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June 26, 2008

Richard L. Beauheim
Sandia National Lab
4100 National Parks Hwy.
Carlsbad, NM 88220

RE: WIPP

Contract No.: 586712

Dear Mr. Beauheim,

Attached please find a draft of the report "Evaluation of Selected Environmental Tracer Data in Ground Water from Seven Wells in the Vicinity of the WIPP Site, New Mexico under Contract # 586712 between the US Geological Survey and Sandia National Laboratories" by L. Niel Plummer and Eurybiades Busenberg. This preliminary document is a summary of our findings under contract 586712 between the US Geological Survey (USGS) and Sandia National Laboratories (SNL). The document interprets analytical results provided to SNL by the USGS for waters from 7 newly-constructed monitoring wells from the Culebra Dolomite in the vicinity of the WIPP Site, NM. These samples were collected by SNL personnel and received by the USGS between June 6, 2006 and August 2, 2007 for analysis. The results of the analyses were transmitted to SNL in February, 2008. This document is for internal use only by Sandia National Laboratories and cannot be cited or made part of the public record until it has been approved for publication by the U.S. Geological Survey. I believe we can take care of the USGS approval requirement at the same time the Sandia Report goes through internal review and approval.

Please do not hesitate to contact us for any additional information or clarifications.

Sincerely,

L. Niel Plummer

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DRAFT
Evaluation of Selected Environmental Tracer Data in Ground Water from Seven Wells in
the Vicinity of the WIPP Site, New Mexico under Contract # 586712 between the US
Geological Survey and Sandia National Laboratories

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INTRODUCTION

As a part of a larger project lead by Sandia National Laboratories (SNL) to re-investigate
ground-water age in the Culebra Dolomite in the vicinity of the Waste Isolation Pilot Project
(WIPP) Site in New Mexico, the US Geological Survey (USGS) received samples of ground
water from seven monitoring wells that were drilled under contract to SNL as a part of the
overall project, and sampled by SNL personnel between June 9, 2006 and August 2, 2007
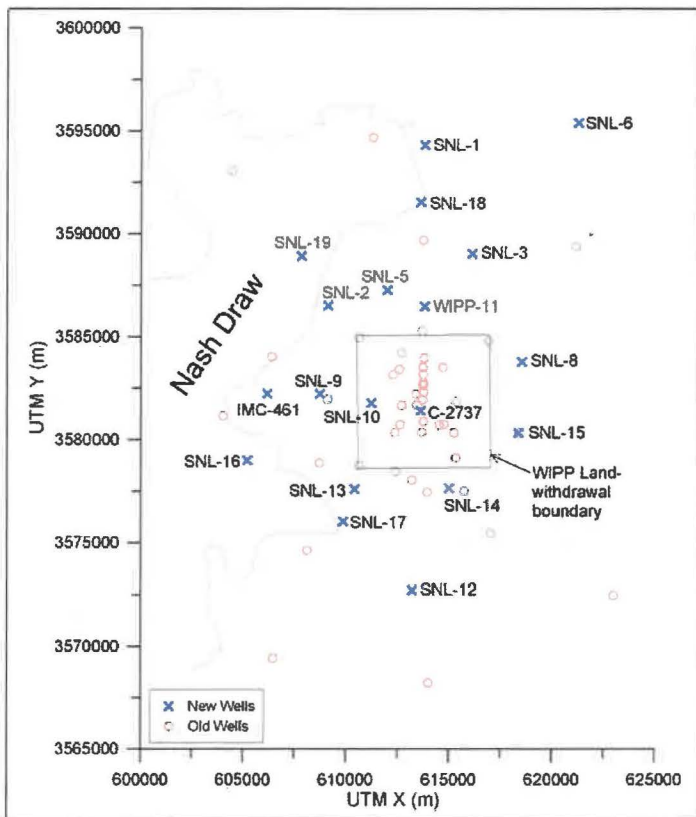(Figure 1).

Figure 1. Approximate location
of WIPP Site monitoring wells
SNL-16, SNL-19, SNL-18,
SNL-17, SNL-10, SNL-14, and
SNL-8 sampled and analyzed as
a part of this study.

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Table 1 summarizes basic information on the 7 monitoring wells including date of completion and date of sampling, general location, land surface elevation, approximate water level, total depth, and depths of the screened interval.

Table 1. Summary of well construction

Sample	Date well completed	Date Sampled	General Location	Altitude Land Surface Feet	Approx-imate water level, Feet below top of casing	Total depth, Feet	Screened Interval, Feet below pad level
SNL-16	4/16/2006	6/9/2006	Nash Draw	3130	223.5	224	189.9 - 216
SNL-19	6/1/2006	7/28/2006	Nash Draw	3220	146.1	358	335.8 - 362
SNL-18	7/20/2006	8/18/2006	East edge of Nash Draw	3373	301.4	559	530.3 - 557
SNL-17	7/20/2006	9/15/2006	East edge of Nash Draw	3235	231.2	366.7	333.7 - 360.
SNL-10	7/6/2006	11/3/2006	West edge of WIPP Land-withdrawal boundary	3375	266.7	626.4	593.3 - 620
SNL-14	6/1/2005	7/30/2007	South of WIPP Land-withdrawal boundary	3366	ND	664	649.5 - 676.
SNL-08	7/6/2005	8/2/2007	East of WIPP Land-withdrawal boundary	3553	500	1012	952 - 978

ND, Not determined

Various methods were used by the driller in well development, including jetting with high-pressure air within the screened interval and introduction of more that 100 barrels (5,500 gallons) of imported water, air lifting, in which air is injected into the well bore above the screen to lift water out of the casing, pumping with submersible pump, and use of a bailer. Information on these development techniques as applied to the 7 monitoring wells, source of imported water, and estimation of the total volume of water removed from the hole in development is summarized in Table 2.

Table 2. Summary of well development

Sample	Date well completed	Date Sampled	Jetted in screened interval, Yes. No	Amount of imported water used in jetting bbls.	Source Imported Water	Air Lifting, Yes, No	Depth of Airlift, Feet	Develop with submersible pump, Yes, No	Approximate Pump Rate, gpm	Duration of Pumping, min.	Volume of water bailed, gallons	Total water removed in initial well development, gallons
SNL-16	4/16/2006	6/9/2006	Yes	100	Eunice City water	No	NA	Yes	14	570	0	7,980
SNL-19	6/1/2006	7/28/2006	Yes	225	WIPP water			Yes	30	195	0	5,850
SNL-18	7/20/2006	8/18/2006	Yes	120	WIPP water	Yes	559	Yes	30	approx. 980	0	29,368
SNL-17	7/20/2006	9/15/2006	No	0	NA	Yes	270 - 328	Yes	31	133	0	4,125
SNL-10	7/6/2006	11/3/2006	Yes	100	Hobbs City water	No	NA	Yes	25	variable	0	ND
SNL-14	6/1/2005	7/30/2007	Yes	100	Double Eagle-City of Carlsbad	No	NA	Yes	12	370	640	5,140
SNL-08	7/6/2005	8/2/2007	Yes	ND [2]	WIPP water	No	NA	No	NA	NA	535	535

[1] Drawdown. Well may sustain discharge of 0.5 gpm.

NA, Not Applicable

ND, Not determined

[2] Blew water from well. Used 450 bbls of WIPP water while drilling well. Well filled with WIPP water while cementing annulus.

Prior to sampling by SNL personnel, each well was again pumped, typically for periods ranging from 0.3 to 4.0 days (Table 3). Electric submersible pumps with stainless steel or Nylon impellors were connected to 200 - 950 feet of galvanized steel pipe with bronze check valves. The wellhead assembly was of metal construction. Nylon tubing carried water to instruments and sampling apparatus. Some gas loss can be expected from sample SNL-8, because a large number of small bubbles were noted in well discharge, likely affecting the least soluble gases, such as SF_6, the most. There was no visible gas loss in discharge from the other 6 wells. Approximately 160,000 to 180,000 gallons of water was pumped from SNL-16, SNL-19, SNL-18, and SNL-17 prior to sampling (Table 3) while only 1,400 to 4,800 gallons of water were pumped from wells SNL-10, SNL-14, and SNL-8) prior to sampling (Table 3). Plots of Specific Conductance as a function of pump time prior to sampling are shown for each well in Appendix 1.

Table 3. Summary of well purging prior to sampling

Well	Start Pumping Date Time	Stop Pumping Date Time	Sample Time Date Time	Days Pumped	Pump Rate, gpm	Volume Pumped, gal.
SNL-16	6/5/06 13:51	6/9/06 14:25	6/9/06 10:38	4.02	27.9	161,593
SNL-19	2/24/06 15:00	2/28/06 12:18	7/28/06 8:57	3.89	29.9	167,837
SNL-18	8/14/06 18:21	8/18/06 12:03	8/18/06 10:10	3.73	29.9	160,557
SNL-17	9/11/06 13:03	9/15/06 13:55	9/15/06 10:22	4.02	31.7	183,799
SNL-10	10/30/06 15:19	11/3/06 16:37	11/3/06 12:50	4.04	0.25	1,465
SNL-14	7/30/07 12:37	7/30/07 20:38	7/30/07 15:20	0.33	10	4,817
SNL-8	7/31/07 13:13	8/2/07 19:25	8/2/07 16:28	2.26	0.54	1,743

The samples received by the USGS were analyzed for the following constituents:

(1) At the USGS Chlorofluorocarbon Laboratory, Reston, VA using gas chromatography procedures: (a) Chlorofluorocarbons (CFCs: CFC-11, CFC-12, CFC-113), (b) Sulfur Hexafluoride (SF_6), (c) Helium-4 (^4He), (d) Dissolved major gases including nitrogen, argon, carbon dioxide, methane and oxygen (N_2, Ar, CO_2, CH_4, and O_2), and (e) other low-level VOCs including chloroform, PCE and TCE.

(2) At the USGS Low-Level Tritium Laboratory in Menlo Park, CA: tritium (^3H) by liquid scintillation counting of enriched samples.

(3) At the University of Waterloo, Environmental Isotope Laboratory, Canada and University of Arizona, AMS Radiocarbon Facility, under contract to the USGS: (a) carbon-14 activity (^{14}C) of dissolved inorganic carbon, and (b) stable carbon isotopic composition ($\delta^{13}C$) of dissolved inorganic carbon.

(4) At the Noble Gas Laboratory of Lamont-Doherty Earth Observatory, Palisades, NY under contract to the USGS: $^3H/^3He$ analyses (including ^4He, Ne, δ^3He).

(5) At the USGS Reston Stable Isotope Laboratory, Reston, VA: $\delta^{13}C$ of selected carbonate rock samples.

The results of the analyses along with details of analytical procedures, QA/QC data, and Chain of Custody documents were transmitted to Sandia in February, 2008 and are not included in this report.

This report gives the analytical results and provides some preliminary interpretation of these data. These results are considered preliminary because they have not been reviewed and approved for publication by the USGS.

Rationale for analysis of the selected environmental tracers

The primary focus of the USGS effort is to provide interpretation of radiocarbon age of dissolved inorganic carbon (DIC) in the 7 new samples collected as a part of the overall investigation. Of concern is whether the measured ^{14}C activity is entirely representative of in-situ, undisturbed, ground-water conditions, or whether the sample has been contaminated, in part, with a fraction of young water that carries a recent, elevated, ^{14}C content in DIC. Traditionally, this check has been performed by measuring tritium in the same samples in which ^{14}C was measured (Lambert, 1987). In old, uncontaminated ground water, tritium would be expected to be nearly zero (certainly <0.1 Tritium Units, TU). This study included measurement of tritium along with a suite of other indicators of young water, including chlorofluorocarbons (CFCs, CFC-11, CFC-12, CFC-113), chloroform and other anthropogenic halogenated VOCs, sulfur hexafluoride (SF_6), and tritium combined with its decay product, ^3He ($^3H/^3He$). Figure 2 shows the historical concentrations of tritium in precipitation in the vicinity of the WIPP site decayed to the year 2006, and atmospheric concentrations (mixing ratios in parts per trillion, ppt) of CFC-11, CFC-12, CFC-113, and SF_6 from 1940 to the year 2006. The atmospheric input functions used to construct Figure 2 and tabulated in Appendix 2.
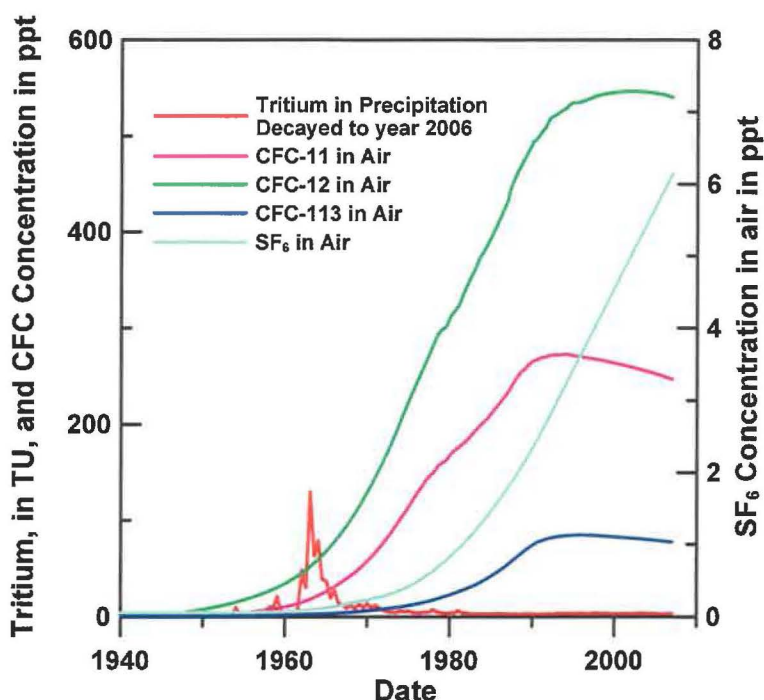
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Figure 2. Plot showing concentrations of tritium in tritium units, TU, in precipitation in the vicinity of the WIPP site from 1940 to 2006 decayed to the year 2006, and mixing ratios of CFC-11, CFC-12, CFC-113, and SF$_6$ in North American air in parts per trillion, ppt, from 1940 to the year 2007.

BACKROUND

Chlorofluorocarbons (CFCs, CFC-11, CFC-12, CFC-113)

Analyses of chlorofluorocarbons (CFCs-- CFC-11, CFC-12 and CFC-113) have been widely used to recognize young waters, i.e., waters that have contacted the atmosphere since about the 1940s (see Busenberg and Plummer, 1992; 2000; Plummer and Busenberg, 2000; Plummer, 2005; IAEA, 2006), or to recognize mixtures of post-1940's water with older water. CFCs have had widespread use in industrial and domestic applications, and consequently, CFC excesses are sometimes detected in ground water from anthropogenic sources, including drilling equipment and lubricants and other substances used in well construction. In some anaerobic ground-water environments, all CFCs can be degraded by microbiological processes. Inspection of the chromatograms from the purge and trap, gas chromatograph with electron-capture detector can identify reducing samples that may have degraded CFCs. Appendix 3 reproduces copies of all the CFC chromatograms measured for the 7 wells. Atmospheric concentrations of CFCs were rapidly increasing before the 1990's, but as a result of the Montreal Protocol on Substances that Deplete the Ozone Layer adopted in 1987, atmospheric concentrations are now declining (Figure 2). Five separate bottles were collected at each well and 3 of these were analyzed for CFCs at the USGS. Details of the analytical procedures are in the data reports of February, 2008.

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Sulfur Hexafluoride (SF₆)

Atmospheric concentrations of SF_6 are currently increasing. There are relatively few industrial and domestic uses of SF_6, in comparison to applications of CFCs (Busenberg and Plummer, 2000, 2007). Furthermore, SF_6 appears to be stable in anoxic environments. SF_6 is detected in post-1970 to modern waters. Although SF_6 is primarily of anthropogenic atmospheric origin, it also occurs naturally (Harnisch and Eisenhauer, 1998; Harnisch et al., 2000; Busenberg and Plummer, 2000). High terrigenic concentrations of SF_6 have been measured in ground water from fractured silicic igneous rocks, from some carbonate aquifers, from some hot springs, and in some ground water from volcanic areas (Busenberg and Plummer, 2000; Koh et al., 2007). Where the terrestrial flux of SF_6 from igneous rocks and mineral grains is high, the relatively small signal from post-1970 atmospheric sources can be completely unrecognizable. Further, low levels of SF_6 enrichment, below concentrations corresponding to modern air-water equilibrium, are difficult to recognize in mixtures with fractions of old water that contain significant amounts of terrigenic SF_6 (Busenberg and Plummer, 2000; Koh et al., 2007). SF_6 was collected in duplicate bottles and both samples were analyzed for SF_6 at the USGS. Details of the analytical procedures are in the data reports of February, 2008. Appendix 4 reproduces copies of all the SF_6 chromatograms measured for the 7 wells.

Tritium (³H)

Tritium is the radioactive isotope of hydrogen with a half-life of 12.32 years. It is produced naturally in the atmosphere. During the late 1950s and particularly in the period 1962-63, large amounts of tritium were injected into the stratosphere due to atmospheric test of nuclear devices. Precipitation in the vicinity of the WIPP site prior to the nuclear weapons testing period contained less than 6 TU, and that water recharged prior to atmospheric testing of nuclear weapons today would contain less than 0.1 TU. Recharge from the mid-1960s in NM would contain today (2006) approximately 100-200 TU. The tritium input function for the WIPP site (Figure 2) was constructed from tritium in precipitation records from the IAEA (International Atomic Energy Agency/World Meterological Organization (IAEA/WMO), 1998), Waco, TX record, and by correlation with several other tritium records in the US (R.L. Michel, U.S. Geological Survey, Menlo Park, CA, written correspondence, 2000). Details of the analytical procedures are in the data reports of February, 2008.

Tritium/Helium-3 (³H/³He)

The $^3H/^3He$ age is based on a helium isotope mass balance used to determine the amount of tritiogenic helium-3 ($^3He_{tri}$) derived from radioactive decay of ^3H in the water sample (Schlosser et al., 1988, 1989). Several conditions may permit solving the helium isotope mass balance for $^3He_{tri}$ for a few water samples from the WIPP site: (1) The sample must contain detectable tritium (greater than approximately 0.5 TU), (2) If the sample contains terrigenic He (helium from mantle and crustal sources), Ne data are needed to define $^3He_{tri}$, (3) The $^3He/^4He$ ratio of the terrigenic He, R_{terr}, must be known, (4) If the amount of terrigenic He is small (<5 % of the dissolved ^4He), the $^3H/^3He$ age may be insensitive to even large uncertainties in R_{terr}, (5) For samples with a large fraction of terrigenic helium, R_{terr} (that of mantle and crustal sources) must be known for the particular sample within approximately 1% or better, and (6) If R_{terr} cannot be defined with sufficient precision to determine age, a range in age can be evaluated for a range in R_{terr}. As a check on the validity of a calculated $^3H/^3He$ age, the age and reconstructed initial tritium ($^3H+^3He_{tri}$), after correction for dilution with old (low tritium) water, should be that of

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tritium in precipitation for that date of recharge. If the calculated initial tritium is less than tritium in precipitation for that date of recharge, then the sample is a mixture, i.e., it has been diluted with low-tritium (old) water.

RESULTS FROM TRITIUM, CFC, VOCs, AND SULFUR HEXAFLUORIDE DATA

The concentrations of tritium, chlorofluorocarbons and sulfur hexafluoride measured in water from the 7 wells are summarized in Table 4. The CFC concentrations are averages of 3 determinations made on 3 separate water samples and those of SF_6 are averages of 2 separate samples.

Table 4: Summary of Tritium, Chlorofluorocarbon and Sulfur Hexafluoride Determinations*

Well	Tritium in TU	Tritium ± 1σ in TU	CFC-11 pg/kg	CFC-12 pg/kg	CFC-113 pg/kg	CFC-11 ppt	CFC-11 ppt	CFC-11 ± 1σ	CFC-12 ppt	CFC-12 ± 1σ	CFC-113 ppt	CFC-113 ± 1σ	SF_6 ppt	SF_6 ppt ± 1σ
SNL-16	0.62	0.09	39.2	47.3	6.4	31.0	31.0	0.4	150.1	5.8	12.2	1.0	42.07	6.20
SNL-19	0.02	0.07	13.4	4.7	0.0	9.6	9.6	4.7	13.6	8.9	0.0	0.0	94.46	2.43
SNL-18	0.19	0.08	28.9	16.8	4.4	23.5	23.5	1.5	54.9	0.4	8.8	0.6	72.81	4.71
SNL-17	0.31	0.08	55.5	56.9	8.8	37.9	37.9	1.2	157.5	7.4	14.7	1.2	3.24	0.05
SNL-10	-0.07	0.07	8.9	5.5	5.4	6.5	6.5	1.6	16.1	1.9	9.6	1.3	0.64	0.02
SNL-14	0.13	0.13	21.9	10.4	2.3	49.3	49.3	21.4	86.9	28.9	11.9	2.9	1.40	0.50
SNL-8	0.1	0.1	180.1	9.2	0.0	271.4	271.4	56.9	53.2	7.6	0.0	0.0	0.25	0.06

* Concentrations in ppt calculated from Henry's Law solubility at 20 °C and 3000 feet altitude. pg/kg, pico grams per kilogram.

Tritium was detected above background counting statistics in 3 of the 7 samples (Table 4), the highest being 0.62 ± 0.09 TU in sample SNL-16. Sample SNL-17 also contains "significant" tritium at 0.31 ± 0.08 TU, and sample SNL-18 contains 0.19 ± 0.08 TU. The tritium concentrations in the rest of the samples do not differ statistically from zero. All of the samples contain CFC-11 and CFC-12 and 5 of the 7 samples contain detectible CFC-113. Detection limits for the CFCs are approximately 0.5 pg/kg for CFC-11 and CFC-12 and 1 pg/kg for CFC-113. All of the samples contain SF_6, which is particularly elevated in samples SNL-16, -19, and -18 indicating a likely terrigenic source for these samples. Based on the tritium data, at least 3 samples contain a young fraction (post-1950s) of water. All samples contain CFCs and may then contain a fraction of post-1940s water or contain CFCs introduced with substances/equipment used in well drilling. All of the samples contain SF_6, which could be of atmospheric (post-1970s) origin in samples SNL-17, -10, -14, and -8. The large excesses of SF_6 in samples SNL-16, -19, and -18 indicate there is terrigenic source of SF_6 in ground water at the WIPP site, and it is not possible to determine if the samples contain both terrigenic and atmospheric sources of SF_6. As all of the samples are from the Culebra Dolomite, it is not understood why water from 3 wells would be elevated in SF_6, and the other are not (Table 4).

Several hypotheses were considered for the origin/introduction of CFCs, tritium and SF_6 in the water samples. These are:

1. Mixing of a young water with old, resident water in the Culebra Dolomite-- the source of the young water being either recent infiltration water that some how reaches the aquifer, or water introduced during drilling,

2. Contamination from substances used in drilling, and
3. Introduction of air used in drilling; both un-fractionated and fractionated air.

It is believed that the first scenario, mixing of recent water, would have the greatest impact on the radiocarbon content of the resident water in the Culebra Dolomite aquifer. Below, we examine the environmental tracer data in light of these possible mechanisms for their introduction to discharge from the wells.

Tracer-Tracer Plots

Plots of the concentrations of one tracer relative to another can be useful in recognizing waters that were in contact with air at various times in the past, the year of this contact, various types of mixtures of these waters, and waters that have concentrations of tracers in excess of simple air-water equilibrium or their mixtures. First we examine the tritium concentration data in relation to CFC-11, CFC-12, and CFC-113 data.

Figure 3 shows the measured tritium and CFC-11 data for waters from the 7 wells in relation to atmospheric input of tritium in precipitation, decayed to the year 2006 and to CFC-11 concentrations in air, in ppt. The water concentrations of CFC-11 were converted to air ppt values using Henry's Law solubility data (IAEA, 2006) at an assumed temperature of 20 °C and altitude of 3,000 feet.
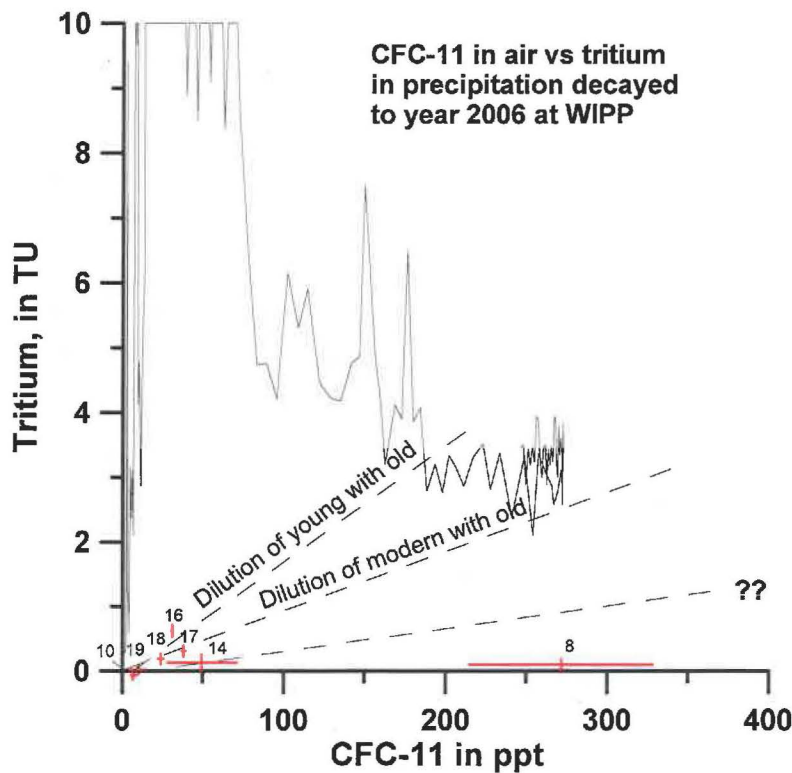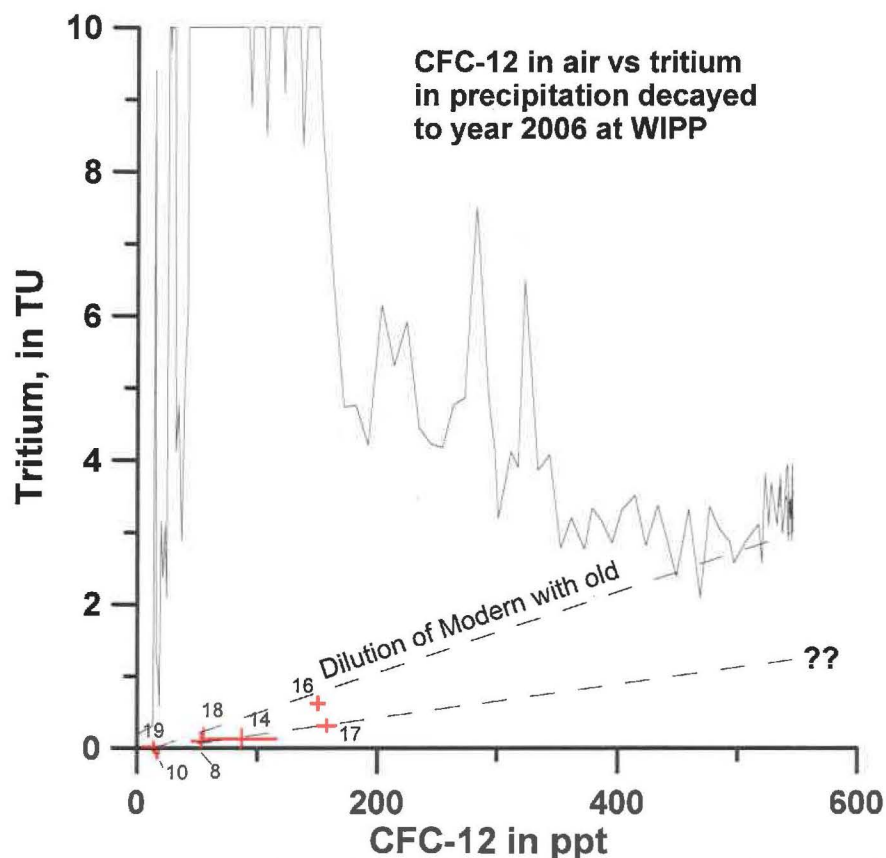

Figure 3. Tracer-tracer plot of tritium and CFC-11. Red crosses show the range of one standard deviation in the measured concentrations and labels correspond to well numbers. Dashed lines show hypothetical binary dilution of young and old water.

The solid line in Figure 3 shows the relation of unmixed waters, if recharged from 1940 (at 0,0) to the year 2006. The large peak in tritium corresponds to about 1963 water. The plot suggests that samples 16, 17, 18, 10, and 19 could be binary mixtures containing a small fraction of modern or near modern water diluted with old tracer-free water. Samples 14 and especially 8 have elevated concentrations of CFC-11 relative to tritium and, if they are binary mixtures, likely contain an excess source of CFC-11.

Figure 4 shows tritium data in relation to that of CFC-12, in a tracer-tracer plot similar to that of Figure 3.

Figure 4. Tracer-tracer plot of tritium and CFC-12. Red crosses show the range of one standard deviation in the measured concentrations and labels correspond to well numbers. Dashed lines show hypothetical binary dilution of young and old water.

Samples SNL-16, and possibly 8, 18, 10, and 19 plot along a dilution line between modern water and old, tracer-free water (Figure 4). Samples 14 and 17 seem to have elevated CFC-12 relative to tritium and either have been impacted by a CFC-12 source or are a dilution of an unknown water that is low in tritium content and elevated in CFC-12. In an expanded scale of Figure 4 (Figure 5), we see that tritium concentration is reasonably well correlated with CFC-12 concentration. This suggests mixing (dilution) of a young fraction and that the tritium and CFC-12 co-occur in the young fraction. The composition of the young fraction probably does not plot along the tritium-CFC-12 input curve, but instead, may represent a water composition low in tritium and elevated in CFC-12.
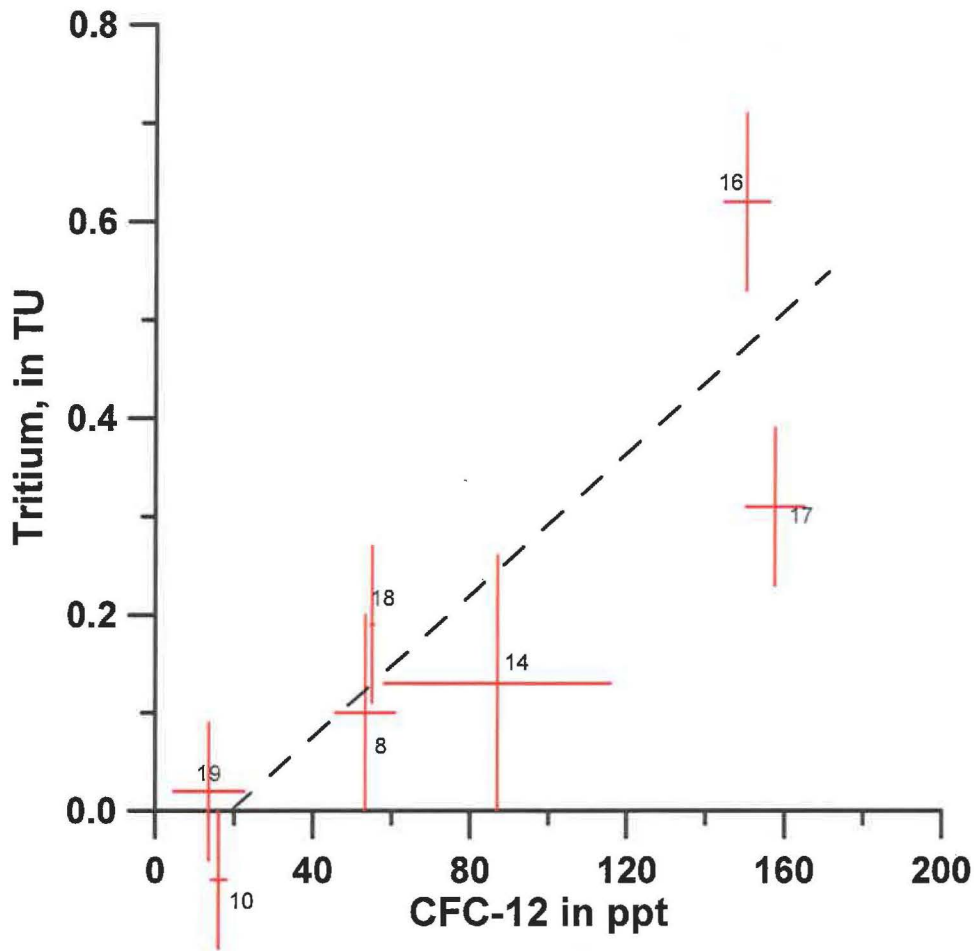
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Figure 5. Plot of tritium and CFC-12; similar to Figure 4, but with expanded tritium scale. Red crosses show the range of one standard deviation in the measured concentrations and labels correspond to well numbers. Dashed lines show hypothetical binary dilution of young and old water.

Only three of the samples have tritium concentrations greater than zero considering the one standard deviation range reported for the measurement, yet all of the points appear to align along a trend (Figure 5). Sample 10 has a negative tritium value only because the background count exceeded the sample count in the liquid scintillation counter. So the actual measurement for sample 10 should be very near zero TU, and plotting again, along the trend with the rest of the samples (Figure 5).

Figure 6 shows tritium data in relation to that of CFC-113, in a tracer-tracer plot similar to that of Figures 3 and 4.
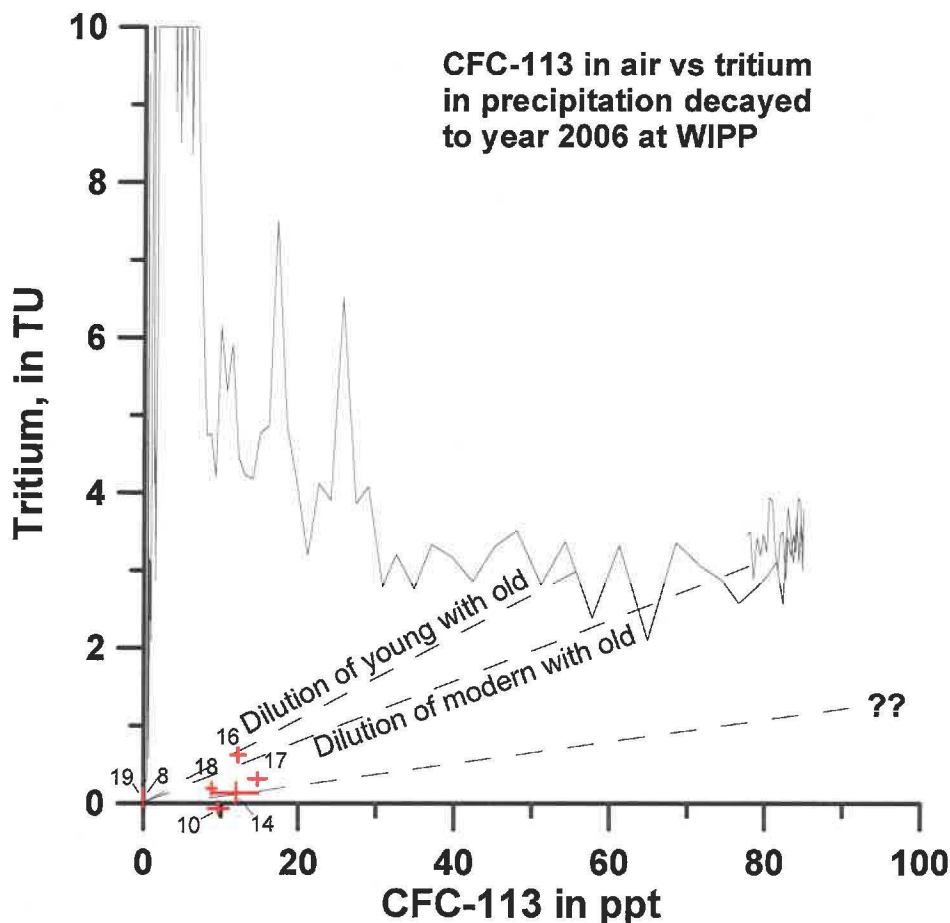
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Figure 6. Tracer-tracer plot of tritium and CFC-113. Red crosses show the range of one standard deviation in the measured concentrations and labels correspond to well numbers. Dashed lines show hypothetical binary dilution of young and old water.

