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Quantifying VOC Emissions for the Strategic Petroleum Reserve

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Abstract

A very important aspect of the Department of Energy's (DOE's) Strategic Petroleum Reserve (SPR) program is regulatory compliance. One of the regulatory compliance issues deals with limiting the amount of volatile organic compounds (VOCs) that are emitted into the atmosphere from brine wastes when they are discharged to brine holding ponds. The US Environmental Protection Agency (USEPA) has set limits on the amount of VOCs that can be discharged to the atmosphere. Several attempts have been made to quantify the VOC emissions associated with the brine ponds going back to the late 1970's. There are potential issues associated with each of these quantification efforts. Two efforts were made to quantify VOC emissions by analyzing VOC content of brine samples obtained from wells. Efforts to measure air concentrations were mentioned in historical reports but no data have been located to confirm these assertions. A modeling effort was also performed to quantify the VOC emissions. More recently in 2011-2013, additional brine sampling has been performed to update the VOC emissions estimate. An analysis of the statistical confidence in these results is presented here. Arguably, there are uncertainties associated with each of these efforts. The analysis herein indicates that the upper confidence limit in VOC emissions based on recent brine sampling is very close to the 0.42 ton/MMB limit used historically on the project. Refining this estimate would require considerable investment in additional sampling, analysis, and monitoring. An analysis of the VOC emissions at each site suggests that additional discharges could be made and stay within current regulatory limits.

A suggested path forward would entail two separate but related efforts. First, additional sampling could be performed on brine samples from the well head to address uncertainties associated with possible VOC emissions from different SPR operations (e.g., leaching,

depressurization). Second, a quantitative air monitoring program could be initiated to quantify the actual VOC emissions from the brine ponds. Several techniques are available and summarized in this document.

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CONTENTS

1 Introduction _____ *9*

2 Prior Work _____ *12*

2.1 VOC Estimates from 1978 EIS _____ 12

2.2 VOC Estimates from 1981 EIS _____ 12

3 RECENT BRINE SAMPLING _____ *15*

4 AIR QUALITY MONITORING _____ *23*

5 Proposed Future Work _____ *25*

5.1 DIAL Measurement Method _____ 25

5.2 FTIR Measurement Method _____ 25

5.3 Passive VOC Measurement Method _____ 26

5.4 Active VOC Measurement Method _____ 26

5.5 Additional Brine Sampling and Analysis _____ 26

6 Path Forward _____ *29*

7 Cited References _____ *31*

8 APPENDIX A: Laboratory Analysis References _____ *32*

FIGURES

.

Figure 1-1. Conceptual model of brine movement during leach operation for SPR salt domes. .. 9
Figure 1-2. Schematic of hypothesized VOC uptake methods by brine during a leach operation in an SPR cavern. 10
Figure 1-3. Conceptual model of brine movement during oil fill. 11
Figure 3-1. VOC emissions estimates for the four SPR sites. 22

TABLES

Table 3-1. VOC estimates for WH-110 15
Table 3-2. VOC estimates for BH-101 15
Table 3-3. Lookup table for f(α,β) 16
Table 3-4. Number of samples needed for a 95% confidence with varying surety and difference desired from cavern WH-110 16

Table 3-5. Number of samples needed for a 95% confidence with varying surety and difference from cavern BH-101 17
Table 3-6. VOC estimates for thirteen caverns. (* - mean data from replicate sampling) 18
Table 3-7. Number of samples needed for a 95% confidence with varying surety and difference desired from thirteen samples. 18
Table 3-8. Number of samples needed for a 95% confidence with varying surety and difference desired from twelve log-transformed samples. 19
Table 3-9. Brine discharges (barrels) at Bryan Mound (BM), Big Hill (BH), West Hackberry (WH), and Bayou Choctaw (BC) for the calendar year 2012. 20
Table 3-10. VOC emission estimates (by current authors) at BM, BH, WH, and BC for the calendar year 2012. 20
Table 3-11. Results of uncertainty analysis and additional brine discharge estimates. 21

NOMENCLATURE

BC	Bayou Choctaw
BH	Big Hill
BM	Bryan Mound
DIAL	Differential absorption light detection and ranging system
DOE	Department of Energy
EIS	Environmental Impact Statement
^{o}F	degrees Fahrenheit
FTIR	Fourier Transform Infrared spectroscopy
MMBbl	million barrels
NMHC	non-methane hydrocarbon
ppm	parts per million
psi	pounds per square inch
RCRA	Resource Conservation and Recovery Act
SNL	Sandia National Laboratories
SPR	Strategic Petroleum Reserve
USEPA	US Environmental Protection Agency
VOC	volatile organic compound
WH	West Hackberry

1 INTRODUCTION

The Department of Energy's (DOE's) Strategic Petroleum Reserve (SPR) program is a vital part of the nation's energy strategy. Managing petroleum reserves also has elements of regulatory compliance. One of the regulatory compliance issues deals with limiting the amount of volatile organic compounds (VOCs) that are emitted into the atmosphere from brine wastes when they are discharged to brine holding ponds. Figure 1-1 shows a conceptual model depicting the brine disposal process for a cavern undergoing leaching operations. In the figure, brackish water is pumped into the salt dome cavern. The walls of the salt dome are enlarged through dissolution, which causes the water in the cavern to approach saturated brine. The brine pool sits underneath a roof blanket of crude oil. Hydrocarbons are transferred to the brine through direct contact with the oil, as well as from mass transfer of gases trapped in the dissolved salt, as illustrated in Figure 1-2. When the brine is in the cavern it is under pressure, at approximately 1,500 psi. The temperature of the brine in the cavern ranges from 100-130°F depending on the incoming brine temperature and residence time in the cavern. In the pipeline exiting the cavern, the pressure is approximately 150 psi. When discharged to the brine ponds the pressure reduces down to atmospheric. Some of the entrained VOCs dissipate to the atmosphere from the surface of the brine pond.

