in these flow tubes is about 114, 41.6 and 11.2 years, respectively (for a porosity of 0.3 and a recharge rate of 1 m/a). Of the total discharge, 33.3% comes from each tube. Multiplying the travel times in each tube by 0.33 and then summing, we obtain a flow-weighted mean travel time of 55.5 years. Now consider flow that crosses the line B-B'. We now have a total of six flow tubes, which includes the three tubes that crossed line A-A'. In this case, each tube contributes 16.7% of the total flow. If we multiply the travel times in each flow tube (155, 78.6, 48.6, 31, 15.7, and 3.71 years) by 0.167 and then sum them, we arrive at a mean

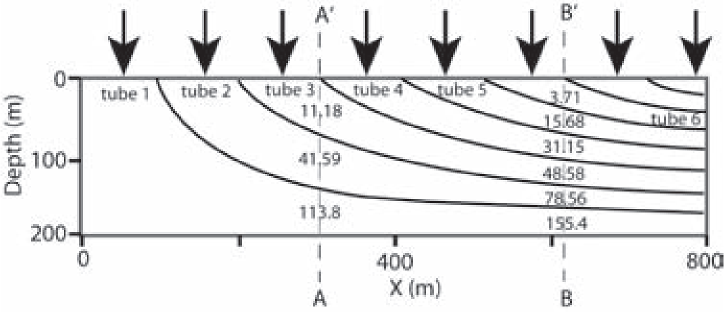

*FIG. 6.2. An illustration of how the mean transit time in an unconfined aquifer of constant thickness and uniform recharge is independent of the horizontal scale. Numbers inside flow tubes represent travel times in years for a recharge rate of 1.0 m/a. At the line A-A' the mean travel time is 55.5 years. At the line B-B' the mean travel time (i.e. average of the travel time in each flow tube) is also 55.5 years. Although water in flow tubes 1, 2 and 3 has increased in age from A-A' to B-B', the addition of younger water in tubes 4, 5 and 6 exactly offsets this increase to produce a mean travel time that is independent of horizontal scale. See text for more details.*

travel time of 55.5 years, the same as for line A-A'. Even though the travel time in tube 1 increases from 114 to 155 years as water moves from the A-A' line to B-B', this increase in age is diluted by the addition of younger water resulting from recharge to the right of the line A-A'.

The independence of the mean transit time to horizontal position is a fundamental attribute of an unconfined aquifer that receives uniform recharge and has a constant thickness. Haitjema (1995) showed how this attribute leads to a mean transit time in the base flow of an idealized watershed that is independent of scale. In other words, where recharge to a watershed is spatially uniform, and the aquifer is of constant thickness, the integrated travel time of water discharging from the system will be the same everywhere, and is related to the aquifer thickness ($L$), recharge rate ($R$) and porosity ($\theta$) as given by Eq. (6.4). The practical significance of this concept is that two of the most fundamental properties of a subsurface flow system (the flow of water per unit area into the system, $R$, and the volume of water in storage per unit area, $L\theta$) can be, in theory, evaluated by collecting flow integrated samples of discharge anywhere in the watershed.

The discharge model described above can be (and historically was) developed without considering the details of the aquifer geometry, but treating the system as a ‘black box’. The basis for the mathematical development of groundwater discharge models is the ‘convolution integral’:

$$C_{out}(t_i) = \int_0^{\infty} C_{in}(t_i - \tau) g(\tau) e^{-\lambda\tau} d\tau \qquad (6.5)$$

where $C_{\mathrm{in}}$ and $C_{\mathrm{out}}$ are the input and output concentrations, respectively, of some tracer, $g(\tau)$ is a weight function that describes the age frequency distribution of the sample, $t_i$ is the time of observation, $\tau$ is the transit time, and the exponential term accounts for first-order decay in the case of a radioactive tracer. For CFCs, the exponential term could also be used to describe biodegradation in some systems. The weighting function, $g(\tau)$, for an unconfined aquifer of constant thickness and uniform recharge is given by:

$$\mathrm{g}(\tau) = \frac{R}{L\theta} e^{-\tau R / L\theta} \qquad (6.6)$$

Because of the exponential term in Eq. (6.6) that describes the frequency distribution of age, this model is known as the ‘exponential’ model. Equation (6.5), together with Eq. (6.6), allows calculation of tracer concentrations in integrated aquifer outflow.

## 6.3. UNCONFINED AQUIFER WITH LINEARLY INCREASING THICKNESS

Consider now an unconfined aquifer with uniform recharge having a thickness that increases linearly in the horizontal direction. A flow net of this aquifer is shown in Fig. 6.3. The distribution of travel times is given by:

$$t = \frac{z\theta}{R} \qquad (6.7)$$

Like the unconfined aquifer of constant thickness, the travel time is independent of the horizontal location in the aquifer.

The horizontal velocity is given by:

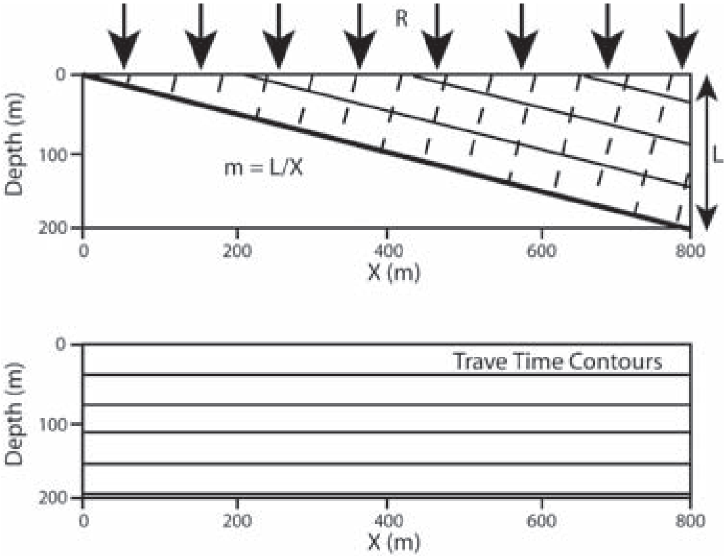

*FIG. 6.3. Unconfined aquifer with linear increasing thickness (L) and uniform recharge (R). The upper diagram is a flow net for this system while the lower diagram shows contours of travel time. The contour interval for travel times is arbitrary, as it depends on the value of recharge.*

$$V_x = \frac{R}{\theta m}, \ m = \frac{\Delta L}{\Delta x} \tag{6.8}$$

Note that Eq. (6.8) is valid only for non-zero values of *m*, which represents the slope of the aquifer bottom.

The vertical velocity is given by:

$$v_z = \frac{R}{\theta} \tag{6.9}$$

The vertical velocity for both the constant thickness and linearly increasing unconfined aquifers is the same at $z = 0$ (i.e. at the water table).

When a groundwater discharge model is applied to the increasing thickness geometry, the mean transit time is given by:

$$\tau = \frac{L\theta}{2R} \tag{6.10}$$

This differs from the constant thickness model by a factor of 2. This is because the aquifer thickness depends on the horizontal location. For a given horizontal length, the total volume of water stored in this system is one half that stored in a system with constant thickness.

The age distribution, $g(\tau)$, for this aquifer is given by:

$$\begin{aligned} g(\tau) &= \frac{R}{L\theta} && \text{for } \tau \le L\theta / R \\ g(\tau) &= 0 && \text{for } \tau > L\theta / R \end{aligned} \tag{6.11}$$

A discharge model of this geometry is also known as a 'linear' model.

## 6.4. CONFINED AQUIFER WITH CONSTANT THICKNESS

We now consider a perfectly confined aquifer (that receives no recharge) that is adjacent to an unconfined aquifer having a uniform recharge rate. A flow net of this system is shown in Fig. 6.4. The age distribution is given by:

$$\begin{aligned} t &= \frac{L\theta}{R}\ln\left(\frac{L}{L-z}\right) + \frac{x^{*}L\theta}{Rx}, && x^{*} \ge 0 \\ t &= \frac{L\theta}{R}\ln\left(\frac{L}{L-z}\right), && x^{*} < 0 \end{aligned} \tag{6.12}$$

where x* is the horizontal distance from the unconfined aquifer (see Fig. 6.4) The age distribution in this system is identical to the constant thickness unconfined model where recharge is occurring, and then becomes a function of horizontal distance in the confined portion of the system. Equation (6.12)

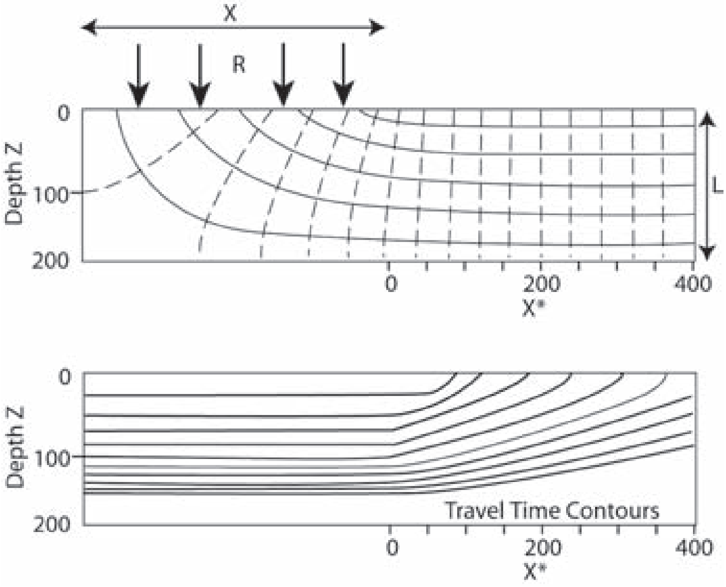

*FIG. 6.4. A confined aquifer of constant thickness that receives recharge from an adjacent unconfined aquifer of constant thickness is shown. The upper diagram is a flow net for this system while the lower diagram shows contours travel time. The contour interval for travel times is arbitrary, as it depends on the values of recharge (R).*

implies that a stratification of age will exist not only in the unconfined aquifer, but will persist in the confined portion of the system as well.

The horizontal velocity is given by:

$$v_x = \frac{Rx}{L\theta} \tag{6.13}$$

Note that once water enters the confined portion of the system (i.e. $x^* > 0$), the horizontal velocity remains constant with horizontal distance (i.e. it is not a function of $x^*$).

The vertical velocity within the confined portion of the system is zero.

The mean transit time for the groundwater discharge model for the confined aquifer is given by:

$$\tau = \frac{L\theta(x + x^*)}{Rx} \tag{6.14}$$

Equation (6.14) indicates that a fundamental attribute of a confined aquifer is that the mean transit time will increase with horizontal distance. If this concept is applied to a watershed, it implies that integrated samples (e.g. from regional springs) should indicate increasing age as a function of scale. Thus, the dependence (confined aquifer) versus independence (unconfined aquifer) of the mean transit time with scale is related to spatial patterns in recharge.

The age distribution function, $g(\tau)$, for a confined aquifer is given by:

$$\begin{aligned} g(\tau) &= 0 \qquad \text{for } \tau < \frac{L\theta x^*}{Rx} \\ g(\tau) &= 0 \qquad \text{for } \tau > \frac{L\theta x^*}{Rx} \end{aligned} \tag{6.15}$$

A discharge model for the confined aquifer described here is known as an ‘exponential piston flow’ model.

## 6.5. CONFINED AQUIFER WITH CONSTANT THICKNESS IN CONFINED PART

As a final aquifer geometry, we consider a confined aquifer that is adjacent to an unconfined aquifer having a uniform recharge rate, but having a thickness that increases with horizontal distance. The thickness of the confined part of this system is constant. A flow net of this system is shown in Fig. 6.5. The age distribution is given by:

$$\begin{aligned} t &= \frac{z\theta}{R} + \frac{x^* L\theta}{Rx}, \qquad x^* \geq 0 \\ t &= \frac{z\theta}{R}, \qquad\qquad\quad x^* < 0 \end{aligned} \tag{6.16}$$

The horizontal and vertical velocities for this system are given by:

$$\begin{aligned} v_x &= \frac{Rx}{L\theta} \\ v_z &= 0 \end{aligned} \tag{6.17}$$

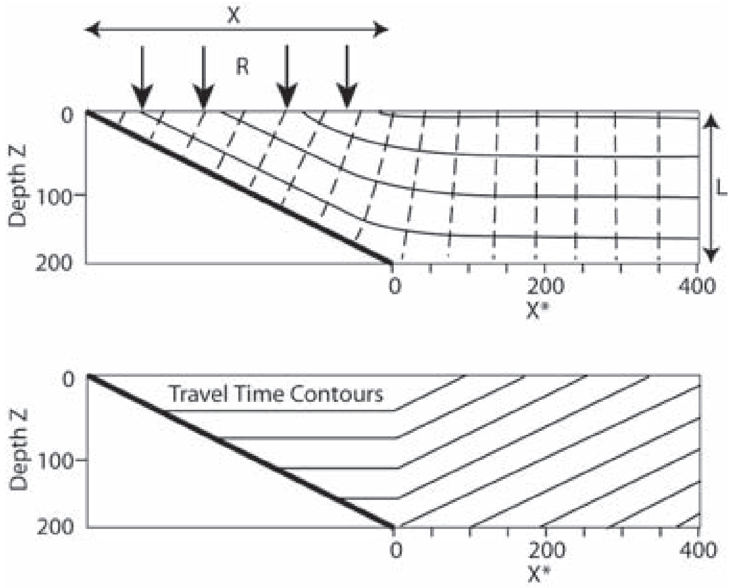

*FIG. 6.5. Confined aquifer of constant thickness that receives recharge from an adjacent unconfined aquifer of linearly increasing thickness. The upper diagram is a flow net for this system, while the lower diagram shows contours travel time. The contour interval for travel times is arbitrary, as it depends on the values of recharge (R).*

For a groundwater discharge model, the mean transit time for this system is given by:

$$\tau = \frac{L\theta}{R}\left(\frac{x^*}{x} + \frac{1}{2}\right) \tag{6.18}$$

The age distribution function, g(τ), for this system is given by:

$$\begin{aligned} &\mathrm{g}(\tau) = \frac{R}{L\theta} && \text{for } \frac{L\theta x^*}{Rx} < \tau \le \frac{L\theta}{R}\left(\frac{x^*}{x} + 1\right) \\ &\mathrm{g}(\tau) = 0 && \text{for all other } \tau \end{aligned} \tag{6.19}$$

This type of discharge model is known as a ‘linear piston flow’ model.

## 6.6. DISCUSSION

Although the four models presented previously are highly idealized, they are useful for understanding general patterns in the age distribution that might be expected in real aquifers. As previously indicated, the choice between a ‘hydrostratigraphy’ model and a ‘discharge’ model depends to a large degree on the type of samples than can be collected. Over small scales in well instrumented systems, it may be possible to collect samples at discrete depths. These values can be compared with estimates, given the age distribution equations for the hydrostratigraphy models, and unknown parameters, such as the recharge rate, can be adjusted in an attempt to minimize the difference between observed and model results. See Chapter 7 for examples of the applications of the hydrostratigraphy models.

At larger scales, it is frequently not possible to obtain sufficient discrete samples to apply a hydrostratigraphy model. In such cases, discharge models are commonly used by collecting samples from discharge points that are thought effectively to include all upstream flow paths. When applying a discharge model to CFC results, the apparent age of the mixture is not the same as the mean age of the mixture because age is not proportional to any of the tracer concentrations. The equations for mean transit time presented previously assume that when all flow tubes mix at the discharge point, the age of water in each flow tube mixes in a linear fashion. For example, if a tube with an age of 10 years mixes with a flow tube having an age of 40 years, the mean transit time equations would yield a mean age for this mixture of 25 years, which is true. However, in the case of CFCs, the relationship between concentration and time is not linear. Thus, the apparent age of this mixture will not generally match that of the mean transit time equations. A water that recharged in 1990 (at sea level and at 20°C) would have a CFC-12 concentration of 1.67 pmol/kg, whereas a water that recharged in 1950 at the same elevation and temperature would have a concentration of 0.018 pmol/kg. If equal parts of this water are mixed, a concentration of 0.84 pmol/kg is obtained. Using the methods described in Chapter 3, an apparent recharge year of this mixture would then be computed that is 1977 instead of 1970. This problem can be avoided by applying actual concentrations to a groundwater discharge model rather than apparent ages. In other words, the convolution integral presented in Eq. (6.5) is solved using the actual relationship between concentration and time that exists for the CFC compound of interest and using the age distribution function, $g(\tau)$, that is appropriate for the system. Unknown model parameters, such as recharge, can then be adjusted in an attempt to minimize the difference between the observed and modelled concentrations. A numerical model known as FLOW PC is available from the IAEA that will

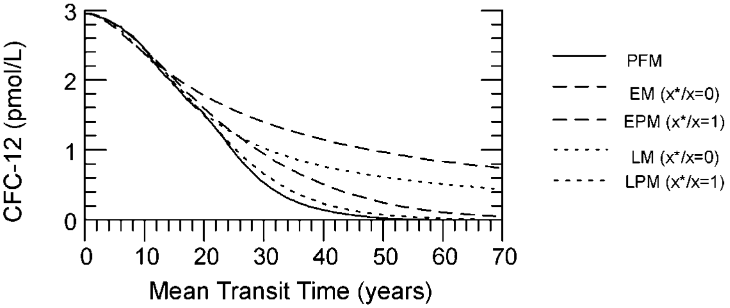

*FIG. 6.6. Concentrations of CFC-12 (pmol/L) as a function of the mean transit time (years) for various groundwater discharge models are shown. The vertical axis represents concentrations that would be observed in 1998 in samples of groundwater discharge in which all aquifer flow paths are mixed together, such as might occur at spring. From Cook and Böhlke (2000).*

numerically integrate the convolution integral of Eq. (6.5) for various age distribution functions, $g(\tau)$, given the relationship between the input concentration and time. Figure 6.6 shows the CFC-12 concentration produced by such a model as a function of the mean transit time, $(\tau)$. The various curves shown in Fig. 6.6 represent the various types of discharge models presented previously (e.g. exponential, linear, etc.).

Because the input functions for the various CFCs are distinct from one another, the mixing of flow paths at a discharge location affects each tracer differently. For example, Fig. 6.7(a) shows the concentrations of CFC-11 and CFC-12 that might exist for samples collected in 2002 from a system in which the exponential model applies. The values for CFC-11 and CFC-12 in an integrated discharge sample are shown for systems in which the mean transit time (in years) is 200, 100, 50, 20, 10, 5 and 1. In other words, if the mean residence time is 50 years, a flow integrated sample of discharge collected in 2002 would have CFC-11 and CFC-12 concentrations of about 100 and 200 pptv, respectively. Also shown in Fig. 6.7 are the curves for the piston flow model. Where the exponential and piston flow curves are similar, the tracer pairs cannot resolve the mixing processes and interpretation of age could be very sensitive to the type of mixing that is assumed. For example, in Fig. 6.7(a) a discharge sample with a CFC-11 concentration of 100 pptv and a CFC-12 concentration of 200 pptv could result from exponential mixing with a mean transit time of 50 years; it could result from piston flow with an age of 29 years, or it could result from binary mixing of about one third modern with two thirds old water. If only CFC-11 and CFC-12 data were available, it would not be

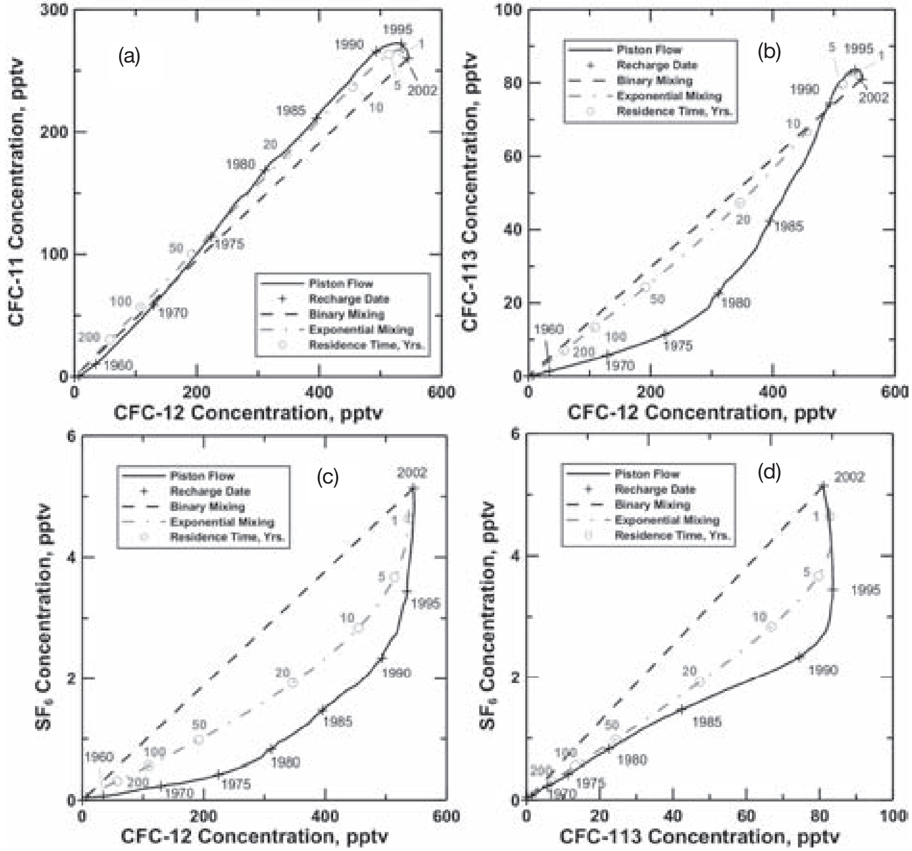

*FIG. 6.7. Tracer plots comparing CFC-11, CFC-12, CFC-113 and $SF_6$ concentrations in pptv for North American air are shown. The solid lines represent unmixed (piston flow) with selected apparent ages ('+'). The dark dashed lines show one example of binary mixing, for the case of water recharged in 2002 diluted with old, CFC-free water. The dash-dot lines represent exponential mixing for residence times of 1 to 200 years. (Modified from Plummer et al. (2003).)*

possible to evaluate the mixing process (i.e. exponential versus binary versus piston flow). This is because the CFC-11 and CFC-12 input curves are rather similar. In contrast, Fig. 6.7(b) shows CFC-113 versus CFC-12, and the exponential and piston flow curves are fairly distinct. For example, a CFC-12 concentration of 200 pptv with a CFC-113 concentration of about 10 pptv would probably represent a water from a piston flow system that is about 28 years old. These values would not be consistent with either the exponential or binary mixing models.

## 6.7. SUMMARY

Simple models regarding groundwater travel times can be divided into two categories:

(1) Groundwater stratigraphy models that predict the distribution of CFC concentrations (or CFC ages) within the aquifer;
(2) Groundwater discharge models that predict the flow weighted concentration of CFCs at discharge points.

These models consider relatively simple aquifer geometries and uniform properties that are not likely to be consistent with most real flow systems. However, these models are useful for understanding general patterns in CFC concentrations in various systems, and for helping to understand the nature of the system itself. For example, if samples are collected from springs within a watershed and if the CFC age of these springs is similar, the flow system might be one in which uniform recharge is occurring. Furthermore, if the porosity and average thickness of the flow system could be estimated, the CFC age (as an approximation of the mean transit time) could be used in Eq. (6.4) to yield the recharge rate. Alternatively, if discrete samples are collected at various depths in an aquifer receiving uniform recharge, then it might be possible to fit either Eq. (6.1) or Eq. (6.7) to the observed data, and thereby obtain an estimate of the recharge rate.

As a final note, it should be pointed out that numerous groundwater flow models exist that are capable of modelling complex aquifers with heterogeneous properties. In many cases, it is probably more appropriate to develop a site-specific model that includes all available information regarding the flow system, rather than relying on the simplified models presented in this chapter.

# Chapter 7

# PRACTICAL APPLICATIONS OF CFCs IN HYDROLOGICAL INVESTIGATIONS

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## 7.1. ESTIMATION OF RECHARGE RATE FROM RATE OF DOWNWARD MOVEMENT USING VERTICAL CFC PROFILES

The distribution of groundwater ages in different types of aquifers under conditions of piston flow is discussed in Chapter 6. In an aquifer of constant thickness and receiving constant recharge, the groundwater age will increase exponentially with depth below the water table. The vertical component of the groundwater velocity will decrease from $R/\varepsilon$ at the water table (R is the recharge rate, $\varepsilon$ is the aquifer porosity), to zero at the base of the aquifer (assuming that the aquifer is underlain by an impermeable aquiclude). If the groundwater age is measured at any discrete depth, then it is possible to calculate the groundwater recharge rate. In practice, collection of a number of samples at discrete depths close to the water table is preferred, and vertical groundwater velocities can then be directly determined from the vertical CFC age gradient. The aquifer recharge rate can be determined from this data, provided that the aquifer porosity is known or can be estimated.

The vertical CFC-12 profile measured at the Sturgeon Falls site, Ontario, Canada, is depicted in Fig. 7.1 (Cook et al., 1995). This site was instrumented with a series of piezometer nests constructed of polyethylene or polyvinyl chloride (PVC) tubing, all with 15 cm screens, permitting excellent vertical resolution of groundwater samples. Concentrations decrease almost linearly

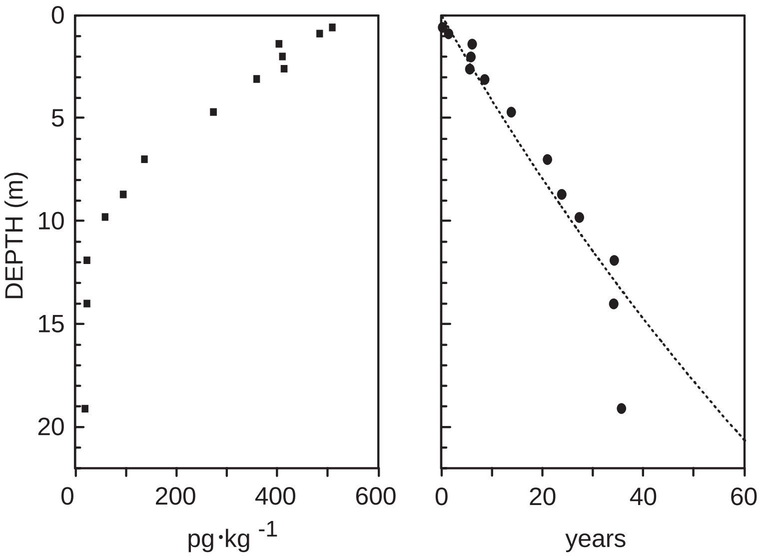

*FIG. 7.1. Profiles of CFC-12 concentration and apparent CFC-12 age in the Sturgeon Falls aquifer are shown. The broken line represents results of a two-dimensional flow model calibrated using tritium data, from Cook et al. (1995).*

with depth, from 510 pg/kg at 0.6 m to less than 50 pg/kg below 10 m. The concentration measured in the uppermost sample is not significantly different from that which would be expected for water in equilibrium with the atmosphere (in 1993, the time of sampling) at a recharge temperature of 3°C. The apparent CFC age increases with depth, from zero at 0.6 m, to 34 years at 11.9 m. The apparent age of 36 years for the sample at 19.1 m appears too young, and is attributed to low levels of contamination, probably introduced during sampling. Apparent CFC-12 ages of 27 and 33 years at 9.8 and 11.9 m depth are in good agreement with $^3$H data obtained at the site. Near the water table, the increase in apparent CFC-12 age with depth is approximately 2.5 a/m. This is equivalent to a vertical water velocity of 0.4 m/a. Multiplying by an aquifer porosity of 0.35, this equates to a groundwater recharge rate of 140 mm/a (see Eq. (6.1a)). For comparison, Cook et al. (1995) estimated an aquifer recharge rate of 130 mm/a using a groundwater flow model calibrated to the CFC-12 data.

Another example of the use of groundwater ages at discrete depths to estimate recharge is discussed in Chapter 9, Section 9.1.

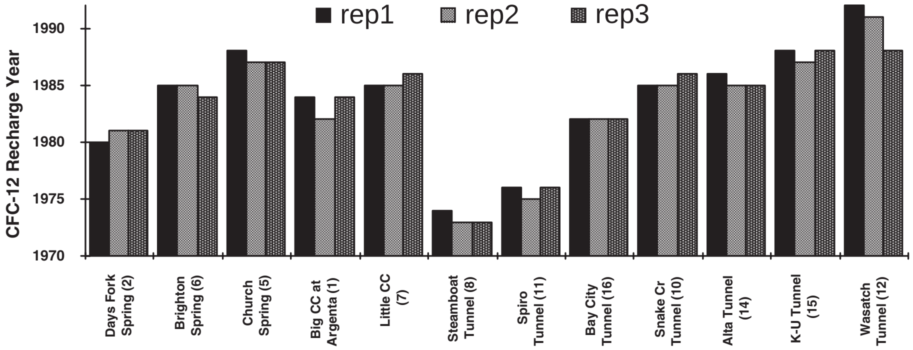

*FIG. 7.2. Apparent CFC-12 recharge year is shown for spring, mine tunnel and stream samples (Big CC at Argenta; Little CC) in the Wasatch Mountains, Utah, USA.*

## 7.2. APPLICATION OF A DISCHARGE MODEL

A simple example of using CFC data in a discharge model is provided by a study of groundwater flow in the Wasatch Mountains, east of Salt Lake City, Utah, USA (Parry et al., 2000). The general objective of this study was to evaluate the extent to which discharge from old mine tunnels would have discharged directly into local streams in the absence of the mine tunnels. The ownership of surface water is distinct from groundwater in this area and the ownership of mine discharge was in dispute.

Figure 7.2 shows apparent CFC-12 ages for samples collected from mine tunnels, springs and directly from stream discharge.

The apparent CFC-12 recharge year for these samples is 1983.4 when the samples from Steamboat Tunnel and Spiro Tunnel, USA (which are in a different watershed), are excluded. Samples were collected in 1996. Assuming that the full range of active subsurface flow paths are sampled by the above results, it is possible to apply a discharge model for an unconfined aquifer. The mean travel time is given by:

$$\tau = \frac{L\theta}{R} \tag{7.1}$$

where $\theta$ is the effective porosity, $R$ the mean recharge rate, and $L$ is the depth of active groundwater circulation (Eq. (6.4)). The recharge rate and porosity are not known precisely for the groundwater system in the Wasatch Mountains, but we can calculate a maximum value for $L$ by assuming reasonable maximum and minimum values for $R$ and $\theta$ of 1 m/a and 0.01, respectively. To a first approximation, if the apparent CFC-12 age (13 years) can be substituted for the mean travel time, the maximum depth of active circulation is computed to be about 1300 m. Because the recharge rate is likely to be a factor of 10 less (based on water balance studies), the probable depth of active circulation is about 130 m. This is consistent with a conceptual model in which the permeability of the upper several hundred metres is enhanced due to fracturing, but rapidly declines at greater depths (Parry et al., 2000).

## 7.3. TRACING FLOW DIRECTION AND VELOCITY USING SPATIAL VARIATIONS — LOSING AND GAINING STREAMS

As discussed in Chapter 6, discharge models that integrate all flow paths in a system can be very powerful for understanding both the flux of water into a system and the volume of water in storage. However, for a discharge model to be valid, a mixed sample of *all* flow paths must be collected. This may occur in regional springs, but is most likely to occur in gaining streams that represent regional discharge points. Discharge models have been successfully applied to base flow in streams using non-volatile environmental tracers, such as tritium (e.g. Taylor et al., 1989). The difficulty of using CFCs in streams arises from gas exchange between the atmosphere and stream water. As groundwater with low CFC concentrations discharges into streams, it is possible for the stream to ‘absorb’ CFCs from the atmosphere, thereby overprinting the CFC signature of groundwater.

Although gas exchange seems likely in virtually all streams, Solomon et al. (1997) pointed out that numerous measurements of CFCs in streams in the western USA indicate that streams are seldom in equilibrium with the atmosphere. To explain this observation, Solomon et al. (1997) developed a simple model of CFC exchange in streams.

The rate of the exchange can be described as:

$$\frac{dC}{dt} = \lambda\left(C - C_{ATM}\right) \tag{7.2}$$

where $C$ is the concentration of the gas in the water, $t$ is time, $\lambda$ (with units of $1/T$) is the gas exchange coefficient, and $C_{ATM}$ is what the gas concentration would be if fully equilibrated with the atmospheric concentration (Clark et al., 1992; Wanninkhof, 1992; Rathbun, 1998).

Shaw (2000) examined the exchange of CFCs by performing a tracer experiment in Little Cottonwood Creek, Utah. Shaw utilized a numerical model of solute transport in streams, that was modified to include gas exchange, developed by Runkle et al. (1998). This model, known as OTIS, solves the following partial differential equation describing the concentration of a solute (e.g. CFCs) in a stream:

$$0 = -\frac{Q}{A}\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial\left(AD\frac{\partial C}{\partial x}\right)}{\partial x} + \frac{q_{LIN}}{A}\left(C_{gw} - C\right)$$
$$+\alpha\left(C_s - C\right) + \lambda_{GAS}\left(C_{ATM} - C\right) \tag{7.3}$$

for the main channel, and:

$$0 = \alpha\frac{A}{A_S}\left(C - C_S\right) \tag{7.4}$$

for the storage zone (Runkel, 1998; Runkel et al., 1999), where $A$ is the main channel cross-sectional area, AS is the storage zone cross-sectional area, $C$ is the main channel solute (e.g. CFC) concentration, $C_S$ is the storage zone concentration, $C_{gw}$ is the lateral inflow concentration, D is the dispersion coefficient, $Q$ is the volumetric flow rate in the stream, $q_{LIN}$ is the lateral inflow rate per unit length of stream, $x$ is the distance, $\alpha$ is the storage zone exchange coefficient, $\lambda$ is the gas exchange coefficient, and $C_{ATM}$ is the atmospheric concentration of CFCs. The gas exchange coefficient describes how rapidly dissolved gases in stream water exchange with the atmosphere. When $\lambda$ is equal to zero, no gas exchanges occur and the CFC concentration of base flow will be equal to the concentration in groundwater discharging into the stream. As $\lambda$ becomes large, the CFC concentration of base flow moves toward being in equilibrium with the atmosphere.

The gas exchange coefficient is a system variable that describes the response of the stream volume to gas exchange at the stream's surface. The actual rate of gas exchange across the surface of the stream to the atmosphere can be described by the gas exchange velocity ($k$) (Wanninkhof, 1992). The gas exchange velocity is a function of turbulence at the surface of the stream, temperature, wind shear and molecular diffusion. The gas exchange coefficient is related to the gas exchange velocity by:

$$\lambda = k/b \tag{7.5}$$

where $b$ is the average depth of the stream. When the stream depth is small, the gas exchange coefficient (l) is large and the stream tends to equilibrate with the atmosphere. In contrast, when the depth is large, l is small and the effect of gas exchange on the stream is small.

For the gaining stream described previously, in which the surface area does not increase downstream, dilution of stream flow by groundwater (having a low CFC concentration) is offset by the uptake of CFCs from the atmosphere, such that a steady state concentration is obtained (Solomon et al., 1997; Shaw, 2000). The steady state concentration will lie somewhere between the concentration in groundwater, and full equilibrium with the atmosphere. Figure 7.3 shows the relationship between the concentration of CFCs in groundwater and the steady state concentration in a gaining stream. When the ratio of the gas exchange velocity to the groundwater specific discharge is small (i.e. a stream

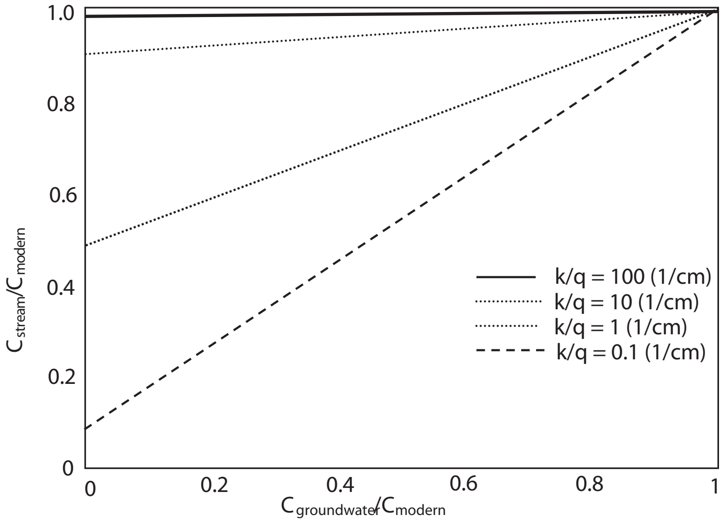

*FIG. 7.3. Relationship between the concentration of CFCs in groundwater (relative to the equilibrium concentration $C_{atm}$ with the modern atmosphere) to the CFC concentration in a gaining stream is shown. This relationship is shown for various values of k/q where k is the gas exchange velocity ($k = \lambda b$; $\lambda$ is the gas exchange coefficient, b is stream depth), and q is the discharge of groundwater into the stream per unit length of stream. When gas exchange is small (i.e. small value for k), and the groundwater specific discharge is large (i.e. large value of q), the concentration of CFC in the stream will approach that of discharging groundwater.*

with a large inflow of groundwater into a deep stream so that gas exchange is minimal), the concentration in the stream will be similar to that of groundwater. In contrast, when the groundwater discharge is small and the stream is shallow, allowing significant gas exchange (i.e. the ratio of $k$ to $q$ is large), the concentration of CFCs in the stream will approach equilibrium with the atmosphere. For the tracer experiment conducted by Shaw (2000), the gas exchange velocity was determined to be 90 cm/h while the discharge of groundwater was 1.6 $cm^2/a$ to give a $k/q$ of about 55 $cm^{-1}$. Thus, for Little Cottonwood Creek, Utah, the concentration of CFCs in the stream should not be at equilibrium with the atmosphere, but rather should reflect both the concentration of discharging groundwater, and the uptake of CFCs from the atmosphere. If the exchange velocity is independently derived, e.g. Shaw (2000), then it may be possible to derive the concentration of CFCs in groundwater by measuring the concentration of CFC in stream flow of a gaining stream.

The practical aspects of the above analysis are twofold. First, gaining streams are not expected to have modern concentrations of CFC unless groundwater discharge is small and the stream is shallow, allowing for significant gas exchange. Second, it may be possible to derive an integrated concentration for groundwater that could be used, for example, in a groundwater discharge model, by measuring CFC concentration in streams.

The above conclusions are consistent with a study of CFCs in the Daly River in northern Australia (Cook et al., 2003). CFC concentrations remained below atmospheric solubility for more than 30 km downstream from a section of the river where CFC-free groundwater is discharging into the river.

## 7.4. IDENTIFYING RECHARGE AREAS

CFCs are found in post-1940s water, thus, their occurrence in groundwater is an indication of the presence of some fraction of relatively recent recharge. Using CFCs to locate recharge areas can be especially useful in arid regions. For example, as a part of an interdisciplinary investigation of the hydrology of the Middle Rio Grande Basin of central New Mexico, USA, approximately 250 radiocarbon, CFC and tritium measurements were made on dissolved inorganic carbon and groundwater from the Santa Fe Group aquifer system. One of the objectives of the study was to identify areas where recent recharge was occurring in the aquifer (Plummer et al., 2001; 2004).

Groundwater samples containing more than 0.2 TU always contained detectable concentrations of CFC-12. The mountain-front groundwater samples containing significant concentrations of tritium also contained 130–1100 pg/kg of CFC-12. As a means of detecting recently recharged water or water samples containing fractions of young water, samples for CFC analysis were routinely collected wherever a closed path could be established between the source and the sampling equipment. Samples where CFCs were not collected included some seeps, wells and windmills that, for various reasons, introduced air into the sample prior to discharge. For these samples, tritium was routinely measured. Because of the low detection limit for CFCs and the stability of CFC-12, CFC-12 provided a useful tracer of young water (post-1940s water) or of samples containing a fraction of young water. The detection of CFC-12 and tritium was limited almost exclusively to wells located in and near the mountains that border the Middle Rio Grande basin along its northern and eastern margin, to wells near arroyos that recharge the aquifer during runoff events, and to wells located in the flood plain and inner valley of the Rio Grande, which extends through the length of the basin (approximately 250 km). Concentrations of CFC-12 were typically less than 2 pg/kg elsewhere in the basin, where depth to water ranged from 100 to more than 300 m in siliciclastic sands.

Therefore, in the absence of tritium measurements, CFCs provided similar information to that obtained from tritium pertaining to young water fractions. The absence of CFC-12 and/or tritium provided useful criteria for screening water samples in which the $^{14}$C activity had not been contaminated with $^{14}$C from atmospheric testing of nuclear bombs.

In the Eastern Snake River Plain of south-east Idaho, USA, CFCs provided a means of recognizing areas where infiltration was occurring through deep unsaturated zones. Figure 7.4 shows a schematic cross-section for an open borehole that penetrates the upper 20 m of the Eastern Snake River Plain aquifer beneath more than 300 m of the unsaturated zone. Analyses of CFCs in air blowing from the annulus of deep wells indicated the presence of air from the mid-1960s in the unsaturated zone that was presumably transported and mixed advectively under barometric pumping (Plummer et al., 2000). Concentrations of CFC-11 and CFC-12 in groundwater indicated apparent recharge dates also from the mid-1960s. These were apparently inconsistent with tritium concentrations of 0.02–0.08 TU. The tritium was presumably low because the bomb tritium was still within the unsaturated zone. However, barometric pumping had introduced CFCs throughout the unsaturated zone, and recharge had resulted in solubility equilibrium CFCs in the groundwater. Thus, at this site the presence of CFCs in groundwater indicates active recharge, while $^{3}$H concentrations, without CFCs, may suggest that no recharge was occurring.

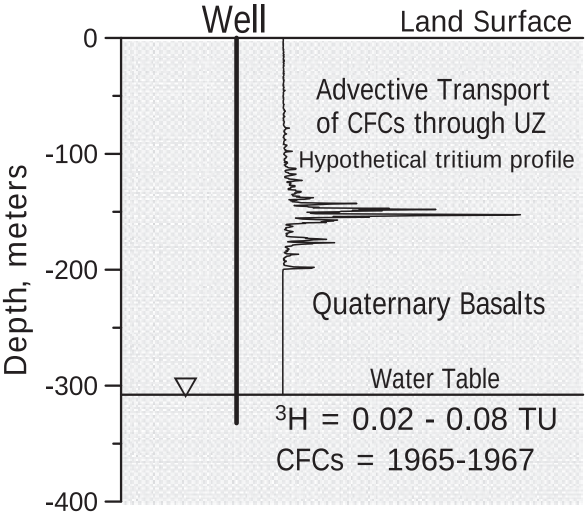

*FIG. 7.4. A schematic illustration is given of an open borehole in Quaternary basalt and sedimentary inter-bed sequences in the Eastern Snake River Plain of south-east Idaho. Depth to water is more than 300 m. Water from the upper 20 m of the aquifer has a tritium content of 0.02–0.08 TU, with CFC-11 and CFC-12 concentrations consistent with apparent recharge dates from the mid-1960s. The presence of CFCs in the aquifer suggests that infiltration of pre-bomb water contacts old air in the unsaturated zone. In this example, CFCs provided evidence that recharge to the Eastern Snake River Plain aquifer is occurring through deep unsaturated zones in this semi-arid environment.*

## 7.5. IDENTIFYING 'SECURE' DRINKING WATER SOURCES — RECOGNIZING LEAKAGE OF SHALLOW WATER INTO WATER SUPPLY WELLS

Because of the low detection limit relative to other environmental tracers, such as tritium, CFCs can play a useful role in lowering the detection of young fractions in well discharge and assessing the susceptibility of public water supplies to contamination from shallow sources. As an example, consider the possibility of a modern, shallow source in equilibrium with North American air recharged at 10°C that mixes with old, pre-CFC water in well discharge. The modern fraction might contain approximately 754, 354 and 97 pg/kg of CFC-11, CFC-12 and CFC-113, respectively. If the minimum detection limit for CFC-11 and CFC-12 is in the range of 0.3–3 pg/kg, it is possible to lower detection of the modern water fraction to the ranges of 0.04–0.4% and 0.08–0.8% in well discharge, based on CFC-11 and CFC-12, respectively. If the shallow, modern source is contaminated with CFCs, as often is the case of shallow water in urban environments, the detection of shallow water in well discharge is potentially many orders of magnitude lower than that determined from low level tritium determinations.

The detection limits of CFCs and other volatile halocarbons using purge and trap gas chromatography with an ECD can be several orders of magnitude below most analytical procedures used for agricultural and industrial contaminants. In many cases, it can be shown that concentrations of halogenated VOCs that are reported as 'background', using conventional GC-MS procedures, are in fact not zero when analysed using purge and trap GC-ECD procedures. Although the concentrations of low level detections of CFCs and other halogenated VOCs in water samples can be orders of magnitude below drinking water standards, the low level detections of CFCs permit a shift in strategy for water supply managers from recognizing water that contains one or more contaminants to screening water supplies that are potentially susceptible to contamination and need to be monitored at higher frequency than those supplies that have lower susceptibility to contamination. By lowering the detection of fractions of shallow water in discharge from public water supplies, long term monitoring has the potential of providing early warning of future contamination problems at the well scale.

There are many ways in which shallow groundwater sources can reach open intervals of public supply wells, including well construction problems, such as leaky casings or leaky seals around the casing. In unconfined, water table aquifers, wells that are not cased deeply enough below the water table are at increased risk of pumping fractions of shallow water, particularly as water levels decline in urban or industrialized areas in which there have been relatively high withdrawals, or as the water table is lowered in the immediate vicinity of the well during use. Hydrogeology also plays a significant role in affecting the extent of shallow water contamination of public supply well discharge. Wells completed in karst or fractured rock can be particularly susceptible to contamination from shallow sources, even at depths of hundreds of metres below the water table. In contrast, public supply wells in sands and gravels that are completed more than 100 m below the water table tend to have low susceptibility to contamination from shallow sources.

There are a growing number of programmes where CFCs have been formally included in source water assessment procedures. In New Zealand, one of the criteria used in drinking water standards for public supply includes residence time estimates based on CFC and/or tritium concentrations in groundwater pumped from wells (Ministry of Health, New Zealand, 2000). Among a number of criteria used to demonstrate the security of groundwater supplies, the New Zealand Drinking Water Standards permit fitting a (lumped parameter) dispersion model to two or more CFC or tritium measurements (Zuber, 1986). Groundwater that is not directly affected by surface or climatic influences was defined to contain less than 0.005% of water estimated to be less than one year old (Ministry of Health, New Zealand, 2000).

In the USA, the Department of Health, Source Water Assessment Program of Virginia (Commonwealth of Virginia, 1999) included detection of CFCs in water from public supply wells as a means of determining the intrinsic natural susceptibility of regional aquifers that serve as public water supplies (see Chapter 9, Section 9.9 for further details).

## 7.6. RECONSTRUCTING THE HISTORY OF CONTAMINANT LOADING TO AN AQUIFER

In dating groundwater with environmental tracers, it is assumed that the aquifer records a history of the tracer concentration recharged over the timescale investigated. Similarly, other substances recharged may also be archived in the groundwater reservoir. When the mixing effects of dispersion are low and transport of the solute is not retarded, a history of solute loading to the aquifer can be reconstructed by measuring solute concentration in dated samples. Groundwater systems are likely to hold valuable records of past environmental change that occurred in recharge areas of the aquifer over periods that are otherwise unobtainable. For example, numerous studies have retrieved records of recharge temperature and excess air achieved in concentrations of noble gases (Mazor, 1972; Andrews and Lee, 1979; Andrews, 1991; Stute and Sonntag, 1992; Stute et al., 1992; 1995; Andrews et al., 1994; Blavoux et al., Clark et al., 1997; Stute and Schlosser, 1999) and $N_2$-Ar (Heaton, 1981; Heaton and Vogel, 1981; Heaton et al., 1986) in groundwater on the radiocarbon timescale. As a test of various dating methods, initial tritium concentrations in recharge waters are often reconstructed by correcting the measured tritium for radioactive decay over the age of the sample (or determining initial $^3H$ from the measured $^3H$ and tritiogenic $^3He$), and comparing the reconstructed initial tritium to local records of tritium in recharge waters (see, for example, Dunkle et al. 1993; Ekwurzel et al., 1994; Plummer et al., 2000).

Groundwater dating permits the retrieval of environmental records from aquifers only over the timescale valid for the particular tracer. Because of their relatively short (recent) timescale, CFCs and $^3H/^3He$ are particularly well suited for retrieving records of human impacts on aquifers. For example, CFC dating of shallow groundwater in agricultural areas of the Atlantic coastal plain of parts of Maryland and New Jersey, USA (Dunkle et al., 1993; Böhlke and

Denver, 1995; Modica et al., 1998; and see Chapter 9, Section 9.1) indicates fairly low rates of nitrate loading to groundwater in the study areas prior to the early 1970s, and rapid loading of nitrate beginning in the early to mid-1970s in Maryland and early 1980s in the New Jersey study. The rapid rise in nitrate concentrations in groundwater apparently reflects changes in the local application rate of fertilizers (Böhlke and Denver, 1995). In many samples from agricultural areas of the Atlantic coastal plain, the maximum nitrate concentration exceeds the USEPA maximum contaminant level (MCL) of 10 mg/L as N. There is considerable interest in retrieving dated records of nitrate loading to groundwater because, unless denitrified in the groundwater system, the groundwater nitrate will eventually discharge to surface waters and estuaries adding nutrients that degrade the aquatic health of the region (Bachman et al., 1998). Using the reconstructed nitrate–age relation for groundwater in Maryland and an exponential model, Böhlke and Denver (1995) found that base flow concentrations of nitrate in a stream receiving discharge from the aquifer could be predicted if the average residence time of water in the aquifer was 20 years. This information can be used to predict the future response of surface waters in the area to changes in land use and to application rates of fertilizers. Spurlock et al. (2000) used CFC dating in conjunction with a one-dimensional transport model to estimate the age and history of herbicides in water from wells in California, USA. Böhlke et al. (2002) used CFC dating to retrieve a record of nitrate recharge rates over a period of several decades beneath changing agricultural land use in Minnesota, USA. Delin et al. (2001) used CFCs and other methods to document local variations in recharge rates of water and agricultural chemicals caused by topographical effects.

