Groundwater & Environmental Services, Inc.
MARYLAND OFFICE

February 15, 2019

Mr. Nick Psenicnik
Oil Control Program
Maryland Department of the Environment
1800 Washington Blvd, Suite 620
Baltimore, Maryland 21230

RE: **2018 ANNUAL REMEDIAL EVALUATION REPORT**
Carroll Independent Fuel/Former Green Valley Citgo
11791 Fingerboard Road
Monrovia, Maryland
OCP Case #2005-0834-FR

Dear Mr. Psenicnik,

Groundwater & Environmental Services, Inc. (GES), on behalf of Carroll Independent Fuel (Carroll), is pleased to submit the 2018 Annual Remedial Evaluation Report for the Carroll/Former Green Valley Citgo facility (Site). Completion of an annual remedial evaluation for the Site was proposed in the *Revised Corrective Action Plan* submitted to the MDE on January 31, 2014 and approved by the Department on October 3, 2014.

In 2018, GES observed continuing, declining trends of MTBE among monitoring and potable wells associated to the case. In addition, review of monitored natural attenuation (MNA) indicator parameters and associated analytical measurements suggests that suitable aerobic and anaerobic conditions exist at the Site to support ongoing biodegradation processes. Therefore, GES recommends the suspension of analytical sample collection for nitrate, ferrous iron and sulfate. It is the opinion of GES that continued verification of improving water quality conditions at the Site and surrounding community can be achieved with analytical sample collection of volatile organic compounds only (including MTBE) in conjunction with the continued field collection of groundwater quality measurements such as ORP and dissolved oxygen.

If you have any questions or would like additional information, please contact the undersigned at 800-220-3606, extension 3726, or Herb Meade at 410-261-5450.

Sincerely,

Peter Reichardt
Project Manager

Enclosure

c: Nick Psenicnik – MDE (2 additional copies & CD)
Ellen Jackson – MDE
Herb Meade – Carroll (e-copy)
Barry Glotfelty – Frederick County Health Department
Samir Andrawos – Timbercrest Limited Partnership
Jennifer Andrawos – Timbercrest Limited Partnership
File – GES, MD (PSID# 770678)

Carroll Independent Fuel Co.

Annual Remedial Evaluation - 2018

Former Green Valley Citgo Station

11791 Fingerboard Road, Monrovia, MD

MDE-OCP Case #2005-0834-FR

February 15, 2019

Annual Remedial Evaluation - 2018

Carroll Fuel – Former Green Valley Citgo
11791 Fingerboard Road
Monrovia, MD 21770

Prepared for:
Carroll Independent Fuel Co.
2700 Loch Raven Road
Baltimore, MD 21228

Prepared by:
Groundwater & Environmental Services, Inc.
1350 Blair Drive, Suite A
Odenton, MD 07727
TEL: 800-220-3726
www.gesonline.com

Date:
February 15, 2019

Pete Reichardt
Project Manger

Dan Drennan, PE
Senior Engineer

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Acronyms

BTEX	Benzene, Toluene, Ethylbenzene and Xylene
CoC	Constituents-of-Concern
DO	Dissolved Oxygen
GAC	Granular Activated Carbon
GES	Groundwater & Environmental Services, Inc.
GVP	Green Valley Plaza
ISCO	In-Situ Chemical Oxidation
MNA	Monitored Natural Attenuation
Max.	Maximum
MDE- OCP	Maryland Department of the Environment - Oil Control Program
µg/L	Micrograms per Liter
mg/L	Milligrams per Liter
mV	Millivolts
MTBE	Methyl tert-butyl ether
MW	Monitoring Well
ORP	Oxidation Reduction Potential
Redox	Oxidation-Reduction
VOC	Volatile Organic Compound

1. Background and Purpose

Completion of an Annual Remedial Evaluation for the Carroll Independent Fuel (Carroll) Former Green Valley Citgo (Site) was proposed in the *Revised Corrective Action Plan* submitted to the Maryland Department of the Environment Oil Control Program (MDE- OCP) on January 31, 2014 and approved by the Department on October 3, 2014. The purpose of the Annual Remedial Evaluation is as follows:

- to report on the analytical trends of constituents-of-concern (CoC), in particular, methyl tert-butyl ether (MTBE), among monitoring and potable wells related to the Site's active MDE-OCP case;
- to evaluate the effectiveness of the monitored natural attenuation (MNA) program now in effect at the Site which has been the primary remedial mechanism since the completion of onsite In-Situ Chemical Oxidation activities (ISCO) in 2012;
- to evaluate the need for additional remedial measures;
- to evaluate the need to add or remove analytical constituents, as well as MNA indicator parameters, from the monitoring program; and
- to evaluate the need to add or remove potable and/or monitoring wells from the current monitoring program, thereby providing a pathway to case closure.

