MICHIGAN DEPARTMENT OF ENVIRONMENTAL QUALITY

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INTEROFFICE COMMUNICATION

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January 22, 2015

To: File for Petroleum Coke (CAS No. 64741-79-3)

From: Michael Depa, Air Quality Division, Toxics Unit

Subject: Toxicity Assessment Update

A previous version of this memo dated February 18, 2014 erroneously attributed Texas Commission on Environmental Quality (TCEQ) basis of the Effects Screening Level (ESL) for petroleum coke to the National Ambient Air Quality Standard (NAAQS) for PM10 (see page 3 for corrected basis).

This memo describes a human health toxicity assessment for the uncalcined form of petroleum coke ("green coke"), which will be herein simply referred to as petcoke. Previously, an AQD assessment of the potential human health concerns for airborne petcoke dust associated with area sources (storage piles) concluded that the storage pile emissions did not pose a significant public health risk for inhalation exposure, based on the available information (Sills, 2013). The purpose of the present assessment was to include an updated and expanded information review and consider if it would be reasonable and appropriate to establish screening levels for petcoke emissions under Rule 225 for application in New Source Review permit reviews.

The conclusion of this assessment is consistent with that of the previous toxicity assessment (Sills, 2013). Human exposure to fine particulate matter (PM) emissions from petcoke storage piles, at sufficiently high concentrations and durations of exposure, could cause respiratory and cardiovascular effects characteristic of PM inhalation exposures. The U.S. Environmental Protection Agency (US EPA) established National Ambient Air Quality Standards (NAAQS) for PM to protect the public health. There is no evidence indicating that PM from petcoke is more potent than other forms of PM that are regulated by the PM primary NAAQS. Also, petcoke dust does not pose a significant carcinogenicity risk, based on negative carcinogenicity findings from chronic animal bioassays in two species and consideration of the elemental composition of petcoke. Therefore, human health concerns for petcoke inhalation exposure from industrial sources may be appropriately addressed via the NAAQS; it does not appear to be appropriate or necessary to establish specific screening levels for petcoke air emissions.

The following information sources were searched as part of the toxicity assessment for petroleum coke: United States Environmental Protection Agency's (US EPA's) Integrated Risk Information System (IRIS), the Registry of Toxic Effects of Chemical Substances (RTECS, 2014), the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLV), National Institute of Occupational Safety and Health (NIOSH) Pocket Guide to Hazardous Chemicals, Chemical Abstract Service (CAS) –Online (1/13/2014), International Agency for Research on Cancer Monographs, National Library of Medicine, Health Effects Assessment Summary Tables, and National Toxicology Program Status Report. The US EPA has not established a reference concentration (RfC) for petroleum coke.

California Office of Environmental Health Hazard Assessment (Cal-OEHHA) has not established reference exposure levels for petroleum coke. The U.S. Agency for Toxic Substances and Disease Registry (ATSDR) has not established a chronic minimal risk level for petroleum coke. Neither the ACGIH nor NIOSH have established occupational exposure levels. A description of petroleum coke is shown below as well as in Appendix A.

> Petroleum coke is a solid material resulting from high temperature treatment of petroleum fractions. It consists of carbonaceous material and contains some hydrocarbons having a high carbon-to-hydrogen ratio.

Table 1 shows the percent composition of major elements found in petroleum coke.

Table 1. Percent Composition of Select Components of Green Coke

Analyte	Green Coke[1]	DBS Coke[2]
Carbon	89.58–91.80	89
Hydrogen	3.71–5.04	
Oxygen	1.30–2.14	
Nitrogen	0.95–1.20	
Sulfur	1.29–3.42	6
Ash (including heavy metals such as nickel and vanadium)	0.19–0.35	See Appendix A
Carbon-Hydrogen Ratio	18:1–24:1	

[1]Congressional Research Service, 2013
[2]Detroit Bulk Storage Sample, Analysis by Hazen Research, Inc., Golden Colorado: Report to Jeff Korniski, MDEQ-AQD Detroit Office, Reported 4-9-2013