Two samples had no detectable CFC-113 (samples SNL-8 and -19). If these samples contain a young fraction, it is diluted below the detection limit of 1 pg/kg (approximately <1% of modern water). We have already shown in Figures 3 and 4 that SNL-8 and -19 contain both CFC-11 and CFC-12, so they are either a dilution or possibly contain fractionated excess air (discussed below). Sample 16 lies on a dilution line of recent (*ca* 1985) water, while samples 17, 18, 10, and 14 appear as if dilution of an end-member low in tritium, but somewhat elevated in CFC-113.

Regardless of the mixing mechanism, the CFC data and to some extent, the tritium data of Figures 3-6, indicate post-1940 introduction of air and/or water or other substances containing CFCs. The presence of detectible tritium in three of the samples indicates that, at least in the cases of these three samples, introduction of post-bomb water.

Next we examine the SF_6 data in relation to tritium (Figure 7) and to CFC-12 (Figure 8). Figure 7 shows the relation between tritium and sulfur hexafluoride. Three samples have large excesses of terrigenic SF_6 (Table 4) and plot well off scale of Figure 7. Only sample SNL-8 has SF_6 and tritium concentrations that might be interpreted as a binary mixture of young and old.

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The other samples (10, 14, and 17) are elevated with SF_6 relative to tritium and likely too contain a terrigenic component.
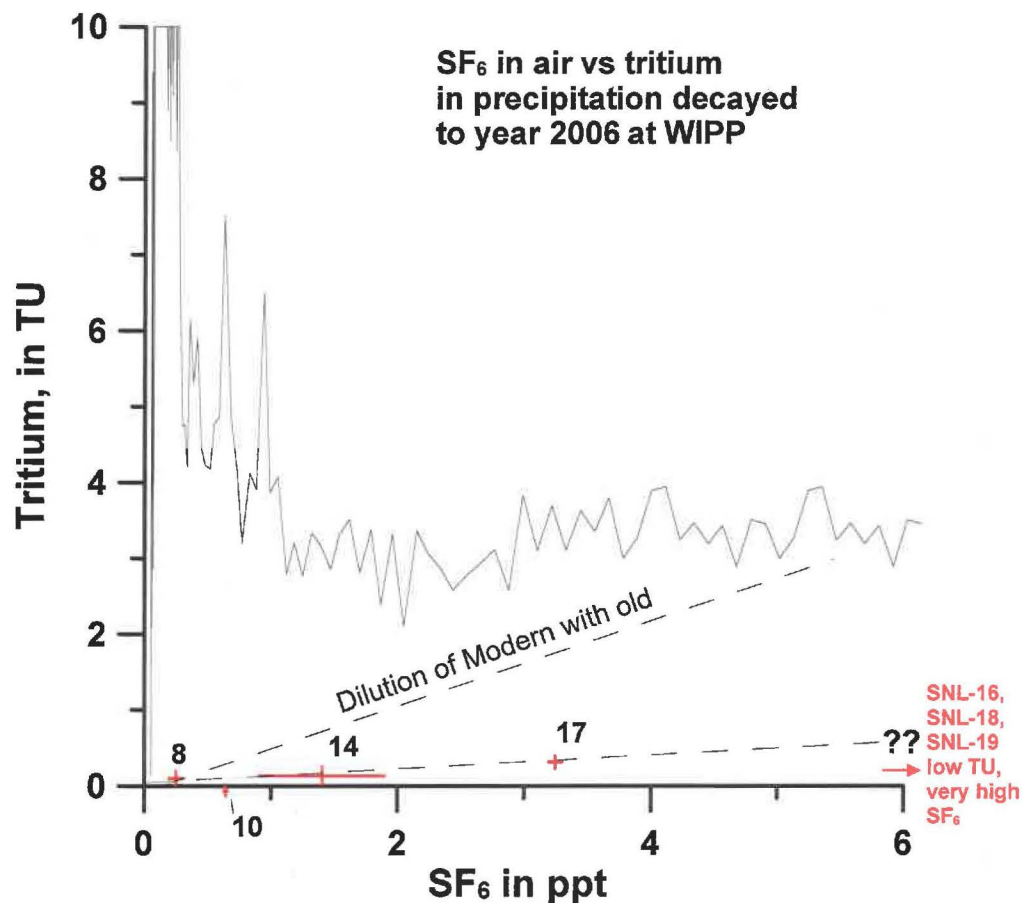

Figure 7. Tracer-tracer plot of tritium and SF_6. Red crosses show the range of one standard deviation in the measured concentrations and labels correspond to well numbers. Dashed lines show hypothetical binary dilution of young and old water.

Samples 8, 10, 14, and 17 could be dilutions of an end-member that is low in tritium and elevated in SF_6 (Figure 7). A different pattern emerges when we examine the SF_6 data in relation to that of CFC-12 (Figure 8).
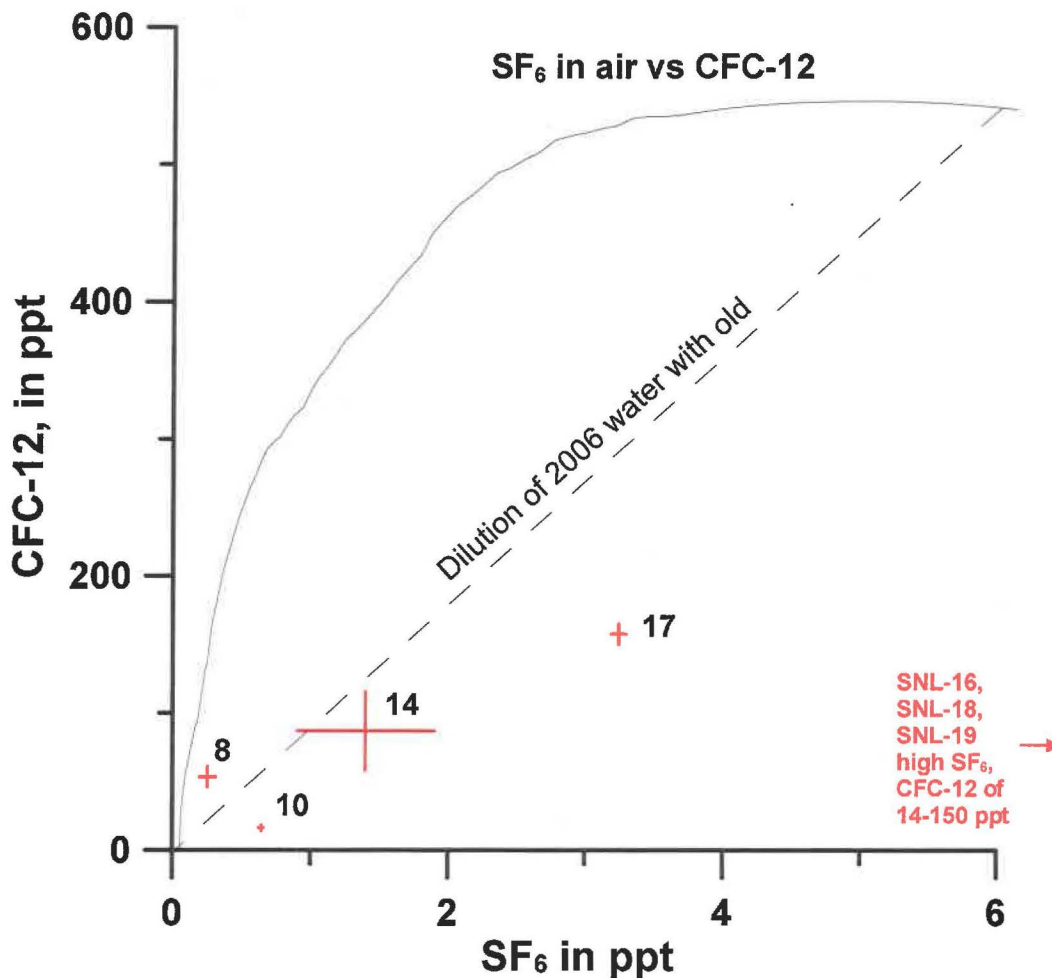
Figure 8. Tracer-tracer plot of SF_6 and CFC-12. Red crosses show the range of one standard deviation in the measured concentrations and labels correspond to well numbers. Dashed lines show hypothetical binary dilution of young and old water.

Three of the samples (Figure 8) are highly elevated in SF_6 (16, 19, and 18), plot well off scale, but have CFC-12 concentrations in the range of water in equilibrium with air (14 to 150 ppt) (Table 4). Samples 8, 10, and 14 are consistent with dilution of a modern air-water equilibrium component with old tracer-free water and sample 17 may also be on that dilution line but with elevated, terrigenic, SF_6. It is important to recall that, while 3 and possibly 4 of the samples on Figure 8 could be dilution of modern water and old water, Figure 7 shows low tritium in all the samples. So it may be that the apparently "modern" water that is diluted in Figure 8 is low-tritium drilling fluid that contains excess air introduced in air-rotary drilling. According to drilling records, water used in drilling was imported from city water supplies off site. This water may be old and low in tritium and CFCs. Injection of air in air-rotary drilling would likely strip excess terrigenic SF_6 and bring the drilling water near equilibrium with air in terms of CFC and SF_6 concentration. It is possible that drilling water was then diluted with old Culebra Dolomite water that is elevated with terrigenic SF_6.

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Contamination from Drilling Equipment or Imported Water

Table 4 gives the average CFC-11, CFC-12, and CFC-113 concentrations in water from the 7 wells, which is expressed as % Modern in Table 5. Percent Modern was computed by converting the measured concentrations to partial pressures at 20 °C and 3,000 feet altitude, using Henry's Law, and computing the ratio to the atmospheric ppt concentration in modern air. Modern air was assumed to correspond to the year 2006, with CFC-11, CFC-12, and CFC-113 mixing ratios of 249.6, 542.4, and 78.5 ppt (Appendix 2). A water sample in equilibrium with the 2006 atmosphere at 20 °C and 3,000 feet altitude would have all three CFC % Modern values at 100 %. Most of the samples are well below Modern air-water equilibrium saturations (Table 5). The last 2 columns of Table 5 average the % Modern for all three CFCs at each well and give the Standard Deviation of the Mean.

Table 5. CFC Concentrations in Percent Modern*

Well	CFC-11 % Modern	CFC-12 % Modern	CFC-113 % Modern	Average % Modern	Standard Deviation
SNL-16	12.4	27.7	15.5	18.5	8.1
SNL-19	3.9	2.5	0.0	2.1	2.0
SNL-18	9.4	10.1	11.2	10.2	0.9
SNL-17	15.2	29.0	18.7	21.0	7.2
SNL-10	2.6	3.0	12.3	5.9	5.5
SNL-14	19.7	16.0	15.2	17.0	2.4
SNL-8	108.7	9.8 (~2)**	0.0	39.5	60.1

* Modern assumed to be the year 2006
** Estimated to be near 2% based on low CFC-113. SNL-8 is contaminated with CFC-11 and other halogenated VOCs.

Typically, in areas where there is CFC contamination of water samples from non-atmospheric sources, such as industrial wastes, drilling equipment, chemicals, etc., CFC excesses can exceed air-water equilibrium values by orders of magnitude (IAEA, 2006). This does not seem to be the case for the samples from the seven monitoring wells in the vicinity of the WIPP site (Table 5). The only sample possibly fitting this scenario is that from well SNL-8 where the CFC-11 concentration is slightly above that of modern air-water equilibrium, while CFC-12 and CFC-113 concentrations are low and consistent with most of the other samples. Two samples have the lowest CFC-11 and CFC-12 concentrations (SNL-10 and SNL-19). These two samples also have the lowest tritium content (Figure 5). Excluding sample SNL-8, the other 6 samples average 12 ± 8 % Modern. Within these 6 samples (excluding SNL-8), there tends to be some consistency among all three CFCs, i.e., samples low in one CFC tend to be low in the other two as well, and similarly for samples with somewhat higher CFC content. The source of the CFCs in the samples is not known, but could be drilling fluid, or imported water used in jetting during well development that has added CFCs from compressed air, or possibly some other form of contact with air. Apparently this source of CFCs also contains tritium (Figure 5). The data of Table 5, giving generally similar % Modern values for all three CFCs in a sample (excluding SNL-8) suggests, for the most part that the CFCs were introduced into the samples approximately according to Henry's Law solubility, and then subsequently diluted.

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The CFCs analyzed (CFC-11, CFC-12, CFC-113) are just 3 of the many other halogenated VOCs detected in the WIPP samples (Appendix 5). The electron-capture detector (ECD) in the purge and trap gas chromatograph is particularly sensitive to halogenated VOCs, such as CFCs, PCE, TCE, chloroform, and others. Chloroform, which is a disinfection byproduct produced during chlorination of drinking water, was present in all samples. Approximate concentrations of chloroform in the 7 samples ranged from about 0.001 to 0.025 ug/L, which is near or significantly below the detection limit by normal GC-Mass Spectrometric analysis. Chloroform was presumably introduced in well development when imported municipal water from various sources (Table 3) was put in the boreholes. The chloroform was subsequently diluted during well development and well pumping, as were the CFCs, and tritium. Figure 5 showed a linear relation with percent young water based on CFC-12 and tritium, but many of the tritium concentrations were particularly low with relatively large standard deviations. Figure 9 shows that the chloroform concentration, expressed as peak area on the GC chromatogram, also varies approximately linearly with the estimated percent imported water based on CFC-12 content.
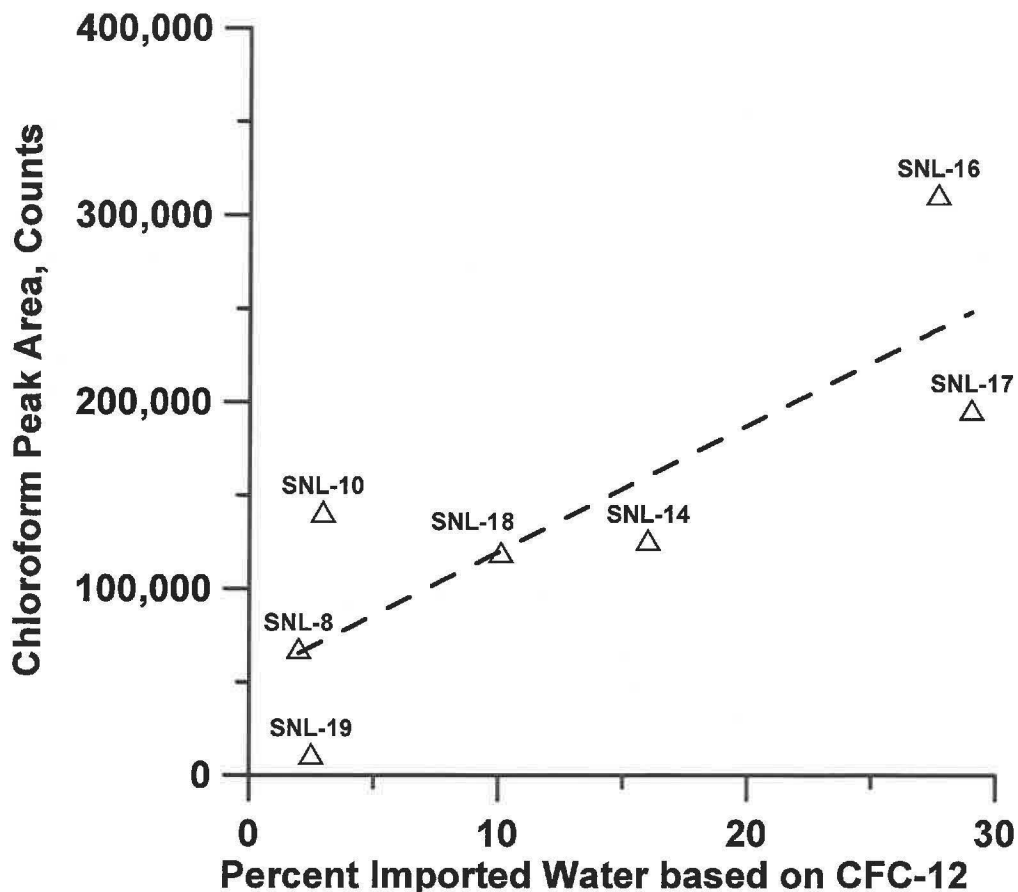

Figure 9. Plot of percent imported water, estimated form the CFC-12 concentration (Table 5) as a function of chloroform concentration, which varies linearly with the chloroform peak area from the GC chromatogram (Appendix 5). It is estimated that the chloroform concentrations in this plot range from about 0.001 to 0.025 ug/L.

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Sample SNL-8 has relatively low chloroform concentration, but has been contaminated with many other halogenated VOCs, including CFC-11, TCE, PCE, methyl chloroform, methyl chloride, and an unknown VOC with retention time of 12.4 minutes (Appendix 5).

Introduction of Air from Drilling Operation

The possibility of introduction of air, either by solubility equilibrium or by injection of excess air into the samples during the operation of air-rotary drilling and jetting in well development was considered.

Solubility Controls

All liquids (drilling mud, lubricants, etc) used in drilling were in contact with air and at least partially saturated with atmospheric gases. These liquids entered the formation to some extent in drilling. Drilling records show that in completing the well, approximately 100 barrels (5,500 gallons) of water from one of several municipal sources in the vicinity of the WIPP Site (cities of Eunice, Carlsbad, Double-Eagle, Hobbs, etc) were put down the hole and, using a high pressure air hose, the screened interval open to the Culebra Dolomite was jetted. The jetting operation added CFCs (and other atmospheric gases) to the water in the borehole and possibly to the aquifer in the vicinity of the well screen in two ways. First, the water standing in the borehole was at least partially saturated with air under the hydrostatic conditions in the borehole. This level of saturation would have been governed by solubility-equilibrium principles. Some of this air-saturated water standing in the casing during jetting likely flowed into the formation. With a large amount of air injection and exhaust of air from the hole in air-rotary drilling, the water in the hole should approach air-water equilibrium at the total pressure and water temperature. This may explain why so many of the samples have % Modern concentrations that agree reasonably well for all three CFCs for a given well (Table 5). Assuming that the jetted water in the borehole approached 100 % Modern in all three CFCs, the % Modern values of Table 5 represent the percent of this air-saturated water that was present when sampling for CFCs was conducted, being mostly diluted with old, CFC-free water. Typical well development involved pumping for up to 4 days prior to sampling. Water from wells SNL-19, SNL-10, and SNL-8 (ignoring the CFC-11 contamination in SNL-8) have the lowest % Modern and, apparently, the lowest fraction of water from the jetting operation. At the other end of the scale, water from wells SNL-16, SNL-17, and SNL-14 have the highest fractions of water from the jetting operation and have not been developed to the same level as wells 19, 10, and 8.

Excess Air

The other way air could have entered the formation during jetting would have been as gas bubbles injected directly through the well screen and into the pore spaces in the Culebra Dolomite. Dissolution of the entrapped gas will eventually occur as the well is pumped, but the process can be very slow (Heilweil et al., 2004), and it is likely that the gas phase was still present during all sampling conducted as a part of this investigation. The dissolution is slow in stagnant water because the film next to the surface of the bubble becomes saturated with the gas, and further dissolution can only occur by diffusion into the aquifer and by advection during pumping bringing less saturated fluid in contact with the gas bubble. The least soluble trace

gases are preferentially concentrated into the gas bubbles. These bubbles constitute one form of excess air; one that has not yet dissolved into the aquifer, but will eventually.

The term "excess air" usually refers to the quantity of air dissolved in ground water that is in excess of air-water equilibrium (Heaton and Vogel, 1981; Aeschbach-Hertig et al., 2000). Excess air is a natural component of air introduced to ground water during recharge events. When excess air (bubbles) is trapped beneath the rising water table within inter-granular spaces or in fractures, it subsequently dissolved under increased hydrostatic pressure. As explained above, excess air can also be injected into ground-water environments during air-rotary drilling, and particularly from jetting procedures within the well screen. If the volume of excess air completely dissolves into old tracer-free water under increased hydrostatic pressure, the ratio of two tracers from dissolved air is equal to that of air and is referred to as un-fractionated excess air (UA model of Aeschbach-Hertig et al., 2000; Holocher et al., 2002). If the quantity of excess air is only partially dissolved, a fractionation results due to the preferential partitioning of lower solubility gases in the bubble (Closed-System Equilibration (CE) model of Aeschbach-Hertig et al., 2000; Holocher et al., 2002). It would seem the latter (fractionated excess air) would more likely apply under conditions of jetting and air rotary drilling than complete dissolution of the excess air (un-fractionated excess air, UA model). Here we consider both models (UA and CE models) to account for the effects of excess air on the interpretation of ground water CFC concentrations.

Un-fractionated Air: CFCs

Figure 10 shows the mole ratios of CFC-11/CFC-12, CFC-113/CFC-11, and CFC-113/CFC-12 in air from 1950 to the present.
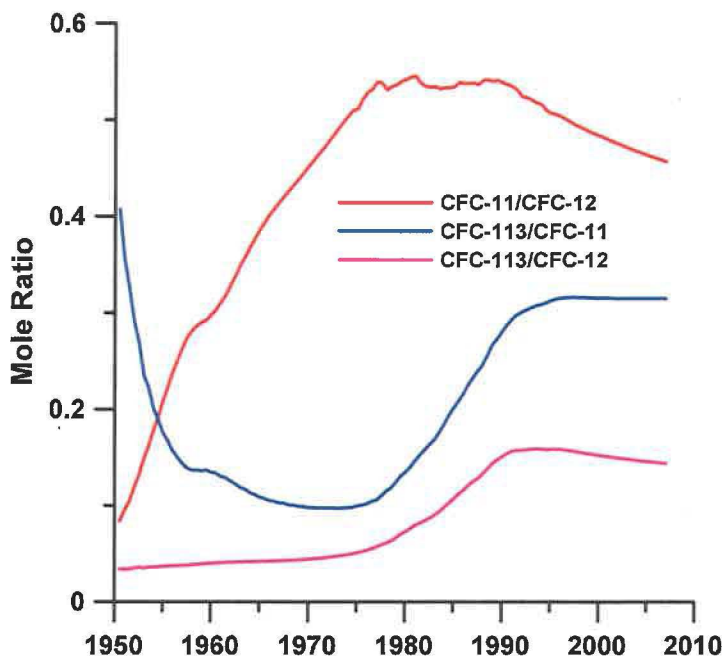

Figure 10. Plot showing mole ratios of CFCs in air between 1950 and the present.

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If air is injected into water and dissolved without gas loss, i.e., un-fractionated air, the dissolved CFC ratios will be those of Figure 10 for the corresponding year of air composition. Air injected and dissolved in 2006 would leave CFC-11/CFC-12, CFC-113/CFC-11, and CFC-113/CFC-12 mole ratios in originally blank, old water of 0.46, 0.31, and 0.14, respectively. Further, all three ratios would have these values corresponding to un-fractionated excess air injected and dissolved in the year 2006.

Table 6 gives the mole ratios of CFC-11/CFC-12, CFC-113/CFC-11, and CFC-113/CFC-12 in the water from the 7 wells.

Table 6. Mole Ratios Assuming Un-fractionated Excess Air*

Well	CFC-11/CFC-12 mol ratio in water	Apparent ratio year CFC-11/CFC-12 year	CFC-113/CFC-11 mole ratio in water	Apparent ratio year CFC-113/CFC-11 year	CFC-113/CFC-12 mole ratio in water	Apparent ratio year CFC-113/CFC-12 year
SNL-16	0.7295	NP	0.1188	1963	0.0867	1983
SNL-19	2.5246	NP	0.0000	old	0.0000	old
SNL-18	1.5117	NP	0.1127	1964	0.1703	1998
SNL-17	0.8589	NP	0.1160	1964	0.0996	1984
SNL-10	1.4336	NP	0.4468	NP	0.6406	NP
SNL-14	1.8444	NP	0.0785	NP	0.1449	1989
SNL-8	17.2125	NP	0.0000	old	0.0000	old

NP Not Possible

The CFC-11/CFC-12 ratio exceeds all historical values of this ratio in air and therefore does not apply to any historical date for un-fractionated air. Three of the samples (Table 6) have CFC-113/CFC-11 ratios of air from 1963-1964, if un-fractionated, which is inconsistent with the date of drilling (2006). The CFC-113/CFC-12 mole ratio is consistent with un-fractionated air from the mid- to late-1980s in 4 of the samples (Table 6); again inconsistent with the date of drilling. None of the samples have ratios consistent with the same age of air. Therefore, it appears the CFCs in the 7 samples cannot be attributed to un-fractionated excess air.

Un-fractionated Air: N_2, Ar

Although the UA model does not account for the observed CFC concentrations, the processes responsible for introduction of CFCs may be quite different from those that, in the past, added primary atmospheric gases to the water samples. Unless of magmatic or other deep crustal origin, virtually all ground water was initially in contact with the atmosphere. It is a common practice to calculate the initial water temperature at time of recharge (recharge temperature) and amount of excess air trapped in recharge waters using the UA model with nitrogen and argon data. The UA model was applied to the measured N_2 and Ar data to estimate recharge temperature and quantities of excess air. The calculations also considered the possibility of excess N_2 from denitrification of soil nitrate. Table 7 summarizes the measured gas concentrations. Each replicate analysis is shown to give an indication of the overall consistency of the data set.

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Table 7. Summary of Dissolved Primary Gas Concentrations, Modeled Excess N_2, Excess Air and Recharge Temperature in pure water*

Sample Name	Date	Salinity, $^o/_{oo}$ as NaCl	Recharge Elevation	N_2 mg/L	Ar mg/L	O_2 mg/L	CO_2 mg/L	CH_4 mg/L	Modeled Excess N_2 in mg/L	Calc. Recharge T °C	Calc. Ex Air cc STP/L
SNL-16	6/9/2006	20.5	3000	25.389	0.641	2.754	10.596	0	3.5	20.1	8.9
SNL-16	6/9/2006	20.5	3000	24.128	0.6213	2.61	10.75	0.0000	3.4	20.1	7.7
SNL-19	7/28/2006	11.0	3000	14.243	0.4869	2.90	7.63	0.0000	1.1	21.1	0.1
SNL-19	7/28/2006	11.0	3000	14.207	0.4858	2.89	7.61	0.0000	1.1	21.2	0.1
SNL-18	8/18/2006	22.0	3373	21.373	0.5522	0.16	3.11	0.0000	4.5	20.1	3.9
SNL-18	8/18/2006	22.0	3373	21.514	0.5531	0.15	3.07	0.0000	4.5	20.4	4.1
SNL-18	8/18/2006	22.0	3373	21.343	0.5513	0.17	3.08	0.0000	4.5	20.2	3.9
SNL-17	9/15/2006	6.1	3000	19.656	0.6143	6.12	8.90	0.0000	0.0	18.2	6.1
SNL-17	9/15/2006	6.1	3000	18.905	0.5990	6.05	8.98	0.0000	0.0	18.7	5.4
SNL-10	11/3/2006	12.1	3000	19.492	0.5943	0.20	0.65	0.0075	0.4	20.0	6.0
SNL-10	11/3/2006	12.1	3000	19.479	0.5968	0.20	0.54	0.0076	0.2	20.1	6.2
SNL-14	7/30/2007	125.2	3000	10.481	0.3126	0.08	0.62	0.0040	1.5	47.7	0.3
SNL-14	7/30/2007	125.2	3000	11.381	0.3281	0.09	0.62	0.0037	2.0	44.8	0.4
SNL-14	7/30/2007	125.2	3000	11.888	0.3357	0.10	0.65	0.0035	2.4	42.9	0.2
SNL-8	8/2/2007	84.8	3000	22.810	0.3985	0.10	0.51	0.0256	11.8	32.3	0.2
SNL-8	8/2/2007	84.8	3000	22.041	0.3887	0.10	0.53	0.0253	11.4	33.2	0.0

* Ex N_2 (from denitrification of paleo soil nitrate) was adjusted to obtain recharge temperatures near 20 °C with at least positive values of excess air.

Two possible initial conditions were considered. In the first scenario, if precipitation infiltrated the unsaturated zone in equilibrium with air, and subsequently gained salt, such as from dissolution of evaporate minerals, the dissolved N_2 and Ar data imply recharge temperatures of 18 to 21 °C in 5 of the samples (SNL-16, 19, 18, 17, and 10) with amounts of excess air of 0.1 to nearly 9 cc/kg and denitrification of 0 to 4.5 mg/L of N_2. Infiltration of freshwater cannot reasonably explain the measured concentrations of N_2 and Ar in samples SNL-14 and SNL-8 which would have recharge temperatures of 32 to nearly 48 °C, possibly low excess air, and, in the case of SNL-8, large excess N_2 from denitrification (Table 7).

Alternatively, the saline waters may have originated from infiltration of marine-evaporative surface waters. The calculations of Table 7 were repeated correcting for the sample salinity in the gas solubility (Table 8).

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Table 8. Summary of Dissolved Primary Gas Concentrations, Modeled Excess N$_2$, Excess Air and Recharge Temperature at Sample Salinity*

Sample Name	Date	Salinity, $^{\circ}/_{oo}$ as NaCl	Recharge Elevation	N$_2$ mg/L	Ar mg/L	O$_2$ mg/L	CO$_2$ mg/L	CH$_4$ mg/L	Modeled Excess N$_2$ in mg/L	Calc. Re-charge T $^{\circ}$C	Calc. Ex Air cc STP/L
SNL-16	6/9/2006	20.50	3000	25.389	0.6411	2.75	10.60	0.0000	1.8	20.1	12.3
SNL-16	6/9/2006	20.50	3000	24.128	0.6213	2.61	10.75	0.0000	1.7	20.1	11.1
SNL-19	7/28/2006	11.00	3000	14.243	0.4869	2.90	7.63	0.0000	0.5	20.1	1.4
SNL-19	7/28/2006	11.00	3000	14.207	0.4858	2.89	7.61	0.0000	0.5	20.2	1.4
SNL-18	8/18/2006	22.00	3373	21.373	0.5522	0.16	3.11	0.0000	2.7	20.2	7.5
SNL-18	8/18/2006	22.00	3373	21.514	0.5531	0.15	3.07	0.0000	2.8	20.1	7.6
SNL-18	8/18/2006	22.00	3373	21.343	0.5513	0.17	3.08	0.0000	2.7	20.2	7.5
SNL-17	9/15/2006	6.10	3000	19.656	0.6143	6.12	8.90	0.0000	0.0	16.7	6.2
SNL-17	9/15/2006	6.10	3000	18.905	0.5990	6.05	8.98	0.0000	0.0	17.1	5.6
SNL-10	11/3/2006	12.10	3000	19.492	0.5943	0.20	0.65	0.0075	0.0	18.0	6.9
SNL-10	11/3/2006	12.10	3000	19.479	0.5968	0.20	0.54	0.0076	0.0	17.6	6.8
SNL-14	7/30/2007	125.20	3000	10.481	0.3126	0.08	0.62	0.0040	0.0	20.2	4.7
SNL-14	7/30/2007	125.20	3000	11.381	0.3281	0.09	0.62	0.0037	0.0	20.1	5.6
SNL-14	7/30/2007	125.20	3000	11.888	0.3357	0.10	0.65	0.0035	0.0	20.6	6.2
SNL-8	8/2/2007	84.80	3000	22.810	0.3985	0.10	0.51	0.0256	9.3	20.0	6.0
SNL-8	8/2/2007	84.80	3000	22.041	0.3887	0.10	0.53	0.0253	9.1	20.0	5.4

* Ex N$_2$ (from denitrification of paleo soil nitrate) was adjusted to obtain recharge temperatures near 20 $^{\circ}$C.

In this case, all seven samples could have recharge temperatures in the range of 17 to 20 $^{\circ}$C, and, with few exceptions, reasonable quantities of excess air and relatively low amounts of denitrifications (Table 8). The exceptions being sample SNL-16 which would require a large amount of excess air, and sample SNL-8 which suggests a large quantity of denitrification.

Fractionated Air: Gas Exchange between Trapped Gas Bubbles and Ground Water

In the case of fractionated excess air, a gas bubble is injected into the aquifer. Part of the bubble dissolves following Henry's Law gas solubility. The remaining volume of gas, which has now been altered in composition due to dissolution of CFCs, (and all other gases) is exhausted from the hole. This fractionation process could have occurred during jetting when gas bubbles partially dissolved in the well bore and then were exhausted from the whole. It also applies to the gas bubbles that remain in the formation.

This section considers the possibility that the dissolved gases (He, Ar, Ne, N$_2$, O$_2$, CFC-11, CFC-12, CFC-113, and SF$_6$) were introduced by the drilling air and/or the air-purging of the wells (i.e. jetting used in well completion). It is assumed that gas bubbles were injected into the formation which subsequently either partially dissolved, as can be described by the closed-system equilibration (CE) model of Aeschbach-Hertig et al. (2000), or completely dissolved, a limiting case of the CE model called the un-fractionated air (UA) model. In the CE model, the initial

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volume, A, of the trapped gas bubbles is reduced by partial dissolution of the bubbles under hydrostatic pressure. The dissolved fraction of any gas present is described by the equation:

$$c_i^A = \frac{(1-F)Ax_i}{1+FAx_i/c_i^E},$$

(1)

where c_i^E and c_i^A are the equilibrium and excess air concentrations of gas i in cm^3/g of water. F is equal to v/q where v is the ratio of final to initial of entrapped gas volumes and q is ratio of dry gas pressure to the pressure of the atmosphere. The term A is the initial volume of entrapped air per mass of water in cm^3/g of H$_2$O. The results of the CE model approach those of the UA model as the fractionation parameter, F, approaches 0. For the condition $F=0$, the dissolved excess air volume is equal to A and the gases completely dissolved (un-fractionated air); for all other conditions the volume of gas that dissolved is less than the volume of trapped gas A.

The CE model was used in an attempt to determine if the measured concentrations of gases could have been introduced during the drilling and/or air-purging processes (jetting) that may have introduced bubbles of gases into the aquifer. In application of the CE model, the following assumptions were made:

1) The ground water in the unaltered aquifer is very old and was initially free of environmental tracers like CFCs;
2) All CFCs were introduced from modern air during drilling and/or air-purging (jetting);
3) He and SF$_6$ were introduced from two sources, modern air during drilling and/or air-purging, and from *in-situ*, terrigenic, sources;
4) In most cases, the ground water was assumed to be anoxic and all the oxygen measured in the samples was assumed to have been introduced during the drilling and/or air-purging of the wells;
5) The concentrations of nitrogen, argon and oxygen introduced during drilling and/or air-purging were the amount in excess of a hypothetical initial solution containing 2 cc/kg of un-fractionated excess air at air-water equilibrium at the sample salinity. It is not understood physically how such an initial condition could exist; only that many of the samples seem to yield "reasonable" results from the CE model if this is indeed the initial condition. Another scenario is that the initial water was dilute infiltration water that subsequently dissolved salts in the formation (Appendix 6), but this leads to calculated negative gas excess using the CE model in three of the samples.
6) Dissolved concentrations of hydrogen, carbon dioxide and methane are affected by geochemical redox reactions in the aquifer and not considered in the CE model calculation.

The calculations using the CE model depend, in part, on the theoretical solubilities of the gases, and on the measured concentrations of the gases in formation waters pumped from the wells. All of the gas solubilities were calculated at an assumed recharge temperature of 20°C and recharge altitude of 3,000 feet with an assumed 2 cc/kg of un-fractionated excess air. It was found that the quantities of dissolved Ar are particularly low in 2 of the samples (SNL-8 and SNL-14). The calculated Ar excess from the CE model is negative for waters from several wells, including SNL-14 and SNL-8, if Ar initially dissolved in pure water, such as during recharge of infiltration. Other samples appear to have large excesses of N$_2$, possibly from in-situ denitrification of soil nitrate, or some other diagenetic and/or redox source. Nitrate and other

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salts of atmospheric origin accumulate in unsaturated zones during arid climatic periods. These salts are mobilized during wet climatic periods and can be transported to the aquifer. In reducing aquifers, the atmospheric nitrate can be reduced to aqueous N_2, leading to an excess of N_2 in the dissolved gas composition, relative to that of Ar and other noble gases of atmospheric origin.