To avoid redundancy, please note that several tables and appendices referenced in this Annual Remedial Evaluation report are included in the **Fourth Quarter 2018 (4Q2018) Monitoring Report** for the Site, *(*which will be submitted concurrently with this report.)

2. Monitoring Since Active Remediation

An ISCO remediation system was in operation at the Site, intermittently, from September 14, 2011 through April 1, 2012. During ISCO system operation, significant reductions in constituent concentrations, including MTBE, were observed. While direct oxidation was likely the dominant factor in the constituent reductions for groundwater in proximity to the injection wells, the constituent reductions occurring further downgradient from the ISCO wells were likely attributed to ongoing natural attenuation processes including the stimulation of microorganisms through oxygen introduction by ISCO (biodegradation).

Since the ISCO system shut-down in 2012, petroleum constituent concentrations in groundwater have continued to reduce while measured groundwater conditions at the Site have continued to demonstrate an environment suitable for both aerobic and anaerobic biodegradation processes. Because MTBE is the only volatile organic compound (VOC) that has been detected above the MDE Action Level since 2009, MTBE is identified as the driving CoC for this MDE-OCP case now in post-remedial monitoring status.

In Fourth Quarter 2017, the monitoring well network was reduced to nine (9) wells which now include: MW-7, MW-14D, MW-17, MW-18S-R and MW-18D, sampled on a quarterly basis, and MW-1, MW-4, MW-5, MW-13, sampled on an annual basis.

3. MTBE Trends for Monitoring Wells

For monitoring performed in 2018, three (3) monitoring wells exhibited MTBE concentrations above the corresponding MDE Action Level of 20 micrograms per liter (µg/L) which included MW-14D (max. of 23 µg/L), MW-18S-R (max. of 570 µg/L) and MW-18D (max. of 29 µg/L).

An updated series of Mann-Kendall statistical analyses were completed to evaluate long-term MTBE trends for eight (8) of the nine (9) total monitoring wells currently comprising the Site monitoring well network. (A Mann Kendall analysis was not performed for MW-5 as this well is historically non-detect for MTBE.) The results of the Mann-Kendall statistical analyses are presented in **Appendix F – Mann Kendall Analyses** of the **4Q2018 Monitoring Report**.

In summary, the updated Mann Kendall analyses demonstrate long-term decreasing MTBE concentration trends with over 99.9% confidence for all active monitoring wells excluding MW-5 and MW-18S-R. As was previously noted, well MW-5 is historically non-detect for MTBE. Well MW-18S-R, installed in 2015, demonstrated a decreasing trend over 16 quarterly events with a confidence factor of 93.0%. The Mann Kendall analyses provided in the **4Q2018 Monitoring Report** support that MTBE concentrations at site monitoring wells have continued to decline since the completion of ISCO remediation activities in 2012.

4. MTBE Trends for Potable Wells

In 2018, five (5) offsite potable well locations were removed from the current monitoring program including 3991, 3993, 3995, 3998 Farm Lane and 3740 Blueberry Court. Currently, the potable well monitoring program for the case consists of the following:

- quarterly sampling and maintenance of four (4) residential, granular-activated carbon (GAC) treatment systems located at 3990, 3992, 3994 and 3996 Farm Lane,
- quarterly sampling and maintenance of the commercial GAC treatment system located at the Green Valley Plaza (GVP) shopping center,
- quarterly sampling of three supply wells related to the GVP GAC treatment system, and
- quarterly “influent-only” sampling of two former residential GAC treatment systems located at 3997 Farm Lane and 3923 Rosewood Road.