Many of the contaminants of interest added to groundwater may be unstable and can degrade, which can result in minimum estimates of historical loading to the aquifer. However, if the degradation product(s) can be measured, the initial concentrations can be reconstructed. For example, Böhlke and Denver (1995) and Böhlke et al. (2002) used the quantity of excess $N_2$ from denitrification to reconstruct the initial nitrate concentration in anaerobic, denitrified samples when developing groundwater records of changing agricultural contamination in recharge. Finally, in samples that are mixtures of young and old, it is usually reasonable to assume that the contaminant is associated with the young fraction. Therefore, in reconstructing the contaminant concentration in the young fraction, the measured concentration must be divided by the fraction of young water in the mixture. Approaches for combining groundwater dating with studies of agricultural recharge records and discharge mixtures are summarized in Böhlke (2002, 2003).

Another example of reconstructing contaminant loading to aquifers from river recharge of a contaminated river is presented in Chapter 9, Section 9.7.

## 7.7. CALIBRATING GROUNDWATER FLOW MODELS

A powerful application of dating groundwater is the calibration of groundwater flow and solute transport models. From a conceptual point of view, age data have the potential to highly constrain flow and transport models because an age sample collected at a point in space represents an integration of the upstream velocity field.

The use of age data as calibration targets in models has been applied in several different modes. In the most straightforward mode, age data are compared with travel times computed using the modelled flow field. Travel times are typically computed using particle tracking routines that numerically differentiate the hydraulic head field that is obtained from a flow model. The computed hydraulic gradients are then combined with hydraulic conductivity values to produce the velocity field. Imaginary particles are then transported from a user-selected starting position through the velocity field to a point of interest. The particles may be transported forward in time (i.e. from a recharge point towards a discharge point), or may be transported backwards in time. The latter is particularly useful for comparing simulated and measured age values. For example, a particle can be placed at the midpoint of a well screen from which it was collected, and then transported backwards until it reaches the water table. Both the flow path and the transport time can be computed. Model parameters, such as recharge rate and hydraulic conductivity, can be adjusted in order to obtain a better fit between observed and computed values. Examples of this approach are found in Reilly et al. (1994), Szabo et al. (1996), Hinkle et al. (1997) and Snyder et al. (1998).

Another approach to calibrating groundwater flow models is to consider vertical profiles of ages in the context of a groundwater stratigraphy model. This approach has already been discussed in terms of estimation of aquifer recharge in Section 7.1. For an unconfined aquifer of constant thickness, the travel time at a given depth is given by Eq. (7.6) (see Chapter 6):

$$t = \frac{L\theta}{R} \ln\left(\frac{L}{L-z}\right) \tag{7.6}$$

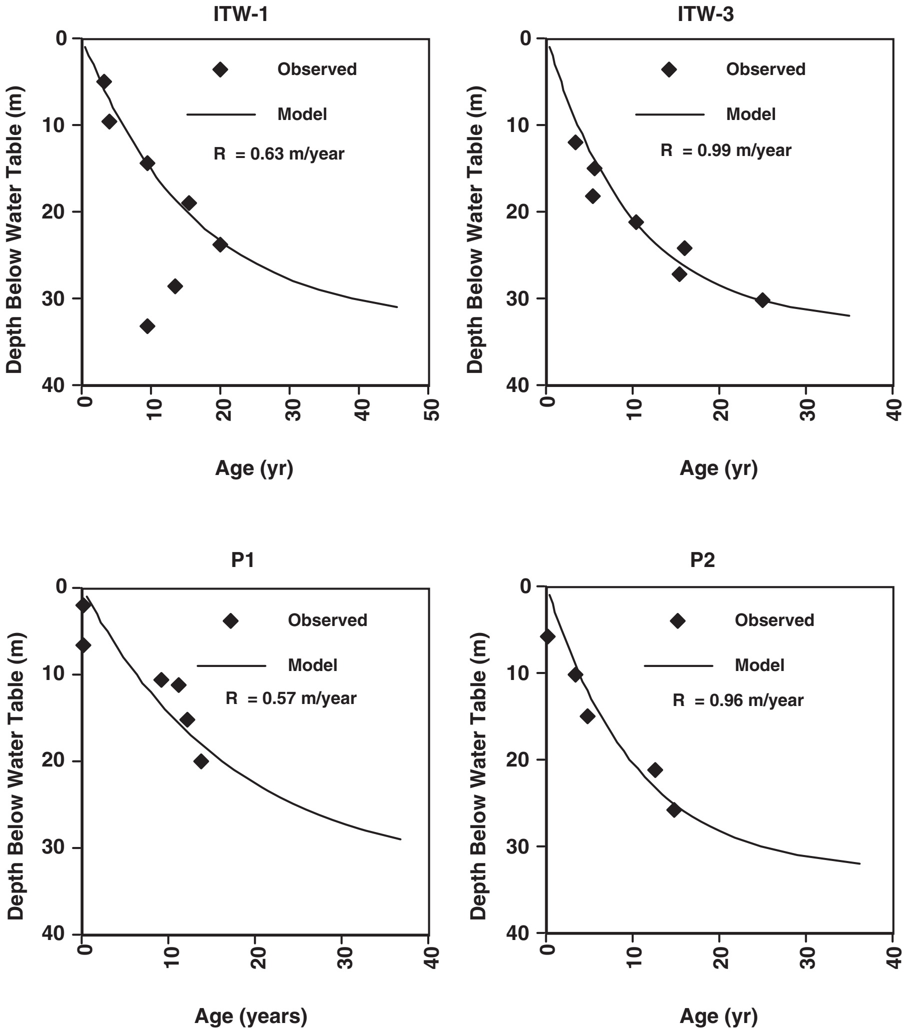

*FIG. 7.5. Observed and simulated distribution of groundwater ages are shown. The simulated values were produced using Eq. (6.1), Chapter 6. The recharge rate was adjusted to produce a best fit between observed and simulated values.*

where $L$ is the aquifer thickness, $\theta$ the porosity, $R$ the recharge rate, and $z$ the depth below the water table. Figure 7.5 shows vertical profiles of ages on Cape Cod, Massachusetts, USA, reported by Solomon et al. (1995). Also shown in Fig. 7.5 is the simulated distribution of ages using Eq. (7.6). The recharge rate ($R$) was adjusted such that the misfit between observed and computed values was minimized.

A final example of using age data to calibrate a groundwater flow model involves a formal inversion procedure. Portniaguine and Solomon (1998) constructed a flow and transport model for an unconfined aquifer on Cape Cod, Massachusetts. A homogeneous hydraulic conductivity was assumed, but a spatially variable recharge rate. The thickness of the aquifer, its porosity and the downstream boundary condition were also allowed to vary within the inversion process. Both age and hydraulic head data were used as calibration targets. The hydraulic head data per se were sensitive to the ratio of recharge flux to hydraulic conductivity. The age data were sensitive to the ratio of recharge to porosity. Together, the age and head data provided a constraint on both boundary values (recharge rates) and hydraulic properties. However, a sensitivity analysis showed that porosity, hydraulic conductivity and recharge are all correlated, and thus a unique inverse solution requires an independent constraint on one of these parameters. Because independent measurements of porosity can typically be made reliably (at least in granular systems), the results of Portniaguine and Solomon (1998) indicate that within limits, the combined use of hydraulic head and age data represent a well posed inverse problem (i.e. one that can have a relatively unique solution).

## Chapter 8

# DATA INTERPRETATION IN REPRESENTATIVE CASES

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## 8.1. INTRODUCTION

This chapter summarizes selected data for CFCs and other environmental tracers in water samples from a variety of hydrogeological environments. Some of the examples are taken from case studies discussed in Chapter 9. Examples are included that have apparently reliable age estimates, as well as samples that have been affected by one or more processes that limit age interpretation. The list of samples supplements examples of 'representative waters' summarized in Plummer and Busenberg (2000). The 25 examples that were selected are discussed in Sections 8.2–8.8. A synthesis of the pattern is presented in Section 8.9.

An effort was made to select examples in which all the reported values apply to a single sample date, but where this was not possible, representative data were included from other sample dates, or estimated on the basis of other samples from the same area. A graphical CFC age pattern is displayed in Table 8.1 for 25 typical examples. Estimated values are given in parentheses in Table 8.2. Table 8.2 includes a narrative explanation of processes that may be affecting the sample, the sample location, sample date, type of well sampled, hydrogeological environment, depth to water, total depth, depth interval sampled, recharge elevation, water temperature, various redox indicators, including dissolved $O_2$, Fe(II), $H_2S$ and $CH_4$ concentrations, various dissolved gas data, including dissolved $N_2$, Ar, Ne and He, an estimate of the recharge temperature and excess air content determined from the $N_2$-Ar data, concentrations of CFC-11, CFC-12 and CFC-113, and the apparent ages, the fraction of young (CFC-bearing) water in the sample (if a mixture of young and old water is assumed), the tritium content, and other age estimates, if available, based on $^3H/^3He$, $^{85}Kr$ and $SF_6$. In some cases, the sample date for a particular measurement differed significantly from that given at the top of the table and was included in parentheses next to the measurement in the table.

Table 8.1 shows some of the apparent CFC age patterns and possible interpretations of CFC data. Each case gives a schematic diagram showing historical air CFC mixing ratios as a function of time (see Chapter 2, Fig. 2.1(a) for further details) with points corresponding to calculated CFC partial pressures from analysis of a water sample. In each case, the plots in Table 8.1 show CFC mixing ratios in the order CFC-12, CFC-11 and CFC-113 from the uppermost to the lowest curve. Some examples discussed in Chapters 8 and 9 are shown in the following section, but for more detailed explanations, see the appropriate sections indicated in the table.

## 8.2. SHALLOW, AEROBIC INFILTRATION WATER (SAMPLE 1)

Sample 1 (Tables 8.1 and 8.2) is an example of an infiltration water that is well dated by a suite of environmental tracers, including CFC-11, CFC-12, CFC-113, $^{3}H/^{3}He$, $^{85}Kr$ and $SF_6$. The sample is from a shallow, aerobic sandy aquifer on the Delmarva Peninsula of Maryland, USA. The $^{3}H/^{3}He$ and $^{85}Kr$ dates are from Ekwurzel et al. (1994) for samples collected in November 1991; the CFC data are averages from Busenberg and Plummer (2000) but were also collected in November 1991, and recalculated assuming a recharge temperature of 11.0°C. Dunkle et al. (1993) reported an estimated apparent age of 8.4 years based on CFC-11 and CFC-12 for an assumed recharge temperature of 9°C for water from this well (KE Be 52) sampled in November 1991. The CFC ages in Table 8.2 were recalculated using a revised air curve.

## 8.3. DATED WATERS FROM SPRINGS, SHENANDOAH NATIONAL PARK AND VICINITY, VIRGINIA, USA (SAMPLES 2 AND 3)

Samples 2 and 3 are from a locality in the Blue Ridge Mountains of Virginia, USA, but represent different origins and hydrogeological environments. Both samples are aerobic and unaffected by microbial degradation or CFC contamination. They were dated using CFCs, $SF_6$ and $^{3}H/^{3}He$ (Plummer et al., 2000; 2001), and discussed in part in Chapter 9, Section 9.4. Sample 2 discharges from a shallow water table spring (Byrd's Nest 3, discharge typically 1.3 L/s) near the crest of the Blue Ridge Mountains (elevation 914 m). The $SF_6$ and $^{3}H/^{3}He$ apparent ages are in nearly complete agreement (2.7 and 2.1 years, respectively). The CFC data are consistent with the young ages obtained from $SF_6$ and $^{3}H/^{3}He$, but because of the levelling off of the atmospheric mixing ratios in the 1990s, the CFC ages have large uncertainties. This is an example of a modern water that can be dated using $^{3}H/^{3}He$ and $SF_6$, but with CFCs the age can be resolved only within the decade of the 1990s to early 2000s.

*Text cont. on p. 114.*

TABLE 8.1. SOME OF THE APPARENT CFC AGE PATTERNS AND POSSIBLE INTERPRETATIONS OF CFC DATA
*(see Table 8.2 for sample information)*

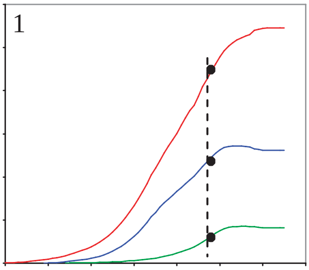
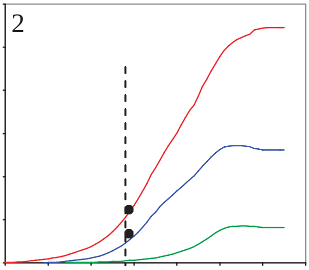
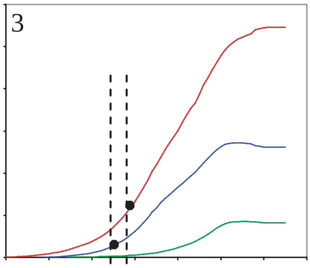
| Pattern of apparent ages | Interpretation | Comments |
|---|---|---|
|  | PF[a]; post-1957 water | Although not exclusive, considerable confidence can be placed in the interpreted apparent age. See Table 8.2, samples 1 and 3 |
| | Mixture of post-1985 waters | Less likely. See Chapter 5, Fig. 5.3 |
|  | PF[a]; pre-1957 water | Although not exclusive, this case is straightforward |
|  | PF[a]; CFC-11 degraded or sample contaminated with CFC-12 | This sample can be generally interpreted as pre-1957 water. However, additional data are required to make detailed interpretations (degradation, contamination, recharge temperature etc.). Check $O_2$ |
| | PF[a]; the estimated recharge temperature is too low | |
| | BM[b]; CFC-11 and CFC-113 degraded. CFC-113 was removed by sorption | See Table 8.2, sample 7. |

TABLE 8.1. SOME OF THE APPARENT CFC AGE PATTERNS AND POSSIBLE INTERPRETATIONS OF CFC DATA (cont.)
*(see Table 8.2 for sample information)*

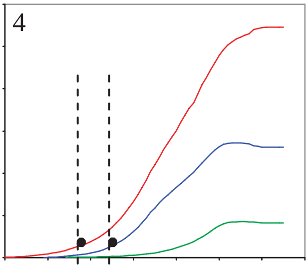
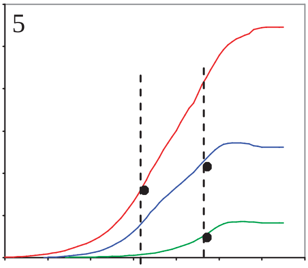
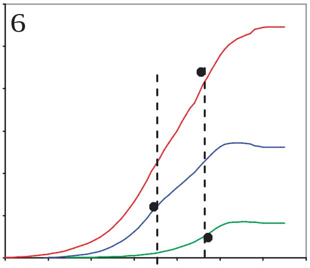
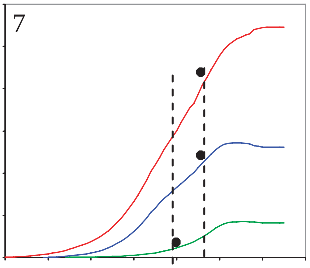
| Pattern of apparent ages | Interpretation | Comments |
|---|---|---|
|  | PF[a]; pre-1957 water; sample contaminated with CFC-11 | See Table 8.2, sample 16. More likely, the CFC-12 is closer to age of the ground water |
| | PF[a]; pre-1957 water; the estimated recharge temperature is too high | Measurements of dissolved gases needed to determine the recharge temperature, and dissolved $O_2$ and $CH_4$ (redox) |
|  | BM[b] or EP[c]; sample contaminated with CFC-11 | |
| | PF[a]; pre-1957 water; sample contaminated with CFC-11 and CFC-113 | Less likely |
|  | PF[a]; post-1957 water; CFC-11 degraded | Potential of degradation? See Table 8.2, sample 17 |
| | BM[b] or EP[c]; sample contaminated with CFC-12 | |
| | Excess air in sample | Dissolved gases. Check $O_2$ |
|  | PF[a]; post-1957 water; CFC-113 sorption | SeeTable 8.2, sample 1 |
| | Sample uniquely contaminated with CFC-11 and CFC-12 | The CFC-113 apparent age is less likely |

TABLE 8.1. SOME OF THE APPARENT CFC AGE PATTERNS AND POSSIBLE INTERPRETATIONS OF CFC DATA (cont.)
*(see Table 8.2 for sample information)*

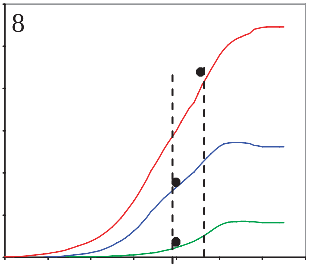
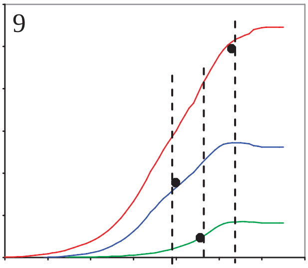
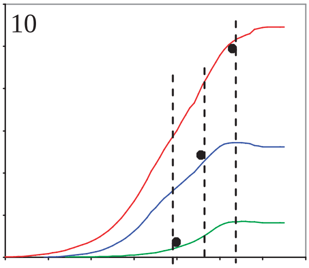
| Pattern of apparent ages | Interpretation | Comments |
|---|---|---|
|  | PF[a]; post-1957 water; sample contaminated with CFC-12 | See Table 8.2, sample 8 |
| | CFC-11 degraded and CFC-113 degraded or sorbed | Less likely because of the greater stability of CFC-113 compared with CFC-11. Check $O_2$ |
|  | CFC-11 and CFC-113 degraded | Potential of degradation? If yes, CFC-12 may not be affected by degradation. See Table 8.2, sample 18. Check $O_2$ |
| | BM[b] or EP[c]; sample contaminated with CFC-12 | This case is likely if there is no indication of degradation |
| | | For other interpretations, see Table 8.2, samples 10, 11 and 12 |
|  | Sample contaminated with CFC-12 and CFC-11 | Apparent age from CFC-113 is more reliable. |
| | CFC-11 and CFC-113 degraded; sorption or retardation has also affected CFC-113 | Potential of degradation? If yes, apparent age from CFC-12 is more likely. Check $O_2$ |

TABLE 8.1. SOME OF THE APPARENT CFC AGE PATTERNS AND POSSIBLE INTERPRETATIONS OF CFC DATA (cont.)
*(see Table 8.2 for sample information)*

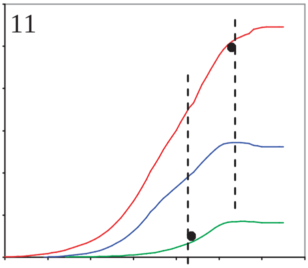
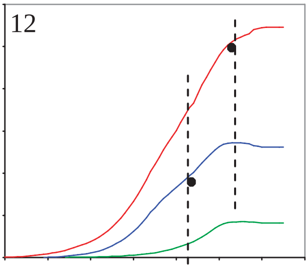
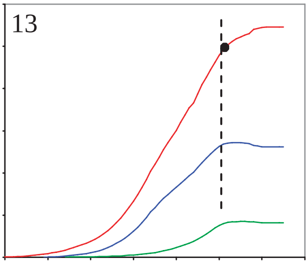
| Pattern of apparent ages | Interpretation | Comments |
|---|---|---|
|  | CFC-11 completely degraded and CFC-113 partially degraded | Potential of degradation? If yes, CFC-12 may not be affected by degradation. Check $O_2$ |
| | Pre-1950 water; sample contaminated with CFC-12 and CFC113 | Less possible. Check $^3H$ |
|  | Pre-1957 water; sample contaminated by CFC-11 and CFC-12 | No reliable apparent age can be assigned. Additional data are needed to make detailed interpretations. Check $O_2$ |
| | CFC-11 degraded. Degradation, sorption or retardation has removed the CFC-113 | |
|  | Pre-1940 water; sample contaminated with CFC-12 | $^3H$ should be measured. See Table 8.2, sample 19. This case is most likely if CFC-12 is high |
| | Post-1940 water; CFC-11 and CFC-113 degraded | This case is most likely if CFC-12 is low. CFC-12 may also be partially degraded. See Section 8.5. Check $O_2$ |
| | | For other interpretations, see Table 8.2, sample 23 |

TABLE 8.1. SOME OF THE APPARENT CFC AGE PATTERNS AND POSSIBLE INTERPRETATIONS OF CFC DATA (cont.)
*(see Table 8.2 for sample information)*

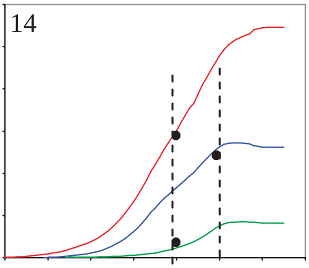
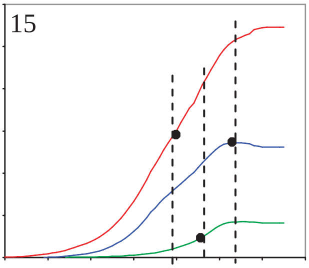
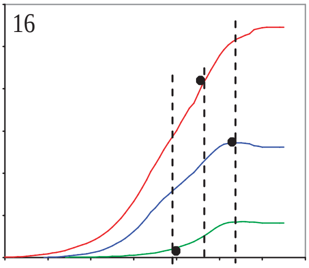
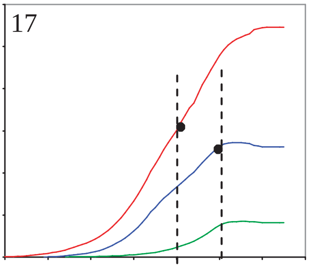
| Pattern of apparent ages | Interpretation | Comments |
|---|---|---|
|  | PF[a]; post-1957 water; sample contaminated with CFC-11 | The more probable apparent age is closer to that based on CFC-12 and CFC-113 |
|  | BM[b] or EP[c]; sample contaminated with CFC-11<br>PF[a]; post-1957 water; sample contaminated with CFC-11 and CFC-113 | See Table 8.2, sample 14 |
|  | PF[a]; post-1957 water; sample contaminated with CFC-11 and CFC-12<br>PF[a]; post-1957 water; estimated recharge temperature is too high | See Table 8.2, sample 13<br>Suggest measurements of dissolved gases to define recharge temperature |
|  | Pre-1940 water; sample contaminated with CFC-11 and CFC-12<br>Post-1957 water; sample contaminated with CFC-11; CFC-113 sorption | $^3$H should be measured to determine the presence of post-1940 fractions.<br>If post-1957 water is assumed, the more probable apparent age is closer to that based on CFC-12 |

TABLE 8.1. SOME OF THE APPARENT CFC AGE PATTERNS AND POSSIBLE INTERPRETATIONS OF CFC DATA (cont.)
*(see Table 8.2 for sample information)*

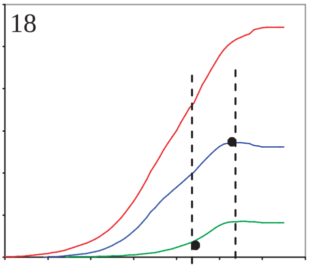
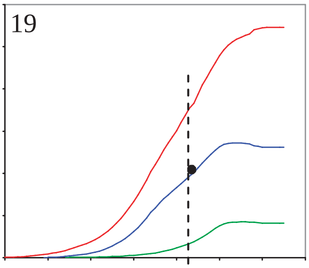
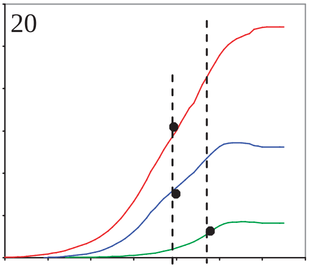
| Pattern of apparent ages | Interpretation | Comments |
|---|---|---|
|  | Pre-1940 water; sample contaminated with CFC-11 and CFC-113 (sampling device) | $^3$H should be measured to determine the presence of post-1940 fractions |
|  | Pre-1940 water; sample contaminated with CFC-11 (sampling device) | $^3$H should be measured to exclude post-1940 fractions |
|  | BM[b] or EP[c] | Usually this is a typical case of BM or EP. See Table 8.2, samples 4 and 21. |
| | PF[a]; post-1975 water; sample contaminated with CFC-113 | |

TABLE 8.1. SOME OF THE APPARENT CFC AGE PATTERNS AND POSSIBLE INTERPRETATIONS OF CFC DATA (cont.)
*(see Table 8.2 for sample information)*

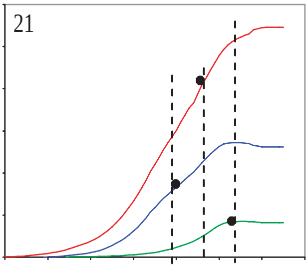
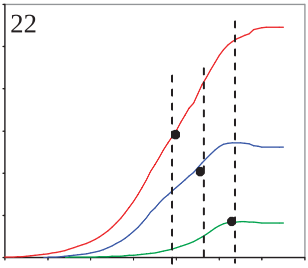
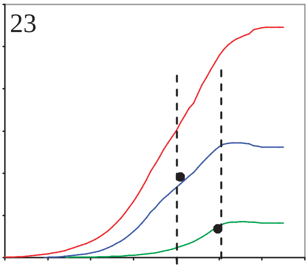
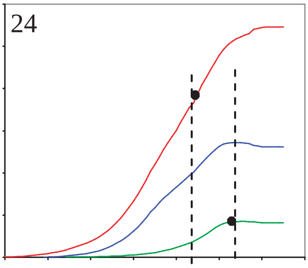
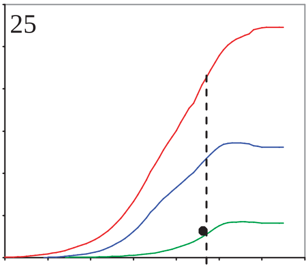
| Pattern of apparent ages | Interpretation | Comments |
|---|---|---|
|  | BM[b] or EP[c]; sample contaminated with CFC-12 | See Table 8.2, sample 6 |
| | BM[b] or EP[c]; CFC-11 degraded | Potential of degradation? |
| | PF[a]; estimated recharge temperature is too low | Suggest measurements of dissolved gases |
| | PF[a]; CFC-113 contaminated and CFC-11 degraded | For other interpretations, see Table 8.2, samples 15, 20 and 24 |
|  | BM[b] or EP[c]; sample contaminated with CFC-11 | The CFC-12 is the more likely apparent age for this sample |
| | Sample contaminated with CFC-11 and CFC-113 | |
|  | Pre-1940 water; sample contaminated with CFC-11 and CFC-113 (sampling device) | $^{3}H$ measurement needed and information on the sample collection procedures may be useful in the data interpretation |

TABLE 8.1. SOME OF THE APPARENT CFC AGE PATTERNS AND POSSIBLE INTERPRETATIONS OF CFC DATA (cont.)
*(see Table 8.2 for sample information)*

| Pattern of apparent ages | Interpretation | Comments |
|---|---|---|
|  | Post-1957 water; CFC-11 degraded; sample contaminated with CFC-113<br>Pre-1950 water; sample contaminated with CFC-12 and CFC-113 | The interpretation is not straightforward. Additional data are required. Check $O_2$ |
|  | Pre-1940 water; sample contaminated with CFC-113 | $^3H$ should be measured and information on the sample collection procedures may be helpful in the data interpretation |

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[a] PF: piston flow conditions or unmixed sample.
[b] BM: binary mixture of young water with old (CFC-free) water.
[c] EP: exponential mixing conditions.

Sample 3 is discharge from a large spring (Hudson Spring, Luray, Virginia, USA, estimated discharge > 60 L/s) that issues from limestone karst at the base of the Blue Ridge Mountains. The source of the water is unknown. The CFC apparent ages are 26.7 (CFC-11 and CFC-12) and 25.2 (CFC-113) years based on piston flow. Using the CFC-113/CFC-12 ratio, the fraction of young water was determined to be 62% with an apparent age of 22 years. Both the piston flow and binary mixing model yield similar ages because the fraction of young water is high, but the binary mixing model age is in closer agreement with the $^3H/^3He$ age (24.4 years) than those based on piston flow. This sample contains an excess of $SF_6$ that is probably of terrigenic origin (Busenberg and Plummer, 2000), and cannot be dated using $SF_6$.

*Text cont. on p. 119.*

## TABLE 8.2. SUMMARY OF REPRESENTATIVE WATER ANALYSES

| Sample number | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Process demonstrated | Shallow, aerobic infiltration water, sandy aquifer, piston flow, agreement in ages | Shallow, water table spring from Blue Ridge Mountains, VA. Piston flow, agreement in age | Spring that discharges somewhat older water near the base of the Blue Ridge Mountains, VA; near piston flow | Binary mixture of young and old water; well in fractured crystalline rock, Blue Ridge Mountains, VA | Old water from fractured rock. Direction of groundwater flow opposite to bedding plane partings | Binary mixture from fractured rock. Direction of groundwater flow parallel to bedding plane partings |
| Location (by state, USA) | MD | VA | VA | VA | PA | PA |
| Date sampled | 1991-11-05 | 1997-09-18 | 1997-09-17 | 1997-08-26 | 1999-05-10 | 1999-05-11 |
| Well type | MW[a] | SP[b] | SP[b] | PW[c] | MW[a] | MW[a] |
| Hydrogeological setting | S[d] | WTS[e] | KLS[f] | FCR[g] | FSR[h] | FSR[h] |
| Depth to water (m) | 5.5 | nd[i] | nd[i] | 61 | 0.8 | 0.5 |
| Total depth (m) | 11 | nd[i] | nd[i] | 198 | 3 | 3 |
| Interval sampled (m) (4) | 0.9 | nd[i] | nd[i] | 183, 191 | 0.6 | 0.6 |
| Recharge elev. (m) | 22.8 | 914 | 305 | 561 | 244 | 244 |
| Water temp. ($^oC$) | 14.8 | 9.9 | 14.2 | 13.4 | 11.8 | 11.3 |
| Dissolved oxygen (mg/L) | 9 | 9.7 | 7.2 | 6.7 | 0.07 | 7.1 |
| Fe(II) (mg/L) | 0 | <0.007 | 0.036 | 0.018 | <0.02 | <0.02 |
| $H_2S$ (mg/L) | 0 | 0 | 0 | 0 | nd[i] | nd[i] |
| $CH_4$ (mg/L) | 0 | 0 | 0 | 0 | 0.41 | 0 |
| $N_2$ (aq) (mg/L) | nd[i] | 17.5 | 18.92 | 21.57 | 23.55 | 20.72 |
| Ar (aq) (mg/L) | nd[i] | 0.637 | 0.689 | 0.737 | 0.7274 | 0.7258 |
| Calc. recharge temp. ($^oC$) | 11 | 10 | 10.1 | 8.2 | 8.9 | (8.8) |
| Calc. excess air (cc/L) | 2.3 | 1.3 | 1.3 | 4 | 2.5 | (2.3) |
| Ne (aq) (ccSTP/g) □$10^{-7}$ | nd[i] | 1.98 | 2.28 | 2.81 | (24.4) | 23.8 |
| He (aq) (ccSTP/g) □$10^{-8}$ | 5.79 | 4.57 | 11.3 | 7.38 | 150 | 9.8 |
| CFC-11 (pg/kg) | 607 | 692 | 198 | 311 | 10.7 | 314 |
| CFC-12 (pg/kg) | 250 | 328 | 96 | 131 | 5.9 | 224 |
| CFC-113 (pg/kg) | 36.2 | 93.7 | 9.5 | 30.4 | 0 | 49 |
| CFC-11 apparent age (a) | 5.3 | 0.2–7.2 | 26.7 | 23.7 | 44 | 25 |
| CFC-12 apparent age (a) | 7.3 | 0 | 26.7 | 24.7 | 49 | 18 |
| CFC-113 apparent age (a) | 9.3 | 2.2 | 25.2 | 17.7 | >46 | 15 |
| Fraction of young water | nd[i] | nd[i] | 0.62 | 0.46 | nd[i] | 0.79 |
| Basis for young fraction | nd[i] | nd[i] | 113/12 | 113/12 | nd[i] | 113/12 |
| Age of young fraction (a) | nd[i] | nd[i] | 21.7 | 11.2 | <49 | 13.4 |
| Tritium (TU) | 16.6 | 7.77 | 2.8 | 9.5 | 2.9 | 9.2 |
| $^3H/^3He$ apparent age (a) | 7.1 | 2.1 | 24.4 | 9.7 | nd[i] | 8.6 |
| $^{85}Kr$ apparent age (a) | 7.7 | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] |
| $SF_6$ apparent age (a) | 7.8 (7/97) | 2.7 | C | 17.7 (10.7) | 35 | 7.9 |

a MW: monitoring well.
b SP: spring.
c PW: production well.
d S--: unconsolidated or poorly consolidated sand aquifer.
e WTS: water table spring.
f KLS: karstic limestone.
g FCR: fractured crystalline rock.
h FSR: fractured sedimentary rock with bedding plane partings.
i not determined (nd).
j DW: domestic well.
k SGC: sand and gravel, with clays.
l GT: glacial till.
m S/SS: mulstone/siltstone.
n FB: fractured basalt with sedimentary interbeds.
o Refers to the interval sampled in metres above the bottom of the well.

## TABLE 8.2. SUMMARY OF REPRESENTATIVE WATER ANALYSES (cont.)

| Sample number | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|
| Process demonstrated | Dating the fraction of river water recharged to a karstic limestone aquifer; mixing ratio determined from Cl and $^{18}O$ | Domestic well in limestone karst, contaminated with CFC-12, but datable with CFC-11 and CFC-113 | Water contaminated by leakage from a landfill completed in unsaturated zone | Monitoring well in contaminate plume of capped landfill in glacial till | Monitoring well downgradient of a capped, but unlined landfill | Water from domestic well in sands and gravel that is probably affected by seepage from septic tank |
| Location (by state, USA) | GA | GA | NM | NY | NY | NM |
| Date sampled | 1991-06-04 | 1993-07-13 | 1996-06-29 | 2001-03-26 | 2001-03-26 | 1996-08-17 |
| Well type | PW[c] | DW[j] | MW[a] | MW[a] | MW[a] | DW[j] |
| Hydrogeological setting | KLS[f] | KLS[f] | SGC[k] | GT[l] | GT[l] | SGC[k] |
| Depth to water (m) | 39 | 9.8 | 33.4 | 1.9 | 1.1 | 69 |
| Total depth (m) | 54.9 | 54.9 | 71 | 4.3 | 7 | 91 |
| Interval sampled (m)[o] | 6.7 | 29.7 | 3 | 3 | 1.5 | 12 |
| Recharge elev. (m) | 70 | 71 | 1520 | 416 | 411 | 1854 |
| Water temp. (°C) | 20.8 | 20.1 | 16.1 | 9 | 9 | 17.4 |
| Dissolved oxygen (mg/L) | <0.1 | 3.6 | 0.07 | 0.04 | 0.4 | 6.8 |
| Fe(II) (mg/L) | 0.06 | 0.004 | 0.1 | 60.3 | 0.55 | nd[i] |
| $H_2S$ (mg/L) | 0.16 | 0 | 0 | nd[i] | nd[i] | nd[i] |
| $CH_4$ (mg/L) | 0.16 | 0 | 0.005 | 9.019 | 0 | 0 |
| $N_2$ (aq) (mg/L) | nd[i] | 20.03 | 17.49 | 11.43 | 20.69 | 16.17 |
| Ar (aq) (mg/L) | nd[i] | 0.69 | 0.541 | 0.3894 | 0.7352 | 0.5558 |
| Calc. recharge temp. (°C) | 17.5 | 16 | 20.9 | 38.5[7.5] | 7.5 | 12.3 |
| Calc. excess air (cc/L) | nd[i] | 3.8 | 5.3 | 0.8 | 2.5 | 2.6 |
| Ne (aq) (ccSTP/g) $\times 10^{-7}$ | 2.45 | | | nd[i] | nd[i] | nd[i] |
| He (aq) (ccSTP/g) $\times 10^{-8}$ | 5.93 | | | nd[i] | nd[i] | nd[i] |
| CFC-11 (pg/kg) | 3.1 | 96 | 5 500 | 83 | 530 | 1.9 |
| CFC-12 (pg/kg) | 6.8 | 3 000 | 45 000 | 74 000 | 4 740 | 10 700 |
| CFC-113 (pg/kg) | 0 | 6 | 31 000 | 92 | 43 | 3 |
| CFC-11 apparent age (a) | nd[i] | 24 | C | 32 | 22 | 46 |
| CFC-12 apparent age (a) | 37 | C | C | C | C | C |
| CFC-113 apparent age (a) | nd[i] | 21 | C | 8 | 19 | 31 |
| Fraction of young water | 0.14 | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] |
| Basis for young fraction | $^{18}O$, Cl | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] |
| Age of young fraction (a) | 22.5 | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] |
| Tritium (TU) | 0.43 | 4 | nd[i] | nd[i] | nd[i] | nd[i] |
| $^{3}H/^{3}He$ apparent age (a) | 22 | 24.9 | nd[i] | nd[i] | nd[i] | nd[i] |
| $^{85}Kr$ apparent age (a) | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] |
| $SF_6$ apparent age (a) | nd[i] | nd[i] | nd[i] | 25 | 26 | nd[i] |

a MW: monitoring well.
b SP: spring.
c PW: production well.
d S--: unconsolidated or poorly consolidated sand aquifer.
e WTS: water table spring.
f KLS: karstic limestone.
g FCR: fractured crystalline rock.
h FSR: fractured sedimentary rock with bedding plane partings.
i not determined (nd).
j DW: domestic well.
k SGC: sand and gravel, with clays.
l GT: glacial till.
m S/SS: mulstone/siltstone.
n FB: fractured basalt with sedimentary interbeds.
o Refers to the interval sampled in metres above the bottom of the well.

TABLE 8.2. SUMMARY OF REPRESENTATIVE WATER ANALYSES (cont.)

| Sample number | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|
| Process demonstrated | Shallow monitoring well in area where infiltration affected by CFC-elevated urban air | Deep monitoring well; contaminated with drilling fluid in the vicinity of the well screen | Monitoring well in low permeability sediment, contaminated by air injection and inadequate well development | Water sample that was probably contaminated with CFC-11 from a sample pump | Shallow low oxygen sampled partially degraded in CFC-11, agreement in CFC-12 and CFC-113 | Possible degradation of all CFCs in soil prior to recharge |
| Location (by state, USA) | NJ | NM | NE | MD | VA | VA |
| Date sampled | 1992-04-30 | 1998-07-31 | 2000-05-22 | 1990-11-14 | 1993-08-12 | 1997-07-29 |
| Well type | MW[a] | MW[a] | MW[a] | MW[a] | MW[a] | MW[a] |
| Hydrogeological setting | S[d] | SGC[k] | MS/SS[m] | S[d] | S[d] | S[d] |
| Depth to water (m) | 4.8 | 222 | 3 | 1.1 | 1.4 | 5.1 |
| Total depth (m) | 8.2 | 463 | 33.5 | 10.4 | 7.0 | 6.7 |
| Interval sampled (m) (4) | 1.5 | 12 | 1.5 | 1 | 0.91 | 0.9 |
| Recharge elev. (m) | 47.2 | 1700 | 1345 | 3.2 | 3 | 18 |
| Water temp. (°C) | 13.8 | 21.9 | 12.8 | 13.6 | 15 | 19.3 |
| Dissolved oxygen (mg/L) | 9 | 1.3 | 2.5 | 0.1 | 0.05 | 6.9 |
| Fe(II) (mg/L) | nd[i] | nd[i] | 0.012 | nd[i] | 0 | 0.043 |
| $H_2S$ (mg/L) | 0 | nd[i] | nd[i] | 0 | trace | nd[i] |
| $CH_4$ (mg/L) | 0 | 0 | 0 | 0 | 0 | nd[i] |
| $N_2$ (aq) (mg/L) | nd[i] | 15.03 | 24.65 | nd[i] | 21.75 | 19.51 |
| Ar (aq) (mg/L) | nd[i] | 0.5133 | 0.6985 | nd[i] | 0.682 | 0.781 |
| Calc. recharge temp. (°C) | nd[i] [13] | 15.9 | 15.9 | 9 | 18.2 | 9.6 |
| Calc. excess air (cc/L) | nd[i] | 2.4 | 11.2 | nd[i] | 6.4 | 1.2 |
| Ne (aq) (ccSTP/g) □$10^{-7}$ | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] |
| He (aq) (ccSTP/g) □$10^{-8}$ | nd[i] | 434 | nd[i] | nd[i] | nd[i] | nd[i] |
| CFC-11 (pg/kg) | 780 | 247 | 251 | 63.1 | 211 | 655 |
| CFC-12 (pg/kg) | 388 | 50 | 132 | 1.7 | 163 | 312 |
| CFC-113 (pg/kg) | 75 | 14 | 35 | nd[i] | 19 | 84.3 |
| CFC-11 apparent age (a) | C | 22 | 24 | 27 | 19 | 12 |
| CFC-12 apparent age (a) | C | 30 | 23 | 45 | 12 | 10 |
| CFC-113 apparent age (a) | 2 | 20 | 15 | nd[i] | 14 | 9 |
| Fraction of young water | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] |
| Basis for young fraction | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] |
| Age of young fraction (a) | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] |
| Tritium (TU) | 10 | nd[i] | <0.8 | -0.2 | nd[i] | 16 (1991) |
| $^{3}H/^{3}He$ apparent age (a) | 2.5 | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] |
| $^{85}Kr$ apparent age (a) | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] |
| $SF_6$ apparent age (a) | nd | C | nd | nd | nd | 2.6 |

a MW: monitoring well.
b SP: spring.
c PW: production well.
d S--: unconsolidated or poorly consolidated sand aquifer.
e WTS: water table spring.
f KLS: karstic limestone.
g FCR: fractured crystalline rock.
h FSR: fractured sedimentary rock with bedding plane partings.
i not determined (nd).
j DW: domestic well.
k SGC: sand and gravel, with clays.
l GT: glacial till.
m S/SS: mulstone/siltstone.
n FB: fractured basalt with sedimentary interbeds.
o Refers to the interval sampled in metres above the bottom of the well.

## TABLE 8.2. SUMMARY OF REPRESENTATIVE WATER ANALYSES (cont.)

| Sample number | 19 | 20 | 21 | 22 | 23 | 24 |
|---|---|---|---|---|---|---|
| Process demonstrated | Methanogenic sand aquifer in which all CFCs have been removed by microbial degradation | Recharge through deep unsaturated zone in contact with a diffusion profile in CFC-11 and CFC-12 | Recharge of pre-bomb water through deep unsaturated zone with advective air transport | Focused recharge through a thick unsaturated zone, little affected by gas exchange | Water from shallow monitoring well that has been naturally gas stripped by methane | Water from shallow monitoring well that has been naturally gas stripped by nitrogen from denitrification |
| Location (by state, USA) | TN | ID | ID | ID | MN | MD |
| Date sampled | 1992-10-02 | 1995-06-15 | 1995-06-14 | 1995-06-13 | 1997-07-09 | 1992-12-23 |
| Well type | PW[c] | MW[a] | PW[c] | PW[c] | MW[a] | MW[a] |
| Hydrogeological setting | S[d] | FB[n] | FB[n] | FB[n] | GDS | S[d] |
| Depth to water (m) | 22.8 | 67.1 | 308 | 242.6 | 1 | 0.8 |
| Total depth (m) | 125.6 | 93.0 | 333 | 216.4 | <7.6 | 4.6 |
| Interval sampled (m)[o] | 24.4 | 29.9 | 25 | 26.2 | 0.91 | 0.9144 |
| Recharge elev. (m) | 77 | 1830 | 1560 | 1560.6 | 261 | 3.9 |
| Water temp. (°C) | 17 | 14 | 16.5 | 10.5 | 9 | 14 |
| Dissolved oxygen (mg/L) | <0.1 | 5 | 6.7 | (7.4) | 0.05 | 0.02 |
| Fe(II) (mg/L) | 5.3 | 0 | nd[i] | 0.049 | nd[i] | nd[i] |
| $H_2S$ (mg/L) | 0.07 | 0 | 0 | nd[i] | 0 | 0 |
| $CH_4$ (mg/L) | 1.3 | 0 | 0 | nd[i] | 9.6 | 0 |
| $N_2$ (aq) (mg/L) | nd[i] | 15.52 | nd[i] | nd[i] | 13.05 | 31 |
| Ar (aq) (mg/L) | nd[i] | 0.554 | nd[i] | nd[i] | 0.51 | 0.668 |
| Calc. recharge temp. (°C) | nd[i] | 13.4 | nd[i] [9] | nd[i] [10.5] | 20.3 [11] | 58 [11] |
| Calc. excess air (cc/L) | nd[i] | 1.4 | nd[i] | nd[i] | -1.4 | 22.9 |
| Ne (aq) (ccSTP/g) □$10^{-7}$ | nd[i] | 1.96 | 2.24 | 2.095 | nd[i] | nd[i] |
| He (aq) (ccSTP/g) □$10^{-8}$ | nd[i] | 5.65 | 7.48 | 5.426 | nd[i] | nd[i] |
| CFC-11 (pg/kg) | 0 | 181 | 61 | 173 | 0 | 235 |
| CFC-12 (pg/kg) | 0 | 111 | 35 | 98.8 | 83 | 203 |
| CFC-113 (pg/kg) | nd[i] | 50 | 6.5 | 19.5 | 0 | 30 |
| CFC-11 apparent age (a) | nd[i] | 22 | 31 | (24) | >50 | 21 |
| CFC-12 apparent age (a) | nd[i] | 19 | 32 | (22) | 27 | 16 |
| CFC-113 apparent age (a) | nd[i] | 7.4 | 26 | (16) | >40 | 14 |
| Fraction of young water | nd[i] | nd[i] | nd[i] | 0.69 | nd[i] | nd[i] |
| Basis for young fraction | nd[i] | nd[i] | nd[i] | 113/12 | nd[i] | nd[i] |
| Age of young fraction (a) | nd[i] | nd[i] | nd[i] | 6.4 | nd[i] | nd[i] |
| Tritium (TU) | 13.8 | 0.93 | 0.1 | 6.2 | nd | 13.4 |
| $^3H/^3He$ apparent age (a) | nd[i] | nd[i] | nd[i] | 6.5 ± 6.5 | nd[i] | nd[i] |
| $^{85}Kr$ apparent age (a) | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] |
| $SF_6$ apparent age (a) | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] | nd[i] |

a MW: monitoring well.
b SP: spring.
c PW: production well.
d S--: unconsolidated or poorly consolidated sand aquifer.
e WTS: water table spring.
f KLS: karstic limestone.
g FCR: fractured crystalline rock.
h FSR: fractured sedimentary rock with bedding plane partings.
i not determined (nd).
j DW: domestic well.
k SGC: sand and gravel, with clays.
l GT: glacial till.
m S/SS: mulstone/siltstone.
n FB: fractured basalt with sedimentary interbeds.
o Refers to the interval sampled in metres above the bottom of the well.

## 8.4. MIXTURES FROM FRACTURED ROCK AND KARSTIC AQUIFERS (SAMPLES 4–7)

Sample 4 is discharge from a water supply well in Shenandoah National Park, Virginia. The well was drilled in crystalline rock and has only two water-bearing zones that intercept the well bore near the bottom of the well (198 m). The well has only 15.8 m of casing. The CFC and $^3$H/$^3$He data indicate that the well probably produces a mixture of young and old water. The mixing may occur in the well bore, but more likely within the fracture network in the vicinity of the well induced by stress from pumping. This sample has CFC apparent ages (piston flow ages) of 24 years (based on CFC-11 and CFC-12), but a CFC signature of binary mixtures of young and old water (CFC-113 apparent age younger than that from CFC-11 and CFC-12). Model calculations suggest the sample contains approximately 46% of water, with an age of 11.2 years (based on the CFC-113/CFC-12 ratio), which agrees well with the $^3$H/$^3$He age of 9.7 years of the young fraction in the sample. Using the value of the young fraction in the mixture determined from CFCs, the dilution corrected $SF_6$ age is similar to that from CFCs and $^3$H/$^3$He dating, 10.7 years.

Samples 5 and 6 are from piezometers located on the north limb of an anticline that is dissected by a stream in fractured siliciclastic sedimentary rocks in the Valley and Ridge geological province of Pennsylvania, USA. Groundwater flow is generally toward the stream and on one side of the stream, groundwater flow is predominantly parallel to the direction of the well developed bedding plane partings and on the other side of the stream, flow is opposite to the direction of bedding plane partings. Burton et al. (2002) found that groundwater flow paths parallel to dip direction in bedding plane partings in the fractured bedrock resulted in a greater proportion of young water arriving at a given discharge point, and groundwater ages near the discharge point significantly younger (sample 6) than for samples from flow paths that are opposite the dip direction (sample 5). Both piezometers were open to only 0.6 m of aquifer. Indications that the sample from well E2-10 (sample 5) contained a high fraction of old water were the low CFC concentrations, with apparent ages of more than 40 years, low $SF_6$ concentration (apparent age 35 years) and high dissolved helium. More than 96% of the dissolved helium was of terrigenic origin, and even though the sample contained a young fraction, as indicated by the $^3$H data, uncertainty in the $^3$He/$^4$He ratio of the terrigenic helium prevented dating by $^3$H/$^3$He. All that can be concluded is that sample 5 contains a high fraction of water older than 49 years (based on the apparent CFC-12 age) and a low fraction of water younger than 49 years. For example, Burton et al. (2002) report results from a nearby piezometer (E3-20 sampled on 11 May 1999) where flow is also opposite the dip direction of bedding plane partings that, by the CFC-113/CFC-12 ratio model contained only 5% of 19 year old water and 95% of pre-CFC water. In contrast, sample 6 is located across the stream from sample 5 where groundwater flow is parallel to the dip direction of the bedding plane partings. The apparent $SF_6$ age was 7.9 years and is similar to the $^3H/^3He$ age of 8.6 years. The sample contains relatively high concentrations of CFCs and tritium, and relatively low helium content. The CFC-113/CFC-12 data indicated an age of 13 years for the young fraction that made up approximately 79% of the sample. Considering an uncertainty of ± 10% in the CFC concentrations, Burton et al. (2002) estimated an uncertainty of ± 3 years in the CFC-113/CFC-12 based age and ± 10% in the value of the fraction of young water in the mixture (see Chapter 9, Section 9.8).