As shown in the previous section, using the UA (un-fractionated air model), samples SNL-8 and -14 have very low Ar, and unrealistically warm recharge temperatures, if the initial solution had low salinity (Table 5). In addition, sample SNL-8 has a large excess of N_2 leading to a calculated large amount of denitrification. Alternatively, if the initial solutions had the salinity as observed in the water samples, initial water temperatures based on N_2 and Ar can be near 20 °C with moderate, but not unrealistic amounts of excess air and relatively low amounts of denitrificaiton (except for sample SNL-8 that still would require approximately 9 mg/L of excess N_2 from denitrificaiton) (Table 8). In order to consistently calculate positive amounts of excess gases using the CE model, it was assumed that each initial solution contained 2 cc/kg of un-fractionated excess air. Further, the initial solubilities of N_2, Ar, and O_2 were calculated in initial waters of the salinity measured for the formation water. Still, the CE model calculations are likely invalid for samples SNL-8 and SNL-14 because a conceptual model of their origin accounting for the low Ar and high N_2 content is not understood. There is insufficient solubility data to calculate the concentrations of CFCs and SF_6 in saline waters, so these solubilities were calculated for pure water. Thus the solubilities assume air-water equilibrium of infiltration of precipitation at some time in the past. This scenario of air-water solubility equilibrium at recharge applies to the permanent atmospheric gases (N_2, Ar, O_2). The transient gases (CFCs and SF_6), in application of the CE model, are presumed to have entered the ground water from dissolution of gases injected into the formation. Here we should use the solubilities of CFCs and SF_6 in the saline formation waters, but, unfortunately the salt effects for brines have not been determined. As a first approximation, we used CFC and SF_6 solubilities in pure water at 20 °C and 3,000 feet altitude. Table 9 summarizes the calculated gas solubilities, c_i^E, used in Equation 1.

Table 9. Equilibrium concentrations used in Equation 1.*

Well	N_2 mol/kg $\times 10^4$	O_2 mol/kg $\times 10^4$	Ar mol/kg $\times 10^5$	He mol/kg $\times 10^9$	Ne mol/kg $\times 10^9$	CFC-12 mol/kg $\times 10^{12}$	CFC-11 mol/kg $\times 10^{12}$	CFC-113 mol/kg $\times 10^{13}$	SF_6 mol/kg $\times 10^{15}$
SNL-16	4.10	2.21	1.08	1.83	7.57	1.71	2.88	2.64	1.45
SNL-19	4.39	2.36	1.15	1.83	7.57	1.71	2.88	2.64	1.45
SNL-18	4.00	2.16	1.06	1.83	7.57	1.71	2.88	2.64	1.45
SNL-17	4.55	2.45	1.19	1.83	7.57	1.71	2.88	2.64	1.45
SNL-10	4.35	2.34	1.15	1.83	7.57	1.71	2.88	2.64	1.45
SNL-14	1.94	1.10	0.54	1.83	7.57	1.71	2.88	2.64	1.45
SNL-08	2.58	1.44	0.70	1.83	7.57	1.71	2.88	2.64	1.45

* The equilibrium concentrations for N_2, O_2 and Ar were corrected for the decrease in solubility by the salinity of the ground waters. The solubilities of all other gases are those in pure water at 20 °C and 3,000 feet altitude.

The measured value of the excess amount of a dissolved gas over an initial condition of solubility equilibrium with 2 cc/kg of un-fractionated excess air, c_i^A, is

$$c_i^A = c_i - c_i^E - c_i^{EX} \qquad (2)$$

where c_i is the measured concentration of the gas in the water sample (Table 10), and c_i^{EX} is the amount of the gas from an initial 2 cc/kg of un-fractionated excess air.

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Table 10. Measured concentration of major and trace gases in the ground water samples.

Well	N_2 mol/kg $\times 10^4$	O_2 mol/kg $\times 10^5$	Ar mol/kg $\times 10^5$	He mol/kg $\times 10^8$	Ne mol/kg $\times 10^8$	CFC-11 mol/kg $\times 10^{12}$	CFC-12 mol/kg $\times 10^{12}$	CFC-113 mol/kg $\times 10^{12}$	SF_6 mol/kg $\times 10^{15}$
SNL-16	8.838	8.381	1.580	4.184*	5.06*	39.2	47.3	6.4	11.90
SNL-19	5.078	9.051	1.218	0.567*	0.904*	13.4	4.7	0.0	28.59
SNL-18	7.643	0.498	1.382	8.22	ND	28.9	16.8	4.4	20.19
SNL-17	6.883	0.190	1.519	0.347*	1.26*	55.5	56.9	8.8	1.02
SNL-10	6.956	0.621	1.491	0.048	ND	8.9	5.5	5.4	0.19
SNL-14	4.016	0.277	0.815	0.83	ND	21.9	10.4	2.3	0.22
SNL-08	8.005	0.317	1.986	3.95	ND	180.1	9.2	0.0	0.05

* He and Ne concentrations determined by mass spectroscopy; all other He concentrations were determined by gas chromatography; ND, not determined.

SNL-10, SNL-14 and SNL-08 contain concentrations of methane of 4.71×10^{-7}, 2.32×10^{-7} and 15.8×10^{-7} mol/kg, respectively.

It was assumed that two cc/kg of un-fractionated excess air at STP was present in the initial ground waters, amounting to 0.697×10^{-4} and 0.833×10^{-6} mol/kg of N_2 and Ar, respectively. The excess air was added to the equilibrium concentrations of N_2 and Ar shown in Table 9.

In the limiting case of only gas injection into the formation during drilling, the CE model should explain all the observed environmental and permanent gas concentrations measured in the ground waters from the seven wells. If it does not, then additional processes, perhaps accompanying gas fractionation, would need to be considered to explain the observed gas concentrations. Some of these processes include microbial degradation in the aquifer or sample bottle (O_2, CFCs), terrigenic sources (H_2, SF_6), denitrification (N_2), mixing and/or other models for incorporation of excess gases (all gases). Model calculations applying the CE model for each of the wells are presented below for the case of initial saline water (for N_2, Ar, and O_2). The calculations are repeated for initial dilute waters (for N_2, Ar, and O_2) in Appendix 6.

A series of plots follow, one for each well, in which model values of c_i^A from Equation 1 are plotted as a function of A, the initial volume of excess air injected into the aquifer at a value of F, the fractionation factor determined by trial and error that best fits the measured values of c_i^A given by Equation 2. In each of the plots, the ordinate is the measured and calculated value of c_i^A. Values of c_i^A were scaled according to the exponent of the mole concentrations given in the legend of each plot, and denoted as "$\times 10^x$" in the ordinate title, where the value of x is exponent from the plot legend for each gas.

SNL-16 contains moderately high concentrations of He and Ne, and a high concentration of terrigenic SF_6. As a result the He, Ne, and SF_6 concentrations are not adequately modeled using the CE model alone. The results of the CE model are presented in Figure 11. The best fit was obtained using a trapped gas volume, A, of 30-42 mL per kg of water and a fractionation factor (F) of 0.37.
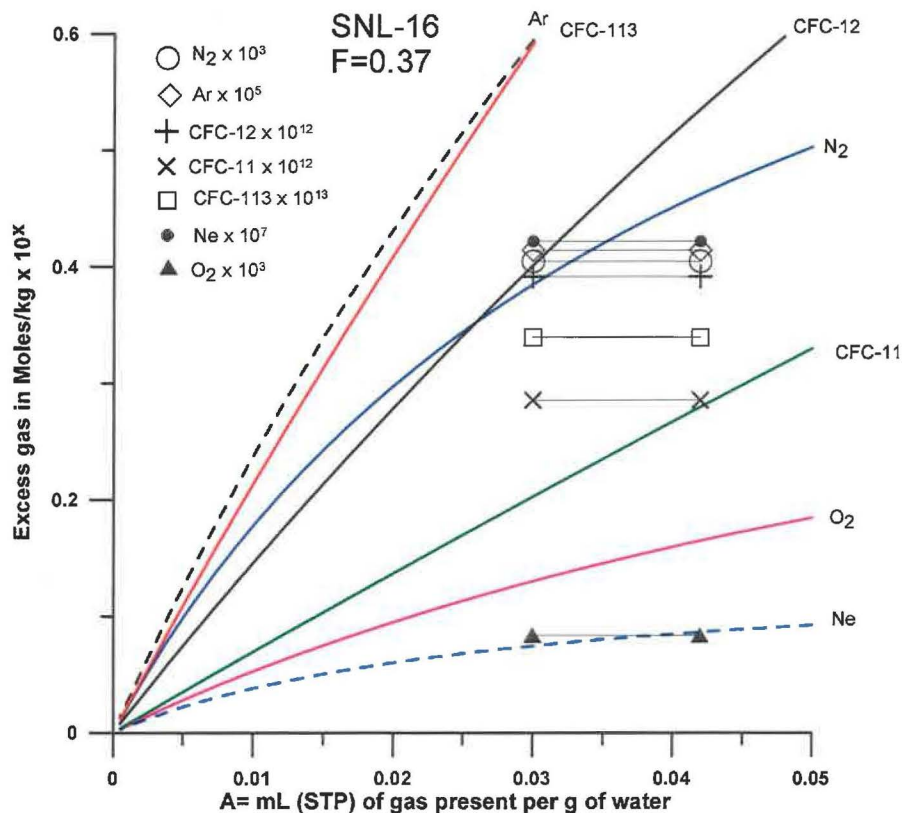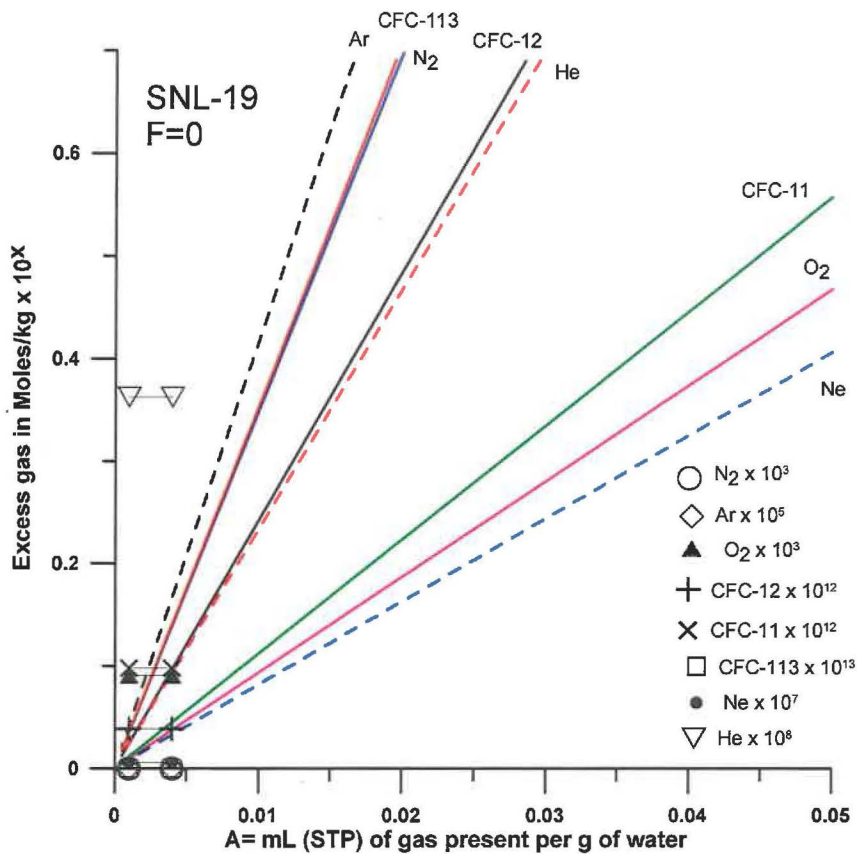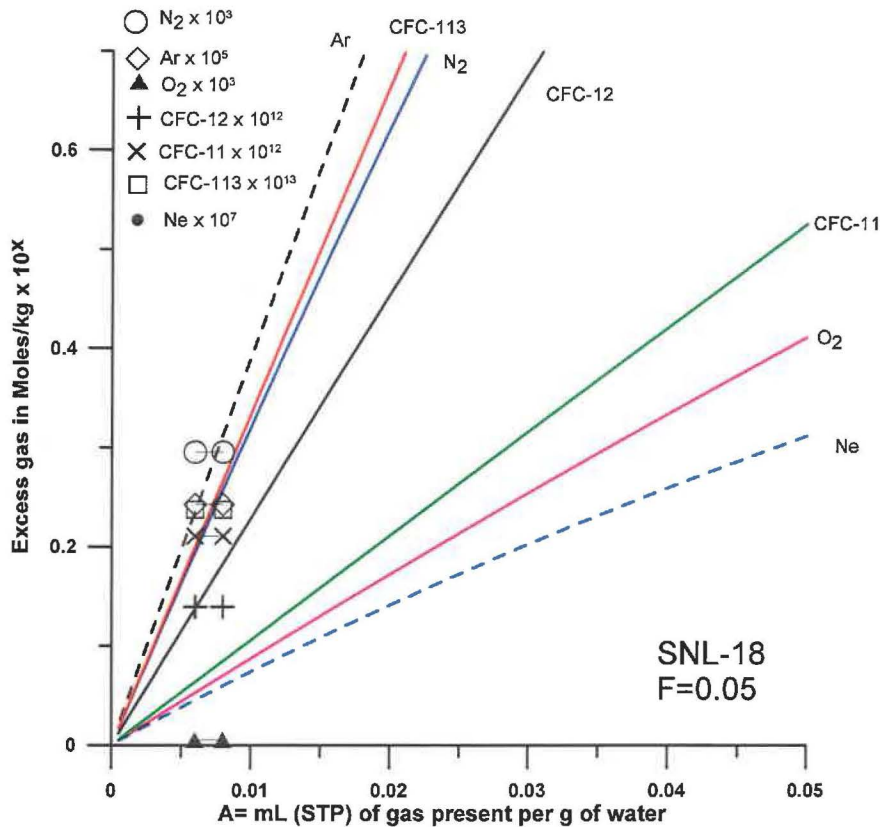
Figure 11. Plot showing the mole fractions of excess gases and environmental tracers as a function of volume of trapped gas for a fractionation factor (F) of 0.37 for SNL-16.

The excess concentrations of N_2 and CFC-12 best fit the model for a trapped gas concentration of 0.030 cc/g of water while the CFC-11 excess concentration better fits the model for a trapped gas concentration 0.042 cc/g of water. The concentration of Ar, O_2 and CFC-113 measured is about 50% too low and does not fit the model. The CFC-113, Ar and O_2 excess concentrations fit a model with a fractionation factor of 0.60.

Water from SNL-19 contains little to no excesses of N_2, Ar, or CFC-113. The results of the CE model are presented in Figure 12. The best fit was obtained using gas volumes of only 0.001-0.004 cc/g of water and a fractionation factor (F) of 0.0.
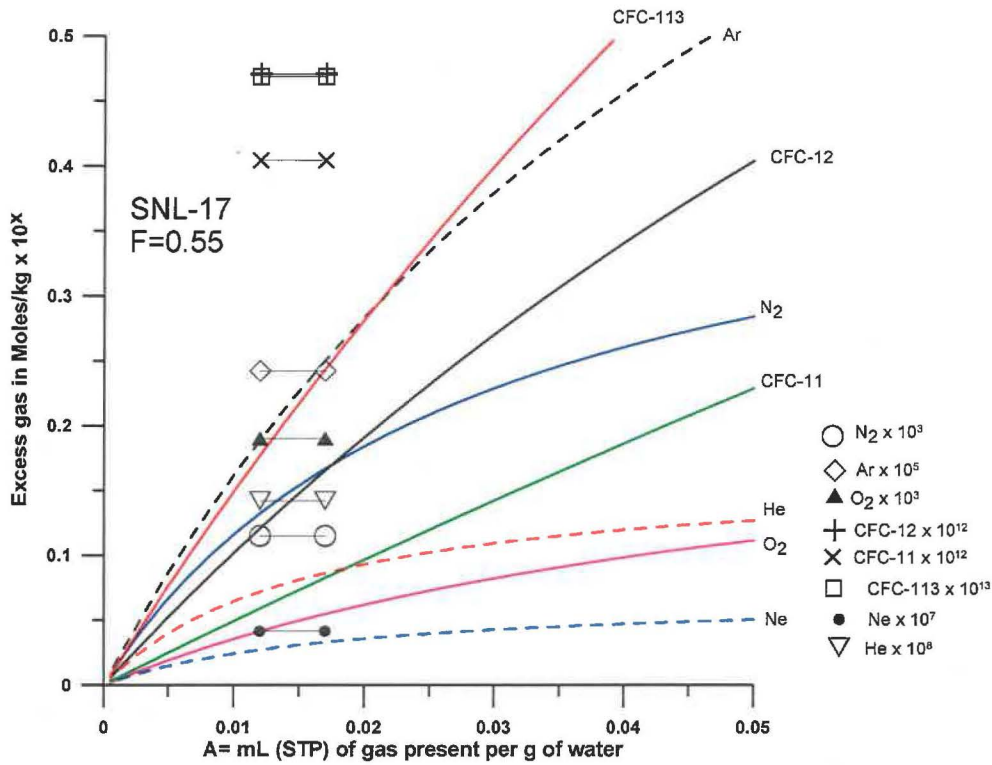
Figure 12. Plot showing the mole fractions of excess gases and environmental tracers as a function of volume of trapped gas for a fractionation factor (*F*) of 0.0 for SNL-19.

The results of the modeling indicate that only a very small amount of gas 0.001-0.004 cc/g of water was trapped and the gas was not fractionated, $F = 0.0$. Water from SNL-19 contains significant concentrations of terrigenic SF_6 and an excess of He that cannot be accounted for by the CE model.

The results of the CE model for water from SNL-18 are presented in Figure 13. The high concentrations of terrigenic He and SF_6 cannot be explained by the CE model alone. The best fit for the other gases was obtained using a gas volume of 0.006-0.008 cc/g of water and a fractionation factor (*F*) of 0.05.
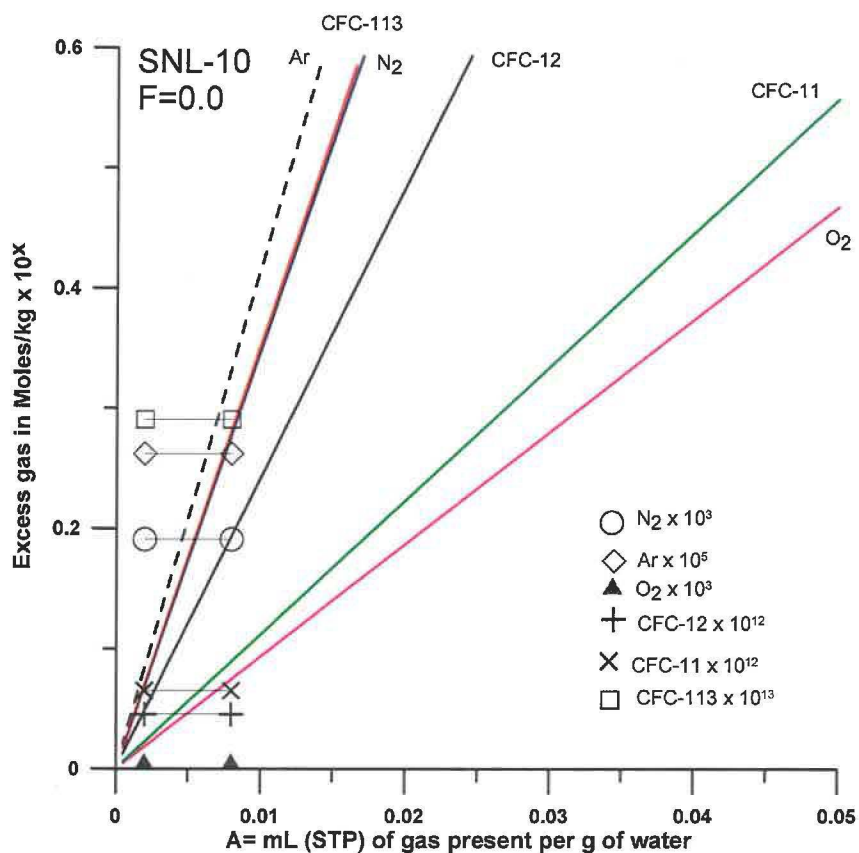
Figure 13. Plot showing the mole fractions of excess gases and environmental tracers as a function of volume of trapped gas for a fractionation factor (*F*) of 0.05 for SNL-18.

The excess concentrations fit the CE model reasonably well, however, the measured CFC-11 concentration is high, possibly due to an additional source of contamination, and the O_2 concentration is low, possibly due to microbial degradation in the aquifer or in the sample bottle prior to analysis.

Water from SNL-17 contains moderately high concentrations of terrigenic SF_6, which cannot be explained by the CE model alone. The results of the CE model for the permanent gases N_2, Ar, He and Ne are presented in Figure 14. The best fit was obtained using a gas volume of 0.012-0.017 cc/g of water and a fractionation factor (*F*) of 0.55. Note that the CFC concentrations are much higher than the modeled values (Figure 14). The CFC-11, CFC-12 and CFC-113 fit an entirely different model (not shown in Figure 13) with 0.020-0.025 cc/g of water of trapped air and a lower fractionation factor (*F*) of 0.25. It is possible that a different physical process introduced the CFCs to water from well SNL-17, than for the other dissolved gases.
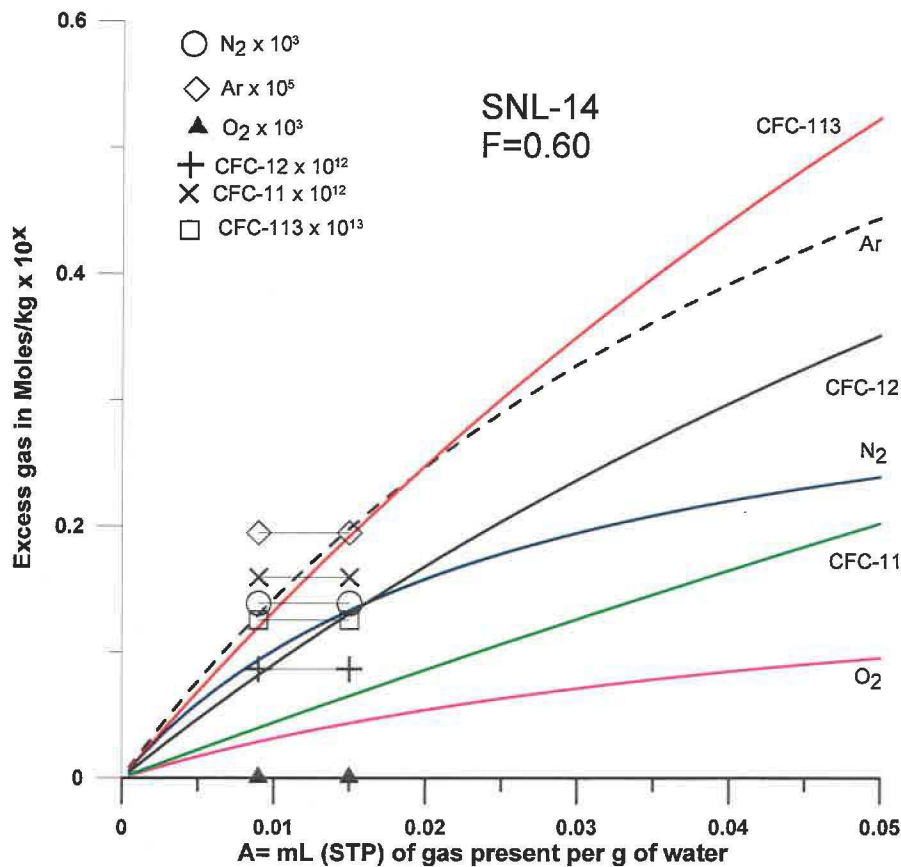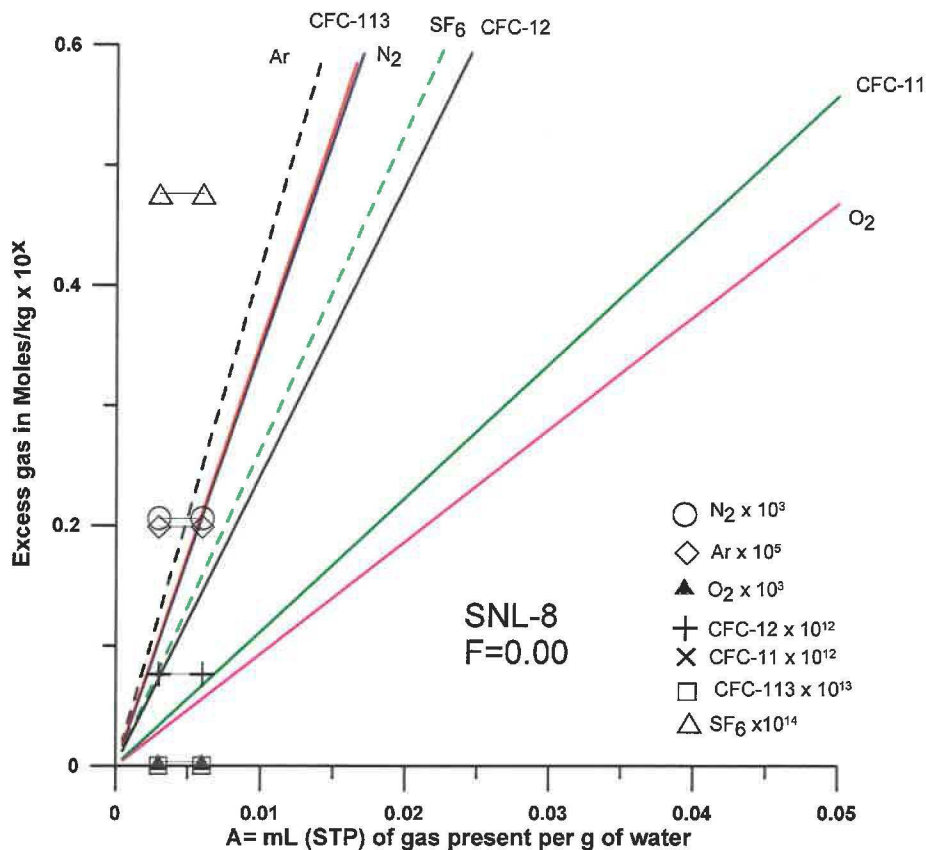
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Figure 14. Plot showing the mole fractions of excess gases and environmental tracers as a function of volume of trapped gas for a fractionation factor (*F*) of 0.55 for SNL-17. Note that the measured CFCs are significantly greater than the modeled concentrations.

Water from SNL-10 contains moderate concentrations of terrigenic He and SF_6. The results of the CE model are presented in Figure 15. The best fit was obtained using a gas volume of 0.002-0.008 cc/g of water and un-fractionated air (*F* = 0.0).

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Figure 15. Plot showing the mole fractions of excess gases and environmental tracers as a function of volume of trapped gas trapped. All the trapped air was dissolved and $F = 0.0$ for SNL-10.

Water from SNL-14 contains high concentrations of terrigenic He and SF_6. The results of the CE model are presented in Figure 16. The best fit was obtained using a gas volume of 0.009-0.015 cc/g of water and a fractionation factor (F) of 0.60.

Figure 16. Plot showing the mole fractions of excess gases and environmental tracers as a function of volume of trapped gas for a fractionation factor (F) of 0.6 for SNL-14.

Water from SNL-14 is similar to that from SNL-18 in that there is an excess of CFC-11, possibly due to a contamination source, and dissolved oxygen concentration is below the modeled value, possibly due to microbial degradation, occurring either in the sample bottle or in the aquifer.

Water from SNL-8 contains very high concentrations of terrigenic He. The CFC-11 concentration is very high and not consistent with the CFC-12 and CFC-113 measured concentrations which suggest that this ground water was contaminated with CFC-11. The results of the CE model are presented in Figure 17. The best fit was obtained using a gas volume of 0.003-0.006 cc/g of water and a fractionation factor (F) of 0.0, based on the N_2, Ar and CFC-12 concentrations.

Information Only

Figure 17. Plot showing the mole fractions of excess gases and environmental tracers as a function of volume of trapped gas for a fractionation factor (F) of 0.0 for SNL-8.

The results for the CE model from Figures 11-17 are summarized in Table 11. A fractionation factor (F) of 0 indicates that all the trapped air was dissolved. The fractionation of the trapped air increases as F approaches 1.0. A is the initial amount of trapped air in cc/g of water. Note that two different models are needed to explain the permanent and environmental gas compositions of water from SNL-17. In almost all cases, the measured CFC-11 concentrations are greater than the modeled CFC-11 concentrations, indicating possibly low-level contamination of CFC-11 in most of the samples. There are many potential sources of the excess CFC-11 from the drilling operation, including rubber hoses used in air injection. SNL-8 appears to be significantly contaminated with CFC-11. Significant excesses of He and SF_6 were present in nearly all the ground waters and are attributed to terrigenic sources.

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Table 11. Summary of results from the CE Model

Well Name	Date Sampled	A (Trapped Air in cc/g H$_2$O)	F (Fractionation factor)	Gases Fitting the CE Model for each sample*
SNL-16	06/09/2006	0.30-0.42	0.37	N$_2$, CFC-12, CFC-11
SNL-19	07/28/2006	0.001-0.004	0.00	N$_2$, O$_2$, CFC-12, CFC-113
SNL-18	08/18/206	0.006-0.008	0.05	N$_2$, Ar, CFC-12, CFC-113
SNL-17	09/15/2006	0.12-0.17	0.55	N$_2$, Ar, Ne
SNL-17	09/15/206	0.20-0.25	0.25	CFC-11, CFC-12, CFC-113
SNL-10	11/03/2006	0.002-0.008	0.00	N$_2$, Ar, CFC-11, CFC-12, CFC-113
SNL-14	07/30/2007	0.09-0.15	0.60	N$_2$, Ar, CFC-12, CFC-113
SNL-08	08/02/2007	0.003-0.006	0.00	N$_2$, Ar, CFC-12

*Other gases, not listed here do not fit the CE Model—see figures of CE model calculations for each sample.

The overall conclusion from the model calculations considering introduction and fractionation of excess air from the drilling operation is that in many cases, the observed concentrations of CFCs, particularly CFC-12, and CFC-113, and permanent atmospheric gases, N$_2$, Ar, could be explained by injection of varying relatively small amounts of air with subsequent partial or in a few cases, complete dissolution of the injected air. These calculations assume an initial condition of N$_2$, Ar, and O$_2$ saturation in initial saline solutions. See Appendix 6 for similar calculations that begin with initial dilute water. In either case, the CE model cannot explain the observed concentrations of SF$_6$ and He which have large excesses relative to the CE model and most likely have additional, terrigenic, sources.

As indicated initially in this report, two general limiting cases were considered for source of anthropogenic contaminants (CFCs and tritium primarily) found in discharge from the newly drilled WIPP site monitoring wells. The first case was gas injection, and it seems from the CE model calculations that this could account for much of the observations. The second case was contamination of formation water from fluids introduced in well construction, particularly in the final stage of well development when imported water from local suppliers was put down the borehole during jetting of the well screen. The wells typically were pumped for up to 4 days prior to sampling. However, it appears that well development and pumping procedures were not sufficient to remove all the effects of drilling, because (1) small amounts of tritium were detected in at least 3 of the wells, (2) there is a correlation of tritium concentration and CFC-12 (Figure 5), (3) all the wells contain chloroform, a disinfection byproduct in many public water supplies, and (4) chloroform and tritium content are correlated with % Modern based on CFC-12 (Figures 5 and 9).

Although mixing of imported water seems a likely source of contamination, there is still the question as to whether air injection can add tritium and carbon-14 to the WIPP waters. Below we examine whether the tritium content (and ^{14}C activity) of the well discharge could be affected by dissolution of excess air, using the CE model results of Table 11.

The Effects of the Dissolution of Humid Air and CO$_2$ Present in the Trapped Air on the Measured Concentrations of Tritium and Carbon-14 of the Samples

The CE model was used to calculate the amount of tritium that could have been added to the ground water by the trapped air that may have been introduced during the drilling and/or air-purging (jetting) of the wells. The tritium contributions were calculated assuming a 100 percent relative humidity, an air temperature of 20°C, and a tritium concentration of the water vapor of

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10 TU. This is a worst case scenario, but the calculations can be used to identify if the humidity of the trapped air was a possible source of tritium observed in some of the ground waters. The CE model results (Table 12) were calculated for an elevation of 3,000 feet where the atmospheric pressure is equal to 0.896 atm. and a vapor pressure of H_2O of 20 mm of Hg. One TU equals one ^3H atom for every 10^{18} atoms of ^1H. One kg of water is equal to 55.5084 moles of H_2O.

Table 12. Calculated increase in the tritium (^3H) concentration of the ground water as a result of the addition of trapped air during the drilling and/or air-purging of the wells.

Well name	Max. trapped air in mL/kg	Water added by the moist trapped air in mol/kg H_2O	^3H atoms added by the moist trapped air ^3H atoms/kg H_2O	Increase in the ^3H conc. due to the added water vapor, in TU
SNL-16	42	5.50E-05	663	9.91E-06
SNL-19	4	5.24E-06	63	9.44E-07
SNL-18	8	1.05E-05	126	1.89E-06
SNL-17	25	3.28E-05	395	5.90E-06
SNL-10	8	1.05E-05	126	1.89E-06
SNL-14	15	1.97E-05	237	3.54E-06
SNL-8	6	6.55E-06	79	1.18E-06

The CE model also was used to calculate the concentration of CO_2 that could have been added to the ground water by the trapped air that may have been introduced during the drilling and/or air-purging (jetting) of the wells. It is reasonable to assume that modern air was used during the air-purging with a CO_2 concentration of 380 parts per million and a ^{14}C activity of 105 percent modern carbon (pmc). Table 13 gives the concentrations of CO_2 that may have been added to the ground water, calculated using Equation 1. The carbon concentration of the ground water was calculated from the alkalinity of the waters.

Table 13. The maximum added CO_2 concentrations from the trapped air calculated using Equation 1.

Well Name	Max. Trapped Air in mL/kg	Max. Added CO_2 In mol/kg	Carbon Conc. in water in mol/kg	Max. increase in C-14 conc. in % Modern Carbon
SNL-16	42	3.33E-07	0.001590	0.0220
SNL-19	4	6.78E-08	0.001475	0.0048
SNL-18	8	1.08E-07	0.001229	0.0093
SNL-17	25	1.28E-07	0.001541	0.0087
SNL-10	8	1.35E-07	0.000754	0.0188
SNL-14	15	1.01E-07	0.000787	0.0134
SNL-08	6	7.62E-08	0.000803	0.0100

The results of Tables 12 and 13 show that the trapped air introduced during the air-purging of the wells could have added only insignificant concentrations of both tritium and ^{14}C to the ground waters.

Still, we have the observation that traces of tritium were detected in water from 3 of the wells, and overall, there appears a trend of tritium, chloroform, and CFC-12 concentration (Figures 5 and 9). Further, all of the samples contain small amounts of ^{14}C and it is not known if that detection is entirely attributed to old formation water or represents a small contamination from drilling fluid or imported water. That the samples contain tritium indicates that there is likely a contamination from water used in the drilling operation.

In the next section we test the possibility of mixing of freshwater containing tritium and ^{14}C used in the jetting process with formation water. This is the other limiting case for introduction of environmental tracers in the well discharge—injection of water from the drilling process. Unfortunately, we do not have any measurements of chemical or isotopic composition of the water sources (city water from various towns in the vicinity; Eunice, Carlsbad, Hobbs, Double Eagle). As they represent quite different sources (Ogallala, Capitan Reef aquifer), it is likely that they have different ^{14}C, DIC, and ^{3}H content.

During the jetting process, some 100 bbls (5,500 gallons) of this external water was put down the borehole while high pressure air was jetted into the well screen. While this process likely injected air into the formation, it also saturated the water column in the borehole with air, including atmospheric CFCs. Some of this air-saturated water flowed through the well screen into the formation, and was probably pushed there under high air and/or hydrostatic pressure. During pump and well development, most of this water was likely removed, but as the CFCs and chloroform data suggest, it is possible that some of it remains (Figures 5 and 9).

Here we consider a carbon isotope mass balance using the CFC data as indicator of fraction of this imported water in well discharge. If the imported water used in the jetting process was saturated with air prior to entering the formation, then the calculated % Modern values of Table 5, based on CFCs, represent percent of imported water that was pumped from wells during sampling. Here we use the average % Modern of all three CFCs of Table 5 as an estimate of percent of imported water, except for well SNL-8 which appears contaminated with CFC-11. Based on the lack of detection of CFC-113 in water pumped from SNL-8, the sample probably contains < 2 percent of imported water.