An updated series of Mann-Kendall statistical analyses was completed to evaluate the long-term, influent MTBE trends for the four (4) remaining residential GAC systems, the GVP GAC system and the two former residential GAC systems related the case. The results of the Mann-Kendall statistical analyses for these potable well locations can be reviewed in **Appendix F – Mann Kendall Analyses** of the **4Q2018 Monitoring Report**.

In summary, the updated Mann Kendall analyses demonstrate long-term decreasing MTBE concentration trends with over 99.9% confidence for all potable wells currently comprising the potable well monitoring program. The Mann Kendall analyses, as provided in the **4Q2018 Monitoring Report**, support that MTBE concentrations at potable well associated to the case have continued to decline since the completion of ISCO remediation activities at the Site in 2012.

5. Monitored Natural Attenuation Data Analysis

Natural attenuation relies upon physical, chemical and/or biological processes to reduce dissolved constituent concentrations in groundwater to acceptable levels. Physical attenuation processes would include dilution and dispersion of the constituents in groundwater. Because MTBE was generally phased-out from gasoline formulations in Maryland from 2005 to 2006, there is no known continuing source to contribute additional MTBE mass to the local groundwater system. The natural movement of groundwater, fed by recurrent precipitation at the surface, is gradually displacing and diluting residual MTBE in both monitoring and potable wells associated to the case. The long-term, declining trends of MTBE for all monitoring and potable wells discussed in the previous section of this report support that natural attenuation processes continue to be effective in reducing MTBE concentrations over time at the Site since the shutdown of the ISCO remediation system. Dilution and dispersion are likely one of the primary natural attenuation mechanisms responsible for continuing declines of MTBE among the active monitoring and potable wells associated to the case.

Another natural attenuation process, the microbial breakdown or biodegradation of MTBE, can also occur when groundwater conditions are suitable to support the appropriate bacterial colonies. As biodegradation can cause changes in groundwater chemistry, the collection of certain field parameters and analysis of select indicator constituents can assist in identifying the dominant (and supporting) biodegradation processes affecting contaminants in groundwater.

The chart below details the anticipated changes in groundwater chemistry during various stages of biodegradation from aerobic to highly anaerobic conditions.

Time →
← Distance from Source

	Aerobic Respiration	Nitrate Reduction	Manganese Reduction	Ferric Iron Reduction	Sulfate Reduction	Methan-ogenesis
	Aerobic	Anaerobic				
Electron Acceptor	O_2	NO_3^-	Mn^{4+}	Fe^{3+} (solid)	SO_4^{2-}	CO_2
Metabolic By-Product	CO_2	N_2, CO_2	Mn^{2+}	Fe^{2+} (dissolved)	H_2S	CH_4 (methane)
Expected Relationship with High BTEX	$O_2 \downarrow$	$NO_3^- \downarrow$	$Mn^{2+} \uparrow$	$Fe^{2+} \uparrow$	$SO_4^{2-} \downarrow$	$CH_4 \uparrow$

5.1 Dissolved Oxygen

During biodegradation, microbial populations in an aquifer can utilize petroleum hydrocarbons, including MTBE, as an energy source through oxidation-reduction (redox) reactions. These reactions often provide complete degradation of hydrocarbons to carbon dioxide and water, but require a terminal electron acceptor. As was suggested in the table above, oxygen is the most thermodynamically favored electron acceptor for these biodegradation reactions, thus dissolved oxygen (DO) concentrations in groundwater can indicate whether aerobic biodegradation is occurring as well as if a system is conducive to support aerobic biodegradation processes. A historical summary of field parameter measurements, including DO, is presented as **Table 4 -**

Historical Monitoring Well Field Parameters Data Summary of the **4Q2018 Monitoring Report**.

