



Shell Chemical Appalachia LLC
300 Frankfort Rd
Monaca, PA 15061

March 27, 2023

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
Malodors 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). The format of this and future malfunction reports has been updated as requested by PADEP.

This malfunction did not pose danger to the public health and safety or the environment. Shell personnel detected faint similar odors during the offsite observations in the vicinity of Gate 3 and Lockhouse 6 across the Ohio River. This offsite odor was considered to be malodor and reported to PADEP. Shell’s 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.

- **Name and location of the facility**
Shell Polymers Monaca
300 Frankfort Road, Monaca PA, 15061
- **Nature and cause of the malfunction or breakdown**
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**
January 25, 2023 at ~09:45AM when a malodor was first detected offsite.
- **The date and time that the malfunction started and ended**
January 25, 2023 beginning at 09:45AM and ending on February 16, 2023 at ~1:58PM when a malodor was last detected offsite.

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

Table 1: Preliminary total estimated excess emissions onsite for the biotreater

Pollutant	Emission Rate (tons)
VOC	0.46
HAP (Total)	0.41
Benzene	0.26
Toluene	0.13

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

Excess emissions for this malodor event have been calculated using the Environmental Protection Agency’s (EPA) updated WATER9 Model, using periodic wastewater sample results for volatile organics and semi-volatile organics taken at the biotreater inlet and flow equalization and oil removal tanks, application of process indicators and operating condition wastewater retention times, and measured flow rates into the biotreaters. Sample results contain volatile organics and Hazardous Air Pollutants (HAPs) including benzene, and toluene; 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

- **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 operational control of flow equalization and oil recovery (FEOR) tank B to receive wastewater which may contain higher levels of hydrocarbons when possible and FEOR A retained wastewater containing lower levels of hydrocarbons. Hydrocarbon-containing wastewater was integrated slowly when possible from FEOR B into the combined flow entering the biotreaters. This minimized hydrocarbons in the biotreaters, allowed time for biodegradation of organic material, and limited hydrocarbon levels that could generate odors.

Odors were minimized through added process wastewater sampling within the ethane cracking unit (ECU) to determine when process wastewater conditions improved or worsened and enabling communication to the WWTP for better wastewater flow management. This sampling also contributed to root cause determination and corrective actions.

Odors were minimized through the closure of a manual valve and isolating the ECU wash oil slop drum, hydrocarbon slop drum, and warm flare drum liquids from the process wastewater system. Operations walked down the piping and hydrocarbon-containing drums within ECU to verify line-ups for pumping. This reduced hydrocarbons entering the wastewater by enabling the pumping and recycling of hydrocarbons back into the closed-loop process.

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

The root cause of offsite detectable odors was determined to be hydrocarbons coming from the ECU leading to the WWTP. The valve was opened in response to an abnormal process condition but was not returned to its normal closed state. This caused pumping of hydrocarbons from the affected drums to be sent to the WWTP for longer than intended instead of recycling back into the process. This led to higher levels of hydrocarbons entering the biotreaters periodically and generating odors. Normal operation is hydrocarbon-containing drums are either recycled back into the process and separated and sent to storage as a byproduct, or loaded out as a waste.

- **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

A management of change was initiated to evaluate and install a car-seal on the manual valve VA-190172-2 isolating the process wastewater from the hydrocarbon-containing drums within ECU. Car-sealing this manual valve closed provides a higher level of control and assurance on the valve operation. Line labeling has also been added to this piping manifold to clearly identify process streams, and approval and notification necessary for valve operation. Car-seals have been added to other valves within ECU to similarly provide a higher level of control against contamination between other process streams that could lead to equipment damage or other malfunctions.

Shell commissioned a project to design and install a temporary enclosed induced air flotation system to improve and increase hydrocarbon removal capacity in the WWTP. 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 for this temporary installation and has been requested from the Air Quality Program through the Request for Determination process. Odors in the future will be minimized by the reduction of hydrocarbons entering the biotreaters and destruction of vapors in the thermal oxidizer. Offsite odor detections have ended prior to implementation of this project but the action began during the event. Performance of this temporary project will be 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**

No follow up report planned. A follow up request for determination or application will be sent as necessary based on PADEP's response to the induced air flotation temporary project.

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

Corrective action to eliminate malodors detectable offsite is considered final. Installation and evaluation of a temporary enclosed diffused air flotation in the WWTP is expected to be commenced in the next month.

