MICHIGAN DEPARTMENT OF ENVIRONMENTAL QUALITY

INTEROFFICE COMMUNICATION

August 4, 2015

To: File for Benzo(a)pyrene equivalent carcinogenic PAHs (CAS No. 50-32-8, and others listed in Table 1)

From: Michael Depa, Air Quality Division, Toxics Unit

Subject: Screening Levels

On February 25, 1993, the Air Quality Division (AQD) established an initial risk screening level (IRSL) and secondary risk screening level (SRSL) for benzo(a)pyrene (B(a)P) at 0.0005 and 0.005 μ g/m³, respectively, both with annual averaging time. At that time, the Environmental Protection Agency (EPA) Integrated Risk Information System (IRIS) did not have an inhalation unit risk (IUR) factor for B(a)P, but did provide an oral slope factor (OSF) of 7.3 per mg/kg/day. The IUR was derived from the OSF as:

IUR = OSF x 20m³/70kg x mg/1000µg IUR = (7.3 kg/mg) x 20m³/70kg x mg/1000µg IUR = 0.00208 (µg/m³)⁻¹

The IRSL and SRSL were derived as follows:

IRSL = 1E-6/IUR, and SRSL = 1E-5/IUR

The Scientific Advisory Panel (SAP 1995a; SAP 1995b; see attached) of the Michigan Department of Environmental Quality recommended that the relative potency factors used by EPA (1993) be applied to the IUR for B(a)P and 6 additional carcinogenic polycyclic aromatic hydrocarbons (PAHs) that cause cancer in the same way that B(a)P does. A method to assess B(a)P and the additional six PAHs is described below. The combined maximum ambient impacts of all 7 carcinogenic PAHs (as B(a)P equivalents) must be below the IRSL. The SRSL can be used in lieu of the IRSL, if appropriate, pursuant to Rule 225(2).

The U.S. Environmental Protection Agency (EPA) Office of Air Quality Planning and Standards (OAQPS) uses an IUR for B(a)P of 0.0011 per μ g/m³ (EPA, 2014). EPA's IUR for B(a)P is based on a value derived by California Office of Environmental Health Hazard Assessment (OEHHA, 2011). EPA OAQPS, OEHHA, and Minnesota Department of Health (MDH, 2014) have different schemes to assess B(a)P and other PAHs, all more inclusive than the EPA's 1993 guidance that SAP advised the AQD to follow.

EPA is conducting a peer review and public comment of the scientific basis supporting the human health hazard and dose-response assessment of polycyclic aromatic hydrocarbon (PAH) that when finalized will appear on the Integrated Risk Information System (IRIS)

database. A webpage was established that includes the draft toxicological review of carcinogenic PAHs by EPA (2010) as well as several rounds of public comment. EPA's Science Advisory Board (SAB) established a review panel called Polycyclic Aromatic Hydrocarbon (PAH) Mixtures Review Panel. Several rounds of public review have been published on the draft 2010 IRIS document and are available on-line (http://cfpub.epa.gov/ncea/iris_drafts/recordisplay.cfm?deid=194584), including a March 2011 SAB report (EPA, 2011) that formalized the review findings and provided comments and concerns. Instead of studying many different approaches to regulating PAHs, including the EPA's OAQPS and California OEHHA and Minnesota's DPH in order to develop an updated IUR, AQD will wait for EPA's IRIS to address the Science Advisory Board comments on EPA IRIS's draft IUR (EPA, 2010) while continuing the SAP recommended approach. The next step in the IRIS review process is an external peer review and public comment. After addressing the comments, the final assessment is scheduled to be posted to the EPA IRIS Web site: http://www.epa.gov/iris/.

The EPA (1993) relative potency factors (RPFs) are listed in Table 1 below.

Table 1. PAH Relative Potency Factors (EPA, 1993)			
Polycyclic Aromatic		Relative Potency	
Hydrocarbon	CAS Numbers	Factor (RPF)	
benz(a)anthracene	56-55-3	0.1	
benzo(a)pyrene	50-32-8	1	
benzo(b)fluoranthene	205-99-2	0.1	
benzo(k)fluoranthene	207-08-9	0.01	
chrysene	218-01-9	0.001	
dibenz(a,h)anthracene	53-70-3	1	
indeno(1,2,3-c,d)pyrene	193-39-5	0.1	
asphalt fumes	8052-42-4	*	
* To be evaluated as a mixture of the above, per SAP (1995a, 1995b)			

In order to determine compliance with the IRSL it is recommended that the ambient impact of the particular PAH be multiplied by the RPF, then summed with all the other carcinogenic PAHs in mixture. An example is shown in Table 2 below.

