

# Aquifer Mapping Program Technical Document: Water Sampling Procedures, Analysis and Systematics

Open-file Report 558

December 2013

New Mexico Tech  
New Mexico Bureau of Geology  
and Mineral Resources



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## BACKGROUND

Groundwater and surface water sampling is often done under the auspices of the Aquifer Mapping Program and other related hydrogeologic studies at the New Mexico Bureau of Geology and Mineral Resources. We use the water samples from wells, springs, and surface water bodies to help interpret the flow path of groundwater, identify the recharge areas, and evaluate groundwater residence time. Since our hydrogeologic studies officially began in 2007, we have developed and implemented our procedures for water sample collection. Water may be sampled for a number of analyses including major ion chemistry, trace metal chemistry, stable isotopes of oxygen and hydrogen, and several naturally occurring environmental tracers, which provide estimates of groundwater age. This document serves as a reference to describe the procedures we use for water sample collection and for sample analyses. We try to adhere to these procedures to the extent that it is possible.

### Laboratories Used

#### Chemistry Laboratory New Mexico Bureau of Geology and Mineral Resources

801 Leroy Place  
Socorro, NM 87801

Analyses of interest: Major ion and trace metal chemistry

#### Stable isotope laboratory New Mexico Institute of Mining and Technology Department of Earth and Environmental Sciences

801 Leroy Place  
Socorro, NM 87801

Analyses of interest: Oxygen and hydrogen stable isotopes

#### Miami Tritium Laboratory University of Miami Rosenstiel School of Marine & Atmospheric Science

4600 Rickenbacker Cswy  
Miami, FL 33149-1098

Analyses of interest: Tritium, chlorofluorocarbons

#### Beta Analytic Inc. 4985 SW 74 Court Miami, Florida 33155 USA

[www.radiocarbon.com](http://www.radiocarbon.com)

Analyses of interest: Carbon-14, carbon isotopes

#### University of Utah Dissolved Gas Service Center

115 South 1460 East Rm. 205  
Salt Lake City, Utah 84112-0112

Analyses of interest: Tritium-helium, other noble gases



## PROCEDURES AND ANALYSIS

### Field parameters

When sampling water at stream, spring or well sites, field parameters are recorded. As wells are purged, sampling is initiated once field parameters have stabilized. Temperature, specific conductance, pH, and dissolved oxygen (DO) are measured in the field with a portable meter (YSI™ Model 556 Multiprobe). For springs, field parameters are typically measured in the spring pool. For wells, field parameters are monitored continuously as the well is purged using an in-line flow cell or flow-through bucket. Sample collection is initiated following parameter stabilization, typically after at least one wellbore volume has purged. Where possible, the oxidation-reduction potential (ORP) is also recorded. The DO probe is calibrated onsite before sampling, at least daily or with any significant elevation or pressure changes. The pH electrode is calibrated weekly against pH 7 and 10 buffers.

### Major ions and trace metals

For major ion and trace metal chemistry, well and spring samples are collected using clean polypropylene containers after three repeated rinses with sample water. Samples for general ion chemistry analyses are collected in 250-ml polypropylene bottles. Water samples for trace metal chemistry are immediately filtered (where possible) through an inline 0.45 µm filter into 125-ml polypropylene bottles and acidified to pH <2 with ultra-pure nitric acid. If a trace metal chemistry sample cannot be field filtered and acidified, it is filtered and acidified upon arrival in the laboratory. All chemistry samples are stored in an ice chest during transport, transferred to the NMBGMR Chemistry Laboratory,

and stored in a refrigerator until analyzed (within 1-2 weeks). Alkalinity (as mg/L HCO<sub>3</sub>) is determined in the NMBGMR Chemistry Laboratory by titration. Laboratory measurements of pH are performed with an Orion 420A meter, and conductivity using a YSI 3200 meter. Chemical analysis for anions (Cl, SO<sub>4</sub> and NO<sub>3</sub>) is performed using a Dionex ICS-5000 ion chromatograph. Cations (Na, K, Ca, and Mg) are analyzed using a Perkin Elmer Optima 5300 DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Trace metals are analyzed with an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) using an Agilent 7500. The quality of the chemical analyses is carefully inspected by analyzing blanks, standards, duplicate samples, and checking ion balances. The ion balance, which is the percent difference between cations and anions, for the analyses is generally within ±5%.

