

February 6, 2012

New Mexico Environmental Department Hazardous Waste Bureau (HWB) 1301 Siler Road, Building B Santa Fe, NM 87507 ✓ Attn: Kristen Van Horn

New Mexico Energy, Minerals and Natural Resources Oil Conservation Division (OCD) 1220 South St. Francis Drive Santa Fe, NM 87505 Attn: Mr. Carl Chavez



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# Re: REPORT #3: Semi-annual Report submittal for Passive Bioremediation (Bio-ventilation) Project for Ultra Low Sulfur Diesel (ULSD) remediation in accordance with NSR Permit No. 0633-M8-R3, Part A.214

Dear Ms. Van Horn and Mr. Chavez:

On October 16, 2010, Western Refining Company, L.P. (Western) - Gallup Refinery (the "facility") was granted New Source Review (NSR) Permit 0633-M8-R3 which, under Part 1.214,, allowed the installation of a Passive Bioremediation (Bio-Ventilation) System for the Ultra Low Sulfur Diesel (ULSD) fuel spill that occurred at the facility. The objective of the bio-ventilation system is to decrease the average VOC concentration over time to a satisfactory standard. As part of this permit allowance, Western is required to submit semi-annual reports to the Agency. This semi-annual report includes monitoring data and analytical results from July 1, 2011 through December 31, 2011 in order to meet the requirements of the NSR permit and provides both a discussion and statistical analysis to the effectiveness of the remediation system.

In addition, Western will attempt to address the questions and/or concerns that were posed by the Agency in its July 22, 2011 email.

# **Question #1:**

"It is not clear if Western is using a dilution kit or not, but that would not account for such high PID readings. Is Western using response factors and not showing that in the data?"

## **Response:**

Western Leak Detection and Repair (LDAR) contractors do not use dilution kits to obtain PID measurements. These measurements are collected from each standpipe individually. The response factor is not shown in the data table but the response





time is included in the "QC Calibration Form" shown under the "Response Time" section. Please refer to the attached "Calibration and Drift Assessment Form."

# **Question #2:**

"Western hasn't commented about the PID numbers being highly variable and may prove difficult to demonstrate remediation is effective."

#### **Response:**

Concentration variability was addressed in Semi-annual Report #2 where a negative trend was established between the time since monitoring began and daily average volatile organic compound (VOC) concentrations. Section 1 of that report presents a regression analysis which indicates a decrease in VOC concentrations over time (i.e. a negative slope) since monitoring began. Furthermore, the daily average VOC concentration shown in that report (15,256 parts per million) has decreased by 6.7 percent to a concentration of 14,233 ppm in the December 2011 monitoring results. Individual fluctuations are attributable to a number of factors including ambient temperature variations, atmospheric and soil moisture contents, individual point source concentrations at time of deposition, and the non-uniformed soil conditions surrounding each individual standpipe. Further statistical evaluation and analysis provides additional assurance that effective remediation is in progress. Please refer to the discussion below for further details.

This report includes several attachments including the Bio-ventilation Monitoring Log (Attachment 1), Linear Regression Statistical Analysis Summary (Attachment 2) and the Daily Average VOC Concentration versus Time graph (Attachment 3). Also included in Attachment 4 is the QA/QC data provided by the LDAR contractor. A detailed discussion of each will follow below.

## **VOC Monitoring and QA/QC Procedures**

LDAR personnel conduct the VOC monitoring using a Flame Ionizing Detector (FID) (TVA-1000) in accordance with the United States Environmental Protection Agency (U.S. EPA) Method 21. LDAR personnel use the QA/QC procedures for VOC monitoring on a daily basis as prescribed by Method 21. As mentioned above, Western LDAR contractors do not use a dilution kit to obtain PID measurements. These measurements are collected from each standpipe individually. The response factor is not shown in the data table but is included in the "QC Calibration Form" shown in the "Response Time" section. Please refer to the attached "Calibration and Drift Assessment Form" in Attachment 4.

## **Monitoring Schedule**

Initial VOC monitoring was conducted on a bi-weekly basis from December 2010 through January 2011 in order to establish a VOC baseline concentration. In February 2011, VOC monitoring frequency was changed from a bi-weekly to a monthly basis. Western conducted



monthly VOC monitoring through June 2011. Beginning on July 1, 2011, Western commenced a quarterly VOC monitoring schedule. One sampling event was conducted in the 3<sup>rd</sup> quarter of 2011 (September 28) and three sampling events were conducted in the 4<sup>th</sup> quarter (November 7, November 15, and December 12) to further assure the validity of the sampling results.

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# **Discussion of Semi-annual Monitoring Period Results**

The daily average VOC concentration for all sampling points combined was calculated for each sampling event and is reflected at the bottom of each column in the Bio-ventilation Monitoring Log. The Daily Average VOC Concentration and Temperature versus Time plot reflects an overall decrease in the VOC concentration from the initial event (December 7, 2010); however, there is an increase from the daily average value in the Semi-annual Report #2. The "overall" average of the system, which is the average of each sampling point combined over all sampling events, in Report #2 is 15,256 ppm and the overall average of the system as shown here is 15,891 ppm. This indicates an overall VOC increase of 635 ppm, which is primarily due to the September 28, 2011 sampling event on which several sampling points [C(8), C(9), C(14), and C(15)] resulted in sampling spikes. These abnormally high values tend to skew the actual trend resulting in a slight increase in the overall system efficiency. Although the exact cause of these sampling spikes is unknown, higher values may be the result of this semi-annual sampling period occurring during the warmer months. Soil temperatures during September reach near their annual peak which increases the volatility of the spilled material.