Table 2. Example PAH Emissions and Application of Rule 225

Pollutant	Initial Risk Screening Level (µg/m³)	Avg. Time	Example PAI* (μg/m³)	RPF**	Relative PAI (µg/m³)
Benzo(a)pyrene	0.0005	annual	2.10E-05	1	2.10E-5
Benz(a)anthracene		annual	4.00E-05	0.1	4.00E-6
Benzo(b)fluoranthene		annual	5.50E-06	0.1	5.50E-7
Benzo(k)flouranthene		annual	5.50E-06	0.01	5.50E-8
Chrysene		annual	5.20E-05	0.001	5.20E-8
Dibenz(a,h)anthracene		annual	5.50E-06	1	5.50E-6
Indeno(1,2,3-cd)pyrene		annual	annual 5.50E-06 0.1 5.50E-7		
Sum = 3.17E-5					
* Predicted Ambient Impact, as determined by air dispersion modeling or other appropriate method. ** Relative Potency Factor; carcinogenic potency relative to benzo(a)pyrene					

In the example above (see Table 2), the sum of relative ambient impacts is $3.17E-5 \mu g/m^3$. Since the combined impact is less than the IRSL of 5E-4 $\mu g/m^3$, the emissions comply with Rule 225(1).

References:

EPA, 1993. Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons. U.S. Environmental Protection Agency, Office of Research and Development, Office of Health and Environmental Assessment, Washington, DC, EPA/600/R-93/089 (NTIS PB94116571). Schoeny R., Poirier K.

http://www.epa.gov/oswer/riskassessment/pdf/1993_epa_600_r-93_c89.pdf

EPA, 2010. Development of a Relative Potency Factor (RPF) Approach for Polycyclic Aromatic Hydrocarbon (PAH) Mixtures: In Support of Summary Information on the Integrated Risk Information System (IRIS) (EXTERNAL REVIEW DRAFT). February 2010. EPA/635/R-08/012A. <u>http://ofmpub.epa.gov/eims/eimscomm.getfile?p_download_id=494851</u>

EPA, 2011. SAB Review of EPA's "Development of a Relative Potency Factor (RPF) Approach for Polycyclic Aromatic Hydrocarbon (PAH) Mixtures (February 2010 Draft)". (PDF, 47 pp., 696,671 bytes), EPA-SAB-11-004. March 17, 2011. <u>http://yosemite.epa.gov/sab/sabproduct.nsf/36a1ca3f683ae57a85256ce9006a32d0/F24FBBB</u> <u>ACA6EEABA852578570040C547/\$File/EPA-SAB-11-004-unsigned.pdf</u>

EPA, 2014. Dose-Response Assessment for Assessing Health Risks Associated With Exposure to Hazardous Air Pollutants. Office of Air Quality Planning and Standards (OAQPS). May 9, 2014. Downloadable excel spreadsheet. Downloaded July 29, 2015. http://www2.epa.gov/sites/production/files/2014-05/table1.xlsx http://www2.epa.gov/fera/dose-response-assessment-assessing-health-risks-associated-exposure-hazardous-air-pollutants

MDH, 2014. Guidance for Evaluating the Cancer Potency of Polycyclic Aromatic Hydrocarbon (PAH) Mixtures in Environmental Samples Minnesota Department of Health. October 31, 2014. <u>http://www.health.state.mn.us/divs/eh/risk/guidance/pahguidance.pdf</u>

OEHHA, 2011. Technical Support Document. "Air Toxics Hot Spots Program Technical Support Document for Cancer Potencies," Appendix B. Chemical-specific summaries of the information used to derive unit risk and cancer potency values. Adoption of the Revised Air Toxics Hot Spots Program Technical Support Document for Cancer Potency Factors [06/01/09] Appendix C Updated 2011. Air Toxicology and Epidemiology. Office of Environmental Health Hazard Assessment (OEHHA). http://oehha.ca.gov/air/hot_spots/2009/AppendixB.pdf

