Shell Chemical Appalachia LLC
300 Frankfort Rd
Monaca, PA 15061

May 18, 2023

Director
Air Protection Section
Mail Code 3AP00
U.S. EPA Region III
1650 Arch Street
Philadelphia, PA 19103-2029

Mark Gorog P.E., Regional Manager Air Quality Program
Pennsylvania Department of Environmental Protection (PADEP)
Southwest Regional Office
400 Waterfront Drive
Pittsburgh, PA 15222

RE: Malfunction Report as per PA-04-00740C and National Response Center Report Incident ID# 1364790 for Malodors and Excess Emissions from Wastewater Treatment Plant (WWTP) Shell Chemical Appalachia LLC

Dear Mr. Gorog,

Shell Chemical Appalachia LLC ("Shell") is submitting this Malfunction Report to the Pennsylvania Department of Environmental Protection (PADEP) for malodors detectable outside the property from the waste water treatment plant (WWTP) (Source ID 502).

This malfunction did not pose danger to the public health and safety or the environment. Shell initiated offsite observations by Shell personnel, and also third-party contractors both on the river and surrounding community areas. Odors were reported offsite periodically throughout the duration of the malfunction. However, no sheen or other indications of impaired water quality was observed on the river at the outfall indicating that hydrocarbons were not entering the environment to the river. A third party contractor monitored the condition of the river during the times when Shell was discharging through Outfall 001. And, a separate third-party contractor conducted offsite odor surveys and hydrocarbon sampling encompassing Route 18 west to Raccoon Creek and east to Beaver Valley Mall area, 376 south to Route 18 and North to Vanport area, and Route 68 west to Lockhouse 6 restaurant and east to Vanport and Beaver areas. Offsite community monitoring with portable analyzers did not indicate the presence of VOCs greater than the background threshold and minimum detection levels.

- **Name and location of the facility**
  Shell Polymers Monaca
  300 Frankfort Road, Monaca PA, 15061

- **Nature and cause of the incident**
  Malodors were detected outside the property. Cause of the odors was hydrocarbons in the WWTP biotreaters.

- **Time when the malfunction or breakdown was first observed**
  April 11, 2023 at ~16:30 when a malodor was first detected offsite

- **The date and time that the malfunction started and ended**
  April 11, 2023 at 14:30 and ending on April 20, 2023 at 15:00 when a malodor was last detected offsite

- **An estimate of the emissions associated with the malfunction**

Pollutant	Emission Rate (tons)[a]	Emission Rate (lbs)
VOC	1.82	3,633
HAP (Total)	1.09	2,182
Benzene	0.22	444[b]
Toluene	0.85	1,705
Napthalene	0.01	24

a – Emissions estimate undergoing final QC.

b – The initial estimated 24-hr benzene release was 300 lbs as described in the calculations below. The final estimated 24-hr benzene release was 219 lbs and a subset of the total 444 lbs based on the final calculations.

- **The calculations that were used to determine that quantity**

  Excess emissions for this malodor event have been calculated by applying biotreater aeration rates to concentrations of VOC and benzene measured on top of the biotreaters during the malfunction. Aeration rate represents the volumetric rate of flow of air introduced at multiple points across the bottom of the biotreater aeration basins and then flowing up through liquid contained in the biotreaters and exiting at the surface level. This flow is converted to standard cubic feet per minute (scfm) using the average measured air temperatures from the on site meteorological station. VOC and benzene concentrations are parts per million by volume (ppmv) as measured periodically by handheld photoionization detector (PID) analyzer. Measured hydrocarbon concentrations and the known aeration rate are then converted to a mass emission rate through multiplication of the molecular weight (MW) of benzene or surrogate representative MW for VOC and division by the standard volume of air in a pound mole (lbmol). Fenceline monitoring data results during the incident period have been applied to estimate other hazardous air pollutants (HAPs) released during the event including toluene and naphthalene.

  Use of the WATER9 WWTP emissions estimation model was not considered to be viable for this calculation due to the lack of a representative inlet water sample to the biotreaters. An inlet sample was not able to be taken as the initial discovery of the incident did not occur until flow into the biotreaters had already ceased and this was outside of regularly scheduled periodic water sampling. Additionally, water flow into the biotreaters ceased during this incident and WATER9 does not produce an emission rate under zero flow conditions.

  Initial emission estimates were performed using a Shell internal dispersion model known

as FRED (for fire, release, explosion, dispersion consequence modelling) with the measured VOC and benzene concentrations on top of the biotreaters and at the fenceline continuous VOC monitors as inputs and guiding data. This is a gaussian model treating the biotreaters as the point of release and modeled a max release rate of 0.02 kg/s of VOC of which 10% was estimated as benzene based on the ratio of monitored benzene to VOC at the time. Max rates were assumed for a 12-hour period and then reduced by 50% for the subsequent 12 hours consistent with the timeline for observed reductions in measured concentrations. This arrived at a 24-hour benzene release quantity of 300 lbs (with a small margin added for conservatism). It was checked against prior worst case WATER9 model runs, found to be reasonably close to those prior worst case results, and considered to be acceptable for purposes of initial reporting. It was not considered acceptable for purposes of final reporting as the FRED model relies on simplified terrain and other assumptions, and estimating the release directly from the source was considered to be the more accurate approach with the available data.

