Shell Chemical Appalachia LLC
300 Frankfort Rd
Monaca, PA 15061

January 13, 2023

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

RE: PA-04-00740C Wastewater Treatment Plant (Source ID 502) Malodor and Excess Emissions Malfunction Report

Dear Mr. Gorog,

Shell Chemical Appalachia LLC ("Shell") is submitting this malfunction report to the Pennsylvania Department of Environmental Protection (PADEP) for odors and excess emissions from the wastewater treatment plant (WWTP)[1] between October 4 and December 13, 2022.

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

- **Nature and cause of the incident**

  On November 6, 2022, Shell personnel detected a odor on site in the vicinity of the WWTP as part of regularly scheduled observations for potentially objectionable odors. Follow up offsite observational rounds by Shell's Emergency Response Team were initiated based upon the strength of the odor and judgement of observer. Shell personnel then detected faint similar odors during the offsite observations in the vicinity of Lockhouse 6 across the Ohio River. This offsite odor was considered to be malodor and reported to PADEP on the following business day.

  Odors had been observed within and around the WWTP on site prior to November 6 and increased observational rounds and area monitoring had already been implemented.[2] This included portable analyzer used to detect VOCs in the WWTP area, more frequent Operator and emergency response team observation rounds, as well as Shell maritime spill operator rounds near the shoreline to detect for odors. Water samples were taken from FEOR Tanks A and B on October 4, 2022 and form the basis for the beginning of the event emissions estimation. December 13, 2022 is the final day of any odors detected by Shell maritime spill operator at the river[3] and marks the

[1] WWTP including two biotreater aeration tanks.
[2] Odors had not been detected offsite by Shell prior to November 6 although olfactory rounds included onsite and offsite rounds.
[3] Contractor rounds were continued through the end of December without additional odor detection.

end of the event. Shell's contractor traveled up and down the river and did not find any other malodors.

Cause of the odors was determined to be the presence of accumulated hydrocarbons in the two biotreater aeration tanks of the WWTP coupled with ambient conditions which carried odors offsite and across the river. Hydrocarbons are received into the biotreater aeration tanks from the upstream flow equalization oil removal (FEOR) Tanks A and B. Source of the hydrocarbons into the FEOR Tanks was traced back to the ethane cracking unit (ECU) process wastewater. Incomplete separation of heavy hydrocarbons and water by the gasoline/water separator within the quench water system is the likely cause of elevated levels of heavy hydrocarbons entering the process wastewater stream from ECU.

Cause of the accumulation of hydrocarbons and biomaterial of top of the biotreaters was determined to be in part due to a misalignment of the skimmer rake, partially missing rubber skirt attached to the rake, and mistiming of the skimmer pump on Biotreater B. This degraded the ability of the skimmer system to remove accumulation from the top of the biotreaters for further processing the by the WWTP.

Corrective action and reduction of hydrocarbons from ECU has been implemented through improving souce control and separation of heavy hydrocarbons within ECU. An ECU wastewater sampling plan has been implemented along with target alarms to ensure streams are within design. This includes total organic carbon (TOC) correlations for ECU wastewater. A management of change project has been initiated for removal of waste oil/pitch from the quench water system in ECU and to limit heavier components from migrating downstream to WWTP.

Corrective action and mitigation of the accumulation of material on top of the biotreaters includes periodic vaccumming of the surface for disposal as a waste as well as utilizing capacity and hold times within each FEOR Tank to allow for additional removal time of hydrocarbons to recovered oil. Corrective action also includes periodic manual operation of the Biotreater B skimmer pump by Operations. Upstream improvements to source control (less hydrocarbons in the wastewater) have also reduced any accumulation and presence of odors. Replacement skimmer blades are on order and a plan to replace the rotating skimmer is in place. Additional assessment will be performed of the entire rotating assembly for any additional scope needed.

Additional long term corrective actions and process improvements are being evaluated or planned for implementation. Additional long term sampling and analysis of the FEOR Tanks is planned for updating modeling and long term emissions calculations.