SAP, 1995a Recommendations of the Scientific Advisory Panel for Asphalt Polycyclic Aromatic Hydrocarbons (PAHs). CAS # 8052-42-4. Report dated: April 14,1995

SAP, 1995b Recommendations of the Scientific Advisory Panel for Polycyclic Aromatic Hydrocarbons (PAHs). Report dated: July 20, 1995

Recommendations of the Scientific Advisory Panel

Asphalt Polycyclic Aromatic Hydrocarbons (PAHs)

CAS # 8052-42-4 April 14,1995

Basis for the current screening level:

The current screening level for asphalt PAHs is based on the EPA cancer unit risk as listed in IRIS for coke oven PAHs. At the time the screening level for asphalt PAHs was developed there was only a unit risk value available for benzo(a)pyrene (B(a)P), even though it was believed that asphalt fumes contain many other PAHs including some that are carcinogenic. Since data on other carcinogenic PAHs were not suitable for determining unit risk values, it was traditionally assumed that all carcinogenic PAHs were equipotent to B(a)P. This approach was recognized to be conservative, as many of the carcinogenic PAHs were likely to less potent than B(a)P. Because this was a conservative approach, and some facilities had difficulty in meeting a screening level based on this approach, the Air Quality Division (AQD) considered other approaches for dealing with the carcinogenic PAHs found in asphalt fume. The approach adopted utilized the unit risk value for coke oven PAHs (a well studied mixture, with a sufficient set of data for conducting a risk assessment to a mixture of PAHs) as a reasonable means to come up with a unit risk value for a complex mixture of PAHs containing known carcinogenic PAHs, likely to occur within asphalt fume.

Summary of the public comment:

Comments were received from the Michigan Asphalt Paving Association (MAPA), who opposed listing asphalt PAHs as a carcinogen, because the existing literature does not provide evidence of asphalt fume as carcinogenic. They commented that OSHA had failed to regulate asphalt fume as a carcinogen, and that OSHA found insufficient dose-response data available to perform a risk assessment. MAPA also commented that a screening level should be established a screening level for each identified PAH, rather than a screening level for the combined mixture. Other comments received were that AQD did not arrive at the screening levels based on Rules 230-232, and did not follow EPA guidelines for carcinogenic risk assessment. Comments were received that anthanthrene, benzo(k)fluoranthene and indeno-1,2,3-cd-pyrene should not be classified as carcinogens.

Response to the public comment:

The Panel spent a considerable amount of time discussing the issues related to the evaluation of asphalt PAHs. The primary difficulty in establishing a screening level for PAHs is that while many of these compounds are considered to be carcinogens, that data are not suitable for calculation of quantitative risk estimates by conventional methods. Since the AQD developed the screening level for asphalt PAHs, the US Environmental Protection Agency has developed a method for doing quantitative risk estimates for various carcinogenic PAHs (EPA 1993). The Environmental Protection Agency (EPA) method for PAH comparisons is similar to the toxic equivalent factor (TEF) methodology utilized for adjusting the potency of various dioxin isomers to a factor of 2,3,7,8-TCDD potency.

In the case of PAHs, EPA used the potency of benzo(a)pyrene as the basis for comparing the potencies of the other carcinogenic PAHs. For each carcinogenic PAH, EPA developed an estimated order of potential potency that is based upon the relative carcinogenic potency compared to B(a)P. EPA developed the estimated

order of potential potency for only a limited number (six in addition to benzo(a)pyrene) of carcinogenic PAHs. These values are listed below.