Sample 7 is from a karstic portion of the Floridan aquifer near Valdosta, Georgia, USA (Plummer et al., 1998a, b). In this case, the source of CFCs and tritium is water from a river that breaches confinement above the Floridan aquifer system through a series of sink holes in the riverbed. The groundwater is anoxic and contains both dissolved $H_2S$ and $CH_4$. CFC-11 and CFC-113 are nearly entirely removed (degraded) in anoxic parts of the aquifer. Using stable isotope and dissolved chloride data, Plummer et al. (1998a) found the mixture contained only 13.9% young (river) water. If not corrected for dilution with old (pre-CFC) water, the apparent CFC-12 age is 37 years. Correcting for dilution, the river water fraction should have contained 48.9 pg/kg of CFC-12 at time of recharge. If the river water was in equilibrium with air during recharge, and CFC-12 has not been significantly degraded in the aquifer, CFC-12 indicates an apparent age of 22.5 years. The reconstructed CFC-12 age compares well with 22 years calculated from the $^3H/^3He$ data. Using the sample date of 1991.6, the young fraction would have recharged in 1969.6 and should have contained nearly five times more CFC-11 than is calculated for the reconstructed young fraction. Apparently both CFC-11 and CFC-113 have been degraded and possibly sorbed in the aquifer. CFC-12 does not appear to have been significantly affected by these processes (see Chapter 9, Section 9.3).

## 8.5. WATER CONTAMINATED WITH ONE OR MORE CFCs (SAMPLES 8–16)

Samples 8–16 (Table 8.2) demonstrate different ways in which groundwater has been contaminated with one or more CFCs, i.e. CFCs have been added in addition to that determined by air–water equilibrium at recharge. Sample 8 is from a domestic well completed in a poorly confined part of the Floridan aquifer near Albany, Georgia, USA. The water is recharged by aerial infiltration into a karstic limestone aquifer, where land use is mostly rural and agricultural. The apparent ages based on CFC-11, CFC-113 and $^{3}H/^{3}He$ are similar, but the sample is clearly contaminated with CFC-12. The source of the CFC-12 contamination is unknown, but effluent from domestic septic tanks is a possibility. One of the strengths of CFC dating is that there are three compounds capable of defining apparent age and, depending on local land use practices, contamination with respect to one or two CFCs does not necessarily preclude the possibility of obtaining a reliable age. The agreement in apparent age from CFC-11, CFC-113 and $^{3}H/^{3}He$ suggests this sample is not significantly mixed with old water.

Sample 9 is from a monitoring well located near a closed and reclaimed landfill in Albuquerque, New Mexico, USA. The water is contaminated with all three CFCs and cannot be dated using CFCs. Although not harmful, the relatively high CFC concentrations indicate that the groundwater near the landfill is probably being affected by anthropogenic sources. Although landfills are anoxic, and microbial degradation of CFCs probably occurs there, landfills are a source of CFC contamination to groundwater. This landfill was constructed within the unsaturated zone, and water has apparently leaked through the landfill to the aerobic aquifer beneath. High concentrations of all three CFCs occur in the aquifer. Because of their low detection limit and generally high concentrations in landfills and other waste sources, a potential application of CFCs is their use as an early warning in assessing susceptibility of wells to contaminant sources.

Samples 10 and 11 are from monitoring wells near a 0.17 km$^2$, unlined landfill that was in operation from 1962 to 1994 in New York, USA. The landfill was capped over approximately 75% of its area in 1996 and the remainder was capped in 2000. The landfill was constructed in glacial till, and is in direct contact with the shallow aquifer. Sample 10 was taken from a monitoring well in the shallow aquifer within the contaminate plume approximately 30 m downgradient of the landfill. Sample 11 is from a monitoring well approximately 366 m downgradient from the landfill. Based on monitoring of water chemistry, there was little evidence that water at the furthest point downgradient (at sample 11) was being influenced by leachate from the landfill. The $N_2$–Ar recharge temperature of sample 11 is indicative of natural recharge in the area, and the absence of dissolved methane suggests the sample is not affected by the landfill. However, the water is probably undergoing iron reduction, as indicated by the low dissolved oxygen and elevated dissolved Fe(II).

Sample 11 has CFC-11 and CFC-113 concentrations in the ‘normal’ range, suggesting apparent ages of 22 and 19 years, respectively, and are only slightly younger than that based on dissolved $SF_6$ (26 years). $SF_6$ does not degrade in anoxic waters (Busenberg and Plummer, 2000), and the $SF_6$ apparent age is consistent with the dates of operation of the landfill, while the CFC-11 and

CFC-113 apparent ages may have been affected both by contamination and degradation. Sample 10, located nearest the landfill, has been affected by degassing as indicated by low concentrations of dissolved $N_2$ and Ar, and an apparent recharge temperature of 38.5°C, more than 30°C warmer than the recharge temperature determined for sample 11. This sample has probably been gas stripped by methane gas formation (9.0 mg/L dissolved methane). Consequently, the CFCs and $SF_6$ have probably been gas stripped and have concentrations lower than that of samples that have not been degassed. Even with gas stripping, the CFC-12 concentration is approximately 100-fold that of modern air–water equilibrium. Traces of methylbutane and isopropyl alcohol were detected by purge and trap GC-MS procedures in sample 11. More than 26 VOCs were identified in sample 10 using purge and trap GC-MS procedures.

Sample 12 is from a domestic well in piedmont sands and gravels along the eastern margin of the Middle Rio Grande Basin in central New Mexico, in an area where the basin receives inflow of old palaeowater from outside the basin. The $^{14}C$ activity of the dissolved inorganic carbon is only 22.0 pMc, indicating a radiocarbon age of more than 10 ka. The sample is aerobic and contains very low concentrations of CFC-11 and CFC-113. In contrast, the sample contains more than 10 000 pg/kg of CFC-12. A likely source of the CFC-12 is effluent from septic tanks in the area. The CFC-11 and CFC-113 concentrations are too low to be used to date the young fraction in the sample. Although none of the CFCs can be used to date the sample, the presence of high levels of CFC-12 indicates the water is being influenced by anthropogenic sources and is susceptible to contamination.

The water in sample 13 is from a shallow monitoring well in a sand aquifer in southern New Jersey, USA, sampled in April 1992, in an area where atmospheric mixing ratio is influenced by air from two large metropolitan areas in the USA: Philadelphia, Pennsylvania and Wilmington, Delaware. It has been suggested that the water shown in sample 13 represents equilibration with urban air, that is, air somewhat enriched in CFCs having mixing ratios greater than that observed at Niwot Ridge, Colorado, USA (Szabo et al., 1996). The land use is rural and agricultural, yet the CFC-11 and CFC-12 concentrations in the water are higher than possible for equilibrium with Niwot Ridge air at that time. At the assumed recharge temperature of 13°C, the measured CFC-11 and CFC-12 concentrations are 110 and 104 pg/kg higher than possible for equilibrium with 1992 Niwot Ridge air. And using the lowest possible recharge temperature of 11°C, the CFC-11 and CFC-12 concentrations still exceed 1992 air–water equilibrium values by 44 and 77 pg/kg. At this site, the CFC-113 was apparently not contaminated, indicating an apparent age of 2 years (13°C recharge temperature), which compares to 2.5 years based on $^3H/^3He$ dating. It was suggested by Szabo et al. (1996) that the contamination of CFC-11 and

CFC-12 in shallow groundwater in the area was due to contamination from urban air, as has been observed in parts of north-eastern USA (Ho et al., 1998).

Samples 14 and 15 are examples of waters that were probably contaminated during drilling and/or well completion. Sample 14 is from a deep monitoring well that was drilled along the eastern mountain front in piedmont sands and gravels near Albuquerque, New Mexico. The well was completed in July 1997 and sampled one year later. The rotary drilling used drilling fluid that circulated through open tanks at the land surface. In completing the well, high pressure air was injected at shallow depths, which lowered the head over the water column and caused the well to be flushed from depth. The sample contains high $^4$He and $SF_6$ of terrigenic origin, indicating old water. The $^{14}$C activity of the dissolved inorganic carbon is 35.4 pMc, indicating an unadjusted radiocarbon age of more than 8 ka. CFCs were low or not detectible in most other deep monitoring wells sampled in the vicinity of Albuquerque, but water from the deep completion at the Matheson piezometer nest (sample 14, Table 8.2) contained more than 240 pg/kg of CFC-11, 50 pg/kg of CFC-12 and 14 pg/kg of CFC-113. The concentrations suggest that this sample was contaminated with some drilling fluid that was nearly in equilibrium with 1998 atmosphere. The ratios of the various CFCs in the sample are significantly different from those of the 1998 atmosphere and, thus, excess air was not the source of CFC contamination in sample 14. Because of the shallow depth for air injection, it is unlikely that the air contamination was due to well development. In this case, the CFC data provided a useful tool to detect monitoring wells that may still contain water in the vicinity of the well screen that contains fractions of drilling fluid.

Sample 15 is from a monitoring well drilled in low permeability mudstones/siltstones in Nebraska, USA. The well was drilled in June 1999, and sampled on two occasions prior to CFC collection in May 2000. It was reported that after removal of the water standing in the well, several days are required for the water level to recover. The $^{14}$C activity of the dissolved inorganic carbon is only 13 pMc and the water contains $< 0.8$ TU. The well was developed by air injection, apparently within the 3 m screened interval. Air injection would probably not significantly affect the $^3$H or $^{14}$C activity of the sample but would likely introduce significant amounts of CFCs in the vicinity of the well screen, which would subsequently dissolve under hydrostatic pressure. Further evidence of air contamination is the relatively high dissolved gas content and high, calculated, excess air (Table 8.2). If 11.2 cm$^3$ of 1999 air dissolved per kg of groundwater (Table 8.2), then this excess air would have contributed 302, 168 and 75 pg/kg of CFC-12, CFC-11 and CFC-113, respectively. The concentrations observed, with the exception of the CFC-113, are similar to the ones calculated from the excess air, which suggests that all CFCs were introduced during the development of the well. In this case, both the CFCs and dissolved gases were useful in recognizing air contaminated groundwater.

Sample 16 is included in Table 8.1 as an example of a water sample that was probably contaminated by the sampling equipment. The sample is from the sand aquifer on the Delmarva Peninsula of Maryland, USA, sampled in November 1991 (Dunkle et al., 1993). The very low tritium content (-0.2 ± 0.3 TU) is consistent with the age of nearly 45 years determined from CFC-12. However, the CFC-11 concentration indicates a recharge date of 1964, and apparent age of 27 years. Water recharged in 1964 on the Delmarva Peninsula would have contained more than 100 TU of tritium in 1991 (Dunkle et al., 1993). The sample was collected using a pump that had a moving internal rubber rotor. Dunkle et al. (1993) noted a young bias of CFC-11 apparent ages relative to CFC-12 in many of the older water samples from Delmarva. The addition of small amounts of CFC-11 from sampling equipment would have less effect on younger water with higher CFC-11 concentrations. Subsequent tests comparing water pumped from deep wells with the pump used by Dunkle et al. (1993) and another pump made of all metal parts showed that the sample pump used earlier introduced CFC-11. Other materials sometimes used in sampling that have been found to contaminate water samples with CFCs are some silicone rubber and plastic tubing used in peristaltic pumps, and plastic impellers and plastic discharge lines used in some pumps.

## 8.6. MICROBIAL DEGRADATION OF CFCs (SAMPLES 17–19)

Samples 17–19 (Table 8.2) demonstrate effects of microbial degradation on CFCs in groundwater. Sample 17 is from anoxic groundwater on the southern Delmarva Peninsula, Virginia. The water contains little or no dissolved oxygen and a trace of hydrogen sulphide. CFC-11 appears to be somewhat degraded, giving an apparent age that is 5–7 years older than those based on CFC-12 and CFC-113. As a general rule, if dissolved oxygen is less than about 0.5 mg/L, it is likely that CFC-11 has been at least partially degraded. However, apparently reliable ages can be obtained from CFC-12 and CFC-113 in such environments.

Sample 18 is from the top 1.6 m of a water table aquifer on the Delmarva Peninsula, Maryland, beneath 5 m of the unsaturated zone. This sample has been interpreted as a case in which degradation of CFCs has occurred in the soil or unsaturated zone prior to recharge (see Chapter 9, Section 9.1). The groundwater sample has a dissolved $O_2$ concentration of 6.9 mg/L and, by comparison, to water from nearby wells at similar depth, the sample was probably denitrified and has lost approximately 20 mg/L $NO_3^-$ to $N_2$ gas that is no longer part of the sample and apparently lost to the unsaturated zone air prior to recharge. The water then apparently re-equilibrated with the major gases but not completely with the trace gases prior to recharge. The apparent age of CFC-11 is greater than that of CFC-113 and CFC-12. The CFC apparent ages are greater than the age based on $SF_6$. Busenberg and Plummer (2000) show that $SF_6$ is highly resistant to microbial degradation and not contaminated by terrigenic sources in the area of sample 18. The $SF_6$ age of 2.6 years is consistent with expected ages from other nearby water table samples (Reilly et al., 1994). Similar results have been observed in about one third of the water table piezometers at Mirror Lake, New Hamsphire, USA (Goode, 1998; Goode et al., 1999). Many of the New Hampshire wells contained dissolved $O_2$, however, the CFCs appeared to be partially degraded, particularly CFC-11 and CFC-113. In addition, some of the New Hampshire soil gas samples were depleted in CFC-11 and CFC-113. Plummer et al. (2001) observed CFC-11 concentrations that indicated apparent ages significantly greater than those based on CFC-12 and CFC-113 in discharge from shallow aerobic springs in Shenandoah National Park, Virginia, USA. The Shenandoah CFC-11 ages are low and precede the turnover in atmospheric concentrations. These results suggest that partial degradation of CFC-11 in organic rich soils may be a fairly common phenomenon.

Sample 19 is from a production well in the Memphis Sand aquifer near the Mississippi River in south-west Tennessee, USA (Parks et al., 1995). The sample contains no detectable dissolved oxygen, and large concentrations of ferrous iron and methane (Table 8.2). CFC-11 and CFC-12 have been entirely removed, presumably by microbial degradation, leaving the impression of pre-1940s water. However, the tritium measurement of 13.8 TU indicates water with a significant post-bomb fraction. As a general rule, all CFCs can be degraded in low sulphate, methanogenic environments. In this case, without the tritium measurement, an erroneous conclusion regarding susceptibility to contamination from shallow sources would have been reached, if based entirely on CFCs.

## 8.7. GROUNDWATER BENEATH DEEP UNSATURATED ZONES (SAMPLES 20–22)

Samples 20–22 are from areas in southern Idaho with deep unsaturated zones (see Chapter 9, Section 9.6). Sample 20 is from a monitoring well in the Snake River Plain (Idaho) aquifer in an area where groundwater is being recharged by seepage from an intermittent stream. The unsaturated zone consists of 16.8 m of alluvial sand that overlies 50.3 m of fractured basalt and sedimentary interbed sequence above the water table. Previous work in the area (Busenberg et al., 1993) has shown that diffusive processes control the unsaturated zone air profile in the sand and basalt. Though the sample may be slightly contaminated with CFC-113, the CFC-11 apparent age is about three years older than that based on CFC-12, consistent with the diffusive process (Cook and Solomon, 1995).

Sample 21 is from a deep stock well in the Snake River Plain aquifer of southern Idaho. The well is 332 m deep with 308 m of unsaturated zone in fractured basalt and associated sedimentary interbeds. The pump draws from the bottom 25 m of open hole. The well was sampled in 1994 and again in 1995 with consistent observations. The tritium content is only 0.08 ± 0.01 TU ($^3$H by helium in-growth), yet the water contains low, but significant concentrations of CFCs (Table 8.2). CFC-11 and CFC-12 concentrations are consistent with equilibration with 1964 air and CFC-113 indicates equilibrium with 1970 air. It is not likely that CFCs could have diffused to such great depths within the past 30 years. However, advective gas flow through fractures driven by barometric pumping and topographical effects possibly introduce CFCs to great depths in the unsaturated zone of these fractured basalts. The apparent CFC ages of 26–32 years indicate equilibration with old air, but not actually the time since recharge. Tritiated infiltration water from the bomb era is apparently still in the unsaturated zone and has not recharged the aquifer. The pre-bomb water at the water table apparently equilibrates with old air and air mixtures that are being transported advectively through the unsaturated zone. If there were no recharge occurring in this semi-arid environment, the presence of CFCs in discharge from the well could indicate that some water is being derived from the top of the water table, perhaps the top 10–20 cm. However, the pump was located at least 10 m below the water table and there was no evidence of excess gases ($N_2$, Ar, He, Ne) in the discharge that would probably be present if water and air from the water table were drawn into the pump. It is more likely that, in this case, the presence of CFCs indicate that some recharge is occurring by infiltration through fractures and sedimentary interbeds in this semi-arid environment.

Sample 22 is from a stock well located approximately 12 km south-west of the Idaho National Engineering and Environmental Laboratory, Idaho, spreading areas. The spreading areas are depressions into which water from the Big Lost River water is diverted to prevent flooding of the Laboratory facilities. An annual average of 8.6 million m$^3$ of water are diverted into the spreading areas, however the amount of water diverted varies from 0 to 43 million m$^3$ annually. The water rapidly enters the unsaturated zone through fractures in the basalts and moves rapidly both horizontally and vertically more than 200 m down to the water table. In a recent tracer experiment, 1,5-naphthalene disulphonate was added to the water in the spreading areas and the tracer was detected in a well completed in a perched water table (with a depth of 80–100 m) and 0.2 km away in 9 days. The tracer was believed to be present in a well sampling the aquifer with a 20.4 m perforated interval starting about 6.5 m below the water table. The first sample from this well was collected 80 days after the release of the tracer but it is likely that the tracer arrival time at this well was much earlier (Nimmo et al., 2002). The water appears to move vertically along fractures, ‘pond’ on low permeability layers of sediments and basalts, and then move horizontally to the next fracture on its way to the water table. There appears to be little or no gas exchange between the recharge and the unsaturated zone atmosphere. The well samples 26 m of the aquifer and based on the CFC-113/CFC-11 ratio, the water is a mixture of 69% recent recharge (6.4 years) with regional groundwater that is several thousand years old. The $^3H/^3He$ age of 6.5 ± 6.5 years is consistent with the CFC age of the young fraction.

## 8.8. GAS STRIPPING AND MICROBIAL DEGRADATION (SAMPLES 23 AND 24)

Samples 23 and 24 (Table 8.2) show evidence of gas stripping and microbial degradation. Products of microbial degradation include carbon dioxide, nitrogen, hydrogen sulphide and methane. As these gases accumulate in groundwater, the sum of the internal partial pressures of all gases can sometimes exceed the hydrostatic pressure at very shallow depths. The result is bubble formation and potential for gas stripping. Gas stripping at the water table will lower the concentrations of all dissolved gases and affect all gas-based dating techniques, including CFCs, $^3H/^3He$, $^{85}Kr$ and $SF_6$.

Sample 23 is from a shallow peat-rich glacial deposit in Minnesota, USA, undergoing methanogenesis. The water contains nearly 10 mg/L dissolved methane and the sum of internal partial pressures of nitrogen, methane, carbon dioxide and argon is 1.07 × (1013.25 hPa). Groundwater ages are not known but are probably less than five years, considering the shallow depth and recharge rate. The dissolved nitrogen and argon concentrations appear to have been partially stripped by gas bubbling at the water table, implying a recharge temperature that is 11°C warmer than the groundwater temperature (Table 8.2). It is likely that methane gas stripping has lowered the concentrations of all dissolved gases in the sample, invalidating dating with any gas-based dating tool. The CFC concentrations observed in water from this well have probably been affected both by microbial degradation and methane gas stripping.

Although CFC-12 has not been entirely removed, it indicates an unrealistic age for this environment.

Sample 24 shows potential for gas stripping by nitrogen from denitrification. The sample is from a monitoring well near agricultural fields on the Delmarva Peninsula, Maryland. Under normal recharge conditions, the dissolved nitrogen and argon concentrations should be similar to those of sample 1 (Table 8.2). However, Sample 24 contains an excess of approximately 11 mg/L of nitrogen (as $N_2$), and the argon content is slightly depleted. This is evidence of strong denitrification and possibly a small amount of gas stripping. The total internal pressure of dissolved gases is 1.35 × (1013.25 hPa), of which dissolved nitrogen totals 1.31 × (1013.25 hPa). Ekwurzel et al. (1994) noted helium loss from this sample and were unable to date the water with $^3H/^3He$. The CFC-11 apparent age is five years older than that based on CFC-12 and may indicate degradation of CFC-11. The CFC-113 and CFC-12 ages of 14–16 years are not inconsistent with the tritium data, but if affected by gas stripping, represent a maximum age.

## 8.9. SCREENING PATTERNS OF CFC APPARENT AGES FOR AN INITIAL ASSESSMENT

As has been discussed in Chapter 4 and demonstrated in this chapter, many processes can modify apparent CFC ages. Therefore, the interpretation of apparent CFC ages may not be always straightforward. For example, six separate apparent CFC ages will be obtained when young water recharged under piston flow conditions is mixed with a fraction of CFC-free water that is slightly contaminated with CFC-12. Three apparent ages will be obtained from the individual CFC concentrations and three from the ratios of CFC-11/CFC-12, CFC-113/CFC-11 and CFC-113/CFC-12. In such cases, it may not be possible to interpret the discordant apparent CFC ages.

Table 8.1 shows some of the patterns observed in the apparent CFC ages. The table can be used in the preliminary interpretation or screening of CFC age data. Emphasis is placed on the patterns that are produced when the CFC concentrations do not exceed air–water equilibrium with modern air, thus permitting the assignment of CFC-based ages.

CFC dating methods do not necessarily result in unique age estimates, and erroneous interpretations may result if age information is based solely on the CFC data. For instance, agreement in the apparent CFC age from all three CFCs implies piston flow (or unmixed sample), and suggests that no other process has altered the CFC concentrations that resulted from water–air equilibrium. Observed agreement in apparent age in itself, however, is not sufficient proof of piston flow (see, for example, Chapter 5, Fig. 5.3(d)).

Care should be exercised even in the qualitative interpretation of CFC data, because apparent CFC ages can be modified by microbial degradation, contamination and other processes. For example, the confirmation or exclusion of post-1940 water may not be reliable without $^3H$ determination because pre-1940 waters can be contaminated by one or more CFCs during collection, storage and analysis. Also, CFCs may be absent in post-1940 waters as a result of biodegradation of the CFCs. For these reasons, $^3H$ analyses can be used to identify possible degradation or contamination with CFCs. With proper care, the scenarios shown in Table 8.1 can be narrowed. Some possible interpretations of the apparent CFC age results can indicate what additional data may be required to confirm or reject other possibilities. In many situations, however, numerous interpretations may be possible and may require extensive multi-component analysis to resolve (see Chapter 1, Section 1.3). The screening process can be useful in determining what additional tools will be needed to provide useful data that can help in the interpretation of the CFC results.

Field measurement of dissolved $O_2$ is highly recommended. The presence of $H_2S$ in the groundwater can be easily detected by its pungent smell and should be noted. Dissolved gases can be used to determine the temperature of recharge, the amount of excess air, the presence or absence of $O_2$, $CH_4$ and excess $N_2$ that is produced by the denitrification of nitrate. The parameters can help narrow the number of possible interpretations.

A careful examination of the chromatograms is also useful. The presence of a $N_2O$ peak indicates that active denitrification is occurring in the aquifer. In nearly all samples undergoing denitrification, CFC-11 is usually at least partially degraded. The presence of a CFC-114 peak usually indicates post-1980s recharge. The presence of $CCl_4$ may indicate post-1920s recharge (Shapiro et al., 2004). Waters with high VOC concentrations are often contaminated to varying degrees with one or more CFCs. Peaks of $CH_3SH$ and $H_2S$ are often present on chromatogram from sulphate reducing waters, and both CFC-11 and CFC-113 are usually partially degraded. Highly anoxic waters can be easily identified by the presence of numerous small peaks, and a very wavy background. Highly anoxic waters usually contain $CH_4$, and CFC-11 and CFC-113 are significantly degraded, while CFC-12 is somewhat degraded. These clues can often help in the interpretation of the apparent CFC age data.

## 8.10. GUIDELINES FOR ASSIGNMENT OF APPARENT CFC AGE

In assigning an apparent age to a water sample based on CFC concentrations, usually all that can truly be relied upon is the measured concentration of the CFC compounds in the sample, and even this assumes that the sample has been collected and analysed using procedures that consistently yield reliable results. Other concerns relate to whether the sample is representative of concentrations occurring in the aquifer or whether the CFC concentrations may have been influenced in some way by the sampling process. Beyond the measured concentrations, all derived age information is regarded as an interpretation and is model dependent. Several guidelines are listed below that can be applied in assigning an apparent (piston flow) age to samples that are typically from narrow intervals in wells, or samples that may be simple binary mixtures of young (CFC-bearing) water with old (CFC-free) water. The guidelines are intended to aid in separating samples that represent simple recharge of water in air–water equilibrium, and simple mixing/dilution, from those that may have been affected by one or more physical/chemical processes beyond that of air–water equilibrium and/or dilution process. For mixtures more complicated than those of simple binary mixing, the CFC data need to be evaluated in terms of expected model results. Some initial screening of samples for possible age information is often possible by comparing CFC concentration data on plots of one tracer in relation to another, such as those in Chapter 5, Figs 5.6 and 5.7, and in relation to expected results from model calculations (see Chapter 6). Figures 8.1 and 8.2 show plots of CFC-11 versus CFC-12 and CFC-113 versus CFC-12 in pptv. Regions are labelled on each figure showing possible scenarios of CFC contamination, CFC degradation, and introduction of excess air. CFC samples unaffected by these processes lie along the piston flow line in Fig. 8.1, or in regions bounded by the piston flow line and the mixing lines shown in Fig. 8.2.

Although the focus of this guidebook is on uses and applications of CFCs in hydrological studies, the level of hydrological understanding will increase significantly as additional tracer and/or supporting data are considered. In general, a multi-tracer approach is recommended.

The criteria listed below can be of some use in recognizing unmixed samples from those that may be mixtures and those that may have been affected by processes, such as microbial degradation or contamination:

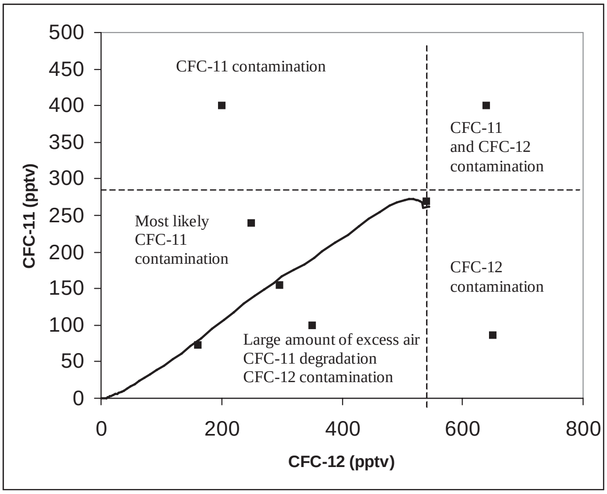

*FIG. 8.1. The tracer plot of CFC-11 versus CFC-12 in pptv shows piston flow line, and regions where samples affected by contamination, degradaton or excess air would plot.*

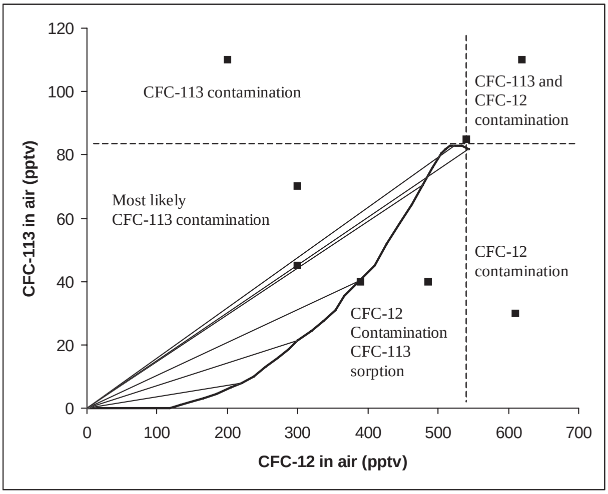

*FIG. 8.2. The tracer plot of CFC-113 versus CFC-12 in pptv shows piston flow line, and regions where samples affected by contamination, degradation or excess air would plot. Broken lines denote binary mixing of young and old components (see Chapter 5, Fig. 5.5).*

— The most reliable result in assigning an apparent age is found when all three CFCs agree in apparent age, within the uncertainties of the data. In calculating the apparent age, it is assumed that a valid recharge temperature and recharge elevation has been assigned for the sample and the analytical data have been converted to gas mixing ratios (pptv) and compared with appropriate local historical air composition. Although agreement in apparent age from all three tracers might be observed under piston flow conditions, the observation is not sufficient to prove piston flow conditions (see Chapter 5, Fig. 5.3(d)).

— If CFC-11 and CFC-12 apparent ages agree and the CFC-113 apparent age is younger than that from CFC-11 and CFC-12, the sample may represent a mixture of old and young water. Methods of estimating the apparent age of the young fraction and the fraction of young water in the mixture are discussed in Chapter 3, Section 3.3 and in Chapter 5, Sections 5.2 and 5.3.

— If the CFC-11 concentration is low (old apparent age) relative to CFC-12 and CFC-113 (indicating younger apparent ages), the CFC-11 may have been degraded somewhat relative to CFC-113 and/or CFC-12. In this case, the more probable apparent age is closer to that based on CFC-12 (and/or CFC-113).

— If binary mixing is assumed and only one CFC compound is considered reliable, the age of the young fraction is less than or equal to the apparent age based on the single CFC compound. If other chemical or isotopic data are available to estimate the fraction of young water in the mixture, it may be possible to estimate the age of the young fraction.

— If all CFCs indicate significantly different apparent ages, in the order from youngest to oldest of CFC-12 apparent age < CFC-113 apparent age < CFC-11 apparent age, all CFCs in the sample may be affected by microbial degradation, and the CFC-12 apparent age is probably least affected. Usually if CFC-11 and CFC-113 are still present in the sample, the CFC-12 has probably not been significantly affected by degradation. However, if microbial degradation is suspected, there should be other indications of anoxic conditions, as indicated below.

— If CFC-11 and CFC-113 are completely removed, it is reasonable to suspect that CFC-12 has been partially degraded as well, resulting in an old bias in the CFC-12 apparent age.

— Data for the concentrations of other dissolved gases can be quite useful in assessing redox conditions. If the environment is aerobic, no CFC degradation can be expected.

— If the dissolved oxygen content is relatively low (< 0.5 mg/L), caution should be exercised in basing results on CFC-11, especially. Inspection of chromatograms from the ECD can indicate conditions undergoing denitrification by the presence of $N_2O$. In samples affected by denitrification (only), CFC-12 and CFC-113 apparent ages can be identical, but CFC-11 can be partially degraded, yielding an apparent CFC-11 age older than that based on CFC-12 and CFC-113. If $H_2S$ is present (sulphate reducing conditions), usually CFC-11 is highly degraded. The CFC-113 apparent age can be a few years older than that based on CFC-12 under sulphate reduction. CFC-12 is often not significantly affected under sulphate reducing conditions. If methane is present, all three CFCs can be degraded. It is probably not possible to date waters with CFCs in most methanogenic environments. If all three CFCs have been degraded, the apparent CFC age is usually noted as ‘younger than the apparent CFC-12 age’. Groundwater environments that undergo methanogenesis typically have low dissolved oxygen, low dissolved sulphate and contain particulate organic matter. These environments can include glacial drift deposits, peats and coal formations.

— The ECD chromatogram provides other evidence of degraded samples. Chromatograms of degraded samples have many extra peaks for halogenated degradation products and display an unstable background.

— Significant contamination with respect to one or more CFCs is evident when the calculated CFC partial pressures exceed the maximum mixing ratios observed in the atmosphere. However, there is a gray area in samples that may be only slightly contaminated, but still in the valid ‘dating range’. Cases of low level contamination sometimes result from local enrichment in air composition or through some land use practices that occur over broad regions. If low level contamination is suspected, there may be additional compounds detected in the analysis from inspection of the chromatogram. If the sample is affected by low level contamination, but not by microbial degradation, a stable background will be observed in the ECD chromatogram. Types of contamination may be regional due to land use in the area. Usually there is a pattern that can be mapped. If the CFCs are partially contaminated (but not degraded), the older apparent age is more likely.

— The success of assigning apparent ages based on CFCs is greatly enhanced as other geochemical and hydrological data are included in the evaluation. Multiple environmental tracers, including $^{3}H$, $^{3}H/^{3}He$, $SF_6$, $^{14}C$, $^{85}Kr$, dissolved gases and redox indicators can be particularly helpful in resolving discordant data. Other useful information includes the type of pump used in sampling, information on the sample collection procedure, and background information on the geological and hydrological setting.

- It is recommended that at least five samples be collected in sequence at each well. Experience has shown that the CFC concentrations are typically highest in water from the first sample relative to the rest of the samples collected, and may represent trace contamination with air, or carry-over from a previous sample. There may not be a ‘right’ apparent age for water from a well because the discharge from the well may not be at a hydraulic steady state.
- No age can be assigned if all CFCs are below detection, other than ‘older than’. No age can be assigned if all the calculated CFC partial pressures exceed the maximum mixing ratios in the atmosphere.
- The apparent age is not necessarily the actual age since confinement. The sample may be affected by other physical processes, such as recharge through deep unsaturated zones, matrix diffusion, hydrodynamic dispersion, complex mixing, all of which are likely to affect the CFC concentrations in the water sample (Chapter 4).

# Chapter 9

# SELECTED CASE STUDIES USING CFC DATA

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## 9.1. DELMARVA, USA

The Delmarva Peninsula, located along the Atlantic coastal plain of the USA (Figs 9.1 and 9.2), consists of a wedge of seaward dipping gravels, sands, silts and clay sediments. The surficial aquifer is unconfined and consists of sands and gravels; the aquifer is underlain by a confining layer consisting of mainly silt and clay. The location of wells, and the flow paths can be found on maps in Dunkle et al. (1993), Reilly et al. (1994) and Böhlke and Denver (1995). The area is intensely farmed and the groundwater chemistry has been profoundly altered by the agricultural practices (Böhlke and Denver, 1995).

The Delmarva has been frequently selected to test the feasibility of the use of various environmental tracers as dating tools because of the relatively

*FIG. 9.1. Map showing the location of areas of case studies presented in this chapter: (1) Delmarva, USA; (2) Sturgeon Falls, Canada; (3) Valdosta, USA; (4) Shenandoah National Park, USA; (5) Eastern Snake River Plain Aquifer, USA; (6) Idaho National Engineering and Environmental Laboratory, USA; (7) Danube River, Hungary; (8) Valley and Ridge Siliciclastics, USA; (9) Virginia, USA; (10) central Oklahoma, USA; (11) Clare Valley, Australia; (12) Grossrinderfeld, Germany; (13) Maikammer, Germany; and (14) Mindanao, Philippines.*

simple hydrology of the aquifer, the presence of a network of multidepth wells with narrow screens installed by the U.S. Geological Survey, and the close proximity of the site to the U.S. Geological Survey Chlorofluorocarbon Laboratory. The apparent age of the groundwater in the Locust Grove watershed (Maryland, USA) has been determined using CFC-11 and CFC-12 (Dunkle et al., 1993; Plummer et al., 1993; Böhlke and Denver, 1995), $^{3}H/^{3}He$ and $^{85}Kr$ (Ekwurzel et al., 1994), CFC-113 and $SF_6$ (Busenberg and Plummer, 2000), and by a numerical simulation procedure (Reilly et al., 1994). The wells at Locust Grove have been sampled numerous times between 1990 and 1998; a summary of the results can be found in Busenberg and Plummer (2000). A comparison of the groundwater ages obtained using various age dating methods for five well nests is shown in Fig. 9.3. A cross-section of the watershed with the wells and the nitrate concentrations is shown in Fig. 9.4. All of the apparent ages are in close agreement.

In an unconfined aquifer, such as the one at the Delmarva Peninsula, areal precipitation minus the loss resulting from transpiration is the source of recharge. At the water table, the vertical velocity component of recharge is

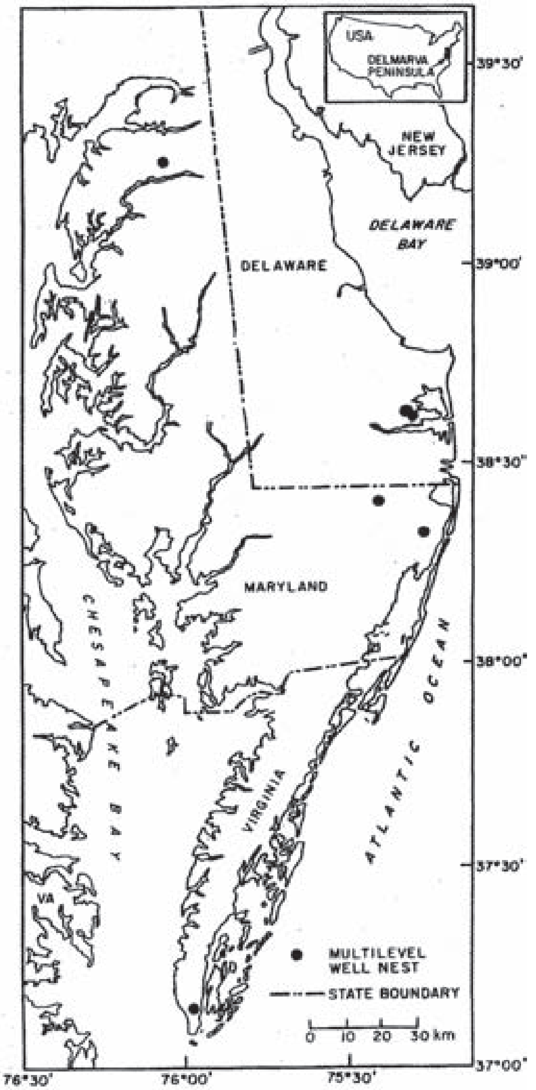


*FIG. 9.2. Map showing the location of well nests sampled for CFCs and other environmental tracers. Locust Grove is located in the north-western corner of this map.*

equal to the recharge rate divided by the porosity of the aquifer. This relation is only valid at the water table or at the groundwater divide; however, a reasonable approximation of the vertical velocity or recharge can be obtained from very shallow wells. The recharge rate then will be approximated by the equation (see Chapter 6):

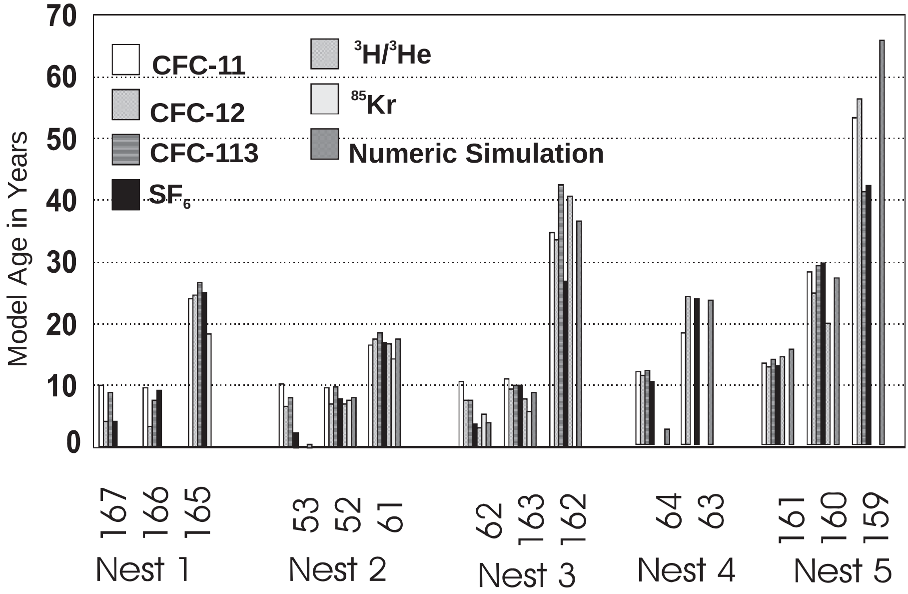


*FIG. 9.3. Comparison of model groundwater ages using six different dating methods at Locust Grove, Maryland, USA.*

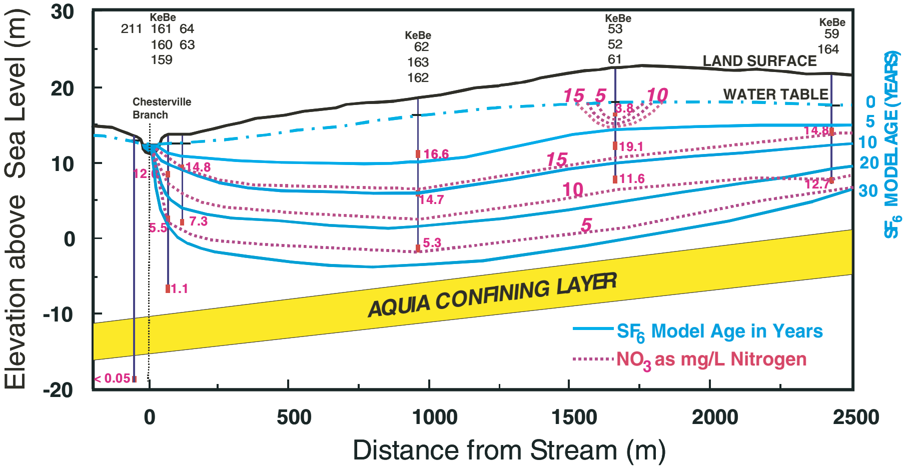


*FIG. 9.4. Cross-section of the Locust Grove, Maryland, USA, watershed shows the $SF_6$ age of the groundwater, as well as the nitrate concentration in the aquifer. Denitrification is occurring in the aquifer in the vicinity of well KeBe 53.*

$$R = z\theta/t \tag{9.1}$$

In the case of the Delmarva Peninsula, hydrodynamic dispersion is small (Ekwurzel et al., 1994; Reilly et al., 1994) and, thus, the tracer derived ages can be used to estimate the vertical component of recharge. Reilly et al. (1994) obtained reasonable rates of recharge using CFC-11 and CFC-12 data for KeBe 59 and KeBe 62, however, the vertical component of recharge for well KeBe 53 was not within the expected range. Significant denitrification has occurred at this site (Fig. 9.4) and the data suggest that some degradation of the CFCs has also taken place. The ages obtained by the three CFCs differ significantly for this groundwater sample with ages of CFC-11>CFC-113>CFC-12>$SF_6$ (sample 18 of Table 8.2 in Chapter 8). The $SF_6$ model age is significantly lower than all CFC model ages, also the $SF_6$ tracer appears to have been minimally affected by degradation. The recharge rate calculated for KeBe 53 with the $SF_6$ model age is within the expected range of recharge for this site (Reilly et al., 1994) while the rates calculated with the CFC ages are too low. The vertical component of the flow velocities has been calculated from environmental tracer model ages in parts of the states of Maryland, Delaware and Virginia. The results can be found in Dunkle et al. (1993), Ekwurzel et al. (1994) and Reilly et al. (1994). Vertical recharge rates of approximately 0.3 m/a were calculated in the northern part of the peninsula and 0.2 m/a at the southern tip. In irrigated areas, the recharge rates were as high as 0.4–0.5 m/a. Böhlke and Denver (1995) also showed that groundwater discharging beneath the local streams had a range of ages that was similar to the range of ages in the surficial aquifer. This provided evidence that the streams were fully penetrating discharge areas with respect to the surficial aquifer.

The natural uncontaminated waters of the Delmarva Peninsula were dilute $Na^+ – Ca^{2+}$ – bicarbonate solutions (Hamilton et al., 1993). The waters in the shallow unconfined aquifer are now $Mg^{2+}$, $Ca^{2+} – NO_3^- – Cl^-$ solutions as a result of the application of dolomite, KCl, nitrogen fertilizers and manure (Böhlke and Denver, 1995). Ages of the waters are stratified, and nitrate concentrations decrease with depth, as shown in Fig. 9.4. The ratio of $N_2$ to Ar is approximately constant in aerobic groundwaters collected near Locust Grove, Maryland. Denitrification in anaerobic waters increases the dissolved $N_2$ concentration of the groundwater. The increase in the dissolved $N_2$ to Ar ratio is the result of anaerobic denitrification of $NO_3^-$. Böhlke and Denver (1995) have shown that there is a direct correlation between the quantity of applied N-fertilizer and the $NO_3^-$ ($NO_3^-$ plus excess $N_2$ from denitrification) concentrations in the groundwater. The $NO_3^-$ in the groundwater increased rapidly after 1970 and the rate of this increase was about one third of the rate of N-fertilizer applied (Fig. 9.5). There were similar increases in the $Mg^{2+}$ and $Cl^-$

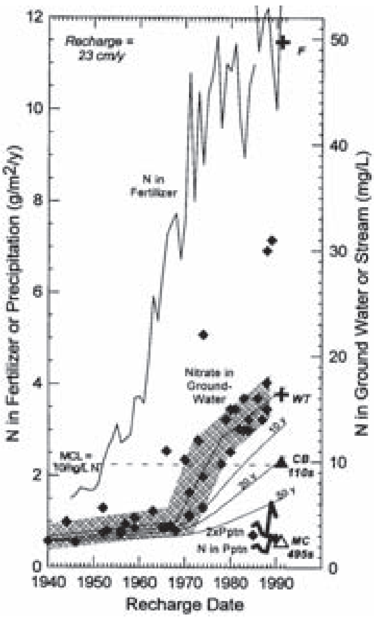


*FIG. 9.5. Comparison of fertilizer nitrogen use and groundwater nitrate concentration corrected for denitrification near Locust Grove, Maryland, USA. (From Böhlke and Denver (1995).)*

concentrations in the post-1970 groundwater that were also attributed to changing agricultural practices. In addition, Böhlke and Denver (1995) showed that the $Mg^{2+}$ and $NO_3^-$ discharge loads in one of the local streams were less than the recharge loads in the watershed and could be explained by applying an exponential mixing discharge model based on the groundwater ages and the agricultural contamination history in the absence of denitrification. Other recent applications of CFCs in the study of denitrification in groundwater are given in McMahon and Böhlke (1996), Böhlke et al. (2002), Puckett et al. (2002), and Puckett and Cowdery (2002).

## 9.2. STURGEON FALLS, ONTARIO, CANADA

The Sturgeon Falls site is located on a relatively flat delta of the Sturgeon River, approximately 5 km from the town of Sturgeon Falls, Ontario, Canada. Surficial deposits consist of fine silty sand, silt, and varved clay and silt, overlying a more permeable regional sand and gravel aquifer below 35 m depth. The groundwater flow system within the surficial silty sand unit has been described by Robertson and Cherry (1989) and Solomon et al. (1993). The water table depth varies seasonally, between approximately 0.2 m in spring, and 1.5 m in late summer. However, because of the fine-grained nature of the surficial sediments at this site, it is likely that the capillary fringe extends to the soil surface during much of the year (Solomon et al., 1993). The mean annual precipitation is estimated to be 990 mm, and the mean annual temperature is 3°C. Fourteen piezometer nests have been installed in the surficial aquifer, to depths of almost 36 m. Piezometers were constructed of polyethylene, PVC tubing or iron pipe, all with 15 cm screens, permitting excellent vertical resolution of groundwater samples. Samples from these piezometer nests have been analysed for CFC-11, CFC-12, CFC-113, $^3$H, noble gases Ne and He, dissolved oxygen and major ions.

Concentrations of dissolved oxygen in the aquifer system decrease with depth (Roberton, 1992). At Nest 28, where flow is mostly vertical, the highest value measured is 5 mg/L at 0.9 m depth. Between 4 and 9 m depth, concentrations are between 0.1 and 0.5 mg/L. Concentrations are below detection limit (0.1 mg/L) below 10 m depth. Robertson (1992) also observed sulphate reduction below 11 m at this site. Concentration profiles of CFC-11, CFC-12 and CFC-113 in Nest 28 are depicted in Fig. 9.6. The concentration of CFC-12 in the groundwater decreases approximately linearly with depth, from 500 pg/kg

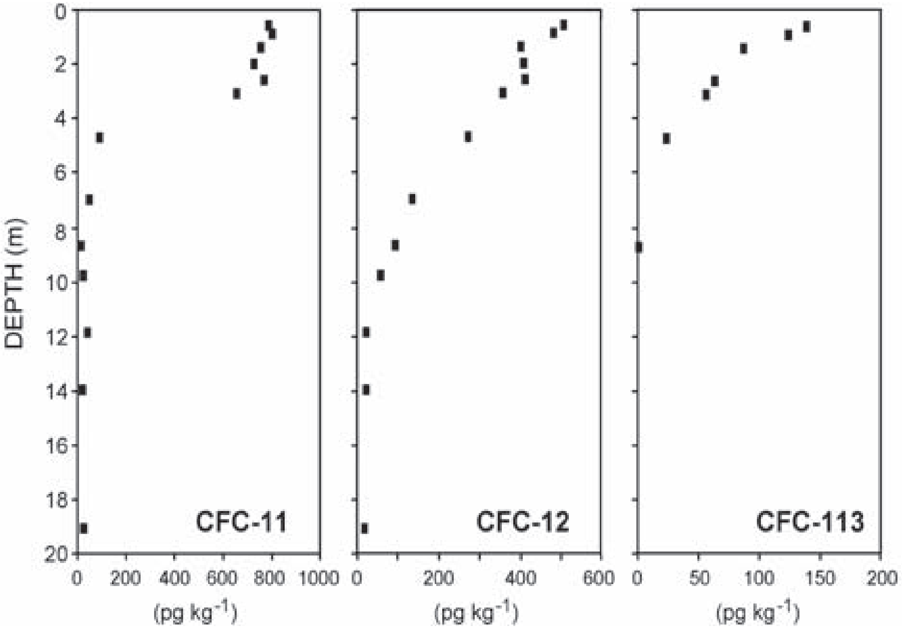


*FIG. 9.6. Measured depth profiles of CFCs at Nest 28.*

near the water table, to less than 50 pg/kg below 10 m depth. The concentration measured in the uppermost sample (510 pg/kg at 0.6 m depth) is not significantly different from that which would be expected for water in equilibrium with the atmosphere at a temperature of 3°C (pg/kg; see below). Concentrations of neon and nitrogen were measured in samples collected in 1986 and 1991 from Nest 28 (Solomon et al., 1993), and used to estimate a recharge temperature of approximately 2°C. Excess air was estimated to be approximately 3 $cm^3$/kg. At this recharge temperature, the presence of 3 $cm^3$/kg of excess air results in CFC concentrations in groundwater being elevated above equilibrium concentrations by less than 2%. This is considerably less than measurement uncertainty, and has been neglected in all of the following calculations. The CFC-113 concentration profile shows a more rapid decrease with depth, reflecting its more rapid increase in the atmosphere in recent years. The sample from 0.6 m depth (139 pg/kg) appears to be in equilibrium with the atmosphere at the estimated recharge temperature of 3°C (163 pg/kg). Concentrations of CFC-113 were less than the detection limit below 8 m depth.