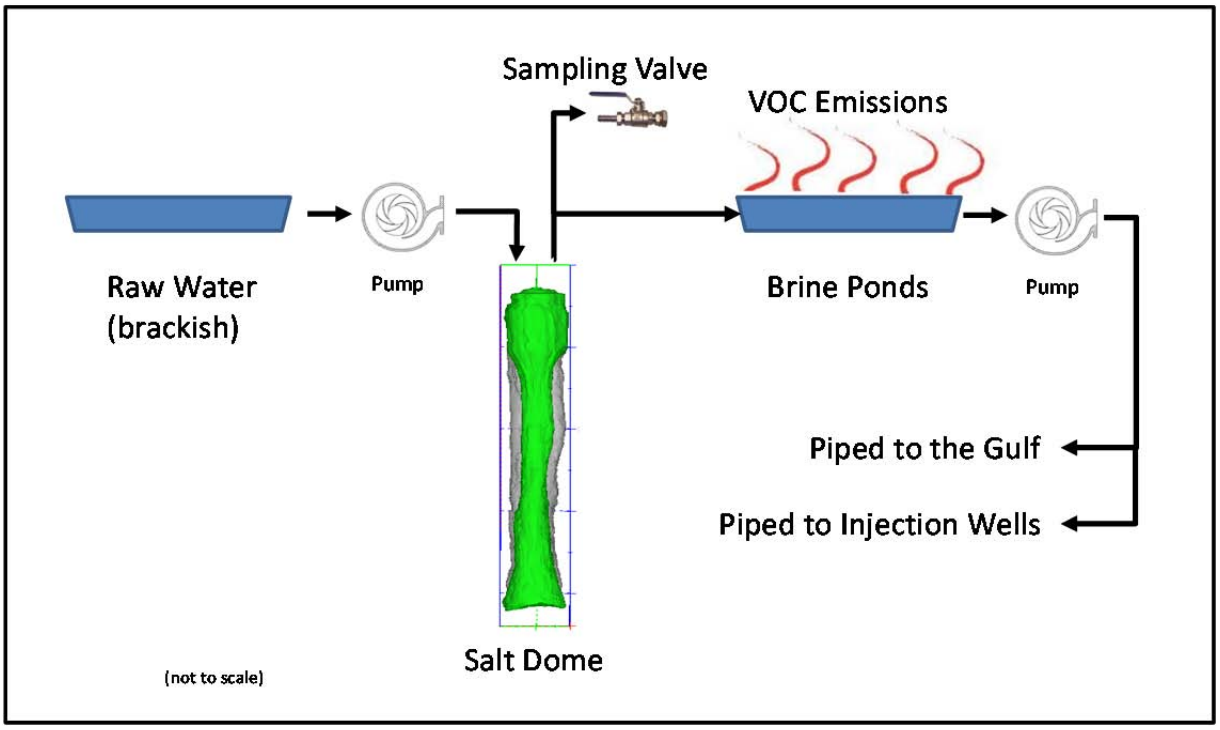

Figure 1-1. Conceptual model of brine movement during leach operation for SPR salt domes.

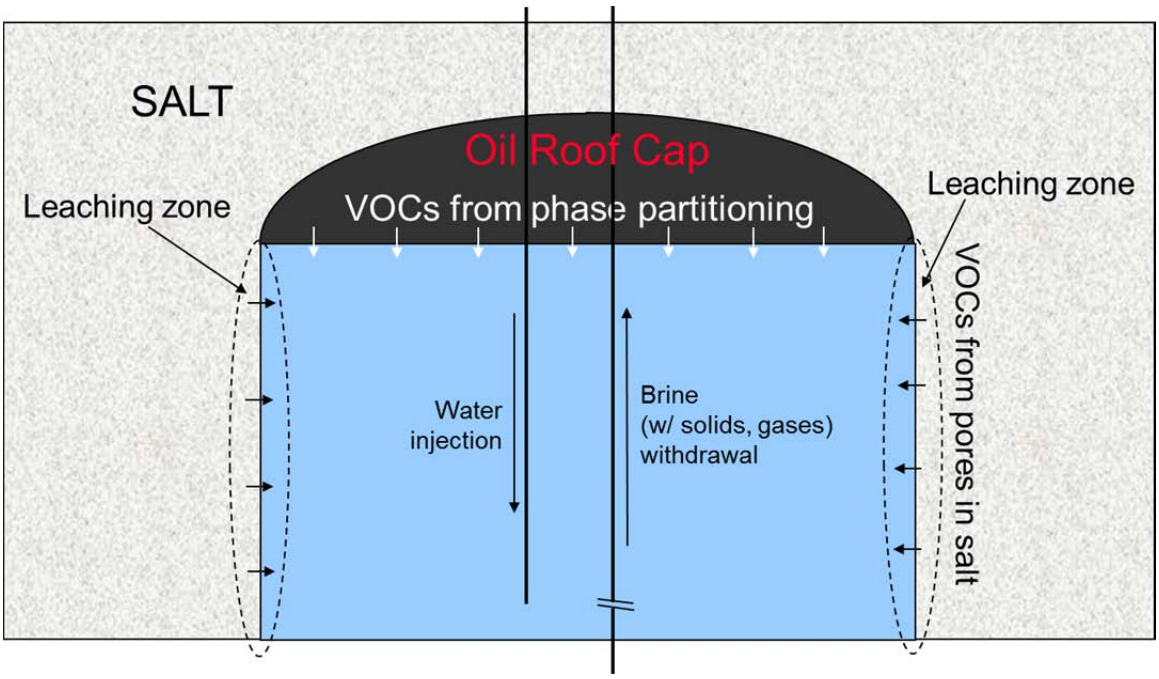

Figure 1-2. Schematic of hypothesized VOC uptake methods by brine during a leach operation in an SPR cavern.

A second operating condition that leads to brine disposal is oil fill, where incoming oil displaces brine from the cavern, as illustrated in Figure 1-3. Brine residence time and temperature in the cavern can vary widely under this scenario. A small brine pool may sit at the bottom of the cavern for years and reach 130°F if the cavern is full and remains in standby. Alternatively, if the cavern was recently drawn down, it will be full of cool, unsaturated brine that leached a lot of new salt and may have released a lot of gas from pores in the salt. If the cavern is quickly re-filled with oil, the brine discharged from that operation will likely have a different VOC make-up than that from a leaching operation or a cavern that was sitting filled for some time.