РАН	Est. Order of Potential Potency
benzo(a)anthracene	0.1
benzo(a)pyrene	1
benzo(b)fluoranthene	0.1
benzo(k)fluoranthene	0.01
chrysene	0.001
dibenzo(a,h)anthracene	1
indeno(1,2,3-cd)pyrene	0.1

The Panel recommends that the above list of estimated order of potential potency values be used to estimate the carcinogenic risk for these PAH compounds. The Panel realizes that the use of the above limited list may not be adequate for all situations, as PAHs are often present as complex mixtures containing many more PAHs, including carcinogenic PAHs other than those identified in EPA's list. The Panel recommends that the 'average' of the estimated order of potential potency be used for the other carcinogenic PAHs. The Panel believes this is a reasonable way to estimate the unknown potency of the other PAHs. The arithmetic mean estimated order of potential potency for the above seven PAHs is 0.3, while the median value is 0.1. It is recommended that the median value of 0.1 be used for those carcinogenic PAHs without estimated order of potential potency values established by EPA. The value should be applied to other carcinogenic PAHs that have been reported to have been found in asphalt fume by some authors, and include: 7Hdibenzo(cg)carbazole, anthanthrene, benzo(e)pyrene, benzo(j)fluoranthene, dibenzo(ah)pyrene, and dibenzo(ai)pyrene.

An example risk assessment for a natural gas fired batch asphalt plant using the methodology recommended by the Panel is provided in Addendum A. This example risk assessment assumes the plant operates continuously for 24 hours per day, 365 days per year. It should be noted that there is a provision in Rule 230, under subsection 10, that allows the use of an average emission rate for determining compliance with the screening level, for facilities that are emitting toxic air contaminants for a period of time less than the screening level averaging time. These emissions are described in Rule 230(10) as intermittent emissions. Specifically this rule states:

(10) The predicted ambient impact of each toxic air contaminant shall be determined using the maximum hourly emission rate in accordance with the provisions of R 336.1240 or R,336.1241, or both, by a screening method using the dilution matrix in table 22, or by any screening method approved by the commission. The level of detail of this ambient impact analysis shall be sufficient to reasonably ensure that all pollutants which result in an ambient concentration of more than 10\$ of the initial screening levels are analyzed. Intermittent emissions are those emissions which are not allowed to be emitted continuously for the entire length of time specified in the averaging time for the appropriate screening level. The ambient impact analysis for intermittent processes may be based on the average emission rate for the appropriate averaging period if the average rate is not less than 10\$ of the maximum hourly rate. An average rate that is less than 10% of the maximum rate may only be used if the applicant can demonstrate, to the satisfaction of the commission, that the proposed new or modified process will not cause or contribute to peak exposures which may result in a violation of the provisions of R 336.1901.

The Panel points out that the case of intermittent emissions is particularly applicable to PAH emissions from asphalt plants. The averaging time for the PAH screening level is annual, while most asphalt plants in Michigan operate only during a limited number of hours ppr day, and for only a portion of the year. Ad"ustment for the reduced number of hours of operation can be utilized in the emission averaging as described in Rule 230(10).

Another method to consider for estimating potency has been developed by the California EPA-Air Resources Board. This group has developed PEF or potency equivalency factors, another similar system to TEFs, for many additional carcinogenic PAHs. The Panel recommends that before adoption and use, these PEFs would need to be reviewed to ensure that they are based on appropriate data, such as a comparison of potencies from animal carcinogen icity studies rather than a comparison of results from in vitro mutagenicity assays.

References:

California EPA-Air Resources Board. 1994. Benzo(a)pyrene as a toxic air contaminant. Part B: Health effects of benzo(a)pyrene.

EPA. 1993. Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons. EPA/600/R-93/089.

Addendum A

Example Risk Assessment for PAHs from an Asphalt Plant

An example of how the estimated order of potential potencies (sometimes referred to as TEF) described in this document for the PAHs could be used to evaluate the risk from exposure to PAHs from an asphalt plant follows in the attached Table 1. For this example it was assumed that a natural gas fired, batch asphalt plant had a stack height of 60 feet, a building height of 30 feet and was located 60 feet from the property line. It was also assumed that this plant produced 350 tons of asphalt per hour, and had a stack flow rate of 56,000 cfm.

The first column in Table 1. lists the PAH''s CAS number. The CAS number is followed by a `c' for the carcinogenic PAH's. The name of the PAH is in the next column of Table 1.