The CFC-11 concentration measured immediately below the water table (785 pg/kg at 0.6 m) is considerably lower than would be expected based on the measured atmospheric concentration of 272 pptv and recharge temperature of 3×C (which would suggest an equilibrium concentration of 1200 pg/kg in the groundwater). The concentration profile also shows a rapid decrease between 3 and 5 m depth, which is not reflected in the other CFCs. The decrease in concentration is coincident with a decrease in dissolved oxygen concentrations in the aquifer, and some degradation of the compound appears to be occurring.

Figure 9.7 depicts apparent groundwater age profiles estimated using $^3$H and CFCs. The error bar depicts the position of the $^3$H peak in 1991. The shaded region depicts the hydraulic age profile calculated using a two dimensional flow model, using the recharge rate obtained from the position of the $^3$H peak. The upper and lower bounds of this region represent the lower and upper bounds of the recharge rate obtained using $^3$H (135 and 170 mm/a, respectively). The solid line bisecting the shaded region represents a recharge rate of 150 mm/a.

The apparent CFC-12 age increases with depth, from zero at 0.6 m, to 34 years at 11.9 m. The apparent age of 36 years for the sample at 19.1 m appears too young, and is attributed to low levels of contamination, probably introduced during sampling. Apparent CFC-12 ages of 27 years and 33 years at 9.8 m and 11.9 m depth are in good agreement with $^3$H data obtained at the site. Near the water table, the increase in apparent CFC-12 age with depth is approximately 2.5 a/m. This is equivalent to a vertical water velocity of 0.4 m/a. Multiplying by an aquifer porosity of 0.35, this equates to a groundwater recharge rate of 140 mm/a. Apparent CFC-113 ages increase linearly with depth,

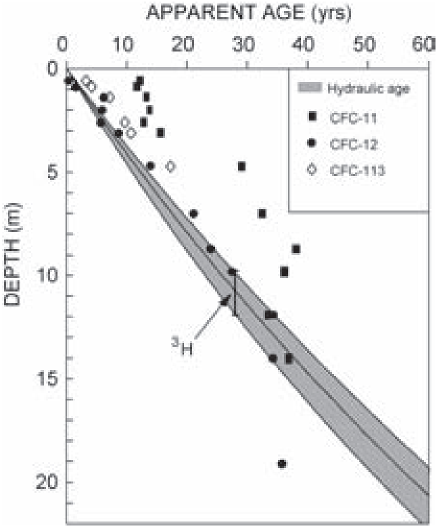


*FIG. 9.7. Apparent groundwater age profiles estimated using $^3$H and CFCs are shown. The error bar depicts the position of the $^3$H peak in 1991. The shaded region depicts the hydraulic age profile calculated using the two-dimensional flow model, using the recharge rate obtained from the position of the $^3$H peak. The upper and lower bounds of this region represent the lower and upper bounds of the recharge rate obtained using $^3$H (135 and 170 mm/a, respectively). The solid line bisecting the shaded region represents a recharge rate of 150 mm/a. Symbols indicate groundwater ages estimated using CFC dating methods on individual piezometer samples.*

but are greater than apparent CFC-12 ages and inferred groundwater model ages at all depths, which led the authors to infer sorption of CFC-113 (see Chapter 4, Section 4.5). Apparent CFC-11 ages are also greater than CFC-11 and CFC-113 ages, which is consistent with microbial degradation of CFC-11.

## 9.3. VALDOSTA, GEORGIA, USA

Groundwater from the Upper Floridan aquifer is the only source of municipal water for the city of Valdosta, Georgia, USA. In the 1980s, analyses of drinking water showed that chlorination of this DOC-rich (referring to dissolved organic carbon) water resulted in the formation of trihalomethanes that exceeded the maximum contaminant limit of 100 μg/L for drinking water. The source of the DOC in the groundwater was river water that recharged the aquifer through sinkholes located in the channel of the riverbed near Valdosta. The study was undertaken to locate, trace, date and determine the fractions of river water that recharged karstic parts of the Upper Floridan (Plummer et al., 1998a, 1998b), and to find a suitable location for a new well field that is free from DOC-rich river water.

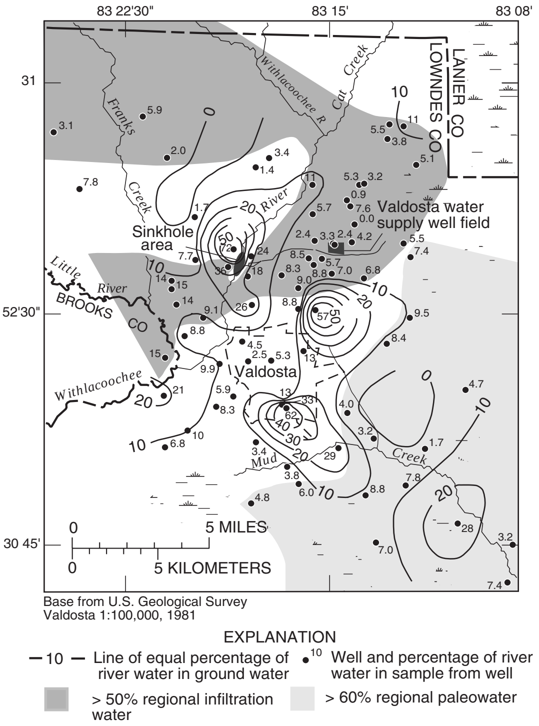
Measurements of dissolved Cl, $^3$H, CFCs, dissolved organic carbon, dissolved $O_2$, $H_2S$, $CH_4$, $\delta^{18}O$ and $^{14}C$ were used to interpret recharge conditions and trace movement of young groundwater within the aquifer in the Valdosta area. Sulphate-reducing and methanogenic conditions persist in the Upper Floridan aquifer in areas impacted by dissolved and particulate organic carbon from river water. In anaerobic parts of the aquifer, CFC-11 and CFC-113 were nearly completely removed by microbial degradation, and/or sorption, but CFC-12 persisted in both sulphate reducing and methanogenic ground water. Mass balance calculations with error simulation using $\delta^{18}O$ and Cl data were used to estimate the mean fractions and associated uncertainty of river water, regional infiltration water, and regional palaeowater in each groundwater mixture sampled. Fractions of river water in groundwater ranged from 0 to 72% and averaged 10%. The influence of river water discharge on the quality of water in the Upper Floridan aquifer was traced from the sinkhole area on the Withlacoochee River, 25 km south-east in the direction of regional groundwater flow. Figure 9.8 shows the calculated percentage of river water in the groundwater mixtures and areas where the aquifer is recharged primarily from regional infiltration through the overlying Miocene semi-confining layers, or where the aquifer is predominantly confined and contains mostly old palaeowater.

Because CFC-11 and CFC-113 were not conservative in the groundwater, CFC ratios could not be used to determine fractions of river water and age of the river water fraction. The river water fractions (determined independently from $\delta^{18}O$ and Cl data) were dated using CFC-12 after correction for dilution, assuming the CFC-12 was derived entirely from river water and that the river was historically in solubility equilibrium with air (Fig. 9.9).

The following assumptions limited the success of CFC dating somewhat:

(1) Historical air–water equilibrium in Withlacoochee River water;
(2) Stability of CFC-12;
(3) Definition of mixing fractions.

Overall, approximately 50% of the 85 water samples obtained from the Upper Floridan aquifer had CFC-12 based ages of the young fraction that were consistent with the $^3$H concentration of the groundwater. $^3$H/$^3$He dating was limited to river water fractions of more than about 10% river water. Dilution of $^3$H and low $^3$H concentration limited $^3$H/$^3$He dating to 16 mixtures out of a total



Base from U.S. Geological Survey
Valdosta 1:100,000, 1981

*FIG. 9.8. Map showing the percentage of river water in groundwater mixtures in the Upper Floridan aquifer near Valdosta, Georgia, USA. In the north-west part of the area, upper confinement is thin and the aquifer is recharged by infiltration. In the south-east, the aquifer is mostly confined and contains old palaeowater (Plummer, 1993). North of the city of Valdosta the aquifer is recharged locally by seepage through a series of sinkholes in the channel of the Withlacoochee River. A trihalomethane contamination problem resulting from chlorination of the DOC-rich river water fraction resulted in location of a new water supply well field east of the sinkhole area. (From Plummer et al. (1998a).)*

of 41 water samples measured. After correction for dilution with (assumed) CFC-free regional infiltration water and regional palaeowater in the Upper Floridan aquifer, the adjusted CFC-12 ages agreed with the $^3$H/$^3$He ages within 5 years or less in 7 of the 9 co-dated mixtures. Calculated velocities of river water in karstic parts of the Upper Floridan aquifer downgradient of the sinkhole area ranged from 0.4 to 8.2 m/d.

Two consistency tests were used to evaluate the overall reliability of the groundwater dating at Valdosta. In the first case, initial $^3$H concentration in Withlacoochee River water was retrieved from measurements of $^3$H and $^3$He in

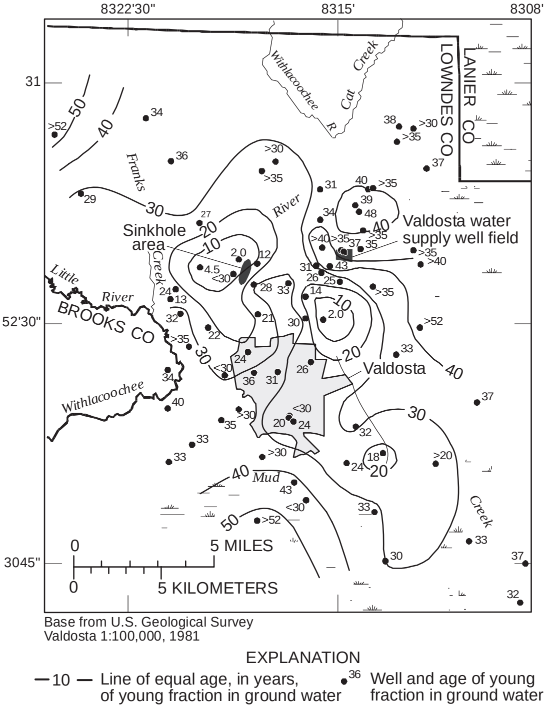


*FIG. 9.9. Ages of the young fraction are shown in groundwater mixtures in the Upper Floridan aquifer near Valdosta, Georgia, USA. (From Plummer et al. (1998b).)*

water from the Upper Floridan aquifer, corrected for dilution, and compared with historical $^{3}H$ concentrations modelled in the Withlacoochee River using a reservoir model. The dilution corrected $^{3}H$ + $^{3}He$ concentrations indicate that $^{3}H$ content of Withlacoochee River water peaked at about 80 TU in the late 1960s. In the second case, geochemical reaction modelling and historical reconstruction of the $^{14}C$ activity of dissolved inorganic carbon (DIC) and DOC in Withlacoochee River water was used to calculate the $^{14}C$ activity of total dissolved carbon (TDC) in water from the Upper Floridan aquifer. The calculated $^{14}C$ activity of TDC in groundwater was compared with the measured $^{14}C$ activity of DIC adjusted for the presence of DOC and $CH_4$ in the Upper Floridan aquifer at Valdosta. In both cases, the agreement in modelled and measured $^{14}C$ values was excellent, supporting the results of both the CFC-12 and $^{3}H/^{3}He$ dating.

## 9.4. SHENANDOAH NATIONAL PARK, USA

Shenandoah National Park covers an area of approximately 800 km$^2$ in the Blue Ridge Mountains of Virginia, USA (Fig. 9.10). Limited groundwater supplies occur in relatively thin (0–24 m, and commonly about 9 m thick) residuum and colluvium that overlie low yielding fractured metabasalts and granodiorites. Approximately 850 springs and seeps have been identified throughout the Park, and most of these have discharges of less than several litres per second (DeKay, 1972). The two largest springs in the Park have maximum discharges of only 20 and 11 L/s. Most of the springs sampled in Shenandoah National Park occur at relatively high altitude (most peaks range in elevation from 600 m to 1200 m) and discharge shallow groundwater from nearby water table sources that can be hydraulically connected to the fracture reservoir. Measurements from a suite of environmental tracers, including $^3$H/$^3$He, CFCs, SF$_6$, $^{35}$S, and δ$^{18}$O and δ$^2$H of water, were compared and used to estimate the residence times of shallow groundwater discharging from 34 springs and 15 wells in the Shenandoah National Park (Plummer et al., 2001).

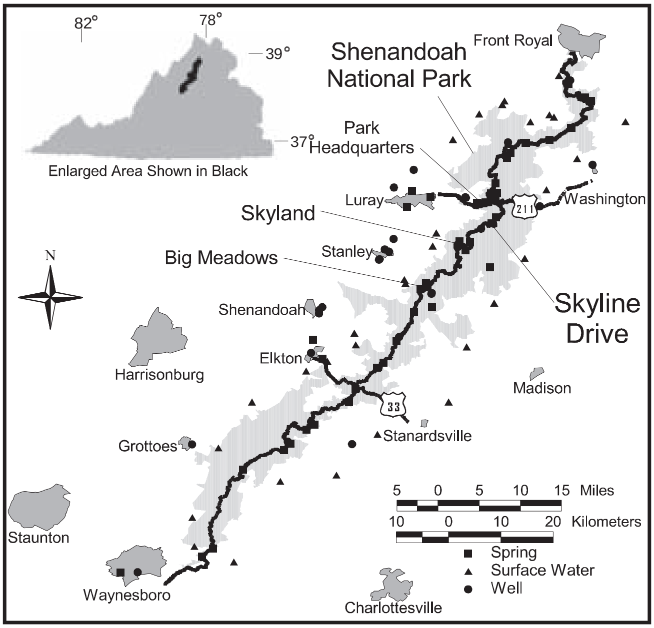


*FIG. 9.10. Location of springs and wells sampled in Shenandoah National Park, USA. From Plummer et al. (2000).*

The measured concentrations of CFC-11, CFC-12, CFC-113, $SF_6$ and $^3H$ for springs and wells are compared with model calculations assuming piston flow, exponential mixing and binary mixing (Fig. 9.11). The model calculations with CFCs are nearly insensitive to expected variations in the amount of excess air, and local air enrichment of 2% in CFC-12. The calculations involving $SF_6$ are also insensitive to local air enrichment of 5%, but depend significantly on variations in excess air.

Concentrations of CFC-11, CFC-12, CFC-113 and $SF_6$ in spring discharge in the Shenandoah National Park are all consistent with young ages but, because of the post-1995 levelling off of the CFC atmospheric growth curves, the CFC-based ages have large uncertainties. CFCs cannot be used to distinguish ages using piston flow or exponential mixing models for waters that recharged in the past decade years. Mean groundwater residence times of 0–3 years were determined for discharge from springs in the Shenandoah National Park based on $SF_6$ and $^3H/^3He$ data.

A few samples, mostly from wells, plot near or within the envelope between the exponential and piston flow models (Fig. 9.11(b) and (c)). These samples lie along hypothetical mixing lines that can be drawn between the piston flow line and old (CFC-free) water, and may be interpreted as binary mixtures of relatively young water with old CFC-free water, however, other alternate mixing scenarios could describe the observed data. Most other samples from wells have CFC-12, and to a lesser extent, CFC-113 concentrations that are as much as two to three times greater than that possible for water in solubility equilibrium with North American air, and have apparently been affected by local anthropogenic sources of CFCs in the Shenandoah National Park. Most waters from springs sampled in August and September 1997 have $^3H$ and $SF_6$ concentrations similar to those of modern waters.

The $^{35}S$ data indicate minimum residence times of 1.5 years (piston flow) and mean ages as old as 15 years (exponential mixing) for atmospheric sulphate in water from five selected springs. However, transport of dissolved sulphate is probably retarded by uptake and exchange of sulphate in plants, and/or soil sorption. If approximately 50% of the $^{35}S$ is lost to the biomass, exponential residence times of 5–7 years for water are possible. A similar transit time of about 5 years for transport through the soils to spring discharge is indicated by the $^{18}O$ data (Plummer et al., 2001).

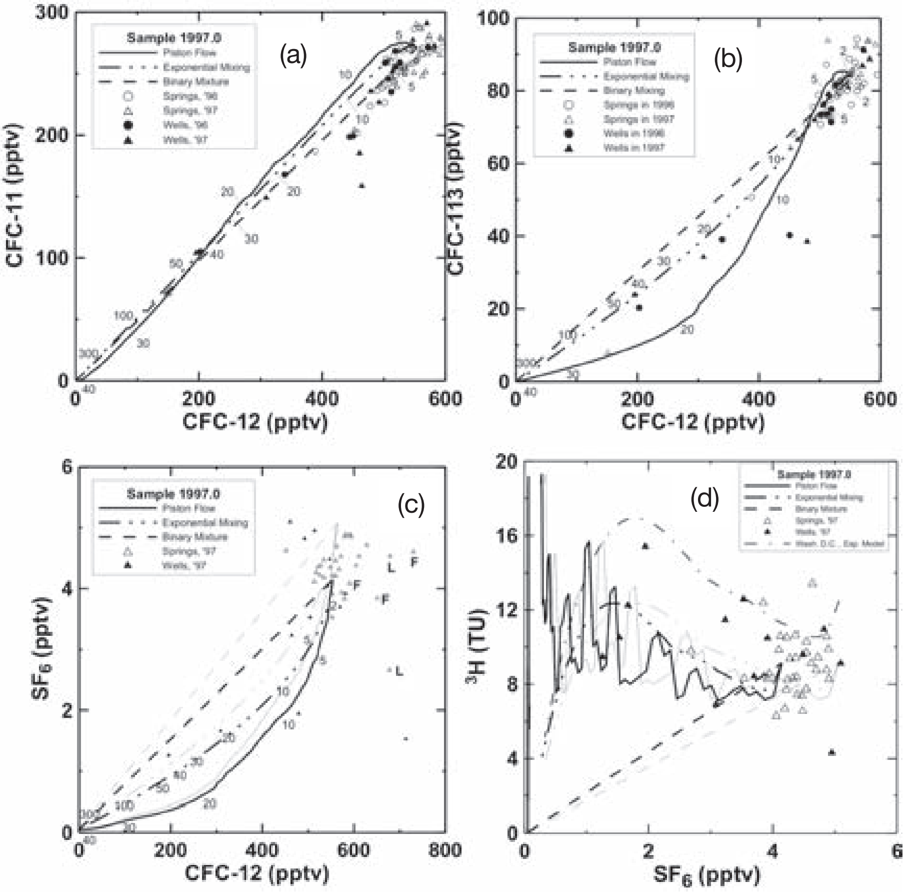


*FIG. 9.11. Comparison of the mixing ratios of (a) CFC-11 and CFC-12; (b) CFC-113 and CFC-12; (c) $SF_6$ and CFC-12 mixing ratios; and (d) $^3H$ activity (TU) and $SF_6$ mixing ratios for springs and wells in the Shenandoah National Park with lines representing piston flow, exponential mixing and binary mixing of young (1997) and old (tracer-free) water. All CFC models were calculated without excess air, but were insensitive to observed variations of 0–2 $cm^3$/kg. Models with $SF_6$ assume 0 excess air (heavy lines) and 2 $cm^3$/kg of excess air added (light lines). The letters on (c) identify samples from Furnace Spring (F) and Lewis Spring (L) that appear to be somewhat contaminated with CFC-12. Two input functions for $^3H$ were considered in (d). The upper line shows results from the exponential model with a tritium record from Washington, D.C., approximately 140 km east of the Shenandoah National Park. The other lines assume a local tritium input function scaled to the Washington, D.C., record. (Modified from Plummer et al. (2001).)*

## 9.5. EASTERN SNAKE RIVER PLAIN AQUIFER, IDAHO, USA

In south-central Idaho, USA, crops are irrigated with surface water diverted from the Snake River through an extensive canal network (Fig. 9.12), or with groundwater pumped from the Eastern Snake River Plain aquifer in

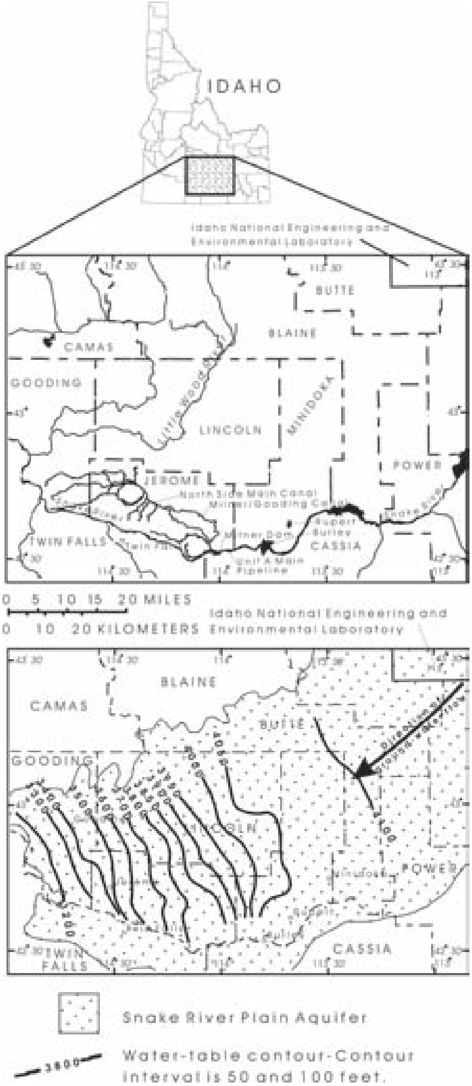


FIG. 9.12. *Location of the Eastern Snake River Plain aquifer and canal system used for irrigation in areas near the Snake River. Water table contours are in feet from the original source (Rupert, 1997) (1 foot = 0.3048 m).*

areas that are topographically too high for surface water irrigation. The plain is underlain by a layered sequence of basaltic lava flows and cinder beds interbedded with aeolian, fluvial and lacustrine sedimentary deposits. Beneath the irrigated areas, the aquifer is recharged significantly by irrigation return flow. Plummer et al. (2000) used stable isotope data ($^{2}$H and $^{18}$O) in conjunction with CFCs and $^{3}$H/$^{3}$He data to determine the fraction and age of irrigation water in groundwater mixtures from farmed parts of the Eastern Snake River Plain aquifer in south-central Idaho. The stable isotope data defined two groups of waters:

(1) Regional background water, unaffected by irrigation and fertilizer application;
(2) Mixtures of irrigation water from the Snake River with regional background water.

The CFC ages were affected by the extent to which irrigation return flow re-equilibrates with air at the land surface, and/or equilibrates with unsaturated zone air during infiltration (typically 100 m thick unsaturated zones in fractured basalt), and the extent to which CFC concentrations were contaminated by agricultural and other anthropogenic sources of CFCs. Interpretation of the $^{3}$H/$^{3}$He ages of water in the Eastern Snake River Plain aquifer was complicated by the introduction of relatively large amounts of excess helium of terrigenic origin (both crustal and mantle-derived helium) with $^{3}$He/$^{4}$He ratios ranging from $\leq 1 \times 10^{-6}$ to more than $1 \times 10^{-5}$.

Waters from irrigated areas commonly had anomalously high concentrations of CFC-11 and to a lesser extent, CFC-12 (see Chapter 4, Section 4.1). It was suggested that the source of the high CFC-11 and CFC-12 concentrations may have been inert ingredients used in pesticides in the area, and recharge of CFC-contaminated irrigation water from the Snake River. The concentrations of CFC-113 in most waters were equal to or less than those for solubility equilibrium with modern air, and apparently less affected by anthropogenic sources. Most air and unsaturated zone air samples from irrigated lands contained significant excesses of CFC-11 above that of North American air. Ages of young water in groundwater mixtures, where the CFCs were not contaminated, were interpreted from the CFC data using ratios of CFC-11/CFC-12, CFC-113/CFC-12 and CFC-113/CFC-11, and from individual CFC concentrations after correction for dilution with CFC-free old groundwater. Most of the waters from irrigated areas had concentrations of at least one CFC compound that was not in excess of that possible for solubility equilibrium with modern air, permitting assignment of CFC-based age in more than 80% of the water samples. Most irrigation water or mixtures of irrigation water and regional background water had high tritium content and low excess helium. For these waters, the $^3H/^3He$ ages of irrigation water in the mixture were well defined and ranged from about 0 to 8 years. The CFC based ages of irrigation water were either in agreement with the $^3H/^3He$ ages or biased older than the $^3H/^3He$ ages by as much as 8–10 years, presumably due to gas exchange with low CFC unsaturated zone air during infiltration.

CFC concentrations and their ratios indicate that the regional background water contains from 5% to about 30% young infiltration water from local precipitation with ages of less than 2 years to 11.5 years. The young fraction in most of the regional background water could not be dated using $^3H/^3He$ because of low tritium concentration and high excesses of terrigenic helium that had a mantle component ($^3He/^4He$ ratios of $1 \times 10^{-6}$ to $10 \times 10^{-6}$).

Although nitrogen fertilizer applications in south-central Idaho are among some of the higher fertilizer applications in the USA, the relatively low residence times of groundwater in irrigated parts of the Eastern Snake River Plain aquifer, and dilution with low-$NO_3^-$ irrigation water from the Snake River lower the potential for $NO_3^-$ contamination in these agricultural areas (Plummer et al., 2000).

## 9.6. IDAHO NATIONAL ENGINEERING AND ENVIRONMENTAL LABORATORY, IDAHO, USA

The Idaho National Engineering and Environmental Laboratory (INEEL) is located in the Eastern Snake River Plain, which is a north-east trending structural basin about 320 km long and 80–110 km wide in south-eastern Idaho, USA (Fig. 9.13). This study site is located north-east of the area described in Section 9.5. The account presented below is a summary of a ten year study of this fractured rock aquifer using multiple tracers (Busenberg et al., 2001, Plummer et al., 2000). Concentrations of CFCs, $SF_6$, He and $^3H$ were used to estimate age of the young fraction of groundwater. These environmental tracers were introduced into the aquifer by natural recharge, return flow of irrigation water, and wastewater disposal at facilities at INEEL. The source of the water and the fraction of young water in the samples also were used to date the groundwater. The data indicate that most groundwater samples are mixtures containing young fractions of water recharged after 1950 and older regional groundwater. Many groundwater samples appear to be a binary mixture of local recharge and very old regional groundwater, and samples from most of the wells are about 20–50% young water that is about 14–21 years old.

Two limiting cases of recharge of the young fraction of groundwater were recognized in samples. Water recharged by rapid focused recharge through the thick unsaturated zone, and water recharged by slow infiltration through the

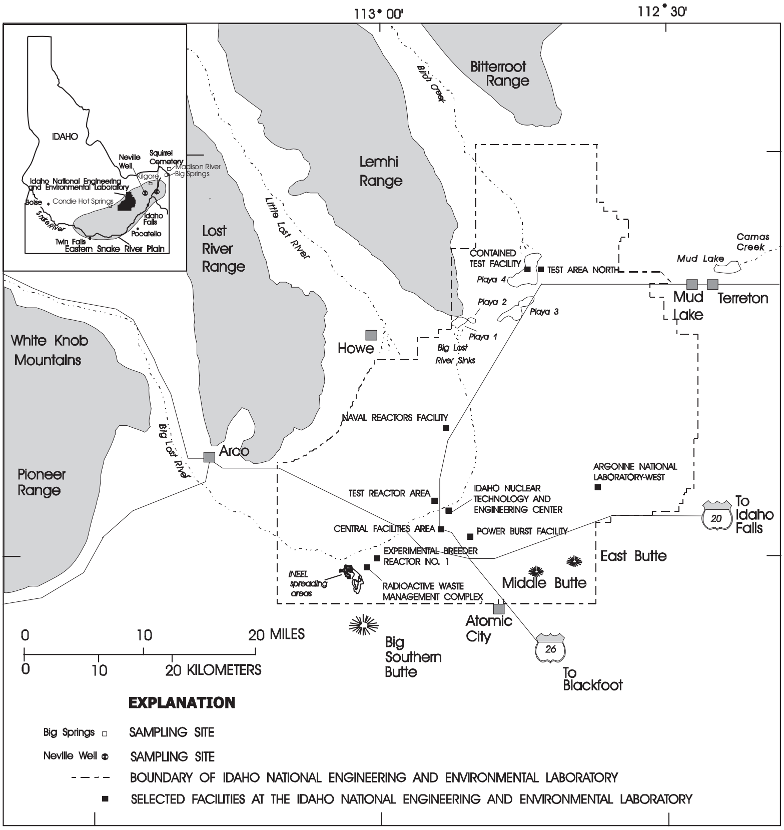


*FIG. 9.13. The location of the Idaho National Engineering and Environmental Laboratory is shown, indicating selected facilities.*

thick unsaturated zone. Water samples from wells that contain a young fraction of water that recharged in the central, western and south-western parts of INEEL are complex mixtures of regional groundwater, agricultural return flow, natural recharge, and artificial recharge from infiltration ponds and injection wells at the various facilities at INEEL. The chemistry and age of the young fraction of the groundwater samples varied greatly and could be correlated with distance from the source of recharge, depth of the open interval below the water table, length of the interval sampled, location of the well with respect to the different sources of recharge. Age increased with distance from the source of recharge and increased with depth below the water table. The young recharge water composes a very small fraction of the total volume of water in the aquifer, and this young water was mainly sampled because most of the wells are completed in the upper 15 m of the aquifer.

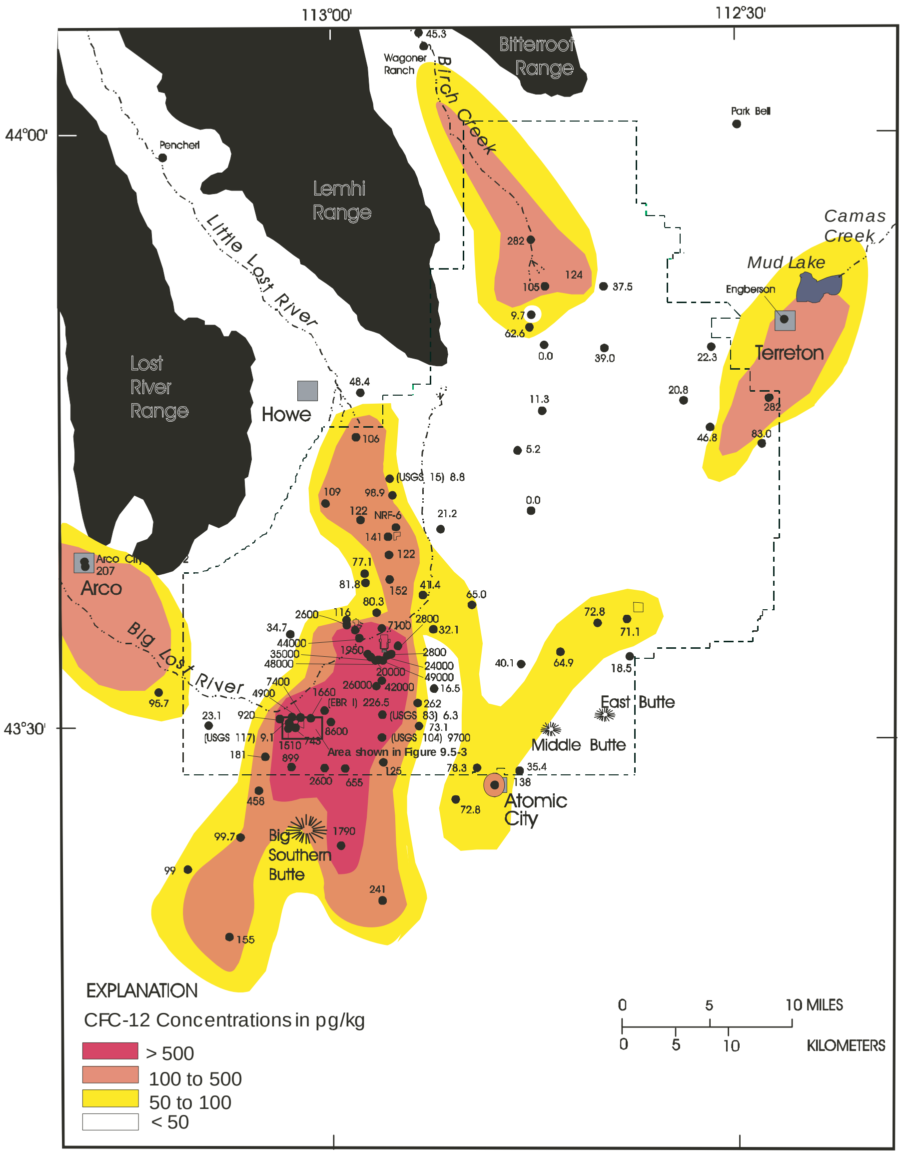


*FIG. 9.14. Concentration of CFC-12 in groundwater at the Idaho National Engineering and Environmental Laboratory and vicinity. Samples with greater than 400 pg/kg are waters with higher than air–water saturations of CFC-12.*

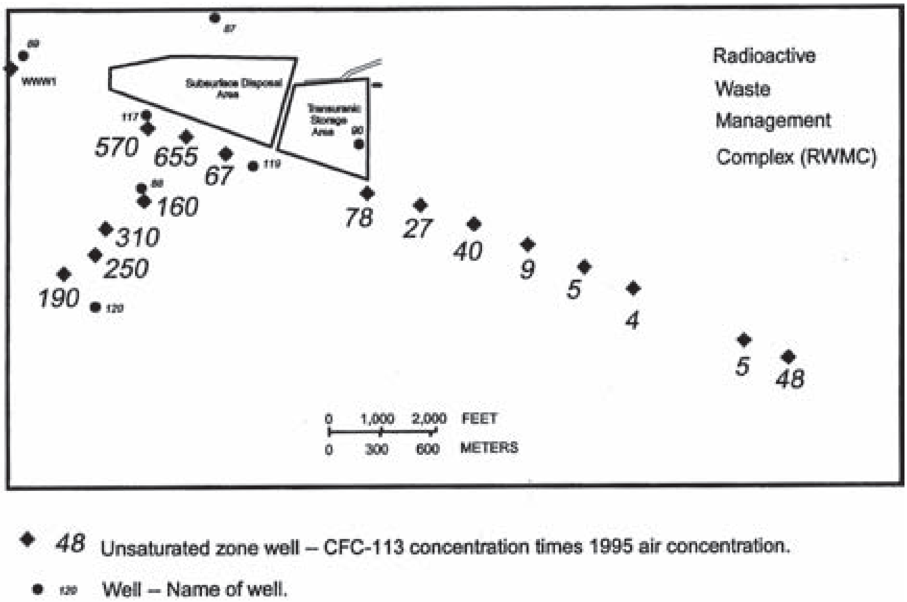


*FIG. 9.15. Soil air concentrations of CFC-113 near the Radioactive Waste Management Complex (INEEL). The numbers next to the piezometers represent how many times greater than the 1995 air mixing ratio (84 pptv) was the concentration of CFC-113 in the soil air. The unsaturated zone air was collected at a depth of 1 m. A large number of barrels full of waste organic oil and solvents were buried within the Subsurface Disposal Areas prior to the 1970s.*

A north-south preferential groundwater flow path was identified with flow velocities of about 3 m/d through the preferential flow path. Flow velocities decreased to 1 m or less per day outside this preferential flow path. Recharge temperatures calculated from dissolved gases were of about 6°C in the underflow of the streams and rivers and between 9 and 13°C in the infiltration recharge and the regional groundwater.

Groundwater near the Radioactive Waste Management Complex (INEEL) contained greater than atmospheric concentrations of CFCs. A large CFC-12 waste plume was recognized that originated near a nuclear fuel reprocessing plant and migrated more than 20 km from the waste injection well and waste infiltration ponds (Fig. 9.14).

Much greater than atmospheric concentrations of CFCs and other halocarbons were found near the Radioactive Waste Management Complex in soil gases obtained from a depth of 1 m (Figs 9.14 and 9.15). The higher than atmospheric concentrations of CFC-113 and other halocarbons were also found

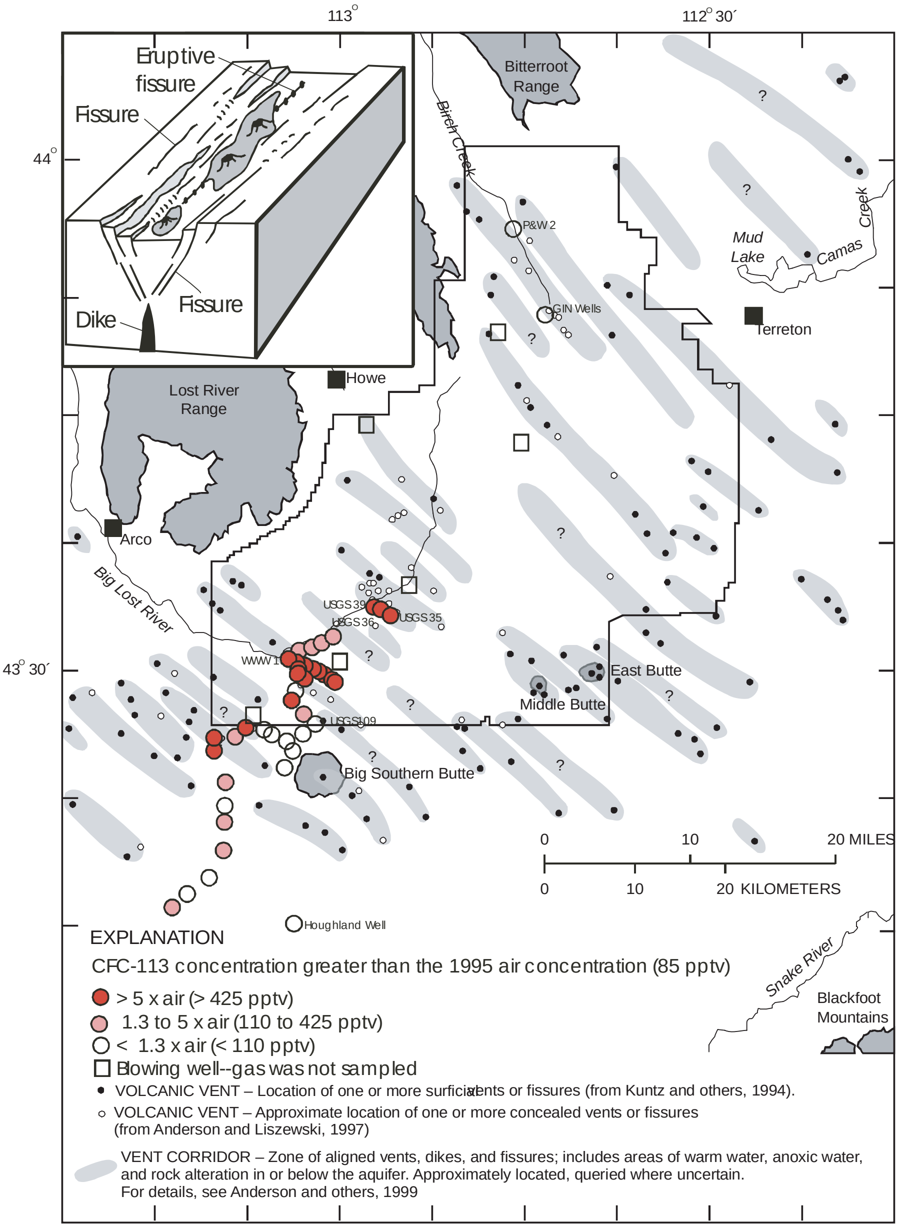


*FIG. 9.16. Distribution of CFC-113 in the unsaturated zone at INEEL. The insert is a conceptual model of a vent corridor and the associated fractures (Anderson et al., 1999). Most gas samples were collected from a depth of 1 m, a few samples were collected from gases blowing from around the annulus of wells.*

in the soils as far as 20 km south of the south-west corner of INEEL (Fig. 9.16). High concentrations of halocarbons also were found in unsaturated zone air blowing from the annulus of some wells in the south-western part of the Laboratory. The advective transport of CFCs and other halocarbons throughout the unsaturated zone probably occurs preferentially both vertically and horizontally along fractures associated with north-western trending vent corridors (Anderson et al., 1999). Barometric pumping appears to be the primary mechanism controlling the distribution of gases in the unsaturated zone in the south-western part of INEEL. Diffusion is the primary mechanism of gas transport in the northern and north-eastern part, in the areas that are covered by thick lacustrine and sedimentary playa deposits.

## 9.7. TRACING AND DATING LEAKAGE FROM THE DANUBE RIVER, HUNGARY

Groundwater systems can preserve long term records of past conditions that existed in recharge areas and are no longer available from other sources. Of particular importance are aquifers with low coefficients of dispersion because they can provide an excellent historical record of natural and anthropogenic changes in the atmosphere and at the recharge areas (Böhlke et al., 1997; Stute et al., 1997).

The Quaternary surficial gravel aquifer that underlies the Little Hungarian Plain is being recharged by bank infiltration from the Danube River in north-western Hungary (Deak et al., 1996). Horizontal groundwater flow is from the north-west to the south-east at a velocity of 530 m/a where the age of the groundwater was obtained from $^3H/^3He$ dating. The groundwater has preserved a unique forty year record of halocarbon contamination of the Danube River (Fig. 9.17). Analyses of waters along the flow path indicate that there was little or no contamination of the groundwater with halocarbons prior to the 1950s. Concentrations of CFC-12 rapidly increased in the early 1960s, then began to decrease from 1970 through 1995 to near air–water equilibrium concentrations. CFC-113 concentrations rapidly increased in the early 1960s, remained fairly high to about 1990 then gradually began to decline. The CFC-11 concentrations are near or below air–water equilibrium up to the mid-1980s, however, the 1993 CFC-11 concentrations in the Danube River and one groundwater recharged in 1990 exceed air–water equilibrium. It is believed that significant degradation of CFC-11 has taken place in the aquifer, and that the CFC-11 concentrations in the groundwater do not represent the level of this tracer in the river through time. Concentrations of methyl chloroform

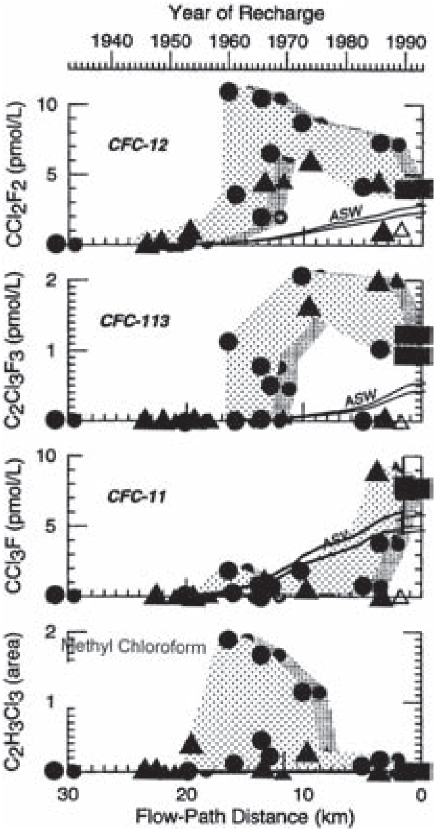


*FIG. 9.17. The figure shows concentrations of halocarbons in municipal wells (circles), monitor wells (triangles) and the Danube River (squares). The air saturation with water (ASW) is shown. In reducing waters CFC-11 and CFC-113 was completely or partially degraded. (From Böhlke et al. (1997).)*

rapidly increased in the early 1950s then rapidly decreased to very low concentrations in 1980. Several other halocarbons show similar histories, with low to non-detectable levels prior to the mid-1950s, then rapid increases in the mid-1960s and declines in concentration in the mid-1980s and 1990s.

The groundwater provides an excellent record of past contamination of the Danube River with halocarbons. The most likely source of the contamination of the Danube River may have been sewage and industrial discharges into the Danube and its tributaries upstream from the recharge areas. CFC concentrations in river water in 1993 were about twice the air–water equilibrium concentration and may represent air–water equilibrium with contaminated air (Frank et al., 1991; Oster et al., 1996).

## 9.8. VALLEY AND RIDGE SILICICLASTICS, PENNSYLVANIA, USA

In the Valley and Ridge geological province of Pennsylvania, USA, CFC and $^3H/^3He$ data were obtained from two arrays of nested piezometers located on the north limb of an anticline in fractured sedimentary rocks (Burton et al., 2002). About one half of the water samples had CFC-113 apparent ages that were younger than those based on CFC-11 and CFC-12, suggesting either binary mixtures of young and old fractions (Plummer and Busenberg 2000), or samples that are slightly contaminated with an excess of CFC-113. Many of the samples with low dissolved oxygen content were affected in part by denitrification (excess $N_2$) and/or methanogenesis (presence of dissolved $CH_4$). These low-oxygen samples may have lost a small fraction of their CFC concentrations as a result of microbial degradation, particularly with respect to CFC-11, which is the most susceptible of the three CFCs measured to biodegradation. Figure 9.18(a) compares the average calculated partial pressures of CFC-11 and CFC-12 to piston flow and binary mixing models. Most of the samples plot outside the range of expected concentrations of CFC-11 and CFC-12, and thus it is possible that the CFC-11 concentrations have been lowered by microbial degradation relative to CFC-12 (Fig. 9.18(a)). Because many of the samples contained low but detectible dissolved $O_2$, the apparent deficiency in CFC-11 may indicate that some mixing of aerobic (CFC-11 bearing) and anaerobic (CFC-11 degraded) waters occurred in the well bore during sampling, resulting in a low bias for CFC-11 relative to CFC-12. Regardless, no age information could be based on the CFC-11 results.

Most of the CFC-12 and CFC-113 mixing ratios plotted within the region bounded by binary mixing lines for mixing of young and old water and the line corresponding to the piston flow model (Fig. 9.18(b)). This indicates that microbial degradation may not have greatly affected the CFC-12 and CFC-113 concentrations. Two samples apparently contained a small excess of CFC-113 relative to CFC-12, and two other samples (not shown in Fig. 9.18(b)) were contaminated with CFC-113 and/or CFC-12.

Most of the water samples with CFC-113 and CFC-12 analyses that plotted within the boundaries of binary mixing and piston flow models were interpreted as binary mixtures of young and old (pre-CFC) water, however, much of the data could be interpreted using other mixing models. Other samples, especially along parts of the east transect arrays pre-date introduction of CFC-113 and ages were estimated as apparent piston flow ages based on the CFC-12 concentration. In mixtures, the piston flow ages provide an estimate of the maximum age of the young fraction, because the CFC concentrations have not been corrected for dilution with old water. If the fraction of young water is near 100%, the piston flow and mixing models yield identical results.

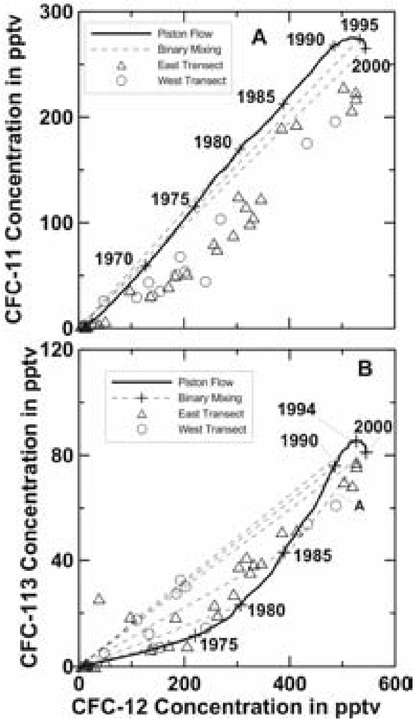


*FIG. 9.18. Comparison of CFC-11, CFC-12 and CFC-113 concentrations in fractured rock from the Valley and Ridge province of Pennsylvania, USA. Concentrations are given in pptv calculated from the measured concentration and recharge temperature based on $N_2$-Ar-Ne data: (a) CFC-11 appears to be degraded relative to CFC-12; (b) most of the CFC-113 and CFC-12 data can be interpreted using piston flow or binary mixtures of young and old water.*

Some samples containing CFC-113 and CFC-12 plotted very close to the line corresponding to piston flow (Fig. 9.18(a)), with recharge dates in the 1970s through the mid-1980s. This suggests that some of the samples are not mixed, or contain only very small fractions of old water. Several samples have CFC-12 and CFC-113 concentrations near that of modern water, or appear to be mixtures of modern water (1998–1999) with small amounts of water from the early to mid-1980s (line A on Fig. 9.18(a)). Although samples that plot within the bounds of piston flow or binary mixing on Fig. 9.18(a) were dated, they may still be affected by trace CFC contamination or minor CFC degradation.

The dating indicates that groundwater travelling on paths parallel to the dip direction of bedding plane parting has younger ages, or a greater component of young water, than does groundwater travelling along paths opposite to the dip direction. Mixtures sampled in transects where flow is parallel to bedding plane dip direction typically contained more than 75% of water with ages of 7–17 years, while samples from transects where flow is opposite to bedding plane dip direction were mostly beyond the CFC and $^3$H/$^3$He dating range. Accumulation of Na and terrigenic He suggested ages greater than 100 years in the old samples.

The uncertainties in the model CFC ages were estimated by varying the $N_2$-Ar recharge temperatures by ±2°C, and the analysed concentrations of CFCs by ±10%. These estimates of uncertainty in recharge temperature and analysed concentrations were typically twice the standard deviation of replicate analyses. The estimated uncertainty in recharge temperature introduced an average variation of ±1.6 years in the CFC-12 based apparent ages, and an average variation of ±0.9 years in the CFC-113 apparent ages. The ages of young water in binary mixtures calculated from the CFC-113/CFC-12 ratio had average uncertainties of ±0.4 years, and an uncertainty in fraction of young water in the mixture of ±5% for uncertainties in recharge temperature of ±2°C.

The estimated uncertainties in CFC concentrations of ±10% introduced an average variation of ±1.5 years in the CFC-12 based apparent ages, and an average of ±1.0 year in the CFC-113 apparent ages. The ages of young water in binary mixtures calculated from the maximum and minimum of the CFC-113/CFC-12 ratio had average uncertainties of ±2.7 years, and the average uncertainty of ±10.1% in fraction of young water in the mixture.