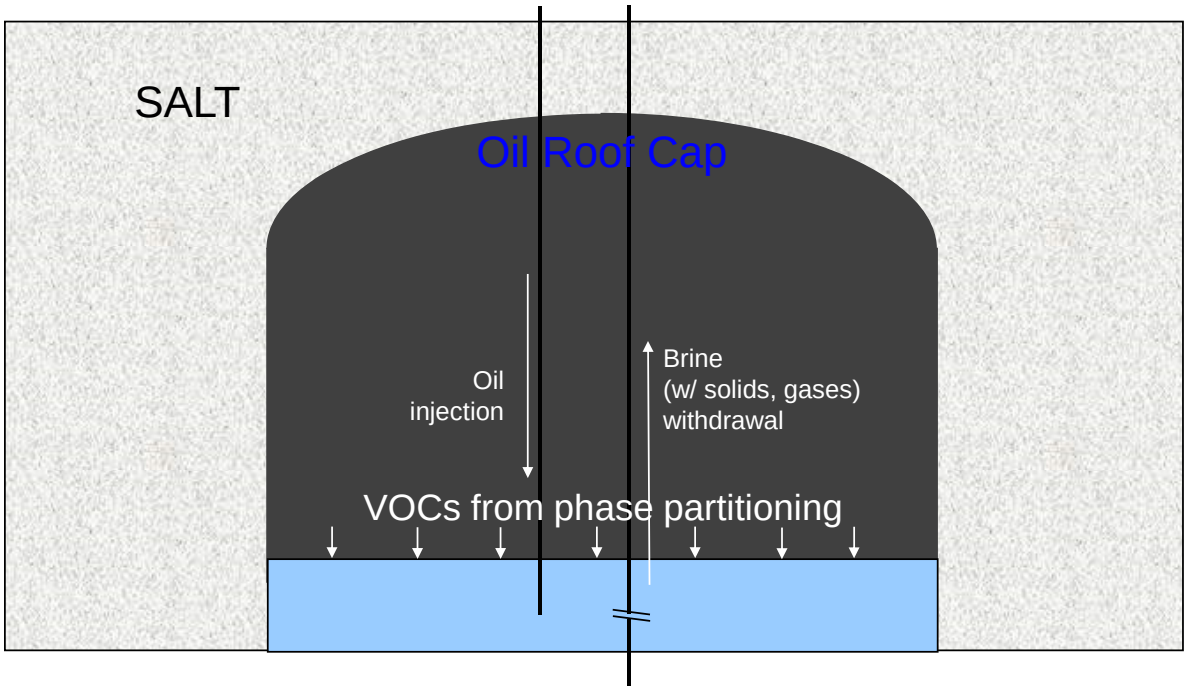

Figure 1-3. Conceptual model of brine movement during oil fill.

The US Environmental Protection Agency (USEPA) has set limits on the amount of VOCs that can be discharged to the atmosphere. Several attempts have been made to quantify the VOC emissions associated with the brine ponds. There are potential issues associated with each of these quantification efforts.

There have been two attempts at quantifying the amount of volatile organic carbon (VOC) emissions from brine ponds based on analyses of brine samples. The first study published in 1978 (DOE, 1978) was the original Environmental Impact Statement (EIS) for the SPR. In this study, the amount of soluble hydrocarbons in brine was estimated from other literature sources and various multipliers assigned to account for the effects of pressure, temperature, etc. No data were collected on actual brine samples or VOC emissions. In the second study (DOE, 1981), an updated EIS published in 1981, twelve samples of brine were collected and VOCs measured from the samples. These data were then used in a series of computer models to predict VOC emissions from the brine ponds. No measurements of VOC emissions were performed in situ to support the EIS emissions estimates. After the Final EIS, there are reports of air quality monitoring occurring at two sites, but the data to support these assertions is not at hand (see below). Additional information regarding these analyses is provided in the next section of this report. Recently, additional brine sampling was performed to address statistical confidence in the VOC emissions estimates. Results of this analysis are provided in this report. Methods exist to directly measure VOC emissions. Some of these methods are summarized in this report for possible consideration for future sampling. Recommendations for future work are also provided in a subsequent section.

2 PRIOR WORK

The SPR program has limits on the amount of VOCs that can be discharged to the atmosphere from their operating facilities. The majority of the VOC emissions come from off-gassing at the surface of the brine ponds. A summary of the VOC emission estimates is provided in this section of the report.

2.1 VOC Estimates from 1978 EIS

The analysis of VOC emissions from the brine ponds in the 1978 EIS (DOE, 1978) was considered a conservative, worst-case scenario due to the lack of measurement data at the time. Data on the concentration of soluble hydrocarbons in brine were shown for 6 different crudes ranged from 7 to 40 ppm, with most data in the 20-30 ppm range. The Murban crude was thought to be representative and conservative at 27.9 ppm for an equilibrium concentration. The effect of temperature on solubility was considered. Cavern temperature was assumed to be 150° F. A multiplier of 1.5 was used to account for the temperature increase. The effect of pressure on solubility was considered. A multiplier of 5.0 was used. The effect of salinity on solubility was considered. A multiplier of 0.15 was used. The net effect of the temperature/pressure/salinity corrections is a multiplier of 1.125. An oil film on the cavern wall was assumed to disperse into the brine. The thickness was assumed to be 50 microns. This would contribute an additional 1.6 ppm to the estimate of VOCs in the brine. The oil-brine interface would contribute some hydrocarbons to the brine in the top 50 feet of the cavern, and then mix with the rest of the brine. A refractory layer is expected to form which would decrease dissolution. The final estimate of dissolved hydrocarbon concentration in the brine emission was 6 ppm.

2.2 VOC Estimates from 1981 EIS

The analysis of VOC emissions from brine was updated in the 1981 EIS (DOE, 1981). Data on the concentration of soluble hydrocarbons in brine were taken from Bryan Mound. Twelve samples were analyzed, with six samples collected on each of two separate days in June 1981. The head space in the samples was sampled and analyzed. The VOCs dissolved in the brine were also measured. A mass balance was performed to estimate the total VOCs present in each sample. The worst case concentrations from cavern 2 were 3.0 ppm for non-methane hydrocarbons (NMHCs). The fraction of NMHC that went to vapor ranged from 50 to 90 percent. A mean vapor partition factor of 0.85 was used to estimate the volatile emissions from the brine. An oil film on the cavern wall was assumed to disperse into the brine. The thickness was assumed to be 50 microns. In an 11 million barrel (MMBbl) cavern this would be an estimated 29.2 barrels of crude available for dissolution, but only half will go into solution and half would rise to combine with the oil/brine interface. The result is an additional 1.0 ppm of dissolved hydrocarbon.

At the beginning of a refill, a dilution factor of 11 is considered appropriate as applied to the initial 3.0 ppm concentration. This yields a 0.27 ppm concentration. The oil film on the wall adds 1.0 ppm, for a starting concentration of about 1.3 ppm. By the end of the fill, the worst case concentration would be in effect at 3.0 ppm. Assuming a linear increase during the fill, the mean

concentration would be 2.2 ppm. Applying the vapor partition coefficient of 0.85 yields a volatile emission of 1.9 ppm during refill.

Computer modeling was also done to estimate VOC emissions. The Single Source Model, CRSTER, was run using meteorological inputs over a year time-frame to determine what day of the year would have the "worst-case" results. The model suggested that June 25 had the maximum 1-hour concentration and yearly maximum 3-hour and 24-hour concentrations. Subsequently, the rural version of the Efficient Gaussian Plume Multiple-Source Air Quality Algorithm Model (RAM) was used to predict VOC emissions throughout the 24-hour day for the maximum predicted effects.