The reportable quantity (RQ) per CERCLA and EPCRA for benzene is 10 lbs within a 24-hour period. While the WWTP is a permitted air emissions source of benzene to the atmosphere, this release was sudden and unplanned and the estimated 24-hr emission rate was determined to be exceeding the expected maximum under the air permit basis.

Calculations have been included as Attachment A.

- **A detailed analysis that sets forth the Root Cause of the malfunction, to the extent determinable**

  Root cause has been determined to be failure of the liquid level indicator in FEOR A to read accurately at low liquid levels. Liquid level indication maintained steady at approximately 2.8 meters of liquid level within FEOR A while normal pumping of FEOR A out to the biotreaters continued and actual liquid level continued to drop (FEOR B was being filled with incoming wastewater at this time). This resulted in pumping higher levels of hydrocarbons from FEOR A into the biotreaters. The liquid level indication of 2.8 meters was higher than both of the low level alarms and the pump interlock level setting in place which are above the designed minimum level indication. Alarm would have alerted the operator of the low liquid level in time to take preventative action while interlock would have automatically shut down the biotreater feed pump to prevent the FEOR A tank dropping to this low level. These alarm and interlock levels were set at 1.57 meters and 1.5 meters, respectively.

  The liquid level indication is provided by guided wave radar instrumentation (597LIT-100) transmitting a microwave pulse down a probe spanning the top to bottom of the tank internally. Design minimum accurate level indication is 0.2 meters, however it does not actually read below ~2.8 meters. The root cause of the frozen and inaccurate liquid level indication is still under investigation pending full inspection of the level indicator to determine the deeper root cause.

- **The steps, if any, that the facility took to limit the duration and/or quantity of emissions associated with the malfunction**

  Odors were minimized through the isolation of both FEOR Tanks A and B from the biotreaters until the situation could be assessed. This prevented introducing any

additional hydrocarbon-containing wastewater into the biotreaters immediately after the initial discovery. Initial discovery was upon tripping biotreater feed pump (P-59704B) offline due to low flow and Operations detecting increased odors at the biotreaters. The inlet flow of relatively low-hydrocarbon wastewater to the FEOR tanks was switched from FEOR B to FEOR A. This allowed the actual liquid level in FEOR A to raise above 2.8 meters and restablish what was believed to be a reliable level indication for operational control. Liquid level in FEOR A was further raised to 5.0 meters and then flow of relatively low-hydrocarbon wastewater from FEOR A into the biotreaters was restablished while maintaining a higher level indication.

Odors were minimized also through ongoing vaccuuming of the top of the biotreaters by third party contractor to remove excess oils and hydrocarbons. Excess oils and hydrocarbons were transported from the site for eventual disposal as a waste at a non-Shell site.

- **An analysis of the measures, if any, that are available to reduce the likelihood of a recurrence of a malfunction resulting from the same Root Cause or contributing causes in the future**

    1. FEOR tank liquid level indicator low level alarms and interlock settings have been raised above the actual minimum accurate liquid level indication of 597LIT-100. These are now set at 4 and 3.5 meters respectively, and will mitigate and prevent the recurrence of this incident. This will provide early operational awareness to correct FEOR levels before low level is reached. This will automatically shut off pumps from FEOR to biotreater and prevent pumping to a low level where higher levels of oils and hydrocarbons could be present.

    2. Shell intends to continue this investigation and make repairs or replacement of the liquid level instrument to restore it to the full design range. This will be contingent upon final determination of the root cause of the failure. Additionally, a second level indicator is under design for installation as a redundant indication. This is also contingent upon final determination of the root cause of the failure of the original instrument. Both actions will reduce the likelihood of a recurrence.

    3. Prior to this incident, Shell commissioned a project to design and install a temporary enclosed induced nitrogen flotation (INF) system to improve and increase hydrocarbon/oil removal capacity in the WWTP. This includes some N2 stripping functionality that further enhances the remove any volatile hydrocarbons. Separated hydrocarbons will be routed to the recovered oil tank and overhead vapors from the enclosed system routed to the spent caustic thermal oxidizer consistent with the original design intent of the WWTP. Approval has been received from the PADEP Water Quality Program and Air Quality Programs for this temporary installation. The WEMCO Depurator had been received and undergoing on-site installation at the time of this incident. It has since completed installation and functionality testing and been placed into service. Odors in the future will be minimized by the reduction of hydrocarbons entering the biotreaters and destruction of vapors in the thermal oxidizer. Performance of this temporary project is being evaluated for potential design of a similar permanent system.