Tritium/Helium-3 Age Results

Samples were collected for tritium/helium-3 age determination, and submitted to the Noble Gas Laboratory of Lamont-Doherty Earth Observatory (LDEO) of Columbia University, Palisades, NY under contract to the USGS. Although the ground-water samples were expected to be old, and well beyond the approximately 30-year dating range of the method, the thought was that, if the samples contained a young (post-bomb) fraction mixed with old water, it may be possible to date the young fraction in the mixture. The amount of terrigenic helium was calculated by subtracting from the measured total dissolved helium (Table 14), the amounts of helium dissolved in solubility equilibrium with air at the recharge temperature and local barometric pressure, and the helium introduced from excess air trapped during recharge, based on the dissolved neon excess (Schlosser et al., 1988, 1989). The term δ^{3}He expresses the percent deviation of the ^{3}He/^{4}He ratio of the sample from that of air (δ^{3}He = (R_s/R_a – 1)x100, where R_s is the ^{3}He/^{4}He ratio of the sample and R_a is that of air (1.384×10^{-6}, Clarke et al., 1976). The measurements that are currently available are summarized in Table 14. Results from other samples are expected, but the results have not been reported to the USGS by LDEO.

Table 14. Summary of $^3H/^3He$ results

Well	Tritium in TU	Tritium ± 1σ in TU	δ^{3}He %	^{4}He (10^{-8} ccSTP/g)	Ne (10^{-8} ccSTP/g)	% Terrigenic He	Δ^{4}He %	ΔNe %	$^3H/^3He$ age yrs	±1σ yrs
SNL-16	0.62	0.09	-55.15	93.79	113.44	65.9	2263	597	79	18
SNL-19	0.02	0.07	-59.74	12.7	20.26	59.6	221.4	25.4	nd	
SNL-18	0.19	0.08	lost	lost	lost	lost	lost	lost	nd	
SNL-17	0.31	0.08	-3.62	7.77	28.26	3.9	98.2	77.1	16	16
SNL-10	-0.07	0.07	lost	lost	lost	lost	lost	lost	nd	
SNL-14	0.13	0.13	not run	not run	not run	not run	not run	not run	nd	
SNL-8	0.1	0.1	not run	not run	not run	not run	not run	not run	nd	

As explained above, samples with low tritium content cannot be dated by the $^3H/^3He$ method, and those with low tritium can have large uncertainties. The terms Δ^{4}He (%) and ΔNe (%) express the amount of He and Ne in the sample that is in excess of solubility equilibrium. Sample SNL-16 has very large Δ^{4}He (%) and ΔNe (%) due to a large amount of excess air in the sample. Samples 19 and 18 also have large excess air. The Ne data were used to correct for excess air assuming un-fractionated excess air. The age of 79 ± 18 years for water from SNL-16 is meaningless as it is well beyond the $^3H/^3He$ dating range, and contains a large fraction of excess air that probably should be corrected using a model that includes gas fractionation. The age of 16 ± 16 years for SNL-17 may be of some use, implying an age range of the young fraction in a mixture of 0-32 years. The calculated initial tritium (tritium + tritiogenic helium-3) is only 0.76 TU for SNL-17. Using the mean age of 16 years and 2006 sample date, precipitation from 1990 would contain about 2.9 TU today. If the16 year age is correct, then sample SNL-17 contains about 26% of 1990 infiltration water diluted with old, tritium-free water. This estimate of percent modern water based on initial tritium is consistent with the range of % Modern values calculated from the CFC data (Table 5); a range of 15.2 to 29.0 % Modern, with average of 21.0 % Modern.

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RADIOCARBON DATA

Sources of ^{14}C

All of the samples contain ^{14}C in their dissolved inorganic carbon (Table 15), but it is not known if that ^{14}C content represents ^{14}C atoms introduced during recharge and isolation from the modern atmosphere or whether the samples have been contaminated by multiple sources of carbon.

Table 15. Summary of ^{14}C activity, δ^{13}C, and evidence of mixing

Well	location	CFC-12 % Modern	Tritium in TU	Tritium ± 1σ in TU	Alkalinity (CaCO₃) mg/L	δ^{13}C in per mil	pmc no ^{13}C corr	C_T*A	Source water
SNL-16	Nash Draw	27.7	0.62	0.09	97	-4.8	7.85	761.7	Eunice
SNL-19	Nash Draw	2.5	0.02	0.07	90	-2.4	11.10	998.7	WIPP
SNL-18	east edge of Nash Draw	10.1	0.19	0.08	75	-2.1	4.63	347.1	WIPP
SNL-17	east edge of Nash Draw	29.0	0.31	0.08	94	-7.0	17.94	1686.7	NA
SNL-10	WIPP, should be old	3.0	-0.07	0.07	46	-5.1	11.75	540.7	Hobbs
SNL-14	WIPP, should be old	16.0	0.13	0.13	48	-2.2	7.07	339.2	Double Eagle
SNL-8	WIPP, should be old	2.0*	0.1	0.1	49	-2.0	13.31	652.0	WIPP

* Estimated

In radiocarbon dating, a mixed age results if there are more than one source of carbon in the sample. The first concern is whether the drilling process created mixed-carbon samples. Although drilling air can be ignored (see above calculations), the CFC, tritium, and chloroform data suggest mixing of water used in drilling with formation water, and that the drilling water was not completely removed during well development and well pumping prior to sampling. Table 15 lists the sources of imported water used in the jetting stage of well development. Unfortunately, there is no information on the chemical or isotopic composition of these source waters. In the case of a simple binary mixture of unaltered Culebra formation water (subscripted fw) with area imported water used in jetting (subscripted iw), a carbon isotope mass balance can be written the well discharge water (subscripted, dw),

$$[C_T \times A]_{dw} = [C_T \times A]_{fw} \times (1-f) + [C_T \times A]_{iw} \times f \qquad (3)$$

where A is the corresponding ^{14}C activity of inorganic carbon in the mixture or end-member water, C_T is the concentration of inorganic carbon in the source water, and f is the fraction of source water from the drilling process. If f is 1, well discharge is 100% drilling fluid, and if f is 0, the water discharged from the well is 100% formation water.

Using the % Modern values based on CFC-12 as representative of % of drilling water in the mixture, Figure 18 shows the quantity, $[C_T \times A]_{dw}$ and a function of f.
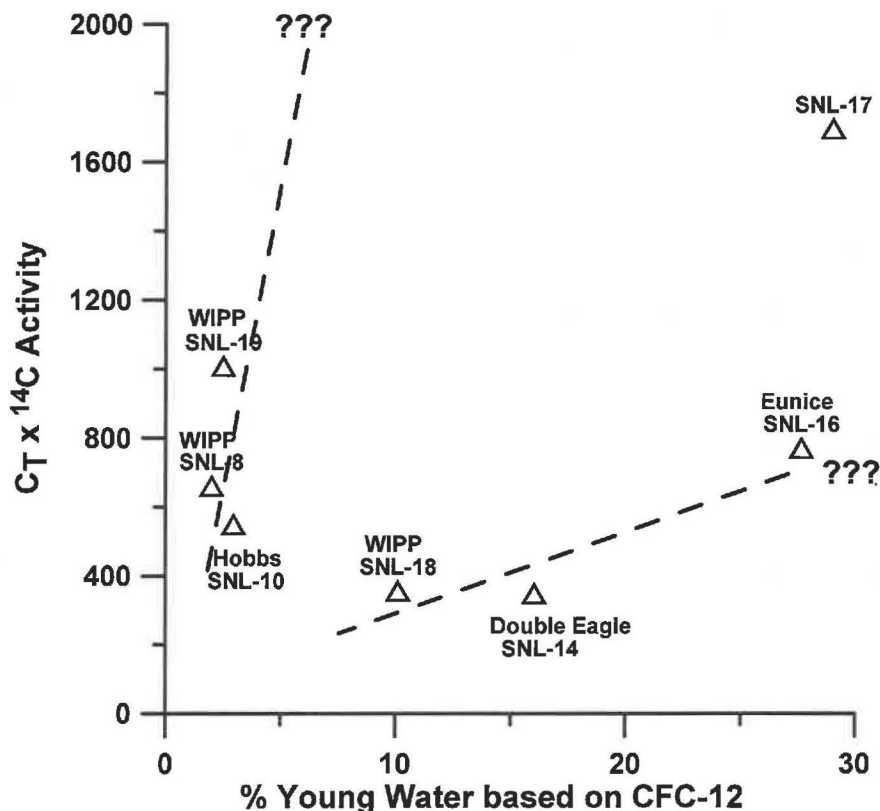
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Figure 18. Plot showing the product of alkalinity (in mg/L as $CaCO_3$) times ^{14}C activity in pmc as a function of percent young water in the mixture determined by CFC-12 (Table 3).

There is a suggestion of two possible mixing lines. One involving water from SNL-18, SNL-14, and SNL-16 implies a relatively low product of $[C_TxA]_{iw}$ in the drilling water, and the other suggests a relatively high value of $[C_TxA]_{iw}$ in drilling water (SNL-10, -8, and -19). Sample SNL-17 appears unrelated to the two groups. This may reflect the fact that imported water was apparently not used in the jetting process for development of this well (though the sample does in fact contain chloroform—an indicator of imported water). Both lines seem to extrapolate to low values of $[C_T x A]_{fw}$ at low fraction of imported water. If the extrapolation to low $[C_T x A]_{fw}$ at low f is correct, then it is implied that the ^{14}C activity, A, may be quite low in the unaltered formation water. However, the mixing fractions are very uncertain. The mixing fraction, f, was based on CFC-12 (Tables 5 and 15), and the value of f for well SNL-8 was estimated to be similar to that of well SNL-19 based on the low CFC-113 content. The suggestion of binary mixing is not nearly so "clear" if the mixing fraction, f, is based on the average of the 3 CFCs, or based CFC-11 or CFC-113. Another complication is that sample SNL-18 seems to lie on a different dilution line than that for samples SNL-19 and SNL-8, though all three were presumably diluted using the WIPP water supply. Further, we do not know values of C_T and A in the various waters imported during drilling (Table 15), or whether the suggested extrapolated values of C_TxA have any bearing on reality.

Given the fact that the imported water from the WIPP supply was used for development of the wells SNL-19, SNL-18 and SNL-8, we assume that the ^{14}C activity of water pumped from these wells has been modified by mixing with WIPP water having a common ^{14}C activity. If the

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chloroform concentrations (Appendix 5) are indicative of the amount of WIPP water in mixtures pumped from these wells, and if the DIC concentration is similar in all 4 wells (WIPP, SNL-19, SNL-18, SNL-8), the ^{14}C activity in WIPP water must be less than approximately 0.4 pmc, implying the ^{14}C activity of DIC from SNL-18 is actually quite low and possibly near zero. This follows from the ratios of the peak areas of chloroform in the samples to that in SNL-19 (Appendix 5). Taking SNL-19 as nearly free of imported water, (ratio of 1), water from SNL-18 has 10.5-fold the chloroform concentration as in SNL-19, and water from SNL-8 has 6-fold that of SNL-19. The ^{14}C activity of DIC from SNL-18 is relatively low, 4.63 pmc. A mass balance on ^{14}C (again assuming that the DIC concentrations of all 4 wells are similar) yields for SNL-18

$$^{14}C_{18} + 10.5\ ^{14}C_{WIPP} = 4.63 \qquad (4)$$

where $^{14}C_{18}$ is the unaffected ^{14}C activity of DIC in water from SNL-18, and $^{14}C_{WIPP}$ is the ^{14}C activity of DIC in the water supply at WIPP. This relation implies that the ^{14}C activity of DIC in the WIPP water supply must be less than approximately 0.4 pmc, as the value of $^{14}C_{18}$ must be $\geq$ 0. Using this estimate of the ^{14}C activity for DIC in water from the WIPP supply, similar relations would imply that the ^{14}C activity of DIC in SNL-19 is approximately 10.7 pmc, and that of SNL-8 is near 10.9 pmc. This calculation also assumes the chloroform concentration in the WIPP water supply was constant on each occasion that water from this supply was used in well development, and that it was stable in the aquifer and sample bottle.

Clearly, these calculations require further measurements to resolve (see Recommendations). Still, the fact remains that all the samples contain chloroform, indicative of imported, chlorinated water, and other halogenated VOCs of anthropogenic origin, including CFCs, and in some cases, tritium, and thus, the samples have been impacted by another source(s) that may contain ^{14}C.

Until the question of possible mixing of imported water can be resolved, no reliable radiocarbon ages can be recommended. In the following, the assumption is made that the samples are representative of unaltered formation water. Given the fact that this is probably an invalid assumption, the derived radiocarbon ages (below) are highly uncertain. The effect of mixing on the radiocarbon age of the unaltered formation water depends on the ^{14}C activity of DIC in the imported water, the amount of DIC in the imported water and the fraction of imported water remaining in the formation. If the imported water has lower ^{14}C activity than the unaltered formation water, the apparent radiocarbon age of the formation water is biased old in mixing, and if the imported water has higher ^{14}C activity than that of the formation water, the apparent radiocarbon age is biased young. Not knowing the fractions of imported water or their ^{14}C activities or DIC content makes it impossible to reliably determine radiocarbon ages of the unaltered formation water.

Conventional and Apparent Radiocarbon Age

The Conventional Radiocarbon Age (Stuiver and Polach, 1977), t, is expressed in years before 1950, the year on which the absolute international radiocarbon standard was based. Since pM is referenced to the year of measurement, the Conventional Radiocarbon Age is

$$t = \frac{5568}{\ln 2} \ln\left(\frac{100}{pM}\right) - \frac{y-1950}{1.029} \qquad (5)$$

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where the number 5568 is the "Libby half-life" of ^{14}C, y is the year of measurement, and the constant 1.029 is the ratio of $\lambda_{5730}/\lambda_{5568}$. λ is the decay constant equal to ln 2 divided by the ^{14}C half-life, and the number 5730 is the modern accepted ^{14}C half-life.

In this report all radiocarbon ages are reported as an "Apparent Age", t_{app}, and analogous to the Conventional Radiocarbon Age, but based on the non-normalized ^{14}C activity, pmc, rather than the normalized, pM, use the modern radiocarbon half-life (5730 yrs), and are not "corrected" for decay of the standard since 1950. Thus, the "Apparent Age", t_{app}, is defined

$$t_{app} = \frac{5730}{\ln 2} \ln\left(\frac{A_o}{pmc}\right) \tag{6}$$

where A_o is the initial ^{14}C activity in pmc at time of recharge. By convention, a value of 100 % is normally assigned to A_o in calculation of the "Apparent Age", but in application, appropriate values of A_o should be evaluated taking into account the initial recharge conditions and the geochemical processes occurring in the recharge areas of aquifers. Geochemical corrections can lower estimates of A_o to values less than 100, and in cases of extensive water-rock reaction, values of A_o as small as 10 % have sometimes been used. In initial systems that are open to isotopic exchange with the atmosphere, A_o can be near 100 pmc. Radiocarbon ages based on the Libby half-life of 5568 years are related to radiocarbon ages based on the modern ^{14}C half-life of 5730 years by the equation

$$t_{Libby} = 0.972 t_{5730} \tag{7}$$

By using the Libby half-life for ^{14}C, the apparent radiocarbon age can be corrected to calendar years using radiocarbon calibration scales (Stuiver et al., 1998), though hardly warranted given the current uncertainties in adjusted radiocarbon ages of the WIPP waters.

Effect of Mixing of DIC into water from the Culebra Dolomite

The calculations below ignore the possible mixing of unaltered Culebra water with imported source water and estimate radiocarbon ages as if the samples were from unaltered sources. Application of radiocarbon dating to the Culebra waters applies to the age of the dissolved inorganic carbon (DIC), and not the water. There needs to be a conceptualization of just how the ^{14}C atoms entered the DIC originally. The radiocarbon age then applies to the time elapsed since the ^{14}C atoms entered the water and were isolated from the atmospheric ^{14}C reservoir.

Two general scenarios were suggested as we examined the dissolved gas data:

(1) infiltration of evolved marine brines, and
(2) infiltration of dilute recharge water that subsequently dissolved evaporate minerals in the subsurface.

In the first case, the surface brine would be expected to be near equilibrium with the atmosphere, yielding a ^{14}C activity of the DIC near 100 pmc at time of infiltration. In this case, the "Conventional Radiocarbon Age" (Stuiver and Polach, 1977), or preferably, "Apparent Radiocarbon Age", which is unadjusted for water-rock reactions may apply; but given the age of the brine, no ^{14}C should be detected.

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In the second case, the initial ^{14}C activity would likely be altered by water-rock reaction, particularly by dissolution of old carbonate minerals, and various adjustment models need to be considered to correct the initial ^{14}C activity for these geochemical reactions. In this report we consider several adjustment models (Tamers, 1975; Ingerson and Pearson, 1964; Mook, 1972; Fontes and Garnier, 1979; Eichinger, 1983), but it is probably invalid to apply these relatively simple adjustment models to the complex brines of the WIPP waters.

Further calculations were made using NETPATH (Plummer et al., 1994), a geochemical mass balance model that is used to reconstruct initial ^{14}C activity that has been corrected for water-rock reaction, but not radioactive decay. The NETPATH calculations began with hypothetical dilute limestone ground water, to which an initial ^{14}C activity of 50-100 pmc was assigned. The waters were then assumed to have contacted evaporate minerals and carbonates during their geochemical evolution. These calculations seem hardly warranted at this time, given the uncertainty in possible contamination of ^{14}C in the formation water, and are used to examine water-rock reactions only. No adjusted ages from NETPATH are presented below, except to show that in most cases, water-rock reaction could lower the initial ^{14}C activity to near zero, alone.

Traditional Adjustment Models

Traditionally, hydrologists have applied some of the well-known inorganic adjustment models (Tamers 1975; Ingerson and Pearson 1964; Mook 1972; Fontes and Garnier 1979; Eichinger 1983) to DIC of water from a single well to estimate adjusted A_o and adjusted ^{14}C ages. This approach is well suited for geochemical systems undergoing relatively simple water-rock reactions, such as carbonate-mineral dissolution, gypsum dissolution, Ca/Na ion exchange, CO_2 gas dissolution, and isotope exchange between soil CO_2, calcite, and dissolved inorganic carbon during recharge. NETPATH (Plummer et al., 1994) was used to calculate adjusted ages based on these traditional adjustment models. Table 16 gives the water chemistry, provided by Hall Environmental.

Table 16. Summary of Water-Quality Data, $\delta^{13}C$, and ^{14}C Activity

Well	pH units	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Cl mg/L	SO$_4$ mg/L	Alk-alinity (CaCO$_3$) mg/L	Br mg/L	F mg/L	NO3+ NO2 mg/L	Sr mg/L	Fe mg/L	$\delta^{13}C$ in per mil	pmc, no ^{13}C corr
SNL-16	7.19	1400	430	4400	290	8600	2500	97	0	2.5	0	18.2	0.02	-4.8	7.85
SNL-19	7.74	850	220	1600	43	2700	2300	90	1.6	1.5	6	11.4	0.03	-2.4	11.10
SNL-18	7.51	1100	360	5200	120	8700	3700	75	5.6	1.7	0	15.9	0.02	-2.1	4.63
SNL-17	7.55	620	150	130	5.3	250	1800	94	0	1.3	2.8	7.8	0	-7.0	17.94
SNL-10	7.92	500	170	1900	72	1100	4400	46	2.3	2.7	0	9.3	nd	-5.1	11.75
SNL-14	7.41	1500	1100	30000	620	47000	6900	48	40	2.5	0	22	0	-2.2	7.07
SNL-8	7.26	2000	3100	47000	1100	77000	6400	49	100	0	0	33	0	-2.0	13.31

These data were speciated in NETPATH using the WATEQ aqueous model to calculate charge imbalance, log P_{CO2}, and selected mineral saturation indices (Table 17).

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Table 17. Summary of WATEQ/NETPATH Results

Well	Sample Date	pH units	T °C	Chg. Bal. %	Calc. Log PCO_2	SI Calcite	SI Dolomite	SI Gypsum	SI Celestite
SNL-16	6/9/2006	7.19	22	1.40	-2.33	0.28	0.39	0.04	-0.13
SNL-19	7/28/2006	7.74	22.5	2.50	-2.86	0.68	1.09	0.01	-0.15
SNL-18	8/18/2006	7.51	23.4	-1.70	-2.74	0.37	0.61	0.10	-0.03
SNL-17	9/15/2006	7.55	22.4	4.10	-2.60	0.49	0.66	-0.03	-0.22
SNL-10	11/3/2006	7.92	21	0.00	-3.32	0.22	0.27	0.03	0.01
SNL-14	7/30/2007	7.41	22*	0.50	-2.95	0.13	0.52	0.18	0.06
SNL-8	8/2/2007	7.26	22*	2.60	-2.89	0.18	1.00	0.22	0.14

* Temperature not available.
Estimated

Table 18 compares values of the Apparent Radiocarbon Age, and adjusted radiocarbon ages from the models of Tamers, Ingerson and Pearson, Mook, Eichinger, and Fontes and Garnier.

Table 18. Summary of Apparent and Adjusted Radiocarbon Ages*

Well	Sample Date	$\delta^{13}C$ in permil	pmc no ^{13}C corr	[1]Calc. Soil Gas CO_2 $\delta^{13}C$ permil	[2]Un-adjusted Apparent ^{14}C Age, ka	Tamers Model Age, ka	Ingerson-Pearson Model Age, ka	Eichinger Model Age, ka	Mook Model Age, ka	Fontes-Garnier Model Age, ka	Fontes-Garnier k value [3]
SNL-16	6/9/2006	-4.8	7.85	-12.33	21.0	15.9	16.3	15.8	50.5	16.7	5.2
SNL-19	7/28/2006	-2.4	11.10	-10.33	18.2	12.7	12.2	11.4	19.1	12.1	-3.3
SNL-18	8/18/2006	-2.1	4.63	-9.84	25.4	20.0	19.3	18.5	26.7	19.3	-4.3
SNL-17	9/15/2006	-7.0	17.94	-14.81	14.2	8.9	10.1	9.7	13.5	10.9	14.7
SNL-10	11/3/2006	-5.1	11.75	-13.28	17.7	12.1	12.8	12.4	15.6	13.4	8.2
SNL-14	7/30/2007	-2.2	7.07	-10.15	21.9	16.4	15.7	15.0	24.0	15.7	-4.3
SNL-8	8/2/2007	-2.0	13.31	-10.01	16.7	11.1	10.3	9.6	19.5	10.3	-4.9

Uses ^{14}C half life of 5730 yrs; $\delta^{13}C$ carbonate minerals = 5 permil.
[1] Open-System assumed
[2] Initial ^{14}C activity = 100 pMC
[3] negative indicates isotopic exchange is rock-dominated, positive for gas-dominated exchange.

Application of NETPATH

Wigley et al. (1978) present Rayleigh distillation and isotope mass-balance models to predict isotopic evolution in carbonate mineral-water systems where both dissolution (incoming carbon) and precipitation (outgoing carbon with isotopic fractionation, including gas evolution) reactions occur, and they propose a general approach for constructing radiocarbon adjustment models for evolutionary waters.

NETPATH (Plummer et al. 1994) incorporates the modeling approach of Wigley et al. (1978) and can be used to construct ^{14}C-adjustment models for complex hydrochemical systems that cannot be treated by previous DIC adjustment models. By combining carbon mass-balance equations with Rayleigh distillation equations for all incoming carbon sources and all isotopically fractionating outgoing carbon phases, the initial ^{14}C (A_o) is adjusted for the modeled geochemical reactions. In radiocarbon dating of DIC in groundwater using NETPATH, the traditional adjustment models are usually applied to the initial water only, where, in the recharge portions of freshwater aquifers, the geochemical reactions are usually relatively simple. In

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general use, the initial and final waters are defined separately in NETPATH. NETPATH is then used to describe the geochemical reactions that reproduce the chemical and $\delta^{13}C$ isotopic composition of DIC in the final water. This, in effect, develops separate adjustment models for each water analysis. The adjustment is applied to the initial ^{14}C to compute the ^{14}C expected in DIC at the final well, as if there were no radioactive decay. The adjusted no-decay ^{14}C activity is then used with the measured ^{14}C activity to compute age of the final water. Further details of radiocarbon dating applications in NETPATH are given in Plummer et al. (1994).

Hypothetical initial waters were constructed to be in equilibrium with calcite and dolomite at CO_2 gas partial pressures of 10^{-2}, $10^{-2.5}$, and 10^{-3} atmospheres, and 15 °C. The initial $\delta^{13}C$ of DIC and ^{14}C activity were assigned the value of -7 permil and 50-100 pmc (closed to open system). Geochemical mass balance models were constructed evolving these initial waters into the 7 water samples from the new WIPP monitoring wells. All of the models considered mass transfer of CO_2 gas, calcite, dolomite, halite, gypsum and Ca/Na ion exchange. Other models included polyhalite and sylvite. Calculations also considered adjustment of water composition for charge imbalance. Regardless of model conditions, no mass transfer models could be found that predicted the observed $\delta^{13}C$ and led to positive radiocarbon ages. All of the models calculated very enriched $\delta^{13}C$ values, due to dissolution of dolomite (in dedolomitization), which also significantly lowered the ^{14}C activity to values below the measured (impossible). This exercise is incomplete and can be resumed if unmixed/uncontaminated formation water can be produced from the new monitoring wells. What the NETPATH calculations do tell us is that the conceptual model for formation of the sampled waters is incorrect. Perhaps consideration of mixing of imported water is needed, or we should consider recharge of marine evaporate brines at the outset that were subsequently contaminated in drilling, but currently, analyses of the imported waters are not available to sort out the mixing question.

SUMMARY AND CONCLUSIONS

Water samples were received from 7 monitoring wells located in the vicinity of the WIPP Site, NM (Table 1, Figure 1). Drilling of these wells was completed between June, 2005 and November, 2006 and the wells were sampled between June 2006 and August 2007. During the drilling process, imported water and air likely entered the formation. In completing the wells, the contract driller used various techniques to develop the wells (Table 2) and remove effects of drilling. Prior to sampling, the wells were pumped for periods of up to 4 days by Sandia National Laboratories personnel. As a means of testing whether traces of drilling fluid remained in the formation, the chemical and isotopic composition of the water was analyzed for a series of environmental tracers that can be indicative of recent water, including CFCs, SF_6, and ^3H. Other measurements included primary dissolved gases (N_2, Ar, CO_2, O_2, CH_4), ^{14}C, and ^{13}C of DIC, He, Ne, and water chemistry, and a suite of halogenated VOCs.

1. All of the samples contain detectible CFC-11 (8.9 - 180.1 pg/kg) and CFC-12 (4.7 - 56.9 pg/kg).

2. Five of the 7 samples contain detectible CFC-113 (2.3 - 8.8 pg/kg).

3. Three of the samples contain detectible tritium, 0.19 ± 0.08, 0.31 ± 0.08, and 0.62 ± 0.09 TU.

4. The CFC data and to some extent, the tritium data of Figures 3-6, indicate post-1940 introduction of air and/or water or other substances containing CFCs. The presence of

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detectible tritium in three of the samples indicates that, at least in the cases of these three samples, introduction of post-bomb water. Together, the CFC, tritium, and chloroform data suggest mixing of water used in drilling with formation water, and that the drilling water was not completely removed during well development and well pumping prior to sampling.

5. The data of Table 5, giving generally similar % Modern values for all three CFCs in a sample (excluding SNL-8) suggests, for the most part that the CFCs were introduced into the samples approximately according to Henry's Law solubility, and then subsequently diluted.

6. All of the samples contain traces (approximately 0.001-0.025 ug/L) of chloroform, a disinfection byproduct of chlorination in municipal water supplies (Appendix 5). The chloroform concentration, expressed as peak area on the GC chromatogram, varies approximately linearly with the estimated percent imported water based on CFC-12 content (Figure 9). Many other halogenated VOCs of anthropogenic origin, including PCE, TCE, and carbon tetrachloride also are present in all the waters.

7. Sample SNL-8 has relatively low chloroform concentration, but has been contaminated with many other halogenated VOCs, including CFC-11, TCE, PCE, methyl chloroform, methyl chloride, and an unknown VOC with retention time of 12.4 minutes. Only 1,743 gallons of water were pumped from SNL-8 prior to sampling,

8. The chloroform and tritium content are linearly correlated with % Modern water indicated by the CFC-12 content.

9. None of the samples have CFC ratios that would result form dissolution of un-fractionated excess air.

10. The Closed-System Equilibrium (CE) model for fractionated excess air was used in an attempt to determine if the measured concentrations of gases could have been introduced during the drilling and/or air-purging processes (jetting) that may have introduced bubbles of gases into the aquifer. The overall conclusion from the model calculations considering introduction and fractionation of excess air from the drilling operation is that in many cases, the observed concentrations of CFCs, particularly CFC-12, and CFC-113, and permanent atmospheric gases, N_2, Ar, could be explained by injection of relatively small amounts of air with subsequent partial or, in a few cases, complete dissolution of the injected air. However, these calculations assume an initial (recharge) condition of N_2, Ar, and O_2 saturation in initially saline solutions, and the CE model does not account for all the dissolved gas concentrations.

11. The detections of tritium and carbon-14 cannot be explained by dissolution of excess air (fractionated or un-fractionated).

12. There are two sources for SF_6, which was detected in all 7 samples: recent air and old formation water that has a large terrigenic component. SF_6 is very insoluble and jetting likely removed some of the SF_6 from water near the well screen. Four of the samples have relatively low concentrations of SF_6 and 3 are highly elevated in SF_6 concentration.

13. A $^3H/^3He$ age of 16 ± 16 years for SNL-17 implies an age range of the young fraction in a mixture of 0-32 years. The calculated initial tritium (tritium + tritiogenic helium-3) is only 0.76 TU for SNL-17, suggesting the sample contains about 26% of 1990 infiltration

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water diluted with old, tritium-free water; a conclusion similar to the mixing suggested by the CFC data (Table 5).

14. All of the samples contain ^{14}C in their dissolved inorganic carbon. The percent modern carbon (pmc) varies from 4.63 to 17.94 pmc (Table 15) corresponding to unadjusted, Apparent Radiocarbon Ages of 14.2 (SNL-17) to 25.4 ka (SNL-18).

15. Application of traditional adjustment models yields a somewhat younger age range of 10.9 to 19.3 ka for these same wells, based on the model of Fontes and Garnier (1979), but the hydrogeologic conceptualization for application of traditional radiocarbon adjustment models to the WIPP waters is not evident.

16. The apparent radiocarbon ages are highly uncertain due to uncertainty in mixing effects. For example, it is possible that DIC in unaffected formation water from SNL-18 has no detectible [14]C. Until the question of possible mixing of imported water can be resolved, no reliable radiocarbon ages can be recommended.

Corrections for water-rock reactions will yield radiocarbon ages younger than the Conventional or Apparent Radiocarbon age. However, if the samples have been contaminated with an external ^{14}C source, such as from imported water elevated in ^{14}C relative to the formation water, the radiocarbon ages could be considerably older (or younger) than implied by the data of Table 18.

In order to determine if the ^{14}C content of the samples could have been compromised in drilling and/or well development, two models were considered to explain the presence of CFCs and tritium. In the first scenario, it was assumed that the imported water that was put down the borehole in jetting was approximately saturated with air in the jetting process and some of this water entered the formation. Based on CFC-12 content, the waters sampled would contain between 3 and nearly 30 % of this air-saturated imported water (Table 5). Only one sample (SNL-17) could be dated using ^{3}H/[3]He, yielding a very uncertain age of the young fraction that ranged from 0 to 32 years and implied the sample contained about 26% of 1990 water, and is consistent with the young fraction from CFCs.

Another series of calculations tested whether the CFCs could have entered the water as un-fractionated or fractionated excess air. If the presence of CFCs indicates introduction of air, the calculations show that the ^{14}C activity of the DIC would likely still be unaffected, though the CFCs would be altered. The calculations show that the CFC concentrations cannot be determined by dissolution of un-fractionated excess air, but may have been introduced by fractionated excess air, which occurs when injected air bubbles partially dissolve. Still, the fractionated air model does not explain all the dissolved gases present in the samples (Table 11).

Regardless of the mechanism for introduction of the CFCs, the CFCs are present in all of the water samples indicating that the samples have contacted young air and/or waters containing CFCs. Mixing of imported water seems to account for most of the observed CFC concentrations (assuming an additional contamination source of CFC-11 from drilling equipment, rubber hose, etc). Also, 3 of the samples have detectible tritium, and actually, all of the samples lie along a dilution trend implied by the fraction of young water determined from CFC-12 content (Figure 5), consistent with model 1. Gas fractionation does not account for the presence of ^{3}H in the waters, nor all of the CFCs or dissolved gas data.

The mixing model implies that the ^{14}C content of DIC measured in discharge from the wells has been compromised, and that the ^{14}C activity of DIC in the unaltered formation water may be considerably lower (or higher) than measured (Figure 18).

Based on the measurements of tritium, CFC-12, chloroform, and inspection of the purging records (Appendix 1), none of the samples are free of waters introduced in drilling and/or well development (Table 19). Three of the purging records give stable values of specific conductance for more than two days of pumping (SNL-19, SNL-17, SNL-16), but all three contain indicators of contamination (CFC-12, and chloroform). The sample from SNL-19 has the lowest concentrations of these indicators and appears the best developed.

Table 19. Summary of well-development indicators

Well	location	Tritium in TU	CFC-12 % Modern	Chloro-form peak area, counts	Source of imported water	pmc, no $\delta^{13}C$ correc-tion	Visual of Specific Conductance pump record, Appendix 1 *	Adequately Purged?
SNL-16	Nash Draw	0.62	27.7	310963	Eunice	7.85	2	no
SNL-19	Nash Draw	0.02	2.5	11375	WIPP	11.10	1	no?
SNL-18	East edge of Nash Draw	0.19	10.1	119446	WIPP	4.63	3	no
SNL-17	East edge of Nash Draw	0.31	29.0	195945	NA	17.94	1	no
SNL-10	WIPP should be old	-0.07	3.0	141253	Hobbs	11.75	3	no
SNL-14	WIPP should be old	0.13	16.0	126111	Double Eagle	7.07	2	no
SNL-8	WIPP should be old	0.1	2.0	68035	WIPP	13.31	1	no

*Conclusion of well development from visual inspection of log of specific conductance during pumping prior to sampling. 1 Steady at least 2 days; 2 No Steady- up and down; 3 Not steady- still rising;

By measuring concentrations of the environmental tracers, CFCs, SF_6, and ^3H, along with dissolved gas composition, $^3H/^3He$, and low-level VOC concentrations, this study demonstrates the difficulty of obtaining un-compromised samples from recently-drilled wells, and the inefficiency of common well-development procedures in removing all the effects of drilling. As a result, environmental isotope signals in old water may be lost or significantly altered by well development practices. Without the environmental tracer data, it would be very difficult to detect the drilling contamination, and assess uncertainty in interpreted radiocarbon age.

RECOMMENDATIONS

Given that the new monitoring wells are in place, nothing can be done to change the steps already taken in their construction and development. Certainly the new monitoring wells are an invaluable asset to the WIPP site as they have been constructed to a high standard. Additional steps could be taken to (1) obtain unaltered samples from these wells, and (2) determine further whether the ^{14}C activity of the formation water was indeed affected in the development process. These are:

1. Further develop the wells and re-sample. Presumably this would be done with a submersible pump, and in steps—pumping for an extended period, sampling for all the chemical, isotopic, and environmental tracers measured here, and repeated in several cycles.

2. Collect samples of the various source waters used in well development and determine major element chemistry, ^{3}H, ^{14}C, δ^{13}C, CFCs, SF$_6$, and low-level halogenated VOCs on these waters (stable isotopes of water should probably be measured as well, but the USGS has not seen these data).

3. Repeat the full suite of sampling on a few selected previously-existing wells at the WIPP Site, if any can be identified that may not have been contaminated in the drilling process in the past.

4. It is expected that the ^{81}Kr results, as they become available, will indicate relatively young waters, have been affected by mixing, and will need to be re-sampled as well. However, if the ^{81}Kr results indicate very old water, further study is needed to explain the presence of CFCs, chloroform, and ^{3}H. One consideration that has not been investigated in this report is the possible role of matrix diffusion, i.e., the slow release of contaminants introduced to the micro porosity of the aquifer rocks during drilling and well development procedures, and then reintroduced to the formation water by diffusion from the rock matrix during well development and pumping prior to sampling. Again, further well development are re-sampling may resolve this question.