### Stable isotopes of hydrogen and oxygen

Stable isotopes of oxygen-18 (<sup>18</sup>O) and hydrogen-2 (deuterium, <sup>2</sup>H) are analyzed from water samples often from precipitation, wells, and streams. Samples are collected in 25 mL amber glass bottles after three repeated rinses. No air bubbles are permitted in the samples, and bottles are kept from direct sunlight. Samples are stored at room temperature in sealed bottles until analysis at the New Mexico Institute of Mining and Technology, Department of Earth and Environmental Sciences Stable Isotope Laboratory on a Picarro Cavity Ringdown Spectrometer (L1102-I Isotopic Water Liquid Sampler). Analytical uncertainties for δ<sup>2</sup>H and δ<sup>18</sup>O are typically less than 1 per mil (‰) and 0.1‰, respectively.

## Tritium

Tritium concentrations can be analyzed in water samples from wells, streams, springs and precipitation. The majority of our samples are processed at Miami Tritium Laboratory by gas proportional counting, subsequent to electrolytic enrichment. Samples are collected according to recommendations described at <http://www.rsmas.miami.edu/groups/tritium/analytical-services/advice-on-sampling/tritium/>. The accuracy of the measurements after enrichment are 0.1 TU or 3.5%, whichever is greater. Samples are stored at room temperature before, during and after shipment.

## Tritium-Helium and noble gases

Tritium/Helium-3 and dissolved noble gas samples may be collected under circumstances which permit it, especially in areas where water is not in contact with air, such as in wells or springs where discharge location is apparent. When possible, these samples are collected using the advanced diffusion samplers, or sometimes the copper tube method, provided by the University of Utah Dissolved and Noble Gas Laboratory. Methods of sample collection are described at <http://www.earth.utah.edu/noble-gasses/how-to.php>. Analyses of gases included N<sub>2</sub>, Ar, Ne, Kr, Xe, <sup>3</sup>He and <sup>4</sup>He, with errors of ± ½ to 1% of value for helium, and ± 1 to 4% of value for all other gases. Samples are stored at room temperature before, during and after shipment. For samples where tritium-helium analyses are run at the University of Utah Dissolved and Noble Gas Laboratory, tritium samples are analyzed there using the helium ingrowth method described at <http://www.earth.utah.edu/noble-gasses/our-lab/tritium.php>. Within the lab, after samples have had sufficient time to decay, the levels of helium-3 are measured on a mass spectrometer producing results with measurement error of ±3% of the value. The detection limit with this method is typically 0.1 TU.

## Carbon isotopes

Water samples can be analyzed for carbon-14 (<sup>14</sup>C) activity and <sup>13</sup>C/<sup>12</sup>C ratios (δ<sup>13</sup>C) to determine groundwater age. For this analysis, water samples are collected in two 500 mL polypropylene bottles, or one 1 L polypropylene bottle, after rinsing three times. Sampling procedures described at <http://www.radiocarbon.com/groundwater-carbon-dating-sampling.htm> are used, with the exception of the addition of NaOH. Samples are kept chilled until shipment for analysis at Beta Analytic ([www.radiocarbon.com](http://www.radiocarbon.com)). The <sup>14</sup>C activity and <sup>13</sup>C/<sup>12</sup>C ratios of the water sample are derived from the dissolved inorganic carbon (DIC) by accelerator mass spectrometry. Measured δ<sup>13</sup>C values are calculated relative to the PDB-1 standard. Results are reported as <sup>14</sup>C activity (in percent modern carbon (pmC)) and as the apparent radiocarbon age (in radiocarbon years before present (RCYBP), where “present” = 1950 CE), with an uncertainty of one standard deviation. We generally do not do corrections for geochemical effects, therefore the reported apparent <sup>14</sup>C ages do not precisely represent the residence time of the water within the aquifer. The <sup>14</sup>C activity and apparent <sup>14</sup>C age are used as a relational tool to interpret hydrologic differences between sample locations.