- **To the extent that investigations of the causes and/or possible corrective action(s) still are underway on the due date of the report, a statement of the anticipated date**

by which a follow-up report will be submitted

Investigation into this malfunction is not yet final and a follow up report will be submitted no later than July 1, 2023

- **Corrective action is final or timeline for implementation**

1. Liquid level low alarms are final and interlock corrective actions are expected to be completed by June 1, 2023.
2. Installation of a second liquid level indicator is pending final design and identification of the specific cause of failure of the original indicator. This is expected to be completed by June 1, 2023.
3. Installation and operation of the temporary INF (WEMCO Depurator) unit is final. (This is under temporary approval by the PADEP Water and Air Quality Programs pending evulation and permitting for a permanent future addition)

If you have any questions regarding this matter, please contact me at (724) 709-2467 or kimberly.kaal@shell.com.

Sincerely,

Kimberly J. Kaal

Kimberly Kaal
Environmental Manager, Attorney-in-Fact

CC:
Scott Beaudway, Air Quality Specialist
Beth Speicher, Environmental Group Manager

Attachment A
Emissions Calculations

WWTP Aeration Rate Emission Calculation

Basis:

Emissions were calculated by applying hydrocarbon concentration measurements on top of the biotreaters to the aeration rate of the biotreaters. Measured concentrations are periodic readings by portable PID analyzer. Calculations begin at 14:30 as the approximate earliest time of abnomal levels of hydrocarbons entering the biotreaters. Hydrocarbon concentration inputs are not changed until a new reading is taken. This adds conservatism to the estimate as measured concentrations decay over time. The initial actual VOC reading was taken at approximately 19:30 and was extrapolated backwards to 14:30 based on the 19:30 benzene to VOC ratio applied to the earliest actual benzene reading. Other HAP emissions are estimated using the ratios of 4/13 fenceline PAMS results which sampled during the peak release. The MW of VOC is applied as toluene as it is the highest concentration measured at the fenceline. This calculation is continued until benzene readings at the top of the biotreaters reach 0 ppmv and VOC readings reach single digit ppmv upon which time WATER9 model calculations will resume based on representative water inlet samples as normal operations.

Formula:

Em = (Ec * Q * 60 * MW) / (385.3 * 10^6)

Where:

Em = Mass emissions rate in lb/hr

Ec = Measured emissions rate in ppmv

Q = Volumetric flow rate in scfm

MW = Molecular weight in lb/lb-mol

Constants:

78.11	lb/lb-mol (Benzene MW)
92.14	lb/lb-mol VOC MW (as toluene)
1.711	m3/s (biotreater aeration rate, per biotreater)
35.3147	ft3/m3 standard conversion
60.4234517	ft3/s (biotreater aeration rate, per biotreater)
3625.407102	cfm (biotreater aeration rate, per biotreater)
385.3	scf/lb-mol standard @ 68F and 1atm
528	R (standard temperature 460R + 68))
60	min/hr
1000000	ppmv
2	# of biotreaters

Fenceline PAMS 4/13 HAP Ratios:

0.781	Toluene
0.204	Benzene
0.011	Naphthalene
0.002	1,3-Butadiene
0.002	Hexane

Emission Calculations:

Start Time	End Time	Hours	Measured Benzene Concentration	Measured VOC Concentration	Biotreater Top Air Temperature Avg	Aeration Rate	Benzene Mass Rate	VOC Mass Rate	Benzene Mass Total	VOC Mass Total	Benzene/ VOC Ratio	PAMS Benzene Ratio	Naphthalene Mass	1,3 Butadiene Mass	Toluene Mass	Hexane Mass	Remaining Unspeciated VOC Mass
MM/DD/YYYY TT:TT	MM/DD/YYYY TT:TT	#	ppmv	ppmv	F	scfm	lb/hr	lb/hr	lbs	lbs	#	#	lbs	lbs	lbs	lbs	lbs
4/11/2023 14:30	4/11/2023 19:30	5	199	1931	72.15	3597.10	8.71	99.68	87.07	996.76	0.09	0.20	4.66	1.03	334.19	0.90	568.92
4/11/2023 19:30	4/12/2023 3:00	7.5	105	1019	54.69	3719.16	4.75	54.38	71.25	815.66	0.09	0.20	3.81	0.84	273.47	0.74	465.55
4/12/2023 3:00	4/13/2023 10:00	31	100	494	61.97	3667.28	4.46	25.99	276.56	1611.62	0.17	0.20	14.80	3.26	1061.51	2.86	252.63
4/13/2023 10:00	4/16/2023 20:00	82	1.1	23	67.92	3625.92	0.05	1.20	7.96	196.24	0.04	0.20	0.43	0.09	30.54	0.08	157.15
4/16/2023 20:00	4/17/2023 10:00	14	1	6	49.44	3757.47	0.05	0.32	1.28	9.06	0.14	0.20	0.07	0.02	4.91	0.01	2.77
4/17/2023 10:00	4/18/2023 10:00	24	0	1.4	42.40	3810.17	0.00	0.08	0.00	3.67	0.00	0.20	0.00	0.00	0.00	0.00	3.67
Sum Total									**444.12**	**3633.02**			**23.77**	**5.23**	**1704.62**	**4.59**	**1450.69**