DISCLAIMER

The USGS was not involved in the drilling or sampling of the seven monitoring wells. We did train Sandia personnel in our sampling protocols. The samples were shipped to the USGS where they were analyzed and reported to Sandia along with details of analytical procedures, QA/QC, detection limits, etc. The interpretations of this report are based on those measured values.

ACKNOWLEDGEMENTS

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APPENDICES

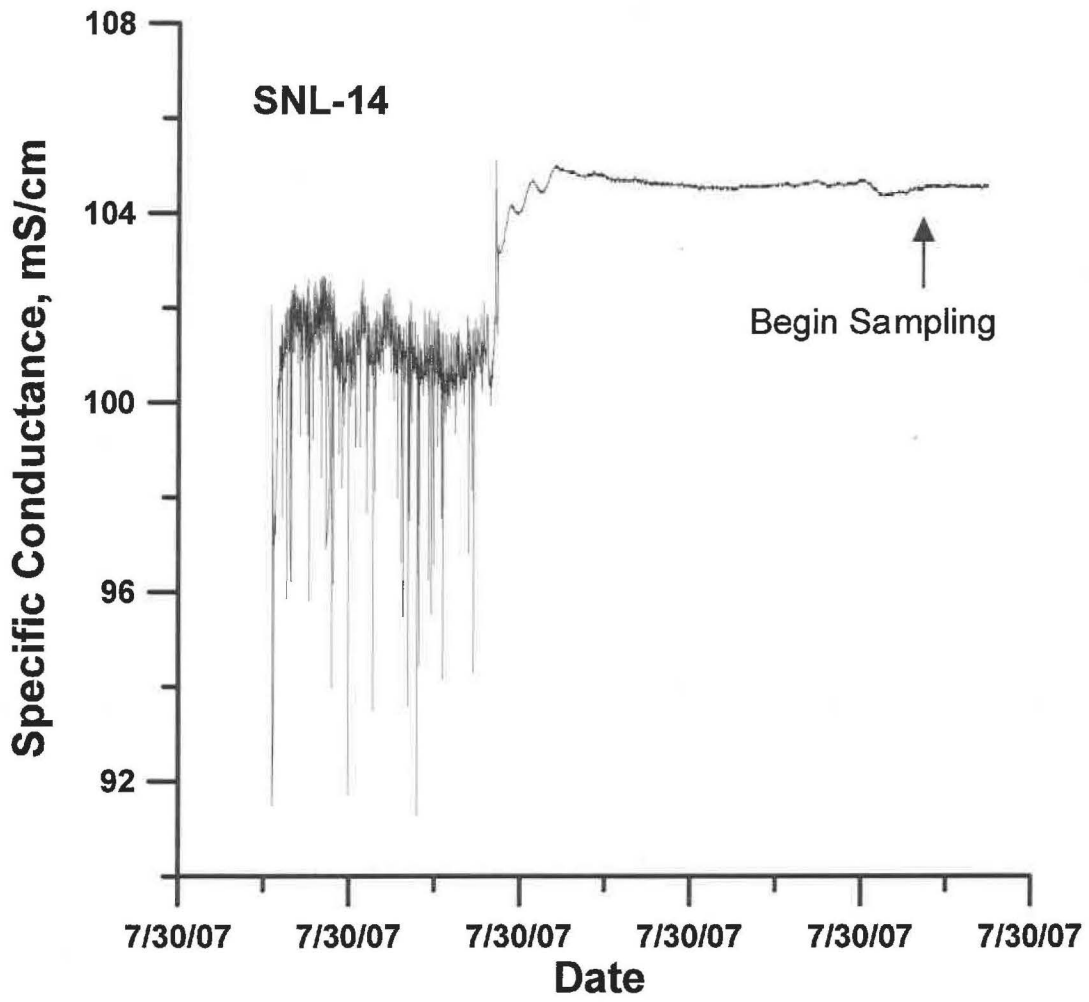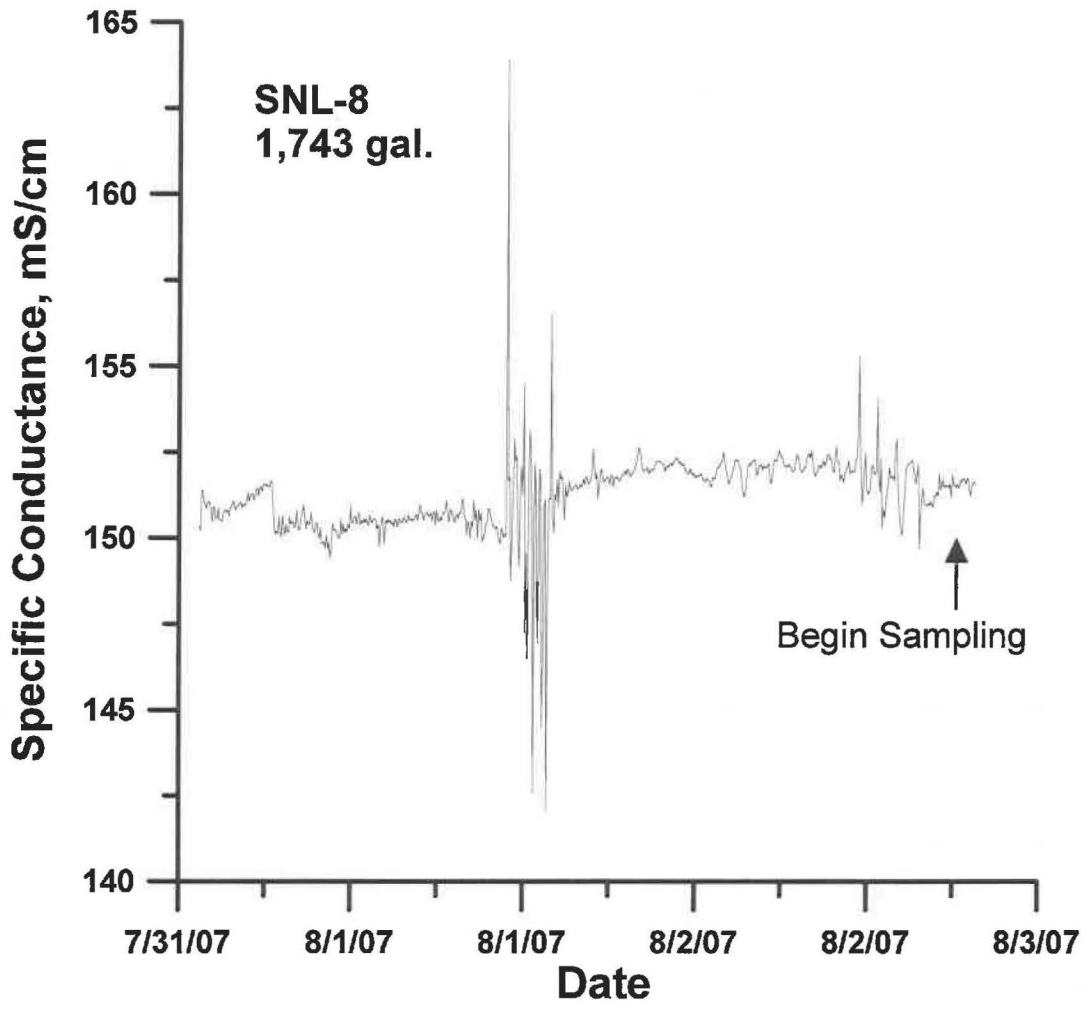Appendix 1: Plots showing Specific Conductance of water pumped from wells prior to sampling.

Appendix 2: Table of CFC and SF_6 mixing ratios in North American Air, and of tritium in precipitation in the vicinity of the WIPP Site decayed to the year 2006, 1940 to 2007.

Appendix 3: CFC Chromatograms from GC Purge and Trap with Electron-Capture Detector

Appendix 4: SF_6 Chromatograms from GC Purge and Trap with Electron-Capture Detector

Appendix 5: Chromatograms of Halogenated VOCs from GC Purge and Trap with Electron-Capture Detector with Retention Times to 30 minutes

Appendix 6: Fractionated Air: Gas Exchange between Trapped Gas Bubbles and Ground Water with Dilute Initial Water

Appendix 1

Plots showing Specific Conductance of water pumped from wells prior to sampling

It is noted that there are some differences between specific conductance values reported to SNL by Hall Environmental and those measured by SNL personnel during pumping prior to sampling, the latter of which appear on the following plots as a function of pump time.

Table A1.1. Comparison of Specific Conductance Values

Well	Spec. Cond. umhos/cm @ 25C from Hall Environ.	Spec Cond. umhos/cm @ 25C Final from purging records	Spec cond Ratio Hall/SNL
SNL-16	35000	25,129	1.39
SNL-19	12000	11,011	1.09
SNL-18	38000	26,722	1.42
SNL-17	3500	3,442	1.02
SNL-10	11000	10,218	1.08
SNL-14	130000	104,680	1.24
SNL-8	280000	151,900	1.84
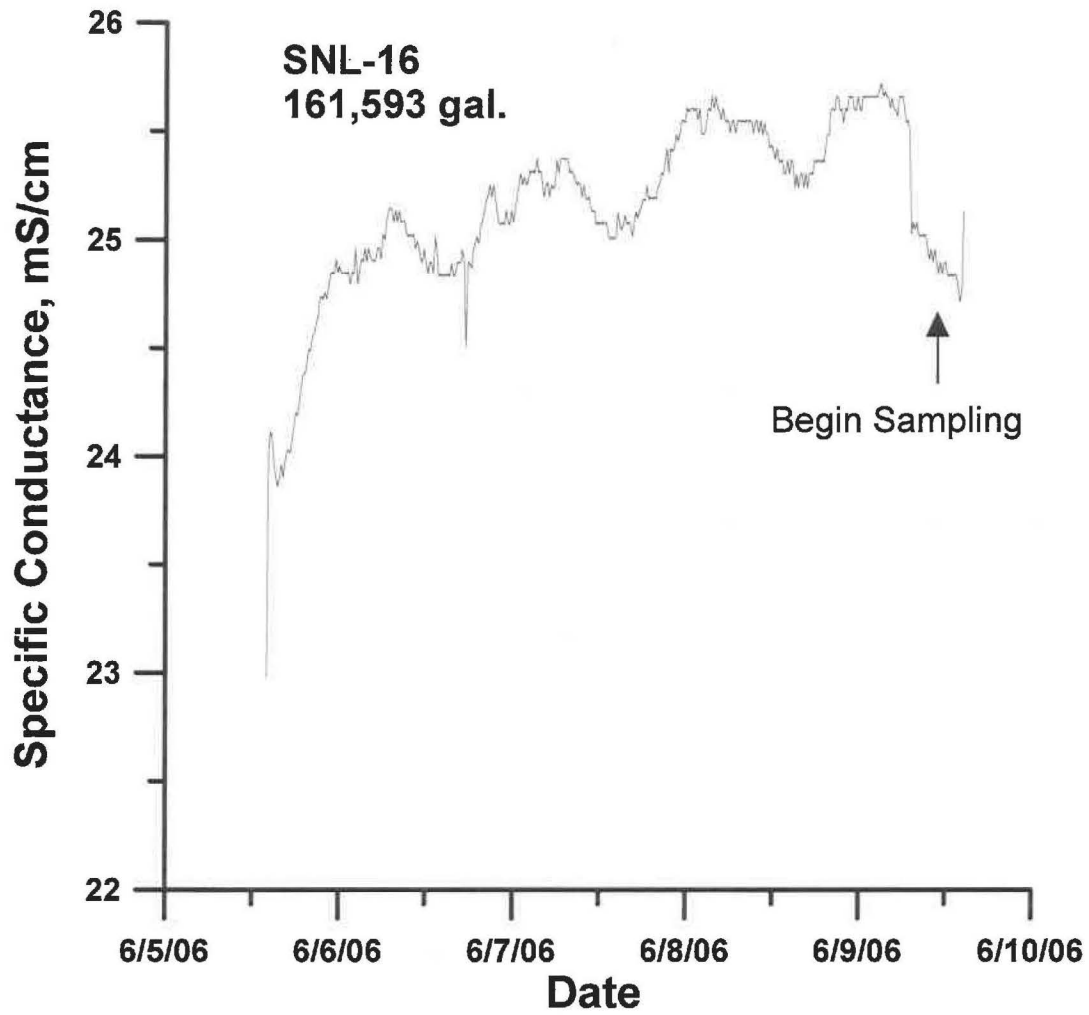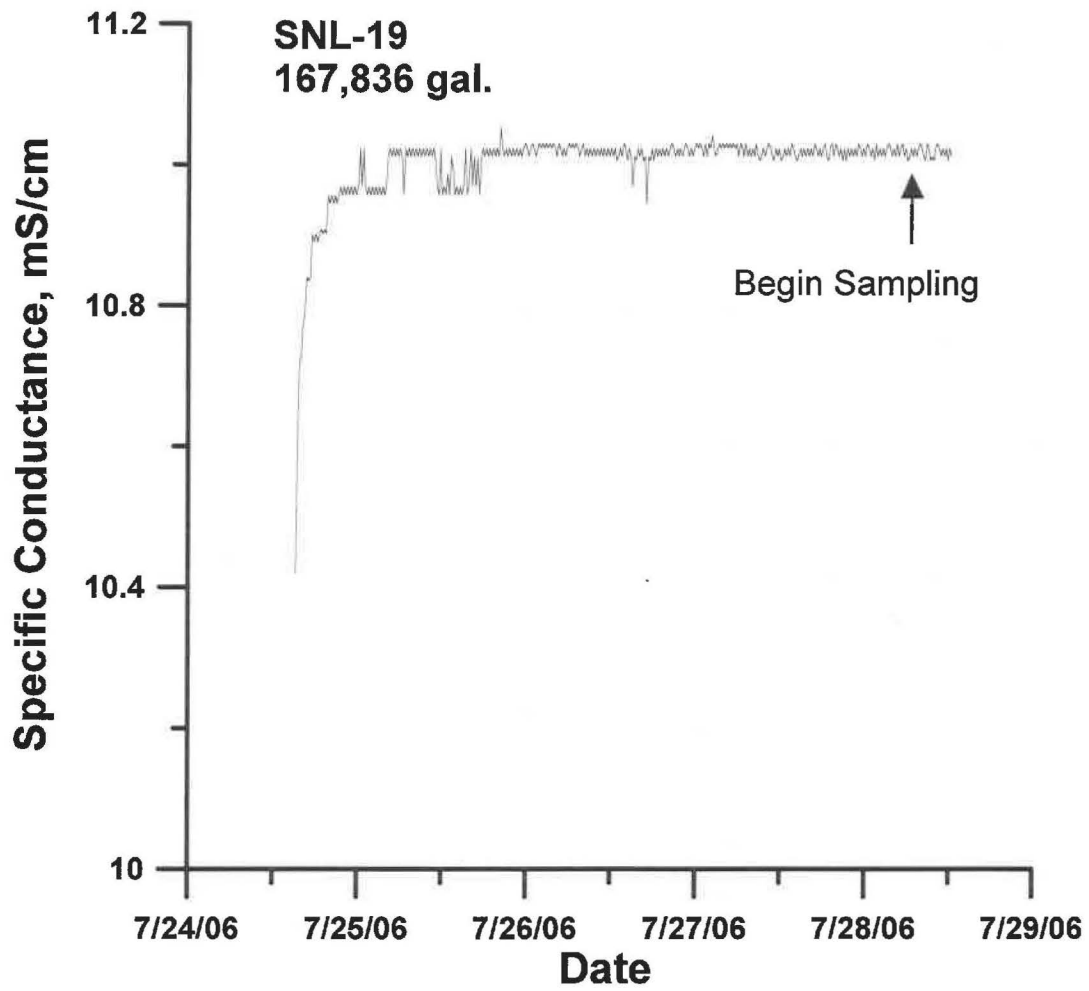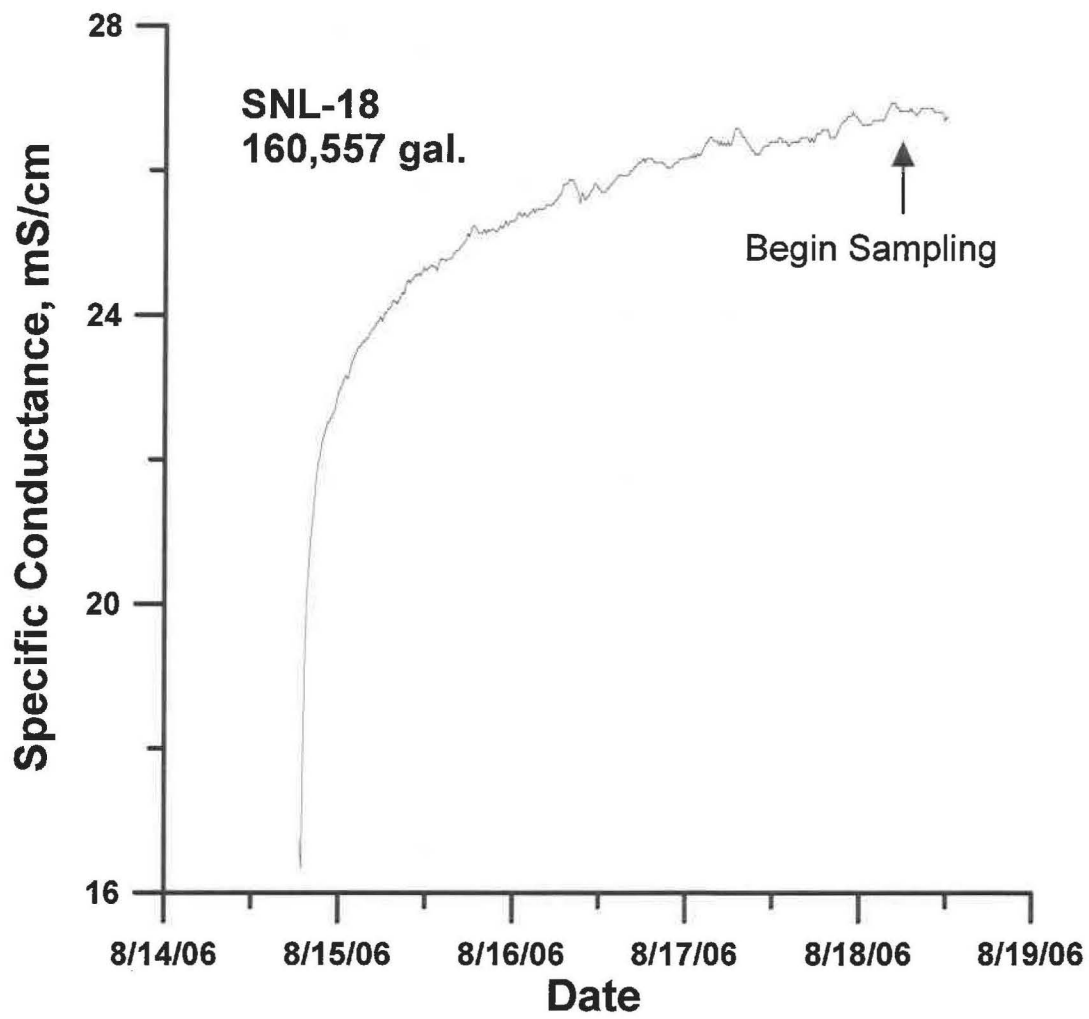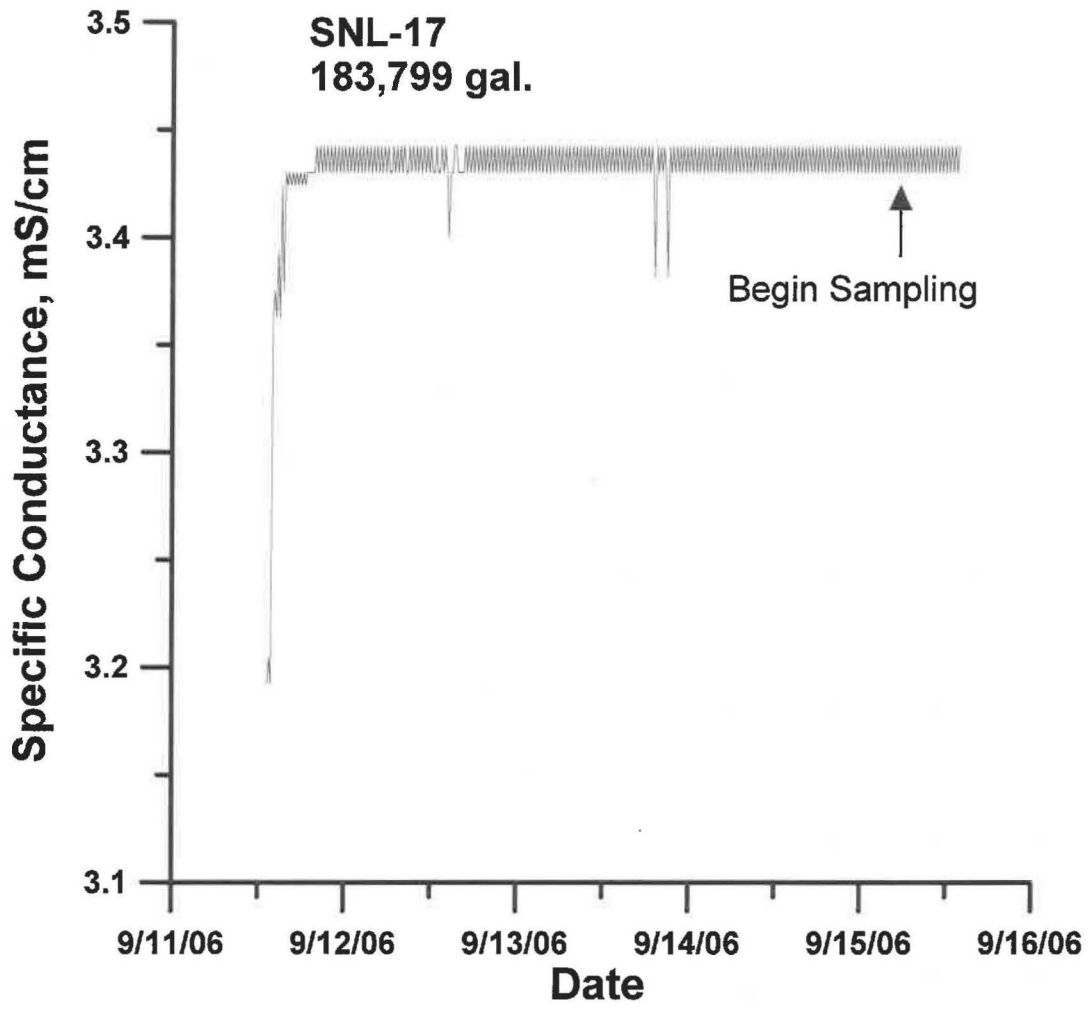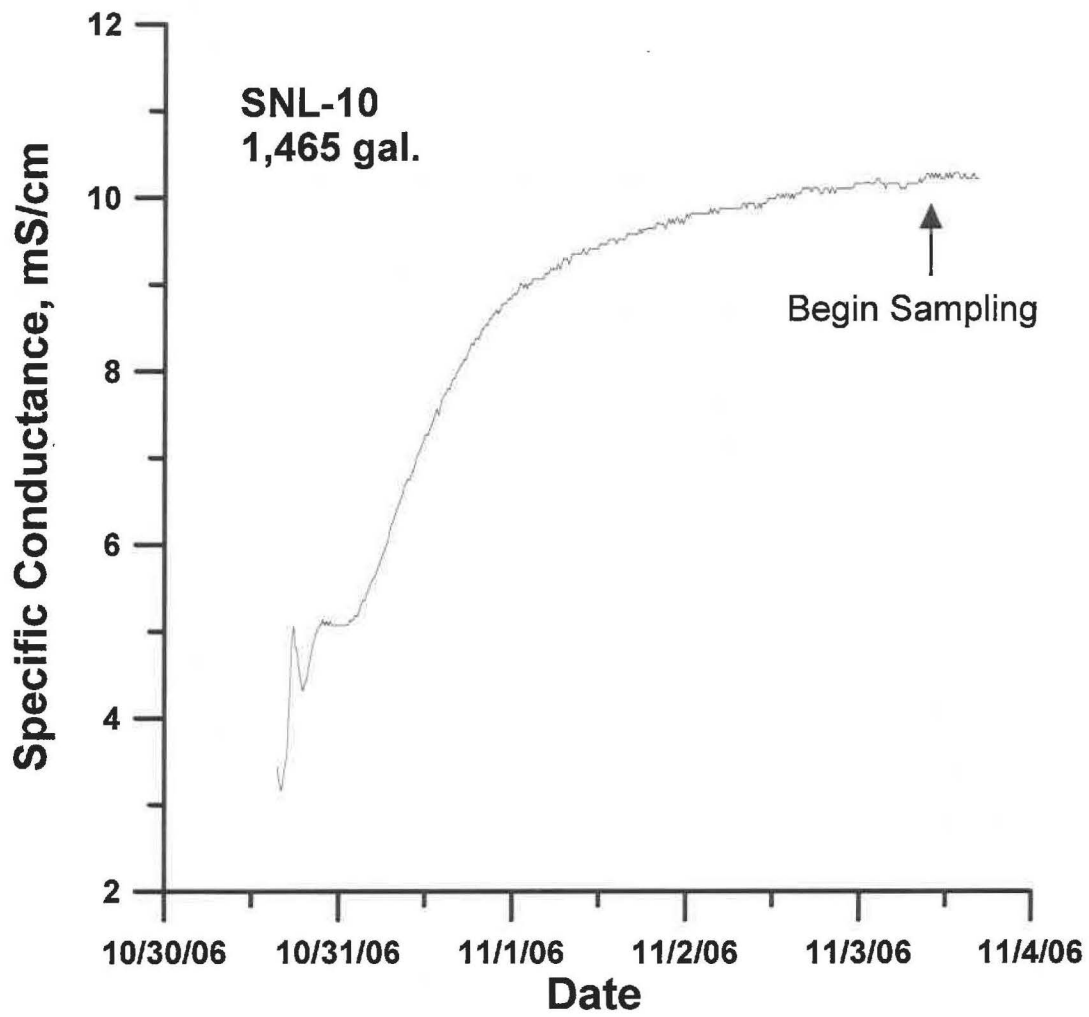
SNL-17
183,799 gal.

Begin Sampling

SNL-8
1,743 gal.

Begin Sampling

Appendix 2

Table of CFC and SF_6 mixing ratios in North American Air, and of tritium in precipitation
in the vicinity of the WIPP Site decayed to the year 2006, 1940 to 2007

Appendix 2: Air-water input functions for tritium, CFCs and SF₆

Date	WIPP Site Tritium in Precipitation decayed to year 2006 *	North American Air			
		CFC-11 ppt	CFC-12 ppt	CFC-113 ppt	SF6 ppt
1940	0.15	0.01	0.34	0.00	0.05
1940.5	0.15	0.01	0.40	0.00	0.05
1941	0.15	0.02	0.48	0.00	0.05
1941.5	0.16	0.02	0.56	0.00	0.05
1942	0.16	0.02	0.66	0.00	0.05
1942.5	0.17	0.02	0.76	0.00	0.05
1943	0.17	0.03	0.88	0.00	0.05
1943.5	0.18	0.03	1.01	0.01	0.05
1944	0.18	0.04	1.18	0.01	0.05
1944.5	0.19	0.04	1.34	0.03	0.05
1945	0.19	0.05	1.56	0.04	0.05
1945.5	0.20	0.05	1.77	0.06	0.05
1946	0.21	0.07	2.15	0.07	0.05
1946.5	0.21	0.08	2.53	0.09	0.05
1947	0.22	0.11	3.11	0.11	0.05
1947.5	0.22	0.14	3.70	0.13	0.05
1948	0.23	0.20	4.37	0.15	0.05
1948.5	0.24	0.25	5.04	0.17	0.05
1949	0.24	0.34	5.76	0.20	0.05
1949.5	0.25	0.43	6.48	0.22	0.05
1950	0.26	0.56	7.28	0.25	0.05
1950.5	0.26	0.68	8.07	0.27	0.05
1951	0.27	0.85	8.93	0.30	0.05
1951.5	0.28	1.02	9.80	0.33	0.05
1952	0.29	1.28	10.69	0.37	0.05
1952.5	0.30	1.53	11.60	0.41	0.05
1953	0.30	1.88	12.59	0.44	0.05
1953.5	0.47	2.22	13.60	0.49	0.05
1954	9.40	2.64	14.74	0.53	0.06
1954.5	1.30	3.06	15.88	0.58	0.06
1955	1.07	3.58	17.15	0.63	0.06
1955.5	0.58	4.09	18.42	0.69	0.06
1956	3.15	4.74	19.90	0.75	0.06
1956.5	2.37	5.38	21.39	0.81	0.06
1957	3.11	6.09	23.06	0.87	0.06
1957.5	2.10	6.81	24.75	0.94	0.06
1958	10.53	7.46	26.50	1.02	0.06
1958.5	9.67	8.11	28.26	1.11	0.06
1959	21.29	8.76	30.22	1.19	0.06
1959.5	4.12	9.42	32.18	1.29	0.06
1960	4.77	10.29	34.52	1.38	0.07
1960.5	2.87	11.17	36.85	1.49	0.07

1961	5.12	12.29	39.48	1.60	0.07
1961.5	6.11	13.42	42.09	1.73	0.08
1962	48.36	14.85	45.10	1.86	0.08
1962.5	30.34	16.28	48.10	1.99	0.08
1963	129.75	18.02	51.61	2.14	0.09
1963.5	63.26	19.76	55.13	2.31	0.10
1964	79.51	21.8	59.2	2.5	0.10
1964.5	38.72	23.9	63.3	2.7	0.11
1965	37.10	26.3	67.9	2.8	0.12
1965.5	19.40	28.6	72.5	3.1	0.13
1966	27.65	31.2	77.6	3.3	0.14
1966.5	14.17	33.8	82.8	3.5	0.15
1967	12.24	36.7	88.5	3.8	0.16
1967.5	8.89	39.7	94.3	4.1	0.18
1968	12.95	43.0	100.7	4.3	0.19
1968.5	8.50	46.4	107.2	4.7	0.20
1969	13.96	50.2	114.4	5.0	0.21
1969.5	9.09	54.1	121.5	5.4	0.22
1970	14.09	58.5	129.3	5.7	0.23
1970.5	8.36	62.9	137.2	6.1	0.25
1971	12.05	67.7	145.5	6.6	0.26
1971.5	8.58	72.5	153.9	7.1	0.27
1972	6.49	77.8	162.9	7.5	0.28
1972.5	4.74	83.2	172.0	8.1	0.30
1973	4.76	89.4	182.0	8.7	0.32
1973.5	4.21	95.5	192.1	9.3	0.34
1974	6.16	102.2	202.9	9.9	0.36
1974.5	5.31	108.9	213.7	10.7	0.39
1975	5.91	114.6	224.0	11.4	0.42
1975.5	4.45	122.1	234.3	12.2	0.45
1976	4.22	128.9	244.2	13.1	0.48
1976.5	4.18	135.1	254.0	14.0	0.52
1977	4.77	142.1	263.3	15.0	0.55
1977.5	4.86	146.7	272.5	16.1	0.59
1978	7.51	150.0	282.4	17.2	0.63
1978.5	4.85	156.5	292.9	18.4	0.68
1979	4.15	159.8	298.1	19.7	0.73
1979.5	3.19	162.6	301.2	21.1	0.77
1980	4.12	168.6	311.2	22.6	0.83
1980.5	3.90	172.8	317.4	24.1	0.88
1981	6.50	176.0	322.7	25.7	0.94
1981.5	3.87	179.7	333.8	27.3	0.99
1982	4.08	183.8	343.6	29.0	1.05
1982.5	2.79	188.3	352.7	30.8	1.12
1983	3.20	193.3	361.6	32.5	1.18
1983.5	2.76	198.0	372.2	34.8	1.25
1984	3.33	201.9	378.6	37.0	1.32
1984.5	3.17	206.0	386.2	39.7	1.39
1985	2.86	211.2	395.4	42.3	1.47
1985.5	3.31	217.3	403.3	45.2	1.54
1986	3.51	223.0	414.6	48.0	1.62
1986.5	2.81	227.9	423.5	51.1	1.70

1987	3.37	233.5	433.6	54.2	1.79
1987.5	2.39	241.0	449.3	57.7	1.87
1988	3.32	248.6	459.5	61.2	1.96
1988.5	2.10	254.0	469.1	64.9	2.05
1989	3.36	257.4	476.7	68.5	2.15
1989.5	3.07	262.0	484.0	71.5	2.24
1990	2.86	265.8	493.5	74.5	2.34
1990.5	2.58	266.9	497.1	76.6	2.44
1991	2.77	269.2	503.4	78.8	2.54
1991.5	2.92	270.1	508.8	80.3	2.65
1992	3.11	271.5	517.7	81.5	2.77
1992.5	2.58	272.2	520.5	82.4	2.88
1993	3.83	272.3	523.0	83.0	2.99
1993.5	3.10	272.4	526.0	83.7	3.10
1994	3.69	272.8	528.2	84.1	3.22
1994.5	3.10	272.2	533.3	84.4	3.33
1995	3.63	271.1	534.7	84.7	3.44
1995.5	3.35	270.5	534.8	84.9	3.55
1996	3.80	269.9	535.7	85.0	3.67
1996.5	3.00	269.2	537.4	85.0	3.78
1997	3.26	268.5	539.3	84.8	3.89
1997.5	3.89	267.8	540.9	84.6	4.00
1998	3.94	267.0	542.1	84.3	4.12
1998.5	3.24	266.2	543.0	84.0	4.23
1999	3.46	265.4	544.0	83.7	4.34
1999.5	3.19	264.5	544.6	83.4	4.45
2000	3.43	263.5	545.1	83.0	4.57
2000.5	2.88	262.6	545.5	82.7	4.68
2001	3.50	261.6	546.0	82.4	4.79
2001.5	3.46	260.6	546.2	82.0	4.91
2002.0	*3.00*	259.5	546.3	81.7	5.02
2002.5	*3.26*	258.4	546.3	81.3	5.13
2003.0	*3.89*	257.2	546.0	81.0	5.24
2003.5	*3.94*	256.1	545.7	80.6	5.36
2004.0	*3.24*	254.9	545.3	80.2	5.47
2004.5	*3.46*	253.6	544.8	79.8	5.58
2005.0	*3.19*	252.3	544.2	79.4	5.69
2005.5	*3.43*	251.0	543.3	79.0	5.81
2006.0	*2.88*	249.6	542.4	78.5	5.92
2006.5	*3.50*	248.2	541.3	78.1	6.03
2007.0	*3.46*	246.8	540.1	77.6	6.14

* IAEA, Robert L. Michel, personal commun. 2008. Italics, estimated.

CFC Chromatograms from GC Purge and Trap with Electron-Capture Detector

Five separate water samples were collected in the field by Sandia personnel. Three samples were analyzed for each well. Approximate retention times for CFC-12, CFC-11, and CFC-113 were 2.84, 4.15, and 6.68 minutes under the instrument configuration used to analyze the samples. Initially the samples were only analyzed only for peaks with retention times of less than 10 minutes, which accounts for the CFCs. Those chromatograms follow for each separate water sample analyzed. The analytical results are summarized in Table 3.

Notes from the laboratory technician on some of the chromatograms indicate that the water foams when striped of dissolved gases in the purge cell. This is common of very saline waters and does not indicated presence of a contaminant. Many of the samples appear to contain at least traces of H_2S (retention time approximately 3.6 minutes) (also apparent in the low-level VOC chromatograms or Appendix 5). Some of the chromatograms have an unsteady background and/or contain many small peaks. This is characteristic of degradation of halogenated VOCs and the numerous small peaks are probably degradation products of other VOCs in the sample. Examples of degraded chromatograms include waters from wells SNL-18, SNL-10, SNL-14, and SNL-8.

Peak size also differs between chromatograms. Peak area is directly proportional to concentration (Table 4). A different analytical system and different ECD was used to analyze the samples for CFCs than was used for low-level VOCs. Generally, there is close correspondence between chromatograms from the CFC and low-level VOC analyses, though a non-linear shift in retention times is noted. There is some uncertainty as to the identification of a peak on the CFC chromatograms with retention time of about 8.4 minutes. This may be the unknown peak with retention time of about 9.4 minutes seen in the low-level VOC chromatograms, though the sensitivity of the ECD to this peak is greater in the CFC system than in the low-level VOC system.