## Chlorofluorocarbons and sulfur hexafluoride

Chlorofluorocarbon (CFC) and sulfur hexafluoride (SF<sub>6</sub>) samples can be collected from wells or springs with no atmospheric exposure, into three 500-mL glass bottles with foil-lined caps. The bottles and caps are thoroughly rinsed with sample water, then filled and capped underwater in a rigid bucket. Sampling follows protocols described at <http://www.rsmas.miami.edu/groups/tritium/analytical-services/advice-on-sampling/cfc-and-sf6/>. Samples are shipped to the University of Miami Tritium Laboratory where they are analyzed using a purge-and-trap gas chromatograph with an electron capture

detector. The limit of detection for the method is  $0.001 \times 10^{-12}$  moles/kg of water (pmol/kg), and  $0.01 \times 10^{-15}$  pmol/kg of water for SF<sub>6</sub>. Precision of CFC-11, CFC-12 and CFC-113 analyses is 2% or less, with SF<sub>6</sub> at 5% or less. The accuracy of the recharge ages is 3 years or less from these measurements.

## Systematics

Understanding of the groundwater systems requires applying these measurements from analyses reviewed above. In the following sections, we describe the applications of measurements as we use them in hydrogeologic studies under the Aquifer Mapping Program.

## Major ion and trace metals

The chemical composition of water samples can provide information about the “life” of the water and the flow path it has traveled from recharge to discharge location, and various other influences within the hydrologic cycle. Important to hydrogeologic studies, we examine the chemical reactions that occur in groundwater – reflected in the major ion and trace metal content – from when it begins as precipitation, travels through the soil and unsaturated zone, then eventually entering the groundwater table within various geologic rock types. The water chemistry is may be affected by environmental factors such as gases and particulates in the atmosphere, anthropogenic inputs such as septic systems or surface water pollution, and the chemical constituents of the soil gas or bedrock through which it flows.

One of the most important ways that we use water chemistry includes correlating the rock sources that have influenced the water chemistry. As groundwater flows through various rock types, such as limestone or granite, it will take up or precipitate various solutes that are measured in the major ion chemistry and trace metals. Using these results we can

also make an assessment of the overall water quality as it pertains to its various uses, including human consumption.

## Stable Isotopes

Stable isotopes of hydrogen and oxygen are useful tools for tracking precipitation through a hydrologic system. The nucleus of most oxygen atoms contains 16 subatomic particles: 8 protons and 8 neutrons. A small fraction of all oxygen atoms (approximately 0.2%) contains 10 neutrons, for a total of 18 subatomic particles in the nucleus. This isotope of oxygen is referred to as oxygen-18, or <sup>18</sup>O. Most hydrogen atoms consist of a single proton in the nucleus orbited by a single electron. A very small fraction of hydrogen atoms (approximately 0.016%) also contains one neutron in the nucleus, for a total of two subatomic particles. This isotope of hydrogen is referred to as deuterium and abbreviated as D.

The isotopic composition of a water sample refers to the ratio of the heavier isotopes to the lighter isotopes (R) for the hydrogen and oxygen that make up the water molecules. Because these stable isotopes are actually part of the water molecule, small variations in these ratios act as labels that allow tracking of waters with different stable isotopic signatures. All isotopic compositions in this report are presented as relative concentrations, or the per mil deviation of R of a sample from R of a standard shown in the equation below:

$$\delta = \left( \frac{R_{sample} - R_{standard}}{R_{standard}} \right) * 1000\text{‰}$$

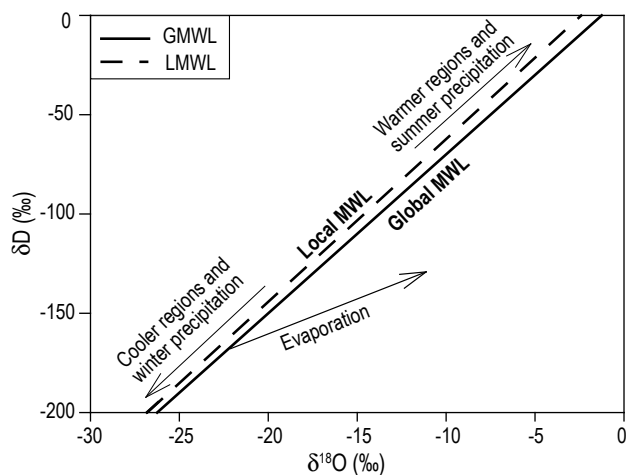
A negative value of δ<sup>18</sup>O or δD indicates that the water sample is depleted in the heavier isotopes with respect to the standard. Vienna Standard Mean Ocean Water (VSMOW) is the reference standard for stable isotopes of hydrogen and oxygen.

