pennsylvania
DEPARTMENT OF ENVIRONMENTAL PROTECTION
BUREAU OF AIR QUALITY

MEMO

TO: Mark Gorog
Environmental Engineer Manager
Southwest Regional Office

FROM: Craig Evans, Chief CC
Air Toxics and Risk Assessment Section
Division of Permits
Bureau of Air Quality

DATE: March 19, 2015

RE: Air Quality Modeling and Inhalation Risk Evaluation
Shell Chemical Appalachia LLC, Potter and Center Townships,
Beaver County, Pennsylvania

Background

Shell Chemical Appalachia LLC (Shell) is proposing to construct a petrochemicals complex in Potter and Center Townships in Beaver County. The proposed petrochemicals plant would be built on approximately 400 acres on the site of the zinc smelter previously owned by the Horsehead Corporation. The proposed complex will be comprised of an ethene manufacturing plant with an average capacity of 1,500,000 metric tons per year. The ethene that is produced will be used to supply feed to three polyethylene production units with a combined annual production of approximately 1,600,000 metric tons of polyethylene. Steam and electricity required for the process will be supplied by natural gas-fired combined cycle (NGCC) cogeneration units (Cogen Units). The project will also include all of the ancillary units needed to support a new standalone complex including effluent treatment, storage, logistics, cooling water facilities, emergency flares, buildings, and warehouses. Excess electricity produced by the Cogen Units will be sold for distribution within the PJM grid for regional use.

The proposed project's seven cracking furnaces will "crack" hydrogen (H_2) out of the ethane (C_2H_6) found in natural gas to produce ethene (C_2H_4). "Tail gas", a byproduct from the cracker furnaces that contains methane and a high concentration of hydrogen, will be used to fuel the process, along with natural gas used to supplement the energy requirements of the process. The ethene that is produced in the cracking furnaces will be used to feed the two gas phase polyethylene manufacturing units and one slurry technology unit. The two gas phase units are each designed to produce 550,000 metric tons per year while the slurry unit is designed to produce 500,000 metric tons per year. Both technologies employ catalysts but use different process equipment and operating conditions to produce each specific grade of polyethylene.

To support the plant operations, three on-site natural gas-fired combustion turbines with duct burners and heat recovery steam generators (HRSGs) will be used to generate the required steam and electricity. These are the NGCC Cogen Units that were previously mentioned. Other ancillary equipment will include four emergency diesel generators and three diesel-driven firewater pumps, two cooling towers, numerous storage tanks and pressure vessels for raw materials and by-products, and a wastewater treatment facility.

On January 28, 2015, the Department of Environmental Protection (DEP) received a report titled "Inhalation Risk Assessment For Petrochemicals Complex Shell Chemical Appalachia LLC Beaver County, Pennsylvania." This report was prepared for Shell by RTP Environmental Associates to support Shell's Plan Approval Application for the petrochemicals project. The DEP's Air Quality Modeling Section performed an independent air quality analysis for a risk assessment on the proposed facility. The DEP's Air Toxics and Risk Assessment Section performed an independent risk assessment and found no unacceptable risks from the proposed operations. The purpose of this memo is to discuss the results of the risk assessment analysis.

Inhalation Risk Assessment

The risk assessment process includes four primary steps: hazard identification, exposure assessment, toxicity assessment, and risk characterization. The hazard identification step involves identifying the compounds of potential concern (COPC) expected to be emitted from the proposed project considering factors such as fuel type, emissions control equipment, feedstock characteristics, etc. COPC emissions data from similar facilities were used in conjunction with manufacturers' specifications and engineering calculations to estimate emission rates from the proposed facility.

These emission rates, in conjunction with the results from the dispersion modeling conducted by the DEP for this facility, were used to estimate the maximum hourly and annual ground level ambient concentrations of the COPC over a defined grid outside the plant perimeter. The DEP's risk assessment analysis includes two inhalation pathway risk scenarios: acute risk and chronic risk for the maximum exposed individual. The COPC identified for the risk assessment are found in Table 1.

The acute risk assessment compares the estimated one hour modeled maximum concentration to an acceptable one hour reference concentration. The maximum exposed individual (MEI) is assumed to live a 70 year lifetime at the point on the receptor grid where the exposure concentration is the highest. However, the EPA assumes a 30 year exposure duration for an adult resident.[1]

The DEP's Air Quality Modeling Section used the AERMOD air dispersion model to perform their analysis. The maximum ground level concentrations (at the MEI location) were determined using the actual COPC emission rates. This procedure was performed for both the acute and the chronic exposure scenarios. More detail pertaining to the air dispersion modeling is available in the memorandum written by the DEP's Air Quality

---

[1] Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities, Chapter 6, Quantifying Exposure, September 2005 http://www.epa.gov/osw/hazard/tsd/td/combust/finalmact/ssra/05hhrap6.pdf

Modeling Section. The results of the DEP's air quality analysis were used for the risk assessment.