- **Time when the incident was first observed, and duration of excess emissions**
  October 4, 2022 and intermittently until December 13, 2022. October 4 is the date of the FEOR Tank A and B water samples which forms the basis for inputs to the emissions model showing the air emissions from the biotreaters. As noted above, odors were not detected offsite by Shell between October 4 and November 6 although olfactory rounds included onsite and offsite rounds (See previous immediately above for duration of event clarification). December 13 is the final day that any odor was detected by the maritime spill operator along the river bank, which coincides with a period of 1 week of relatively lower stable TOC readings from FEOR Tank A and B samples.

- **Estimated rate of excess emissions**

Excess emissions for this malodor event have been calculated based upon an updated WATER9 Model, using FEOR Tank A and B water samples for speciated VOCs collected on October 4, using periodic FEOR Tank TOC sample results as indicators of elevated or low hydrocarbons, and measured flow rates into the biotreaters. The air emissions were modeled for what would have been emitted from the biotreaters. Sample results from each FEOR Tank contain volatile organics and HAPs including benzene, toluene, styrene, and naphthalene; with trace amounts of other HAPs present. All have been used as inputs to the updated model.

WATER9 Model outputs, inputs from sample results speciation, and inputs design parameters have been included as Attachment A.

Pollutant	Emission Rate (tons)
VOC	2.71
HAP (Total)	2.49
Benzene	2.01
Toluene	0.37
Styrene	0.05
Naphthalene	0.01

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

Sincerely,

Kimberly Kaal

Kimberly Kaal
Environmental Manager, Attorney-in-Fact

CC:
Scott Beaudway, Air Quality Specialist
Anna Hensel, District Supervisor

Attachment A
WATER9 Model Ouputs and Inputs

Table 1 **Air Emissions Calculations, Wastewater Treatment Plant, Water9 Output - Air Emissions, Malfunction Case**
Shell Chemical Applachia LLC