Using EPA's current AP42 emission factors (see attached Table 11.1-11 taken from the AP42 document) for PAHs from natural gas fired, batch asphalt plants and the above assumptions, it is possible to determine stack concentrations for the individual PAHs as follows.

stack concentration (mg/m3) = $\frac{(lbs/ton) \times (350 \text{ tons/hr}) \times (453600 \text{ mg/lbs})}{(56000 \text{ cf/min}) \times (0.0283 \text{ m3/cf}) \times (60 \text{ min/hr})}$

Given the above conditions (stack height, building height and distance to property line) it is also possible estimate the predicted ambient impact utilizing the attached dilution matrix (Table 22 from Rule 230). The dilution matrix provides an estimate of the dilution that occurs from the stack to the property line. This value is called the dilution factor (df).

annual df = $\frac{16511}{10 \text{ X}}$ = 62.5

ambient concentration = <u>stack concentration</u> dilution factor

Adjustments to the df, for screening levels (ITSL) with periods other than annual averaging times were made according to the instructions in Table 22. This adjustment will allow direct comparison of the column under ambient ug/m3 to the ITSL column. Note that none of the listed PAHs are estimated to have ambient concentrations greater than the associated ITSL.

For the carcinogenic PAHs, the last column in Table 1. identifies the level of risk associated with the calculated ambient concentration. The risk can be calculated from the estimated order of potential potency factor (sometimes referred to as TEF) and the potency for benzo(a)pyrene of 0.0021 (ug/m3)-1 as follows.

risk = (ambient concentration) x (potency) x (TEF)

For this example, the total carcinogenic risk (5.1E-08) is less than one in a million (1E-06), indicating that a plant with these conditions would meet the initial risk screening level (IRSL).

Table 1. Example Risk assessment for a Natural Gas Fired Batch Asphalt Plant

CAS #	PAH	Emission <u>Factor (lb/ton)</u>		Amb. Conc. ug/m3	ITSL (ug/m3)	Risk with TEFs
56-49-5 3-methvlcholanthr				<u> </u>	<u></u>	
57-97-6 7,12-dimethylbenz						
194-59-2 c 7H-dibenzo(cg)						
779-02-2 9-methylanthrace	ene					
83-32-9 acenaphthene		1.2E-06	0.002	0.32057	210	
208-96-8 acenaphthylene		8.6E-07	0.00144	0.22974	35	
120-12-7 c anthanthrene						
191-26-4 anthracene		3.1E-07	0.00052	0.08281	1000	
56-55-3 c benzo(a)anthrac		4.5E-09	7.5E-06	0.00012		2.5E-08
238-84-6 benzo(a)fluorene	•					
50-32-8 c benzo(a)pyrene						
205-99-2c benzo(b)flucran		5E-09	0.0000075	0.00012		2.5E-08
243-17-4 benzo(b)fluorene						
205-12-5 benzo(c)fluorene						
195-19-7 benzo(c)phenant						
192-97-2 c benzo(a)pyrene						
191-24-2 benzo(ghi)peryle						
205-82-3 c benzo(j)fluoran						
207-O8-9 c benzo(k)fluora	nthrene	0 - 00				o 15 10
218-01-9 c chrysene		6E-09	0.00001	0.00016		3.4E-10
91-07-1 coronene						
53-70-3 c dibenzo(ah)anth						
189-64-0 c dibenzo(ah)pyr						
189-55-9 c dibenzo (ai) py						
132-65-0 dibenzothio-oher	1e	0.45.07				
206-44-0 fluoranthene		3.1E-07	0.00052	0.08281	140	
86-73-7 fluorene		2.00E-06	0.00334	0.53428	140	
193-39-5 c indeno(123-cd)						
613-12-7 methylanthracen	e		0.07040	44.0400	1.10	
91-20-3 naphthalene	lara	4.2E-05	0.07012	11.2198	140	
91-58-7 naphthalene, 2-ch						
91-57-6 naphthalene, 2-me	etriyi					
198-55-0 perylene			0.00554	4 5000	0	
85-01-8 phenanthrene		3.3E-06	0.00551	1.5868	2	
213-46-7 picene		6 25 09	0.0004	0.01656	100	
129-00-0 pyrene		6.2E-08	0.0001	0.01656	100	
217-59-4 triphenylene					1-1-	
					tota	l = 5.1E-08

No emission factor was available from EPA's AP42 Table 11.1-11 for these PAHs therefore, stack and ambient concentrations, comparison to screening levels (ITSL), and potential risk could not be estimated for those PAHs.

