Public Health Subcommittee
Maine Air Toxics Advisory Committee

Recommendations for the Toxicity Factor for Polycyclic Aromatic Hydrocarbons and Polycyclic Organic Matter

Revised June 23, 2004

1.0 Introduction

The Public Health Subcommittee of the Maine Air Toxics Advisory Committee (ATAC) was charged with providing the ATAC with recommendations as to how polycyclic aromatic hydrocarbons (PAHs) and polycyclic organic matter (POM) should be ranked within the overall Air Toxics Priority List. This charge stemmed from the ATAC's recognition that there was overlap in the mixtures of POM/PAH included in the initial Strawman Priority List as well as significant complexity in the available toxicological data on individual chemicals in the POM/PAH categories and uncertainty in the application of these data to mixtures of POM/PAH. In order to address the charge, the Subcommittee conducted closer evaluation of the emissions data, toxicological data, estimates of health risks from POM/PAH exposure, and information used by other groups (i.e., California EPA).

This memo conveys the recommendations of the Subcommittee with respect to ranking POM/PAH and outlines the relevant information that lead to the recommendations, including other options for ranking that the Subcommittee considered.

2.0 Recommendations of the Subcommittee

The Public Health Subcommittee of the Air Toxics Advisory Committee recommends that POM/PAH be ranked by applying a toxicity weight to the sum of POM/PAH emissions in each source category. The Subcommittee recommends that POM/PAH from residential wood burning be ranked using a toxicity weight of 6400 coupled with an estimate of total POM/PAH emissions (summed across all categories of reported emissions). This toxicity weight is based on the World Health Organization's unit risk of 90 per mg/m3 for benzo(a)pyrene as an indicator for exposure to a mixture of POM/PAH. The toxicity weight incorporates an assumption that benzo(a)pyrene represents approximately 1% of total POM/PAH emissions from residential wood burning. Emissions factors for residential wood combustion both from the National Emissions Inventory (NEI) and from Bostrom (2002) support the assumption of 1% BaP.

The Subcommittee recommends that the same toxicity weight be applied to mobile sources of POM/PAH emissions. The assumption of 1 % BaP for mobile sources is also supported by mobile source emission estimates from the NEI. The emissions inventories for other categories show the B(a)P/Total POM ranges from 0-4% of the mixture, with the mean and median value being 1%. Wood burning makes up 80% of total PAH/POM emissions, and as discussed above, the B(a)P ratio is also 1% for these source categories. There is a significant degree of uncertainty in both the activity data and emission factors used to derive the PAH/POM inventory, which could out-weigh the precision derived from source specific toxicity factors for this project. Therefore, for purposes of the ATPL ranking only, the subcommittee recommends that POM/PAHs from other source categories also be rank by using a toxicity weight of 6400 coupled with an estimate of total POM/PAH emissions (summed across all categories of reported emissions).

Finally, the Subcommittee recommends that, in ranking POM/PAH within the ATPL, DEP take into consideration qualitative information on the particular susceptibility of children to health effects of POM/PAH, as outlined by the California EPA.

3.0 Overview of Ranking within Air Toxics Priority List

In the MATI process, ranking emissions of toxic air contaminants for Maine involves ranking by the product of the total emissions of each toxicant (in pounds) by a unitless toxicity weight. The toxicity weight is based on USEPA's standard quantitative values relating dose to health response[1]. Further detail on the toxicity weight is available in the Revised Draft Prioritized List of Air Toxics For the State of Maine & Basis Statement.

In order for a chemical (or chemical group) to be numerically ranked in this scheme, there must be quantitative estimates of the chemical's in-state emissions and a toxicity weight applicable to the chemical. Absent either of these values, the chemical cannot be quantitatively ranked within the ATPL. This does not imply that the chemical cannot be given priority in the Maine Air Toxics Initiative, as qualitative methods for ranking can be applied.

4.0 Overview of POM/PAH Mixtures

The broadest category of POM/PAH is polycyclic organic matter. This category includes all compounds with more than one benzene ring and with a boiling point greater than or equal to 212 F. POM compounds are formed from combustion and generally exist as particulates in ambient air. Importantly, POM includes compounds that have substituted moieties such as nitro substitutions. The total number of POM compounds that exist is not known, as there are millions of theoretical compounds meeting the description of POMs. Only a small fraction of these have been identified and chemically analyzed. A much smaller fraction of these has been tested for toxicological effects.