SNL-16 #1

SNL-16#1 WIPP   6/15/06 12:16:03 PM   wt = 52.80 m/-0.15

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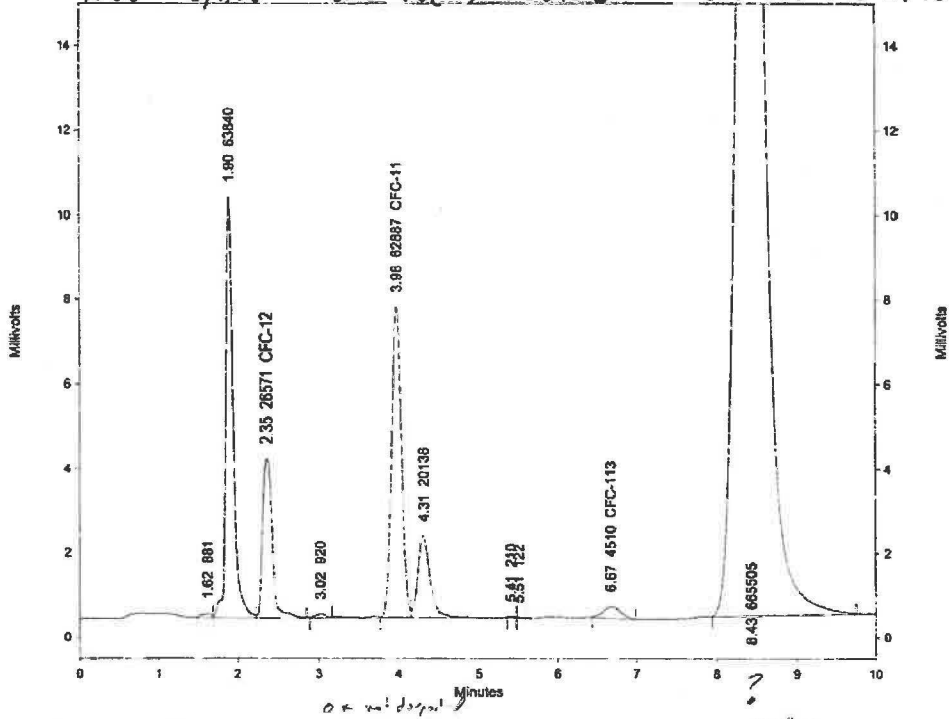
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Detector 2 Results (Original)

Retention Time	Area	Channel	Name
1.62	881	Detector 2	
1.90	63840	Detector 2	
2.35	26571	Detector 2 24950	CFC-12
3.02	920	Detector 2	
3.98	62887	Detector 2	CFC-11
4.31	20138	Detector 2	
5.41	210	Detector 2	
5.51	122	Detector 2	
6.67	4510	Detector 2	CFC-113
8.43	665505	Detector 2	

Begin Sandia WM

water foams when stripped with N_2

62

SNL-16 #2

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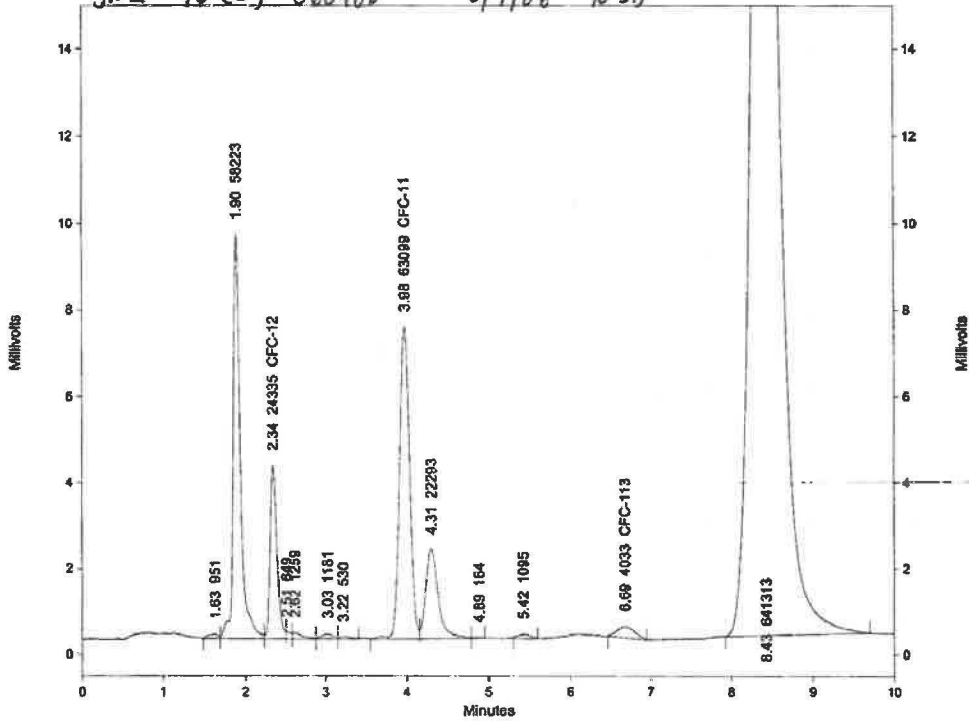
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Detector 2 Results (Original)

Retention Time	Area	Channel	Name
1.63	951	Detector 2	
1.90	58223	Detector 2	
2.34	24335	Detector 2	CFC-12
2.51	649	Detector 2	
2.62	1259	Detector 2	
3.03	1181	Detector 2	
3.22	530	Detector 2	
3.98	63099	Detector 2	CFC-11
4.31	22293	Detector 2	
4.89	164	Detector 2	
5.42	1095	Detector 2	
6.69	4033	Detector 2	CFC-113
8.43	641313	Detector 2	

Sandia

63

SNL-16 #3

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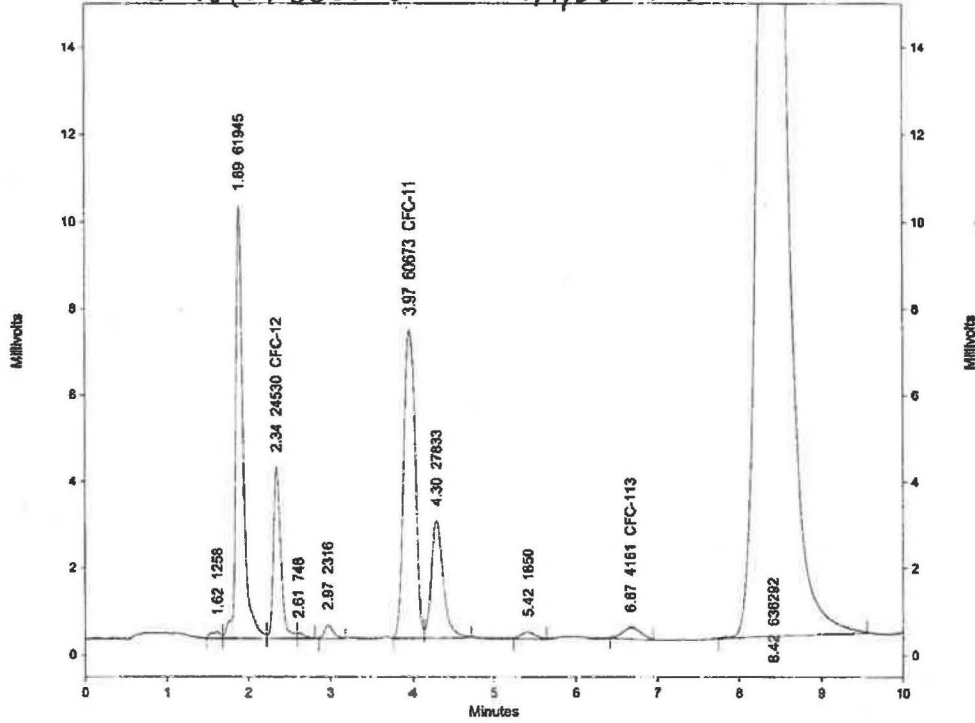
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Detector 2 Results (Original)

Retention Time	Area	Channel	Name
1.62	1258	Detector 2	
1.89	61945	Detector 2	
2.34	24530	Detector 2 23661	CFC-12
2.61	748	Detector 2	
2.97	2316	Detector 2	
3.97	60673	Detector 2	CFC-11
4.30	27833	Detector 2	
5.42	1850	Detector 2	
6.67	4161	Detector 2	CFC-113
8.42	636292	Detector 2	

Sardia 1 well 3eq

64

SNL-19 #1

x1   SNL-19(1) - 012006   8/31/06 9:32:52 AM   wt = 3234 #3-0

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C:\ChromQuest\METHODS\NEWGC1.met Page 1 of 1 (9)
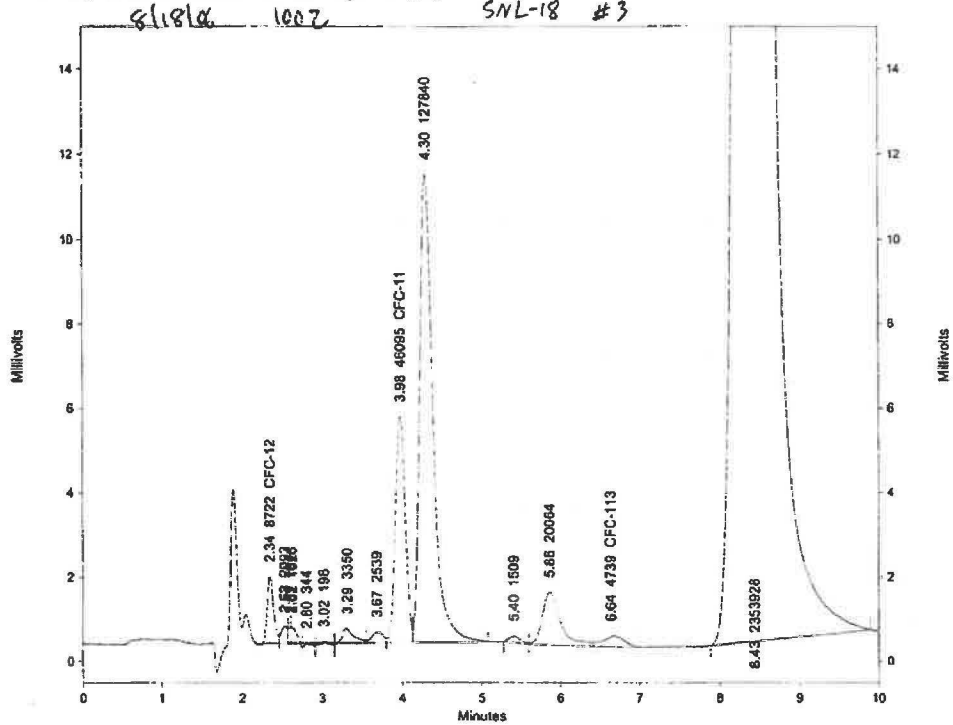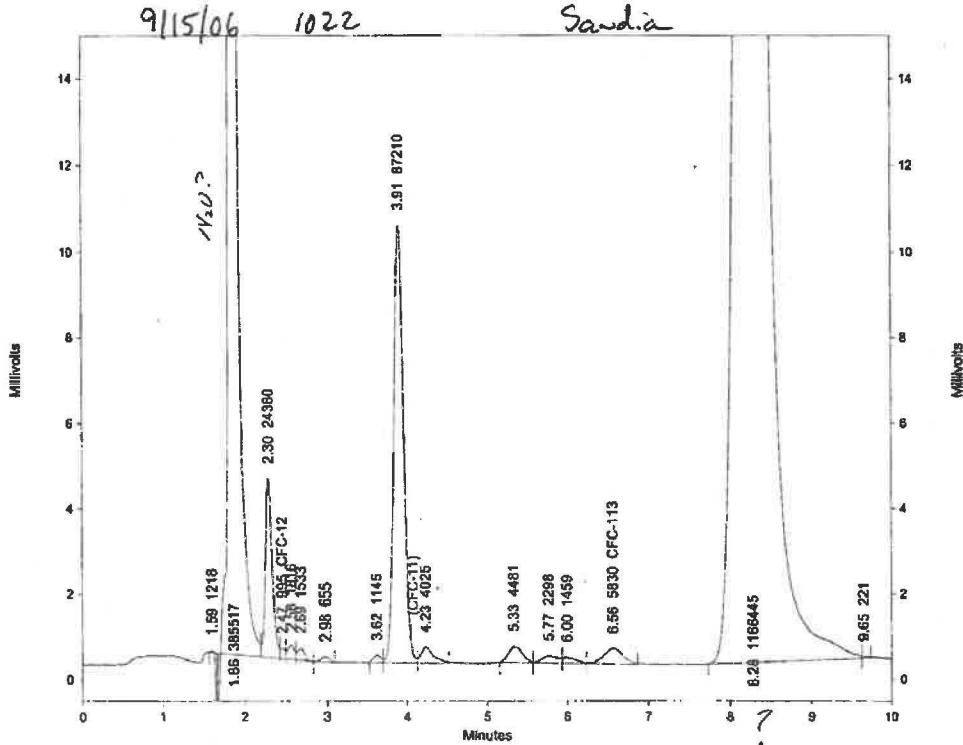
7|28|06   857   WIPP SNL-19   #1
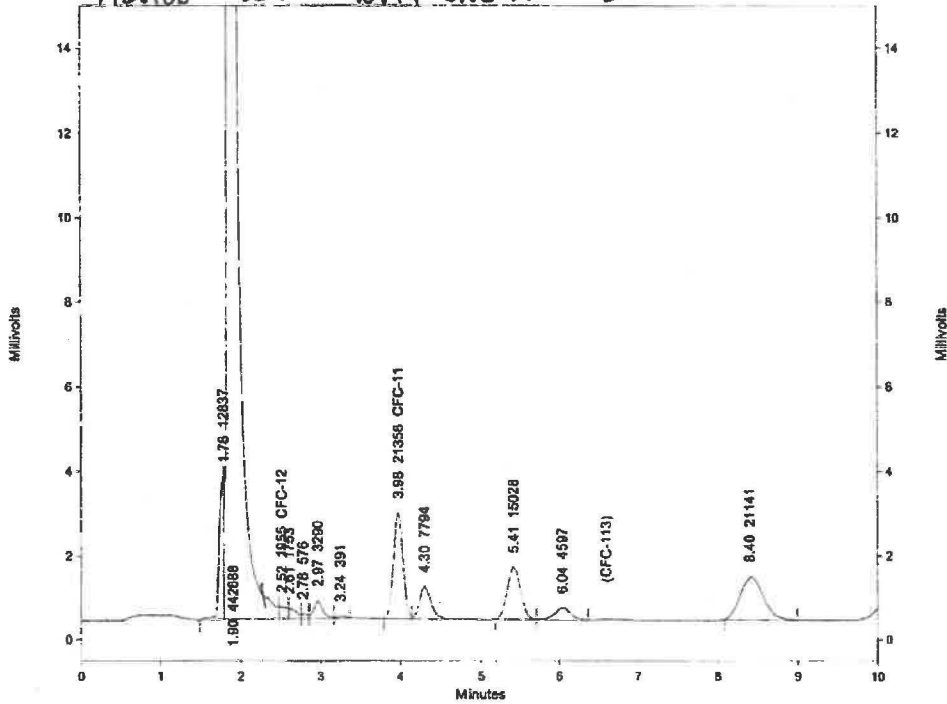
NMCOtollrupert083106a9 G:\CFC Sequences\NewGc\NMtoll\NMCOtollrupert083106a.seq
C:\ChromQuest\METHODS\NEWGC1.met Page 1 of 1 (9)
Detector 2 Results (Original)   do not signif.

Retention Time	Area	Channel	Name
1.78	12837	Detector 2	
1.90	442688	Detector 2	
2.52	1955	Detector 2 382-7	CFC-12
2.61	1753	Detector 2	
2.78	576	Detector 2	
2.97	3290	Detector 2	
3.24	.391	Detector 2	
3.98	21358	Detector 2	CFC-11
4.30	7794	Detector 2	
5.41	15028	Detector 2	
6.04	4597	Detector 2	
		Detector 2	CFC-113
8.40	21141	Detector 2	

65

SNL-19 #2

7/28/06   857   SNL-19 #2
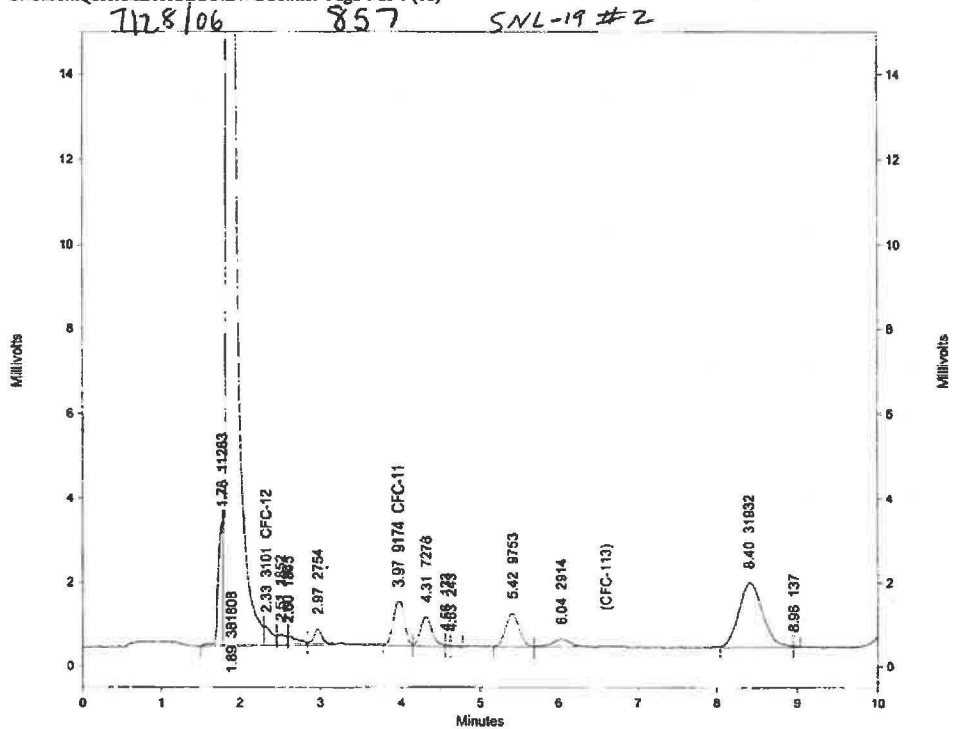
Detector 2 Results (Original)

Retention Time	Area	Channel	Name
1.78	11283	Detector 2	
1.89	381808	Detector 2	
2.33	3101	Detector 2	CFC-12
2.51	1852	Detector 2	
2.60	120	Detector 2	
2.60	1845	Detector 2	
2.97	2754	Detector 2	
3.97	9174	Detector 2	CFC-11
4.31	7278	Detector 2	
4.56	133	Detector 2	
4.63	243	Detector 2	
5.42	9753	Detector 2	
6.04	2914	Detector 2	
		Detector 2	CFC-113
8.40	31932	Detector 2	
8.96	137	Detector 2	

66

Information Only

SNL-19 #3

*J SNL-11067 U12006 8/31/06 10:03:34 AM WT = 52.10 HS=0

NMCOtollrupert083106a11 G:\CFC Sequences\NewGc\NMtoll\NMCOtollrupert083106a.seq
C:\ChromQuest\METHODS\NEWGC1.met Page 1 of 1 (11)

7/28/06   857   SNL-19 #3
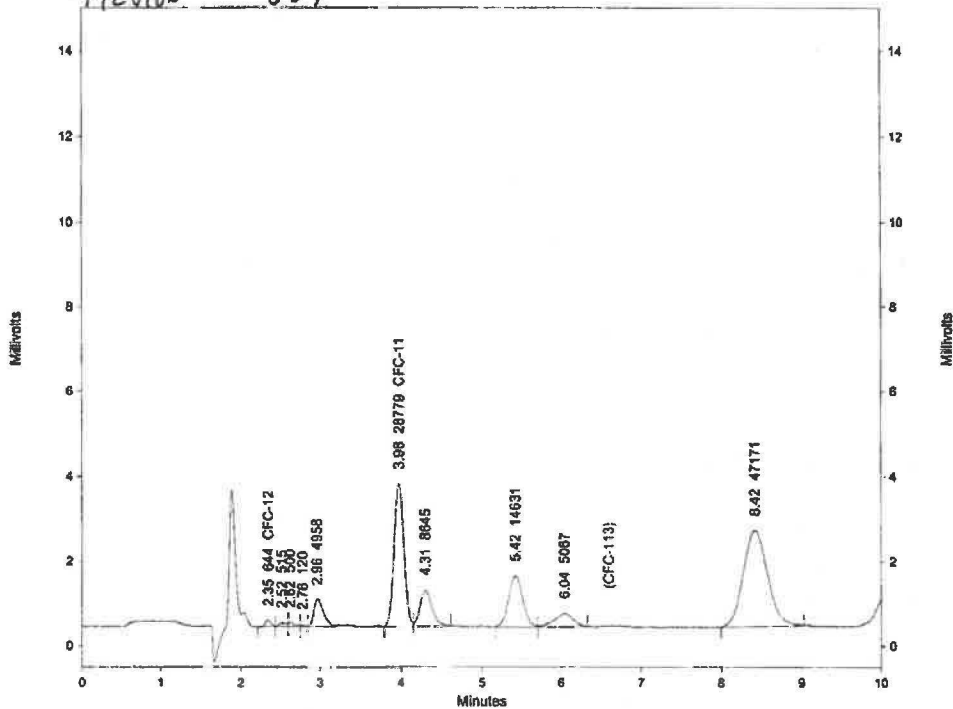
NMCOtollrupert083106a11 G:\CFC Sequences\NewGc\NMtoll\NMCOtollrupert083106a.seq
C:\ChromQuest\METHODS\NEWGC1.met Page 1 of 1 (11)
Detector 2 Results (Original)

Retention Time	Area	Channel	Name
2.35	644	Detector 2	CFC-12
2.52	515	Detector 2	
2.62	500	Detector 2	
2.78	120	Detector 2	
2.96	4958	Detector 2	
3.98	28779	Detector 2	CFC-11
4.31	8645	Detector 2	
5.42	14631	Detector 2	
6.04	5067	Detector 2	
		Detector 2	CFC-113
8.42	47171	Detector 2	

67

SNL-18 #1

#1   SNL-18 (C) 08 1306   8/31/06 10:17:12 AM   WL-52.13 H=0.10

NMCOtollrupert083106a12 G:\CFC Sequences\NewGc\NMtoll\NMCOtollrupert083106a.seq
C:\ChromQuest\METHODS\NEWGC1.met Page 1 of 1 (12)

8/18/05   1002   SNL-18 #1
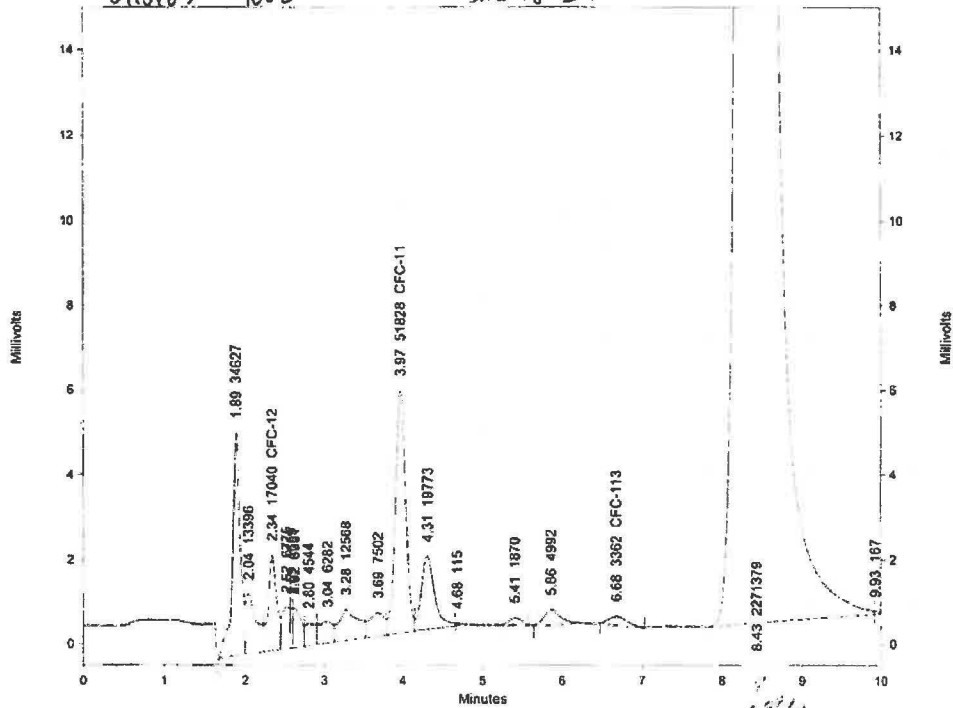
NMCOtollrupert083106a12 G:\CFC Sequences\NewGc\NMtoll\NMCOtollrupert083106a.seq
C:\ChromQuest\METHODS\NEWGC1.met Page 1 of 1 (12)
Detector 2 Results (Original)

Retention Time	Area	Channel	Name
1.89	34627	Detector 2	
2.04	13396	Detector 2	
2.34	17040	Detector 2 8584	CFC-12
2.52	6775	Detector 2	
2.59	1659	Detector 2	
2.62	6351	Detector 2	
2.80	4544	Detector 2	
3.04	6282	Detector 2	
3.28	12568	Detector 2	
3.69	7502	Detector 2	
3.97	51828	Detector 2 47792	CFC-11
4.31	19773	Detector 2	
4.68	115	Detector 2	
5.41	1870	Detector 2	
5.86	4992	Detector 2	
6.68	3362	Detector 2	CFC-113
8.43	2271379	Detector 2	
9.93	167	Detector 2	

68

SNL-18 #2

F 2   JNL - 18(C) U 518V8   8/31/06 10:38:37 AM   Wt - 2L-61 H 3 - C1 1C

NMCOtollrupert083106a13 G:\CFC Sequences\NewGc\NMtoll\NMCOtollrupert083106a.seq
C:\ChromQuest\METHODS\NEWGC1.met Page 1 of 1 (13)

8/18/06 100Z   SNL-18 # 2
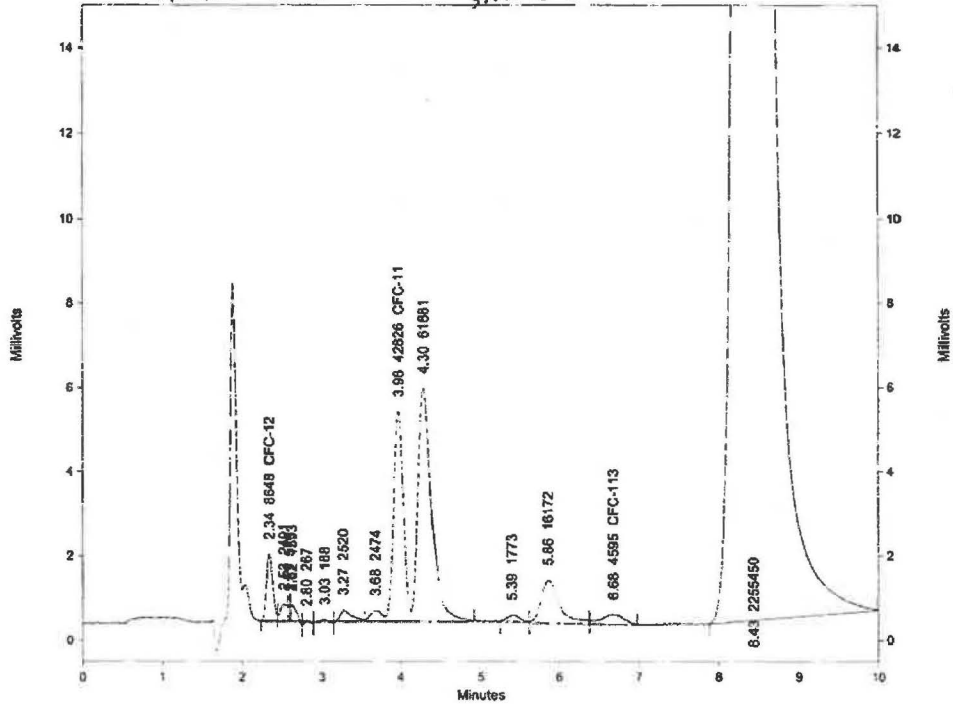
NMCOtollrupert083106a13 G:\CFC Sequences\NewGc\NMtoll\NMCOtollrupert083106a.seq
C:\ChromQuest\METHODS\NEWGC1.met Page 1 of 1 (13)
Detector 2 Results (Original)

Retention Time	Area	Channel	Name
2.34	8648	Detector 2	CFC-12
2.53	2401	Detector 2	
2.59	576	Detector 2	
2.62	1553	Detector 2	
2.80	267	Detector 2	
3.03	188	Detector 2	
3.27	2520	Detector 2	
3.68	2474	Detector 2	
3.98	42826	Detector 2	CFC-11
4.30	61881	Detector 2	
5.39	1773	Detector 2	
5.86	16172	Detector 2	
6.68	4595	Detector 2 2917	CFC-113
8.43	2255450	Detector 2	

69

SNL-18 #3

8|18|06   1007   SNL-18   #3

Detector 2 Results (Original)

Retention Time	Area	Channel	Name
2.34	8722	Detector 2	CFC-12
2.53	2093	Detector 2	
2.59	794	Detector 2	
2.62	1626	Detector 2	
2.80	344	Detector 2	
3.02	198	Detector 2	
3.29	3350	Detector 2	
3.67	2539	Detector 2	
3.98	46095	Detector 2	CFC-11
4.30	127840	Detector 2	
5.40	1509	Detector 2	
5.86	20064	Detector 2	
6.64	4739	Detector 2	CFC-113
8.43	2353928	Detector 2	

70

SNL-17 #1

9/15/06   1022   Sandia

CTbrown110306b23 G:\CFC Sequences\NewGc\COmcmahon101606.seq C:\ChromQuest\METHODS\NEWGC1.met Page 1 of 1

Detector 2 Results
(Reprocessed)

Retention Time	Area	Channel	Name
1.59	1218	Detector 2	
1.86	385517	Detector 2	
2.30	24380	Detector 2	
2.47	995	Detector 2	CFC-12
2.58	1816	Detector 2	
2.69	1533	Detector 2	
2.98	655	Detector 2	
3.62	1145	Detector 2	
3.91	87210	Detector 2	
		Detector 2	CFC-11
4.23	4025	Detector 2	
5.33	4481	Detector 2	
5.77	2298	Detector 2	
6.00	1459	Detector 2	
6.56	5830	Detector 2	CFC-113
8.28	1166445	Detector 2	
9.65	221	Detector 2	

Sandia

71

SNL-17 #2

SNL-17(C) Sandia   11/3/06 1:45:20 PM   wt=52.46 H2-0.70

CTbrown110306b24 G:\CFC Sequences\NewGc\Connetecticut\CTbrown110306b.seq C:\ChromQuest\METHODS\NEWGC1.met
Page 1 of 1 (24)

#2 9/15/06   1022

Detector 2 Results (Original)

Retention Time	Area	Channel	Name
1.58	316	Detector 2	
1.86	180627	Detector 2	
2.30	24318	Detector 2	CFC-12
2.47	709	Detector 2	
2.57	2525	Detector 2	
2.68	1591	Detector 2	
2.98	1019	Detector 2	
3.90	82932	Detector 2	CFC-11
4.24	3569	Detector 2	
5.32	4007	Detector 2	
5.79	1768	Detector 2	
6.55	5112	Detector 2	CFC-113
8.26	693428	Detector 2	

72

SNL-17 #3

SNL-17L   June 20   11/3/06 2:03:06 PM   wt = 52.13 H2 = 0.70

CTbrown110306b25 G:\CFC Sequences\NewGc\Connetecticut\CTbrown110306b.seq C:\ChromQuest\METHODS\NEWGC1.met
Page 1 of 1 (25)   #3   9/15/06   1022
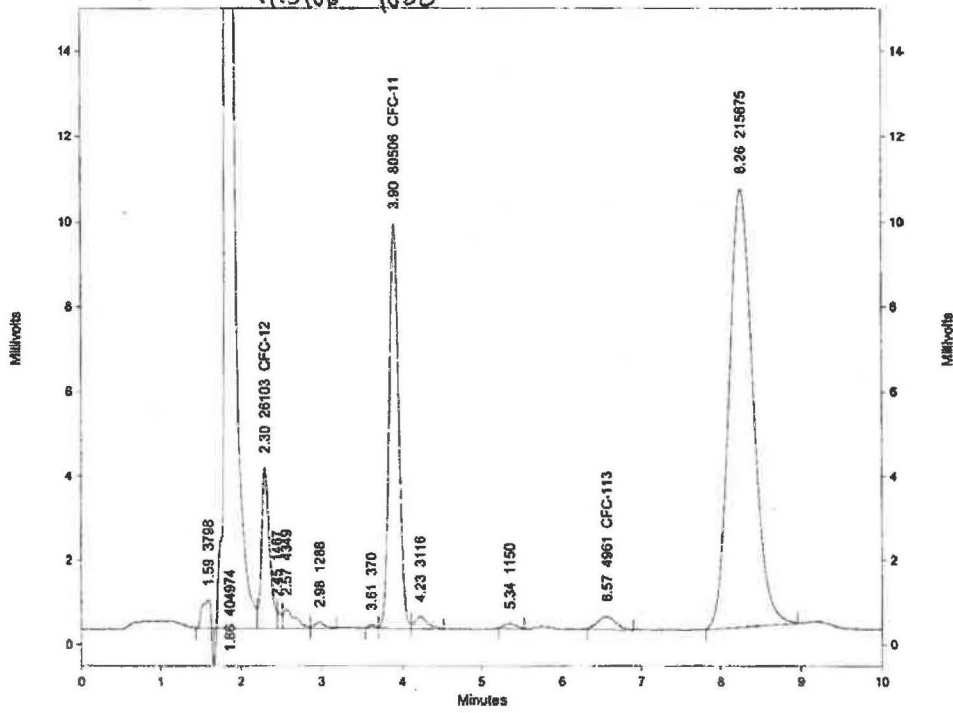
CTbrown110306b25 G:\CFC Sequences\NewGc\Connetecticut\CTbrown110306b.seq C:\ChromQuest\METHODS\NEWGC1.met
Page 1 of 1 (25)

Detector 2 Results (Original)

Retention Time	Area	Channel	Name
1.59	3798	Detector 2	
1.86	404974	Detector 2	
2.30	26103	Detector 2	CFC-12
2.45	1467	Detector 2	
2.57	4349	Detector 2	
2.98	1288	Detector 2	
3.61	370	Detector 2	
3.90	80506	Detector 2	CFC-11
4.23	3116	Detector 2	
5.34	1150	Detector 2	
6.57	4961	Detector 2	CFC-113
8.26	215675	Detector 2	

73

SNL-10 #1

110306   1250   11/3/06

NVrosen121406e25 G:\CFC Sequences\NewGc\Nevada\NVrosen111606\NVrosen121406e.seq
C:\ChromQuest\METHODS\NEWGC1.met Page 1 of 2 (25)

Detector 2 Results (Original)

Retention Time	Area	Channel	Name
1.68	202	Detector 2	
1.72	211	Detector 2	
1.89	8516	Detector 2	
2.04	5476	Detector 2	
2.20	198	Detector 2	
2.33	2865	Detector 2	CFC-12
2.60	6635	Detector 2	
2.64	994	Detector 2	
2.74	2854	Detector 2	
2.83	44	Detector 2	
3.28	54793	Detector 2	
3.64	16268	Detector 2	
3.96	15291	Detector 2	CFC-11
4.29	74757	Detector 2	
5.40	6049	Detector 2	
5.86	31977	Detector 2	
6.67	6332	Detector 2 3920	CFC-113
7.05	261	Detector 2	
8.41	23713	Detector 2	
8.93	7578	Detector 2	