Because a water molecule is made up of both hydrogen and oxygen, it is advantageous to evaluate δD and δ<sup>18</sup>O data simultaneously. Figure 1 shows a graph with δD on the y-axis



and  $\delta^{18}\text{O}$  on the x-axis. On such a plot, the isotopic compositions of precipitation samples collected worldwide plot close to a line called the global meteoric water line (GMWL) due to the predictable effects of evaporation and condensation (Craig, 1961). In general, precipitation in warmer regions will plot toward the heavier end of the GMWL (less negative values), and precipitation from cooler regions will plot towards the lighter end (more negative values). At any given location, a seasonal trend may be evident with winter precipitation plotting on the GMWL toward the lighter end and summer precipitation toward the heavier end. The GMWL represents a global average variation in the isotopic composition of precipitation. In a study such as this, it is necessary to collect local precipitation and define a local meteoric water line (LMWL), whose slope and y-intercept (deuterium excess) may vary slightly from the GMWL due to local climatic conditions.

The effects of evaporation are illustrated in Figure 1. As precipitation evaporates, the isotopic composition of the residual water evolves away from the meteoric water line (global or local) along an evaporation line, whose slope depends on the conditions under which evaporation has taken place.



**Figure 1.** Stable isotope systematics.

## Tritium

Tritium ( $^3\text{H}$ ) is a short-lived radioactive isotope of hydrogen with a half-life of 12.32 years, and is a commonly-used tracer for determining the relative age of groundwater less than fifty years old. The vast majority of hydrogen atoms consist of a single, positively-charged proton in the nucleus of the atom and a single, negatively-charged electron orbiting the nucleus. The nucleus of the tritium isotope of hydrogen also includes two neutrons, for a total of three subatomic particles. Tritium concentrations are expressed in Tritium Units (TU), wherein one TU indicates a tritium-hydrogen atomic abundance ratio of  $10^{-18}$  (Clark and Fritz, 1997).

Tritium is produced naturally in the stratosphere by cosmic radiation, and enters the hydrologic cycle via precipitation. Large volumes of anthropogenic tritium were produced between 1951 and 1962 by atmospheric testing of thermonuclear weapons, creating a “bomb” tritium spike in groundwater that has been used as a tracer in many hydrologic investigations (e.g., Rabinowitz et al., 1977). By 1990, bomb-levels of tritium had decreased in the atmosphere and tritium concentrations have mostly returned to naturally occurring levels. Use of the tritium isotope for dating modern groundwater now relies upon the largely natural  $^3\text{H}$  signal (Clark and Fritz, 1997).

Unlike most environmental tracers, tritium atoms are directly incorporated into the water molecule and thus are not subject to alteration when exposed to atmospheric gases. Without knowing the background tritium concentration during recharge, a rather complicated input function must be assumed, and in most cases the absolute age of groundwater cannot be precisely determined using  $^3\text{H}$  alone. Tritium is nevertheless a very useful tracer for making qualitative assessments of groundwater residence time. Waters with a concentration of 5 to 15 TU are considered to be modern groundwater, less than 5 – 10 years old. Tritium concentrations of 0.8 to 4 TU probably represent a mixture of recent and sub-modern recharge. Water samples less

than 0.8 TU are assumed to be sub-modern, recharged prior to 1952 (Clark and Fritz, 1997).

Atmospheric concentrations of tritium display significant spatial and seasonal variations. The greatest increase in tritium concentrations in the atmosphere occurs during the spring in mid-latitude zones due to displacement of the jet stream (Clark and Fritz, 1997).

### Tritium-helium and noble gases

Tritium is subject to radioactive decay by beta emission to yield its daughter product, helium-3 ( $^3\text{He}$ ). By measuring  $^3\text{H}$  together with its daughter,  $^3\text{He}$ , a true radiometric groundwater age can be determined that does not rely on a tritium input function (Solomon and Sudicky, 1991). Under ideal circumstances, the tritium-helium method of dating groundwater is remarkably accurate for water samples less than 40 years old (Clark and Fritz, 1997; Kazemi et al., 2006).

In addition to tritiogenic helium produced by tritium decay, other sources of  $^3\text{He}$  include mantle-derived helium; nucleogenic helium produced by radioactive decay of uranium and thorium nuclides in the earth's crust; and atmospheric helium, which includes an excess air component. Numerous observations have shown that groundwater frequently contains more atmospheric gas than can be accounted for by equilibrium solubility with the atmosphere. This excess air is probably a result of transient rise in the water table that does not fully displace the gas phase, but it can also be artificially introduced during well construction or development (Cook et al., 2006). Additionally, excess air can be a problem if air bubbles remain in the sampling equipment when the sample is collected, or if air bubbles are produced by a submersible pump in the well (Solomon and Cook, 2000).