Review of the DO field measurements collected in 2018 from the nine (9) active monitoring wells in the network demonstrates the following:

- DO concentrations for wells MW-1, MW-4, MW-5 and MW-13 were measured once in Fourth Quarter 2018 as these wells are now sampled on an annual frequency. DO concentrations for the annual wells in the Fourth Quarter 2018 ranged from 5.09 to 6.48 milligrams per liter (mg/L), with an average DO concentration, at 5.78 mg/L.
- DO concentration for shallow well MW-7 ranged from 2.69 to 4.33 mg/L, measured during four quarterly events, with an average concentration of 3.53 mg/L.
- DO concentration for shallow well MW-17 ranged from 1.86 to 2.60 mg/L, measured during four quarterly events, with an average concentration of 2.31 mg/L.
- DO concentration for shallow well MW-18S-R ranged from 2.01 to 4.49 mg/L, measured during four quarterly events, with an average concentration of 3.05 mg/L.
- DO concentration for bedrock well MW-14D ranged from 0.28 to 0.95 mg/L, measured during four quarterly events, with an average concentration of 0.69 mg/L.
- DO concentration for bedrock well MW-18D ranged from 0.49 to 0.82 mg/L, measured during four quarterly events, with an average concentration of 0.65 mg/L.

In summary, shallow wells MW-1, MW-4, MW-5, MW-7, MW-13, MW-17 and MW-18S-R continue to demonstrate DO concentrations exceeding 2.0 mg/L on average, which is a suitable DO concentration to support aerobic biodegradation of petroleum constituents, including MTBE, at these particular wells. The fact that DO is reduced in the monitoring wells with historically higher levels of MTBE (MW-7, MW-17, and MW-18S-R) compared with the upgradient wells with historically lower levels of MTBE (MW-1, MW-4, MW-5, and MW-13) indicates that aerobic biodegradation has occurred.

Conversely, bedrock wells MW-14D and MW-18D continue to demonstrate DO concentrations ranges below 1.0 mg/L, which indicates a water quality condition conducive to anaerobic biodegradation processes.

5.2 Oxidation Reduction Potential

Oxidation-Reduction Potential (ORP) is a measurement of electron activity and can be an indicator of the relative tendency of groundwater to accept or transfer electrons. ORP is used as an indicator parameter for biodegradation and can identify regions of a groundwater system that are under oxidizing (aerobic) or reducing (anaerobic) conditions. A summary of field parameter measurements, including ORP, is presented as **Table 4 – Historical Monitoring Well Field Parameters Data Summary** of the **4Q2018 Monitoring Report**.

Review of the ORP field measurements collected in 2018 from the nine (9) active monitoring wells in the network demonstrates the following:

- ORP values for annual monitoring wells MW-1, MW-4, MW-5 and MW-13 were measured during the Fourth Quarter 2018 event. ORP values for the annual wells ranged from 59 to 94.8 millivolts (mV), with an average ORP value, at 78.8 mV.
- ORP values for shallow well MW-7 ranged from 37.2 to 390.2 mV, measured during four quarterly events, with an average value of 164.5 mV.
- ORP values for shallow well MW-17 ranged from -10.2 to 265.7 mV, measured during four quarterly events, with an average value of 107.9 mV.
- ORP values for shallow well MW-18S-R ranged from -46.2 to 240.5 mV, measured during four quarterly events, with an average value of 87.2 mV.
- ORP values for bedrock well MW-14D ranged from -185.6 to -60.9 mV, measured during four quarterly events, with an average value of -125.4 mV.
- ORP values for bedrock well MW-18D ranged from -214.1 to -94.1 mV, measured during four quarterly events, with an average value of -146.7 mV.

In summary, ORP measurements obtained in 2018 from the seven (7) shallow wells and two (2) bedrock wells support the conclusions presented in the previous section of this report that the shallow monitoring wells continue to exhibit conditions (positive ORP values) conducive for aerobic biodegradation while the two bedrock wells demonstrated (negative) OPR values which are conducive for anaerobic biodegradation processes.

5.3 Nitrate

In 2018, GES collected nitrate analytical samples from all nine (9) active monitoring wells during a given quarterly or annual monitoring period. Nitrate analysis has been performed to establish if nitrate reduction contributes to the observed historical decline of petroleum constituent concentrations, including MTBE, at monitoring and potable wells associated to the case.

Review of the nitrate analytical results collected in 2018 from the nine (9) active monitoring wells in the network demonstrates the following:

- Nitrate concentrations for annual monitoring wells MW-1, MW-4, MW-5 and MW-13 were measured during the Fourth Quarter 2018 event. Nitrate for the annual wells ranged from 1.8 to 2.2 mg/L, with an average nitrate concentration of 2.0 mg/L.
- Nitrate concentrations for shallow well MW-7 ranged from 2.3 to 3.0 mg/L, measured during four quarterly events, with an average concentration of 2.7 mg/L.
- Nitrate concentrations for shallow well MW-17 ranged from 2.8 to 3.2 mg/L, measured during four quarterly events, with an average concentration of 3.0 mg/L.
- Nitrate concentrations for shallow well MW-18S-R ranged from 2.2 to 3.5 mg/L, measured during four quarterly events, with an average concentration of 2.9 mg/L.