Sandia

74

SNL-10 #2

#2 SNL-10 12/14/06 1:41:36 PM wt = 3251 HS = 0.24

NVrosen121406e26 G:\CFC Sequences\NewGc\Nevada\NVrosen111606\NVrosen121406e.seq
C:\ChromQuest\METHODS\NEWGC1.met Page 1 of 2 (26)

11/3/06   1250
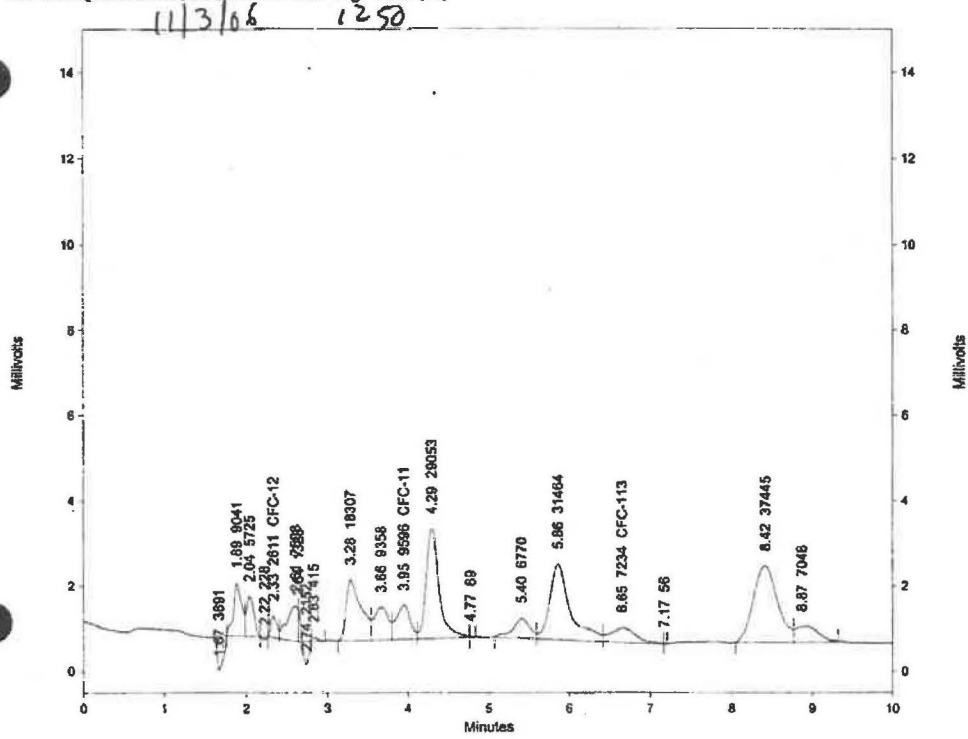
NVrosen121406e26 G:\CFC Sequences\NewGc\Nevada\NVrosen111606\NVrosen121406e.seq
C:\ChromQuest\METHODS\NEWGC1.met Page 1 of 2 (26)

Detector 2 Results (Original)

Retention Time	Area	Channel	Name
1.67	3891	Detector 2	
1.89	9041	Detector 2	
2.04	5725	Detector 2	
2.22	228	Detector 2	
2.33	2611	Detector 2	CFC-12
2.61	7508	Detector 2	
2.64	1328	Detector 2	
2.74	2152	Detector 2	
2.83	415	Detector 2	
3.28	18307	Detector 2	
3.66	9358	Detector 2	
3.95	9596	Detector 2	CFC-11
4.29	29053	Detector 2	
4.77	89	Detector 2	
5.40	6770	Detector 2	
5.86	31464	Detector 2	
6.65	7234	Detector 2 3834	CFC-113
7.17	56	Detector 2	
8.42	37445	Detector 2	
8.87	7048	Detector 2	

75

Information Only

SNL-10 #3

#3 SNL-10   12/14/06 1:54:45 PM   wt = 32.87 HS = 0.24
NVrosen121406e27 G:\CFC Sequences\NewGc\Nevada\NVrosen111606\NVrosen121406e.seq
C:\ChromQuest\METHODS\NEWGC1.met Page 1 of 2 (27)

11/3/06   1250
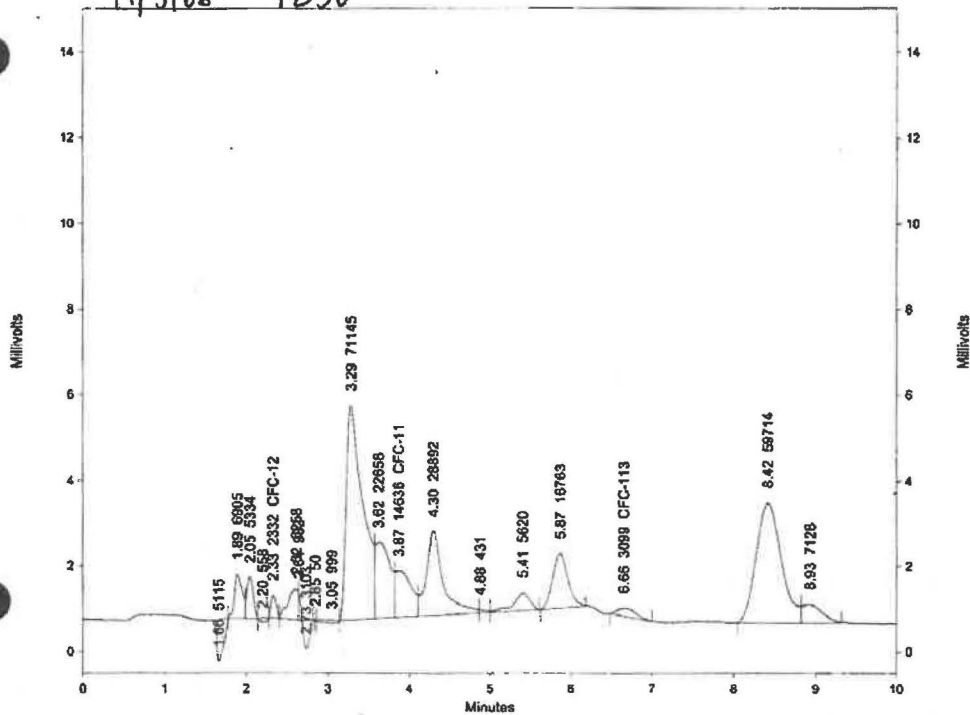
NVrosen121406e27 G:\CFC Sequences\NewGc\Nevada\NVrosen111606\NVrosen121406e.seq
C:\ChromQuest\METHODS\NEWGC1.met Page 1 of 2 (27)

Detector 2 Results (Original)

Retention Time	Area	Channel	Name
1.66	5115	Detector 2	
1.89	6905	Detector 2	
2.05	5334	Detector 2	
2.20	558	Detector 2	
2.33	2332	Detector 2	CFC-12
2.62	6258	Detector 2	
2.64	982	Detector 2	
2.73	3103	Detector 2	
2.85	50	Detector 2	
3.05	999	Detector 2	
3.29	71145	Detector 2	
3.62	22658	Detector 2	
3.87	14636	Detector 2	CFC-11
4.30	28892	Detector 2	
4.88	431	Detector 2	
5.41	5620	Detector 2	
5.87	16763	Detector 2	
6.66	3099	Detector 2	CFC-113
8.42	59714	Detector 2	
8.93	7128	Detector 2	

76

SNL-14 #1

M. Hillesheim   W Deyong   SNL-14(C)-073007 #1   33.76   0.6C
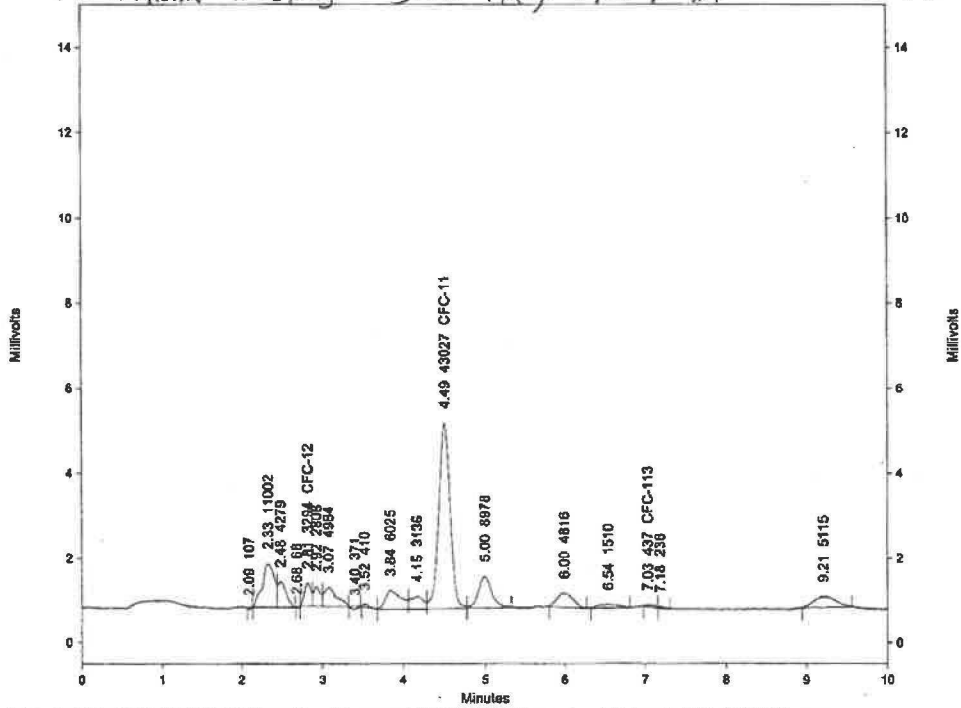
PAseniorNMtoll121307a012 C:\ChromQuest\Sequence\GC2 NEWGC\Pennsylvania\PAseniorNMtoll121307a.seq
C:\ChromQuest\Methods\GC2.met Page 1 of 1 (12)

GC2 Results (System
(12/13/2007 11:05:43 AM)
(Original))

Retention Time	Area	Channel	Name
2.09	107	GC2	
2.33	11002	GC2	
2.48	4279	GC2	
2.68	68	GC2	
2.81	3294	GC2	CFC-12
2.92	2808	GC2	
3.07	4984	GC2	
3.40	371	GC2	
3.52	410	GC2	
3.84	6025	GC2	
4.15	3136	GC2	
4.49	43027	GC2	CFC-11
5.00	8978	GC2	
6.00	4816	GC2	
6.54	1510	GC2	
7.03	437	GC2	CFC-113
7.18	236	GC2	
9.21	5115	GC2	

1049

77

SNL-14 #2

SNL -14 (c) - 073007   # 2   33.70   0.80

GC2 Results (System
(12/13/2007 11:19:21 AM)
(Original))

Retention Time	Area	Channel	Name
2.34	13064	GC2	
2.65	3200	GC2	
2.83	4945	GC2	CFC-12
2.92	4152	GC2	
3.08	5647	GC2	
3.38	0	GC2	
3.53	3051	GC2	
3.86	2021	GC2	
4.16	2026	GC2	
4.50	22076	GC2	CFC-11
5.01	12196	GC2	
6.02	3801	GC2	
7.06	1633	GC2	CFC-113
9.23	7297	GC2	
9.63	97	GC2	

78

SNL-14 #3

SNL - 14(c) - 073007 #3   33.78   1.30

GC2 Results (System
(12/13/2007 11:59:02 AM)
(Original))

Retention Time	Area	Channel	Name
2.00	806	GC2	
2.34	11789	GC2	
2.49	4177	GC2	
2.83	6186	GC2	CFC-12
2.91	3028	GC2	
3.10	5528	GC2	
3.52	1776	GC2	
3.87	2884	GC2	
4.16	2148	GC2	
4.50	19842	GC2	CFC-11
5.00	9345	GC2	
6.03	4576	GC2	
7.10	1586	GC2	CFC-113
9.24	4709	GC2	

SNL-8 #1

SNL -8(c) 080207 #1   34.85   1.21

GC2 Results (System
(12/13/2007 10:37:33 AM)
(Original))

Retention Time	Area	Channel	Name
2.21	5152	GC2	
2.34	11214	GC2	
2.52	27368	GC2	
2.84	3590	GC2	CFC-12
2.95	5602	GC2	
3.12	13459	GC2	
3.33	1533	GC2	
3.55	1217	GC2	
3.83	41184	GC2	
4.15	18057	GC2	
4.51	265641	GC2	CFC-11
5.00	58699	GC2	
6.03	22944	GC2	
6.48	1491	GC2	
6.67	2034	GC2	
		GC2	CFC-113
9.24	14370	GC2	
9.70	94	GC2	

80

SNL-8 #2

SNL -8(c) 080207 #2   34.88   1.21

GC2 Results (System
(12/13/2007 10:50:13 AM)
(Original))

Retention Time	Area	Channel	Name
2.18	6424	GC2	
2.32	16257	GC2	
2.49	24465	GC2	
2.81	4294	GC2	CFC-12
2.94	4488	GC2	
3.10	14060	GC2	
3.30	995	GC2	
3.52	2756	GC2	
3.82	26680	GC2	
4.15	14322	GC2	
4.50	190137	GC2	CFC-11
4.99	53768	GC2	
6.02	18616	GC2	
6.54	2847	GC2	
		GC2	CFC-113
8.29	297	GC2	
8.41	185	GC2	
9.21	8420	GC2	

81

SNL-8 #3

SNL -8(c) - 080207 #3   37.74 (27

GC2 Results (System
(12/13/2007 11:44:31 AM)·
(Original))

Retention Time	Area	Channel	Name
2.19	6747	GC2	
2.32	15032	GC2	
2.51	23925	GC2	
2.81	4410	GC2	CFC-12
2.93	4531	GC2	
3.11	13301	GC2	
3.30	1020	GC2	
3.52	695	GC2	
3.82	34358	GC2	
4.14	15533	GC2	
4.50	325236	GC2	CFC-11
5.00	51357	GC2	
6.01	15229	GC2	
		GC2	CFC-113
9.23	7226	GC2	

82

SF₆ Chromatograms from GC Purge and Trap with Electron-Capture Detector

Three separate water samples were collected in the field by Sandia personnel in 1 L gas bottles with polycone seal for analysis of SF_6. Two of these samples normally were analyzed for each well, and the third if there was not agreement between the first two. The SF_6 retention time is approximately 2.42 minutes. In most cases there was no separate gas phase in the sample bottle, but in the case of SNL-14, a 23 mm diameter gas bubble formed. In calculating the SF6 concentration of the sample it was assumed that the gas in the gass bubble was in equilibrium with the analyzed water sample and the moles of SF_6 calculated in the bubble were added to the water sample. The following pages show copies of the SF6 chromatograms. In some cases the pen did not record the chromatogram traces, but the peak was integrated and recorded electronically.

SF$_6$, SNL-16

SNL-16 wipp 6-9-06 1107   Sandia

CHANNEL A   SM062113.RAW INJECT 06/21/06 09:44:55

2.A DATA CAPTURED TO: c:\labnet\sf606\florida\SM062113.RAW

```
1206sf.fil              06/21/06 09:44:55   CH- "A" PS- 1.

FILE 1.    METHOD 0.    RUN 89    INDEX  1

PEAK#    AREA%      RT     AREA BC

   1      100.      2.11   631176 01

TOTAL    100.             631176

2.A Sending Report...Done
```

Same   Sandia   SNL-16

CHANNEL A   SM062114.RAW INJECT 06/21/06 10:07:26

2.11

2.A DATA CAPTURED TO: c:\labnet\sf606\florida\SM062114.RAW

```
1206sf.fil              06/21/06 10:07.26   CH- "A" PS- 1.

FILE 1.    METHOD 0.    RUN 90    INDEX  1

PEAK#    AREA%      RT     AREA BC       ✓

   1      100.      2.11   778010 01

TOTAL    100.             778010

2.A Sending Report...Done
```

84

SF$_6$, SNL-19

SNL-19   7-28-06   919

CHANNEL A   SK090515.RAW   INJECT 09/05/06 11:11:40
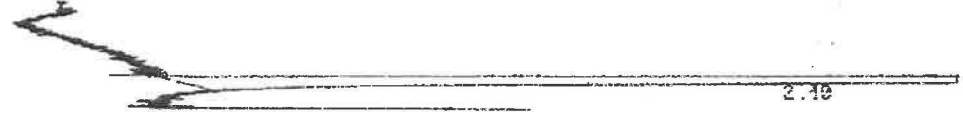
2.A DATA CAPTURED TO: c:\labnet\sf606\florida\SK090515.RAW

1206sf.fil   09/05/06 11:11:40   CH- "A" PS- 1.

FILE 1.   METHOD 0.   RUN 227   INDEX 1

PEAK#	AREA%	RT	AREA BC
1	100.	2.4	1889408 01
TOTAL	100.		1889408

2.A Sending Report...Done

Same

CHANNEL A   SK090516.RAW   INJECT 09/05/06 11:26:04
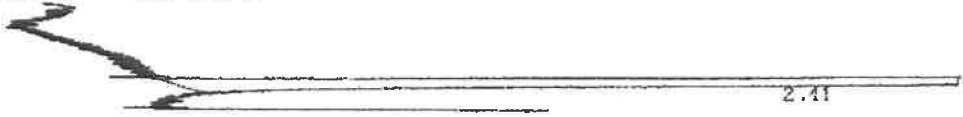
2.A DATA CAPTURED TO: c:\labnet\sf606\florida\SK090516.RAW

1206sf.fil   09/05/06 11:26:04   CH- "A" PS- 1.

FILE 1.   METHOD 0.   RUN 228   INDEX 1

PEAK#	AREA%	RT	AREA BC
1	100.	2.41	1959457 01
TOTAL	100.		1959457

2.A Sending Report...Done

FI-0
AT-32
PT-1000

SF$_6$, SNL-18

SNL-18 8-18-06 1002   NM Sandia

CHANNEL A   SK090513.RAW INJECT 09/05/06 10:36:32
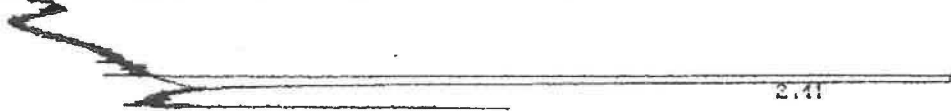
2.0 DATA CAPTURED TO: c:\labnet\sf606\florida\SK090513.RAW

1206sf.fil   09/05/06 10:36:32   CH- "A" PS- 1.
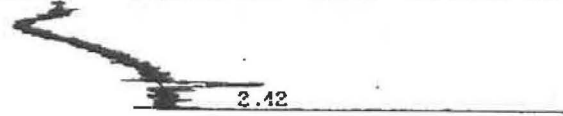
FILE 1.   METHOD 0.   RUN 225   INDEX   1

PEAK#   AREA%   RT   AREA BC

  1   100.   2.11 1296472 01

TOTAL   100.   1296472

  2.0 Sending Report...Done

                    Same

CHANNEL A   SK090514.RAW INJECT 09/05/06 10:59:18
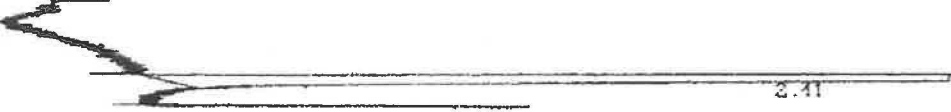
2.0 DATA CAPTURED TO: c:\labnet\sf606\florida\SK090514.RAW

1206sf.fil   09/05/06 10:59:18   CH- "A" PS- 1.

FILE 1.   METHOD 0.   RUN 226   INDEX   1

PEAK#   AREA%   RT   AREA BC

  1   100.   2.11 1420850 01

TOTAL   100.   1420850

  2.0 Sending Report...Done

SF$_6$, SNL-17

Toff- Sandia

SNL-17   9-15-06   1022

CHANNEL A   IA092909.RAW   INJECT 09/29/06 08:33:23

2.40

2.A DATA CAPTURED TO: c:\labnet\sf606\newyor~1\IA092909.RAW

1206sf.fil   09/29/06 08:33:23   CH- "A"   PS- 1.

FILE 1.   METHOD 0.   RUN 106   INDEX 1

PEAK#   AREA%   RT   AREA BC

1   100.   2.4   68151 01

TOTAL   100.   68151

2.A Sending Report...Done

Same   SNL-17

CHANNEL A   IA092910.RAW   INJECT 09/29/06 09:07:03

2.41

2.A DATA CAPTURED TO: c:\labnet\sf606\newyor~1\IA092910.RAW

1206sf.fil   09/29/06 09:07:03   CH- "A"   PS- 1.

FILE 1.   METHOD 0.   RUN 107   INDEX 1

PEAK#   AREA%   RT   AREA BC

1   100.   2.41   69752 01

TOTAL   100.   69752

2.A Sending Report...Done

END   Toll

87

SF$_6$, SNL-10

Sandia -   SNL·10   Deyonge DuHaers / Chace   11-3-0.   1252

CHANNEL A   SK120703.RAW   INJECT   12/07/06 06:15:27

2.41
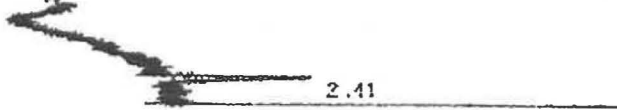
2.A DATA CAPTURED TO: c:\labnet\sf606\florida\SK120703.RAW

1296sf.fil   12/07/06 06:15:27   CH- "A"   PS- 1.

FILE 1.   METHOD 0.   RUN 320   INDEX   1

PEAK#	AREA%	RT	AREA	BC
1	100.	2.41	15850	01
TOTAL	100.		15850	

2.A Sending Report...Done

Same

CHANNEL A   SK120704.RAW   INJECT   12/07/06 06:30:34

2.39
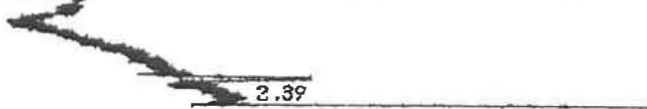
2.A DATA CAPTURED TO: c:\labnet\sf606\florida\SK120704.RAW

1296sf.fil   12/07/06 06:30:34   CH- "A"   PS- 1.

FILE 1.   METHOD 0.   RUN 321   INDEX   1

PEAK#	AREA%	RT	AREA	BC
1	100.	2.39	15213	01
TOTAL	100.		15213	

2.A Sending Report...Done

88

SF$_6$, SNL-14

SNL-14c   7-30-07   1848   23mm

CHANNEL A   JW081709.RAW   INJECT   08/17/07 08:49:38

2.42

2.A DATA CAPTURED TO: c:\labnet\sf607\indiana\JW081709.RAW

1206sf.fil   08/17/07 08:49:38   CH- "A" PS- 1.

FILE 1.   METHOD 0.   RUN 324   INDEX   1

PEAK#   AREA%   RT   AREA BC

  1   100.   2.42   12319 01 13289

TOTAL   100.   12319

2.A Sending Report...Done

Same   23mm

CHANNEL A   JW081710.RAW   INJECT   08/17/07 09:03:55

2.43
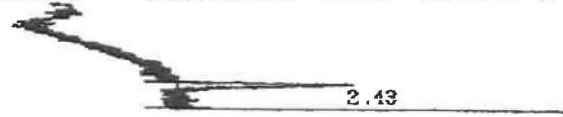
2.A DATA CAPTURED TO: c:\labnet\sf607\indiana\JW081710.RAW

1206sf.fil   08/17/07 09:03:55   CH- "A" PS- 1.

FILE 1.   METHOD 0.   RUN 325   INDEX   1

PEAK#   AREA%   RT   AREA BC

  1   100.   2.43   22248 01 ✓

TOTAL   100.   22248

2.A Sending Report...Done

89

SF$_6$, SNL-14 (continued)

SNL-14C   3rd bottle   7-30-07   1848   26mm

CHANNEL A   JW091711.RAW   INJECT 09/17/07 09:31:53

2.A DATA CAPTURED TO: c:\labnet\sf607\indiana\JW091711.RAW

2.43   2521

SF$_6$, SNL-8

SNL-8c   8-2-07   1628   Jegun   Sandia   15 mm

CHANNEL A   JW081707.RAW   INJECT   08/17/07 08:19:21

2.A DATA CAPTURED TO: c:\labnet\sf607\indiana\JW081707.RAW

2.42 - 4533

NO DATA, CHANNEL A

2.A Sending Report...Done

Same   SNL-8c   15 mm

CHANNEL A   JW081708.RAW   INJECT   08/17/07 08:33:35

2.44 - 3249

2.A DATA CAPTURED TO: c:\labnet\sf607\indiana\JW081708.RAW

NO DATA, CHANNEL A

2.A Sending Report...Done

91

Chromatograms of Halogenated VOCs from GC Purge and Trap with Electron-Capture Detector with Retention Times to 30 minutes

An analytical system is available in the USGS Chlorofluorocarbon Laboratory that recognizes many more halogenated VOCs; those having retention times up to 30 minutes. On June 19, 2008, one additional achieved CFC bottle was analyzed on this system for additional halogenated VOCs for each of the seven monitoring wells. This permitted identification of, in addition to the CFCs, the presence of methyl chloride (present in all samples), 1,1-dichloroethylene (present in all but SNL-17), carbon tetrachloride (present in all but SNL-17), chloroform (present in all samples), TCE (present in all samples), PCE (present in all samples), and methyl chloroform (present in SNL-16, SNL-17, SNL-8). The presence of these VOCs was determined by running standards containing the compounds and matching peaks with retention times. The concentrations were not quantified.

The ECD is particularly sensitive to halogenated VOCs and can detect these compounds at concentrations more than 1,000-fold below the usual USEPA mass spectrometric analysis. Although some of these halogenated VOCs are naturally occurring in air of marine origin, the peak areas observed in the WIPP samples are, in many cases, indicative of anthropogenic origin. Previous analyses of old ground water from throughout the US do not show significant detections of these compounds. Further, many of the halogenated VOCs, including chloroform, are disinfection by-products of chlorination in municipal water systems, and would not be present in old, unaffected water. Other compounds were present in the samples, but have not been identified, and are marked as unknown or with a question mark on the chromatograms.

The approximate retention times of the recognized halogenated VOCs identified in the samples run on June 19, 2008 are, in minutes, 2.6 (CFC-12), 3.6 (H_2S, not a VOC but detected by the ECD), 4.4 (CFC-11), 4.9 (methyl chloride), 6.0 (1,1-dichloroethylene), 7.2 (CFC-113), 9.4 (unknown), 10.3 (carbon tetrachloride), 12.4 (unknown), 15.8 (chloroform), 16.3 (TCE), 20.5 (PCE), and 23.3 (methyl chloroform). Copies of the low-level VOC chromatograms follow. The first chromatogram shows the retention time of a chloroform standard, followed by a chromatogram of blank air passed through the purge cell, then one chromatogram for each well, and finally, a chromatogram of a 5 cc air standard.

Inspection of the chromatograms below shows a relatively large range of low-level VOC concentrations present in the 7 samples. Overall, sample SNL-19 has the lowest concentrations of halogenated VOCs of the seven wells. The peak area for chloroform is 11,375 counts, which is perhaps on the order of 0.001 ug/L chloroform, and the lowest concentration of chloroform among the 7 samples. If the chloroform peak area (which varies linearly with concentration) is indicative of fraction of municipal water being pumped from the wells, then the fraction of municipal water in discharge from well SNL-16 is 27-fold larger than that of well SNL-19. And similarly, for wells SNL-18, SNL-17, SNL-10, SNL-14, and SNL-8, the chloroform factors are 10-, 17-, 12-, 11-, and 6-fold greater than water from SNL-19.

Figure 9 shows that the chloroform concentration of the samples, expressed as peak area recorded in the GC chromatograms, varies linearly with the estimated % Modern based on CFC-12 (Table 4).

Sample SNL-8 has relatively low chloroform concentration, but has been contaminated with many other halogenated VOCs, including CFC-11, TCE, PCE, methyl chloroform, methyl chloride, and an unknown VOC with retention time of 12.4 minutes.

Chloroform Standard

Chloroform   T = 24.4   BP = 749.4

Gas std. with Chloroform
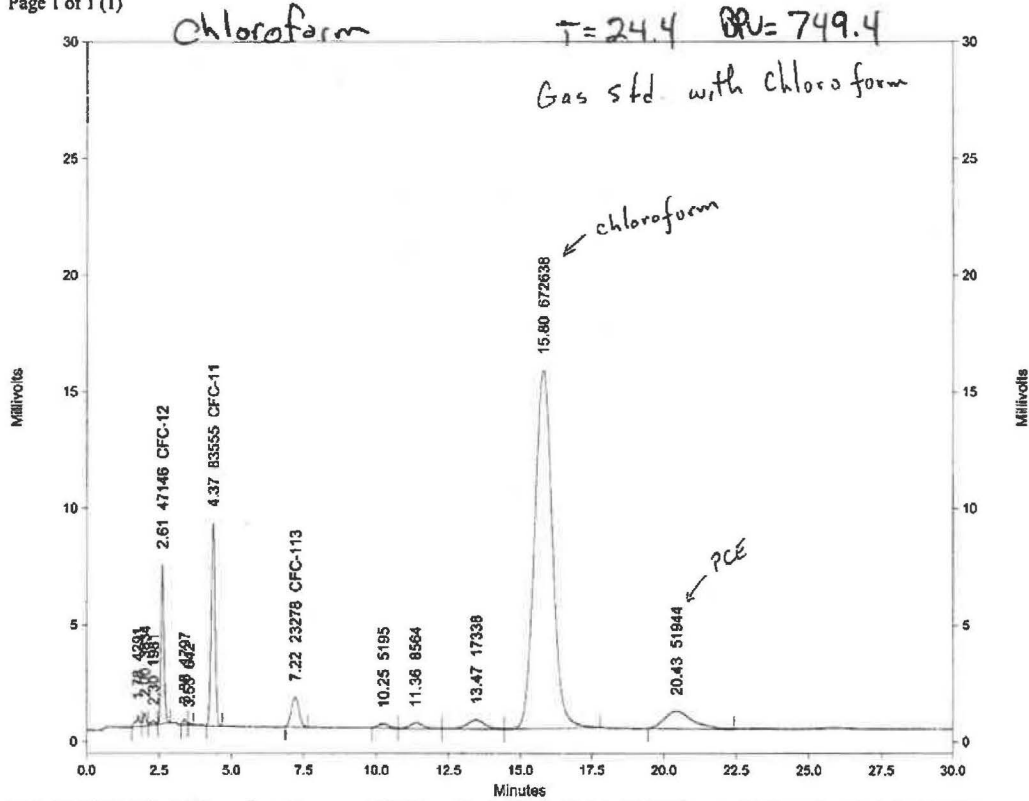
GC3 Results (System
(6/18/2008 10:09:05 AM)
(Original))

Retention Time	Area	Channel		Name
1.78	4291	GC3		
2.00	3834	GC3		
2.30	1981	GC3		
2.61	47146	GC3	CFC-12	CFC-12
3.38	1797	GC3		
3.53	642	GC3		
4.37	83555	GC3	CFC-11	CFC-11
7.22	23278	GC3	CFC-113	CFC-113
10.25	5195	GC3		
11.36	8564	GC3		
13.47	17338	GC3	?	
15.80	672638	GC3	chloroform	
20.43	51944	GC3	PCE	

94

Blank gas through purge cell

Blank water
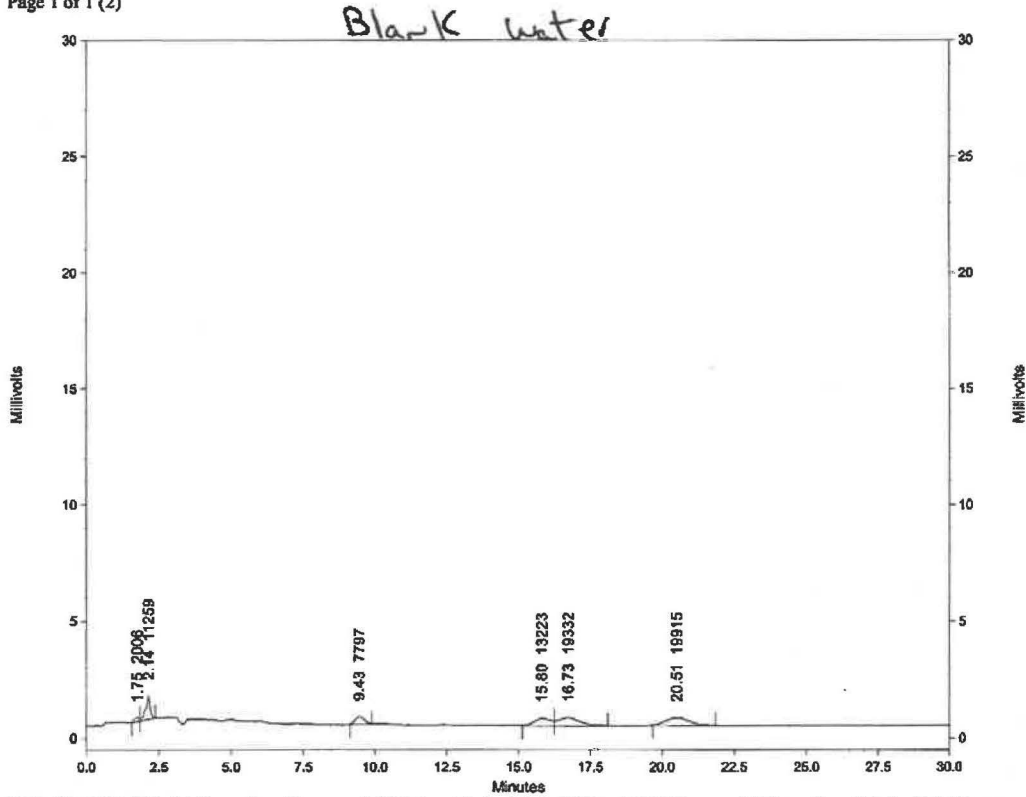
GC3 Results (System
(6/18/2008 10:47:27 AM)
(Original))

Retention Time	Area	Channel	Name
1.75	2006	GC3	
2.14	11259	GC3	
		GC3	CFC-12
		GC3	CFC-11
		GC3	CFC-113
9.43	7797	GC3	
15.80	13223	GC3	
16.73	19332	GC3	
20.51	19915	GC3	

SNL-16

NMtoll061808a003 C:\ChromQuest\Sequence\GC3\COrupert\COrupert072307a.seq C:\ChromQuest\Methods\GC3.met Page 1 of 2

GC3 Results (System
(6/18/2008 11:26:01 AM)
(Original))

Retention Time	Area	Channel	Name
1.75	1837	GC3	
2.05	3633	GC3	
2.12	12543	GC3	
2.28	2323	GC3	
2.62	29494	GC3	CFC-12
3.36	2381	GC3	
3.64	4098	GC3	
4.05	1963	GC3	
4.38	194499	GC3	CFC-11
4.87	16174	GC3	
6.00	2655	GC3	
7.22	6213	GC3	CFC-113
9.42	16772	GC3	
10.26	1142	GC3	
11.17	14470	GC3	
12.35	44848	GC3	
15.85	310963	GC3	
16.34	128011	GC3	
20.67	257528	GC3	
23.38	31844		

96

SNL-19

7/28/06   857

NMtoll061808a007 C:\ChromQuest\Sequence\GC3\New Mexico\NMtoll\NMtoll061808a.seq C:\ChromQuest\Methods\GC3.met
Page 1 of 2 (10)
GC3 Results (System
(6/18/2008 2:18:45 PM)
(Original))

Retention Time	Area	Channel	Name
1.71	2008	GC3	
1.94	40057	GC3	
2.09	1520684	GC3	
2.51	17103	GC3	CFC-12
2.68	9677	GC3	
2.82	6929	GC3	
2.95	8362	GC3	
3.31	5195	GC3	
3.60	13668	GC3	
3.73	5033	GC3	
3.95	4691	GC3	
4.32	18786	GC3	CFC-11
4.83	29208	GC3	
5.32	143	GC3	
5.99	930	GC3	
7.20	1372	GC3	CFC-113
9.41	40153	GC3	
10.06	951	GC3	
11.16	72680	GC3	
12.31	5174		
15.80	11375		
16.61	13439		
20.44	25273		