A subcategory of POM is polycyclic aromatic hydrocarbons (PAH). Although these two categories are sometimes used interchangeably, PAH are sometimes distinguished as POM without substituted moieties. Within the category of PAH, USEPA uses subcategories known as the "15-PAH" and "7-PAH" groups. The "7-PAH" group includes the 7 PAHs classified as probable human carcinogens by USEPA:

[1] For the Risk-Screening Environmental Indicators model, USEPA devised a system of unitless toxicity weights calculated from the following equations:

Toxicity weight = 0.5 / Reference Dose (in mg/kg-d)
Toxicity weight = 1.8 / Reference Concentration (in mg/m3)
Toxicity weight = Slope Factor (in risk per mg/kg-d) / 0.0005
Toxicity weight = Unit Risk (in risk per mg/m3) / 0.00014

These equations are also used by DEP in the Air Toxics Priority List to calculate toxicity weights benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, and indeno(1,2,3-c,d)pyrene. The "15-PAH" group includes the seven "carcinogenic" PAHs as well as eight PAHs traditionally treated as noncarcinogenic: fluorene, acenaphthylene, acenaphthene, anthracene, benzo(g,h,i)perylene, fluoranthene, phenanthrene, and pyrene. USEPA occasionally uses a variant of this category, the "16-PAH" group that includes naphthalene.

5.0 POM/PAH Emissions Data

Information on emissions of POM/PAH is generally in one of three forms: emissions of individual compounds, emissions of the "7-PAH" or "15/16-PAH" groups, or emissions of unspecified POM/PAH. Summing the emissions from these subcategories will generate an estimate of total POM/PAH emissions. If the ATAC concludes that it is appropriate to consider efforts to mitigate POM/PAH emissions, these efforts will affect total POM/PAH, and will likely be aligned along emission source types (e.g., wood combustion, mobile sources, etc.). For these reasons, the Subcommittee recommends that total POM/PAH emissions[2] be ranked (rather than 7-PAH or 15/16-PAH groups), and that POM/PAH be ranked by source category.

Based on the work of the Inventory Subcommittee of the ATAC, it appears that wood burning is the primary source of POM/PAH emissions in Maine, accounting for approximately 80% of total POM/PAH emissions. While the Inventory Subcommittee acknowledges that this estimate is subject to some uncertainty, this figure, along with estimates by USEPA and others, suggests that the major source of POM/PAH emissions is likely residential wood burning. Mobile sources are another significant source category, but represent a much smaller contribution to total.

6.0 Toxicological Data

POM/PAHs have been shown to have immunotoxic and reproductive effects, among others. However, the primary health endpoint associated with POM/PAHs is carcinogenicity. POM/PAH exposures have long been known to cause cancers, and available toxicological data suggest that cancer is a much more sensitive endpoint than noncancer effects of POM/PAH (Bostrom et al., 2002). Thus, the focus of this toxicological review for POM/PAH was carcinogenicity. Toxicological data for the carcinogenic effects of individual POM/PAH in animals are available for a few individual PAH compounds. Epidemiological data on the carcinogenicity of mixtures of POM/PAH to humans exposed primarily in occupational settings (coke oven workers, gas workers, aluminum smelters, etc.) are also available.

6.1 Animal Data on Inhalation Carcinogenicity. Robust toxicological data are available for only a handful of individual compounds in the POM/PAH categories. The most well studied compound in the group is benzo(a)pyrene, which has long been studied for its

[2] This recommendation also stems from consideration of the toxicological data (see Section 6.0). The toxicological data on total POM/PAH is considered superior to the data on individual compounds that would be used to rank the "7-PAH" or "15/16-PAH" groups.

carcinogenic properties. An oral cancer slope factor of 7.3 per mg/kg-day is available for benzo(a)pyrene from USEPA's IRIS database, the premier source for toxicity values within the agency. This slope factor was estimated using data from animal bioassays. A variety of groups have estimated inhalation unit risk values for benzo(a)pyrene from animal data where the only exposure was to benzo(a)pyrene (with no concurrent exposure to other PAHs). These unit risk estimates range from 0.28 per mg/m3 to 400 per mg/m3 (Bostrom et al., 2002). California's Environmental Protection Agency (CA-EPA) estimated an inhalation unit risk of 0.0011 per ug/m3 (or 1.1 per mg/m3) using animal data for benzo(a)pyrene.