- Nitrate concentrations for bedrock wells MW-14D and MW-17D were all non-detect (detection limit =0.25 mg/L), measured during four quarterly events.

In summary, nitrate was found stable and at consistent concentrations among all seven (7) shallow wells at the Site in 2018 while the deep wells MW-14D and MW-17D were recurrently non-detect for nitrate. Therefore, it can be concluded that:

- the seven shallow wells existed at a predominately aerobic condition through the year (and thus, would not require or deplete nitrate as part of ongoing biodegradation processes at these wells) while;
- non-detect nitrate concentrations at bedrock wells MW-14D and MW-18D indicates that nitrate is not available to be used as an electron acceptor and nitrate reduction has not been a significant biodegradation mechanism in the deeper wells.

5.4 Ferrous Iron and Sulfate

Ferrous iron and sulfate groundwater samples are only collected from monitoring wells which exhibit a field-measured DO value of $\leq$ 1.0 mg/L during a given monitoring period. Based on field measurements of DO obtained in 2018, only bedrock wells MW-14D and MW-17D were analyzed for both ferrous iron and sulfate and this occurred during all four quarters of 2018.

Review of the ferrous iron and sulfate analytical results collected in 2018 demonstrates the following:

- Ferrous iron concentrations for bedrock well MW-14D ranged from 0.048 to 0.12 mg/L, measured during four quarterly events, with an average concentration of 0.07 mg/L;
- Ferrous iron concentrations for bedrock well MW-18D ranged from non-detect (<0.015 mg/L) to 0.93 mg/L, measured during four quarterly events, with an average concentration of 0.43 mg/L (using half the concentration value of the detection limit (0.075 mg/L) as the non-detect value);
- Sulfate concentrations for bedrock well MW-14D ranged from 13.1 to 19.4 mg/L, measured during four quarterly events, with an average concentration of 15.3 mg/L; and
- Sulfate concentrations for bedrock well MW-18D ranged from 5.3 to 7.4 mg/L, measured during four quarterly events, with an average concentration of 6.6 mg/L.

Time-series plots comparing historical MTBE concentrations (beginning in 2014) with ferrous iron and sulfate concentrations for both MW-14D and MW-18D are attached as **Figures 1 and 2**, respectively.

Review of **Figures 1 & 2** indicates the following:

- Sulfate concentrations at MW-14D have depleted over time as MTBE concentration has declined, indicating that sulfate reduction was likely occurring near this well. Since the MTBE concentrations dropped to lower levels, there is no longer an obvious sulfate trend, but there is still sufficient sulfate present to support biodegradation.

- Ferrous iron concentrations over time at MW-14D have remained low and do not present obvious visual correlations in trend. Iron reduction is not considered a significant biodegradation mechanism near this well.
- MTBE, ferrous iron and sulfate concentrations at MW-18D generally fluctuate in tandem but do not show an obvious trend. The increases in ferrous iron may indicated that iron reduction has occurred near this well. The sulfate concentrations indicate that there is sufficient sulfate present to support biodegradation.

6. Conclusion

In summary, statistical analysis of long-term MTBE concentrations for both monitoring and potable wells associated to the MDE-OCP case support the observation of continuing, declining trends.

Field parameter measurements and analytical results collected in 2018 among the nine (9) monitoring wells comprising the network indicate that suitable aerobic and anaerobic conditions exist at the Site to support ongoing biodegradation processes. As these biological processes reduce over time, the ongoing dilution and dispersion of MTBE from the local aquifer system will allow for the continued natural attenuation of MTBE.