Toxicity assessment involves the identification of the adverse health effects posed by an individual compound and relates the development of these effects to the level of exposure. The toxic potential of a chemical may depend on exposure route and duration as well as the mode of action. In an inhalation risk assessment the health risk value potentially posed by each COPC is mathematically applied to the modeled exposure concentration to provide the estimated risk level.

Risk Factors and Their Application

For cancer risk, the risk value is determined using an inhalation unit risk factor (URF) expressed as risk per unit concentration ($m^3/\mu g$). The URF is multiplied by the modeled exposure concentration to derive the individual cancer risk for each carcinogenic COPC which is then summed along with all other individual COPC cancer risks to calculate a total excess lifetime cancer risk (ELCR). The Department's acceptable total ELCR level is one-in-one hundred thousand (1×10^{-5}).

For noncancer risk, the risk value is determined using a reference concentration (R*f*C) expressed in mass per cubic meter of air (typically mg/m^3). An R*f*C is "an estimate of a continuous inhalation exposure for a given duration to the human population (including susceptible subgroups) that is likely to be without an appreciable risk of adverse health effects over a lifetime."[2] The R*f*C is divided into the modeled exposure concentration of the COPC (expressed in the same units of concentration) to derive the hazard quotient (HQ) which is then summed along with all other individual COPC HQ's to calculate a total hazard index (HI). The Department's acceptable total HI level is 0.25.

The acute health risk benchmark is the short term (one hour) exposure inhalation reference concentration. An HQ of 1.0 or less indicates that a compound poses no threat of an adverse effect on a one hour exposure basis rather than a chronic basis. The acute R*f*C for each COPC should not be exceeded by its respective modeled maximum hourly concentration - the predicted maximum one hour hazard quotient (the modeled acute exposure concentration divided by the acute R*f*C) should be no greater than 1.0.

Risk Factor References (Table 3)

As a reference for chronic human health inhalation risk values for the COPC, DEP follows the hierarchy provided by the U.S. Environmental Protection Agency's (EPA) Office of Solid Waste in the "Human Health Risk Assessment Protocol" (HHRAP), Appendix 2-A. This list is recommended by EPA "for acquiring human health toxicity data to be used in performing risk assessments of hazardous waste combustion facilities" and is ranked as follows: [3]

---

[2] EPA IRIS Glossary, http://www.epa.gov/iris/gloss8_arch.htm (accessed 8/21/12).

[3] Human Health Risk Assessment Protocol, Appendix A-2, EPA530-R-05-006, September 2005. p. A-2-33. www.epa.gov/osw/hazard/tsd/td/combust/finalmact/ssra/05hhrapapa.pdf (accessed 8/3/12).

1. EPA's Integrated Risk Information System (IRIS)
2. EPA's Provisional Peer Reviewed Toxicity Values (PPRTVs)
3. Other Toxicity Values (including California Environmental Protection Agency (Cal EPA) Reference Exposure Levels (RELs), Agency for Toxic Substances and Disease Registry (ATSDR) Minimal Risk Levels (MRLs), and Health Effects Assessment Summary Tables (HEAST) toxicity values

The Department uses the following hierarchy of acute risk values[4] for the acute risk assessment:

1. Short-Term Exposure Limit/40
2. Ceiling/10
3. 3 x Time-Weighted Average/20
4. Immediately Dangerous to Life or Health/20

Results

There is one chronic scenario and one acute scenario that have been assessed for the COPC.

The chronic scenario is:

1. Maximum Exposed Individual (MEI) Non-Cancer Risk (Table 1)

   Hazard Index: COPC HI = 0.0754

2. Maximum Exposed Individual (MEI) Cancer Risk (Table 1)

   Excess Lifetime Cancer Risk: COPC ELCR = 7.86×10^{-6}

The acute scenario is:

1. Maximum Exposed Individual (MEI) Acute Non-Cancer Risk (Table 2)

   Hazard Quotient: All COPC HQ's are less than 1.0

The MEI is the individual who is exposed to the modeled maximum ground-level concentrations. The risks for the two scenarios are not unacceptable.