6.2 Epidemiological Data. There are several inhalation cancer unit risk estimates for PAHs with benzo(a)pyrene as the indicator substance for exposure to a mixture of PAHs. In essence, these unit risk estimates are based on quantitative measured or estimated exposure to benzo(a)pyrene in a setting where individuals are exposed to a mixture of PAHs. These studies differ from the animal data in that exposure is to a *mixture* of PAHs, rather than to benzo(a)pyrene in isolation. In the epidemiological studies, benzo(a)pyrene is used as an indicator of total PAH exposure. The unit risk estimates for PAHs with BaP as an indicator range from 23 to 430 per mg/m3 (Bostrom et al., 2002). The World Health Organization (WHO) Air Quality Guidelines for Europe has advocated a unit risk value of 90 per mg/m3 for BaP as an indicator of total PAH exposure based on a study of coke-oven workers (Bostrom et al., 2002).

6.3 Relative Potency Estimates. Although there are inadequate data to estimate the cancer potency (or unit risks) for individual PAHs other than BaP, there are animal data to suggest how individual PAH potencies compare with BaP. Several groups have used these data to develop estimates of relative potency. These relative potency values relate the potency of an individual compound with that of a well-studied compound like BaP. Table 1 shows the relative potency systems that have been developed and were reported in Bostrom et al. (2002).

As Bostrom et al. (2002) note, however, these relative potency systems should be used with caution, as a number of studies on mixtures of PAHs have shown that they may interact metabolically. Further, several groups have suggested that animal data should not be used to estimate cancer risks from PAH exposure in man. The Dutch (RIVM, 1989, as cited in Bostrom, 2002) concluded that the uncertainties in extrapolating from animal data on BaP to effects in man were too high to justify risk assessment for humans. Canada (Muller, 1997 as cited in Bostrom, 2002) compared risk estimates using animal data on individual PAHs with risks based on human epidemiological data and reported that the risks based on the individual PAHs underestimated risk based on epidemiological data by almost two orders of magnitude. After reviewing these and other reports, Bostrom et al (2002) stated,

> "We do not recommend the use of experimental animal data on single PAH substances for purposes other than relative potency rankings. The epidemiological data on lung cancer in coke-oven workers are still the best basis for a quantitative risk estimate, and we accept the unit risk estimate

in the WHO Air Quality Guidelines for Europe (9 x 10-5 per ng/m3 B[a]P as an indicator of the total PAH mixture."

Table 1. Relative Potency Estimates for Individual PAHs Compared with B(a)P.

Compound	Chu and Chen (1984	Clement (1986)	Nisbet and LaGoy (1992)	RIVM (1989)	CARB (1994)	Health Canada (1994	Ontario (1997)	Larsen and Larsen (1998)
Anthracene			0.01	0				0.0005
Phenanthrene			0.001	0.01			0.00064	0.0005
Benz(a)anthracene	0.013	0.145	0.1	0 - 0.04	0.1		0.014	0.005
Benzo(c)phenanthrene							0.023	0.023
Chrysene	0.001	0.0044	0.01	0.05 - 0.89	0.01		0.026	0.03
Fluoranthene			0.001	0 - 0.06				0.05
Pyrene		0.081	0.001					0.001
Benzo(a)pyrene	1	1	1	1	1	1	1	1
Benzo(e)pyrene		0.004						0.002
Benzo(b)fluoranthene	0.08	0.14	0.1		0.1	0.06	0.11	0.1
Benzo(j)fluoranthene		0.061			0.1	0.05	0.045	0.05
Benzo(k)fluoranthene	0.04	0.066	0.1	0.03 - 0.09	0.1	0.04	0.037	0.05
Cyclopenta(cd)pyrene		0.023					0.012	0.02
Dibenzo(a,h)anthracene	0.69	1.11	5				0.89	1.1
Anthanthrene		0.32					0.28	0.3
Benzo(g,h,i)perylene		0.022	0.01	0.01 - 0.03			0.012	0.02
Dibenzo(a,e)pyrene					1		1	0.2
Dibenzo(a,h)pyrene					10		1.2	1
Dibenzo(a,i)pyrene					10			0.1
Dibenzo(a,l)pyrene					10		100	1
Indeno(1,2,3-c,d)pyrene	0.017	0.232	0.1	0 - 0.08	0.1	0.12	0.067	0.1

Source: Bostrom et al., 2002.

7.0 Calculation of Toxicity Weights Using Available Toxicity Data

Table 2 shows a variety of potential toxicity weights for individual POM/PAH and mixtures of POM/PAH. For its Risk-Screening Environmental Indicators (RSEI) model[3], USEPA used the oral slope factor to calculate a toxicity weight that was applied to both oral and inhalation exposures to PAH. In the RSEI model, USEPA grouped all PAHs together and applied the toxicity weight for benzo(a)pyrene to the mixture. In other words, USEPA assumed that all PAHs have the same potency as benzo(a)pyrene in the RSEI model. The toxicity weight applied to inhalation exposure to total PAHs was 15,000.