Summary of Inhalation Studies

Sprague-Dawley rats and Cynomolgus monkeys were exposed to dust aerosol concentrations (0, 10.2, and 30.7 mg/m^3) of micronized delayed process petroleum coke for 6 hr/day, 5 days/week over 2 years (Klonne et al., 1987). With the exception of pulmonary effects, particularly in the rats, no significant adverse treatment-related effects were observed. Both dust-exposed groups of both species exhibited a gray to black discoloration of the lung, an observation consistent with pulmonary deposition of the coke dust, as well as increased absolute and/or relative lung weight values. The pulmonary histopathology in the monkeys was limited to the deposition and phagocytosis of the test material by pulmonary macrophages. The rats also exhibited these responses, but with concomitant signs of chronic inflammation and focal areas of fibrosis, bronchiolization, sclerosis, squamous alveolar metaplasia, and keratin cyst formation. No difference in the mortality rate was observed between the control and exposed groups of rats. Lastly, no significant increases in chromosomal aberrations were observed in rodents of the 10.2 or 30.7 mg/m^3 exposure groups when examined after 5 days, 12 months, and 22 months of exposure. The lowest dose (10.2 mg/m^3) was identified as the lowest-observed-adverse-effect-level (LOAEL).
A combined reproductive/developmental toxicity screening test with petroleum coke dust showed no reproductive or developmental effects following inhalation exposure in rats; however, pulmonary inflammation (macrophage accumulation, lymphocyte hyperplasia and squamous metaplasia of respiratory epithelium) was observed in all exposed parental animals (EPA, 2011). The no-observed-adverse-effect-level (NOAEL) for reproductive/developmental toxicity is 300 mg/m^3, the highest concentration tested.

Health Benchmarks for Petroleum Coke

Texas Commission on Environmental Quality (TCEQ) regulates petroleum coke for air permit evaluations using Effects Screening Levels (ESLs). The TCEQ has 2 interim ESLs for petroleum coke:

1. Short-term: 50 µg/m³ (PM10) 1-hour averaging time
2. Long-term: 5 µg/m³ (PM10) annual averaging time

The TCEQ ESLs for petroleum coke are based on the National Institute for Occupational Safety and Health (NIOSH) Reference Exposure Level (REL) for Particles Not Otherwise Regulated (PNOR) (Lee, 2015).

A potential ITSL could be developed for further consideration, from the Klonne, et al. (1987) study. Both rats and monkeys exhibited lung inflammation effects at the lowest dose test: 10 mg/m³. Given that monkeys have lung structure and function similar to humans it was deemed appropriate to use monkeys for the development of a screening level. The animal and human dose were considered equivalent. The experimental dose was adjusted for continuous exposure by multiplying the dose by the number of hours per day and number of days per week the animals were exposed.

Adjusted Dose = experimental dose x 6hr/24hr x 5days/7days
Adjusted Dose = 10 mg/m³ x 6/24 x 5/7
Adjusted dose = 1.79 mg/m³

A potential ITSL was calculated as follows:

Potential ITSL = (Adjusted Dose)/(UF_A x UF_L x UF_H)

Where UF is an uncertainty factor, and the appropriate UF values consistent with risk assessment practice would be:

UF_A = 3 to10 for extrapolating between animals (monkeys) and humans (interspecies extrapolation)
UF_L = 10 for extrapolating from lowest-observed-adverse-effect-level (LOAEL) to NOAEL
UF_H = 10 for the protection of sensitive individuals (intraspecies extrapolation).

The potential ITSL is then:

Potential ITSL = (1.79 mg/m³)/((3 to10) x 10 x 10) x 1000 µg/mg
Potential ITSL = 2 to 6 µg/m³ with 1 significant figure (annual averaging time)

This potential ITSL is based on a chronic inhalation study adjusted for continuous exposure and derived using uncertainty factors to adjust for lifetime exposure, therefore an appropriate averaging time would be annual average. The value of the potential ITSL of 2 to 6 µg/m^3 (annual average), including a total uncertainty factor of 300 to 1000, may be compared to the annual primary NAAQS for $PM_{2.5}$ of 12 µg/m^3 based on a wealth of human epidemiology studies and the peer review and scrutiny afforded a national ambient air quality standard. It would not be reasonable and appropriate to establish an ITSL for petcoke at the level of the above potential ITSL based on an animal bioassay and a relatively large uncertainty factor, when there is no evidence indicating that the NAAQS levels would not be protective for the petcoke toxicity findings (a chronic monkey LOAEL of 10 mg/m^3, adjusted to 1.79 mg/m^3).

Concerns for the potential for petcoke dust exposures to pose a carcinogenicity hazard are not supported by the negative bioassay findings in two species as summarized above. Additionally, Sills (2013) considered the levels of two carcinogens (nickel and benzo(a)pyrene) that have been reported as constituents of petcoke, and found that under some worst-case assumptions such as lifetime continuous exposure to petcoke dust at the

PM2.5 NAAQS of 12 µg/m^3 (annual average), the reported levels of these two constituents would be associated with a plausible upper bound lifetime incremental cancer risk of approximately 0.5 in one million and 10 in one million, respectively. These findings, along with the negative carcinogenicity findings from animal bioassays, do not suggest the need to address the potential cancer risk of specific petcoke constituents.