[4] *NIOSH Pocket Guide to Chemical Hazards* http://www.cdc.gov/niosh/npg/default.html

Table 1 – Summary of DEP's Air Quality Analysis Results for Chronic Risk Scenario for Maximum Exposed Individual

Compounds of Potential Concern	Chronic Cancer Risk	Concentration (µg/m³)	Chronic Non Cancer HQ	Concentration (µg/m³)
1,3-Butadiene	**1.14E-06**	3.81E-02	**0.01941639**	3.88E-02
2-Methylnaphthalene	-	8.98E-08	-	8.86E-08
3-Methylchloranthrene	4.24E-11	6.74E-09	-	6.64E-09
7,12-Dimethylbenz(a)anthracene	4.25E-09	5.99E-08	-	5.90E-08
Acenaphthene	-	7.95E-07	-	8.20E-07
Acenaphthylene	-	1.55E-06	-	1.60E-06
Acetaldehyde	3.32E-11	1.51E-05	0.00000169	1.52E-05
Acrolein	-	3.06E-06	0.00015519	3.10E-06
Anthracene	-	2.16E-07	-	2.23E-07
Arsenic	3.23E-09	7.48E-07	0.00004920	7.38E-07
Barium	-	1.45E-05	0.00002854	1.43E-05
Benz(a)anthracene	1.23E-11	1.11E-07	-	1.15E-07
Benzene	**2.03E-06**	2.60E-01	**0.00868161**	2.59E-01
Benzo(a)pyrene	5.19E-11	4.72E-08	-	4.91E-08
Benzo(b)fluoranthene	2.13E-11	1.94E-07	-	2.00E-07
Benzo(g,h,i)perylene	-	4.49E-09	-	4.43E-09
Benzo(k)fluoranthene	4.78E-12	4.34E-08	-	4.45E-08
Beryllium	1.08E-10	4.49E-08	0.00000222	4.43E-08
Biphenyl	-	1.63E-05	0.00004193	1.68E-05
Cadmium	7.41E-09	4.12E-06	0.00040592	4.06E-06
Chromium VI	**2.98E-07**	2.48E-05	**0.00295563**	2.36E-05
Chrysene	2.91E-12	2.64E-07	-	2.73E-07
Cobalt	2.83E-09	3.14E-07	0.00005166	3.10E-07
Copper	-	2.80E-06	-	2.76E-06
Dibenz(a,h)anthracene	7.06E-11	5.88E-08	-	6.46E-08
Dichlorobenzene	4.94E-11	4.49E-06	0.00000001	4.43E-06
Ethylbenzene	1.96E-08	7.84E-03	0.00000780	7.73E-03
Ethylene Oxide	-	0.00E+00	-	0.00E+00
Fluoranthene	-	6.90E-07	-	7.12E-07
Fluorene	-	2.17E-06	-	2.24E-06
Formaldehyde	6.33E-09	4.87E-04	0.00004927	4.83E-04
n-Hexane	-	3.20E-01	0.00046477	3.25E-01
Indeno(1,2,3-cd)pyrene	7.76E-12	7.05E-08	-	7.86E-08
Lead	2.21E-11	1.84E-06	0.00001212	1.82E-06
Manganese	-	1.42E-06	0.00002805	1.40E-06
Mercury	-	9.73E-07	0.00000320	9.59E-07
Methanol	-	3.33E-02	0.00000170	3.40E-02
Molybdenum	-	3.62E-06	-	3.57E-06
Naphthalene	**4.34E-06**	1.28E-01	**0.04241949**	1.26E-01
Nickel	3.77E-09	7.86E-06	0.00055352	7.75E-06
PAH (as benzo(a)pyrene)	6.57E-10	5.97E-07	-	5.96E-07
n-Pentane	-	8.56E-03	0.00000843	8.43E-03
Phenanthrene	-	6.93E-06	-	7.16E-06
Phenol	-	5.81E-06	0.00000003	5.92E-06
Propane	-	5.27E-03	-	5.19E-03
Propylene Oxide	2.91E-11	7.88E-06	0.00000026	7.86E-06
Pyrene	-	6.43E-07	-	6.63E-07
Selenium	-	8.98E-08	0.00000000	8.86E-08
Styrene	-	4.38E-02	0.00004353	4.36E-02
Toluene	-	9.10E-02	0.00001811	9.06E-02
Vanadium	-	7.57E-06	-	7.46E-06
Xylenes	-	2.97E-03	0.00002951	2.95E-03
ELCR	**7.86E-06**	**HI**	**0.07542977**	

$$Modeled\ Maximum\ Exposure\ Concentration * Unit\ Risk\ Factor\ (URF) = Chronic\ Cancer\ risk$$

$$\frac{Modeled\ Maximum\ \ Exposure\ Concentration}{Reference\ Concentration\ (RfC)} = HQ$$