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
WATER9 Model Ouputs and Inputs

Wastewater Treatment Plant, Malfunction Emissions
Shell Polymers Monaca

Incident Start Time:
Incident End Time:

1/25/2023
2/16/2023

Timeline Run Start Date	Timeline Run End Date	Timeline Run Number of Days	FEOR- T Flowrate (l/sec)	Sample Date/Location	Malfunction Start Date	Malfunction Start Date	Malfunction Number of Days	% of Emissions Based on Days	Total VOC Emissions (tons)	Total HAP Emissions (tons)	Benzene Emissions (tons)	Phenol Emissions (tons)	Toluene Emissions (tons)	Ethylbenzene Emissions (tons)	Xylene Emissions (tons)	Styrene Emissions (tons)	Naphthalene Emissions (tons)	POM (minus naphthalene) Emissions (tons)
1/15/2023	2/8/2023	24.625	63.3	10/4/2022 FEOR A	1/25/2023	2/8/2023	15	60.9137	0.0701	0.0281	0.0183	0.0000	0.0079	0.0000	0.0002	0.0013	0.0005	0.0000
1/15/2023	2/8/2023	0.375	7.0	1/10/2023 FEOR B	1/25/2023	2/8/2023	0.375	100.0000	0.0032	0.0032	0.0019	0.0000	0.0010	0.0000	0.0000	0.0001	0.0002	0.0000
2/9/2023	2/9/2023	0.5	69.4	2/9/2023 Biotreater Inlet	2/9/2023	2/9/2023	0.5	100.0000	0.2488	0.2488	0.1548	0.0000	0.0762	0.0063	0.0000	0.0111	0.0005	0.0000
2/9/2023	2/10/2023	1.5	67.6	2/9/2023 Biotreater Inlet; diluted by 6.5	2/9/2023	2/10/2023	1.5	100.0000	0.1059	0.1059	0.0689	0.0000	0.0340	0.0028	0.0000	0.0000	0.0002	0.0000
2/11/2023	2/11/2023	1	61.5	2/9/2023 Biotreater Inlet; diluted by 6.5, then another 6.5	2/11/2023	2/11/2023	1	100.0000	0.0099	0.0099	0.0064	0.0000	0.0032	0.0003	0.0000	0.0000	0.0000	0.0000
2/12/2023	2/20/2023	8.875	58.0	10/4/2022 FEOR A	2/12/2023	2/16/2023	5	56.3380	0.0214	0.0086	0.0056	0.0000	0.0024	0.0000	0.0001	0.0004	0.0001	0.0000
2/12/2023	2/20/2023	0.125	6.4	1/10/2023 FEOR B	2/12/2023	2/16/2023	0.125	100.0000	0.0010	0.0010	0.0006	0.0000	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000
									0.4602	0.4054	0.2564	0.0000	0.1250	0.0094	0.0002	0.0129	0.0015	0.0001

**Wastewater Treatment Plant, Water9 Emission Inputs
Shell Polymers Monaca**

Data Sources

Marked_Air_Plan_Approval.pdf - plan approval assumptions vetted by Operations.
3/13/2023 email Process Engineering for the Biotreater agitated/quiescent fractions

Waste Stream Input Assumptions

Water9 Parameter	FEOR-T	CT-BLOW
Solids (ppm)	162	20
Oil (ppm)	24	
Dissolved Solids (ppm)	5,000	1,896
Temp (C)	25	25

Wastewater Treatment Plant Unit Inputs into Water9

Diffused air biotreatment	Water9 input	Water9 input
1 Description of unit		Diffused air bio -
	Diffused air bio - unit 28	unit 29
2 Wastewater temperature (C)	25	25
3 length of aeration unit (m)	24.8	24.8
4 width of aeration unit (m)	24.8	24.8
5 depth of aeration unit (m)	6.1	6.1
6 fraction of surface agitated by air	0.72	0.72
7 fraction of surface quiescent	0.28	0.28
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)	17.2	17.2
4 secondary clarifier depth (m)	6.1	6.1
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
	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 temp. 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