## 9.9. SUSCEPTIBILITY OF PUBLIC WATER SUPPLIES TO SHALLOW CONTAMINATION, VIRGINIA, USA

Approximately 40% of all water used for public supply in the USA is from groundwater sources (Solley et al., 1998). Under Section 1453 of the 1996 Amendments to the USEPA Safe Drinking Water Act (Public Law 104-182), states are required to develop source water assessment programmes to:

(1) Delineate the boundaries of the assessment areas in the state from which one or more water systems receive supplies of drinking water;
(2) Make an inventory of potential sources of contamination within the assessment areas;
(3) Evaluate the susceptibility of the public water supplies in the delineated areas to contamination.

As a component of the Source Water Assessment Program for the state of Virginia, the U.S. Geological Survey, working with the Virginia Department of Health, conducted a study of the intrinsic natural susceptibility of regional aquifers in the state that serve as public water supplies (Commonwealth of Virginia, 1999; Nelms et al., 2002; 2003). More than 100 wells and springs in the fractured rock and unconsolidated aquifers of Virginia were sampled between 1999 and 2000 for a suite of environmental tracers, including CFCs, $^3H/^3He$, $^3H$ and $SF_6$. The fundamental premise of the study was that the tracer information can be used to determine the susceptibility to contamination of aquifers used for drinking water supplies. A CFC concentration greater than 5 pg/kg was used as a threshold to indicate that parts of the aquifer sampled have a component of young water (younger than 50 years) and, therefore, are susceptible to near surface contamination. More than 95% of the samples from the fractured rock aquifers contained concentrations of CFCs above this threshold. No relation between the presence of CFCs and depth of the wells (36–290 m) or water bearing zones (12–290 m) was evident. Several samples contained concentrations of CFCs in excess of the air–water equilibrium, indicating a contaminated shallow source. Other volatile halocarbon compounds were qualitatively identified in water samples during the CFC analysis by purge and trap gas chromatography with an ECD. Although the concentrations of all VOCs detected are below drinking water standards, the presence of CFCs and other halocarbon compounds indicates the susceptibility of the fractured rock aquifers to contamination. In contrast, water samples from 31 wells in the confined unconsolidated aquifers of the coastal plain of Virginia having water bearing zones of depths (28–344 m) similar to those in the fractured rock aquifers did not contain CFCs and had adjusted radiocarbon ages older than 10 000 years. Figure 9.19 compares GC–ECD chromatograms of water samples from a deep and shallow public supply well in coastal plain sands of Virginia, indicating that shallow wells in the coastal plain sands are susceptible to contamination but those in deep sands are not.

For comparison, Fig. 9.20 shows a chromatogram from a public supply well with total depth similar to that shown for the deep well in Fig. 9.19, but in fractured rock. This chromatogram is representative of water from most public supply wells sampled in Virginia as a part the USGS/VDH Virginia Aquifer Susceptibility Study (Nelms et al., 2002; 2003).

Results from this study indicated that CFCs and other environmental tracers measured in groundwater samples provide a useful tool for classifying aquifers in terms of susceptibility to contamination and that virtually all wells and springs in the fractured rock aquifers of Virginia are susceptible to contamination.

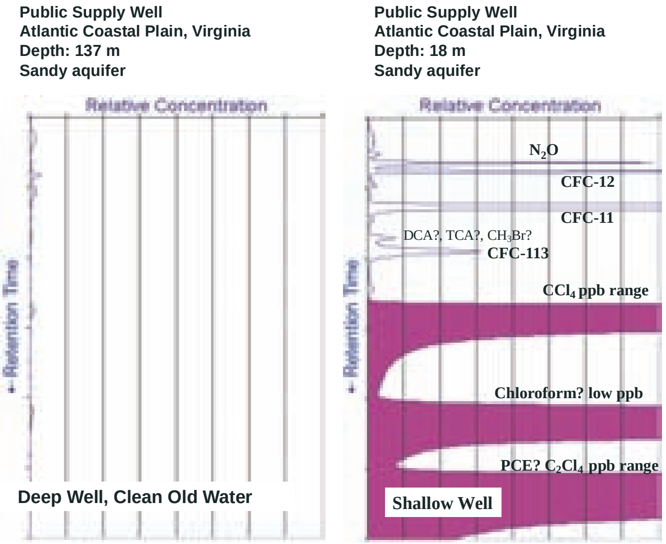


*FIG. 9.19. Comparison of two GC–ECD chromatograms of water from public supply wells in a sandy aquifer in the Atlantic coastal plain of Virginia. The sample on the left is from a depth of approximately 126–134 m in coastal plain sands and is virtually free of CFCs and other halocarbons. The sample on the right is from a screened interval of 13.4–18 m depth and contains all three CFCs and significant detections of other halocarbon compounds.*

Approximately 50% of the population in the USA and 97% of the population in rural areas of the USA rely on groundwater as a source of domestic supply (Mlay, 1990). Groundwater, however, is subject to many potential sources of contamination in urban, suburban and rural areas. Contamination of groundwater with VOCs is of particular concern because many VOCs are known or suspected carcinogens. In a study of low level detections (pg/kg) of selected halogenated VOCs in untreated groundwater samples used for drinking water, at least three different VOC compounds were detected in 100% of the water samples collected from 413 domestic and public supply wells from throughout the USA (Shapiro et al., 2004), indicating that most drinking water from domestic and public supply well groundwater sources in the USA already has at least a trace imprint of human activity. A previous study of drinking water wells in the USA, including domestic and public supply wells, primarily in rural areas (Squillace et al., 2002), detected at least one VOC, or pesticide compound, or anthropogenic nitrate in 70% of wells, with a minimum detection limit of ppb for VOCs and pesticides. Most of the VOC concentrations reported by Shapiro et al. (2004) were only qualitatively

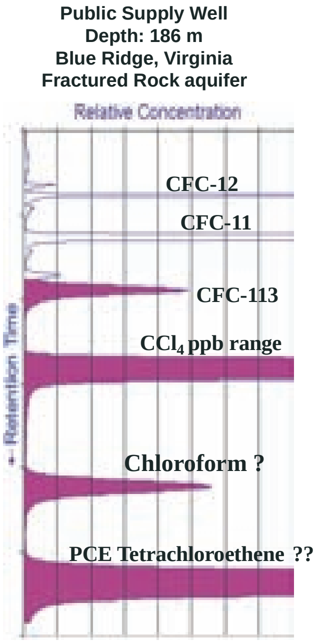


*FIG. 9.20. The GC–ECD chromatogram of a water sample is shown from a public supply well in fractured rock in the Blue Ridge province of Virginia. The well has a total depth of 186 m with 175 m of casing and a single water bearing fracture at 186 m.*

assessed, but were very low, and none were above any existing drinking water standards.

The Shapiro et al. (2004) study focused on drinking water wells with no obvious nearby sources of VOC contamination, and related VOC detections and concentrations to the apparent CFC-12 age of groundwater for the past sixty years. The very low concentrations of some of the VOCs were attributed to atmospheric sources, but VOC concentrations were generally higher in the younger groundwater than possible for atmospheric inputs alone. The study of Shapiro et al. (2004) indicates that there has been an increase in VOC contamination of groundwater used for drinking water in the USA, from the middle of the twentieth century to the present. The likely sources of these contaminants are spills, leaking underground storage tanks, landfills and other mechanisms associated with the widespread manufacture, use and disposal of these compounds (see Chapter 4, Section 4.1) and, to a lesser extent, atmospheric sources. The high frequency of detection of VOCs in drinking water sources (Shapiro et al., 2004) can be, at least in part, attributed to well construction practices. Wells constructed for production purposes usually intercept large intervals of aquifers, including relatively shallow depths that are more likely to be affected by anthropogenic sources than deep groundwater. There is also potential for drawdown of shallow groundwater around the annulus of wells with high capacity pumps.

## 9.10. EXAMPLES OF CFCs IN SURFACE WATERS, USA

Some detailed reports of CFC concentrations in surface waters can be found in Busenberg and Plummer (1992), Clark et al. (1995), Böhlke et al. (1997), Plummer et al. (1998) and Plummer et al. (2000). Some of these results were discussed in Chapter 4, Section 4.1 regarding CFC contamination sources to aquifers.

In March 1991, surface waters were sampled in central Oklahoma, USA, to evaluate the hypothesis that sewage returns and sewage disposal ponds are major sources of CFCs in natural waters. Another objective of this survey was to determine if there was any correlation between the previously identified groundwater anomalies and surface water contamination. The rivers and streams were sampled for CFCs upstream and downstream from major sewage treatment plants; the results are given in Busenberg and Plummer (1992).

Of the 57 sites sampled, 53% had elevated concentrations of CFCs and all but two of the contaminated sites were downstream from sewage disposal ponds and sewage returns into rivers and streams (Fig. 9.21). The two other contaminated sites were lakes, and these sites were located next to picnic areas. All surface water sites upstream from sewage treatment plants and sewage returns into streams were not contaminated with CFCs. Two sites downstream from sewage returns were visited on two separate occasions weeks apart, and were found to be significantly contaminated on both occasions.

A match was found between the Oklahoma City CFC-12 and CFC-11 surface water anomaly and the groundwater anomaly (Fig. 9.22). Similar matches were also found between surface and groundwater anomalies at other locations in the study area. The close matches between surface water and groundwater anomalies suggest that contaminated river and stream water may recharge the alluvium and terrace deposits of central Oklahoma. The recharge may occur through seepage from disposal ponds but may also occur during periods of flooding when contaminated water moves from the river into bank storage. The contaminated water then reached some of the alluvium and terrace deposit wells.

Of the surface water samples, 46% appear not to have been contaminated with CFCs and 14% of the surface water sites had concentrations of CFCs at or

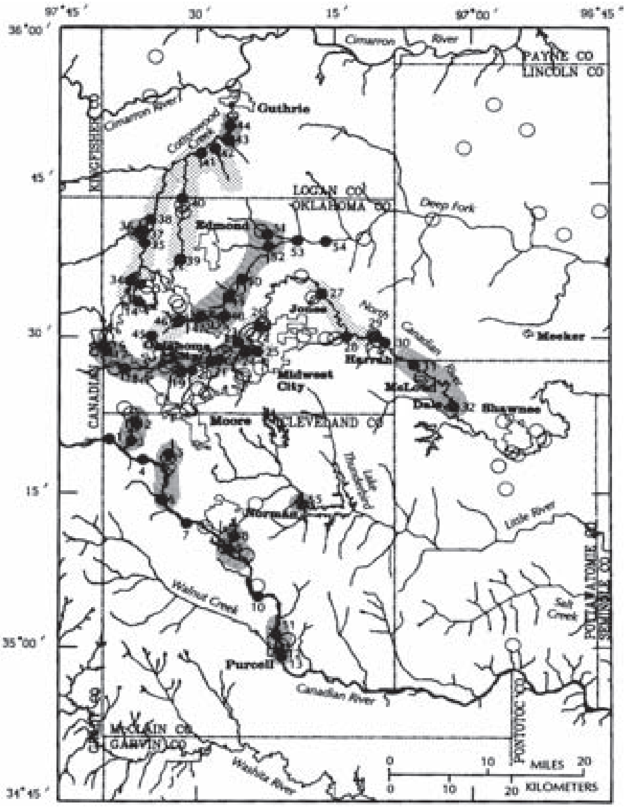


*FIG. 9.21. Concentrations of CFC-12 in central Oklahoma surface waters are shown. Solid circles are the location of sites sampled in March 1991 and the open circles are the location of sewage treatment plants or sewage returns into streams. Hatched areas represent locations where the CFC-12 concentrations were significantly higher than air–water equilibrium. The stippled areas represent surface water concentration significantly lower than air–water equilibrium, at all other locations, the surface water was in equilibrium with air. (From Busenberg and Plummer (1992).)*

near equilibrium with air. In the rest of the samples, both the CFC-12 and CFC-11 concentrations were significantly lower than the air–water equilibrium concentration. All these sites are located in rural areas and the less than air equilibrium concentrations may represent locations where there is significant discharge of old groundwater to the stream.

Several investigations report time series of CFC concentrations in streams and rivers. Monthly samples of a river water in south Georgia, southeast USA, over a 13 month period in 1992–1993 showed that CFC-113 was

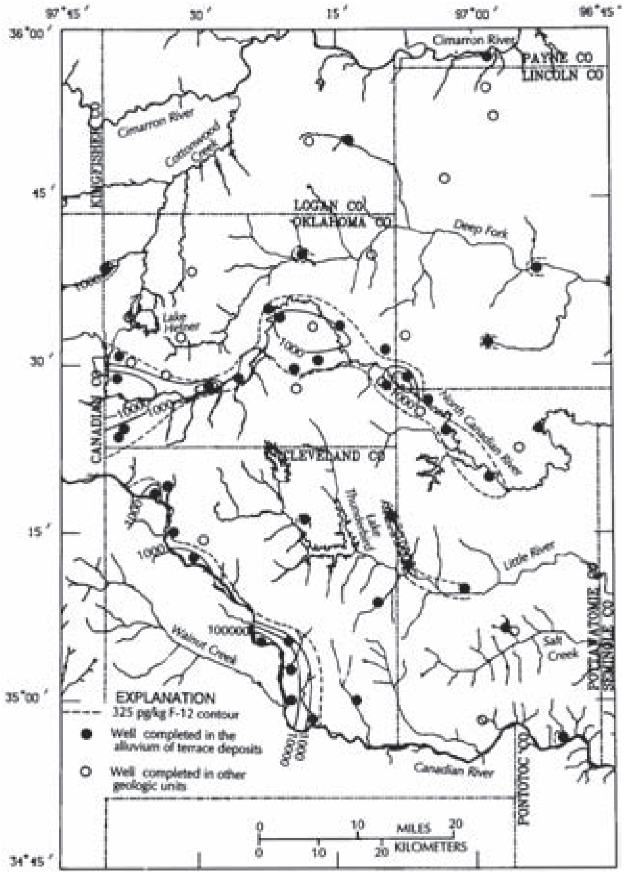


*FIG. 9.22. The concentration of CFC-12 in groundwater in central Oklahoma is indicated. Note that the contours are logarithmic. The dashed lines represent air–water equilibrium. There is a close correlation between surface water anomalies and groundwater contamination. (From Busenberg and Plummer (1992).)*

always near saturation (0.9–1.5 times saturation); CFC-12 was typically near saturation (1.0–1.5 times), but with occasional periods of oversaturation of nearly six times, and CFC-11 was usually oversaturated by 5–20 times, with one sample 137 times saturation (Plummer et al., 1998b). CFC-11, CFC-12 and CFC-113 concentrations in 104 samples of surface water from the Rio Grande and associated drains and laterals near Albuquerque, New Mexico, averaged 109 ± 28, 149 ± 74, and 112 ± 19 (± 1$\sigma$)% of the respective air–water equilibrium values over a five month period in 1997 (Plummer et al., 1997; 2004).

Agricultural irrigation water in canals diverted from the Snake River in southern Idaho, 1995, were mostly near saturation with air values of CFC-12 and CFC-113, but contained CFC-11 excesses that ranged from factors of 1.2 to nearly 12 times saturation (Plummer et al., 2000). The CFC-11 contaminated irrigation water probably contributes to an observed excess of CFC-11 in groundwater from irrigated areas in southern Idaho (see Section 9.5 and Chapter 4, Section 4.2).

These studies show that, once contaminated, surface waters can be slow to re-equilibrate with air. The relatively low diffusion coefficients for CFCs and the rate of mixing in surface waters contribute to the slow exchange of CFCs between surface waters and air. Along reaches of streams that receive net discharge of groundwater (gaining streams), the CFC concentrations of surface water can reflect that of the local and upstream groundwater sources. If old water discharges to streams (Böhlke and Denver, 1995; Modica et al., 1998;), relatively low CFC concentrations can be found in stream samples that persist over kilometre scale distances due to the slow re-equilibration with air (Solomon et al., 1997). Along reaches of streams where there is net loss of surface water to an aquifer, groundwater CFC concentrations can be affected by the CFC concentration in the stream at time of recharge (see, for example, Böhlke et al., 1997), depending on relative saturation state of the river. Plummer et al. (1998b) reconstructed CFC-12 concentrations in groundwater recharged from a river and showed that in most cases the historical water in the river, from a rural area in Georgia, was near solubility equilibrium with air. It is more likely that in urban areas or in areas downstream of urban areas, historical concentrations of CFCs in rivers were contaminated (Busenberg and Plummer, 1992; Clark et al., 1995; Böhlke et al., 1997). Consequently, because of contamination, it is often not possible to date river water after it has seeped into groundwater systems.

## 9.11. FRACTURED ROCK AQUIFERS, CLARE VALLEY, SOUTH AUSTRALIA

The Clare Valley, located approximately 100 km north of Adelaide, Australia, lies within the Northern Mount Lofty Ranges, and forms part of the Adelaide geosyncline. The geology consists of low grade metamorphic, folded and faulted rocks of Proterozoic age. Rock types within the Clare Valley consist primarily of shales, siltstones, sandstones, dolomites and quartzites. The area receives a mean annual rainfall of approximately 650 mm. Groundwater stored within the fractured rock aquifers is of variable quality (200–8000 mg/L total

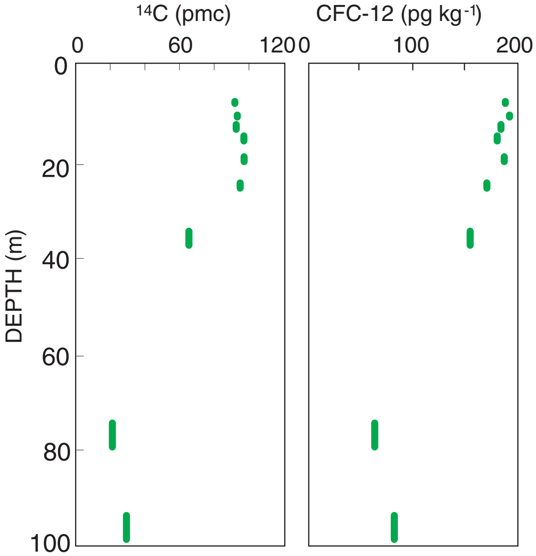


*FIG. 9.23. Vertical profiles are shown of $^{14}$C and CFC-12 obtained from a piezometer nest installed in Mintaro Shale.*

dissolved solids), and is used for stock and domestic supplies, and for irrigation of vineyards.

A piezometer nest has been installed for groundwater sampling in the Mintaro Shale, located on the west limb of the Hill River syncline, where strata dip at high angles to the east, with the majority of fractures and bedding planes oriented vertically. At this site, a 200 mm diameter bore was drilled to 100 m depth, and a 250 mm bore to 26.4 m depth. A nest of six 50 mm PVC piezometers was installed in the 250 mm bore, and four 50 mm piezometers in the 200 mm bore. (The two bores were spaced only 5 m apart.) Screen lengths range from 0.5 to 6 m, being longer in the deeper piezometers. Gravel packs were used around the screens, which were separated using cement plugs. The nest of 10 piezometers allows groundwater samples to be collected from depths between 8 and 100 m below the land surface.

Cook and Simmons (2000) used $^{14}$C and CFC-12 concentrations to estimate vertical flow rates at the Pearce Road site, by assuming that flow occurred through vertical, planar, parallel fractures and that matrix properties were spatially uniform (Fig. 9.23). In the case of a constant source, conservative tracer, subject to radioactive decay, concentrations within the fracture, $c$, are related to the vertical flow rate within the fractures, $V_w$, by:

$$\ln\left(\frac{c}{c_0}\right)=\frac{-\lambda z}{V_w}\left[1+\frac{\theta_m D^{1/2}}{b\lambda^{1/2}}\tanh\left(BD^{-1/2}\lambda^{1/2}\right)\right] \tag{9.2}$$

where $c_0$ is the initial concentration, $b$ is the fracture half-aperture, $B$ is the fracture half-spacing, $\theta_m$ is the matrix porosity, $D$ is the diffusion coefficient within the matrix, $\lambda$ is the decay constant and $z$ is depth. Equation (9.2) can be used to relate $^{14}$C concentrations within fractures to vertical groundwater flow rates, where $\lambda = 1.21 \times 10^{-4}\cdot a^{-1}$ is the decay constant for $^{14}$C. Equation (9.2) also approximates the relationship between $V_w$ and CFC-12 concentration, where the decay constant, $\lambda$, is replaced by the exponential growth rate for CFC-12, $k \approx 0.06\ a^{-1}$.

Expressed in terms of apparent age gradients, Eq. (9.2) becomes:

$$V_w=\left[1+\frac{\theta_m D^{1/2}}{b\lambda^{1/2}}\tanh\left(BD^{-1/2}\lambda^{1/2}\right)\right]\Big/\left[\frac{\delta t_a}{\delta z}\right] \tag{9.3}$$

where $t_a$ is the apparent CFC-12 (or $^{14}$C) age.

The vertical CFC-12 age gradient apparent in the upper six piezometers (i.e. between 5 and 25 m depth) is approximately $\delta t_a/\delta z = 0.1\ a\cdot m^{-1}$ (2 years over 20 m). A mean fracture spacing of $2B = 0.16$ m and hydraulic conductivity of $K = 0.1\ m\cdot d^{-1}$ was assumed, based on outcrop measurements and single well pumping tests, respectively. These values together imply a mean fracture aperture of $2b = 64\ \mu m$. Values for matrix diffusion coefficient and matrix porosity were assumed to be $D = 10^{-4}\ m^2\cdot a^{-1}$ and $\theta_m = 0.02$, respectively. Thus $V_w = 256\ m\cdot a^{-1}$, and hence $R = 102\ mm\cdot a^{-1}$. A sensitivity analysis on this calculation showed that estimated recharge rate is particularly insensitive to the estimated hydraulic conductivity. In particular, an order of magnitude error in the hydraulic conductivity would result in a factor of two error in the estimated fracture aperture and minimum fracture velocity, but less than a 5% error in the estimated recharge rate. The estimated recharge rate is sensitive to the fracture spacing, and to the matrix porosity and matrix diffusion coefficient (Cook and Simmons, 2000).

## 9.12. REMEDIATION TIMESCALE FOR NITRATE POLLUTED GROUNDWATER AT GROSSRINDERFELD, GERMANY

Twelve wells and springs in the vicinity of a water pump station near Grossrinderfeld, Germany, were sampled for CFC and nitrate concentrations. The nitrate concentration in this area varied between about 5 and 70 mg/L. The

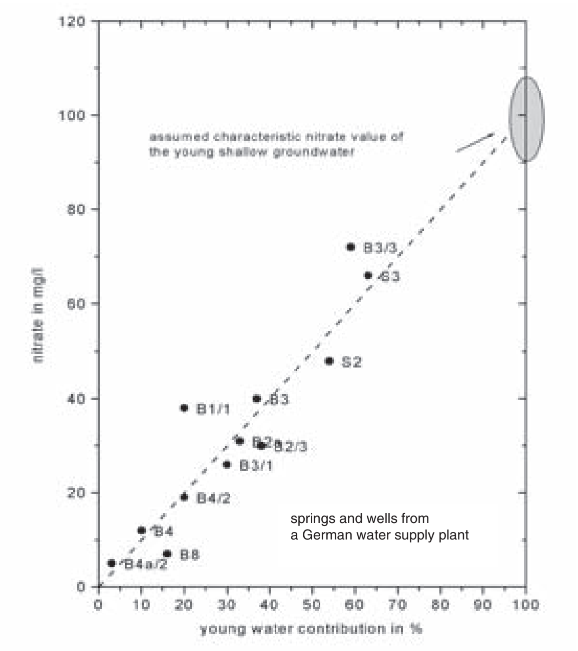


*FIG. 9.24. Relationship shown between nitrate concentration and per cent young water as determined using CFC data with a binary mixing model.*

main question concerned future scenarios for nitrate concentrations in the pumped water, depending on remediation measures to be taken to reduce nitrate concentrations below the allowed limit of 50 mg/L for drinking water.

The measured CFC concentrations of the groundwater were interpreted using two very simple model approaches. First, a binary mixing model was applied with the end members of: (a) young groundwater having ages between 0 to 10 years; and (b) old, CFC-free groundwater. On the basis of the measured CFC concentration, the contribution of the young water component in the water sample could be calculated. Figure 9.24 shows a good correlation between this parameter and the nitrate concentration, implying that the variation in nitrate concentration could be explained by the extent of young water admixture. Extrapolation of the regression line suggests that the recent shallow groundwater could have a typical value of about 100 mg/L nitrate.

The second approach assumes an exponential model (see Chapter 6, Section 6.1). Using the measured CFC concentration, the mean residence time of the water can be derived. The plot of calculated mean residence times against nitrate concentration shows decreasing nitrate with increasing mean

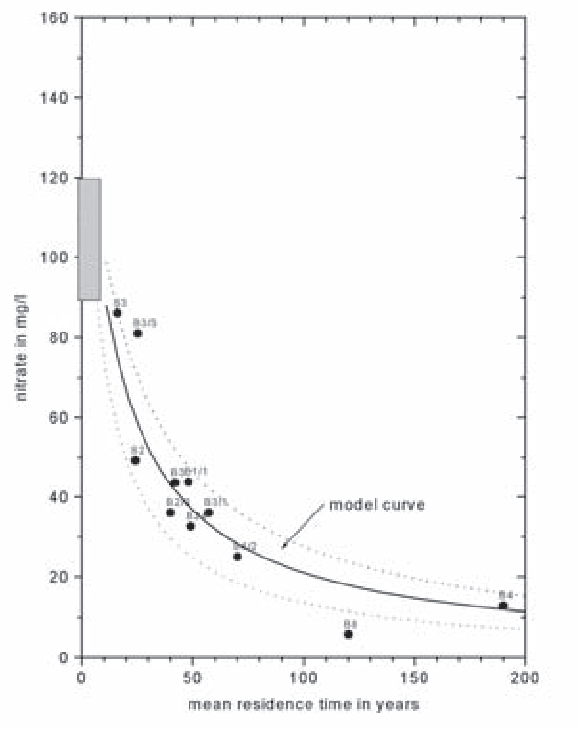


*FIG. 9.25. Nitrate concentration as a function of the mean residence time. The model curve is for an exponential model (see Chapter 6). The mean age for samples was compiled using CFC data.*

residence time (Fig. 9.25). The solid line shows the relationship between CFC derived mean residence time and nitrate concentration in aquifer outflow that would be predicted using an exponentially increasing nitrate input, scaled to a reasonable value of 100 mg/L for modern recharge. The broken lines show the same exponential increase, but scaled to modern recharge concentrations of 90 and 120 mg/L. Again the actual measurement data fit very well to these model assumptions for the temporal structure of the nitrate input (exponential increase) and the distribution of the groundwater arrival time (exponential mixing model).

In this case, both models are acceptable approximations for the real flow pattern and provide a first insight for a prediction of future nitrate values to be expected for the different wells and springs.

An example for such a prediction for future nitrate concentrations in a well is given in Fig. 9.26 (from a well of another investigation area). It shows the

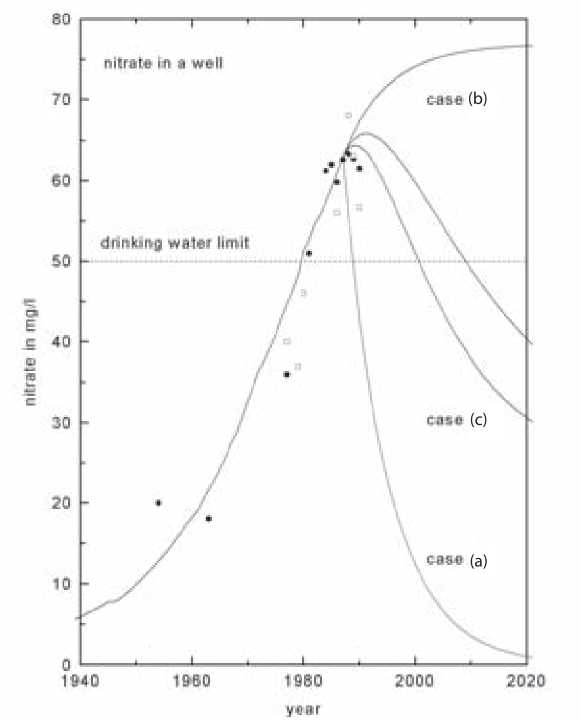


*FIG. 9.26. Model depicting nitrate concentrations as a function of time, based on an exponential model with a mean residence time of 8 years, based on a nitrate input function that increases approximately linearly between 1940 and 1988. Cases (a), (b) and (c) show predictions for nitrate concentrations in aquifer outflow based on different nitrate input scenarios: case (a) nitrate input decreases to zero immediately (1988); case (b) continued nitrate input; case (c) exponential decrease of nitrate input to the level back to the 1960 concentration, with timescales of 10 years (lower curve) and 20 years (upper curve). From Oster et al. (1996).*

calculated long term increase of nitrate in a single well having a mean residence time of about 8 years (exponential mixing). A good agreement exists between the exponential model and the measured historical nitrate data. Assuming the validity of this model for the given well nitrate values, simulations can be undertaken about the future development of nitrate concentrations. This can be done, for example, if the following assumptions relating to the future nitrate input in the groundwater system are made:

- Case (a): the nitrate input stops immediately;
- Case (b): continued nitrate input at the level of 1988;

— Case (c): the nitrate input drops over a timescale of 10 or 20 years, respectively, down to the 1960 value.

The completely unrealistic case (a) of no further nitrate input shows only the time span the system will react in decreasing nitrate concentrations in the well. In case (b), the nitrate concentration of the well will reach a steady state value of about 70–80 mg/L nitrate within the next 10–20 years. As there are some actions taken in the recharge area to reduce the nitrate input into the groundwater, case (c) describes what perhaps could happen as the most realistic case. This scenario indicates decreasing nitrate concentrations reaching the 50 mg/L drinking water limit in about one to two decades, depending on the timescale necessary to reduce the nitrate input into groundwater to 15 mg/L. For further examples, see Böhlke (2002) who considered a wide range of applications of environmental tracers to agricultural contamination studies.

## 9.13. TRACING OF CONTAMINATED SHALLOW GROUNDWATER IN A DEEP AQUIFER SYSTEM, GERMANY

The area of investigation is situated at the edge of the Rhine River valley and the mountains of the Palatian Forest in the western part of Germany. Some decades ago, the drinking water was mainly provided by springs from the forest valleys (nitrate below 5 mg/L). Owing to the increasing population, wells were drilled to satisfy the water demand. The groundwater from the shallow, sandy aquifer located in the intensive farming area (wine, vegetables) typically has an increasing nitrate concentration — in the particular case of the Maikammer community up to about 120 mg/L nitrate (see Fig. 9.27). The task of this investigation was to check the possibilities of minimizing the nitrate load in order to safeguard the independent, decentralized water supply of the community for the future.

Owing to the lack of deep piezometers, it was necessary to get more information from the well itself. A depth specific, low budget sampling technique with two pumps shows that below 80 m the water is almost free of nitrate and very low in CFCs and tritium as well. The mean inflow of nitrate rich water occurs at a comparatively great depth between 60 and 80 m below surface (well Rans 2). In this deep interval the environmental tracers (CFCs, tritium) also have significant concentrations, so the groundwater must contain post-1950 recharge. It is noteworthy that the CFC-11/CFC-12 ratio is different from the atmospheric input. A CFC excess, that is a concentration higher than atmospheric values, with rather high CFC-11 (> 50 pmol/L) and moderately high CFC-12 (about 5 pmol/L) concentrations were found upstream in an old inoperative well, Rans 1, and also in a newly drilled shallow piezometer.

The CFC-12 and nitrate data at the various sampling sites fit nicely with a binary mixing approach with two characteristic end members having high and low nitrate concentration (see Table 9.1 and Fig. 9.28). These findings indicate that the nitrate and CFC-rich waters originate from the same shallow groundwater regime. The question arises as to what mechanism allows the penetration of shallow, nitrate-rich groundwater characterized by a CFC excess to the deep aquifer. Two causes seem possible: (a) geological 'windows' connect the shallow and deep aquifer layers; or (b) the old, inactive well Rans 1 has acted as a hydraulic window over the years.

As a consequence of these findings, the upper screens of the well Rans 1 were sealed to about 60 m below surface. This resulted in an immediate dropping of the nitrate concentration from 120 to about 60 mg/L. But the stable end member-2 nitrate concentration of less than 30 mg/L was not affected at

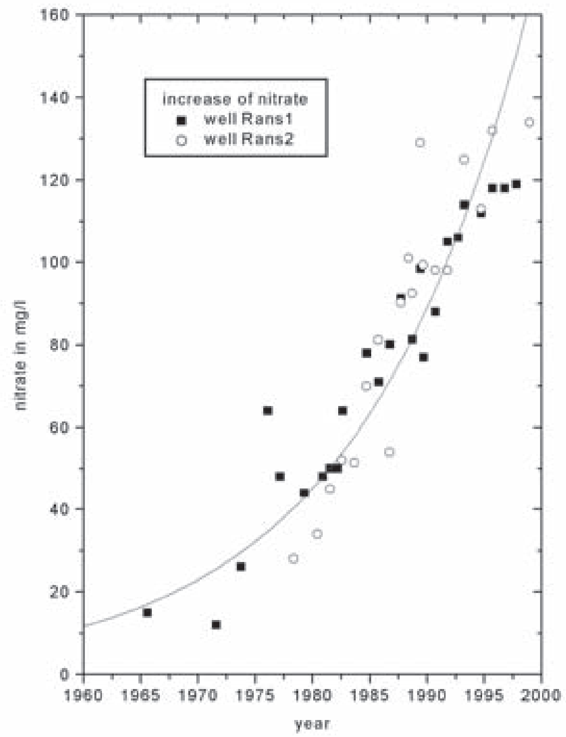


*FIG. 9.27. Time series of nitrate concentrations in two wells in Maikammer, Germany.*

TABLE 9.1. CHARACTERISTICS OF END MEMBER WATERS

| End member 1:<br>shallow groundwater<br>(< 60 m below surface) | End member 2:<br>(> 60 m below surface) |
|---|---|
| Anthropogenic influenced with:<br>— CFC-12, CFC-11 conc. in excess<br>— CFC-113 conc. near detection limit<br>— Nitrate conc. about 120 mg/L | Natural properties:<br>— CFC-12, CFC-11 low concentration<br>— CFC-113 conc. near detection limit<br>— Nitrate conc. about 10 to 30 mg/L |

this time. As the CFCs showed further excess values, it can be concluded that residual shallow water masses still play an important role in the deep aquifer system.

A confirmation of this theory is provided by the temporal variation of the CFC and nitrate concentration with pumping (following a resting phase of the well). In analogy to a relaxation process, the concentration of nitrate (and

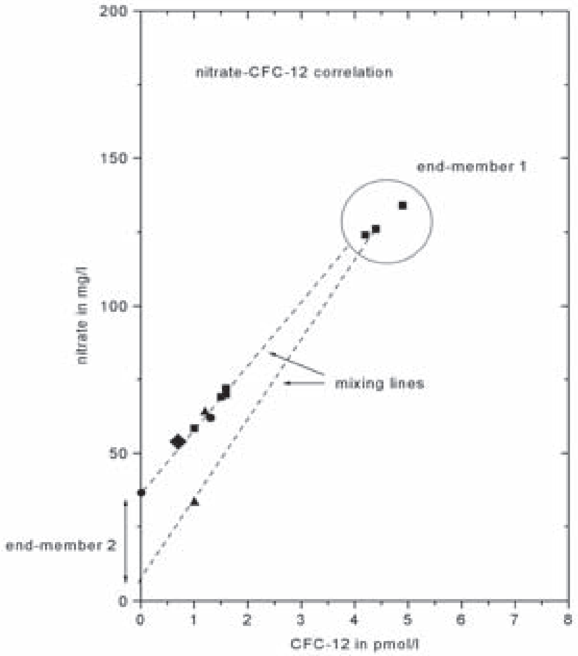


*FIG. 9.28. Water mixing scenario and nitrate CFC-12 content of assumed end members.*

CFCs) increases until reaching a steady state value of about 60 mg/L nitrate. This behaviour is interpreted as the contribution of the residual water component increasing while the pump is working. Three pumping tests in the last two years show that the timescale of the relaxation process increases from a long term point of view. Owing to the natural groundwater flow and mixing processes, the contribution of the residual water masses decreases with time. This explanation indicates that through the elimination of the hydraulic window (well Rans 1), the natural remediation of the deep aquifer leads to a long term decrease in the nitrate contamination.

Despite a low budget investigation and the lack of deep piezometers, this example shows that just a few CFC measurements are sufficient to detect an anomalous water component in a deep groundwater. Moreover, the results point to the basic hydraulic processes responsible for the contamination of the deep aquifer system. A knowledge of this mechanism in ideal situation even permitted the elimination of the deep penetration and the subsequent remediation of the deep aquifer system.

In general, these examples show that owing to the low detection limit and the almost ideal transport properties of the CFCs in groundwater, the site-

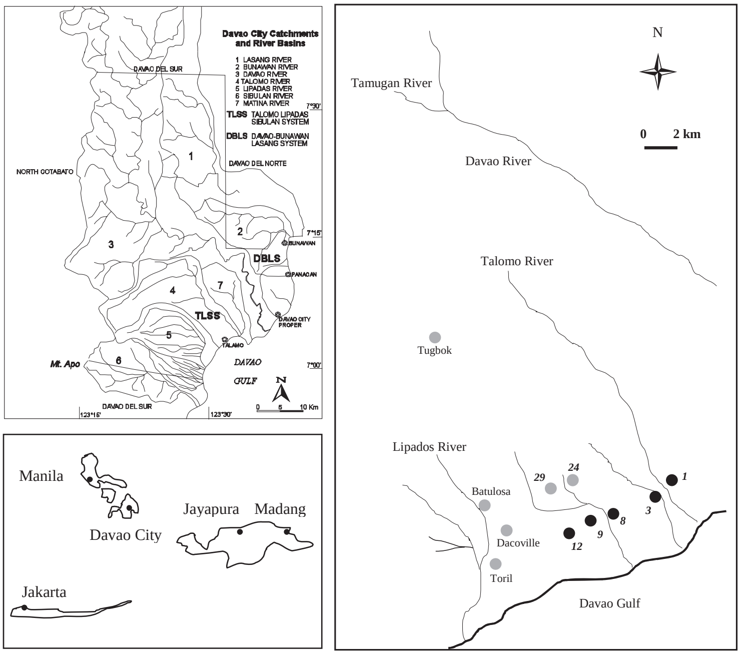


*FIG. 9.29. Map showing the study area and location of wells.*

specific CFC excess is a sensitive indicator for identifying unfavourable water components in the subsurface. Besides drinking water management, such features are also useful for monitoring mineral water or brewing applications. In addition, landfill–groundwater and surface–groundwater interaction are possible areas where similiar investigations could be of benefit. It seems that, especially in densely populated countries, the CFC excess is of similar importance to the CFC age dating tool under normal conditions.

## 9.14. EQUATORIAL LOW TRITIUM ACTIVITY REGION IN MINDANAO, PHILIPPINES

Davao City is located in the south-eastern part of the island of Mindanao, southern Philippines (see Fig. 9.29). Groundwater is the most important source of fresh water in the region and supplies 97% of the Davao City water requirements. Significant urban growth in the past two decades is reflected in the remarkable rise in water production, from 27 000 $m^3$/d in 1981 to about 200 000 $m^3$/d in 2001. Rapid urbanization without adequate zoning control poses long term environmental problems. For example, there is no existing sewerage system for Davao City. Domestic wastewater flows commonly through a series of septic tanks to settle the solid wastes. Overflow water from these tanks flows directly into the storm drainage system which discharges into the rivers and eventually into the Davao Gulf. The city's urban and development areas are concentrated on a narrow coastal strip averaging 5 km in width and extending 56 km along the Davao Gulf. It is also in the coastal area where most of the production wells are located and where heavy abstraction is concentrated. In view of this situation, water management issues, particularly those concerning recharge and vulnerability of the groundwater to pollution, need to be addressed.

The study area is within the Talomo-Lipadas-Sibulan-System, which has an upper unconfined aquifer composed of sand, gravel and occasional boulders that are tapped by shallow domestic wells. The deeper aquifer is being tapped by wells of the Davao City Water District. Many wells are constructed with filter screens of about 60 m length, tapping depths between 30 and about 120 m below the land surface. The lithology indicates that most of the wells are in sand and gravel layers with no clear confining layer on the top, but with the occurrence of some clay lenses. No data are available about the lithology at depths of more than 150 m. The city is traversed by two major river systems, the Davao River and Talomo River. These two river systems flow through the city and carry domestic, solid and liquid wastes to the Davao Gulf south of the city.

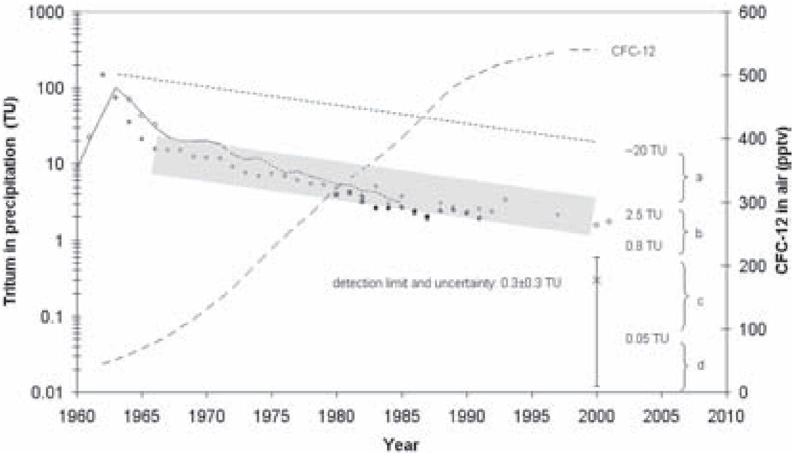


*FIG. 9.30. Semi-log plot of the smoothed record of $^3H$ in precipitation in the study region and CFC-12 concentrations. Open squares: Jakarta, Indonesia; solid circles: Jayapura, Indonesia; solid squares: Madang, Papua New Guinea; open circles: Manila, Philippines (data from GNIP, IAEA/WMO 2001). The solid line shows the predicted annual mean concentration of $^3H$ in precipitation over the time period 1960–1986 for Manila (Doney et al., 1992). The dashed line shows the path of decay of $^3H$ in groundwater if recharged from precipitation in the early 1960s. Similarily, the gray rectangle represents the $^3H$ decay pattern of most groundwaters recharged since the late 1960s. The long-short dashed curve shows the historic atmospheric concentrations of CFC-12. For tritium ranges (a) to (d), see text.*

The applicability of $^3$H in this study area for groundwater dating and detection of recent recharge is quite limited. Conclusive groundwater ages can be derived only for water originating from the $^3$H bomb-peak time in the early 1960s ($^3$H range *a* in Fig. 9.30). As can be seen in Fig. 9.30, even for unmixed water with 0.8–2.5 TU (range *b*), dating with $^3$H alone is only qualitative at best, being able only to recognize post-1965 water. No further quantification of groundwater ages is possible by the $^3$H data alone. The same conclusion holds in the case of groundwater mixtures, where the possibility to characterize mixing end members is quite limited except in the case of high level tritium contributions from the early 1960s. Considering the quite low prevailing $^3$H concentrations in the region and a $^3$H detection limit of about 0.6 TU in water (at the 2$\sigma$ level), as it applies to the Davao samples, a groundwater sample with a $^3$H value of 0.3 ± 0.3 TU could be interpreted as tritium-free pre-1950 recharge ($^3$H range *d*), but it could potentially contain more than 50% of post-1965 recharge ($^3$H range *c*). The $^3$H range *c* is typical for groundwater mixtures of pre-1950 water with a $^3$H-bearing contribution. In this region, water recharged prior to the 1950s should contain in the year 2000 less than 0.05 TU. Due to the low $^3H$ concentrations in the region, and the unavoidable uncertainty in the $^3H$ measurement, there is little room for any data interpretation with $^3H$ concentrations below 0.8 TU.

In contrast to $^3H$, the CFC-12 atmospheric concentration increased from 1965 to 1990 from about 68 to 540 pptv (Fig. 9.30), and CFC-11 from about 28 to 270 pptv, respectively. Thus, from the CFC data an apparent age of groundwater recharged between 1965 and 1990 can be estimated with an uncertainty of a few years. The further interpretation of apparent CFC ages depends, however, on an assessment whether the CFC concentrations have been altered by degradation or contamination, or have been diluted by mixing with old water.

CFCs are sensitive indicators for recognition of recent recharge. CFCs can be routinely detected in water at concentrations down to 0.3–1 pg/kg (see Chapter 1, Section 1.1). Water in solubility equilibrium with post-1993 air, recharged at approximately 28°C and 1013.25 hPa total pressure, contained about 320, 170 and 40 pg/kg of CFC-11, CFC-12 and CFC-113, respectively. Therefore, the low detection limit of CFCs permits the recognition of a very small admixture of recent recharge to old water, which could not be detected by $^3H$.

In 2000, samples from selected wells and surface waters in Davao City were collected and analysed for tritium, CFC and stable isotopes. CFC analysis was repeated for the same locations in 2001 and 2002. Because $^3H$ records for precipitation in the area of Davao City are not available, the interpretations relied on the recorded $^3H$ of precipitation in the region (Jakarta and Jayapura, Indonesia; Madang, Papua New Guinea; and Manila, Philippines) (see Fig. 9.30).

Analyses of water samples collected between 2000 and 2002 from seven rivers in the study area (see Fig. 9.29) showed that the river water samples had CFC-11, CFC-12 and CFC-113 concentrations at or near equilibrium with air (with min. 0.75 and max. 1.23 times saturation). Although the data indicate that the rivers in the study area have not been contaminated with CFCs recently, the history of CFC contamination in the study area is unknown.

No data were available about redox potential and dissolved oxygen content of the samples. The chromatograms and CFC ratios, however, provide no evidence for possible CFC degradation (see Chapter 8).

Water samples from six wells contained $^3H$ below 0.5 TU, of which five samples did not contain detectable CFCs. Because both $^3H$ and CFCs are not detected, these water samples can be interpreted as pre-1950 waters. The wells with pre-1950s waters are all located along the coast (Production Well 1, 3, 8, 9 and 12 in Fig. 9.29, represented by black points).

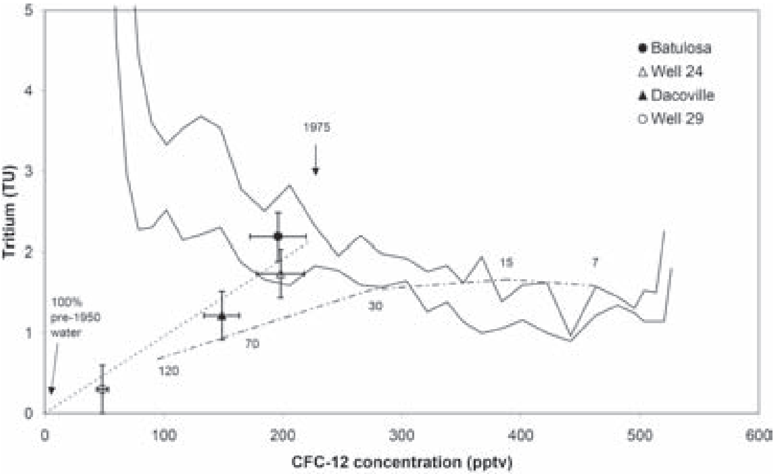


*FIG. 9.31. Tracer plots comparing well $^{3}H$ data with concentrations of CFC-12 in (pptv) with uncertainties being ±0.3 TU for $^{3}H$ and ±10% for CFC-12. The data are compared with models of piston flow (two solid lines, representing the lower and upper bounds of the estimated $^{3}H$ concentrations in the region, see Fig. 9.30), exponential model (long-short dashed line with numbers attached indicating mean residence times), and binary mixing (dashed line).*

Water samples from four wells contained detectable CFCs; these include samples from Batulosa Well, Well 24, Dacoville Well and Well 29. The measured concentrations of CFC-12 and $^{3}H$ for these wells are compared with model calculations assuming piston flow, exponential mixing and binary mixing (Fig. 9.31). These samples lie along a mixing line that can be drawn between the piston flow line and old water, and may be interpreted as diluted samples from the mid-1970s with old pre-1950 water. CFC-11 and CFC-113 data can be interpreted similarly. However, due to low concentrations the recharge date of the young water can only be roughly estimated by CFC-113 to be between mid-1970s and mid-1980s. All these wells are located north-west to those wells that did not contain detectable $^{3}H$ and CFCs, and upgradient from Davao Gulf (represented by gray points in Fig. 9.29).

Two samples, Toril Well (1.8 TU) and Tugbok Well (1.8 TU) contained $^{3}H$ concentrations higher than 1 TU but did not contain CFCs. One possible explanation is that the two samples contained fractions of young water that were recharged during the time when the CFC concentrations were relatively low and $^{3}H$ was high (see Fig. 9.30). Other possibilities could be microbial degradation of CFCs in the aquifer or a possible contamination of the samples with tritium. No conclusive explanation could be found for this effect.

The fact that old CFC-free and tritium-free waters are located along the coastline of the Davao Gulf may indicate upward leakage following the hydraulic gradient, being eventually intensified by increased groundwater exploitation, whereas CFC- and $^3$H-bearing water samples are located more upgradient in the inland area. Water chemistry and $\delta^{18}$O data of all wells indicate mixing of three different water types in varying proportions. The four samples in Fig. 9.31 would all be in agreement with a simple binary mixing model between an old CFC- and $^3$H-free component and another one of about thirty years' age. Both other simple groundwater flow assumptions (piston flow and exponential mixing) cannot explain all four data satisfactorily.

## Chapter 10

# POTENTIAL USE OF OTHER ATMOSPHERIC GASES

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## 10.1. SULPHUR HEXAFLUORIDE ($SF_6$)

Sulphur hexafluoride is a colourless, odourless, non-flammable, non-toxic, stable gas with excellent electrical insulating and arc-quenching properties, and is mainly used as an electrical insulator in high voltage switches and transformers. Industrial production of $SF_6$ began in 1953 with the introduction of gas-filled electrical switches and production has increased from nearly zero in 1953 to 85 700 t of $SF_6$ in 1995 (Maiss and Brenninkmeijer, 1998). $SF_6$ has received significant recent interest because of its high greenhouse warming potential which is estimated to be 23 900 times that of $CO_2$ (Climate Change 1995) and is the second highest value measured. $SF_6$ was one of the six gases covered by the Kyoto Global Warming Protocol Agreement of 1997.