In relatively young groundwater the contribution of nucleogenic and mantle helium is insignificant, and the most important correction that must be made is for excess air. This correction can be made by analysis of the

concentrations of some noble gases such as neon, or from the nitrogen-argon ratio in the sample (Kazemi et al., 2006).

The ratio of helium-3 to helium-4 is a common parameter that is measured during noble gas analysis (Solomon, 2000). Because primordial helium derived from mantle sources consists of the  $^3\text{He}$  isotope – the same isotope of helium produced by radioactive decay of tritium in groundwater – it must be accounted for when conducting studies of groundwater residence time using tritium-helium methodology. Elevated  $^3\text{He}/^4\text{He}$  ratios in groundwater samples indicate that those waters may contain a significant percentage of mantle-derived helium-3 (Newell et al., 2005; Crossey et al., 2006). Analyses that we have obtained provide ratios of  $^3\text{He}/^4\text{He}$  ratios in the sample compared to ratios of  $^3\text{He}/^4\text{He}$  in the atmosphere ( $R/R_a$ ). The  $^3\text{He}/^4\text{He}$  ratio of the atmosphere is considered a constant, so any variation in the  $R/R_a$  number is a result of the  $^3\text{He}/^4\text{He}$  ratio from the sample.

### Carbon isotopes

Carbon-14 is a naturally-occurring radioactive isotope of carbon that is produced naturally in the atmosphere by cosmic radiation. Carbon-14 was also produced by atmospheric thermonuclear testing during the mid-20<sup>th</sup> century, similar to tritium.  $^{14}\text{C}$  radioactivity of inorganic carbon in water is expressed in units of percent modern carbon (PMC) relative to the abundance of  $^{14}\text{C}$  in atmospheric  $\text{CO}_2$ . Once isolated from atmospheric and soil gases, the abundance of  $^{14}\text{C}$  decreases at a rate governed by its half-life of 5,730 years. The PMC of a water sample can be used to estimate its residence time up to ~50,000 radiocarbon years before present (rcbyp). An accurate estimate of residence time in closed systems requires correction of measured PMC values for the effects of carbon mass transfer during geochemical reactions with carbonate host rock along groundwater flow paths.

Carbon-13 ( $^{13}\text{C}$ ) is a naturally-occurring stable isotope of carbon.  $^{13}\text{C}/^{12}\text{C}$  ratios of inorganic

carbon in water are expressed in the per mil (‰) difference ( $\delta^{13}\text{C}$ ) between a sample and the PeeDee Belemnite standard (PDB). The PDB is defined to have a  $\delta^{13}\text{C}$  value of 0 ‰. Typical  $\delta^{13}\text{C}$  values are near 0 ‰ for marine carbonates and -7 to -8 ‰ for atmospheric  $\text{CO}_2$ . A combination of equilibrium and kinetic fractionation that takes place during the uptake of  $\text{CO}_2$  by plants via photosynthesis and the release of  $\text{CO}_2$  in the soil by plant and microbial respiration results in soil  $\text{CO}_2$  being isotopically depleted with respect to atmospheric  $\text{CO}_2$ .  $\delta^{13}\text{C}$  values for  $\text{CO}_2$  respired from soils range from -27 to -14 ‰ (Amundson et al., 1998). The  $\delta^{13}\text{C}$  of inorganic carbon in water can serve as an indicator of water/rock/gas interactions along groundwater flow paths (Kalin, 2000) and is often used to correct measured groundwater PMC values for the effects of carbon mass-transfer geochemical reactions with carbonate host rock.

### Chlorofluorocarbons and sulfur hexafluoride

Chlorofluorocarbons (CFCs) are a class of volatile, synthetic compounds of carbon, chlorine and fluorine that have been used in refrigeration and other industrial applications since the 1930s (Plummer and Busenberg, 2000). The CFC compounds most commonly used in hydrologic studies are CFC11, CFC12, and CFC113 (Plummer et al., 2006). Atmospheric concentrations of CFC compounds increased in a quasi-exponential fashion from the 1950s through 1980s (Fig. 2), and the history of their concentrations is well-known or has been reconstructed from production/release data. Because CFCs contribute to destruction of the ozone layer, their production has been limited by international agreements, and in response atmospheric concentrations of CFCs have leveled off and begun to decrease since the 1990s.