The results of the brine sample analyses reported in the 1981 EIS do not appear to be documented anywhere else. Nowhere in this document do they reference a study that details the acquisition and analysis of these samples. The samples were collected in June 1981. A check in the Sandia National Laboratories (SNL) SPR library for data reports produced in 1981 came up negative. There are correspondences in the library that have yet to be cataloged into the system, and a cursory check of these resources also came up negative. It would appear that the first time the sample data were published is in the actual 1981 EIS report. The modeling to support the VOC emissions projections also appears for the first time in the 1981 EIS report, including tables of representative model outputs.

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3 RECENT BRINE SAMPLING

SPR recently commissioned brine sampling from twelve wells and conducted laboratory analysis tests on these samples for VOC concentrations. The intent of this sampling was to compare results to the previous sampling performed for the 1981 EIS to see if the results might lend themselves to a different estimate of VOC emissions. The results of these laboratory extraction tests are being compared to previous VOC concentration estimates/assumptions made for permitting of VOC emissions from the brine ponds.

Two wells, the West Hackberry WH-110 and Big Hills BH-101, were sampled in December 2011 and March 2012, respectively. Four samples were collected and analyzed for the former well and three for the latter. The laboratory reports for these samples are reproduced in Appendix A. Table 3-1 shows a summary of the pertinent results as they pertain to estimated VOC concentrations that could lead to VOC emissions for the West Hackberry samples.

Table 3-1. VOC estimates for WH-110

Sample	Gas MW	Wt% VOC	GLR	ton/MMBbl
WH-110-1	29.7	8.05	0.09	0.28
WH-110-2	29.7	8.05	0.05	0.16
WH-110-3	29.7	8.05	0.11	0.36
WH-110-4	29.7	8.05	0.06	0.20
Mean	29.7	8.05	0.08	0.25
Standard Deviation	0	0	0.028	0.089

In Table 3-1, the Gas MW column represents the molecular weight of all gases in the sample. The Wt% VOC represents the weight percent of NMHC VOCs present. The GLR represents the Gas-to-Liquid Ratio of the sample. The last column represents the estimated concentration of VOCs in the samples as tons per million barrels. Table 3-2 summarizes results as they pertain to estimated VOC concentrations for the Big Hill samples.

Table 3-2. VOC estimates for BH-101

Sample	Gas MW	Wt% VOC	GLR	ton/MMBbl
BH-101-1	29.55	6.16	0.06	0.14
BH-101-2	30.11	9.01	0.02	0.07
BH-101-3	29.94	11.3	0.02	0.09
Mean	29.87	8.82	0.03	0.10
Standard Deviation	0.29	2.58	0.023	0.036

The regulatory limit established for VOC emissions is 0.42 ton/MMBbl. The results from these two wells are well within this limit. In a review of these data, however, a question was raised as to the statistical significance of this many samples and the ability to draw conclusions from the data.

The USEPA (2009) provides guidance (referred to as Unified Guidance) on statistical sampling as it relates to groundwater monitoring at Resource Conservation and Recovery Act (RCRA)

permitted facilities. These statistical techniques have some applicability to the VOC emission issue. There are other statistical methods to derive confidence levels for sampling design, but this RCRA recommended method is arguably the method to use for this purpose.

The Unified Guidance suggests that a minimum data set should contain at least 4 samples, but that 8 or more is preferable for statistical significance. This is a general rule of thumb. A more definitive estimate of the number of samples desired can be made with the following equation:

$$n = f(\alpha, \beta) \times ((2 \times \sigma^2)/\delta^2)$$

where:

n = number of samples

$f(\alpha, \beta)$ = a functional relationship derived from a lookup table

α = significance level, where $(1-\alpha)$ = confidence level

β = power level, where $(1-\beta)$ = surety level

σ = standard deviation

δ = difference desired to detect

The lookup table for $f(\alpha, \beta)$ is shown in Table 3-3.

Table 3-3. Lookup table for f(α,β)

	β			
α	0.05	0.1	0.2	0.5
0.05	13	10.5	7.9	3.8
0.01	17.8	14.9	11.7	6.6

The Unified Guidance suggests that a 95% confidence level is typical for statistical analyses. The surety is generally up to the user, but could be anywhere from 80% to 95%. With the limited data provided for the two wells that were sampled, the standard deviation of the data is probably not accurate and therefore will bias the estimate of the number of samples desired. With more data, the estimate may change. The δ parameter (i.e., difference desired to detect) is a measure that should be decided by the project lead. In the following recommendations this parameter is put forth as a percent difference from the mean estimate.

The data set for well WH-110 had a mean VOC concentration of 0.25 tons/MMBbl, and a standard deviation of 0.089 tons/MMBbl. Assuming that the desired confidence is 95%, a table of results can be developed for several different values of surety and δ. Table 3-4 shows a range of sample numbers for varying values of surety and δ for WH-110.

Table 3-4. Number of samples needed for a 95% confidence with varying surety and difference desired from cavern WH-110.

	δ (% of mean)					
(1-β) (%)	5	10	15	20	25	50
95	1309	327	145	82	52	13
90	1057	264	117	66	42	11
80	795	199	88	50	32	8

To understand this information, the cell highlighted in yellow has a value of 11, which in this context represents the number of samples needed to be 90% sure that 95% of the time you will be within 50% of the mean. If you want to be more sure or be closer to the mean, the number of samples needed will increase. So in contrast, if you want to be 95% sure that 95% of the time you will be within 5% of the mean you would need to collect 1309 samples.

The data set for well BH-101 had a mean VOC concentration of 0.10 tons/MMBbl, and a standard deviation of 0.036 tons/MMBbl. Similar to the above analysis, Table 3-5 shows a range of sample numbers for varying values of surety and difference desired for BH-101.

Table 3-5. Number of samples needed for a 95% confidence with varying surety and difference from cavern BH-101

	δ (% of mean)					
(1-β) (%)	5	10	15	20	25	50
95	1352	338	150	84	54	14
90	1092	273	121	68	44	11
80	822	205	91	51	33	8

It should be noted that the mean and standard deviations for the two wells appear to be significantly different. If more data existed, a quantitative comparison of the two data sets could be made to determine if they are statistically different (e.g., t-test comparison). However, there is an algorithm referred to as Cohen's Rule of Thumb that allows a quick look at differencing of means that can be applied to evaluate the relative difference in these two data sets. The 'effect size', or d, is defined as:

$$d = (\mu_1 - \mu_2) / (\text{sqrt}(\sigma_1^2 + \sigma_2^2) / 2)$$

where:

μ = mean

Subscripts denote two different data sets. For the two data sets for the two wells the effect size, d, is estimated at 2.2. Cohen's guidelines are as follows:

d ~ 0.2 is a small effect size

d ~ 0.5 is a medium effect size

d ~ 0.8 is a large effect size

So with a d ~ 2.2 this denotes a large effects size, indicating that the two data sets are likely statistically different.