$SF_6$ is primarily of anthropogenic origin but also occurs naturally (Harnisch and Eisenhauer, 1998; Busenberg and Plummer, 2000). The troposphere mixing ratio of $SF_6$ has increased from a steady state value of 0.054 ± 0.009 to about 5 parts per trillion during the past 40 years (Busenberg and Plummer, 1997; 2000). The atmospheric history of $SF_6$ is now well established (Maiss and Levin, 1994; Maiss and Brenninkmeijer, 1998) and the mixing fraction of $SF_6$ is currently increasing at a rate of about 6% per year (Fig. 10.1(a)) while those of the CFCs are nearly constant or decreasing (Geller et al., 1997).

The natural background concentration constitutes about 1.0% of the 2001 total atmospheric partial pressure. Small but significant concentrations of $SF_6$ were measured in 16 minerals and rocks of igneous metamorphic, hydrothermal and sedimentary origin (Busenberg and Plummer, 2000). Concentrations of $SF_6$ were generally highest in silicic igneous rocks and lowest in mafic rocks. Significant concentrations of $SF_6$ may be present in some diagenetic fluids. Concentrations of $SF_6$ significantly higher than equilibrium with modern air–water were measured in groundwater from fractured silicic igneous rocks, from some hot springs, and in some groundwater from volcanic areas

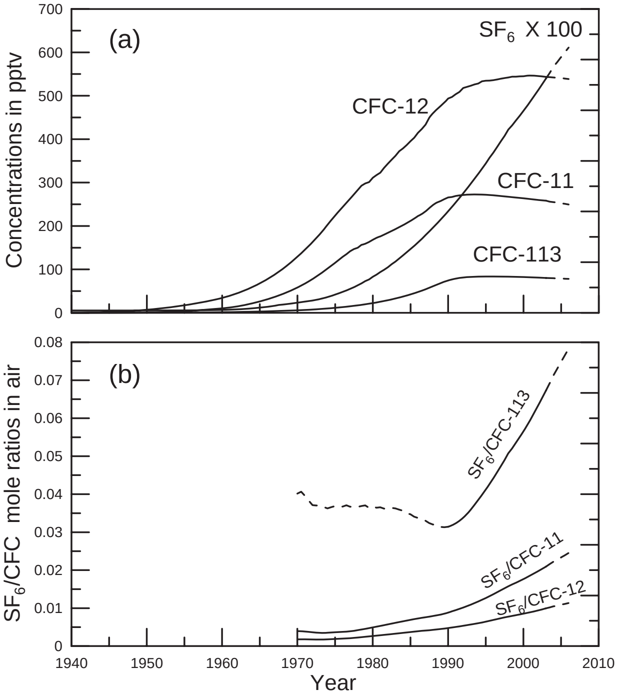

*FIG. 10.1. Shown are: (a) historical concentrations of CFCs and $SF_6$ in the North American atmosphere; and (b) historical ratios of $SF_6$ to CFCs in the North American atmosphere.*

(Busenberg and Plummer, 2000). Concentrations of $SF_6$ may be a useful natural tracer of igneous and volcanic fluids. Where the terrestrial flux of $SF_6$ from igneous rocks and mineral grains is high, groundwater cannot be dated by the $SF_6$ method.

$SF_6$ has been extensively used in many studies as a natural atmospheric tracer (Lovelock and Ferber, 1982; Levin and Hesshaimer, 1996; Patra et al., 1997; Geller et al., 1997; Hall and Waugh, 1998; Zahn et al., 1999; Reddmann et al., 2001). The gas has been injected into the oceans to determine longitudinal dispersion, diapycnal and isopycnal diffusion, and mixing (Ledwell et al., 1986; Watson et al., 1987; Ledwell and Watson, 1988; Ledwell and Watson, 1991; Watson et al., 1991; King and Saltzman, 1995; Law et al., 1998; Ledwell et al., 1998; Vollmer and Weiss, 2002), and air–sea gas exchange and dispersion (Watson et al., 1991; Wanninkhof, 1992; Wanninkhof et al., 1993, 1997; Asher and Wanninkhof, 1998). $SF_6$ has been used to study longitudinal dispersion, gas exchange and mixing in lakes, rivers and estuaries (Wanninkhof et al., 1985, 1987; Clark et al., 1994; Maiss et al., 1994a, 1994b; Clark et al., 1996; Cole and Caraco, 1998; Hibbs et al., 1999; van Bodegom et al., 2001; von Rohden and Ilmberger, 2001; Salhani and Stengel, 2001; Frost and Upstill-Goddard, 2002; Ho et al., 2002; Vollmer et al., 2002); in the study of soil venting (Olschewski et al., 1995); has been used to label drilling air in fractured rock studies (Davidson, 2002), and as a hydrological tracer (Wilson and Mackay, 1993; Upstill-Goddard and Wilkins, 1995; Wilson and Mackay, 1995, 1996; Gamlin et al., 2001; Vulava et al., 2002). As with CFCs, $SF_6$ is measured by gas chromatography with an ECD (Busenberg and Plummer, 2000).

The dating range of water with $SF_6$ is from 1970 to modern, and the $SF_6$ method is particularly useful in dating very young (post-1993) groundwater (Busenberg and Plummer, 2000; Śliwka and Lasa, 2000; Bauer et al., 2001; Zoellmann et al., 2001). It has been used to study the deep water renewal times in Lake Issyk-Kul, Kyrgystan, and the $SF_6$ model ages agreed closely with the $^3H/^3He$ ages (Hofer et al., 2002). The ratios of $SF_6$ to CFC partial pressures are useful in dating groundwaters that recharged after the 1990s (Fig. 10.1(b)).

The procedure that is used to calculate the Henry's Law constant for $SF_6$ is the same as that for CFCs (see Chapter 3). The $K_H$ for $SF_6$ solubility in pure water and sea water have been determined at 1013.25 hPa total pressure between 273–313 K and for salinities of 0–40‰ (Bullister et al., 2002) (Fig. 10.2). Table 10.1 gives the least squares fitting parameters to the temperature, and salinity dependence of $K_H$ for $SF_6$ concentration units of mol·kg$^{-1}$ ·(1013.25 hPa)$^{-1}$ and mol·L$^{-1}$·(1013.25 hPa)$^{-1}$:

$$\ln K_H = a_1 + a_2\left(\frac{100}{T}\right) + a_3 \ln\left(\frac{T}{100}\right) + S\left[b_1 + b_2\left(\frac{T}{100}\right) + b_3\left(\frac{T}{100}\right)^2\right] \quad (10.1.)$$

where $T$ is the temperature in degrees kelvin and $S$ is the salinity in parts per thousand (‰). Corrections for excess air are very important for $SF_6$, due to its low solubility in water (Busenberg and Plummer, 2000).

The following example demonstrates the use of $SF_6$ in dating groundwater in a sand aquifer of the Atlantic Coastal Plain, USA. The Locust Grove watershed, located on the Delmarva Peninsula, USA, is an unconfined, surficial aquifer consisting of sands and gravels, and ranges in thickness from about 25 m at the southern part of the watershed to about 5 m in the northern part. The surficial aquifer is underlain by a confining layer consisting of mainly silt and clay. The geographical location, the location of wells, and the flow paths can be found on maps in Dunkle et al. (1993), Reilly et al. (1994) and Böhlke and Denver (1995). The area is intensely farmed and the groundwater

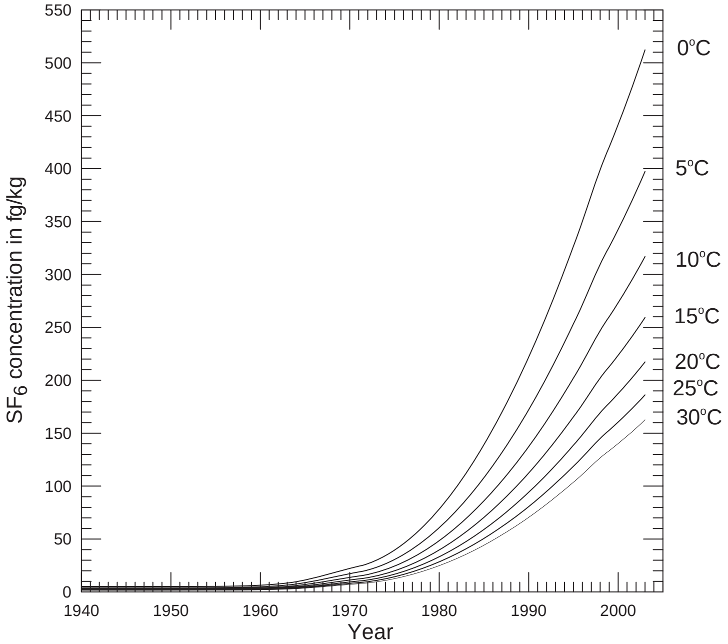

*FIG. 10.2. Concentration of $SF_6$ (femtograms per kilogram (fg/kg)), in water as a function of temperature in equilibrium with North American air at 1013.25 hPa total pressure.*

chemistry has been profoundly altered by the agricultural practices (Böhlke and Denver, 1995). The concentrations of agricultural chemicals in the groundwater can be used to estimate the relative ages of the water at this site (Böhlke and Denver, 1995). The $SF_6$ derived age and nitrate concentrations in the aquifer are shown in cross-section in Fig. 9.4 in Chapter 9. $SF_6$ ages are in

TABLE 10.1. CONSTANTS FOR CALCULATION OF $K_H$ FOR $SF_6$ (BULLISTER et al., 2002), Eq. (10.1)

| $K_H$ | $a_1$ | $a_2$ | $a_3$ | $b_1$ | $b_2$ | $b_3$ |
|---|---|---|---|---|---|---|
| $Mol \cdot kg^{-1} \cdot (1013.25\ hPa)^{-1}$ | –98.7264 | 142.803 | 38.8746 | 0.0268696 | –0.0334407 | 0.0070843 |
| $Mol \cdot L^{-1} \cdot (1013.25\ hPa)^{-1}$ | –96.5975 | 139.883 | 37.8193 | 0.0310693 | –0.0356385 | 0.00743254 |

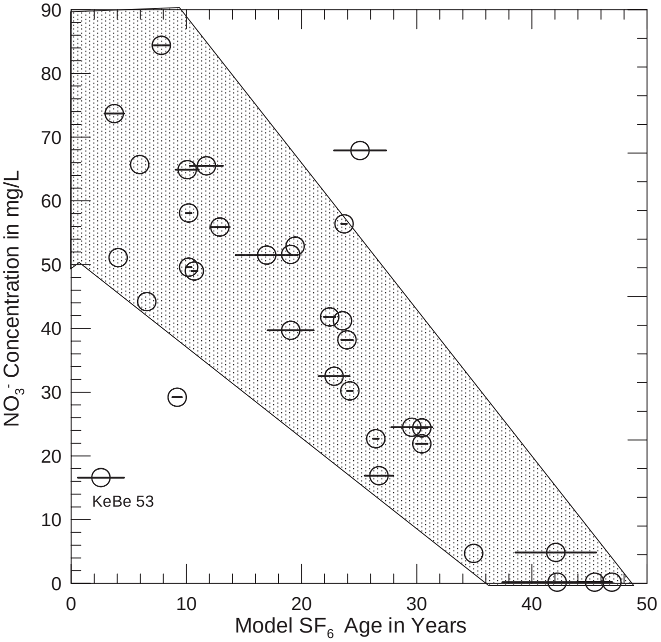

*FIG. 10.3. Shown are concentrations of nitrate in groundwater, as mg $NO_3$ per litre, from the Locust Grove, Maryland, watershed as a function of the $SF_6$ age. The results indicate an increase in fertilizer application in the past 35 years. The nitrate in KeBe 53 was reduced to $N_2$.*

good agreement with those obtained with other dating methods at the site (see Fig. 9.3 in Chapter 9). Figure 10.3 clearly shows the effect of increased fertilizer use in the past 30 years at this site. The nitrate concentration in most of the upper 10–15 m of the aquifer exceeds the U.S. Environmental Protection Agency (USEPA) maximum contaminated level (MCL) of 10 mg/L as nitrogen.

$SF_6$ has been successfully used to date groundwaters in a number of multi-tracer studies (Bauer et al., 2001; Zoellman et al., 2001; Katz et al., 2001; Plummer et al., 2001; Hofer et al., 2002; Vulava et al., 2002). The $SF_6$ dating method yields excellent results in clastic sediments even in urban areas that are often contaminated with CFCs and other VOCs. However, results have been less reliable for groundwaters obtained from glacial tills, fractured igneous rocks (Busenberg et al., 1998, 2001) and from carbonate aquifers (Katz et al., 2001; Busenberg and Plummer, 2000) where the natural background $SF_6$ was often significant, and in some cases, exceeded the anthropogenic fraction. $SF_6$ can be elevated in urban air (Santella et al., 2003).

## 10.2. TRIFLUOROMETHYL SULPHUR PENTAFLUORIDE ($CF_3SF_5$)

Trifluoromethyl sulphur pentafluoride has been detected in the atmosphere and may prove to be useful as a future dating tool. Its historical atmospheric mixing ratio has been determined from dated Antarctic firn-air. The present atmospheric mixing ratio is about 0.13 pptv or about 40 times lower than that of $SF_6$, and the $CF_3SF_5$ concentration is increasing at a rate of 6% per year (Sturges et al., 2000). The atmospheric lifetime of the tracer is estimated to be between 650 and 950 years (Takahashi et al., 2002). $CF_3SF_5$ has received considerable recent interest because it is the most powerful greenhouse gas per molecule that has been detected in the atmosphere (Sturges et al., 2000; Nielsen et al., 2002). The tracer is believed to be a by-product of the manufacture of some fluorochemicals (Santoro, 2000).

## 10.3. HCFC-22 ($CHF_2CL$)

HCFC-22 has been suggested as a possible dating tool for groundwater. HCFC-22 is widely used in cooling devices, and is at present used as a temporary replacement of CFCs because it has a short lifetime (about 12 years) in the atmosphere (Montzka et al., 1999). Production and release data into the atmosphere for this tracer are known (Midgley and Fisher, 1993). Its global atmospheric mixing ratio was 137 pptv in 1999 and the concentration is rapidly increasing at a rate of 5.1 pptv per year (Elkins et al., 2001). Measurements of the tracer in sea water indicate that HCFC-22 does not significantly hydrolyse and may be stable in aerobic sea water (Lobert et al., 1994). There are no known measurements of HCFC-22 in groundwater where the HCFC-22 is of atmospheric origin only. HCFC-22 can be produced by the anaerobic degradation of CFC-12 and is not stable in reducing waters (Lesage et al., 1992; Deipser and Stegmann, 1997).

Analytical difficulty in measuring environmental concentrations of HCFC-22 in groundwater is the main reason why this tracer has not been used to date aerobic groundwater. HCFC-22 can be measured with $O_2$-doped carrier gas with ECDs from a sample volume of less than 100 mL of water (Lobert et al., 1994) or from significantly larger volumes by GC-MS (Montzka et al., 1993). HCFC-22 will eventually be replaced by other refrigerants that do not contain halides and do not damage the ozone layer.

A large number of other HCFC and HFC compounds are currently used as short term replacements for CFCs (Mangani et al., 2000; Shira et al., 2001; Elkins et al., 2001). Even though the concentrations of these compounds are rapidly increasing in the atmosphere, they hydrolyse readily in water and have relatively short atmospheric lifetimes. Many of the short term CFC replacements are unstable in aerobic and anaerobic groundwater environments.

## 10.4. PERFLUOROCARBONS

Perfluorocarbons have atmospheric lifetimes of tens of thousands of years (Harnisch et al., 1996), and do not hydrolyse in water or sea water (Harnisch et al., 1996). Their composition is given by the equation $C_nF_{n+2}$ where $n$ is an integer and C and F represent the elements carbon and fluorine. $CF_4$ is the perfluorocarbon with the highest atmospheric mixing ratio of about 80 pptv. The main difficulty in using $CF_4$ is the high natural background, which comprises about half of the present atmospheric mixing ratio (Harnisch et al., 1996).

$C_2F_6$ has been detected in the atmosphere and the present concentration is about 2.6 pptv. It is believed to be a by-product of aluminium manufacture (Ramanathan et al., 1985) and unlike $CF_4$, $C_2F_6$ is entirely of anthropogenic origin (Harnisch et al., 1996). Atmospheric mixing ratios of this tracer are increasing at a rate of about 6.8% per year (Fabian et al., 1987). Other aliphatic perfluorocarbons are probably present in the atmosphere at much lower concentrations. Even though $C_2F_6$ appears to be an ideal tracer for dating, at the present time, very large quantities of water are required to obtain detectable amounts of the tracer, and limits its use as a hydrological age dating tool.

Aromatic perfluorocarbons have also been detected in the atmosphere and the most abundant of this group is hexafluorobenzene (Lovelock and Ferber, 1982). Their concentrations are low and their atmospheric histories are not known at this time.

## 10.5. TRIFLUOROACETATE OR TFA ($CF_3COO^-$)

Trifluoroacetate is produced in the environment through the oxidation of the hydrochlorofluorocarbon and hydrofluorocarbon repacements of CFCs (HCFC-123, HCFC-124, HCFC-134a and HFC-227ea) producing trifluoroacetyl halides that hydrolyse in the atmosphere to produce TFA (Bott and Standley, 1998). Other precursors are halothane and isoflurane anaesthetics, and the widely used trifluoroacetic acid. An additional very important source of TFA may be the thermal decomposition products of fluoropolymers coatings of cooking utensils (Ellis et al., 2001). Frank et al. (2002) reported uniform concentrations of about 200 ng/L of TFA in all ocean water. The presence of

TFA even in very old sea water and from remote locations indicates that there is an unknown natural source of TFA and that the oceans are the final sink of TFA (Frank et al., 2002).

The salts of TFA are highly soluble in water, and concentrate in water through evaporation (Tromp et al., 1995). Even though TFA is not believed to degrade in water, there is some laboratory evidence suggesting that it degrades in some organic-rich salt marsh sediments (Visscher et al., 1994). The atmospheric TFA is removed by rain and environmental concentrations are believed to be highly variable (Wujcik et al., 1998). It is also believed that local sources are very important (Frank et al., 1996). Even though TFA may not be suitable as a precise dating tool, its presence at elevated concentrations in groundwater indicates recharge after 1950.

Trifluoroacitic acid has a high vapour pressure and is fairly easy to measure in water using headspace chromatography (Bowden et al., 1996; Zehavi and Seiber, 1996).

## Chapter 11

# COMPARISON OF THE CFC TECHNIQUE WITH OTHER TECHNIQUES ($^3$H, $^3$H/$^3$He, $^{85}$Kr)

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## 11.1. INTRODUCTION

The applications of CFC technique to solve specific hydrological problems are discussed in Chapters 7, 8 and 9. It should be pointed out that very often interpretations of CFC data need to rely extensively on additional data. Measurements of concentrations of dissolved gases, such as dissolved oxygen, to determine if there is potential for microbial degradation, can be extremely useful. Noble gas measurements are useful in defining recharge temperature and excess air. Measurements of dissolved nitrogen and argon can also be used to determine recharge temperature and excess air and recognize environments undergoing denitrification. Measurements of dissolved methane are useful in recognizing environments in which all three CFCs can be degraded (see Plummer and Busenberg, 2000).

Isotope techniques are also useful tools. Tritium measurements have proven particularly useful in helping to validate CFC apparent ages. In cases of mixing young water with old water (old water on the >1000 year timescale), $^{14}C$ can be useful in estimating mixing fractions. Noble gas dating techniques, such as those based on $^{3}H/^{3}He$ and $^{85}Kr$ measurements, may provide more reliable dating information in CFC-contaminated environments or methanogenic environments. In general, the CFC technique is most likely to be successful in rural settings, with shallow water tables, where the groundwater is aerobic, and not impacted by local contaminant sources. When applied in other hydrological or geological environments, multiple dating techniques, whenever possible, should be applied to prevent erroneous conclusions. All dating techniques have certain advantages and limitations in the application to specific hydrological problems. Consequently, a multi-tracer approach to groundwater dating is recommended (see Chapter 1, Section 1.3 and Chapter 8, Section 8.9).

## 11.2. $^{3}H$ TECHNIQUE

Tritium is the radioactive isotope of hydrogen that has a half-life of 12.32 years (Lucas and Unterweger, 2000). Environmental tritium occurs in precipitation from two sources. Tritium from the natural source is produced by the interaction of cosmic radiation with atmospheric gases. The second source is human-made and is derived principally from nuclear weapons testing and nuclear reactors. Since 1952, the second source has overwhelmed the first and, therefore, the $^{3}H$ input from precipitation is represented by a series of pulses with the largest pulse occurring during 1963–1964. The shape of the $^{3}H$ input differs significantly from the relatively smooth input functions for CFCs. Furthermore, unlike CFCs, concentrations of tritium in precipitation are much lower in the southern hemisphere than in the northern hemisphere. Significant spatial variations also occur on smaller scales, so that uncertainty in input function can sometimes limit interpretation.

Because of various meteorological processes and atmospheric moisture sources (Rozanski et al., 1991), it generally is necessary to construct a local record of '$^{3}H$-in-precipitation' for a particular region being studied. Several scaling procedures exist for reconstruction of local $^{3}H$ records on the basis of records from parts of the USA (Michel, 1989), and reports from the IAEA for other parts of the world.

Knowledge of the tritium concentration of precipitation in the area under study is a prerequisite for data interpretations based on tritium concentrations in groundwater. Recharge temperature and altitude do not have to be known. Direct age estimation using tritium concentrations is difficult due to the complicated shape of the input function. Reconstruction of local $^{3}H$ records for precipitation can be used, to a first approximation, to infer some aspects of

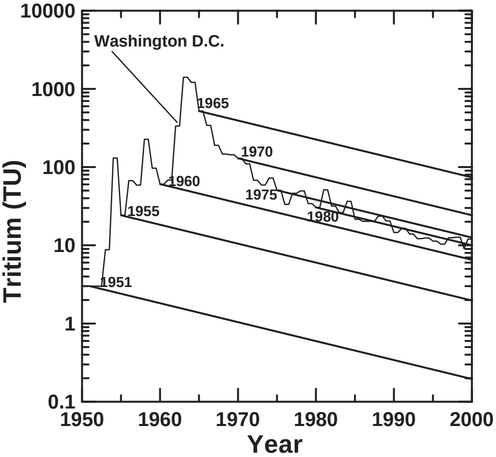

*FIG. 11.1. A smoothed record of $^3$H in precipitation at Washington, D.C, is shown. Parallel lines show the path of decay of $^3$H in groundwater if recharged from precipitation in the years 1951, 1955, 1960, 1965, 1970, 1975 and 1980.*

groundwater age. For example, a smoothed record of $^3$H in precipitation in Washington, D.C., is shown in Fig. 11.1. On the semi-log plot of Fig. 11.1, a series of parallel lines define the decay paths of points along the precipitation input function over time. For example, water recharged prior to the 1950s should contain, in 2000, less than 0.1 TU. Water recharged in 1965 would contain approximately 70 TU. The $^3$H input function of Fig. 11.1 is greatly smoothed (half-year intervals). In actuality, $^3$H in precipitation is quite variable with season and even individual precipitation events. It is also apparent that, because of the multiple peaks in $^3$H content of precipitation, decay lines (Fig. 11.1) can intercept multiple possible years of recharge. During the past 25 years, the $^3$H content of precipitation decreased at approximately the same rate as $^3$H decay and, consequently, meteoric water recharged since about 1975 and sampled in the late 1990s to 2000 contains about 10 TU in the Washington, D.C., area (Fig. 11.1); thus, dating with $^3$H alone is only qualitative at best. Still, the $^3$H data can be quite useful in recognizing post-bomb waters, and in comparison with concentrations of other atmospheric tracers, the $^3$H concentration can be very useful in recognizing groundwater mixtures. Furthermore, terrigenic sources of $^3$H are negligible, and $^3$H is not affected by microbial degradation processes.

In most cases, $^3$H is used as an event marker. Tritium is the only radioactive isotope whose behaviour is identical to that of water. For this reason, the processes that will normally affect CFC-based ages, such as retardation, sorption and chemical processes (see Chapter 4), have practically no impact on tritium. Because the bomb peak dominates $^{3}H$ input, $^{3}H$ distributions in groundwater are more greatly affected by hydrodynamic dispersion than those of the CFCs and $^{85}Kr$ (see Chapter 4, Section 4.8).

In general, the tritium technique alone cannot be used to identify the mixing of waters even in the simplest cases. In cases of mixing of young water with old water, the apparent age can be determined by the $^{14}C$ technique then (old water on the >1000 year timescale). If mixing has been identified by the CFC technique, $^{3}H$ can also be of help in checking the mixing percentage obtained from CFC calculations. Because of the low detection limit of CFCs (1 pg/kg), CFCs are significantly more sensitive indicators of mixing and contamination than tritium.

An unfavourable opinion on the tritium dating technique has sometimes been formed due to the fact that: (a) $^{3}H$ concentrations in the atmosphere and in precipitation have declined to the low natural concentrations; and (b) in groundwater the tritium signal from the human-made source has also decreased to a point where it is difficult to distinguish from natural levels. This is partly so for the southern hemisphere, where $^{3}H$ fallout levels from atomic bomb testing were much lower than in the northern hemisphere. It should be pointed out, however, that the tritium method cannot be replaced by the CFC-based technique completely and $^{3}H$ will continue to be a valuable tracer.

Tritium concentrations in the atmosphere may increase in the future due to the development of nuclear power plant programmes.

Further development of the technique will enable the detection limit for tritium to be lowered. This will extend the range of groundwater dating even though the initial tritium concentrations of groundwater are at the level of the natural source. Without complications introduced by human-made sources of tritium, data interpretations will be more straightforward.

On a broader timescale, the atmospheric concentrations of the CFCs are beginning to decrease. In the decades ahead, although the time range of dating by the CFC technique will be extended, the method alone will probably no longer be able to provide unambiguous apparent groundwater ages (see Chapter 3, Section 3.6). The use of CFCs in conjuction with other tracers (including $^{3}H$) may help to overcome this ambiguity, and increase the precision of the CFC ages.

Even though $^{3}H$ concentrations may not be suitable for precise age determinations, the $^{3}H$ data are invaluable when combined with CFC concentrations, particularly near urban areas where shallow groundwaters may be contaminated with CFCs (see Chapter 4). Tritium measurements can be used to identify contaminated groundwaters. A useful test is to reconstruct initial tritium concentrations in precipitation using the CFC apparent age and measured tritium content for comparison with expected historical tritium-precipitation data (see Busenberg and Plummer, 1992; Dunkle et al., 1993; Ekwurzel et al., 1994; Plummer et al., 1998). Consistencies between the CFC and tritium concentrations may provide greater confidence in data interpretation.

## 11.3. $^3H/^3He$ TECHNIQUE

Tritium derived $^3He$ (tritiogenic helium) is built up in the groundwater as the contained tritium decays. Therefore, the $^3H/^3He$ ratio decreases with age. In principle, the age of groundwater can be determined by simultaneous measurement of $^3H$ and $^3He$ (Jekins and Clarke, 1976; Torgersen et al., 1977, 1979; Poreda et al., 1988; Schlosser et al., 1988, 1989; Solomon et al., 1992).

Sampling and analytical procedures for the $^3H/^3He$ method require complicated and sophisticated techniques. This is perhaps the primary drawback of this method.

This technique can be used to date groundwater that is not more than a few years old. The ability to date very young water is of considerable advantage in comparison with CFC dating of young water. Because growth of atmospheric concentrations of CFCs has slowed since 1988, CFC ages are difficult to resolve in post-1990 water. Because the $^3H/^3He$ method involves measurement of a parent-daughter ratio, this technique does not require that the tritium input function be known. This method can be used to reconstruct the initial tritium concentration (if dispersion is minimal) and provide an independent check of the results obtained from CFC data. For a binary mixture consisting of old (tritium-free) and newly recharged water, the $^3H/^3He$ ages are independent of mixing fractions, and can define the age of the young fraction in the mixture, provided the old fraction does not contain a large component of terrigenic helium. Similar to tritium, the common effects that will affect CFC-based ages, such as local contaminant sources and chemical processes, do not have an impact on it. For age calculation using $^3H/^3He$ data, however, the recharge temperature, excess air and other sources and sinks which result from possible gains and losses of $^3He$ other than tritiogenic $^3He$ should be identified and corrected. Hydrodynamic dispersion affects more greatly the ages determined from $^3H/^3He$ technique than that from CFCs. $^3H/^3He$ ages near the tritium bomb peak are most seriously affected (see Cook and Solomon, 1997).

This technique requires that the $^3He$ is being retained in the sample. When the $^3H/^3He$ dating method is used to date groundwater that is recharged through thick unsaturated zones, then the $^3H/^3He$ age of water at the $^3H$ bomb peak (ignoring problems of dispersion) may be considerably less than the time which has elapsed since peak tritium fallout. The difference will be equal to the travel time of $^3H$ through the unsaturated zone (see Chapter 3, Section 3.4). In the case of a fluctuating water table, it appears that the $^3$H/$^3$He clock is set at the seasonal low water table (Cook and Solomon, 1997; Cook et al., 1996). The fact that the $^3$H/$^3$He clock is 'reset' to zero at the water surface has advantages over the CFCs for some applications (the CFC clock does not reset to zero at the water surface due to a lower diffusion coefficient and lower concentration gradients) (Cook et al., 1996). For example, in the study of Lake Titicaca, $^3$H/$^3$He is found to be a better indicator than CFCs to measure the 're-aeration' rate. $^3$H/$^3$He age is reset immediately to zero when the water moves to the surface, but CFC age is not reset to zero (IAEA, unpublished data, 2000). In another example, Shapiro et al. (1999) showed that the $^3$H/$^3$He 'clock' was reset by $^3$He gas exchange from a small pond of treated wastewater that recharged a sand and gravel aquifer (see Chapter 3, Section 3.4).

$^3$H/$^3$He technique alone cannot be used to identify mixing between old and newly recharged water. Combined with the CFC technique, it can be used to determine the age of the newly recharged water and provide a check of the results obtained from CFCs.

Because this technique measures the tritium signal retained in the groundwater, it still can be used in the next decades. Even when the tritium in groundwater is no longer measurable, the presence of $^3$He will indicate post-1952 recharge. For further information on the $^3$H/$^3$He technique, the reader is referred to Solomon and Cook (2000).

## 11.4. $^{85}$Kr TECHNIQUE

Krypton-85 is a radioactive noble gas with a half-life of 10.76 years. Similar to tritium, its natural source (cosmogenic production) has been overwhelmed by a second (human-made) source since the 1950s. Unlike tritium, however, except for a few years of stability around 1970, the specific activity of $^{85}$Kr in the atmosphere has steadily increased; rather good mixing of $^{85}$Kr in the atmosphere and a certain gradient between the northern and southern hemisphere are observed (see Rozanski and Florkowski, 1978).

Sampling can be done with plastic containers. There are no significant natural sources or sinks of the isotope. Contamination by local sources does not have a significant impact on this technique. The primary limitation of the $^{85}$Kr method for routine use is the large sample size (120–360 L) and time consuming analytical procedures.

Similar to CFCs, the input of $^{85}$Kr has increased along a smooth gradient. Therefore, data interpretations with the $^{85}$Kr method in terms of water ages are more or less straightforward. Compared with tritium, the $^{85}$Kr technique can provide more unambiguous apparent ages. Because the $^{85}$Kr specific activity is measured, recharge temperature, altitude and excess air do not have to be known. $^{85}$Kr is chemically inert in groundwater and it is affected only by radioactive decay and hydraulic properties of the aquifer. Therefore, chemical processes do not have a significant impact on $^{85}$Kr-based ages. Dispersion may have a small effect on $^{85}$Kr-based ages.

When $^{85}$Kr is used to date groundwaters that are recharged through thick unsaturated zones, the time lag for transport of the atmospheric gas through the unsaturated zone should be considered (see Chapter 3, Section 3.4).

The $^{85}$Kr technique alone cannot be used to identify mixing between old and newly recharged waters. Combined with other techniques, it can be used to calculate the mixing percentage and this can provide a check of the results obtained from other tracers. Because of its high detection limit, it may be less reliable than CFCs for waters recharged in the late 1940s and 1950s. It is also difficult to detect any newly recharged water component if the percentage of the younger water is less than 10%.

Atmospheric concentrations of $^{85}$Kr are expected to continue to increase in the foreseeable future. That will allow the technique to be used in the next decades. Further development of the technique and increase of $^{85}$Kr in the atmosphere will probably make this technique more practical. Additional information on the $^{85}$Kr technique is given by Loosli et al. (2000).

## 11.5. SUMMARY

Two groups of environmental tracers can be recognized (Plummer et al., 1993): event markers and passive environmental tracers. The first group, event markers, refers to the occurrence of a meteorological perturbation or some environmental event that can be detected in groundwater. Examples of event markers are the detection of the mid-1960s bomb pulse in $^3$H or in initial $^3$H ($^3$H + $^3$He$_{tri}$), or recognition of the bomb pulse in $^{36}$Cl or $^{14}$C in groundwater. Passive environmental tracers determine temporal information through recognition of a continuous, known atmospheric input of an environmental tracer. Examples of passive environmental tracers are the CFCs, $SF_6$, $^{85}$Kr and some environmental tracers of cosmogenic origin that have a generally constant atmospheric input, such as $^{32}$Si (Morgenstern et al., 1995) and $^{35}$S (Tanaka and Turekian, 1995; Michel and Turk, 1995; Sueker et al., 1999; Michel et al., 2000; Böhlke et al., 2001; Plummer et al., 2001). Table 11.1 summarizes and compares some characteristics of selected passive environmental tracers and event markers as they apply to age interpretation on the 0–50 year timescale. Additional background information on dating of young groundwater is given by Plummer (in press).

## TABLE 11.1. COMPARISON OF ADVANTAGES AND LIMITATIONS OF CFCs, $^3$H/$^3$He, $^{85}$Kr, SF$_6$, $^{14}$C, $^{36}$Cl AND $^3$H DATING

| Characteristic | CFCs | $^3$H/$^3$He | $^{85}$Kr | SF$_6$ | $^{14}$C (E[a]) | $^{36}$Cl (E[a]) | $^3$H (E[a]) |
|---|---|---|---|---|---|---|---|
| Approximate dating range | 1950+ | 1965+ | Past 30 years | 1970+ | Mid-1960s | Late 1950s | Post-1950, mid-1960s |
| Ease of field collection | Moderate to easy | Easy | Difficult | Easy | Easy (AMS[b]) | Easy | Easy |
| Interference from terrigenic sources? | No | Yes | No | Yes | No | No | No |
| Interference from anthropogenic (non-atm) sources? | Yes | No | No | No | No | No | No |
| Date contaminated sites (landfills, septic, etc.)? | No | Yes | Yes | No | No | Yes | Yes |
| Date urban sites? | Limited | Yes | Yes | Yes | Yes | Yes | Yes |
| Relative effect of hydrodynamic dispersion | Low | Moderate to high | Low | Low | Moderate | Low | Moderate to high |
| Affected by sorption? | Yes | No | No | No | No | No | No |
| Degraded microbially? | Yes | No | No | No | Yes | No | No |
| Sensitive to recharge temperature? | Low to moderate | Low | Low | Moderate | No | No | No |
| Sensitive to excess air | Low to moderate | Low | Low | Moderate | No | No | No |
| Need atmospheric input function to date? | Yes | No | Yes | Yes | Yes | Yes | Yes |
| Can date aerobic waters? | Yes | Yes | Yes | Yes | Yes | Yes | Yes |
| Can date anaerobic waters? | No (limited CFC-12) | Yes | Yes | Yes | Yes | Yes | Yes |

[a] E: event marker.

[b] AMS: accelerator mass spectrometry.

# Chapter 12

# SAMPLING AND ANALYTICAL METHODS

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## 12.1. GENERAL REQUIREMENTS

When water samples are taken for the analysis of CFCs, regardless of the sampling method used, contamination of samples by contact with atmospheric air (with its 'high' CFC concentrations) is a major concern. This is because groundwaters usually have lower CFC concentrations than those waters which have been exposed to the modern air. Some groundwaters might not contain

CFCs and, therefore, are most sensitive to trace contamination by atmospheric air. Thus, extreme precautions are needed to obtain uncontaminated samples when groundwaters, particularly those with older ages, are sampled.

It is recommended at the start of any CFC investigation that samples from a CFC-free source be collected and analysed, as a check upon the sampling equipment and methodology. The CFC-free source might be a deep monitoring well or, alternatively, CFC-free water could be carefully prepared in the laboratory. It is especially important that all tubing, pumps and connection that will be used in the sampling campaign be checked in this manner (see Section 12.2 and Chapter 4, Section 4.1).

## 12.2. COLLECTING GROUNDWATER

In all cases, wells should be purged before sampling. It is recommended that field parameters, such as specific conductivity, water temperature, dissolved oxygen and pH be monitored in a flow-through cell during well purging and sampling to recognize if transient phenomena occur in the purging cycle, which could indicate unreliable CFC samples. After the well has been purged, as indicated by stability in field parameters, samples can be collected either using a special purpose ultra-clean pump, using existing pumps in bores that have these equipped, or using bailer methods.

Well purging criteria for sampling groundwaters for purgeable organic compounds have been discussed in detail in the literature (Gibs and Imbrigiotta, 1990). Gibs and Imbrigiotta (1990) showed that after purging three casing volumes, purgeable organic concentrations stabilized in only 55% of the wells. They also showed that the purgeable organics did not necessarily stabilize after the field parameters stabilized and that the hydrological characteristics of the aquifer, the nature of the organics compounds present, and the well construction must be considered in sampling for VOCs. Multiple timed samples should be collected for CFC analysis. The U.S. Geological Survey recommends the collection of 5 samples over a period of 30 min or more to ascertain that samples are representative of concentrations in the aquifer. Samples 2, 3 and 5 are analysed for CFCs. If inconsistencies are found in the results, the rest of the samples are then analysed.

Several types of pumps that have been used to sample monitoring wells include a portable electric pump with steel impeller, capable of discharging up to about 30 L/min (Grundfos pump model Rediflow 2), and a stainless steel piston-type pump driven by compressed nitrogen (Bennett pump or oil-free compressed air) that discharges water at about 4 L/min. During purging, the pump is usually located above the screened interval and lowered to a position at the top of the screened interval during sampling. The pump discharge is usually split at the pump using a fabricated stainless steel 'Y' dividing the discharge between a 6 mm nylon line and 6 mm refrigeration-grade copper line. In sampling large diameter wells, where it is sometimes not feasible to completely purge the well casing, the Bennett pump can be positioned just above the open interval while a pump of larger capacity, placed well above the open interval, is used to maintain a steady flow into the well. Springs have been sampled either with a Bennett pump or peristaltic pump (Plummer et al., 2001). Normally, the Bennett pump is placed in the opening of the spring where maximum discharge occurs. In springs with low flow, such as some seeps, a stainless steel drive point with a screened opening is placed in the spring (seep) and pumped with a peristaltic pump (Modica et al., 1998).

Peristaltic pumps have been successfully used to sample very small diameter piezometers and multiport wells with narrow tubing. A copper or nylon tube is lowered into the piezometer and is connected to a 20 cm length of Viton tubing that is inserted through the head of the pump. After purging, the Viton tubing is discarded. A new piece of Viton tubing is added, and after some more purging, the piezometer is sampled for CFCs. The new piece is used to purge the next well and is replaced before sampling the next well. This procedure prevents cross-contamination of groundwater samples.

When sampling from bores installed with permanent pumps, several factors have to be taken into account. Municipal and domestic wells should be sampled as close as possible to the well head, to minimize the risk of sample contamination through the tubing and any headspace gas therein. The sample line should be connected to the pump upstream of any water treatment, such as chlorination, which may add chemicals to the pump discharge or, if not possible, the treatment should be discontinued during sampling. The pump should run continuously during purging and sample collection. Sample collection should be taken upstream of any pressure tank or other storage tank. Refrigeration-grade copper or nylon lines are recommended in making the connection between the pump and sampling equipment. Because of the risk of contamination, it is important to ensure reliability of the data, either by comparing ages obtained with different CFCs, or by comparing CFC ages with those obtained using other tracers (e.g. $^3$H/$^3$He). Studies in which water samples have been collected using existing pumps on production bores include Busenberg and Plummer (1992), Johnston et al. (1998), Plummer et al. (1998a, 1998b), Plummer et al. (2000).

Pumping of groundwater can sometimes cause shallow water to be drawn into open intervals in wells. Connections to the land surface can occur through poorly sealed well casings and/or through the natural fracture network in consolidated rocks. Some production wells in fractured Permian sandstones in

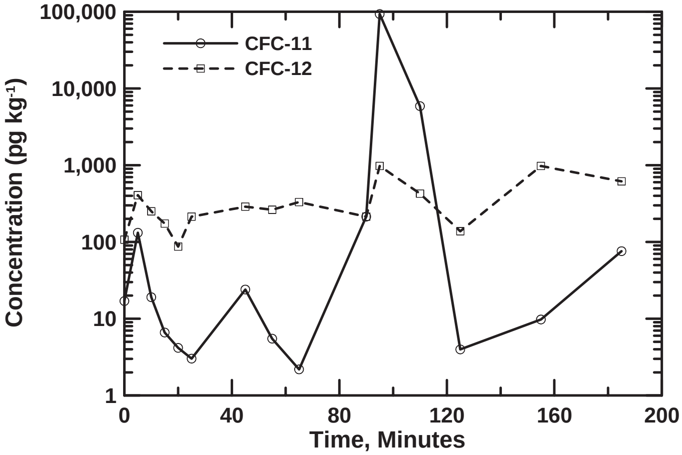

*FIG. 12.1. Concentrations (pg·kg$^{-1}$) of CFC-11 and CFC-12 in discharge from a water supply well in fractured sandstone from central Oklahoma, USA. (Modified from Busenberg and Plummer (1992).)*

central Oklahoma, when sampled over periods of as much as 3 hr, showed transient periods in which anomalous concentrations of CFC-11 were discharged from the well (Fig. 12.1) (Busenberg and Plummer, 1992). The CFC data shown in Fig. 12.1 are from a well that discharges more than 16 L/s and has been in production for many years. The $^{14}C$ activity of the dissolved inorganic carbon in the water was 3.5% modern carbon (pMc), and the water contained <0.1 TU of tritium. It was concluded that the presence of CFCs and the transient in CFC-11 (Fig. 12.1) represented a small quantity of shallow, CFC-11 contaminated water that had been drawn into the well bore during pumping (Busenberg and Plummer, 1992).

Cook et al. (1995, 1998) have developed nitrogen bailer methods for collecting groundwater samples without the need for an ultra-clean pump. The bailer was first used at the Sturgeon Falls field site (see Chapter 9, Section 9.2), where the narrow diameter of many of the piezometers at this site (9 mm ID) posed special problems in CFC sampling. After first purging the wells with a triple-tube pump, CFC samples were collected using a 6 mm OD nylon tube bailer. A 25 m length of nylon tubing with a check valve on the lower end was lowered down the wells to be sampled. Water filled the tubing under gravity. When necessary, a hand vacuum pump was used to draw additional water into the tubing. A 10 m column of water in the nylon tubing was required to provide a sufficient volume of water for a single sample. Because the water table was at only 1.5 m depth, degassing did not affect the measured CFC concentrations.

Once the tubing was sufficiently full, the tubing was pressurized by attaching ultra-high purity (UHP) nitrogen to the upper end, and the tubing was withdrawn from the well. With the nitrogen still attached, the check valve was removed (with the tubing crimped to prevent water loss), and the tubing attached to the ampoule filling system (see Busenberg and Plummer, 1992, Fig. 1). After flushing the ampoule with UHP $N_2$ (from a second tank) for 2 min, the water was forced into 50 mL borosilicate glass ampoules using nitrogen pressure. The nylon tubing was found to introduce large amounts of carbon tetrachloride contamination in water samples collected, but comparisons with the sampling technique of Busenberg and Plummer (1992) found it to produce only trace levels of CFC contamination. Estimated levels of introduced contamination are < 5 pg/kg for CFC-12 and CFC-113, and approximately 20 pg/kg for CFC-11.

Cook et al. (1998) subsequently modified the bailer for use in larger diameter wells. In the modified design, a 75 cm length of 1 in. (2.54 cm) diameter stainless steel tubing was used as the bailer, thus providing a larger volume of water, and minimizing contact with the nylon tubing. The one-way valve is attached to the lower end of the SS tubing, and the nylon tubing is attached to the upper end. In this system, the bailer is pressurized with UHP nitrogen before it is lowered to the required sampling depth. (The pressure is set to be slightly greater than the in situ head, so that no water will enter the bailer as it is being lowered in the well.) Once the bailer is at the required sampling depth, the pressure is released at the surface, and water enters the bailer. After waiting a few minutes for the bailer to fill, the nylon tubing is again pressurized, although this time a pressure of only approximately 100 kPa is needed firmly to close the one-way valve. The bailer is then withdrawn from the well and attached to the ampoule filling system as described above.

## 12.3. SAMPLING CFCs IN GLASS AMPOULES

The water samples are preserved in the field by sealing them into 62 mL borosilicate glass ampoules by fusing the neck (Busenberg and Plummer, 1992). The apparatus for collecting and sealing water samples in ampoules is shown in Fig. 12.2. The apparatus is connected to the well with a copper or aluminium tube, however, nylon tubing can also be used. Except for water discharge lines, all other tubing in contact with the water is stainless steel. The ampoule is connected to the apparatus by tightening nut B; the Teflon ferrules form an airtight seal between the glass and the stainless steel union tee. The well water is allowed to flow through the tubing and the three-way valve V1

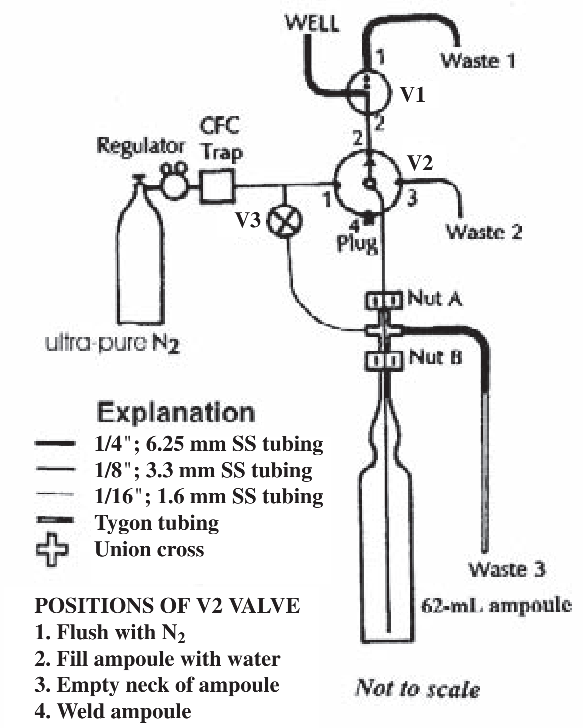

*FIG. 12.2. Apparatus to collect groundwater samples without contact with air and flame seal the water in borosilicate ampoules. (See text for details.)*

(position 1, waste) to waste line 1 for a few minutes, thoroughly flushing the tubing and valve with well water. At the same time, ultra-pure nitrogen that has passed through a molecular sieve (MS13X) trap to remove traces of CFCs flows through the rest of the apparatus flushing out air. This gas flow is split into two streams.

Part of the gas moves through the needle valve (V3) across the union cross. This gas flow is always on and the flow rate is adjusted between 75 and 150 $cm^{3/}$min with the needle valve V3. The gas flow keeps air out of the apparatus and ampoule. The second gas flow is turned on when V2 is set at position 1 (flush ampoule with $N_2$). The gas travels through V2 down the stainless steel tube and is released at the bottom of the glass ampoule, this flow rate is maintained between 250 and 750 $cm^3 \cdot min^{-1}$. The gas escapes up along the neck of the ampoule in the space between the outer wall of the steel tube and the inner glass surface, out through the union cross into waste line 3. The purpose of the $N_2$ purge is to remove all air from the ampoule. The gas flow can be adjusted by changing the applied $N_2$ pressure with the gas regulator. In order to fill the ampoule with water, the four-way valve (V2) is turned to position 2 (fill with water) and then the three-way valve (V1) is turned to position 2 (water). The flow of water is directed down through the 1/8 in. (3 mm) stainless steel tubing to the bottom of the ampoule. The water displaces the ultra-pure $N_2$ which escapes upwards through the neck of the ampoule across the union cross into waste line 3. After the ampoule fills with water, the water is allowed to continue flowing, and this overflow mixes with the ultra-pure $N_2$ in the union cross and is carried to waste line 3. In this manner, the ampoule is rinsed with several hundred $cm^3$ of well water. The upper nut (A) on the union cross is slightly loosened and the ampoule is lowered, raising the stainless steel tube to a position inside the neck of the ampoule. The water flow direction is changed to waste line 1 by turning the three-way valve (V1) to position 1 (waste). The Tygon tubing leading to waste line 3 is pinched and then the four-way valve (V2) is turned to position 3 (empty neck of ampoule). This procedure forces out water from the neck of the ampoule. Valve V2 is turned to position 4 (weld ampoule) and the upper nut (A) of the union cross is slightly loosened and the lower part of the apparatus holding the ampoule is lowered, raising the stainless steel tube outside the neck of the ampoule. Nut A is tightened and immediately the ampoule is fused shut with an oxygen-MAPP (methyl acetylene propadiene stabilized fuel) gas torch about 2 cm above the water level while ultra-pure $N_2$ is flowing across the union cross to prevent the contamination of the sample with air. Normally, 5 samples are collected at each well at time intervals of 5–20 min, and in some cases, up to 40 samples were collected at 5 min intervals to observe the effect of purging on CFC concentrations. The welded ampoules are allowed to cool and are stored for future analysis. Further details of the U.S. Geological Survey sampling procedures can be found at: *http://water.usgs.gov/lab/cfc/*.

## 12.4. SAMPLING IN GLASS BOTTLES

Two methods are used for collecting water samples in glass bottles for the analysis of dissolved CFCs. Analyses of water samples have shown that both methods of sample collection, if properly done, do not introduce contamination and the samples can be stored for several months without measurable changes of CFC concentration.

**Method 1.** The water samples are collected in the field in 500 mL narrow neck glass bottles with glass stoppers. The sealed glass bottles are submerged in metal containers also filled with sample water. This procedure creates an efficient molecular-diffusion barrier against contamination of the inner sample bottle. The metal containers are those normally used for food storage and preservation with airtight rubber O-ring sealing. This procedure can protect the samples from contamination during shipment. The large sample size allows in principle the additional measurement of $SF_6$.