Air Emissions

	Case 1: High Hydrocarbon Flow Case				Case 2: Low Hydrocarbon Flow Case				Total Malfunction Period
Component	Case 1 Emission Rate (g/s)	Case 1 Emission Rate (lb/hr)	Case 1 Emissions (lbs/ malfunction period)	Case 1 Emissions (tons/ malfunction period)	Case 2 Emission Rate (g/s)	Case 2 Emission Rate (lb/hr)	Case 2 Emissions (lbs/ malfunction period)	Case 2 Emissions (tons/ malfunction period)	Emissions (tons/ malfunction period)
Benzene	7.05E-01	5.595	4,028.6	2.014	1.06E-02	0.084	82.8	0.041	2.056
Phenol	3.21E-08	0.000	0.0	0.000	3.46E-08	0.000	0.0	0.000	0.000
Toluene	1.22E-01	0.968	697.1	0.349	4.43E-03	0.035	34.6	0.017	0.366
Ethylbenzene	1.20E-03	0.010	6.9	0.003	0.00E+00	0.000	0.0	0.000	0.003
Xylene	6.80E-04	0.005	3.9	0.002	8.85E-05	0.001	0.7	0.000	0.002
Styrene	1.67E-02	0.133	95.4	0.048	7.98E-04	0.006	6.2	0.003	0.051
Naphthalene	2.58E-03	0.020	14.7	0.007	2.49E-04	0.002	1.9	0.001	0.008
2 Methylnaphthalene	7.09E-04	0.006	4.1	0.002	0.00E+00	0.000	0.0	0.000	0.002
Acenaphthene	6.94E-05	0.001	0.4	0.000	0.00E+00	0.000	0.0	0.000	0.000
Acenaphthylene	1.09E-04	0.001	0.6	0.000	0.00E+00	0.000	0.0	0.000	0.000
Fluorene	4.99E-05	0.000	0.3	0.000	0.00E+00	0.000	0.0	0.000	0.000
Anthracene	1.44E-05	0.000	0.1	0.000	0.00E+00	0.000	0.0	0.000	0.000
Phenanthrene	4.77E-07	0.000	0.0	0.000	0.00E+00	0.000	0.0	0.000	0.000
Fluoranthene	2.43E-07	0.000	0.0	0.000	0.00E+00	0.000	0.0	0.000	0.000
Pyrene	8.05E-07	0.000	0.0	0.000	0.00E+00	0.000	0.0	0.000	0.000
Cyclopentadiene	1.60E-03	0.013	9.1	0.005	1.73E-03	0.014	13.5	0.007	0.011
Other Pentanes	6.16E-03	0.049	35.2	0.018	0.00E+00	0.000	0.0	0.000	0.018
Other Hexanes	1.02E-02	0.081	58.3	0.029	9.06E-03	0.072	70.8	0.035	0.065
Other Heptanes	5.18E-04	0.004	3.0	0.001	4.61E-04	0.004	3.6	0.002	0.003
Other Octanes	2.13E-03	0.017	12.2	0.006	2.13E-03	0.017	16.6	0.008	0.014
Propyl (-n) Benzene	1.96E-03	0.016	11.2	0.006	0.00E+00	0.000	0.0	0.000	0.006
1,2,4-Trimethylbenzene	6.22E-04	0.005	3.6	0.002	0.00E+00	0.000	0.0	0.000	0.002
Other Nonanes	6.91E-03	0.055	39.5	0.020	3.00E-03	0.024	23.4	0.012	0.031
1,2,4,5 Tetramethylbenzene (1)	6.17E-04	0.005	3.5	0.002	6.00E-04	0.005	4.7	0.002	0.004
1,2,4,5 Tetramethylbenzene (2)	9.20E-04	0.007	5.3	0.003	9.95E-04	0.008	7.8	0.004	0.007
Butyl Benzene	5.87E-04	0.005	3.4	0.002	0.00E+00	0.000	0.0	0.000	0.002
Other Decanes+	8.64E-03	0.069	49.4	0.025	8.47E-03	0.067	66.1	0.033	0.058
Total VOC	8.90E-01	7.063	5,085.6	2.543	4.26E-02	0.338	332.8	0.166	2.709
Total POM (excluding Naphthalene)	9.53E-04	0.008	5.4	0.003	0.00E+00	0.000	0.0	0.000	0.003
Total HAP	8.49E-01	6.739	4,852.1	2.426	1.62E-02	0.128	126.2	0.063	2.489

Notes

1) Emission Rate (g/s) calculated in WATER9

2) Malfunction period was from 10/04/2022 to 12/13/2022, which is:

71 days

1704 hours

Malfunction period separated between 2 cases (High and Low Hydrocarbon Flows)

Case 1: High Hydrocarbon Flow Case: 30 days

720 hours

Case 2: Low Hydrocarbon Flow Case: 41 days

984 hours

Table 2 **Air Emissions Calculations, Wastewater Treatment Plant, Water9 Composition Inputs, Malfunction Case**
Shell Chemical Applachia LLC