Table 2 – Summary of DEP's Air Quality Analysis Results for Acute Risk Scenario

Compounds of Potential Concern	DEP Max 1-Hr Conc (µg/m³)	DEP Acute HQ
1,3-Butadiene	2.25E+00	0.0081984364
2-Methylnaphthalene	1.40E-04	0.0000000467
3-Methylchloranthrene	1.00E-05	0.0000001351
7,12-Dimethylbenz(a)anthracene	9.00E-05	-
Acenaphthene	1.20E-02	0.0000033222
Acenaphthylene	2.36E-02	0.0000023560
Acetaldehyde	6.43E-02	0.0000142867
Acrolein	2.01E-02	0.0010040000
Anthracene	3.14E-03	0.0000116296
Arsenic	1.14E-03	0.0057000000
Barium	1.42E-02	0.0001896000
Benz(a)anthracene	1.59E-03	0.0000530000
Benzene	1.68E+01	**0.0839698000**
Benzo(a)pyrene	6.60E-04	0.0000220000
Benzo(b)fluoranthene	2.83E-03	-
Benzo(g,h,i)perylene	1.00E-05	0.0000000003
Benzo(k)fluoranthene	5.60E-04	0.0000294737
Beryllium	7.00E-05	0.0002800000
Biphenyl	1.38E-03	0.0000092000
Cadmium	6.30E-03	**0.0210000000**
Chromium VI	1.01E-02	0.0010140000
Chrysene	3.90E-03	0.0001300000
Cobalt	4.80E-04	0.0001600000
Copper	2.75E-03	0.0011000000
Dibenz(a,h)anthracene	8.80E-04	-
Dichlorobenzene	6.83E-03	0.0000009107
Ethylbenzene	2.04E-01	0.0000149765
Ethylene Oxide	0.00E+00	-
Fluoranthene	1.03E-02	-
Fluorene	3.26E-02	-
Formaldehyde	4.30E-01	0.0070187755
n-Hexane	4.94E+01	0.0018284763
Indeno(1,2,3-cd)pyrene	1.06E-03	-
Lead	2.85E-03	0.0003800000
Manganese	2.17E-03	0.0000289333
Mercury	1.48E-03	0.0001480000
Methanol	2.51E+00	0.0003093218
Molybdenum	3.56E-03	0.0000079111
Naphthalene	3.13E+00	0.0016666720
Nickel	1.20E-02	0.0053155556
PAH (benz(a)pyrene RfC)	8.70E-04	0.0000290000
n-Pentane	8.41E+00	0.0000467226
Phenanthrene	1.04E-01	-
Phenol	1.16E-03	0.0000001933
Propane	5.17E+00	0.0000191631
Propylene Oxide	1.15E-02	0.0000159306
Pyrene	9.50E-03	-
Selenium	1.40E-04	0.0000046667
Styrene	1.14E+00	0.0002684729
Toluene	2.37E+00	0.0001692779
Vanadium	7.44E-03	0.0000042514
Xylenes	4.92E-01	0.0000302488

$$\frac{Modeled\ Maximum\ Exposure\ Concentration}{Reference\ Concentration\ (RfC)} = Hazard\ Quotient$$