Regardless of individual daily spikes or seasonal impacts, the overall daily average VOC concentration has decreased over time as indicated by the negative slopes consistently calculated in the Linear Regression Statistical Analysis Summary. The initial daily average VOC concentration on December 7, 2010 was measured as 27,847 ppm and the daily average from December 12, 2011 was measured at 9,463 ppm. The data indicates that there is an average negative slope of -23.6 ppm per day with a 60.0% probability that this trending slope exists. Further detail and explanation of the statistical analysis will be provided below to further describe these calculations and provide additional confirmation on the bio-ventilation remediation system's VOC reduction progress.

The graph of the "Daily Average VOC Concentration versus Time" illustrates the reduction in VOC concentration over time. The individual spikes on 12/27/2010 (42,589 ppm), 2/17/2011 (28,850 ppm), and 9/28/2011 (34,654 ppm) tend to skew the overall trending slope and therefore reduces the overall efficiency. These individual fluctuations are not uncommon and, as mentioned before, are partially due to ambient temperature variations, individual point source concentrations at time of deposition, and the non-uniformed soil conditions surrounding each individual standpipe. However, by fitting an exponential curve to the daily average VOC concentration one can see a definitive decrease in the overall VOC concentrations in the system. As expected, the bio-ventilation system's daily average VOC concentration has a high initial concentration with an exponential decay over time.

The relative outside temperature has been plotted in conjunction with the daily average VOC concentration in the "Daily Average VOC Concentration versus Time' graph as a mode of comparison. There appears to be a correlation between the outside temperature and the VOC



concentration; however, several other variables contribute to the overall VOC concentrations and impact the significance of the temperature and VOC concentration correlation. Also, the temperature represents the average daily atmospheric temperature and does not reflect the soil temperature thus the correlation is time lagging. Concentrations tend to increase in the late summer months when the soil temperature is near its annual peak and appear to be declining again as the winter months approach and ground temperatures again decrease.

The daily average VOC concentration per sampling event has been trending downward from February 2011 which is indicative of a reduction in VOC Concentration. The initial VOC concentration measured on December 7, 2010 was 27,847 ppm. From December 7, 2010 to February 2011, the daily concentrations ranged from the initial value of 27,847 ppm to a maximum concentration of 42,589 ppm (December 27, 2010), to a minimum value on January 21, 2011 of 6345 ppm. In February 2011, monthly sampling began and on February 17, 2011 the daily average VOC concentration was 28,850 ppm. Over the next four months (I.e., March 2011 through June 2011) the daily average declined significantly relative to the first three months of sampling with a minimum of 82 ppm (March 22, 2011) and a maximum of 7,881 ppm (June 28, 2011). The overall average VOC concentration of all thirteen daily sampling events is 15,891 ppm which represents a 42% overall reduction in the VOC concentration from the initial sampling event (27,847 ppm). In Semi-annual Report #2, the overall daily average was 15,256 ppm thus there has been an increase in the overall average of 635 ppm that equates to an overall increase of 4.2% within this semi-annual monitoring period. This increase is primarily due to individual VOC fluctuations or spikes at standpipes # 8, 9, 14, and 15.

The major focus should be on the overall efficiency of the system and not individual fluctuations. These individual VOC fluctuations should be dampened using statistical analysis in order to analyze the system more effectively thus a linear regression analysis was applied to each monitoring point to determine if there is indeed a statistically valid negative trend in the VOC concentrations over the monitoring period.

The overall average slope was -23.56 ppm per day which indicates a declining trend in the VOC concentration over time. The F-value calculated in the regression analysis, and shown in Attachment 2, is compared to the F-distribution to determine the probability that a given F-value occurs by chance. Subtracting this probability from 1 provides a measure of the likelihood that the established linear trend exists between the VOC concentration and time. The average probability of a linear trend existing is 0.60 (60%); however, similar to the analysis above the data is skewed due to the sample spikes at several sampling locations. Many of the sampling locations indicate negative trends with greater than 95% confidence.

## Conclusion

Passive bioremediation (bio-ventilation) of ultra low sulfur diesel (ULSD) for spill material in order to augment reduction of VOC concentration is a time dependent process. The objective of the bio-ventilation system is to decrease the average VOC concentration over time to a satisfactory standard and monthly VOC monitoring through December 2011 per the requirements of the NSR permit has been performed in order to evaluate the effectiveness of the bio-ventilation system. Although several higher than average sampling measurements





occurred within the last semi-annual period, the average VOC concentrations at most all monitoring locations appears to be decreasing. To confirm this statement, a linear regression statistical analysis was performed in order to fit a linear trend line through the VOC concentration versus time data set. The trend line indicates that a negative slope exists in this data set and for the majority of the sampling locations greater than 95% confidence that this trend line is statistically valid exists.

Western intends to continue the quarterly sampling routine until satisfactory remediation has occurred and will submit to the Agency additional semi-annual progress reports approximately thirty days after the end of each semi-annual period. If you should require any additional information or assistance in this matter, please contact me at the number listed below or via e-mail.

Sincerely,

Beck Larsen, CHMM/REM/PG Environmental Engineer Western Refining Southwest

Direct Line: (505) 722-0258 e-mail: <u>Thurman.larsen@wnr.com</u>

Cc: File Attachment: #4- Qa/Qc Data; Calibration and Drift Assessment Form



**Bio-Ventilation Monitoring Log** Attachment 1

Passive Bioremediation Project Semi-Annual Report for July 1 – December 31, 2011 Western Refining Company, L.P. – Gallup Refinery

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