The results of sampling these two wells do not provide the confidence that is likely required to quantify VOC emissions. Therefore additional sampling was recommended. Given that the cost of sampling and analysis is not trivial, there may be a need to perform a cost-benefit analysis to assess the target sampling design.

Eleven more samples were collected from caverns between November 2012 and January 2013. This included wells from West Hackberry (WH), Bryan Mound (BM), Big Hill (BH), and Bayou Choctaw (BC). Table 3-6 shows the VOC results for these additional eleven samples. The mean results from the replicates of the previous two samples collected are also included. The means and standard deviations of all 13 samples are shown in Table 3-6 as well.

Table 3-6. VOC estimates for thirteen caverns.
(* - mean data from replicate sampling)

Sample	Gas MW	Wt% VOC	GLR	ton/MMBbl
WH-115	28.83	6.93	0.05	0.13
WH-107	30.14	4.48	0.08	0.14
WH-011	21.16	3.78	0.22	0.23
WH-103	28.80	1.21	0.12	0.05
WH-104	29.05	5.51	0.11	0.23
BM-113	28.33	6.22	0.14	0.32
BC-018	40.28	23.39	0.08	0.98
WH-106	30.45	12.29	0.11	0.54
BC-019	29.07	0.60	0.15	0.03
BC-101	32.64	8.76	0.005	0.02
BH-101	28.41	0.073	0.005	0.00
WH-110*	29.7	8.05	0.078	0.25
BH-101*	29.87	8.82	0.03	0.10
Mean	29.75	6.93	0.09	0.23
Standard Deviation	4.08	6.10	0.06	0.27

These data range from 0.0 to 0.98 tons/MMBbl. The mean VOC concentration of the thirteen samples is 0.23 tons/MMBbl and a standard deviation of 0.27 tons/MMBbl. With this relatively large standard deviation compared to the mean it can be concluded that there is significant variability in the results. One factor that may contribute to this variability is the operational history of the wells prior to sampling. The West Hackberry wells WH-103, WH-104, WH-107, WH-110, and WH-115 had undergone depressurization. Wells BM-113, BH-101, and WH-106 had undergone leaching. Well BC-018, with the highest VOC concentration, had undergone a fill operation.

The results of these sample analyses represent conditions at a point in time associated with the sampling events. They do not necessarily represent long-term release conditions.

An analysis of the confidence associated with these results is shown in Table 3-7.

Table 3-7. Number of samples needed for a 95% confidence with varying surety and difference desired from thirteen samples.

	δ (% of mean)					
(1-β) (%)	5	10	15	20	25	50
95	13899	3475	1544	869	556	139
90	11226	2806	1247	702	449	112
80	8446	2112	938	528	338	84

Again, noting the highlighted cell in Table 3-7, the data suggest that 112 samples would provide a 90% surety that 95% of the time the concentration will be within 50% of the mean. This is a

large number of samples with significant cost associated with acquiring and analyzing that many samples. These results are significantly different from the previous analysis of WH-110 and BH-101 because the standard deviation (i.e., variability) for the thirteen samples is markedly higher. Two of the samples in the data set are significantly higher than the rest, BC-018 and WH-106. As mentioned, BC-018 had undergone a fill operation and WH-106 a leaching operation. Other leached wells, BM-113 and BH-101, had lower concentrations than WH-106. Additional scrutiny of the sampling analysis processes for BC-018 and WH-106 might also provide some insights into why the concentration results were as high as they were.

Another aspect to consider is the operations in each of the caverns sampled. One would expect the brine concentration to be different for a fill operation versus depressurization or leaching. It might be advantageous to collect more samples to characterize each type of operation. The variability for each operation might be less than the overall variability, and therefore the confidence might be greater for fewer samples collected.

The Unified Guidance method cited above to estimate the recommended sample size for a desired confidence statement assumes that the data are parametric, or rather that they are normally distributed. A method exists to test whether a distribution is normal, called the Probability Plot Correlation Coefficient Test for Normality (Filliben, 1975). A series of calculations are made from the rank-ordered data set and the Poisson ratio, r, calculated. If the data are normally distributed the Poisson ratio should be close to a value of 1. The Poisson ratio was calculated for the 13 data points shown above with the result equal to 0.87. This value is not considered close enough to unity to describe the distribution as normal. Next, the data were log-transformed and the Poisson ratio recalculated. The one data point with a zero value was left out of this analysis because it cannot be log-transformed. The Poisson ratio, r, was calculated at 0.99 for this case. Therefore, the data are lognormally distributed. The Unified Guidance method was reapplied to the log-transformed data. Table 3-8 shows the results of this analysis.

Table 3-8. Number of samples needed for a 95% confidence with varying surety and difference desired from twelve log-transformed samples.

	δ (% of mean)					
(1-β) (%)	5	10	15	20	25	50
95	3729	932	414	233	149	37
90	3012	753	335	188	120	30
80	2266	567	252	142	91	23

Again, noting the highlighted cell in Table 3-8, the data suggest that 30 samples would provide a 90% surety that 95% of the time the concentration will be within 50% of the mean. This is a large number of samples with significant cost associated with acquiring and analyzing that many samples. The 13 samples already acquired would reduce the preliminary future sampling matrix to ~30 – 13 = ~17 more samples. Given that the methodology was already developed and demonstrated as part of the early sampling effort in 2011-2012, a reasonably straightforward schedule and budget could be developed for the 17 remaining samples if this pathway is required sometime in the future.

The stated regulatory limit of 0.42 tons/MMBbl of VOCs released does not account for any variations in the amount of brine pumped at each of the SPR sites. Total VOC release limits exist for each of the four sites, which are: Bryan Mound - 9.42 tons/yr; Big Hill - 13.15 tons/yr; West Hackberry - 22.22 tons/yr; and Bayou Choctaw - 1.26 tons/yr. Another approach to assessing the potential VOC release amount would be to estimate the total release of VOCs from the brine actually discharged from the caverns to the brine ponds for each site and compare to the release limits. In order to estimate the tons of VOCs released at each site annually an estimate of the amount of brine pumped to the ponds each year is needed. Table 3-9 has a summary of the brine pumped for each site broken down monthly and as a yearly total for the calendar year 2012 (data provided by DM Petroleum Operations).

Table 3-9. Brine discharges (barrels) at Bryan Mound (BM), Big Hill (BH), West Hackberry (WH), and Bayou Choctaw (BC) for the calendar year 2012.