Note: The averaging times for the ambient concentrations corresponds to the averaging times for the ITSL, the two columns directly comparable.

Recommendations of the Scientific Advisory Panel Polycyclic Aromatic Hydrocarbons (PAHs) July 20, 1995

In the past, for purposes of the evaluation of carcinogenic PAHs predicted ambient impacts for compliance with Rule 230 - 232, there has only been a screening level value available for benzo(a)pyrene (B(a)P). Screening levels have not been available for other carcinogenic PAHs since toxicity data on other carcinogenic PAHs, were not suitable for deriving unit risk values. During the evaluation of other carcinogenic PAHs, it was traditionally assumed that all carcinogenic PAHs were equipotent to B(a)P. This approach was recognized to be conservative, as limited available data (in most cases *in vitro* data) indicate that many of the carcinogenic PAHs were likely to be less potent than B(a)P. Therefore, the Panel and the Air Quality Division (AQD) considered other approaches for dealing with the carcinogenic PAHs.

The primary difficulty in establishing a screening level for PAHs is that while many of these compounds are considered to be carcinogens, data are not suitable for calculation of quantitative risk estimates by conventional methods. In lieu of having actual specific PAH toxicity data, the Panel found that the next best method for assessing the carcinogenic risk from exposure to PAHs was a method from the US Environmental Protection Agency, which provides comparative potency estimates (EPA 1993). At this time, the Panel recommends that this methodology may be utilized for sources emitting carcinogenic PAHs, whenever more specific data regarding PAH containing mixtures are not available. The Environmental Protection Agency (EPA) method for PAH comparisons is similar to the toxic equivalent factor (TEF) methodology utilized for adjusting the potency of various dioxin isomers to a factor of 2,3,7,8-TCDD potency. In the case of PAHs, EPA used the potency of benzo(a)pyrene as the basis for comparing the potencies of the other carcinogenic PAHs. For each carcinogenic PAH. EPA developed an estimated potential potency that is based upon the relative carcinogenic potency compared to B(a)P. EPA developed the estimated potential potencies for a limited number (six in addition to benzo(a)pyrene) of carcinogenic PAHs. These values are listed in the following table.

PAH	Estimated Potential Potency
benzo(a)anthracene	0.1
benzo(a)pyrene	1
benzo(b)fluoranthene	0.1
benzo(k)fluoranthene	0.01
chrysene	0.001
dibenzo(a,h)anthracene	1
indeno(1,2,3-cd)pyrene	0.1

The Panel recommends that the above list of estimated potential potency values be used to estimate the carcinogenic risk for these PAH compounds. The Panel realizes that the use of the above limited list may not be adequate for all situations, as PAHs are often present as complex mixtures containing many more PAHs, including carcinogenic PAHs other than those identified in EPA's list. The Panel recommends that the "average" of the estimated potential potencies be used for the other carcinogenic PAHs. The Panel believes this is a reasonable way to estimate the unknown potency of the other PAHs. The arithmetic mean of potential potencies for the above seven PAHs is 0.3, while the median value is 0.1. It is recommended that the median value of 0.1 be used for those carcinogenic PAHs without estimated potential potency values established by EPA.

Another method to consider for estimating potency has been developed by the California EPA-Air Resources Board. This group has developed PEF or potency equivalency factors, another similar system to TEFs, for many additional carcinogenic PAHs. The Panel recommends that before adoption and use, these PEFs would need to be reviewed by a national body such as, but not limited to, the EPA or the National Academy of Science (NAS) to ensure that they are based on appropriate data.

For their information and to get an idea on how wide an impact this evaluation might have, the Panel requested a list be compiled of facilities/sources that may be emitting PAHs. However, the AQD staff found that there is no easily available listing of these types of facilities. The AQD Permit Section compiled a partial listing of PAH sources that includes: coal combustion; oil combustion; charcoal manufacturing; coke production; incineration of scrap wood; municipal waste incinerators; woodstoves; fireplaces; and hot-mix asphalt plants.

References:

California EPA-Air Resources Board. 1994. Benzo(a)pyrene as a toxic air contaminant. Part B: Health effects of benzo(a)pyrene. EPA. 1993. Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons. EPA/600/R-93/089.9.