Sample Data - Input into Water9

Component	Carbon Atoms	Component Molecular Weight (lb/lb-mol)	HAP?	POM?	FEOR-A - 16479 Concentration Sample Result (ug/L)	FEOR-A - 16479 Concentration Sample Result (mg/L)	FEOR-B - 16480 Concentration Sample Result (ug/L)	FEOR-B - 16480 Concentration Sample Result (mg/L)	Case 1: High Hydrocarbon Flow Case FEOR-T (input into Water9) Concentration (mg/L)	Case 2: DLow Hydrocarbon Flow Case FEOR-T (input into Water9) Concentration (mg/L)
Benzene	6	78.11	X		341.0	0.3410	299,000.0	299.0000	22.7404	0.3410
Phenol	6	94.11	X		19.3	0.0193		0.0000	0.0179	0.0193
Toluene	7	92.15	X		187.0	0.1870	66,200.0	66.2000	5.1380	0.1870
Ethylbenzene	8	106.16	X			0.0000	608.0	0.6080	0.0456	0.0000
Total Xylenes	8	106.16	X		6.9	0.0069	622.0	0.6220	0.0530	0.0069
Styrene	8	104.15	X		15.6	0.0156	4,160.0	4.1600	0.3264	0.0156
Naphthalene	10	128.17	X	X	13.6	0.0136	1,710.0	1.7100	0.1408	0.0136
2-Methylnaphthalene	11	142.2	X	X		0.0000	197.0	0.1970	0.0148	0.0000
Acenaphthene	12	154.21	X	X		0.0000	43.4	0.0434	0.0033	0.0000
Acenaphthylene	12	152.19	X	X		0.0000	83.2	0.0832	0.0062	0.0000
Fluorene	13	166.22	X	X		0.0000	51.5	0.0515	0.0039	0.0000
Anthracene	14	178.23	X	X		0.0000	24.2	0.0242	0.0018	0.0000
Phenanthrene	14	178.23	X	X		0.0000	81.3	0.0813	0.0061	0.0000
Fluoranthene	16	202.25	X	X		0.0000	11.1	0.0111	0.0008	0.0000
Pyrene	16	202.25	X	X		0.0000	22.1	0.0221	0.0017	0.0000
1,3-Cyclopentadiene	5	66.1			30.1	0.0301		0.0000	0.0278	0.0301
* 1-Buten-3-yne, 2-methyl-	5	66.1				0.0000	1,420.0	1.4200	0.1065	0.0000
* 1,3-Cyclopentadiene, 1-methyl-	6	80.13			147.0	0.1470	246.0	0.2460	0.1544	0.1470
* Ethylidenecyclobutane	6	82.14			21.6	0.0216		0.0000	0.0200	0.0216
* Cyclobutane, ethenyl-	6	82.14				0.0000	200.0	0.2000	0.0150	0.0000
* 1-Penten-3-yne, 2-methyl-	6	80.13				0.0000	10.5	0.0105	0.0008	0.0000
* 1,4-Cyclohexadiene, 1-methy-	7	94.15			8.4	0.0084		0.0000	0.0077	0.0084
* Bicyclo[2.2.1]hept-2-ene, 1-methyl	7	94.15				0.0000	18.0	0.0180	0.0014	0.0000
* 3-Oxabicyclo[3.3.0]octan-2-one,6-	8	138.16			13.5	0.0135		0.0000	0.0125	0.0135
* Bicyclo[2.2.1]hept-2-ene, 2-methyl	8	108.18			24.9	0.0249		0.0000	0.0230	0.0249
* 9-Oxabicyclo[6.1.0]non-4-ene	8	124.18				0.0000	31.2	0.0312	0.0023	0.0000
n-Propyl Benzene	9	120.19				0.0000	457.0	0.4570	0.0343	0.0000
1,2,4-Trimethylbenzene	9	120.19				0.0000	148.0	0.1480	0.0111	0.0000
* 1H-Indene,3a,4,7,7a-tetrahydro	9	120.19			12.8	0.0128	23.3	0.0233	0.0136	0.0128
* Bicyclo[2.2.1]hept-2-ene, 5-ethenyl	9	120.19			29.6	0.0296	901.0	0.9010	0.0950	0.0296
* Indene	9	116.16			9.3	0.0093	21.3	0.0213	0.0102	0.0093
* Tricyclo[3.3.0.0(2,8)]octan-3-one	9	136.19				0.0000	19.5	0.0195	0.0015	0.0000
Benzene, 1,2,4,5-tetramethyl-(01)	10	134.22			10.5	0.0105	14.4	0.0144	0.0108	0.0105
Benzene, 1,2,4,5-tetramethyl-(02)	10	134.22			17.4	0.0174		0.0000	0.0161	0.0174
Butylbenzene	10	134.22				0.0000	139.0	0.1390	0.0104	0.0000
* Benzene, 2-ethyl-1,4-dimethyl-	10	134.22			10.8	0.0108	14.4	0.0144	0.0111	0.0108
* 2,4-Dimethylstyrene	10	132.2			8.5	0.0085		0.0000	0.0079	0.0085
* Benzene,1,3-diethyl-	10	134.22			23.2	0.0232		0.0000	0.0215	0.0232
* Benzene,1-methyl-3-propyl-	10	134.22			13.7	0.0137		0.0000	0.0127	0.0137
* cis-8-Methyl-bicyclo(4,3,0)non-3,7	10	134.22			49.1	0.0491	64.5	0.0645	0.0503	0.0491
* Benzene, 1-methyl-3-(1-methylethyl)-	10	134.22			9.5	0.0095	12.9	0.0129	0.0097	0.0095
* 1,4,4a,5,8,8a-Hexahydro-naphthalen	10	134.22			13.2	0.0132	21.4	0.0214	0.0138	0.0132
* Benzene,1-methyl-2-propyl-	10	134.22				0.0000	19.1	0.0191	0.0014	0.0000
* 1-Phenyl-1-butene	10	132.2				0.0000	11.8	0.0118	0.0009	0.0000
* Benzene, 1,2,3,5-tetramethyl-	10	134.22				0.0000	22.6	0.0226	0.0017	0.0000
* Benzene, pentamethyl-	11	148.24			7.3	0.0073		0.0000	0.0067	0.0073
* 5-Phenylbicyclo[2.2.1]hept-2-ene	13	170.25			12.0	0.0120	13.1	0.0131	0.0121	0.0120