Sulfur hexafluoride is an inert gas widely used as a gas-phase electrical insulator.  $\text{SF}_6$  has a very long atmospheric lifetime (up to 3,200 years: Ravishankara et al., 1993) and is detectable to very low levels using gas

chromatography. Unlike CFCs, atmospheric concentrations of sulfur hexafluoride have continued to increase monotonically in the atmosphere since about 1970 (Fig. 2), rendering this compound particularly useful for evaluating the age of groundwater recharged in the last few decades (Busenberg and Plummer, 2000).

Chlorofluorocarbons and sulfur hexafluoride enter the hydrologic cycle through precipitation as dissolved gas. The amount of gas dissolved in groundwater is dependent upon recharge temperature and recharge elevation (lower temperatures and higher elevations result in lower atmospheric and groundwater CFC concentrations). Therefore, recharge elevation and temperature need to be estimated to calculate the age of a water sample. Incorrect estimation of these parameters will result in erroneous dates.

Used as a groundwater tracer, CFC compounds can provide virtual year-to-year dating sensitivity for water recharged before 1990. Estimates of residence time for groundwater recharged since the 1990s are somewhat ambiguous because of declining CFC levels beginning in the late 20<sup>th</sup> century (Plummer and Busenberg, 2000; Phillips and Castro, 2003; International Atomic Energy Agency, 2006). However, CFC concentration ratios (e.g., CFC113/CFC12) may also be used to determine groundwater age. Using CFC concentration ratios has extended the application of these tracers for groundwater dating into the 21<sup>st</sup> century. The use of CFC ratios has particular application to quantifying binary mixtures of young groundwater (containing CFCs) and pre-modern groundwater (zero CFC concentration), since the CFC ratio can be used to define the age and volumetric fraction of the young component (Han et al., 2001, 2007; Plummer et al., 2006).

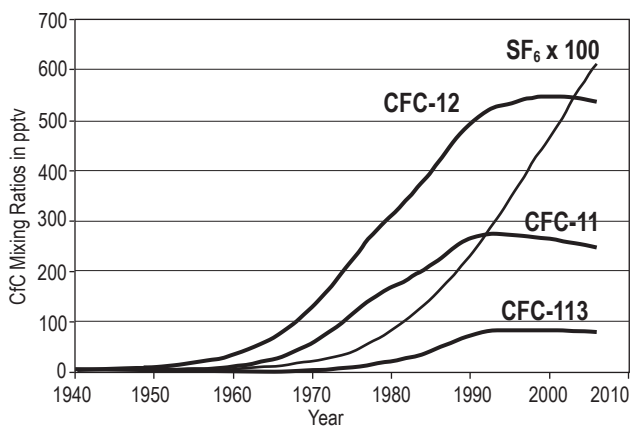
When using CFCs to date groundwater samples, the CFC12 date is usually considered the most reliable. CFC12 has the highest atmospheric concentrations (Fig. 2) and thus has the highest absolute concentrations in natural water samples. CFC113 has the lowest atmospheric concentrations and was introduced into the atmosphere later than the other two

## SUMMARY

CFC species. CFC11 has a greater potential for contamination and microbial degradation (Plummer and Busenberg, 2000).

The simplest model for estimating groundwater age based on CFC concentrations is the piston flow model, which assumes that after recharge occurs, the tracer becomes incorporated into a parcel of water and moves through the aquifer to points of discharge at the mean velocity of groundwater. Hydrodynamic dispersion and molecular diffusion are considered negligible, and the age based on the piston flow model is referred to as the apparent age of the groundwater sample (Bethke and Johnson, 2002a; 2002b). Other models of groundwater age distribution include exponential models and binary mixing models, which assume mixing of two groundwater sources of different ages (Plummer et al., 2006; Solomon et al., 2006).

Using the analyses of major ion chemistry, trace metal chemistry, stable isotopes of oxygen and hydrogen, and several naturally occurring environmental tracers, combined with detailed geologic and hydrologic data, we are able to develop schematic hydrogeologic models that depict groundwater in the subsurface. These results are publicly available through numerous open file reports at the New Mexico Bureau of Geology, with links available from the Aquifer Mapping Program webpage. Our results are applicable in policy development, education, water and land use management, and assessment of water quality for multiple purposes and beneficiaries in New Mexico.



**Figure 2.** CFC and SF<sub>6</sub> atmospheric concentrations over time.

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