Monthly Summary of Brine Discharges (BBL)				
	BM Brine	BH Brine	WH Brine	BC Brine
JANUARY 2012	2,804,693	2,057,379	2,211,576	823
FEBRUARY 2012	77,061	1,425,099	1,119,842	2,010
MARCH 2012	967,623	1,681,885	19,068	0
APRIL 2012	475,665	1,300,187	40,841	3,023
MAY 2012	2,438,180	2,118,946	865,033	5,416
JUNE 2012	2,635,278	2,033,966	2,685,758	597
JULY 2012	3,409,817	2,276,871	2,312,491	2,298
AUGUST 2012	2,268,865	3,175,055	2,137,450	1,380
SEPTEMBER 2012	785,728	2,786,517	2,448,803	732
OCTOBER 2012	334,199	386,423	147,513	0
NOVEMBER 2012	213,680	164,538	152,477	730
DECEMBER 2012	698,225	226,245	1,407,205	273,106
YEARLY TOTAL	17,109,014	19,633,111	15,548,057	290,115

For the purpose of this analysis, these discharges will be considered representative as a yearly estimate for each of the sites. From the 13 brine samples recently collected and analyzed for VOC content the mean result was 0.23 ton/MMBbl, with a standard deviation of 0.27 ton/MMBbl. If the mean is used as a representative concentration for all four sites and the discharge amounts shown in Table 3-9 used to assess the total estimated VOC releases, the results are shown in Table 3-10. Also shown in Table 3-10 is the regulatory limit for each site.

Table 3-10. VOC emission estimates (by current authors) at BM, BH, WH, and BC for the calendar year 2012.

	BM Brine	BH Brine	WH Brine	BC Brine
VOC emissions, mean [tons/yr]	3.76	4.32	3.42	0.06
Permit limit [tons/yr]	9.42	13.15	22.22	1.26

Based on the recent VOC data, Table 3-10 shows that there is a considerable difference between the allowable VOC emissions and the estimated discharge. SPR may be able to discharge considerably more brine than previously estimated. There should be some consideration, however, for the uncertainty in the data.

It is desirable to specify a confidence statement in developing a recommendation for the allowable discharge of brine. Specifying a 95% confidence bound on the data would be consistent with the Unified Guidance. The 95% confidence bound applied to the mean will yield both lower and upper confidence limits, thereby providing a 90% confidence interval (e.g., with 5% on each tail of the distribution, the difference is 90%). A standard confidence limit based on the central limit theorem is not appropriate for this data set due to the fact that it is not parametric. Fortunately, there is a non-parametric confidence bound technique that can be used based on work put forth by Guttman (Woo, 1989). The confidence bound is calculated as:

$$\text{Confidence bound} = (2.68 \times \sigma) / (n^{1/2})$$

The lower confidence limit is therefore the mean minus the confidence bound, and conversely the upper confidence limit is the mean plus the confidence bound. The lower and upper confidence limits for the VOC emission concentrations are calculated at 0.033 ton/MMBbl and 0.43 ton/MMBbl, respectively. The upper confidence limit therefore represents a 95% confidence limit. Incidently, the upper confidence limit is close in value to the regulatory limit of 0.42 ton/MMBbl. If the VOC emission estimates are carried out for the confidence limits, there is a 90% confidence interval predicted for the difference between the lower and upper confidence limits. Table 3-11 shows the results of these additional calculations.

Table 3-11. Results of uncertainty analysis and additional brine discharge estimates.

	BM Brine	BH Brine	WH Brine	BC Brine
Brine discharge to ponds, 2012 [barrels]	**17,109,014**	**19,633,111**	**15,548,057**	**290,115**
VOC emissions, lower confidence limit [tons/yr]	**0.56**	**0.64**	**0.51**	**0.01**
VOC emissions, mean [tons/yr]	**3.76**	**4.32**	**3.42**	**0.06**
VOC emissions, upper confidence limit [tons/yr]	**7.39**	**8.48**	**6.72**	**0.13**
Permit limit [tons/yr]	**9.42**	**13.15**	**22.22**	**1.26**
Additional discharge to meet limit* [barrels]	**3,684,576**	**6,969,734**	**10,847,977**	**261,257**

** - difference between the permit limit and the upper confidence limit emission estimate*

Figure 3-1 shows the VOC emission estimates in a graphical form. Even the upper confidence limit estimates of the VOC emissions are considerably below the permit limits for the individual sites. The difference between the estimated 95% upper confidence limit and the permit limit translates into additional discharge that could be realized. An estimate of the additional discharge, in barrels, that could be realized if VOC limits were attained is shown in Table 3-11 as well. These data obviously assume that the VOC concentrations obtained from recent laboratory testing translate into emissions once released to the brine ponds. This is thought to be a conservative assumption. Additional sample collection and testing may be desired to increase confidence in the results. Issues already mentioned include the representativeness of the samples depending on operations (e.g., fill, leach) and variability associated with each cavern. Actual

measurements of VOC emissions might also be considered. Options for VOC emission measurements are identified in the next section of this report.