Notes

1) FEOR-A and FEOR-B samples from Environmental Service Laboratories, INC. lab results from 10/04/2022 sample

2) If daily TOC reading is ≥ 84.76 mg/l, FEOR-T is calculated assuming the following contributions from FEOR-A and FEOR-B:

FEOR-A	92.5	% contribution to FEOR-T
FEOR-B	7.5	% contribution to FEOR-T

This assumption is based off of: Wastewater is fed to the biotreater from one FEOR at a time, and high hydrocarbon flow will trickle in from the other FEOR. A conservative case is 5-10% of high hydrocarbon FEOR to be trickled in, therefore, an average of the high hydrocarbon FEOR of 7.5% will be used for the spilt of FEOR A/B.

3) If daily TOC reading is < 84.76 mg/l, FEOR-T is assumed 100% FEOR-A. See 'Input_FEOR_A_B_T' tab for backup.

4) A subset of components above were not available within the Water9 database (desginated with an *), so they were grouped by carbon atoms and input into Water9 according to:

Component	Case 1 Concentration (mg/L)	Case 2 Concentration (mg/L)
Pentanes	0.107	0.000
Hexanes	0.190	0.169
Heptanes	0.009	0.008
Octanes	0.038	0.038
Nonanes	0.120	0.052
Decanes+	0.150	0.147

Note: for Hexanes, n-Hexane is only surrogate available in Water9, so it was chosen for the model, but n-Hexane is not present and will be treated as 'Other Hexanes'

Table 3 **Air Emissions Calculations, Wastewater Treatment Plant, Water9 Data Inputs, Malfunction Case**
Shell Chemical Applachia LLC

Waste Stream Input Assumptions

Water9 Parameter	FEOR-T	CT-BLOW
Flow (l/s)	57.6	89
Solids (ppm)	162	20
Oil (ppm)	24	
Dis Sol (ppm)	5,000	1,896
Temp (F)	41	42

Waste Set Inputs assumed from the company supplied data: *Marked_Air_Plan_Approval.pdf*
FEOR-T Flow - See 'Input_FEOR_A_B_T' tab for backup

Wastewater Treatment Plant Unit Inputs into Water9

Unit Inputs assumed from the company supplied data: *Marked_Air_Plan_Approval.pdf*