Table 3 – Summary of DEP's Risk Factors

Chemical Name	CAS No.	RfC ($\mu g/m^3$)	Chronic RfC reference	URF ($m^3/\mu g$)	URF Reference	Acute RfC (mg/m3)	STEL (mg/m3)	Ceiling (mg/m3)	TLV (mg/m3)	IDLH (mg/m3)	Reference
1,3-Butadiene	106-99-0	2.00	EPA IRIS	0.00003	EPA IRIS	0.275	11		2.2		OSHA
1,4-Dichlorobenzene	106-46-7	801.5	Cal EPA	0.000011	Shell	7.5	301				ACGIH
2-Methylnaphthalene	91-57-6	NR		NR		3					Shell
3-Methylchloranthrene	56-49-5	NR		0.0063	CalEPA	0.074					Shell
7,12-Dimethylbenz[a]anthracene	57-97-6	NR		0.071	CalEPA						
Acenaphthene	83-32-9	NR		NR		3.6					Shell
Acenaphthylene	208-96-8	NR		NR		10					Shell
Acetaldehyde	75-07-0	9.00	EPA IRIS	2.2E-06	EPA IRIS	4.5		45			ACGIH
Acrolein	107-02-8	0.02	EPA IRIS	NR		0.02	0.8				NIOSH
Anthracene	120-12-7	NR		NR		0.27					Shell
Arsenic	7440-38-2	0.015	Cal EPA	0.00431	EPA IRIS	0.0002		0.002			NIOSH
Barium	7440-39-3	0.5	HEAST	NR		0.075			0.5		ACGIH
Benz[a]anthracene	56-55-3	NR		0.00011	CalEPA	0.03			0.2		Shell
Benzene	71-43-2	30.00	EPA IRIS	7.8E-06	EPA IRIS	0.2	8				ACGIH
Benzo[a]pyrene (PAH)	50-32-8	NR		0.0011	CalEPA	0.03			0.2		OSHA
Benzo[b]fluoranthene	205-99-2	NR		0.00011	CalEPA						
Benzo[g,h,i]perylene	191-24-2	NR		NR		30					Shell
Benzo[k]fluoranthene	207-08-9	NR		0.00011	CalEPA	0.019					Shell
Beryllium	7440-41-7	0.02	EPA IRIS	0.0024	EPA IRIS	0.00025	0.01				ACGIH
Biphenyl	92-52-4	0.4	PPRTV	NR		0.15			1		NIOSH
Cadmium	7440-43-9	0.01	ATSDR	0.0018	EPA IRIS	0.0003			0.002		ACGIH
Chromium III	16065-83-1	NR		NR		0.075			0.5		ACGIH
Chromium VI	18540-29-9	0.008	EPA IRIS	0.012	EPA IRIS	0.01		0.1			OSHA
Chrysene	218-01-9	NR		0.000011	CalEPA	0.03			0.2		OSHA
Cobalt	7440-48-4	0.006	PPRTV	0.009	PPRTV	0.003			0.02		ACGIH
Copper	7440-50-8	NR		NR		0.0025	0.1				ACGIH
Dibenz[a,h]anthracene	53-70-3	NR		0.0012	CalEPA						
Ethylbenzene	100-41-4	1000	EPA IRIS	2.5E-06	CalEPA	13.6	543				ACGIH
Ethylene Oxide	75-21-8	30	Cal EPA	0.000088	CalEPA	0.225	9				OSHA
Fluoranthene	206-44-0	NR		NR							
Fluorene	86-73-7	NR		NR							
Formaldehyde	50-00-0	9.8	ATSDR	0.000013	EPA IRIS	0.0615	2.5				OSHA

Indeno[1,2,3-cd]pyrene	193-39-5	NR		0.00011	CalEPA						
Lead	7439-92-1	0.15	NAAQS	0.000012	CalEPA	0.0075			0.05		ACGIH
Manganese	7439-96-5	0.05	EPA IRIS	NR		0.075	3				NIOSH
Mercury	7439-97-6	0.30	EPA IRIS	NR		0.01		0.1			OSHA
Methanol	67-56-1	20000	EPA IRIS	NR		8.125	325				NIOSH
Molybdenum		NR		NR		0.45			3		ACGIH
Naphthalene	91-20-3	3.00	EPA IRIS	0.000034	CalEPA	1.875	75				NIOSH
n-Hexane	110-54-3	700	EPA IRIS	NR		27			180		ACGIH
Nickel	7440-02-0	0.014	Cal EPA	0.00048	EPA IRIS	0.00225			0.015		NIOSH
n-Pentane	109-66-0	1000	PPRTV	NR		180		1800			NIOSH
Phenanthrene	85-01-8	NR		NR							
Phenol	108-95-2	200	Cal EPA	NR		6		60			NIOSH
Propane	74-98-6	NR		NR		270			1800		OSHA
Propylene Oxide	75-56-9	30	EPA IRIS	3.7E-06	EPA IRIS	0.7125			4.8		ACGIH
p-Xylene	106-42-3	100	EPA IRIS	NR		16.275	651				ACGIH
Pyrene	129-00-0	NR		NR							
Selenium	7782-49-2	19.99	Cal EPA	NR		0.03			0.2		ACGIH
Styrene	100-42-5	1001	EPA IRIS	NR		4.25	170				ACGIH
Toluene	108-88-3	5000	EPA IRIS	NR		14	560				NIOSH
Vanadium	7440-62-2	NR		NR		1.75				35	NIOSH