97

SNL-18

8/18/06   1002
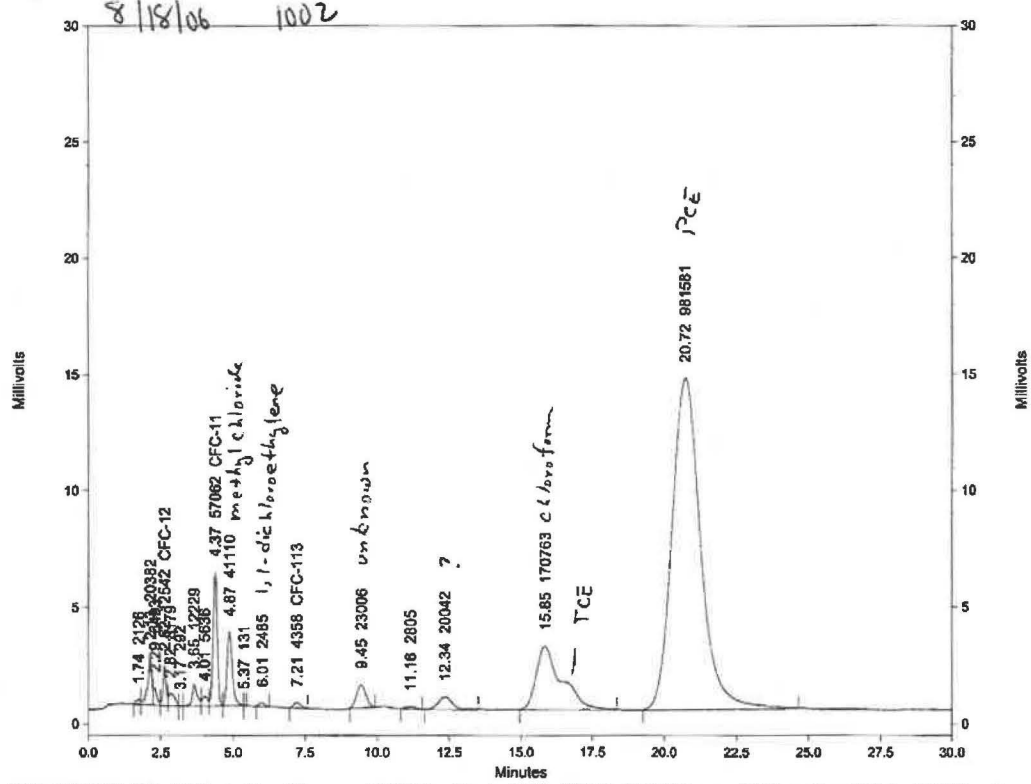
GC3 Results (System
(6/18/2008 12:34:49 PM)
(Original))

Retention Time	Area	Channel	Name
1.74	2126	GC3	
2.13	20382	GC3	
2.29	6493	GC3	
2.62	12542	GC3	CFC-12
2.82	8179	GC3	
3.17	292	GC3	
3.65	12229	GC3	
4.01	5636	GC3	
4.37	57062	GC3	CFC-11
4.87	41110	GC3	
5.37	131	GC3	
6.01	2485	GC3	
7.21	4358	GC3	CFC-113
9.45	23006	GC3	
11.16	2805	GC3	
12.34	20042	GC3	
15.85	170763	GC3	
20.72	981581	GC3	

SNL-17

9/15/06   1022

NMtoll061808a004 C:\ChromQuest\Sequence\GC3\New Mexico\NMtoll\NMtoll061808a.seq C:\ChromQuest\Methods\GC3.met

Page 1 of 2 (5)

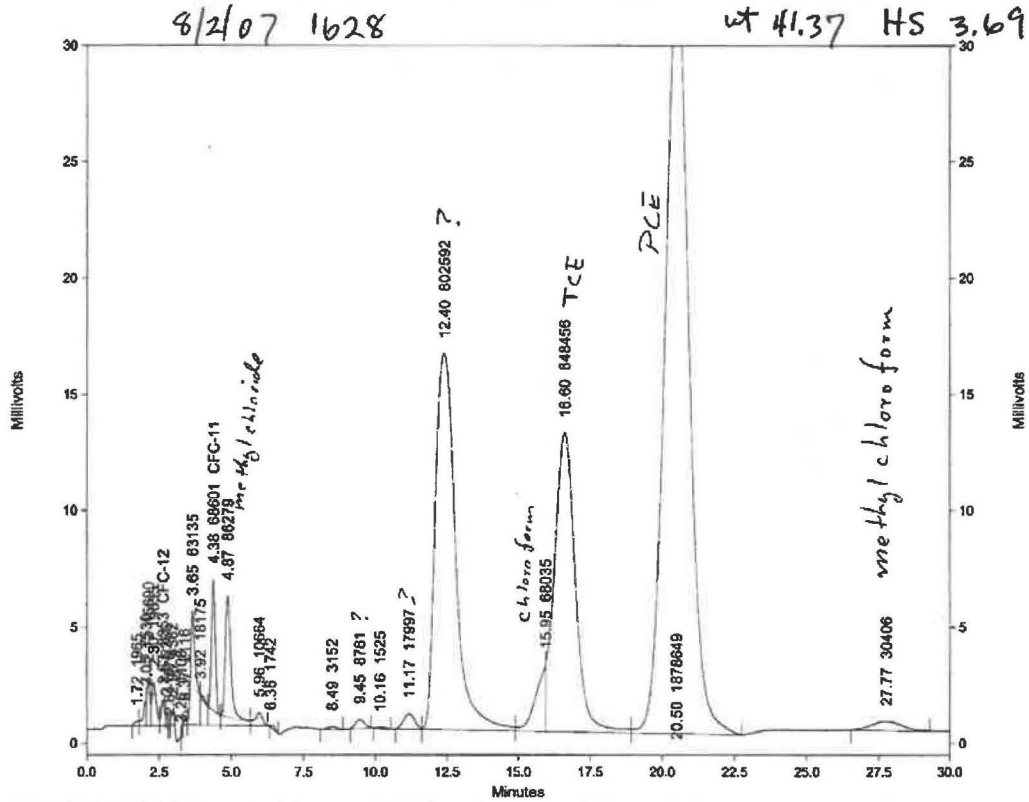GC3 Results (System
(6/18/2008 12:00:29 PM)
(Original))

Retention Time	Area	Channel	Name
1.21	11556	GC3	
1.63	7143	GC3	
1.78	6206	GC3	
2.02	3861	GC3	
2.13	19847	GC3	
2.26	3210	GC3	
2.63	107890	GC3	CFC-12
2.93	2185	GC3	
3.37	15768	GC3	
3.59	2526	GC3	
3.96	266	GC3	
4.39	1331286	GC3	CFC-11
4.87	17722	GC3	
5.97	941	GC3	
6.61	2514	GC3	
7.23	36839	GC3	CFC-113
9.44	114643	GC3	
10.27	180209	GC3	
11.17	7288	GC3	

99

SNL-10

SNL-10

6/19/2008 2:57:35 PM
NMtoll061808a008 C:\ChromQuest\Sequence\GC3\COrupert\COrupert072307a.seq C:\ChromQuest\Methods\GC3.met Page 1 of 2

11/03/06   1250   ₩ 40.34   HS 0.80

GC3 Results (System
(6/19/2008 2:57:10 PM)
(Reprocessed))

Retention Time	Area	Channel	Name
1.70	1894	GC3	
1.98	6070	GC3	
2.09	18979	GC3	
2.21	6185	GC3	
2.57	17969	GC3	CFC-12
2.67	3265	GC3	
2.87	4270	GC3	
3.06	3795	GC3	
3.32	1383	GC3	
3.60	107173	GC3	
3.89	949	GC3	
4.34	65551	GC3	CFC-11
4.82	4595	GC3	
5.93	4290	GC3	
6.47	1298	GC3	
7.20	7283	GC3	CFC-113
8.34	2388	GC3	
9.40	20147	GC3	
9.84	13215	GC3	

100

SNL-14

07/30/07   1937

NMtoll061808a010 C:\ChromQuest\Sequence\GC3\New Mexico\NMtoll\NMtoll061808a.seq C:\ChromQuest\Methods\GC3.met

Page 1 of 2 (16)
GC3 Results (System
(6/18/2008 4:06:21 PM)
(Original))

Retention Time	Area	Channel	Name
1.71	3822	GC3	
1.78	1272	GC3	
1.96	6360	GC3	
2.07	18426	GC3	
2.18	6862	GC3	
2.55	17693	GC3	CFC-12
2.63	1610	GC3	
2.85	2641	GC3	
2.96	1491	GC3	
3.11	1613	GC3	
3.29	6169	GC3	
3.58	11252	GC3	
3.95	3321	GC3	
4.32	76409	GC3	CFC-11
4.82	31227	GC3	
5.90	848	GC3	
7.15	4560	GC3	CFC-113
9.41	6894	GC3	
10.18	1240	GC3	

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SNL-8

8/2/07 1628   wt 41.37   HS 3.69

GC3 Results (System
(6/19/2008 2:59:33 PM)
(Reprocessed))

Retention Time	Area	Channel	Name
1.72	1965	GC3	
2.05	7530	GC3	
2.12	15690	GC3	
2.30	19633	GC3	
2.63	8353	GC3	CFC-12
2.74	2265	GC3	
2.84	676	GC3	
2.96	4362	GC3	
3.26	1108	GC3	
3.37	2116	GC3	
3.65	63135	GC3	
3.92	18175	GC3	
4.38	68601	GC3	CFC-11
4.87	86279	GC3	
5.96	10664	GC3	
6.36	1742	GC3	
		GC3	CFC-113
8.49	3152	GC3	
9.45	8781	GC3	

5 cc of air standard

5cc   7173 25.8

5 cc Air standard
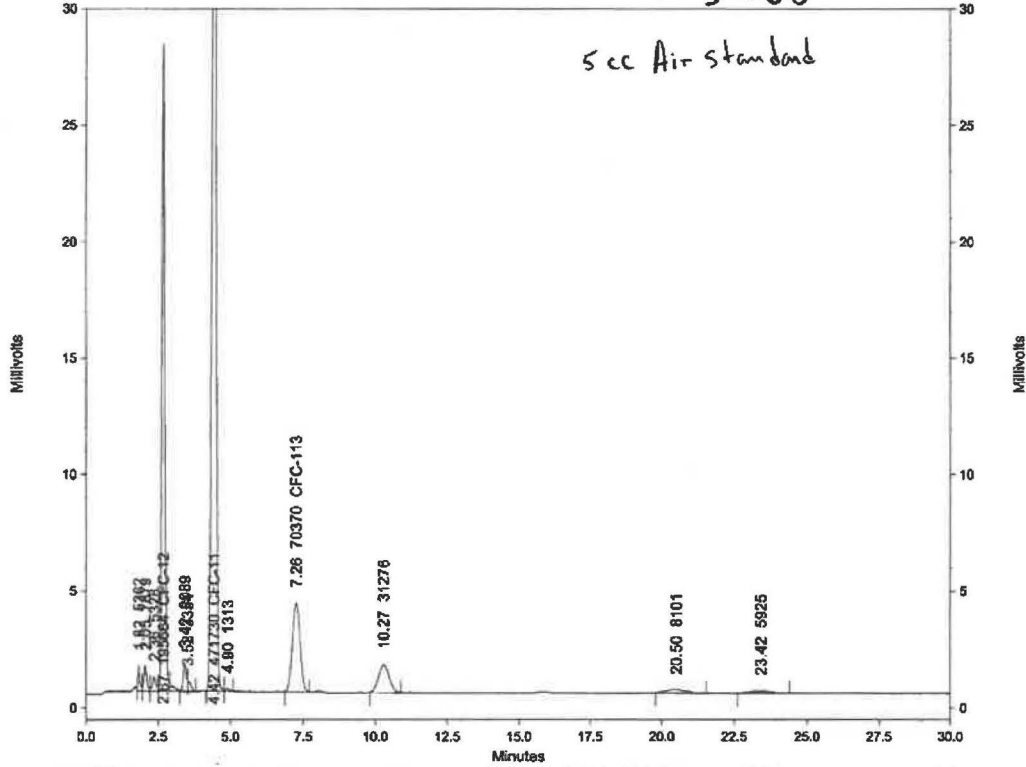
GC3 Results (System
(6/18/2008 4:50:43 PM)
(Original))

Retention Time	Area	Channel	Name
1.82	5362	GC3	
2.05	7879	GC3	
2.36	5328	GC3	
2.67	195664	GC3	CFC-12
3.42	9089	GC3	
3.52	3354	GC3	
4.42	471730	GC3	CFC-11
4.90	1313	GC3	
7.26	70370	GC3	CFC-113
10.27	31276	GC3	
20.50	8101	GC3	
23.42	5925	GC3	

103

Fractionated Air: Gas Exchange between Trapped Gas Bubbles and Ground Water with Dilute Initial Water

This section repeats the previous calculations given in the main body of this report that determines whether the CE model for fractionated excess air can fit the dissolved gas data. In the main body of this report the initial condition assumed the initial solubilities of N_2, Ar, and O_2 were those for initial saline waters. Now we consider the possibility that the initial waters were fresh water, with and without 2 mL/kg of excess air. The calculations then consider the possibility that the dissolved gases (He, Ar, Ne, N_2, O_2, CFC-11, CFC-12, CFC-113, and SF_6) were introduced and/or modified by the drilling air and/or the air-purging of the wells (i.e. jetting used in well completion). It is assumed that gas bubbles were injected into the formation which subsequently either partially dissolved, as can be described by the closed-system equilibration (CE) model of Aeschbach-Hertig et al. (2000), or completely dissolved, a limiting case of the CE model called the un-fractionated air (UA) model. In the CE model, the initial volume, A, of the trapped gas bubbles is reduced by partial dissolution of the bubbles under hydrostatic pressure.

These calculations assume that:

1) fresh waters initially equilibrated with the atmosphere at $20^\circ C$,

2) at an elevation of 3000' before recharge and gas confinement, and

3) the waters contained 2mL/kg of excess air.

The overall result is that the measured concentrations of N_2 and Ar (and O_2) are lower than the equilibrium concentrations with excess air in SNL-19, SNL-14 and SNL-08, leading to calculated negative amounts of fractionated excess air—which is impossible. Also the Ar concentration in SNL-18 is lower than the equilibrium concentration with excess air—another impossibility. Since most ground water contain some excess air, it is highly unlikely that 4 of the 7 waters recharged under these conditions.

We next consider the possibility that:

1) fresh waters equilibrated with the atmosphere at $20^\circ C$,

2) at an elevation of 3000' before recharge and gas confinement,

3) no excess air was introduced during recharge of the ground waters, and

4) the salts were dissolved in the aquifer after the confinement of the gases.

In SNL-14, the measured concentration of N_2 was greater than the fresh water equilibrium concentration. Also in wells SNL-14, SNL-19 and SNL-8, the measured Ar concentrations were slightly smaller than the calculated equilibrium concentrations. The results of the simulations are presented below in Figures A6.1 through A6.7.

SNL-16 contains moderately high concentrations of He and Ne, and a high concentration of terrigenic SF_6 that are not adequately modeled using the CE model alone. The results of the CE model are presented in Figure A6.1. The best fit for Ar, O_2 and CFC-113 was obtained using a trapped gas volume, A, of 25-33 mL per kg of water and a fractionation factor (F) of 0.55. The N_2 and CFC-12 fit a model with a lower fractionation factor and trapped air concentrations of 25-33 mL per kg of water.
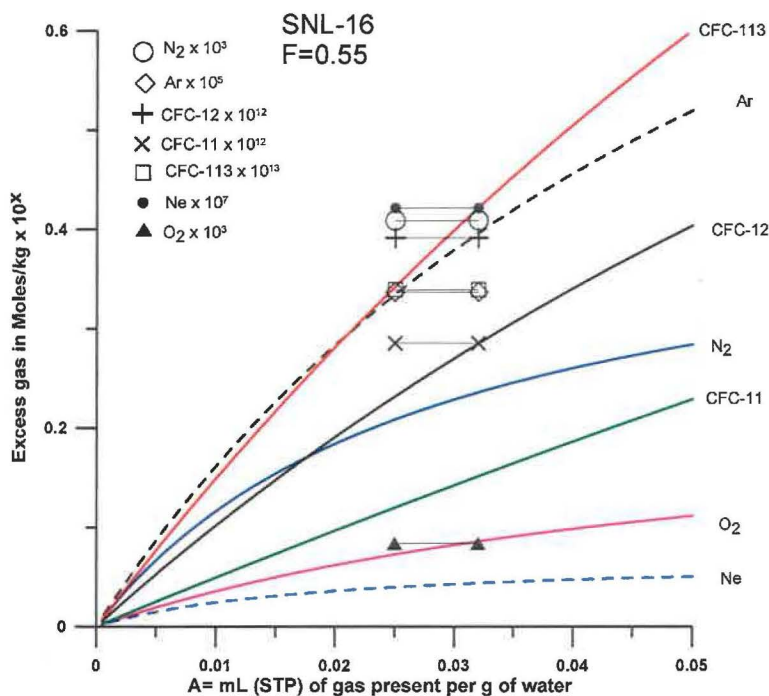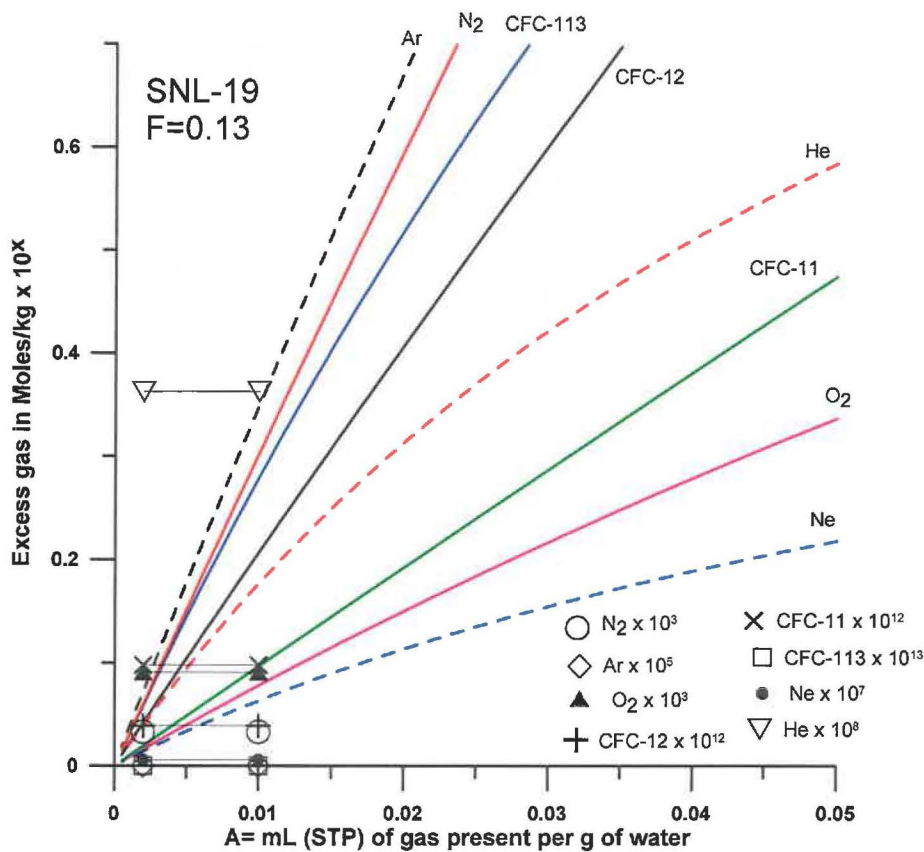

Figure A6.1. Plot showing the mole fractions of excess gases and environmental tracers as a function of volume of trapped gas for a fractionation factor (F) of 0.55 for SNL-16.

Water from SNL-19 contains little to no excesses of N_2, Ar, or CFC-113. The results of the CE model are presented in Figure A6.2. The best fit was obtained using gas volumes of only 0.002-0.010 cc/g of water and a fractionation factor (F) of 0.13. Water from SNL-19 contains significant concentrations of terrigenic SF_6 and an excess of He that cannot be accounted for by the CE model.
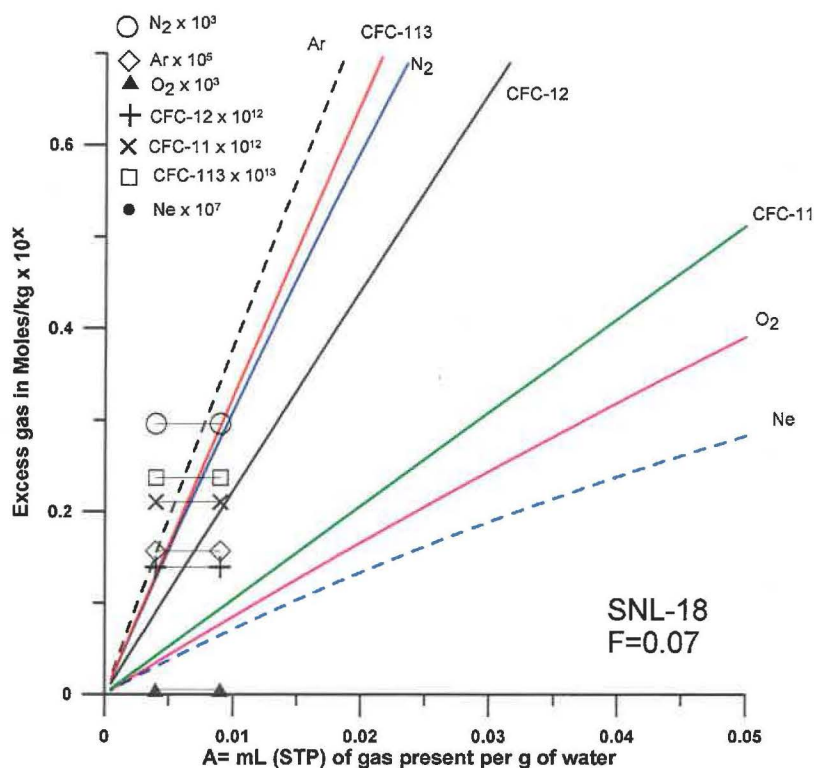
Figure A6.2. Plot showing the mole fractions of excess gases and environmental tracers as a function of volume of trapped gas for a fractionation factor (*F*) of 0.13 for SNL-19.

The results of the CE model for water from SNL-18 are presented in Figure A6.3. High concentrations of terrigenic He and SF_6 and cannot be explained by the CE model alone. The best fit was for the other gases was obtained using a gas volume of 0.004-0.009 cc/g of water and a fractionation factor (*F*) of 0.07. The excess concentrations fit reasonably well the CE model, however, the measured CFC-11 concentration is high, possibly due to an additional source of contamination, and the O_2 concentration is low, possibly due to microbial degradation in the aquifer or in the sample bottle prior to analysis.

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Figure A6.3. Plot showing the mole fractions of excess gases and environmental tracers as a function of volume of trapped gas for a fractionation factor (F) of 0.07 for SNL-18.

Water from SNL-17 contains moderately high concentrations of terrigenic SF_6, which cannot be explained by the CE model alone. The results of the CE model for the permanent gases N_2, Ar, He and Ne are presented in Figure D. The best fit was obtained using a gas volume of 0.011-0.015 cc/g of water and a fractionation factor (F) of 0.35. Note that the CFC concentrations are much higher than the modeled values (Figure A6.4). The CFC-11, CFC-12 and CFC-113 fit an entirely different model.
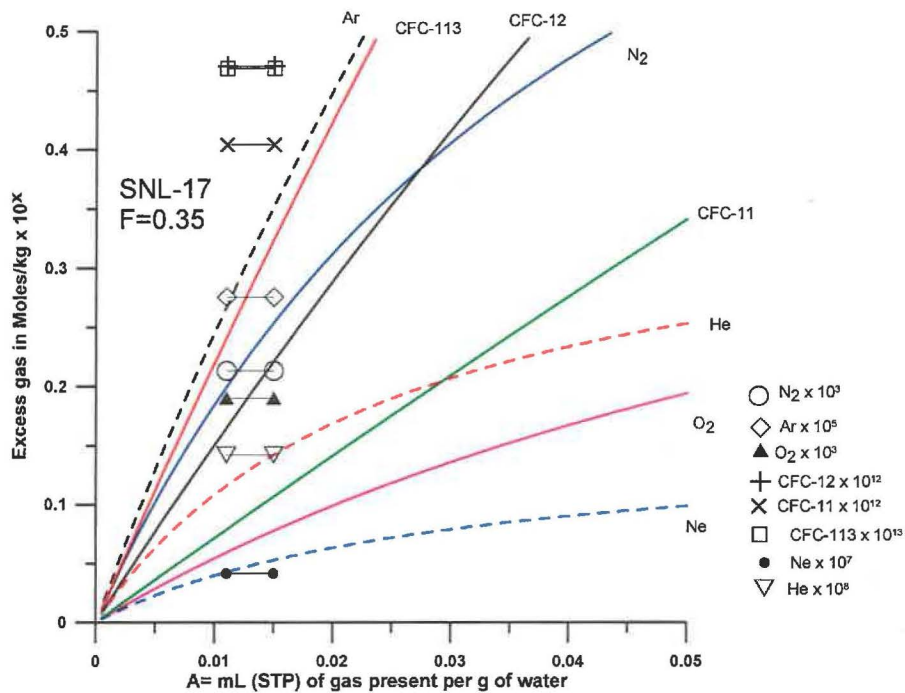
Figure A6.4. Plot showing the mole fractions of excess gases and environmental tracers as a function of volume of trapped gas for a fractionation factor (F) of 0.35 for SNL-17. Note that the measured CFCs are significantly greater than the modeled concentrations.

Water from SNL-10 contains moderate concentrations of terrigenic He and SF_6. The results of the CE model are presented in Figure A6.5. The best fit was obtained using a gas volume of 0.002-0.008 cc/g of water and un-fractionated air (F = 0.0).
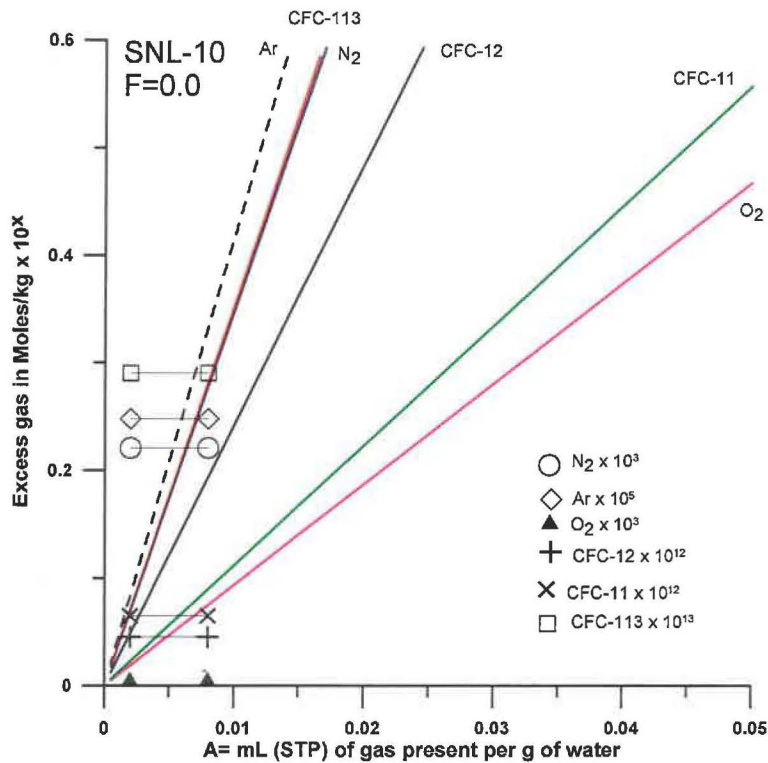
Figure A6.5. Plot showing the mole fractions of excess gases and environmental tracers as a function of volume of trapped gas trapped. All the trapped air was dissolved and $F = 0.0$ for SNL-10.

Water from SNL-14 contains high concentrations of terrigenic He and SF_6. The modeled concentrations of N_2 and Ar were greater than the measured concentrations. The results of the CE model are presented in Figure A6.6. The CFC-12 and CFC-113 best fit a model with a fractionation factor of 0.60 using a gas volume of 0.004-0.008 cc/g. Water from SNL-14 is similar to that from SNL-18 in that there is an excess of CFC-11, possibly due to a contamination source, and dissolved oxygen concentration is below the modeled value, possibly due to microbial degradation, either in the sample bottle or in the aquifer.
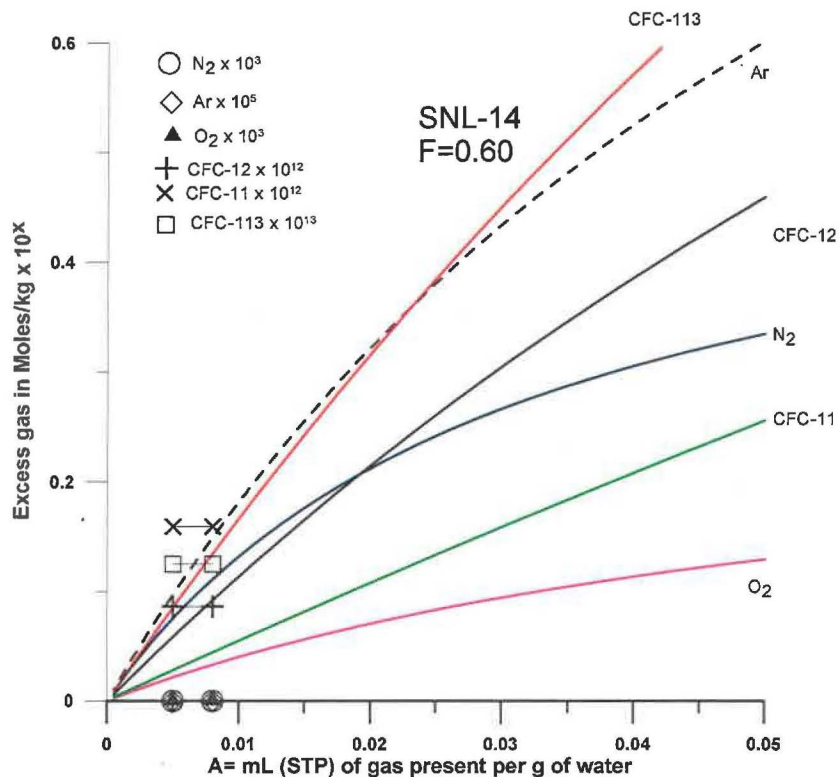
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Figure A6.6. Plot showing the mole fractions of excess gases and environmental tracers as a function of volume of trapped gas for a fractionation factor (F) of 0.6 for SNL-14. Fresh water, no excess air; F=0.50; A=0.04-0.08; CFC-12, CFC-113.

Water from SNL-8 contains very high concentrations of terrigenic He. The CFC-11 concentration is very high and not consistent with the CFC-12 and CFC-113 measured concentrations which suggest that this ground water was contaminated with CFC-11. The results of the CE model are presented in Figure A6.7. The best fit was obtained using a gas volume of 0.003-0.006 cc/g of water and a fractionation factor (F) of 0.5, based on the N_2 and CFC-12 concentrations.
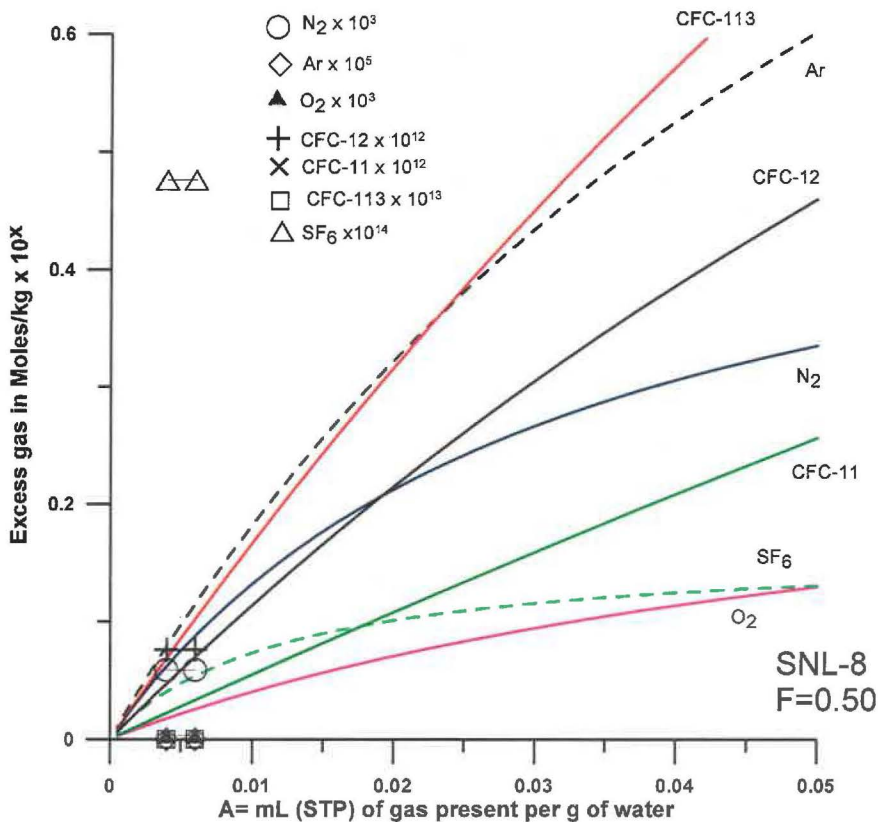
110

Figure A6.7. Plot showing the mole fractions of excess gases and environmental tracers as a function of volume of trapped gas for a fractionation factor (F) of 0.5 for SNL-8.

The results for the CE model from Figures A6.1-A6.7 are summarized in Table A6.1. A fractionation factor (*F*) of 0 indicates that all the trapped air was dissolved. The fractionation of the trapped air increases as *F* approaches 1.0. *A* is the initial amount of trapped air in cc/g of water. Note that two different models are needed to explain the permanent and environmental gas compositions of of water from SNL-17. The modeled N_2 and Ar results for SNL-14 are negative indicating the gases were not introduced by partial dissolution of a trapped bubble during recharge. In almost all cases, the measured CFC-11 concentrations are greater than the modeled CFC-11 concentrations, indicating possibly low-level contamination of CFC-11 in most of the samples. There are many potential sources of the excess CFC-11 from the drilling operation, including rubber hoses used in air injection. SNL-08 appears to be significantly contaminated with CFC-11. Significant excesses of He and SF_6 were present in nearly all the ground waters and are attributed to terrigenic sources.

Table A6.1. Summary of results from the CE Model, assuming fresh water recharge at 20°C at an elevation of 3000' and the presence of no excess air in the ground waters.

Well Name	Date Sampled	A (Trapped Air in cc/g H_2O)	F (Fractionation factor)	Gases Fitting the CE Model for each sample*
SNL-16	06/09/2006	0.25-0.33	0.55	Ar, O_2, CFC-113
SNL-19	07/28/2006	0.002-0.010	0.13	N_2, O_2, CFC-12, CFC-113
SNL-18	08/18/206	0.004-0.009	0.07	N_2, Ar, CFC-12, CFC-113
SNL-17	09/15/2006	0.011-0.017	0.35	N_2, Ar, Ne, He
SNL-10	11/03/2006	0.004-0.008	0.00	N_2, Ar, CFC-11, CFC-12, CFC-113
SNL-14	07/30/2007	0.09-0.15	0.50	CFC-12, CFC-113
SNL-08	08/02/2007	0.003-0.006	0.50	N_2, CFC-12

*Other gases, not listed here do not fit the CE Model—see figures of CE model calculations for each sample.

The overall conclusion is that it is unlikely that the N_2 and Ar were introduced during recharge of fresh water at 20°C at 3000' elevation if 2mL/kg of excess air was present in the recharge and if the salts were added into the ground water in the aquifer. It is possible to explain the N_2 and Ar concentrations in six of the seven wells if no excess air was present in the recharge. The model calculations considering introduction and fractionation of excess air from the drilling operation is that in many cases, the observed concentrations of CFCs, particularly CFC-12, and CFC-113, could be explained by injection of varying relatively small amounts of air with subsequent partial or in a few cases, complete dissolution of the injected air. In nearly every case, CFC-11 concentrations are significantly greater than the modeled calculations suggesting contamination with CFC-11. Since in most ground waters contain a small amount of excess air, either no excess was introduced during recharge of these ground waters or equilibrium was between air and water that contain significant salt concentrations. The CE model cannot explain the observed concentrations of SF_6 and He which have large excesses relative to the CE model and most likely have additional, terrigenic, sources.