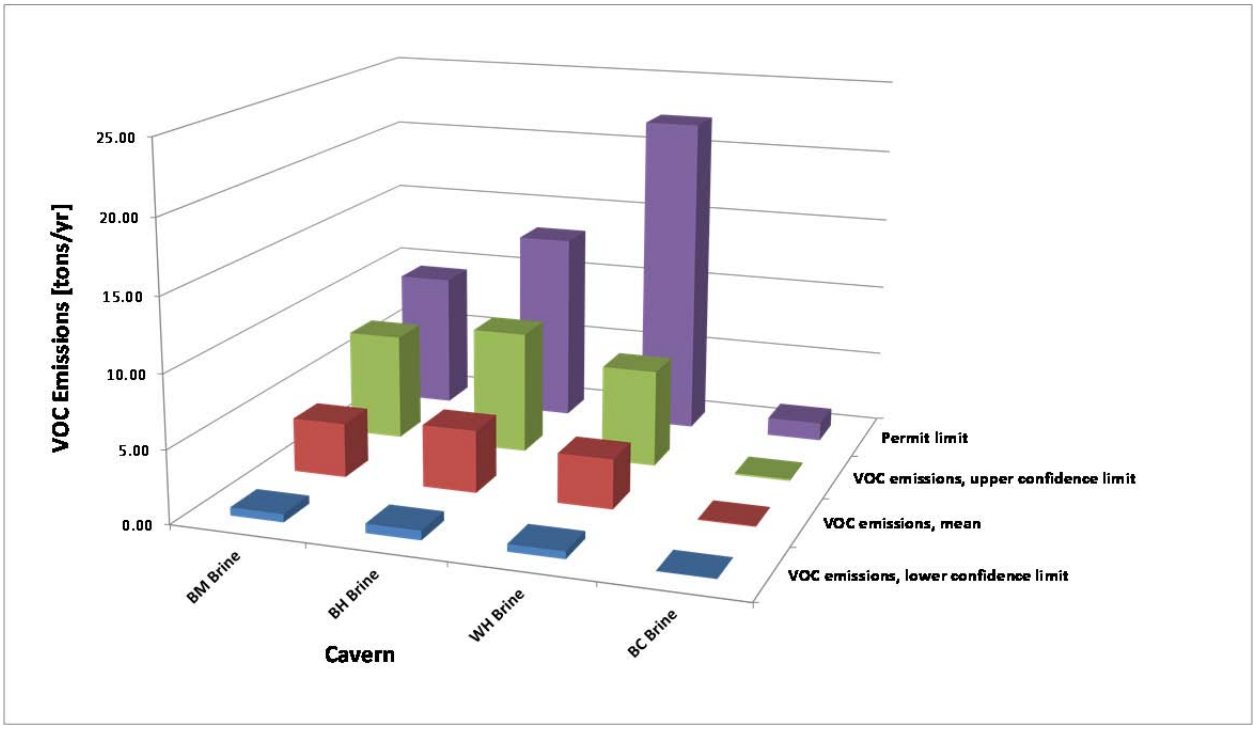

Figure 3-1. VOC emission estimates for the four SPR sites based on current brine study data and reported brine discharges for CY2012.

4 AIR QUALITY MONITORING

It is possible that air quality monitoring may have been performed to quantify VOC emissions at one or more SPR sites. In DOE (1992), there is an interesting statement on page 7-19: "Actual emissions may be substantially lower than the conservative maximum estimates. For example, at the Sulphur Mines site, hydrocarbon emissions from the brine pond, slop oil tank, pump seals, and valves totaled 9.4 tons from 1979 to 1984. This implies that measurements may have been taken at this site. The reference document cited is Petroleum Operations and Support Services (1983). However, the Document Number associated with this reference, 124-84-AS-001, appears to be for the 1983 annual report, not the 1982 annual report that is listed in the title. Which document they are referring to is problematic, because neither document appears to list the emissions amounts in the quote from DOE (1992). In the Petroleum Operations and Support Services (1983) document there is mention of an air quality monitoring program being started at Bryan Mound in the fall of 1982 and continuing for one year. The monitoring was supposed to include nonmethane hydrocarbons. The 1983 annual report, Petroleum Operations and Support Services (1984), mentions the results of the air quality monitoring at Bryan Mound by stating: "An internally conducted fugitive hydrocarbon emissions monitoring program was fully implemented during 1983 at Bryan Mound. All monitoring data indicated negligible fugitive emissions of volatile organic carbon (VOC) compounds during 1983." However, no data are provided in this report. No references are provided for the data. There is mention that quarterly reports required by the Texas Air Control Board permit were submitted on schedule during 1983. A search of the SNL SPR library did not find any mention of these quarterly reports. So, in summary, there may or may not have been VOC air monitoring performed at the Sulphur Mines site.

It appears that VOC air monitoring of some sort occurred at the Bryan Mound site during a one year period from 1982 to 1983, but the data are not readily attainable.

There are several methods available to quantify VOC emissions, which are presented in the next section.

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5 PROPOSED FUTURE WORK

There have been several attempts at quantifying the amount of VOC emissions from brine ponds. Two of these attempts did not actually measure the VOC emissions, but rather estimated them based on either literature data or laboratory data from brine samples (DOE [1978] and DOE [1981]). The SPR literature (DOE, 1992) makes claims to some measurements being taken in situ to estimate VOC emissions but no data or documentation of the efforts can be located. Measurement techniques exist to better quantify the VOC emissions from brine ponds than was done in the late 1970's and early 1980's. Several options are identified in this section of the report.

5.1 DIAL Measurement Method

There is a measurement device on the market that purports to have the ability to quantify VOC emissions in air. This system is called the differential absorption light detection and ranging system (DIAL). USEPA (2006) had the following to say regarding the performance of the DIAL system:

> The DIAL technique has been used extensively in Europe and more recently in Canada. As currently configured it uses both ultraviolet (UV) and infrared (IR) lasers to measure criteria pollutants (NOx, SO_2, and O_3) and light aromatic (benzene, toulene, ethylbenzene, and xylene) in the UV, and methane and total hydrocarbon plumes in the IR. DIAL is capable of providing a 2-dimensional contour of concentrations across a scanning plane. By combining this concentration contour with separately obtained wind speeds, a contaminant flux can be calculated. The DIAL system has been validated in European studies for hydrocarbon emissions. Estimated fluxes obtained by the DIAL system are generally assumed to be conservative.

The DIAL technique looks quite promising as a method for quantifying VOC emissions from brine ponds. In performing a literature search on the Internet it appears that there may not be any providers of this technology in the United States. A firm does exist in the United Kingdom that offers consulting services to perform this type of work. Additional work would need to be done to evaluate the feasibility of deploying this technology if the SPR is interested.

5.2 FTIR Measurement Method

A technique employing Fourier Transform Infrared (FTIR) spectroscopy analyses can identify and quantify certain organic and inorganic compounds in complex mixtures by measuring the unique infrared absorbance of each compound in the gas-phase. By comparing to reference spectra the compounds of interest are identified and quantified. With this method the FTIR device could be used to scan across the surface of the brine pond and get a two-dimensional representation of the concentration distribution of each of the compounds of interest that are emitting from the surface of the pond. This information could be gathered at multiple elevations to quantify a gradient. Coupling this with meteorological data the flux of VOCs could be determined. It might be wise to perform this monitoring operation under differing meteorological conditions to understand the range of results and the temporal variation that may be applicable. There are multiple commercial providers of this technology in the US. If SPR is interested in quantifying VOC emissions based on measuring the off-gassing from the brine ponds, this method appears to have the most promise for success. Additional research should be

undertaken to evaluate the pros and cons of employing this method for measuring the VOC emissions from the brine ponds.

5.3 Passive VOC Measurement Method

A passive VOC measurement technique might also be used to quantify VOC emissions from the brine ponds. There is an ASTM standard called "D7758 - Standard Practice for Passive Soil Gas Sampling in the Vadose Zone for Source Identification, Spatial Variability Assessment, Monitoring, and Vapor Intrusion Evaluations". This standard was developed for two main purposes: to identify the nature and extent of subsurface contamination of VOCs, and to evaluate the potential for VOC intrusion/migration into buildings. The passive techniques described in this standard rely on sorbent media in canisters to get a time-averaged mass estimate of VOC emissions. The sorbent media is analyzed in the laboratory to determine the mass of VOCs sorbed in the media. The techniques identified in the standard are intended for use in soil or at the land surface but could be modified slightly for use in estimating VOC emissions from a brine pond. Placement of the canisters could be a challenge if it was deemed necessary to get a vertical flux estimate from the surface of the brine pond. An alternative might be to place canisters at different elevations at the edge of the pond in the downwind direction to assess the amount of VOCs leaving the pond. This data coupled with meteorological data could result in estimates of VOC emission rates and cumulative mass amounts of release. These measurements should be performed at different times of the year to assess the temporal variation of the VOC emissions. One attractive aspect of the passive canister methods is that they may be able to quantify lower emission rates due to the nature of the long-term sorption occurring in the media of the canisters. The challenge in employing this type of approach is how to get the canisters placed in representative locations to make appropriate emissions measurements.