For the National Air Toxics Assessment (NATA), USEPA used emission factors for the four highest PAH source categories (accounting for approximately 77% of PAH

[3] This model was developed to rank environmental releases from point sources reporting to the Toxics Release Inventory.

emissions) coupled with estimates of BaP "equivalents"[4] to calculate unit risk values for mixtures of PAHs. The BaP equivalents used relative potency estimates from CA-EPA and an inhalation unit risk estimate CA-EPA developed for BaP (1.1 per mg/m3). Using the emission factors for residential wood burning, primary aluminum production, wildfires and prescribed burning, and electric generation with bituminous cyclone boilers, USEPA estimated the BaP equivalents to be approximately 5% as a percentage of total PAH and 18% as a percentage of the 7-PAH group.

If the ATAC chose this approach to rank POM/PAH in Maine, toxicity weights would have to be calculated. Using the BaP equivalents estimates and the CA-EPA unit risk for BaP, one can calculate toxicity weights of 1400 (for the 7-PAH group) and 400 (for total PAHs). The former would be combined with emissions data for the 7-PAH group, while the latter would be combined with emissions data for total POM/PAH.

An alternative would be to use the WHO unit risk for BaP as an indicator of total PAH exposure. The toxicity weight for BaP as an indicator would be 640,000, but this toxicity weight would only be appropriate if combined with emissions data on BaP itself. In order to apply this weight to emissions of total POM/PAH, one would first estimate what fraction of the total POM/PAH emission consists of BaP itself. Using the emission factors used by USEPA for the NATA risk assessment, one can calculate that BaP represents up to 2% of the total POM/PAH emissions. Using data provided by Bostrom et al. (2002) on emissions of PAHs from domestic burning of wood, one can calculate that BaP may represent approximately 1% of the total PAH emissions (as the 17 measured PAHs). Finally, using NEI data for Maine, DEP has estimated that BaP represents about 1% of total POM/PAH emissions from residential wood burning. These percentages can be combined with the toxicity weight based on the WHO unit risk (640,000) to calculate toxicity weights for POM/PAH mixtures of 12,800 (assuming 2% BaP) or 6400 (assuming 1% BaP). These toxicity weights could be combined with emissions data on total POM/PAH to rank these groups of chemicals.

Table 2. Potential Toxicity Weights for POM/PAH

	Unitless Toxicity Weights		
Chemical/Mixture	**RSEI**	**NATA**	**WHO**
B(a)P	15,000	8,000	640,000
7-PAH		1,400	
16-PAH		400	
POM		400	
POM/PAH assuming 1% BaP[a]			6400
POM/PAH assuming 2% BaP[a]			12800

a. See text for explanation.

[4] BaP "equivalents" were calculated by multiplying the emission factor (in pounds chemical per ton of the source category such as per ton of wood combusted or per ton of aluminum produced) by the relative potency of the chemical as estimated using animal data.

While the uncertainty in applying toxicity weights based on animal data (as in the NATA values above) lies in the extrapolation of effects in animals to effects in humans, the uncertainty in applying the toxicity weights calculated above (based on the WHO unit risk and estimates of what fraction of total POM/PAH is BaP) lies in large part in the uncertainty in defining the percentage of total POM/PAH represented by BaP. Available estimates appear to support a value of 1% BaP for residential wood burning. It is important to recognize the uncertainties in considering various approaches to ranking POM/PAH.

8.0 Estimates of POM/PAH Cancer Risks in NATA

In the NATA, USEPA reported that the highest median countywide risk estimates for total POM exposure ranged from 1 in 1 million to 3 in 1 million (Cumberland and York counties). USEPA did a separate assessment using emissions and toxicity data for the 7-PAH group. For that group, the highest median countywide risk estimates ranged from 3 in 10 million (or 0.3 in 1 million) to 1 in 1 million (Cumberland county). Because the NATA assessment used unit risk estimates and relative potency values based on animal data, it is important to reiterate the cautions offered by Bostrom et al. (2002). Based on discussion in that paper, it is possible that these risk estimates may be underestimated as much as 2 orders of magnitude.