It may be noted that the inorganic constituents of petcoke, as described in Appendix A, may also be anticipated to be present as natural constituents in topsoil, and therefore also present in airborne dust originating from topsoil erosion and atmospheric suspension. Appendix A includes a column for the Michigan topsoil concentrations for the inorganic constituents of petcoke, for information purposes and to help lend perspective to the consideration of petcoke dust health concerns.

Discussion

Petroleum coke has no observed carcinogenic, reproductive, or developmental effects. Inhalation exposure to high concentrations of petroleum coke dust can lead to an inflammatory response in the lungs of both humans and animals. As noted above, animal toxicity studies of repeated-dose and chronic inhalation have shown respiratory inflammation attributed to the non-specific effects of dust particles rather than the specific effects of petroleum coke. On this basis, it seems most appropriate to evaluate the emissions and impacts pf petroleum coke and its risk of inflammatory effects on the lung in terms of particulate matter less than 10 µm in diameter (PM10) or 2.5 µm in diameter (PM2.5). The health-protective primary NAAQS for PM2.5 are appropriate for evaluating the impacts of processes that emit petroleum coke dust.

References:

Congressional Research Service. 2013. Petroleum Coke: Industry and Environmental Issues. Anthony Andrews, Richard K. Lattanzio. Octorber 29, 2013. 7-5700. www.crs.gov, r43263. https://www.hsdl.org/?view&did=746955

EPA. 2011. Petroleum Coke Category. Hazard Characterization Document. U.S. Environmental Protection Agency June, 2011.

Klonne DR, Burns JM, Halder CA, Holdsworth CE, Ulrich CE. 1987. Two-year inhalation toxicity study of petroleum coke in rats and monkeys. American Journal of Industrial Medicine 11:375-389.

Lee, Jong Song, Ph.D. 2015. Personal communication. Mr. Lee is a toxicologist with the Texas Commission on Environmental Quality, Toxicology.

Sills, R. 2013. Petroleum Coke: Summary of Composition and Evaluation of Inhalation Toxicity. April 12, 2013. Unpublished MDEQ-AQD report.

TCEQ. 2014. Texas Commission on Environmental Quality. Toxicology. Effects Screening Levels (ESLs). http://www.tceq.texas.gov/toxicology/esl/ESLMain.html

Appendix A: Detailed Analysis of Coke Samples for Comparison

Sample	Delayed Process Green Coke - 2003 Sample 1				API Sample #4-1-140 2	Micronized Delayed Process Green Coke – 1981 sample 3		DBS Green Coke[6]	Mich. Top Soil[7]
	pellet (initial)4	pellet (final)5	micro-nized (initial)	micro-nized (final)	Delayed Process Coke	1981 Analysis	1984 Analysis	MDEQ 2013	MDEQ 2005
Avg. Particle Size, Mass Median Aerodynamic, µm	2000*	2000*	2.3/3.3*		5**	3.1	3.1		
Elemental Analysis, % wt									
Carbon					89.93	89.97	89.58	89.8	
Hydrogen					3.71	5.04	3.89		
Oxygen					1.3	1.62	2.14		
Sulphur	7.4		5.8		3.36	3.27	3.42	6	
Nitrogen					1.1	1.1	1.2		
Other Analysis, % wt									
SiO2					0.04	<0.04	<0.02		
Ash					0.21	0.19	0.28		
Trace Metals, ppm									
Al (aluminum)	321	205.1	300.2	250.7					4572
As (arsenic)	<19.3	<2.3	<29.6	<2.3	<0.001	0.3	0.7	ND	5.67
B (boron)	<19.3		<29.6						
Ba (barium)	<19.3	7.74	<29.6	6.9				1.8	37.7
Be (beryllium)	<9.6		<14.8					ND	<0.2
Bi (bismuth)	<19.3		<29.6						
Ca (calcium)	178	81.7	121.6	158.7					
Cd (cadmium)	<9.6		<14.8					ND	<2
Co (cobalt)	<9.6	1.9	<14.8	1.7				0.88	<5
Cr (chromium)	<9.6	3.9	<14.8	4.6				ND	12.9
Cu (copper)	<11.6	1.8	<17.8	2.3				ND	10.1
Fe (iron)	310	215.9	247	276.1				78	9547
Hg (mercury)					<1	<1	<0.01	ND	<0.1
K (potassium)	<28.9	10.9	<44.4	20.5					
Li (lithium)	<9.6	<1.2	<14.8	<1.16					4.5
Mg (magnesium)	77.4	50.3	60.9	65.5					1576
Mn (manganese)	<19.3	5.3	<29.6	7.3				1.4	475
Mo (molybdenum)	<19.3	16.7	<29.6	16.0				20	<5
Na (sodium)	133	87.8	114.6	99.0					
Ni (nickel)	367.1	319.6	351.7	304.6	95	78	85	190	8.8
P (phosphorus)	<19.3	19.8	30.3	25.0					
Pb (lead)	<19.3	4.88	<29.61	7.4				ND	11.7
Pd (palladium)		<6.9		<6.9					
Pt (platinum)		3.8		4.5					
S (sulfur)	73920		58060						
Sb (antimony)	<48.2		<74.0					ND	
Se (selenium)	<19.3		<29.6		4.5	<0.2	<0.5	ND	<1
Si (silicon)	743.2	86.75		204					
Sn (tin)	<28.9	<2.3		<2.3					
Ti (titanium)	12.9	11.7	<14.8	14.4					94.5
V (vanadium)	1938	1559	1805	1580	145	140	130	470	20.9
Zn (zinc)	12.0	8.9	<14.8	11.2				2.2	43.2