Diffused air biotreatment	Water9 input	Water9 input
1 Description of unit	Diffused air bio - unit 28	Diffused air bio - unit 29
2 Wastewater temperature (C)	25	25
3 length of aeration unit (m)	26.7	26.7
4 width of aeration unit (m)	26.7	26.7
5 depth of aeration unit (m)	7.9	7.9
6 fraction of surface agitated by air	0.8	0.8
7 fraction of surface quiescent	0.2	0.2
13 if there is plug flow, enter 1	0	0
14 Overall biorate (mg/g bio-hr)	19	19
15 Aeration air flow (m3/s)	1.711	1.711
16 activated sludge biomass (g/l)	2	2
17 If covered, then enter 1	0	0
18 special input	0	0
19 pH (enter 0 for no pH adjustment)	0	0

Circular clarifiers	Water9 input	Water9 input
1 Description of unit	Clarifier 1 - unit 2	Clarifier 2 - unit 7
2 Wastewater temperature (C)	25	25
3 secondary clarifier diameter (m)	19.3	19.3
4 secondary clarifier depth (m)	5.6	5.6
5 clarifier solids removal efficiency	0.7	0.7
6 waterfall drop height (cm)	20	20
7 clarifier weir/circumference	0.5	0.5
8 Center well present, =1	0	0
10 number of identical units in parallel	1	1
19 pH (enter 0 for no pH adjustment)	0	0

Open sump	Water9 input
1 Description of unit	Biosluge sump - unit 16
2 Underflow T (C)	25
3 Total water added at the unit (l/s)	0
4 Area of openings at unit (cm2)	50
5 Radius of drop pipe (cm)	5
6 Drop length to conduit (cm)	61
7 Open surface=1	1
8 Subsurface entrance=1	0
9 subsurface exit =1	0
10 radius of underflow conduit (cm	12
11 distance to next unit (cm)	500
12 slope of underflow conduit	0.015
13 Open surface of liquid at the unit (cm2)	90000
14 flow entrance depth under surface	10
15 depth of liquid in sump (cm)	168

16 velocity air at opening (ft/min)	88
17 municipal waste in conduit =1	0
18 Assume equilibrium in unit, =1	0
19 pH (enter 0 for no pH adjustment)	0

Storage tank	**Water9 input**	**Water9 input**
1 Description of unit	Biosluge holding - unit 13	Biosludge tank - unit 12
2 Wastewater temperature (C)	25	42
3 Open surface area of tank (m2)	16.6	34.2
4 Density of liquid in tank (g/cc)	1	1
5 tank wast Mwt, water=18	18	18
6 unit storage time (days)	0	0
7 tank paint factor	0.6	0.6
8 tank diameter	4.6	6.6
9 tank vapor space height (m)	0.64	1.1
10 diurnal tamp. Change (deg. C)	11	11
11 tank height (m)	3.2	5.5
12 oil in composite wastewater (Wt. %)	0	0
13 Product factor crude oil =0.75 else 1.0	1	1
19 pH (enter 0 for no pH adjustment)	0	0

DAF or grit separator	**Water9 input**
1 Description of unit	Sand Filter - unit 30
2 Wastewater temperature (C)	42
3 KL unit surface (m/s)	0.001
4 Pretreatment length (m)	3.6
5 Pretreatment width (m)	2.7
6 Pretreatment depth (m)	3
7 air flow (m3/s)	0.193
8 oil in composite wastewater (Wt. %)	0
9 fraction surface covered with float	0
10 Oil molecular weight	180
11 Density of oil (g/cc)	1
12 active biomass, (g/l)	0
13 number units in parallel	0
15 vent air emission control factor	0
16 cover vent rate (m3/s per m2 surface)	0.02
17 If covered, then enter 1	1
19 pH (enter 0 for no pH adjustment)	0

Weir, waterfall	**Water9 input**
1 Description of unit	Outfall - unit 9
2 Underflow T (C)	42
3 Total water added at the unit (l/s)	0
4 waterfall width at surface (m)	3
5 waterfall drop height (cm)	20
6 tailwater depth (m)	0.1
7 Open surface=1	1
8 Subsurface entrance=1	1
9 subsurface exit =1	0
10 radius of underflow conduit (cm)	12
11 distance to next unit (cm)	500
12 slope of underflow conduit	0.015
19 pH (enter 0 for no pH adjustment)	0