9.0 CA-EPA Prioritization of Toxic Air Contaminants under Children's Environmental Health Protection Act: Rationale for Ranking POM in Tier 1

Under a mandate from California's Children's Environmental Health Protection Act, CA-EPA conducted an evaluation of the unique susceptibility of children to the health effects of POM. The goal of the evaluation was to determine whether POM should be ranked within the top tier (Tier 1) of toxic air contaminants that could cause infants or children to be susceptible to illness. CA-EPA concluded that POM should be ranked in Tier 1 based on both greater exposures to children and on evidence of greater toxicological susceptibility. The major findings of CA-EPA's review are as follows:

- Many PAHs and PAH mixtures have been shown to be carcinogenic to animals and/or humans. Carcinogen exposure early in life may have greater overall impact than exposure to adults. Experimental data suggest young animals may be more sensitive to the carcinogenicity of certain PAHs and PAH derivatives.
- Prenatal PAH exposure is associated with numerous noncancer effects, including teratogenesis, low birth weight, immunotoxicity, loss of fertility, and hematopoietic effects, even at doses that do not cause maternal toxicity.
- PAHs are transplacental carcinogens[5], and the sensitivity and diversity of tumor sites is greater in transplacental carcinogenesis.
- Children's exposures to PAHs are generally higher than adults' exposures in the same setting.

[5] In transplacental carcinogenesis, toxicants circulating in the maternal bloodstream cross the placenta and render the fetus more susceptible to cancer.

10.0 Options Considered for Ranking POM/PAH:

Several options were considered for ranking POM/PAH within the Air Toxics Priority List, including:

1. *Use toxicity weight(s) calculated from WHO risk estimate assuming 1% or 2% BaP applied to total POM/PAH emissions estimates*. This approach is preferred over other quantitative approaches because it makes use of information on the health effects of mixtures of POM/PAHs rather than effects of individual compounds. The uncertainty in this approach stems from the need to estimate the contribution of BaP to total POM/PAH emissions, as well as uncertainty in the degree to which wood combustion emissions are similar to coke oven emissions (WHO unit risk is based on a study of exposures to coke oven emissions).
2. *Use toxicity weight based on CA-EPA unit risk and relative potencies for 16-PAH group and apply to total POM emissions*. Note that this approach may underestimate carcinogenicity by up to 2 orders of magnitude.
3. *Use NATA risk estimate with CA-EPA prioritization to qualitatively rank*. NATA estimated median cancer risks up to 3 in 1 million for exposure to POM in Maine. Note that the NATA risk estimate, because it relies on toxicity values developed from animal data and relative potency values, may underestimate risks by up to 2 orders of magnitude
4. *Develop risk assessment of wood burning in Maine, and use outcome to determine prioritization for POM/PAH and other air toxics released from wood burning*. In 1989, the Environmental Health Unit in the Bureau of Health developed a risk assessment for residential wood combustion emissions. Since that time, there have likely been changes in residential wood combustion patterns, and there have been changes in toxicological data for *POM/PAH*. One option for addressing PAH emissions from residential wood burning is to prepare an updated risk assessment of residential wood combustion in Maine.
5. *Implement monitoring program to measure indicator POM/PAHs and compare with proposed guidelines.* At present, there are no data on ambient levels of POM/PAH in Maine. Estimates of POM/PAH emissions from residential wood combustion (the major source of emissions) are generally believed to be uncertain. One option for evaluating the public health impact of POM/PAHs in ambient air is to develop a program for monitoring a subset of indicator compounds such as BaP, fluoranthene, etc. The resulting data could be compared with available ambient air guidelines in order to better understand the potential public health concerns associated with these emissions. A monitoring program would require both time and financial resources to implement. If not used for ranking purposes, this option could be considered as a next step if POM/PAH are ranked high within the ATPL.

11.0 References

Bostrom, C-E., P. Gerde, A. Hanberg, et al. 2002. Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air. Environ. Health Perspectives 110 (Suppl. 3): 451-489.

CA-EPA, 1994. Benzo(a)pyrene as a Toxic Air Contaminant. Prepared by the California Air Resources Board and the Office of Environmental Health Hazard Assessment. July.

CA-EPA, 2001. Prioritization of Toxic Air Contaminants – Children's Environmental Health Protection Act: Polycyclic Organic Matter.

Maine Air Toxics Advisory Committee, Revised Draft Prioritized List of Air Toxics For the State of Maine & Basis Statement, May 2004 (Available from Maine Department of Environmental Protection, Augusta, ME).

USEPA, Undated. Estimating Carcinogenic Potency for Mixtures of Polycyclic Organic Matter (POM) for the 1996 National-Scale Assessment. (at www.epa.gov\ttn\atw\sab\appendix-h.pdf)