All parts of the glass bottle and the metal container are placed in a metal bucket (a) (see Fig. 12.3). Groundwater for CFC analysis is transferred through a nylon or a refrigeration-grade copper tubing (b) (see Section 12.2 and Chapter 4, Table 4.1) directly to the bottom of the glass bottle (c). The metal bucket is continuously rinsed with sample water. In this manner, the entire sampling equipment in the bucket is rinsed with plenty of water to remove adsorbed CFCs from the surfaces before sampling is initiated. After rinsing, the bottle (c) is closed with the glass stopper (d) and secured with a metal joint clip (e). The glass bottle (c) is then immersed in the metal container (f). The container is sealed with cap (g) (with O-ring lip) and secured with the clamp (h). The sealed metal containers are shipped to the laboratory for analysis.

**Method 2.** Water samples are collected in the field in 50 mL glass bottles fitted with metal foil-lined caps. The metal foil cap liner provides a tight seal and the air and CFCs adsorbed on the metal surface are easily washed away by rinsing with sample water.

The empty glass bottle is put in a metal container. The sample water is flushed through a suitable tubing (copper, stainless steel or nylon) directly to the bottom of the glass bottle. The bottle is filled with water until it overflows.

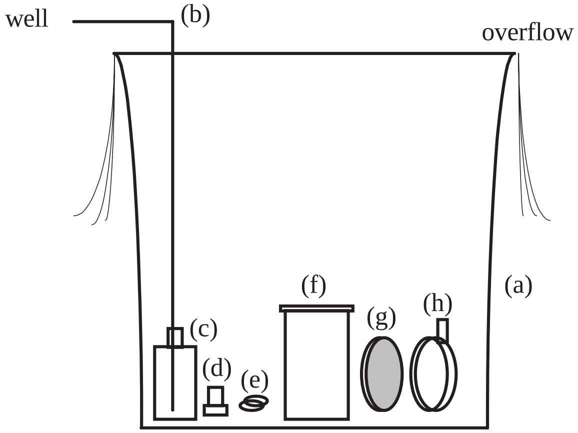

*FIG. 12.3. Apparatus for collecting groundwater samples by using large sized 500 mL glass bottles and metal container without contact to air: (a) metal bucket; (b) tubing; (c) narrow neck glass bottle; (d) glass stopper; (e) stainless steel clip (f) metal containe; (g) container cover with rubber O-ring sealing; (h) clamp.*

The bottle should continue to overflow the bottle until the metal container overflows. The cap should be filled with water and tapped under water to dislodge air bubbles. The cap should be inserted loosely in the cap holder under water. The cap should then be positioned close to the bottle so that the cap is rinsed with the overflowing water from the bottle (Fig. 12.4). At least 2 L of water should be allowed to flow through the bottle and out of the metal container. In this manner, the inner surface of the glass bottle and the cap are rinsed with plenty of water to remove adsorbed atmospheric air and CFCs before sampling is initiated. After this flushing period, the tubing is pulled out of the glass bottle and the glass bottle is closed inside the container with the cap. After closure of the sample, the sample should be turned in order to check for the absence of any gas bubbles. However, such gas bubbles may appear after some time due to pressure and temperature changes in the bottle. It is recommended that the caps be taped to the glass bottles to prevent loosening of during transport.

Note the following:

— More than one glass bottle can be put in the metal containers at one time. However, the bottles and caps should be rinsed in turn sufficiently to ensure that the air and CFCs adsorbed on the inner surface are removed from each bottle.

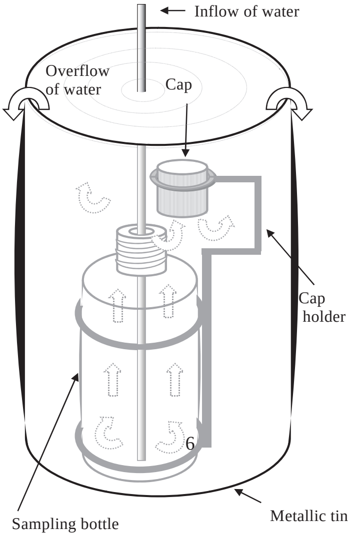

*FIG. 12.4. Apparatus for collecting groundwater samples by using small sized 50 mL glass bottles without contact to air.*

— Air bubbles should not be present in the bottle after sampling. Dissolved air in the sample can produce air bubbles in the bottle after some time. This is normal and a correction is applied, if necessary, to account for the CFC content in the headspace of the bottle.

For further details, see Collection and Preservation of Water Samples for Chlorofluorocarbon Analysis in Glass Bottles with Foil-lined Caps, U.S. Geological Survey Chlorofluorocarbon Laboratory, Reston, VA (2003) at: *http://water.usgs.gov/lab/cfc/sampling/newmethod.htm*

## 12.5. SAMPLING USING COPPER TUBES

Water samples for dissolved noble gases have historically been obtained using copper tubes that are sealed with external pinch clamps. This technique can also be used for CFC samples (Jean-Baptiste, 1994; Hofer and Imboden, 1998.) When sampling flowing wells or when a CFC-free pump is used, copper tubes (typically 3/8 in. (or about 9.5 mm) OD by 30 in. (or 76.2 cm) long) can be attached directly to the discharge line. After purging a minimum of 10 tube volumes (more is better), external pinch clamps can be installed (see Fig. 12.5) or can be crimped with a cold welding tool. For monitoring wells that are not equipped with a pump, a one-way valve can be attached to one end of the copper tube, making it similar to a conventional bailer. To facilitate flushing, a metal bottle having a larger ID than the copper tube can be attached to the upper end as shown in Fig. 12.6.

When using copper tubes, the following precautions should be taken:

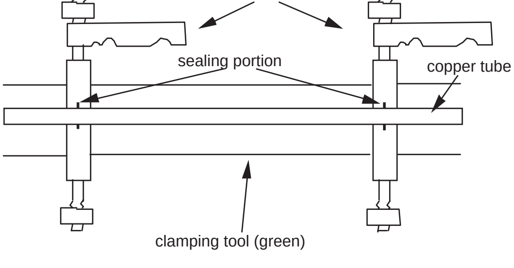

*FIG. 12.5. Copper sampling tube with external pinch clamps.*

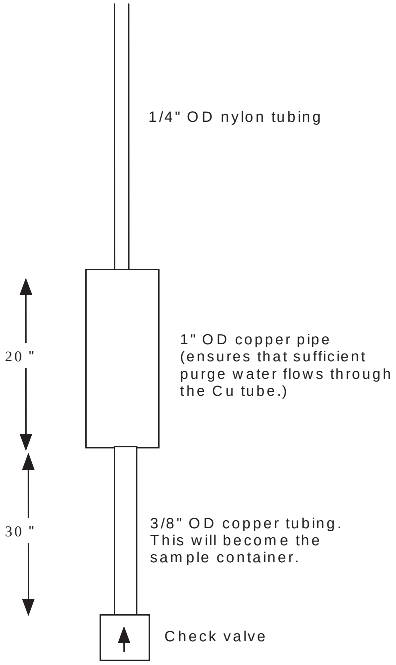

*FIG. 12.6. The diagram shows a Cu tube sampler when used as a 'bailer' (1 in. = 25.4 mm).*

- The copper tubing should be checked for CFC contamination. If the tubing has been stored near a refrigeration system it may be contaminated.
- It is well known that dissolved oxygen reacts with copper tubing. Hofer and Imboden reported an $O_2$ uptake rate of 14 $\mu$mol·kg$^{-1}$·d$^{-1}$. This gives rise to anoxic degradation of CFC-11. Hofer and Imboden reported a degradation rate of 0.0026 pmol·kg$^{-1}$·d$^{-1}$ for CFC-11 at 22°C. No degradation of CFC-12 was detected within 200 days. Thus, a degradation correction for CFC-11 must be made and it is best to analyse the samples within about 30 days of collection to minimize the correction. The degradation rate declines with decreasing temperature so storing samples at low temperature is advisable.

Although CFC-11 is not as stable in copper tubes as in borosilicate glass, the copper tube method has several practical advantages. The primary advantage is that minimal field equipment is needed and thus the method is suitable for sampling at remote sites. Also, the system can be used when a CFC free sampling pump is not available.

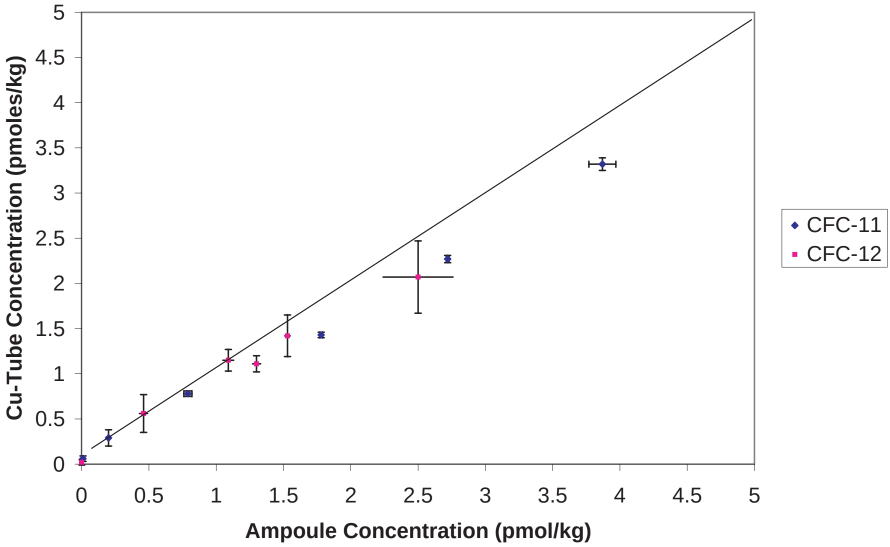

*FIG. 12.7. Comparison of the copper tube sampling method with the ampoule method. (After Heilweil et al. (2000).)*

A comparison between the ampoule and copper tube method was conducted by Heilweil et al. (2000) and is shown in Fig. 12.7. Duplicate samples containing various amounts of CFCs were collected from wells and a stream in the central Virgin River Basin, Utah. Samples in glass ampoules were analysed at the U.S. Geological Survey, while samples in copper tubes were analysed at the University of Utah. For CFC-12 there is good agreement between both methods with essentially all samples agreeing within the stated uncertainty. For CFC-11, there is good agreement for values less than about 2 pmol/kg, but the copper tube samples have consistently lower concentrations for values greater than 2 pmol/kg. Hofer and Imboden (1998) reported anoxic degradation of CFC-11 (but not CFC-12) in copper tubes, which is qualitatively consistent with the results of Heilweil et al. (2000).

## 12.6. ANALYSIS OF CFCs IN WATER AT THE U.S. GEOLOGICAL SURVEY CHLOROFLUOROCARBON LABORATORY

CFCs are determined in the laboratory using a purge and trap gas chromatography procedure with an ECD. This section describes details of the measurements, including determination of the gas volume in the headspace of

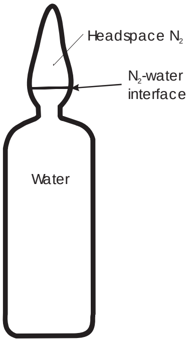

*FIG. 12.8. Ampoules used to sample water for CFCs. The location of the water-*$N_2$ *interface is marked with a pen. The volume of the headspace is determined after the analysis of the sample by filling the top of the ampoule to the mark with water and then determining the weight of the water by difference.*

the ampoule, the apparatus for measuring CFC concentrations, the procedure for introducing the water into the stripping cell, and the measurement procedures.

The analytical procedure determines the CFC concentration of the water. The CFC content of the aquifer sample is partitioned between the water and the gas in the neck of the ampoule, therefore, the CFCs in the headspace are calculated and added to the measured concentrations in the water (Fig. 12.8). The partial pressure of the CFCs in the aquifer are calculated from the concentrations in the water, the water temperature, and the volumes of water and headspace (Busenberg and Plummer, 1992). The volume of the headspace in the neck of the ampoule is calculated from the weight of water required to fill the void space. The headspace is independently evaluated for every ampoule after the CFC analysis and is approximately 2% of the volume of water in the ampoule.

The analytical system (Fig. 12.9) is similar to the design of Bullister and Weiss (1988); for additional information, refer to Busenberg and Plummer (1992).

Contamination of the samples with air is a major concern, because introduction of as little as 0.01 $cm^3$ of modern air during sampling is detectable and can be a serious problem with older water samples. Figure 3 in Busenberg and Plummer (1992) shows the procedures used to transfer the water samples from the ampoules to the stripping cell to eliminate contact with the laboratory atmosphere.

The pre-scored ampoule is inserted into the Tygon sleeve, then several litres of ultra-pure $N_2$ are passed through the Tygon sleeve and released into

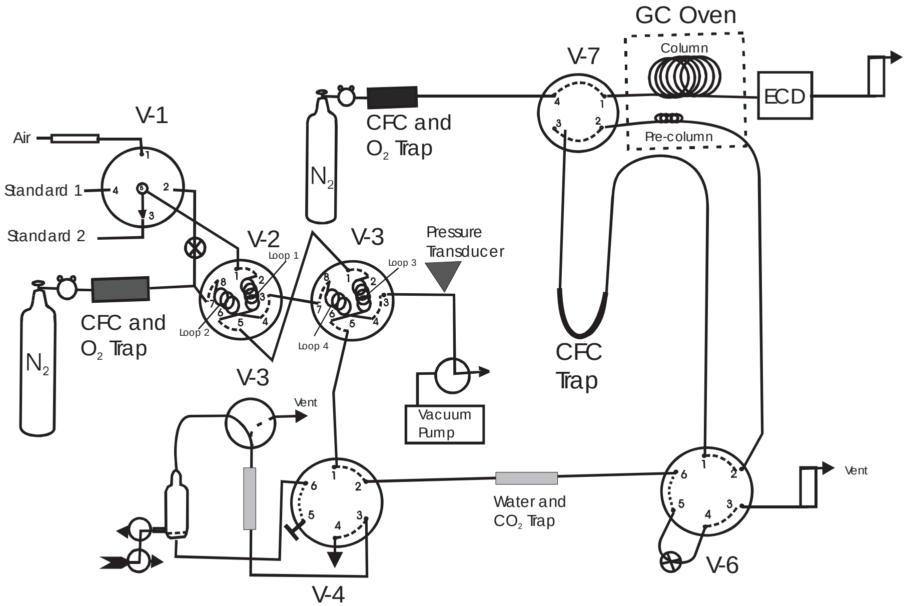

*FIG. 12.9. The CFC analytical system used to pre-concentrate and measure CFCs in groundwater and air samples.*

the laboratory by means of the valve while the intake valve of the stripping cell is closed. This procedure removes all the air from around the neck of the ampoule. Next, the valve is closed and the intake valves are flushed with ultra-pure $N_2$ gas. The borosilicate ampoule is broken along the pre-scored neck by bending the Tygon tube, the union nut is loosened slightly, and the stainless steel tube is lowered to the bottom of the ampoule. The union nut is immediately tightened, allowing further flushing of the intake valves with about 15–20 mL of sample, which is disposed of in the waste receptacle. The intake valves are now turned, filling the stripping cell with the sample (about 25–35 mL). When the desired volume of sample is introduced into the cell, the intake valves are turned, emptying the rest of the sample into the waste receptacle. The stripping of the water sample begins at this point and continues for the next 5 min. After the CFC trap is isolated, the empty ampoule is removed and replaced by a new ampoule in preparation for the analysis of the next sample. After stripping the water sample for 5 min, the intake valves are turned, emptying the cell into a pre-weighed beaker; the intake valves are then closed. The chromatography phase then begins and continues for the next 10 min. The weight of the water is recorded to the nearest 0.01 g.

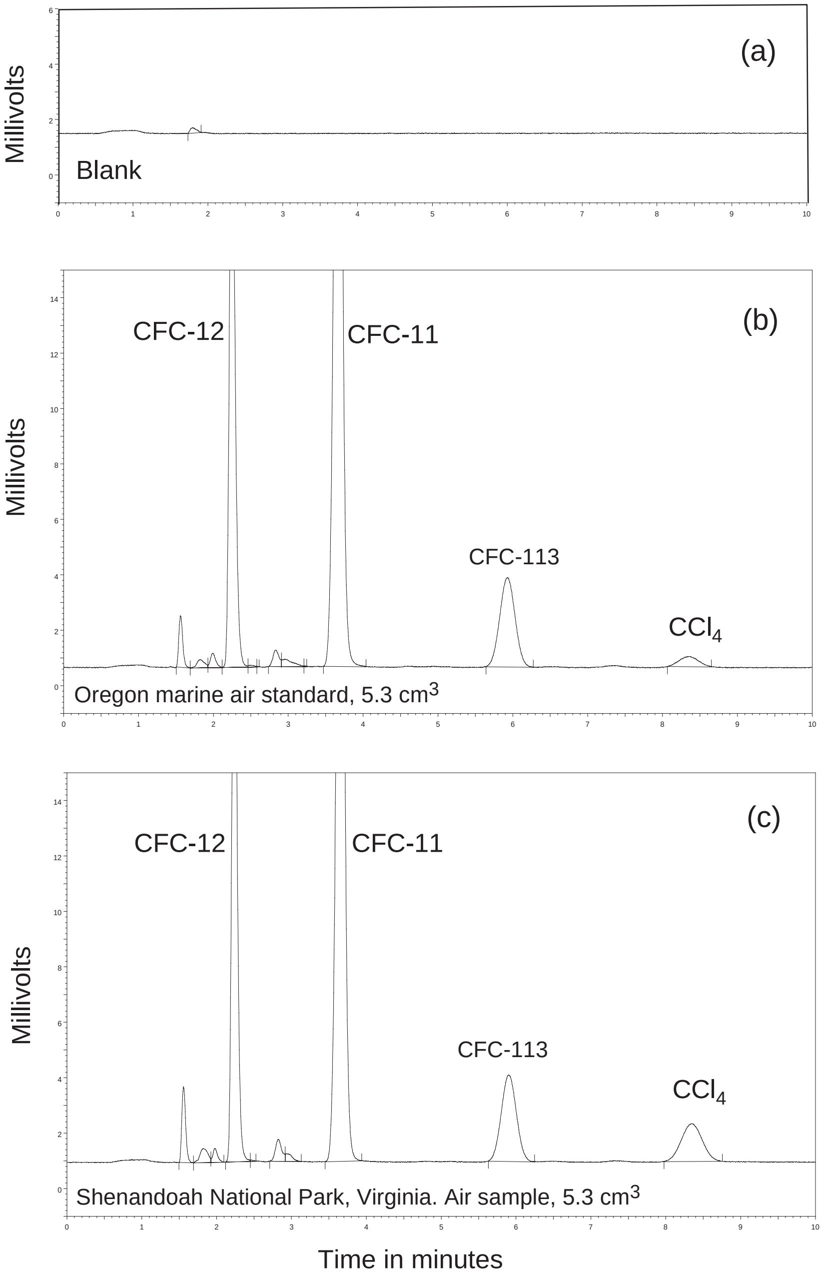

*FIG. 12.10. Sample chromatograms from the U.S. Geological Survey Chlorofluorocarbon Laboratory show: (a) an instrument blank of 5.3 $cm^3$ of ultra-pure $N_2$ carrier gas; (b) 5.3 $cm^3$ of Oregon marine air standard; (c) 5.3 $cm^3$ of 2001 air from the Air Monitoring Station at Shenandoah National Park, Virginia.*

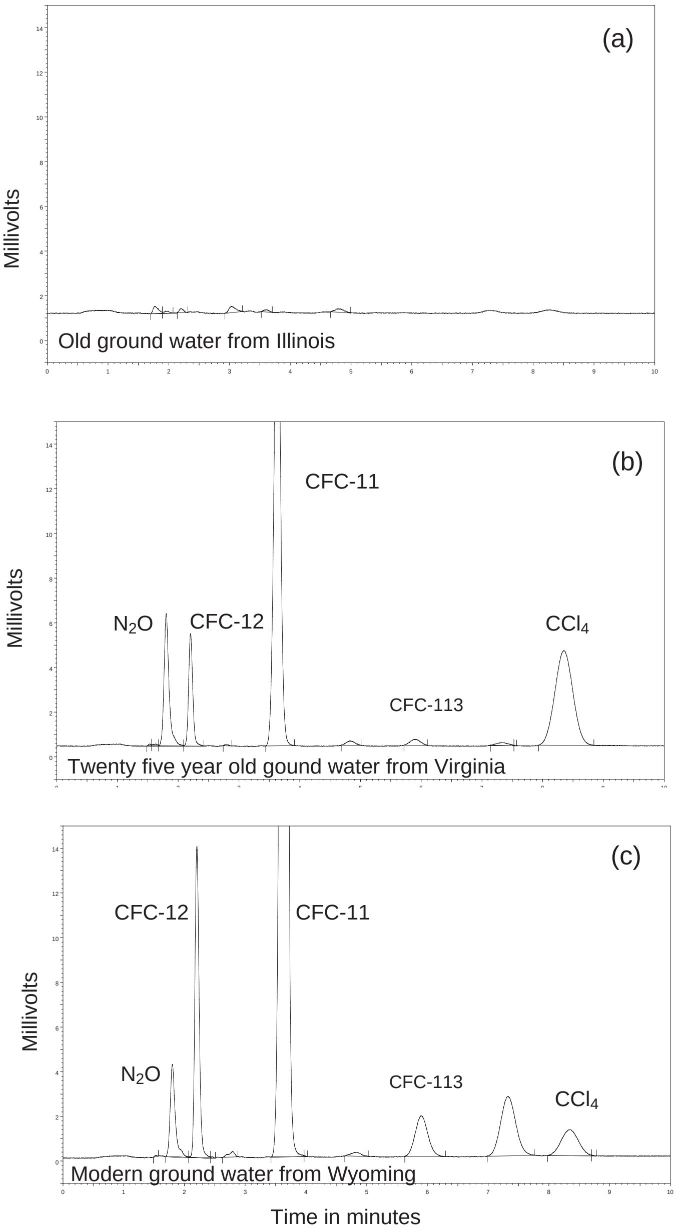

*FIG. 12.11. Chromatograms from the U.S. Geological Survey Chlorofluorocarbon Laboratory show: (a) an old, nearly blank sample; (b) a water sample that is approximately 25 year old water from Hudson Spring, Luray, Virginia (sample 3 of Table 8.2); (c) a water sample from Wyoming that is approximately modern (year 2001).*

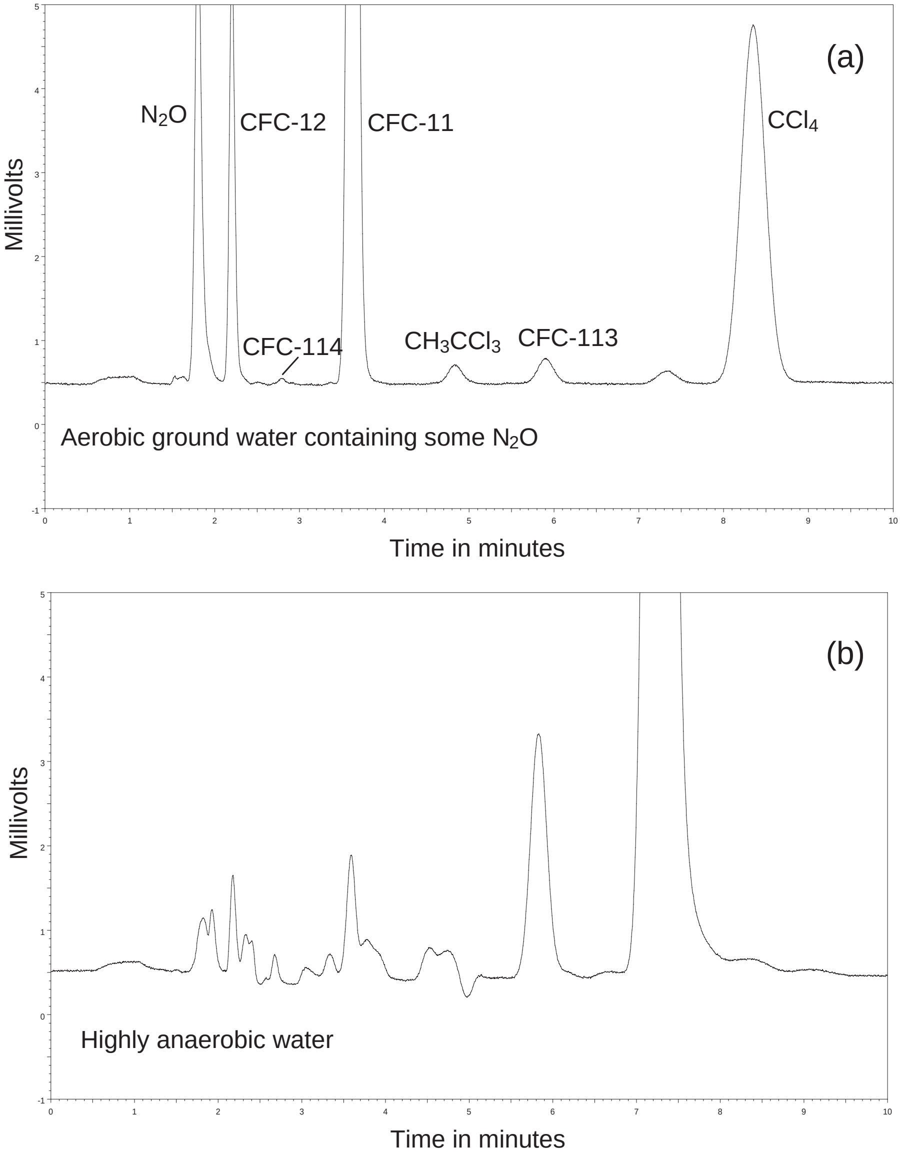

*FIG. 12.12. Chromatograms from the U.S. Geological Survey Chlorofluorocarbon Laboratory show: (a) an example of a nearly clean, aerobic water with a stable background that is typical of oxic groundwater samples; and (b) an example of a highly degraded anoxic water sample. Many of the peaks in sample (b) are degradation products of the CFCs and other halocarbons that were originally present in the sample. The unstable background of the chromatogram in (b) is characteristic of anoxic waters.*

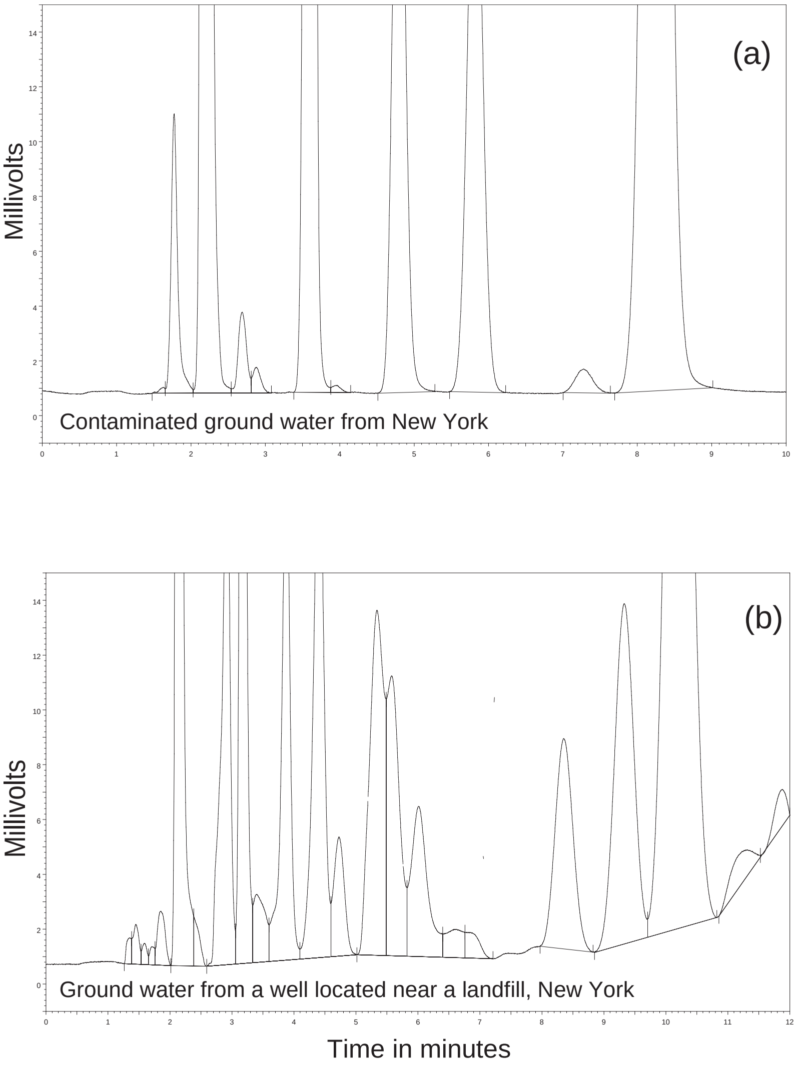

*FIG. 12.13. Chromatograms from the U.S. Geological Survey Chlorofluorocarbon Laboratory show: (a) an oxic water sample located downgradient of a capped landfill in the state of New York that is beginning to be affected with VOCs leached from the landfill; and (b) a highly contaminated anaerobic water sample in the contaminant plume beneath a capped landfill in the state of New York. (Plummer and Busenberg, unpublished data (2001).)*

The purged CFCs are quantitatively collected in a cold trap consisting of a column of Porapak-T and Porasil-C held at –30°C. The CFCs are released by heating this trap to 95°C. Initial separation of the CFCs from other VOCs takes place in a pre-column of Porasil-C. After CFCs pass through the pre-column into the Porasil-C column, the carrier gas flow in the pre-column is reversed. This procedure prevents other VOCs and halocarbons with higher retention times from entering the analytical column, and back-flushes the pre-column. The concentrations of CFCs are measured with an ECD. Figures 12.10–12.13 show examples of typical chromatograms that can be obtained using the GC-ECD analytical system described previously. Further details are given at: http://water.usgs.gov/lab/cfc.

## 12.7. PRESERVATION OF SAMPLES

The effect of storage of waters with trace concentrations of CFCs can often result in the contamination of the sample with CFCs. The contamination occurs if plastics, rubbers or polymers are in contact with the sample. Commonly, significant amounts of CFCs are dissolved in polymers and can seriously contaminate the samples (Reynolds et al., 1990; Bullister, 1984). In addition, CFCs can diffuse from the air through the polymers into the sample (Bullister, 1984). Uptake of halocarbons by the container materials can also be a major problem (Reynolds et al., 1990). CFC-11 and CFC-12 concentrations of groundwater samples fused into borosilicate-glass ampoules remained unchanged on storage times of 0.5–4 years (Fig. 12.14). Very often the CFC concentrations in some surface waters can rapidly degrade in ampoules on storage (Plummer et al., 1998). Many factors influence the rate of degradation of CFCs of surface waters in ampoules, including temperature, presence and absence of light, and amount of particulate organic carbon in the sample (Fig. 12.15).

The use of glass bottles with glass stopcocks or glass bottles sealed with aluminium foil (sampling methods 1 and 2 in Section 12.4) in principle can avoid any contamination problem, as no polymers or grease is used for tight closure of the sampling container. The preservation of the original CFC concentrations using method 1 is documented in Table 12.1 for a time period of up to one year. A CFC-free deep well was used for testing of any contamination during sampling and during storage for both methods. The results presented in Table 12.2 verify that no significant contamination with CFCs could be detected within one year's storage time. Additional data on storage in glass bottles (method 2) are given in Shapiro et al. (2004) and consistent with the results shown in Tables 12.1 and 12.2.

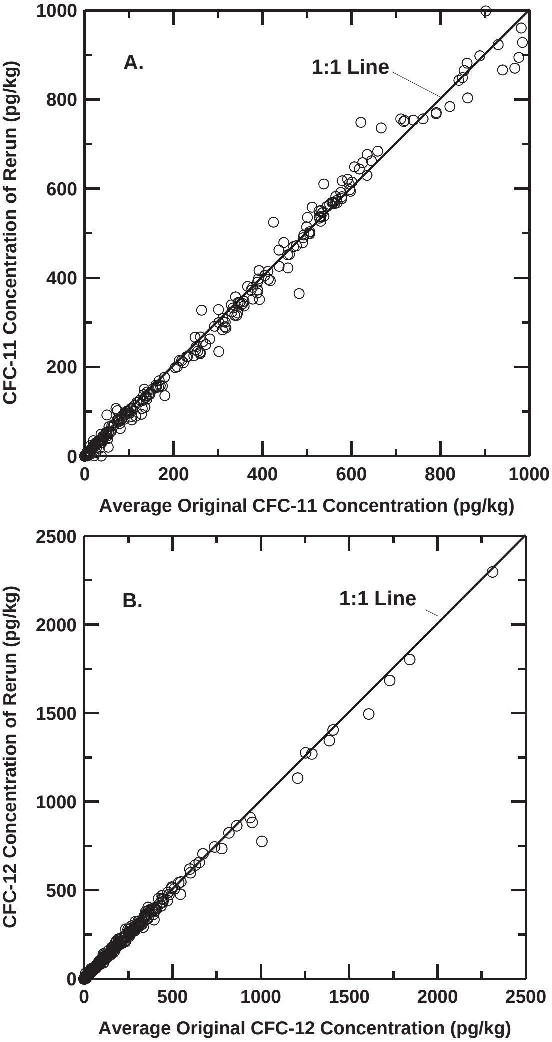

*FIG. 12.14. Graphs comparing the averages of three separate analyses of: (a) CFC-11; and (b) CFC-12 from 356 sites that were initially analysed within several months of collection (average original analysis) with replicate analyses ('rerun' analyses) of CFC-11 and CFC-12 analysed after periods of 0.5–4 years of storage in fused borosilicate ampoules. The 'rerun' groundwater samples were analysed in the U.S. Geological Survey Chlorofluorocarbon Laboratory in the spring of 2001, and were from throughout the USA. The comparison excludes samples from wells that did not discharge a constant CFC composition, as determined from the three original analyses, and apparently were influenced by some hydraulic characteristics of the well or sampling procedure. These plots demonstrate the stability of CFC-11 and CFC-12 in groundwater samples on storage in fused borosilicate ampoules. Modified from Shapiro et al. (2004).*

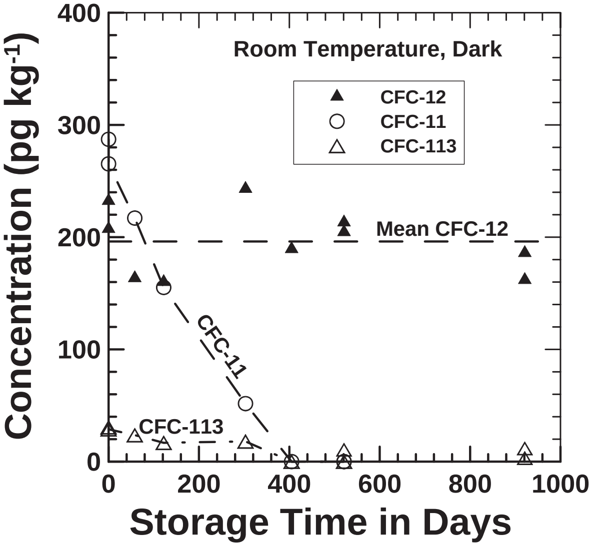

*FIG. 12.15. Concentrations of CFC-11, CFC-12 and CFC-113 in sealed ampoules of Withlacoochee River water from south-east Georgia, USA, show degradation of CFC-11 and CFC-113 and apparent stability of CFC-12. Modified from Plummer et al. (1998b).*

TABLE 12.1. CONCENTRATIONS OF CFC-11, CFC-12 AND CFC-113 OF A GROUNDWATER SAMPLE COLLECTED IN REPLICATE GLASS BOTTLES IN OCTOBER 1996, FROM WACHENHEIM, GERMANY
*(the samples were collected in 500 mL glass bottles and sealed in metallic tins. The water samples were analysed at the Isotope Hydrology Laboratory, IAEA.)*

| Date of analysis | CFC-12 (pmol/kg) | CFC-11 (pmol/kg) | CFC-113 (pmol/kg) |
|---|---|---|---|
| 1996-12-19 | 1.48 ± 0.08 | 2.78 ± 0.03 | 0.26 ± 0 |
| 1996-12-20 | 1.49 ± 0.08 | 2.86 ± 0.04 | 0.25 ± 0.01 |
| 1997-01-23 | 1.61 ± 0.15 | 2.82 ± 0.02 | 0.25 ± 0.01 |
| 1997-02-24 | 1.42 ± 0.01 | 2.79 ± 0.04 | 0.28 ± 0 |
| 1997-11-11 | 1.43 ± 0.06 | 2.66 ± 0.03 | 0.25 ± 0.01 |

TABLE 12.2. CONCENTRATIONS OF CFC-11, CFC-12 AND CFC-113 OF A DEEP GROUNDWATER SAMPLE COLLECTED IN SEVERAL REPLICATE BOTTLES ON 13 JUNE 2000, FROM GRAFENDORF, AUSTRIA

*(the samples were analysed after periods of 0.5–1.5 years of storage in glass bottles. The groundwater samples were analysed in the Isotope Hydrology Laboratory, IAEA.)*

| Date of analysis | CFC-12 (pmol/kg) | CFC-11 (pmol/kg) | CFC-113 (pmol/kg) | Remark (mL bottle) |
|---|---|---|---|---|
| 2000-09-13 | ND[a] | ND | ND | 500 — in container |
| 2000-10-03 | ND | ND | ND | 50 |
| 2000-10-03 | ND | ND | ND | 50 |
| 2000-10-03 | ND | ND | ND | 50 |
| 2000-10-10 | ND | 0.07 | ND | 50 |
| 2000-10-10 | ND | 0.09 | ND | 50 |
| 2001-05-11 | ND | ND | ND | 50 |
| 2001-05-11 | ND | ND | ND | 500 — in container |
| 2001-05-17 | ND | ND | ND | 50 |
| 2001-05-17 | ND | 0.05 | ND | 50 |
| 2001-05-17 | ND | 0.09 | ND | 50 |
| 2001-12-10 | ND | ND | ND | 50 |
| 2001-12-10 | 0.21 | 0.55 | 0.11 | 50[b] |
| 2001-12-11 | ND | ND | ND | 50 |

[a] ND: not detected.

[b] The aluminium foil in the bottle cap was damaged.

# Appendix I

## PHYSICAL AND CHEMICAL PROPERTIES OF CFCs

TABLE I.1. PHYSICAL AND CHEMICAL PROPERTIES OF CFCs. SOLUBILITIES AND DIFFUSION COEFFICIENTS ARE TAKEN FROM COOK AND HERCZEG (2000) AND COOK AND SOLOMON (1995)

| Compound | CFC-11 | CFC-12 | CFC-113 |
|---|---|---|---|
| Molecular formula | $CCl_3F$ | $CCl_2F_2$ | $CCl_2FCClF_2$ |
| Molecular weight (g/mol) | 137.37 | 120.91 | 187.38 |
| Boiling point (°C) | 23.82 | –29.79 | 47.7 |
| Melting point (°C) | –111 | –158 | –36.4 |
| Solubility in water (mol $kg^{-1}$ $(1013.25\ hPa)^{-1}$) | $2.11\ 10^{-2}$ (10°C)<br>$1.04\ 10^{-2}$ (25°C) | $5.48\ 10^{-3}$ (10°C)<br>$2.92\ 10^{-3}$ (25°C) | $6.53\ 10^{-3}$ (10°C)<br>$2.98\ 10^{-3}$ (25°C) |
| Diffusion coefficient in water at 25°C and 1013.25 hPa ($cm^2\ s^{-1}$) | $1.01\ 10^{-5}$ | $1.08\ 10^{-5}$ | |
| Diffusion coefficient in air at 25°C and 1013.25 hPa ($cm^2\ s^{-1}$) | 0.082 | 0.091 | 0.073 |

## Appendix II

## INPUT FUNCTIONS

The North American air curves that are used to date groundwater by the U.S. Geological Survey Chlorofluorocarbon Laboratory are given in Table II.1. The mixing ratios for CFCs from 1976 to 1992 are based on air sample data collected at Niwot Ridge Observatory, Colorado and analysed by the Climatic Monitoring and Diagnostic Laboratory of NOAA (Elkins et al., 1993). The post-1992 mixing ratios are based on in situ gas chromatograph measurements at Niwot Ridge also collected and analysed by NOAA; the data are available at: *http://www.cmdl.noaa.gov/; http://ftp.cmd.noaa.gov/hats/.*

The pre-1976 values are based on production and release data that are available from AFEAS (*http://www.afeas.org/*) (see Chapter 2, Section 2.1 for further details). The $SF_6$ mixing ratios were compiled from data obtained from various sources and measurements by the authors at Big Meadows Air Monitoring Station, Shenandoah National Park, Virginia (see Busenberg and Plummer (2000) for further details). Walker et al. (2000) tabulated separate air curves for the northern and southern hemispheres. Complete references and details are given in Chapter 2, Section 2.1. The ALE/GAGE/AGAGE CFC data are available at: *http://cdiac.esd.ornl.gov/ftp/ale_gage_agage/agage/ and http://gaslab.ucsd.edu/pub/cfchist/.*

The CFC data in Table II.1 are presented on the SIO-98 scale, as are most of the CFC data of this report. The CMDL/NOAA CFC-12 2001, CFC-11 1992, and the CFC-113 2002 scales are 1.64% lower, 0.64% higher and 1.79% higher than the SIO-98 scale, respectively (Bradley Hall, CMDL/NOAA, written communication, 2004). These differences in CMDL/NOAA-SIO scales were derived from in situ measurements as of October 2003 based on 1999–2003 data comparisons at the NOAA observatory in American Samoa. The data in Table II.1 can be converted to the CMDL/NOAA scale using the scaling factors given previously. Specifically, to convert CFC-12 air mixing ratios in Table II.1 to the CMDL/NOAA CFC-12 2001 scale, multiply the CFC-12 values in Table II.1 by 1.0164. To convert CFC-11 air mixing ratios in Table II.1 to the CMDL/NOAA CFC-11 1992 scale, multiply the CFC-11 values in Table II.1 by 0.9936. To convert CFC-113 air mixing ratios in Table II.1 to the CMDL/NOAA CFC-113 2002 scale, multiply the CFC-113 values in Table II.1 by 0.9821. Further details on calibration of the CMDL/NOAA standards are available at: *http://http.cmdl.noaa.gov/hats/Standards/standard_trees/*

Data on the SIO-93 scale can be converted to the SIO-98 scale by multiplying the SIO-93 CFC-12, CFC-11 and CFC-113 values by 1.0053, 1.0082 and 1.0038, respectively (Walker et al., 2000).

TABLE I.2. ATMOSPHERIC MIXING RATIOS OF CFC-11, CFC-12, CFC-113 AND $SF_6$ IN NORTH AMERICAN AIR AND CFCs IN SOUTHERN HEMISPHERE AIR COMPILED BY THE U.S. GEOLOGICAL SURVEY CHLOROFLUOROCARBON LABORATORY. THE CFC DATA ARE ON THE SIO-98 SCALE. THE POST-2003 VALUES (IN ITALICS) WERE ESTIMATED FROM TRENDS IN THE ATMOSPHERIC MIXING RATIOS.