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	pellet (initial)4	pellet (final)5	micro-nized (initial)	micro-nized (final)	Delayed Process Coke	1981 Analysis	1984 Analysis	MDEQ 2013	MDEQ 2005
Benzene Extract, % wt					1.79	2.08	2.64		
PAHs, ppm									
Naphthalene	3.6	3.6	11	11					
1-methyl naphthalene	2.7	3.1	10	12					
2-methyl naphthalene	11	12	26	26					
Acenaphthene	ND	0.18	ND	0.51					
Acenaphthylene	ND	0.12	ND	0.5					
Fluorene	0.34	0.37	1.5	1.5	11	ND	ND		
Phenanthrene	0.69	0.64	7.8	8.2	ND	ND	ND		
Anthracene	ND	0.29	3.3	3.6					
Pyrene	1.3	1.2	8.6	10	ND	165	158		
Fluroanthene	ND	0.1	1.4	1.6					
Benzofluorenes					ND	ND	ND		
Benzo(a)anthracene	0.58	0.59	7.1	8	544				
Benzp(a,b)anthrcene						280	287		
Chrysene	0.88	1.1	9.4	10	126	210	255		
Benzo(a)pyrene	1.8	1.7	11	13	440	175	190		
Benzo(e)pyrene					110	85	134		
Beno(b)fluoranthene	0.52	0.62	3.8	3.9	ND	ND	ND		
Benzo(k)fluoranthene	ND	ND	ND	1.5					
Perylene					ND				
Methyl benzo(a)pyrene					ND	ND			
Benzo(g,h,i)perylene	1.1	1.4	8.7	12	439	120	167		
Dibenzo(a,h)anthracene	0.49	0.51	4.1	4.3	ND	NQ	ND		
Benzo(g,h,i)fluoranthene					ND	ND	ND		
Indeno(1,2,3-cd)pyrene	0.34	0.45	3.5	3.3					
Dimethylbenz(a)anthracene							ND		
Methylbenzo(g,h,i)perylene							377		
Coronene					ND	ND	ND		

Toxicology study(s) in which samples were used:
1 OECD 203 Fish acute toxicity test; OECD 202 Invertebrate acute toxicity test; OECD 201 Algal growth inhibition test; OECD 208 Seedling emergence and growth of terrestrial plants; OECD 207 Earthworm acute toxicity test; OECD 421 Reproduction/developmental toxicity screening test
2 Mouse dermal carcinogenicity study; *Salmonella* assay; mouse lymphoma cell assay
3 Rat chronic inhalation study; Monkey chronic inhalation study; *Salmonella* assay; Rat *in vivo* cytogenicity assay
4 initial refers to analyses conducted prior to initiation of the toxicology studies
5 final refers to analyses conducted following completion of the toxicology studies
6 DBS = Detroit Bulk Storage sample. Trace metals analysis by MDEQ Lab. Reported 4-9-2013 ; Carbon, sulfur analysis by Hazen Research, Inc., Golden Colorado: Report to Jeff Korniski, MDEQ-AQD Detroit Office, Reported 4-9-2013**7** Michigan Background Soil Survey 2005. Huron–Erie glacial lobe. Mean (average) topsoil values. http://www.michigan.gov/documents/deq/deq-whm-hwp-Michigan-Background-Soil-revJuly2005_248097_7.pdf
ND = not detected
NQ = detected, but not quantifiable Blank cells = analysis not performed
* values are average mean particle size
** size not measured; value estimated from scanning electron micrographs
References: Aveka, Inc., 2003; CONCAWE, 1993; Chevron Products Company, 2003, 2005; Lancaster Laboratories, Inc., 2003, 2005.