5.4 Active VOC Measurement Method

An active VOC measurement technique might also be used to quantify VOC emissions from the brine ponds. There is an ASTM standard called "D7663 - Standard Practice for Active Soil Gas Sampling in the Vadose Zone for Vapor Intrusion Evaluations". This standard was developed to evaluate the potential for VOC intrusion/migration into buildings. With the active sampling techniques, a vacuum is applied to a sampling tube and air is drawn into a canister or a sorbent tube. Measurements of VOC concentrations could be made on site with the proper analytical measurement devices present. Otherwise the canisters or tubes would be sent to a laboratory for analysis. The standard provides formulas for calculating the VOC concentrations based on sampling parameters and the analytical results. As with the passive VOC measurement method, the locations for sampling above the surface of the brine ponds or downwind of the ponds could be a challenge. These measurements should be performed at different times of the year to assess the temporal variation of the VOC emissions. If the VOC concentrations are too low relative to the detection limits of the analytical measurement devices, then this method will not be suitable.

5.5 Additional Brine Sampling and Analysis

Another option available to quantify the VOC emissions is to continue the prior practice of sampling the brine and performing calculations to estimate the releases. The recent brine sampling and statistical analysis raised some questions about the variability associated with the cavern operations and potential release amounts. The range of the results was arguably significant. The sampling and analysis procedures for the two highest concentration results

should be scrutinized in more detail prior to finalizing any conclusions. Additional sampling might be informative in order to address the variability in VOC composition from different caverns and different SPR operations (e.g., leaching, fill, depressurization).

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6 PATH FORWARD

A number of options have been identified to address the issue of VOC emissions from brine ponds. Quantifying the VOC emissions through direct measurement is preferable to sampling upstream and extrapolating the results from laboratory measurements. This approach is not without some uncertainty, but may provide additional insights into quantifying the VOC emissions. So in order of preference, the following techniques should be considered:

- FTIR measurements
- Brine sampling and additional data scrutiny to address uncertainty

Whatever approach is chosen, a scope of work would need to be developed to identify the actions to be taken, the products to be realized from the work, as well as time and cost estimates to perform the work.

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7 CITED REFERENCES

Department of Energy (DOE), 1978, Final Environmental Impact Statement, Strategic Petroleum Reserve, Seaway Group Salt Domes, DOE/EIS-0021, UC-11, 13, 92, U.S. Department of Energy, Washington, D.C., June 1978.

Department of Energy (DOE), 1981, Final Supplement to Final Environmental Impact Statements, Strategic Petroleum Reserve, Phase III Development, Texoma and Seaway Group Salt Domes, DOE/EIS-0021, 0029, U.S. Department of Energy, Washington, D.C., October 1981.

Department of Energy (DOE), 1992, *Draft Environmental Impact Statement on the Expansion of the Strategic Petroleum Reserve*, Volume 2 of 3, Chapters 6-13, DOE/EIS-0165-D, Washington, D.C., October 1992.

Filliben, J.J., 1975, "The Probability Plot Correlation Coefficient Test for Normality", *Technometrics*, Vol. 17, No. 1. (Feb., 1975), pp. 111-117.

Petroleum Operations and Support Services, Inc., *1982 Annual Environmental Monitoring Report, Strategic Petroleum Reserve*, U.S. Department of Energy, Strategic Petroleum Reserve Project Management Office, New Orleans, LA, March 31, 1983, Document Number 124-83-AS-001.

Petroleum Operations and Support Services, Inc., *1983 Annual Environmental Monitoring Report, Strategic Petroleum Reserve*, U.S. Department of Energy, Strategic Petroleum Reserve Project Management Office, New Orleans, LA, March 31, 1984, Document Number 124-84-AS-001.

U.S. Environmental Protection Agency (USEPA), 2006, *VOC Fugitive Losses: New Monitors, Emission Losses, and Potential Policy Gaps*, 2006 International Workshop, Office of Air Quality Planning and Standards, Research Triangle Park, Office of Solid Waste and Emergency Response, Washington, DC, October 25-27, 2006.

U.S. Environmental Protection Agency (USEPA), 2009, Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities, Unified Guidance, EPA 530/R-09-007, U.S. Environmental Protection Agency, Office of Resource Conservation and Recovery, Program Implementation and Information Division, Washington, D.C., March 2009.

Woo, G., 1989, "Confidence Bounds on Risk Assessments for Underground Nuclear Waste Repositories." *Terra Nova*, Volume 1, p. 79-83, Blackwell Publications, Oxford, England.

8 APPENDIX A: LABORATORY ANALYSIS REFERENCES

Filename	Cavern	Sampling date	Sampling location	GLR
				scf/bbl
38670 Preliminary Data.xlsx	BH101	3/15/2012	Wellhead	0.06
38670-5012048437.xlsx	BH101	3/19/2012	Wellhead	0.06
39812-5012128466.xlsx	WH115	11/8/2012	Wellhead	0.05
39813-5012128458.xlsx	WH107	11/8/2012	Wellhead	0.08
39814-5012128460.xlsx	WH011	11/8/2012	Wellhead 11A	0.22
39815-5012128461.xlsx	WH103	11/8/2012	Wellhead	0.12
39816-5012128467.xlsx	WH104	11/8/2012	Wellhead	0.11
39946-5013018377.xlsx	BM113	12/13/2012	Wellhead	0.14
39976-5013018433.xlsx	BC018	12/18/2012	Wellhead	0.08
39988-5013018429.xlsx	WH106	12/21/2012	Wellhead	0.11
40043-5013018432.xlsx	BC019	1/19/2013	Wellhead	0.15
40044-5013018439.xlsx	BC101	1/9/2013	Wellhead	0
4014-5013028425.xlsx	BH101	1/29/2013	wellhead	0
40041-5013018448.xlsx	WH109	1/8/2013	Wellhead	0.19

The individual lab reports for each of the above samples have been archived in the Sandia SPR library. The current contact for access to the SPR library is Carolyn Kirby (clkirby@sandia.gov)

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Wayne Elias (wayne.elias@hq.doe.gov) for distribution to DOE SPR Program Office, Washington, DC

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