*(http://water.usgs.gov/lab/cfc/background/air_curve.html)*

| Year | NH CFC-12 | SH CFC-12 | NH CFC-11 | SH CFC-11 | NH CFC-113 | SH CFC-113 | NH $SF_6$ |
|---|---|---|---|---|---|---|---|
| 1940.0 | 0.34 | 0.15 | 0.01 | 0.01 | 0.00 | 0.00 | 0.05 |
| 1940.5 | 0.40 | 0.21 | 0.01 | 0.01 | 0.00 | 0.00 | 0.05 |
| 1941.0 | 0.48 | 0.27 | 0.02 | 0.01 | 0.00 | 0.00 | 0.05 |
| 1941.5 | 0.56 | 0.33 | 0.02 | 0.01 | 0.00 | 0.00 | 0.05 |
| 1942.0 | 0.66 | 0.39 | 0.02 | 0.01 | 0.00 | 0.00 | 0.05 |
| 1942.5 | 0.76 | 0.47 | 0.02 | 0.02 | 0.00 | 0.00 | 0.05 |
| 1943.0 | 0.88 | 0.55 | 0.03 | 0.02 | 0.00 | 0.00 | 0.05 |
| 1943.5 | 1.01 | 0.65 | 0.03 | 0.02 | 0.01 | 0.00 | 0.05 |
| 1944.0 | 1.18 | 0.75 | 0.04 | 0.02 | 0.01 | 0.00 | 0.05 |
| 1944.5 | 1.34 | 0.87 | 0.04 | 0.03 | 0.03 | 0.00 | 0.05 |
| 1945.0 | 1.56 | 0.99 | 0.05 | 0.03 | 0.04 | 0.01 | 0.05 |
| 1945.5 | 1.77 | 1.16 | 0.05 | 0.04 | 0.06 | 0.01 | 0.05 |
| 1946.0 | 2.15 | 1.32 | 0.07 | 0.04 | 0.07 | 0.03 | 0.05 |
| 1946.5 | 2.53 | 1.53 | 0.08 | 0.05 | 0.09 | 0.04 | 0.05 |
| 1947.0 | 3.11 | 1.74 | 0.11 | 0.06 | 0.11 | 0.06 | 0.05 |
| 1947.5 | 3.70 | 2.12 | 0.14 | 0.07 | 0.13 | 0.08 | 0.05 |
| 1948.0 | 4.37 | 2.49 | 0.20 | 0.08 | 0.15 | 0.09 | 0.05 |
| 1948.5 | 5.04 | 3.06 | 0.25 | 0.11 | 0.17 | 0.11 | 0.05 |
| 1949.0 | 5.76 | 3.64 | 0.34 | 0.14 | 0.20 | 0.13 | 0.05 |
| 1949.5 | 6.48 | 4.30 | 0.43 | 0.20 | 0.22 | 0.15 | 0.05 |
| 1950.0 | 7.28 | 4.96 | 0.56 | 0.25 | 0.25 | 0.17 | 0.05 |
| 1950.5 | 8.07 | 5.67 | 0.68 | 0.34 | 0.27 | 0.20 | 0.05 |
| 1951.0 | 8.93 | 6.38 | 0.85 | 0.43 | 0.30 | 0.22 | 0.05 |
| 1951.5 | 9.80 | 7.16 | 1.02 | 0.56 | 0.33 | 0.25 | 0.05 |
| 1952.0 | 10.7 | 7.94 | 1.28 | 0.68 | 0.37 | 0.28 | 0.05 |
| 1952.5 | 11.6 | 8.79 | 1.53 | 0.86 | 0.41 | 0.31 | 0.05 |

TABLE I.2. ATMOSPHERIC MIXING RATIOS OF CFC-11, CFC-12, CFC-113 AND $SF_6$ IN NORTH AMERICAN AIR AND CFCs IN SOUTHERN HEMISPHERE AIR COMPILED BY THE U.S. GEOLOGICAL SURVEY CHLOROFLUOROCARBON LABORATORY. (cont.)

| Year | NH CFC-12 | SH CFC-12 | NH CFC-11 | SH CFC-11 | NH CFC-113 | SH CFC-113 | NH $SF_6$ |
|---|---|---|---|---|---|---|---|
| 1953.0 | 12.6 | 9.64 | 1.88 | 1.03 | 0.44 | 0.34 | 0.05 |
| 1953.5 | 13.6 | 10.5 | 2.22 | 1.29 | 0.49 | 0.38 | 0.05 |
| 1954.0 | 14.7 | 11.4 | 2.64 | 1.54 | 0.53 | 0.42 | 0.06 |
| 1954.5 | 15.9 | 12.4 | 3.06 | 1.89 | 0.58 | 0.45 | 0.06 |
| 1955.0 | 17.1 | 13.4 | 3.58 | 2.23 | 0.63 | 0.50 | 0.06 |
| 1955.5 | 18.4 | 14.5 | 4.09 | 2.66 | 0.69 | 0.54 | 0.06 |
| 1956.0 | 19.9 | 15.9 | 4.74 | 3.08 | 0.75 | 0.59 | 0.06 |
| 1956.5 | 21.4 | 17.1 | 5.38 | 3.60 | 0.81 | 0.64 | 0.06 |
| 1957.0 | 23.1 | 18.5 | 6.09 | 4.12 | 0.87 | 0.70 | 0.06 |
| 1957.5 | 24.7 | 19.9 | 6.81 | 4.77 | 0.94 | 0.76 | 0.06 |
| 1958.0 | 26.5 | 21.5 | 7.46 | 5.41 | 1.02 | 0.82 | 0.06 |
| 1958.5 | 28.3 | 23.0 | 8.11 | 6.50 | 1.11 | 0.89 | 0.06 |
| 1959.0 | 30.2 | 24.7 | 8.76 | 7.16 | 1.19 | 0.96 | 0.06 |
| 1959.5 | 32.2 | 26.3 | 9.42 | 7.80 | 1.29 | 1.04 | 0.06 |
| 1960.0 | 34.5 | 28.2 | 10.3 | 8.51 | 1.38 | 1.13 | 0.07 |
| 1960.5 | 36.9 | 30.1 | 11.2 | 9.20 | 1.49 | 1.21 | 0.07 |
| 1961.0 | 39.5 | 32.3 | 12.3 | 10.1 | 1.60 | 1.31 | 0.07 |
| 1961.5 | 42.1 | 34.4 | 13.4 | 10.9 | 1.73 | 1.41 | 0.08 |
| 1962.0 | 45.1 | 37.0 | 14.9 | 12.0 | 1.86 | 1.52 | 0.08 |
| 1962.5 | 48.1 | 39.4 | 16.3 | 13.1 | 1.99 | 1.63 | 0.08 |
| 1963.0 | 51.6 | 42.3 | 18.0 | 14.5 | 2.14 | 1.76 | 0.09 |
| 1963.5 | 55.1 | 45.1 | 19.8 | 15.8 | 2.31 | 1.89 | 0.10 |
| 1964.0 | 59.2 | 48.5 | 21.8 | 17.5 | 2.47 | 2.03 | 0.10 |
| 1964.5 | 63.3 | 51.8 | 23.9 | 19.2 | 2.66 | 2.18 | 0.11 |
| 1965.0 | 67.9 | 55.7 | 26.3 | 21.2 | 2.85 | 2.35 | 0.12 |
| 1965.5 | 72.5 | 59.5 | 28.6 | 23.1 | 3.06 | 2.52 | 0.13 |
| 1966.0 | 77.6 | 63.9 | 31.2 | 25.4 | 3.28 | 2.71 | 0.14 |
| 1966.5 | 82.8 | 68.1 | 33.8 | 27.6 | 3.53 | 2.90 | 0.15 |
| 1967.0 | 88.5 | 73.1 | 36.7 | 30.2 | 3.77 | 3.12 | 0.16 |

TABLE I.2. ATMOSPHERIC MIXING RATIOS OF CFC-11, CFC-12, CFC-113 AND $SF_6$ IN NORTH AMERICAN AIR AND CFCs IN SOUTHERN HEMISPHERE AIR COMPILED BY THE U.S. GEOLOGICAL SURVEY CHLOROFLUOROCARBON LABORATORY. (cont.)

| Year | NH CFC-12 | SH CFC-12 | NH CFC-11 | SH CFC-11 | NH CFC-113 | SH CFC-113 | NH $SF_6$ |
|---|---|---|---|---|---|---|---|
| 1967.5 | 94.3 | 77.9 | 39.7 | 32.7 | 4.06 | 3.34 | 0.18 |
| 1968.0 | 100.7 | 83.5 | 43.0 | 35.6 | 4.33 | 3.59 | 0.19 |
| 1968.5 | 107.2 | 88.8 | 46.4 | 38.3 | 4.66 | 3.84 | 0.20 |
| 1969.0 | 114.4 | 95.0 | 50.2 | 41.6 | 4.98 | 4.13 | 0.21 |
| 1969.5 | 121.5 | 101.0 | 54.1 | 44.8 | 5.35 | 4.41 | 0.22 |
| 1970.0 | 129.3 | 108.0 | 58.5 | 48.6 | 5.73 | 4.74 | 0.23 |
| 1970.5 | 137.2 | 114.7 | 62.9 | 52.3 | 6.15 | 5.07 | 0.25 |
| 1971.0 | 145.5 | 122.3 | 67.7 | 56.6 | 6.57 | 5.45 | 0.26 |
| 1971.5 | 153.9 | 129.6 | 72.5 | 60.7 | 7.05 | 5.83 | 0.27 |
| 1972.0 | 162.9 | 137.8 | 77.8 | 65.4 | 7.54 | 6.26 | 0.28 |
| 1972.5 | 172.0 | 145.6 | 83.2 | 70.0 | 8.10 | 6.69 | 0.30 |
| 1973.0 | 182.0 | 154.6 | 89.4 | 75.3 | 8.65 | 7.18 | 0.32 |
| 1973.5 | 192.1 | 163.2 | 95.5 | 80.4 | 9.29 | 7.68 | 0.34 |
| 1974.0 | 202.9 | 173.1 | 102.2 | 86.4 | 9.93 | 8.25 | 0.36 |
| 1974.5 | 213.7 | 182.5 | 108.9 | 92.2 | 10.67 | 8.81 | 0.39 |
| 1975.0 | 224.0 | 193.0 | 114.6 | 98.6 | 11.39 | 9.46 | 0.42 |
| 1975.5 | 234.3 | 202.9 | 122.1 | 104.7 | 12.23 | 10.11 | 0.45 |
| 1976.0 | 244.2 | 213.3 | 128.9 | 111.1 | 13.07 | 10.86 | 0.48 |
| 1976.5 | 254.0 | 223.1 | 135.1 | 117.1 | 14.02 | 11.60 | 0.52 |
| 1977.0 | 263.3 | 233.2 | 142.1 | 123.4 | 14.99 | 12.45 | 0.55 |
| 1977.5 | 272.5 | 242.6 | 146.7 | 129.3 | 16.09 | 13.31 | 0.59 |
| 1978.0 | 282.4 | 252.2 | 150.0 | 135.3 | 17.19 | 14.28 | 0.63 |
| 1978.5 | 292.9 | 261.1 | 156.5 | 140.8 | 18.44 | 15.26 | 0.68 |
| 1979.0 | 298.1 | 267.7 | 159.8 | 145.0 | 19.70 | 16.38 | 0.73 |
| 1979.5 | 301.2 | 273.5 | 162.6 | 148.8 | 21.14 | 17.50 | 0.77 |
| 1980.0 | 311.2 | 283.3 | 168.6 | 154.3 | 22.59 | 18.78 | 0.83 |
| 1980.5 | 317.4 | 292.3 | 172.8 | 159.3 | 24.15 | 20.06 | 0.88 |
| 1981.0 | 322.7 | 301.0 | 176.0 | 163.8 | 25.72 | 21.05 | 0.94 |
| 1981.5 | 333.8 | 308.8 | 179.7 | 167.8 | 27.34 | 22.50 | 0.99 |

TABLE I.2. ATMOSPHERIC MIXING RATIOS OF CFC-11, CFC-12, CFC-113 AND $SF_6$ IN NORTH AMERICAN AIR AND CFCs IN SOUTHERN HEMISPHERE AIR COMPILED BY THE U.S. GEOLOGICAL SURVEY CHLOROFLUOROCARBON LABORATORY. (cont.)

| Year | NH CFC-12 | SH CFC-12 | NH CFC-11 | SH CFC-11 | NH CFC-113 | SH CFC-113 | NH $SF_6$ |
|---|---|---|---|---|---|---|---|
| 1982.0 | 343.6 | 317.6 | 183.8 | 172.2 | 28.96 | 23.70 | 1.05 |
| 1982.5 | 352.7 | 325.5 | 188.3 | 176.1 | 30.76 | 25.60 | 1.12 |
| 1983.0 | 361.6 | 334.5 | 193.3 | 180.6 | 32.55 | 26.94 | 1.18 |
| 1983.5 | 372.2 | 342.5 | 198.0 | 184.5 | 34.80 | 28.10 | 1.25 |
| 1984.0 | 378.6 | 351.5 | 201.9 | 188.8 | 37.03 | 29.79 | 1.32 |
| 1984.5 | 386.2 | 359.4 | 206.0 | 192.5 | 39.70 | 31.40 | 1.39 |
| 1985.0 | 395.4 | 369.4 | 211.2 | 197.6 | 42.3 | 33.8 | 1.47 |
| 1985.5 | 403.3 | 378.2 | 217.3 | 202.2 | 45.2 | 36.0 | 1.54 |
| 1986.0 | 414.6 | 387.9 | 223.0 | 207.2 | 48.0 | 38.6 | 1.62 |
| 1986.5 | 423.5 | 396.5 | 227.9 | 211.5 | 51.1 | 41.0 | 1.70 |
| 1987.0 | 433.6 | 407.0 | 233.5 | 217.3 | 54.2 | 44.1 | 1.79 |
| 1987.5 | 449.3 | 416.3 | 241.0 | 222.4 | 57.7 | 47.0 | 1.87 |
| 1988.0 | 459.5 | 426.7 | 248.6 | 228.2 | 61.2 | 50.2 | 1.96 |
| 1988.5 | 469.1 | 435.8 | 254.0 | 233.4 | 64.9 | 53.3 | 2.05 |
| 1989.0 | 476.7 | 445.8 | 257.4 | 238.2 | 68.5 | 56.6 | 2.15 |
| 1989.5 | 484.0 | 454.4 | 262.0 | 242.3 | 71.5 | 59.7 | 2.24 |
| 1990.0 | 493.5 | 464.2 | 265.8 | 247.1 | 74.5 | 63.0 | 2.34 |
| 1990.5 | 497.1 | 472.7 | 266.9 | 251.2 | 76.6 | 66.1 | 2.44 |
| 1991.0 | 503.4 | 480.8 | 269.2 | 254.4 | 78.8 | 68.8 | 2.54 |
| 1991.5 | 508.8 | 487.4 | 270.1 | 256.8 | 80.3 | 71.2 | 2.65 |
| 1992.0 | 517.7 | 493.6 | 271.5 | 259.2 | 81.5 | 73.9 | 2.75 |
| 1992.5 | 520.5 | 498.4 | 272.2 | 260.9 | 82.3 | 76.4 | 2.86 |
| 1993.0 | 523.0 | 503.5 | 272.3 | 262.1 | 82.7 | 78.2 | 2.97 |
| 1993.5 | 526.0 | 507.0 | 272.4 | 262.6 | 83.0 | 79.8 | 3.09 |
| 1994.0 | 528.2 | 511.6 | 272.8 | 263.6 | 83.2 | 80.5 | 3.20 |
| 1994.5 | 533.3 | 514.7 | 272.2 | 263.8 | 83.5 | 81.5 | 3.32 |
| 1995.0 | 534.7 | 518.6 | 272.0 | 263.9 | 83.6 | 82.1 | 3.44 |
| 1995.5 | 534.8 | 520.9 | 271.3 | 263.5 | 83.7 | 82.2 | 3.57 |
| 1996.0 | 535.7 | 524.3 | 271.0 | 263.3 | 83.6 | 82.4 | 3.69 |

TABLE I.2. ATMOSPHERIC MIXING RATIOS OF CFC-11, CFC-12, CFC-113 AND $SF_6$ IN NORTH AMERICAN AIR AND CFCs IN SOUTHERN HEMISPHERE AIR COMPILED BY THE U.S. GEOLOGICAL SURVEY CHLOROFLUOROCARBON LABORATORY. (cont.)

| Year | NH CFC-12 | SH CFC-12 | NH CFC-11 | SH CFC-11 | NH CFC-113 | SH CFC-113 | NH $SF_6$ |
|---|---|---|---|---|---|---|---|
| 1996.5 | 537.4 | 526.2 | 269.5 | 263.1 | 83.5 | 82.7 | 3.82 |
| 1997.0 | 539.3 | 529.2 | 269.0 | 263.0 | 83.4 | 82.8 | 3.95 |
| 1997.5 | 540.9 | 530.6 | 268.0 | 262.1 | 83.3 | 82.8 | 4.08 |
| 1998.0 | 542.1 | 533.0 | 267.3 | 262.0 | 83.2 | 83.1 | 4.22 |
| 1998.5 | 543.7 | 533.8 | 266.3 | 261.1 | 83.0 | 82.8 | 4.32 |
| 1999.0 | 544.0 | 536.1 | 265.6 | 260.9 | 82.8 | 82.7 | 4.43 |
| 1999.5 | 544.6 | 536.7 | 264.2 | 259.9 | 82.6 | 82.3 | 4.54 |
| 2000.0 | 545.1 | 538.2 | 263.8 | 259.4 | 82.3 | 81.9 | 4.65 |
| 2000.5 | 546.3 | 539.2 | 263.2 | 258.7 | 82.1 | 81.7 | 4.77 |
| 2001.0 | 546.5 | 539.8 | 261.8 | 257.9 | 81.7 | 81.4 | 4.89 |
| 2001.5 | 546.1 | 540.4 | 260.8 | 256.9 | 81.3 | 81.0 | 5.01 |
| 2002.0 | 545.3 | 541.2 | 260.1 | 256.3 | 81.0 | 80.8 | 5.14 |
| 2002.5 | 544.7 | 541.4 | 258.6 | 255.3 | 80.6 | 80.4 | 5.27 |
| 2003.0 | 543.3 | 541.7 | 258.1 | 254.2 | 80.3 | 80.2 | 5.40 |
| 2003.5 | 542.8 | 541.5 | 256.1 | 253.0 | 79.9 | 79.8 | 5.53 |
| 2004.0 | 542.1 | 541.2 | 255.1 | 252.1 | 79.6 | 79.4 | 5.67 |
| 2004.5 | 541.2 | 540.8 | 253.5 | 251.0 | 79.1 | 79.1 | 5.78 |
| 2005.0 | 540.3 | 540.2 | 252.4 | 250.0 | 78.8 | 78.7 | 5.89 |
| 2005.5 | 539.7 | 539.6 | 251.0 | 248.9 | 78.4 | 78.3 | 6.00 |
| 2006.0 | 538.7 | 538.6 | 249.6 | 247.8 | 78.1 | 78.0 | 6.11 |

# Appendix III

# DATA EVALUATION SOFTWARE

Useful software for evaluating CFC data is described in this section. Several of the programs are included in the electronic version of this Guidebook on the CD-ROM that accompanies this volume, or can be downloaded from *http://www.iaea.org/programmes/rial/pci/isotopehydrology/*.

## III.1. QCFC

QCFC is an easy to use interactive Microsoft Excel spreadsheet program for carrying out quick calculations in hydrological studies using CFCs as time dependent tracers. This program is developed to: (1) provide a practical tool for quick calculations on the time dependent CFC values in air and water using known input functions; and (2) provide a software tool for the needs of teaching and training.

Selectable input values include water CFC concentrations, air CFC concentrations and a date (year) for the corresponding atmospheric CFC concentration. In this spreadsheet program, the independent and dependent variables are interchangeable. This feature allows the user to start from any known value(s) (set as independent variable(s)) to calculate the unknown value(s) (set as dependent variable(s)). In addition, the interactive feature of this program allows the user to assess the effects of changing values more easily. Finally, this program has demonstrated that the two basic methods of mathematical modelling, i.e. the solution of direct and inverse problem, can be combined in one single spreadsheet by proper program design.

The calculations in this program are based on the air–water equilibrium and take into account temperature, salinity, altitude and historical CFC concentrations in the atmosphere, as well as local elevation factors. Except for excess air, other processes that may modify CFC equilibrium concentrations in water such as ‘point-source’ contamination, microbial degradation, matrix sorption/retardation, mixing of waters of different age and hydrodynamic dispersion are not considered separately, but rather considered in a single factor (saturation factor).

The program can be downloaded from: *http://www.iaea.org/programmes/rial/pci/isotopehydrology/* and is included on the CD-ROM that accompanies this Guidebook. For instructions on use of the software, see Section III.10.

## III.2. USGS-CFC2004

This Microsoft Excel program is used by the U.S. Geological Survey Chlorofluorocarbon Laboratory to assist in the preliminary interpretation of results of CFC analysis of groundwater. This program includes the piston flow model, the exponential model and binary mixing model. It also permits dating using the ratios of CFC concentrations and permits construction of mixtures of two water samples, both of which may contain CFCs. Finally, this program can be used to observe the sensitivity of the calculated piston age to uncertainties in the recharge temperature and elevation. The program is included on the CD-ROM that accompanies this Guidebook. For instructions on the use of this software, see Section III.10.

## III.3. TRACERMODEL1

TRACERMODEL1, written by J.K. Böhlke, is a Microsoft Excel spreadsheet program to determine hypothetical concentrations of atmospheric environmental tracers in water samples with several different age distributions. It is designed to permit plotting of ages and tracer concentrations in a variety of different combinations to facilitate interpretation of measurements. TRACERMODEL1 includes several different types of graphs that are linked to the calculations. The spreadsheet and accompanying graphs can be modified for specific applications. For example, the selection of atmospheric environmental tracers can be changed to reflect analytes of interest, the input tracer data can be modified to reflect local conditions or different timescales, and the analytes of interest can include other types of non-point-source contaminants, such as nitrate (Böhlke, 2002).

TRACERMODEL1 contains two Excel workbooks: TRACERMODEL1a and TRACERMODEL1b. TRACERMODEL1a consists of two worksheets and several charts. The first worksheet (‘models’) contains the tracer calculations for hypothetical age distributions, and the second worksheet (‘samples’) contains measurements for representative samples for comparison with the models (real data can be substituted here). TRACERMODEL1b is similar to TRACERMODEL1a, except that TRACER-MODEL1b includes provision for evaluating $^{3}$H–$^{3}$He data. The program is included on the CD-ROM that accompanies this Guidebook. For instructions on the use of this software, see Section III.10.

## III.4. GASFLOW

GASFLOW, written by P. G. Cook and translated into Visual Basic code in Microsoft Excel by K. Solomon, solves the one-dimensional flow equation for combined gas and liquid flow in the unsaturated zone. Diffusion occurs in both the liquid and vapour phases, and convection only in the liquid phase. Retardation due to sorption on the solid phase is included in the model. It is assumed that exchange between the liquid, gas and solid phases is instantaneous. Instructions on its use can be found in the Excel workbook. The program can be found on the accompanying CD-ROM.

## III.5. CFC

The Microsoft Excel based program CFC is a comprehensive tool for CFC laboratory data handling, created at the IAEA Isotope Hydrology Laboratory and tailored for the needs of CFC analysing laboratories. It includes many more data evaluation procedures than QCFC, but requires a sound understanding of CFCs and of processes possibly affecting measured concentrations. The IAEA Isotope Hydrology Laboratory can be contacted for details, or to obtain a copy of this program.

## III.6. FLOWPC

This program includes several lumped-parameter models for the interpretation of environmental tracer data in steady state flow approximations (Maloszewski and Zuber, 1996). It includes the piston flow model, the exponential flow model, the linear model, two combined models for piston flow and exponential/linear flow, and the dispersion model. The program is available from the IAEA and is included on the accompanying CD-ROM.

## III.7. TRACER

TRACER (Bayari, 2002) is an Excel workbook for calculating the mean residence time of groundwater based on the environmental CFC-11, CFC-12 and tritium concentrations using piston, exponential, linear, exponential piston flow and linear piston flow lumped-parameter models. The program is available from: *http://www.iamg.org/CGEditor/index.htm*.

## III.8. LUMPED

LUMPED (Ozyurt and Bayari, 2003) is a Visual Basic code for the analysis of mean residence time in groundwater systems based on measurements of tritium, CFC-11, CFC-12, CFC-113, $SF_6$ and $^{85}Kr$. A total of 15 different lumped-parameter models are considered. The program is available from: *http://www.iamg.org/CGEditor/index.htm* 
or from *http://www.sukimyasilab.hacettepe.edu.tr/english/software.shtml*

## III.9. BOXMODEL

This is an Excel workbook program to evaluate environmental tracer data by the box model approach. Atmospheric tracer input data are convoluted using three different approaches (piston flow, exponential mixing, dispersion) and mean residence times calculated for environmental tracers in aquifers. The data are compared with measured sample data. The program can be downloaded from: *http://www.baum.ethz.ch/ihw/boxmodel_en.html* written by K. Zoellmann, W. Kinzelbach and W. Aeschbach-Hertig). For instructions on the use of this software, see Section III.10.

## III.10. INSTRUCTIONS ON THE USE OF THE SOFTWARE PROGRAMS

### III.10.1. QCFC

QCFC is the IAEA spreadsheet program for evaluation of CFC data written by L.F. Han.

Main window

This window contains input boxes for the parameter/factor values and independent variables (boxes with blue colour). It also contains output boxes for the calculated results (boxes with yellow colour) and two graphs. The values can be changed using the scrollbars. The output results and the graphs respond interactively to reflect the change in the values.

There are three sets of variables: recharge date, CFCs in water and CFCs in air. The three sets of variables are interchangeable by choosing one of the options:

- Set CFCs in water as independent variables;
- Set CFCs in air as independent variables;
- Set date as independent variable.

If one set of variables is chosen as independent variables, the scrollbars associated with the variables are activated and the scrollbars associated with the other sets of variables are dimmed. The dimmed scrollbars indicate that the variables are dependent variables.

The scrollbar associated with the upper graph is independent of the variables. It is only used for reading out the recharge date based on CFC ratios.

### Window for editing input functions

Up to three sets of input functions can be created and maintained in the template sheet. By clicking one of the ‘set as default’ buttons in this window the user can switch quickly from one set of input functions to another.

### Using the spreadsheet

The program facilitates insight into the interrelationship of parameters relevant for applying CFCs as a dating tool. The user is guided to pay attention to the basic parameters, such as elevation of study area, the average temperature of recharging water and its salinity, and excess air. The saturation and dilution factors are also considered. The effects of those parameters on calculated results are easily visible.

By choosing ‘set CFCs in water as independent variables’ and taking the measured CFC concentrations as input, the user can quickly convert CFC water concentrations into dry air concentrations (pptv) at sea level and obtain apparent recharge dates. The user can also re-evaluate published CFC data to perform exercises or to learn basic skills of groundwater dating with CFCs, i.e. to obtain age information by combining measured CFC concentrations in water and other relevant information (input function, recharge temperature and altitude, etc.).

The use of ‘set CFCs in air as independent variables’ helps to assess questions on CFC tracer behaviour for different parameter values. It also reveals any effect of CFC contamination due to past local CFC emission (industry, waste disposal).

The option to ‘set date as independent variable’ allows the user to easily calculate air and water CFC concentrations for any point in time and to forecast and estimate expected CFC concentrations for field studies to be undertaken.

The option to change CFC input functions allows the user to easily evaluate data from distinctly different locations. It is well known that the input functions are considerably different in highly industrialized areas (western Europe, USA) compared with rural regions or oceanic sites (islands).

Details about methods of calculations are summarized in the on-line help pages in the program.

### III.10.2. USGS-CFC2004

USGS-CFC2004 is the spreadsheet program for preliminary evaluation of CFC data (E. Busenberg and L.N. Plummer). This program is used by the U.S. Geological Survey Chlorofluorocarbon Laboratory to assist in the preliminary interpretation of results of CFC analysis of groundwater. The Microsoft Excel program consists of several sub-sheets.

Definitions

The following definitions are common to all sub-sheets in USGS-CFC2004:

- All input fields or their headings have a yellow background throughout the program;
- Required input fields have bold headings;
- Green background fields contain explanations, comments and caution statements;
- Columns with blue backgrounds should not be altered and these columns should be hidden;
- In all the figures, blue, red and green lines represent CFC-12, CFC-11 and CFC-113, respectively;
- Ages of other data are found at the intersection of horizontal dashed lines with curves of the same colour. The age or other data can be obtained by placing the pointer on the intersection and a pop-up box appears with the pertinent data.

Setting up the program

Setting up the program in the ‘RESULTS’ sheet involves the following:

- *CFC enrichment factors*: Cells E12, E13, and E14 are used to correct the air curves for any local enrichment of CFCs. Normally, the contents of the cells should remain as 1.00 and the program will use the northern hemisphere air concentrations. If local enrichment is present, then the content of the cells can be changed to reflect this. For example, a factor of 1.05 for CFC-12 should be entered to represent a 5% enrichment in the concentration of CFC-12 in air. The program will multiply the entire

CFC-12 air curve by this factor. The local air curve in this example will be used to calculate the apparent CFC-12 ages of the samples. The northern hemisphere air curve, as well as the local air curves, are shown in Fig. 1 of the 'INPUT' sheet.

— *Recharge elevation units*: Cell E15 determines the recharge elevation units that will be used throughout the worksheet. An input of 0 is used if the elevations of recharge are entered in metres, while 1 should be used if elevations are entered in feet.

— *Units of CFC concentration*: Cell E16 determines the units of input of the CFC concentrations in columns R, S and T. An input of 0 indicates that the unit of concentration of CFCs is entered as picomoles/kg, while an input of 1 is required if the concentrations are entered as picograms/kg.

— *Date of sampling*: The date format of column G is set for the entry of dates in order of month/day/year. For example, an entry of 1/3/01 represents the date 3 January 2001. The date of sampling is a required entry because it is used to calculate the apparent age in years of the groundwater. The date format of column G can be changed in the Excel program through the following steps: Format—Cells—Date—(select preferred date format).

— *Sensitivity of calculated age to the recharge temperature*: Cell U15 should be set at 0.0 in order for this program to calculate the correct apparent ages of the groundwater. The program can be used to rapidly evaluate the sensitivity of the calculated apparent ages to the recharge temperature. For example, an entry of 2.0 can be used to determine the sensitivity of the calculated ages if the recharge temperature of all the samples (column V) were higher by 2°C. An entry of –3.0 can be used to evaluate the sensitivity of calculated apparent ages for a recharge temperature that is 3.0°C lower than the temperature entered in column V. The program does not accept temperatures below 0°C.

— *Sensitivity of calculated age to the recharge elevation*: Cell U16 should be set at 0.0 in order for this program to calculate the correct apparent ages of the groundwater. The program can be used to rapidly evaluate the sensitivity of the calculated apparent ages to the recharge elevation. For example, an entry of 200 can be used to determine the sensitivity of the calculated ages if the recharge elevation of all the samples (column V) were higher by 200 m or ft. An entry of –300 can be used to evaluate the sensitivity of calculated apparent ages for a recharge elevation that is 300 m or ft lower than the elevations entered in column W. The program does not accept elevations below sea level.

### Input

Input in the USGS-CFC2004 'RESULTS' sheet includes the following (required entries are in bold):

- **Column E: Name of sample.**
- Column F: Number, if more than one sample was collected from the same source.
- **Column G: Date of sampling.**
- Column H: Time of sampling.
- **Column R: Measured CFC-12 concentration in sample (if determined).**
- **Column S: Measured CFC-11 concentration in sample (if determined).**
- **Column T: Measured CFC-113 concentration in sample (if determined).**
- Column U: Concentration of 'excess air' present in the sample. The content of 'excess air' is often less than 2 $cm^3$ STP/kg of water, but can be substantially higher in samples recharged along floodplains of rivers, or arroyos, or where recharge occurs through fractured rocks (see Chapter 4, Section 4.4). Place 0.0 or an estimate of the 'excess air' concentration that is appropriate for the recharge conditions of your sample if the 'excess air' concentration has not been determined.
- **Column V: Recharge temperature.** The temperature of recharge of the groundwater sample, which may or may not be the same as the temperature of the water (see Chapter 4, Section 4.3). If the recharge temperature has not been calculated from permanent gas concentrations, then enter here the mean annual air temperature of the recharge location.
- **Column W: Recharge elevation.** The elevation at the location of recharge (see Chapter 3 and Table 3.2). The recharge elevation can differ significantly from the elevation of the water sample at time of collection.
- **Column Y: Salinity of the groundwater in parts per thousands.** For most dilute ground and surface waters enter 0.00. (See Chapter 3 and Table 3.2.)

### Output

Output of 'RESULTS' sheet:

- Calculated partial pressures are in columns AM through AO;
- Apparent piston flow dates of recharge are given in columns AP through AU;
- Apparent piston flow ages are given in years in columns BM through BR (see Chapter 3);

- Ratio ages calculated from two CFCs in years are given columns BS through BX. The fraction of young water in the binary mixture of young and CFC-free water is also given where applicable (see Chapter 5).

‘INPUT’ sheet:

Input up to five numbers from column A of the ‘RESULTS’ sheet in columns B16 to B20 of the INPUT sheet. The program evaluates several lumped-parameter models in the next five sheets. If there are multiple analyses of the same sample, it is recommended that all replicates be evaluated at one time.

Figure 1 on this sheet is a plot of the air mixing ratios (Table II.1) that were used to calculate the groundwater ages. If an enrichment factor was used, then both the local (solid lines) and the northern hemisphere (dashed line) will be shown.

‘SENSITIVITY’ sheet

On Fig. 1 of the ‘SENSITIVITY’ sheet are plotted the following samples selected in the ‘INPUT’ sheet:

- To observe the sensitivity of the calculated piston age to uncertainties in the recharge temperature, the input in °C in cell B4 will be added to the recharge temperature entered in column V of the ‘RESULTS’ sheet;
- The input in °C in cell B5 will be subtracted from the recharge temperature entered in column V of the ‘RESULTS’ sheet;
- To observe the sensitivity of the calculated piston age to uncertainties in the recharge elevation, the input uncertainty in cell B8 will be added to the recharge elevation entered in column W of the ‘RESULTS’ sheet;
- The input uncertainty in cell B9 will be subtracted from the recharge elevation entered in column W of the ‘RESULTS’ sheet;

The output will show the date of recharge and the error bars represent the uncertainty in the recharge date. Samples are colour coded for identification — see table in ‘SENSITIVITY’ sheet.

‘PISTON’ sheet

In Fig. 1, the piston flow recharge dates can be obtained at the intersection of the horizontal dashed lines with the air curves of the same colour.

The local (solid line), as well as the northern hemisphere (dashed line), air mixing curves are given. The age of the samples can be evaluated with and without the local enrichment factor.

The samples were selected to be evaluated in the 'INPUT' sheet.

'RATIO' sheet

Ratio ages are valid only if (Chapter 3, Section 3.3 and Chapter 5):

- The two CFCs are not contaminated or their air water equilibrium concentrations were not altered in any way;
- The ratio age is valid only if it is younger or the same as the piston age of the two CFCs used to calculate the ratio.

On Fig. 1 of this sheet, the ratio age is obtained at the intersection of the horizontal dashed lines with the ratio curves of the same colour. The recharge date of the young fraction with the local and northern hemisphere air can be determined from Fig. 1.

The per cent of young water in a binary mixture of young and CFC-free water can be determined on Fig. 2. Required input is the age of the young water to the nearest 0.5 year. The per cent of young water in the mixture can be obtained from this figure. Both the local air as well as the northern hemisphere air are shown.

'BINARY' sheet

The atmospheric partial pressure ratios of CFC-11/CFC-12, CFC-113/CFC-12 and CFC-113/CFC-11 are plotted in Figs 1–3, as follows:

- The solid black curves represent piston flow models plotted using the local air curves;
- Unmixed waters should plot on the piston flow line;
- The dashed lines represent binary mixtures of young and CFC-free water. Mixtures fall on straight lines representing mixtures of various age waters with CFC-free waters;
- Mixtures of 2000, 1995, 1990, 1985 and 1980 waters with CFC-free water are represented by red, blue, green, orange and brown dashed lines, respectively;
- The fraction of young water can be estimated from the location of the sample on the binary mixing lines;

— Set A of the three figures plots all the samples in the worksheet while set B plots the samples selected (up to five samples) in the 'INPUT' sheet.

### 'MIXTURE' sheet

This sheet permits construction of mixtures of two water samples, both of which may contain CFCs. The two samples mixed are defined by their (assumed) apparent age. A graph shows the concentrations (in pptv) of up to five samples selected in 'INPUT' for each CFC.

### 'EXPONENTIAL' sheet

Required input is the date of sampling that is entered to the nearest 0.5 year.

— The exponential model is assumed (Chapter 6).
— Figure 1 (Excel workbook) gives exponential model CFC partial pressures of groundwater samples with average residence times of 1–1000 years. Figure 2 (Excel workbook) is a similar plot of the average residence times of 1–100 years.
— If the exponential model applies, the average residence time of a sample is represented by the intersection of the horizontal dashed line with the exponential model curve of the same colour.
— The samples shown were selected in the 'INPUT' sheet.

Table 1 below Fig. 1 (Excel workbook) gives the CFC concentrations as a function of the residence time of the groundwater. Also given is the apparent piston flow age for any given exponential residence time.

### 'AIR2004' sheet

The 'AIR2004' sheet is the revised air mixing ratios of CFCs that are used in this program to date northern hemisphere groundwater. The mixing ratios are given on the SIO-98 scale (Table II.1).

## III.10.3. TRACERMODEL1. Excel workbook for calculation and presentation of environmental tracer data for simple groundwater mixtures (J.K. Böhlke, U.S. Geological Survey, *jkbohlke@usgs.gov*)

### Introduction

Atmospheric environmental tracers commonly used to date groundwater on timescales of years to decades include CFC-11, CFC-12, CFC-113, $SF_6$, $^{85}$Kr, $^3$H and $^3$H/$^3$H$^0$, where $^3$H$^0$ refers to initial tritium ($^3$H + tritiogenic $^3$He) (Cook and Herczeg, 2000). Interpretation of age from environmental tracer data may be relatively simple for a water sample with a single age, but the interpretation is more complex for a sample that is a mixture of waters of varying ages. A mixture can be a natural result of convergence of flow lines to a discharge area such as a spring or stream, or it can be an artefact of sampling a long-screen well. TRACERMODEL1 contains a worksheet that can be used to determine hypothetical concentrations of atmospheric environmental tracers in water samples with several different age distributions. It is designed to permit plotting of ages and tracer concentrations in a variety of different combinations to facilitate interpretation of measurements. TRACERMODEL1 includes several different types of graphs that are linked to the calculations. The spreadsheet and accompanying graphs can be modified for specific applications. For example, the selection of atmospheric environmental tracers can be changed to reflect analytes of interest, the input tracer data can be modified to reflect local conditions or different timescales, and the analytes of interest can include other types of non-point-source contaminants, such as nitrate (Böhlke, 2002). Previous versions of this workbook have been used to evaluate field data in studies of groundwater residence time and agricultural contamination (Böhlke and Denver, 1995; Focazio et al., 1998; Katz et al., 1999; Katz et al., 2001; Plummer et al., 2001; Böhlke and Krantz, 2003; Lindsey et al., 2003).

### Calculations

Calculations are based on equations given in Cook and Böhlke (2000), some of which were modified slightly from those of previous authors (Vogel, 1967; Zuber, 1986). Equations summarized here relate the concentration of a tracer in a sample collected at a specific time ($C_{s,ts}$) to the tracer concentrations in recharging waters of all ages represented in the sample. A water sample is considered to be a mixture of sub-parcels, each of which has a tracer concentration appropriate for the time it entered the system ($C_{\text{in,ti}}$), adjusted for first-order decay. The tracer concentration in the sample is given by the sum of the fractional contributions of all sub-parcels in the sample. The fractional contributions of the sub-parcels are given by various assumptions about their age–frequency distribution in the sample. Because the commonly used atmospheric environmental tracers are transient (their concentrations in air have changed over time), the tracer concentrations in any water sample will depend not only on the age distribution, but also on the date the sample was collected.

In the Piston Flow Model (PFM), all the water in the sample has a single age (by definition equal to the mean age or residence time $\tau_{\mathrm{PFM}}$) (Chapter 3), and the time it entered the system (*ti*) is equal to ts–τ. In this case, the concentration of a tracer in a sample collected at time *ts*, is given by:

$$C_{\mathrm{s,ts}} = C_{\mathrm{in},(ts-\tau_{\mathrm{PFM}})} \qquad (1)$$

In the Binary Mixing Model (BMM), the sample is a mixture of two subparcels, one of which is young and contains measurable tracer and one of which is too old to have measurable tracer (Chapter 5). As currently formulated in the model worksheet, the young subparcel is assumed to have a discrete age. In this case, the concentration of a tracer in a sample collected at time *ts*, is given by:

$$C_{s,ts} = X_{\mathrm{young}} \cdot C_{\mathrm{in},(ts-\tau_{\mathrm{young}})} \qquad (2)$$

where $X_{\mathrm{young}}$ is the fraction of the sample consisting of the young sub-parcel and $\tau_{\mathrm{young}}$ is the age of the young sub-parcel. Given a value of $\tau_{\mathrm{young}}$ (which could be zero for dilution of modern water), the worksheet returns tracer concentrations for mixtures ranging from 0 to 100% young, in 10% increments.

In the Exponential Mixing Model (EMM), the sample consists of an infinite number of sub-parcels that have an exponential age distribution and an overall mean age of $\tau_{\mathrm{EMM}}$ (Chapter 6, Section 6.1). This could correspond to certain simple situations, such as discharge from a spring or long-screen well in a homogeneous aquifer with evenly distributed recharge. In this case, tracer concentrations are calculated by stepping forward numerically through time and adding appropriate increments for each sub-parcel. At each time step:

$$C_{s,ti} = C_{s,(ti-1)} + [1/\tau_{\mathrm{EMM}}] \cdot [C_{in,ti} - C_{s,(ti-1)}] \qquad (3)$$

where $C_{s,ti}$ is the concentration of tracer in the mixture at time *ti*, $C_{s,(ti-1)}$ is the concentration in the mixture at the previous time step, and $C_{in,ti}$ is the concentration in the new recharge added to the mixture in the time step.

In the Exponential Piston Model (EPM), the sample consists of an infinite number of sub-parcels that have an exponential age distribution

(EMM), but the whole assemblage is shifted in time (Chapter 6, Section 6.3). This could correspond to a situation in which an aquifer receives distributed recharge in an upgradient unconfined area, then continues beneath a downgradient area that does not receive recharge (e.g. confined area). The EMM age distribution is established in the recharge area, then all sub-parcels in the mixture age together as the water moves laterally beneath the area without recharge. The same result would be obtained for a perfectly soluble tracer in the reverse situation in which the sample represents an aquifer receiving distributed recharge following piston flow through an unsaturated zone. That is, the EPM model and its reverse (PEM) would be indistinguishable for a tracer like $^3$H. The procedure used in the model worksheet for the EPM is as follows:

- Assign an age to the PFM part of the flow system ($\tau_{PFM}$) and a ratio of $\tau_{PFM}/\tau_{EMM}$ and use these values to calculate the total mean age ($\tau_{EPM}$) and the mean age of the EMM part of the system ($\tau_{EMM}$);
- Locate the EMM tracer concentration result corresponding to $\tau_{EMM}$ for a displaced sample date of ts–$\tau_{PFM}$;
- Add first order decay to the displaced EMM result for the time represented by $\tau_{PFM}$ (decay was already accounted for in the EMM calculation).

Explanation of workbook TRACERMODEL1a

- *General:* TRACERMODEL1 consists of two worksheets and several charts. The first worksheet ('models') contains the tracer calculations for hypothetical age distributions and the second worksheet ('samples') contains measurements for representative samples for comparison with the models (real data can be substituted here). In the models worksheet, bold italic entries in shaded boxes are entries made by the user. All other entries should be left alone except when modifying the calculations. The models worksheet is arranged as follows.
- *Column A:* Times (in years) for tracer input values. The time interval for the input data (cell A6, currently two rows per year) is used in the decay equation and elsewhere. This can be changed to accommodate other input data sets (e.g. annual, monthly, etc.), as long as the table is filled at the corresponding timescale for all tracers of interest and the entry in cell A6 is correct.
- *Columns C–G:* Tracer input values. The current entries (CFC-11, CFC-12, CFC-113, $SF_6$, $^3$H) represent atmospheric abundances in the mid-Atlantic region of North America. The current entries for the gases are

atmospheric mixing ratios in parts per trillion by volume (pptv) from Table II.1. Model output in these units is generalized and can be compared with measurements from water samples if the measurements have been converted to equilibrium mixing ratios at appropriate temperatures and pressures. Alternatively, the input tracer values can be replaced with equilibrium aqueous concentrations for a specific set of conditions. The entries for $^3$H are from the Washington, D.C. record (IAEA GNIP; R.L. Michel, private communication, 2004). Concentrations of $^3$H before 1959 and after 2000 are estimated. Cells C6:G6 contain half-lives for the tracers, which can be altered to evaluate effects of first-order decay. An alternative tracer (e.g. $^{85}$Kr or nitrate) can be substituted for a current one simply by replacing the entries in one of these columns.

- *Columns J–N:* Interactive exponential mixing model. The mean age can be changed here (cell J6) for a quick comparison of different tracers in a sample collected at any time. This section is independent of the larger calculation blocks to the right.
- *Columns S–Z:* Comparison of PFM, EM, EPM and BMM results for a single tracer (currently CFC-11). For PFM (columns S and T), EMM (columns U and V), and EPM (columns W and X), mean ages are tabulated with corresponding tracer concentrations. For BMM (columns Y and Z), results for mixtures of varying proportions of old and young water are given. Important entries here are the sample date (cell S6, applies to all models), the ratio of $\tau_{PFM}/\tau_{EMM}$ (cell W6, for the EPM model), and the age of the young fraction (cell Z6, BMM model). The values of mean age considered by the EMM calculations (cells AD6–BL6) can be altered if necessary (entries in this section are used for all tracers in the worksheet).
- *Columns AA–BL:* The worksheet block for EMM calculations for various mean ages and collection times. These data are used to fill in the summaries in columns S–Z and they also are used directly in some types of graphs (see below).
- *Columns BO–IV:* Four more blocks of data and calculations identical to those in columns S–BL, but for different tracers. The calculations in these other blocks refer to the input data and half-lives in appropriate columns from C–G.
- *Graphs:* Representative plot types are shown to illustrate different approaches to data evaluation. Hypothetical tracer concentrations from any of the models can be plotted against sample dates, mean ages and each other. Measurements added to these and other related plots can be evaluated for concordance with different model assumptions, for

concordance among different tracers in a sample, and for evidence of degradation or contamination. Measured values are shown in the tracer-tracer plots for three hypothetical samples that yield concordant results for different age distributions. All tracer measurements in each of these samples are consistent if interpreted as follows: sample 1 has a single discrete age ($\tau_{PFM}$) of 14 years; sample 2 is a binary mixture in which the young sub-parcel is 60% of the sample and has an age ($\tau_{young}$) of 14 years; sample 3 is an exponential mixture with a mean age ($\tau_{EMM}$) of 14 years. Other graphics programs may provide additional options for the presentation of the data.

Explanation of workbook TRACERMODEL1b

- *General:* TRACERMODEL1b is similar to TRACERMODEL1a except that TRACERMODEL1b includes provision for evaluating $^3H$–$^3He$ data. This is done by treating $^3H$ both as a stable species ($^3H^0$) and as a radioactive species ($^3H$) and reserving one block of calculations for the ratio $^3H/^3H^0$. The remaining two calculation blocks can be used for any other tracers (currently CFC-12 and $SF_6$).
- *Columns S–BL:* This block is different from all the others because the results are calculated directly by dividing the model results for radioactive $^3H$ ($^3H$) by the model results for ‘stable’ $^3H$ ($^3H^0$). Results of these calculations can be compared to $^3H$–$^3He$ measurements by assuming $^3H^0 = {}^3H$ + tritiogenic $^3He$ (see ‘samples’ worksheet).

Disclaimer

The current version of TRACERMODEL1 contains several modifications from previous versions that have not been tested fully. Any errors or suggestions may be directed to the author. Also, because the worksheets are not protected from accidental changes, users are advised to keep unaltered backup copies.

### III.10.4. Use of spreadsheet Boxmodel for age determination with tritium and CFCs (W. Aeschbach, U. Beyerle, K. Zoellmann and W. Kinzelbach)

The box model approach described previously is implemented as an Excel spreadsheet workbook. The Excel workbook is called Boxmodel_V3.xls (by Zoellmann and Aeschbach) and is provided on the CD-ROM accompanying this Guidebook. It allows the interpretation of environmental tracer data ($^3H$, $^3He_{tri}$, $^{85}Kr$ and CFCs) taken from groundwater samples. The interpretation is based on the box model approach (see the workbook, Chapter 6, and Fig. 5.6).

The use of this workbook in the interpretation of measured concentrations of environmental tracers in wells is described in the following section. All that is needed to run it is a computer equipped with the software Excel. A simplification used in this workbook is that the input data are assumed to be constant over the year, which could be unrealistic for systems with very small residence times.

The workbook consists of 17 separate sheets, comprising INTERFACE, Tr in Graph, CFC in Graph, Kr in Graph, Transfer Exp Graph, Transfer Disp Graph, Output Graph, Tau Graph, Tritium Input, CFC Input, 85Kr Input, Piston Flow Model, Exponential Model, Dispersion Model, Output (tau), Output (t) and CFC Converter. They are described in the following sections.

## INTERFACE

The sheet 'INTERFACE' contains the input parameters that can be changed by the user (black bordered cells):

- *Model Code:* Enter the desired transfer function (pm, exp or dm) that is used for convoluting the input function (pm = Piston Flow Model, exp = Exponential Model, dm = Dispersion Model).
- *Tau [a]:* Enter a value for the mean residence time in years for the pm, exp or dm model. The Transfer Function Graph is calculated for this value only. In the Tau Graph on the other hand the output concentrations for the required year are shown as function of Tau for a whole range of Tau values.
- *Tau Step [a]:* This value determines the step width for the Tau Graph in years.
- *Delta [a]:* Dispersion Parameter for the Dispersion Model. This value has no effect if the Piston Flow or the Exponential Model is used.
- *Tritium Factor:* Defines a scaling factor for the tritium input function.
- *Tracer Code:* Enter a code (tr, cfc, kr, he) for the desired tracer: tr = tritium; cfc = chlorofluorocarbons CFC-11 or CFC-12 depending on the input function provided (see sheet CFC Input); kr = $^{85}$Kr and he = tritiogenic $^{3}$He (i.e. $^{3}$He which originates from the tritium decay during groundwater flow).
- *Year of Observation:* This value determines for which time the concentrations are calculated (Tau Graph). This should be the year of your tracer measurement.

— *C_obs:* Enter here the measured tracer concentrations in the same units as the corresponding input function is given in. These values are not needed for the computation of the other graphs. But the comparison of those lines with the computed graphs allows the age dating. They are therefore drawn in the same graph as the computed output. Note that the measured CFC concentration of the groundwater sample (e.g. in pg/kg) must be transformed to pptV according to the solubility, which depends on the groundwater temperature and the altitude of the recharge area (see sheet CFC Converter) as the input function is given in these units.

Tr in Graph, CFC in Graph, Kr in Graph

These three sheets show the input functions of tritium ($^3$H), CFC-12 or CFC-11 and $^{85}$Kr derived from the Tritium Input, CFC Input, $^{85}$Kr Input data sheets.

Transfer Exp Graph, Transfer Disp Graph

These sheets show transfer functions based on the parameters (Tau and Delta) given in the User Interface Sheet.

Output Graph

This sheet shows the resulting output concentration for the desired transfer function as a function of time *t* (year of observation) for the given parameters Tau and Delta. The intersection of this curve with the observed concentration (red line) should be in agreement with the chosen residence time (Tau). This agreement can be obtained iteratively. But one can also proceed to the Tau Graph for a more convenient method.

Tau Graph (= Residence Time Graph)

This sheet shows the resulting output concentration for the desired transfer function as a function of the parameter Tau (and implicitly Delta) for a given time *t* (year of observation). The intersection of this curve with the observed concentration (red line) identifies the ‘correct’ mean residence time (Tau).

### Tritium Input, CFC Input, $^{85}$Kr Input

These three sheets contain the data of the input functions of tritium ($^{3}$H), CFC-12 or CFC-11 and $^{85}$Kr. The tritium concentrations were derived from monthly averaged precipitation and have to be adapted to your local tritium input function. They are given in Tritium Units (TU). The CFC data are given in pptV and are derived from global CFC measurements. If necessary they have to be adjusted to your local conditions. The $^{85}$Kr input function can be strongly dependent from the investigated area and should be modified if local atmospheric concentrations are known.

### Exponential Model, Dispersion Model, Output(tau) and Output(t)

These four sheets contain the calculation algorithms providing the data for the different graphs. *The user should not change them.*

### CFC Converter

This sheet allows one to convert the measured CFC concentration in pg/kg in water to a corresponding atmospheric concentration in pptV.

## Appendix IV

## REPRESENTATIVE LIST OF CFC LABORATORIES

CSIRO Land and Water,
Private Bag 2,
Glen Osmond SA 5064, Australia
P.G. Cook
Email: Peter.G.Cook@csiro.au

Isotope Hydrology Laboratory,
International Atomic Energy Agency,
P.O. Box 100, Wagramer Strasse 5,
A-1400 Vienna, Austria
L.F. Han
Email: L.Han@iaea.org, Isotope.Hydrology.Lab@iaea.org

Institute of Geology and Geophysics,
Chinese Academy of Sciences,
Qijiahuozi, Beijing, 100029, China
Z.H. Pang
Email: pangzh@mail.igcas.ac.cn

Geological Survey of Denmark and Greenland (GEUS),
Department of Geochemistry,
Øster Voldgade 10,
DK-1350 Copenhagen, Denmark
T. Laier
Email: tl@geus.dk

Spurenstofflabor,
Bornweg 10,
D-67157 Wachenheim, Germany
H. Oster
Email: Harald.Oster@t-online.de

Institute of Environmental Physics/Oceanography,
University of Bremen,
Otto Hahn Allee,
D-28359 Bremen, Germany
J. Sueltenfuss
Email: noblegas@uni-bremen.de
*http://www.noblegas.uni-bremen.de*

GNS
Water Dating Laboratory,
Lower Hutt, New Zealand
M. Stewart
Email: m.stewart@gns.cri.nz
*http://www.gns.cri.nz/services/groundwater/cfc.html*

Radioisotope Hydrology Group,
Radiation and Isotope Application Division,
Pakistan Institute of Nuclear Science and Technology,
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*http://www.eawag.ch/research_e/w+t/e_index.html*

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Water Chemistry Laboratory,
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Email: nozyurt@hacettepe.edu.tr, serdar@hacettepe.edu.tr

United States Geological Survey,
432 National Center,
Reston, VA 20192, United States of America
L. N. Plummer, E. Busenberg
Email: cfc@usgs.gov
*http://water.usgs.gov/lab/cfc*

Dissolved Gas Laboratory,
135 East 1460 South,
Salt Lake City, Utah 84112, United States of America
D.K. Solomon
Email: ksolomon@mines.utah.edu

University of Miami/RSMAS
Tritium Laboratory,
4600 Rickenbacker Causeway,
Miami, FL 33149, United States of America
J. Happell / C. Grall
Email: jhappell@rsmas.miami.edu, cgrall@rsmas.miami.edu
*http://www.rsmas.miami.edu/groups/tritium/*

LDEO CFC Laboratory,
Lamont–Doherty Earth Observatory,
P.O. Box 1000,
Palisades, New York 10964, United States of America
W.M. Smethie, Jr.
Email: bsmeth@ldeo.columbia.edu

UWSP Dissolved Gas Laboratory,
College of Natural Resources,
800 Reserve Street,
University of Wisconsin — Stevens Point,
Stevens Point, WI 54481, United States of America
B.A. Browne
Email: bbrowne@uwsp.edu

# ABBREVIATIONS

| | |
|---|---|
| AFEAS | Alternative Fluorocarbons Environmental Acceptability Study (USA) |
| AGAGE | advanced GAGE |
| ALE | atmospheric lifetime experiment |
| CDIAC | Carbon Dioxide Information Analysis Center (USA) |
| CMDL | Climate Monitoring and Diagnostics Laboratory (NOAA) |
| DIC | dissolved inorganic carbon |
| DOC | dissolved organic carbon |
| ECD | electron capture detector |
| GAGE | global atmospheric gases experiment |
| GC-MS | gas chromatography-mass spectrometry |
| GNIP | global network of isotopes in precipitation |
| ID | internal diameter |
| MCL | maximum contaminant level |
| MLD | million litres per day |
| NOAA | National Oceanic and Atmospheric Administration (USA) |
| OD | outside diameter |
| pMc | per cent of modern carbon |
| pptv | parts per trillion ( $= 10^{12}$) by volume |
| SIO | Scripps Institution of Oceanography |
| STP | standard temperature and pressure (0°C, 1013.25 hPa) |
| TDC | total dissolved carbon |
| TU | tritium unit ( $= [^3H]/[^1H] = 10^{-18}$) |
| UHP | ultra-high purity |
| USEPA | United States Environmental Protection Agency |
| USGS | United States Geological Survey |
| VOC | volatile organic compound |

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* See the Editorial Note at the beginning of this Guidebook regarding the style followed for the references.

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Development of the chlorofluorocarbon (CFC) technique as a tool for dating groundwater has occurred over approximately the last 20 years, and a number of research publications have documented its use in specific aquifers. This publication is intended to facilitate a comparative analysis of CFC and isotope techniques and a wider use of the CFC technique under appropriate conditions by providing a description of its scientific basis, sampling and measurement methods, interpretation and limitations of data, and a variety of case studies.

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