With conditions that support biodegradation processes established at all existing monitoring wells, the low level concentrations of MTBE, and the unlikely scenario of MTBE significantly rebounding in the local aquifer system due to an absent onsite source, GES recommends the suspension of analytical sample collection for nitrate, ferrous iron and sulfate. It is the opinion of GES that continued verification of improving water quality conditions at the Site and surrounding community can be achieved with analytical sample collection of VOCs only (including MTBE) in conjunction with the continued field collection of groundwater quality measurements such as ORP and dissolved oxygen.

References

US EPA (2005) *Monitored Natural Attenuation of MTBE as a Risk Management Option at Leaking Underground Storage Tank Sites*, EPA 600-R-04-179 https://archive.epa.gov/ada/web/pdf/20017i6r.pdf

GES (2019) *Fourth Quarter 2018 Monitoring Report-Former Green Valley Citgo-Carroll Independent Fuel Company*, *11791 Fingerboard Road, Monrovia, MD, OCP Case #2005-0834-FR*

Figures

Figure 1 – MTBE vs. Ferrous Iron and Sulfate Concentrations MW-14D

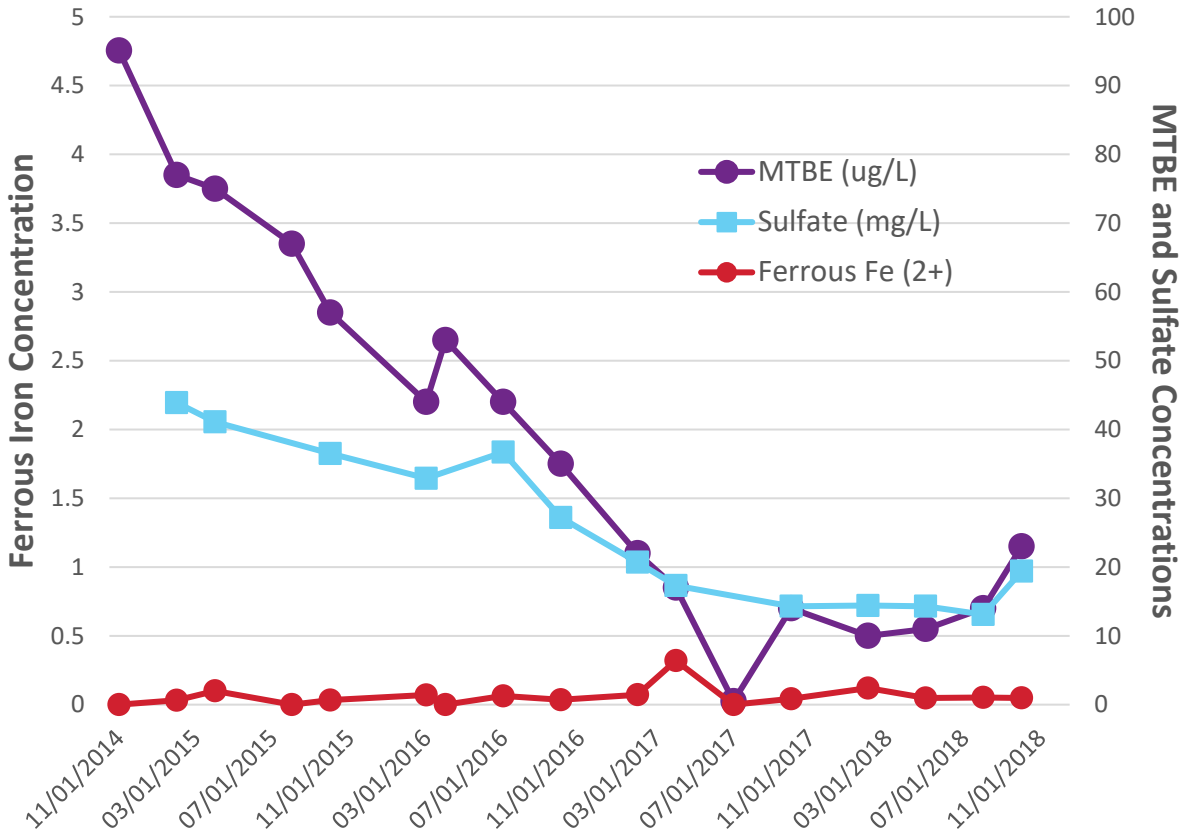

Figure 2 – MTBE vs. Ferrous Iron and Sulfate Concentrations
MW-18D