Wastewater Treatment Plant, Summary of Analytical Data
Shell Polymers Monaca

Sample Date Sample Time Sample ID Sample Location Analytical Method Lab					10/4/2022 9:50 16479 FEOR A EPA 624/625 ESL	1/10/2023 14:00 29034 FEOR B EPA 624.1/625.1 Eurofins	2/9/2023 12:00 180-15833-1 Biotreater Inlet EPA 624.1/625.1 Eurofins	2/9/2023 12:00 180-15833-1 Biotreater Inlet; diluted by 6.5 EPA 624.1/625.1 Eurofins	2/9/2023 12:00 180-15833-1 Biotreater Inlet; diluted by 6.5, then another 6.5 EPA 624.1/625.1 Eurofins
Component	Carbon Atoms	Component Molecular Weight (lb/lb-mol)	HAP?	POM?	Concentration Sample Result (mg/L)	Concentration Sample Result (mg/L)	Concentration Sample Result (mg/L)	Concentration Sample Result (mg/L)	Concentration Sample Result (mg/L)
Benzene	6	78.11	X		0.3410	13.0000	78.0000	12.0000	1.8462
Phenol	6	94.11	X		0.0193				
Toluene	7	92.15	X		0.1870	8.3000	49.0000	7.5385	1.1598
Ethylbenzene	8	106.16	X				3.7000	0.5692	0.0876
Total Xylenes	8	106.16	X		0.0069				
Styrene	8	104.15	X		0.0156	0.4100	3.7000		
Naphthalene	10	128.17	X		0.0136	1.6000	0.3900	0.0600	0.0092
2-Methylnaphthalene	11	142.2	X	X					
Acenaphthene	12	154.21	X	X		0.0770	0.0059	0.0009	0.0001
Acenaphthylene	12	152.19	X	X		0.0480	0.0019	0.0003	0.0000
Fluorene	13	166.22	X	X		0.0900	0.0032	0.0005	0.0001
Anthracene	14	178.23	X	X		0.0110	0.0005	0.0001	0.0000
Phenanthrene	14	178.23	X	X		0.0980	0.0037	0.0006	0.0001
Fluoranthene	16	202.25	X	X		0.0110	0.0007	0.0001	0.0000
Pyrene	16	202.25	X	X		0.0130	0.0009	0.0001	0.0000
Benzo(a)anthracene	18	228.29	X	X		0.0014			
Chrysene	18	228.29	X	X		0.0013			
1,3-Cyclopentadiene	5	66.1			0.0301				
* 1-Buten-3-yne, 2-methyl-	5	66.1							
* 1,3-Cyclopentadiene, 1-methyl-	6	80.13			0.1470				
* Ethylidenecyclobutane	6	82.14			0.0216				
* Cyclobutane, ethenyl-	6	82.14							
* 1-Penten-3-yne, 2-methyl-	6	80.13							
* 1,4-Cyclohexadiene, 1-methyl-	7	94.15			0.0084				
* Bicyclo[2.2.1]hept-2-ene, 1-methyl	7	94.15							
* 3-Oxabicyclo[3.3.0]octan-2-one,6-	8	138.16			0.0135				
* Bicyclo[2.2.1]hept-2-ene, 2-methyl	8	108.18			0.0249				
* 9-Oxabicyclo[6.1.0]non-4-ene	8	124.18							
n-Propyl Benzene	9	120.19							
1,2,4-Trimethylbenzene	9	120.19							
* 1H-Indene,3a,4,7,7a-tetrahydro	9	120.19			0.0128				
* Bicyclo[2.2.1]hept-2-ene, 5-ethenyl	9	120.19			0.0296				
* Indene	9	116.16			0.0093				
* Tricyclo[3.3.0.0(2,8)]octan-3-one	9	136.19							
Benzene, 1,2,4,5-tetramethyl-(01)	10	134.22			0.0105				
Benzene, 1,2,4,5-tetramethyl-(02)	10	134.22			0.0174				
Butylbenzene	10	134.22							
* Benzene, 2-ethyl-1,4-dimethyl-	10	134.22			0.0108				
* 2,4-Dimethylstyrene	10	132.2			0.0085				
* Benzene,1,3-diethyl-	10	134.22			0.0232				
* Benzene,1-methyl-3-propyl-	10	134.22			0.0137				
* cis-8-Methyl-bicyclo[4,3,0]non-3,7	10	134.22			0.0491				
* Benzene, 1-methyl-3-(1-methylethyl)-	10	134.22			0.0095				
* 1,4,4a,5,8,8a-Hexahydro-naphthalen	10	134.22			0.0132				
* Benzene,1-methyl-2-propyl-	10	134.22							
* 1-Phenyl-1-butene	10	132.2							
* Benzene, 1,2,3,5-tetramethyl-	10	134.22							
* Benzene, pentamethyl-	11	148.24			0.0073				
* 5-Phenylbicyclo[2.2.1]hept-2-ene	13	170.25			0.0120				
Pentanes	5				0				
Hexanes	6				0.1686				
Heptanes	7				0.0084				
Octanes	8				0.0384				
Nonanes	9				0.0517				
Decanes +	10+				0.1473				

*A subset of components above were not available within the Water9 database (designated with an *), so they were grouped by carbon atoms and input into Water9 as Pentanes, Hexanes, Heptanes, Octanes, Nonanes and Decanes.

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