

# **Toxicity-Weighting: A Prioritization Tool for Quality Assurance of Air Toxics Inventories**

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## **ABSTRACT**

Implementation of the residual risk, area source, and other HAP programs requires high quality inventories of Hazardous Air Pollutants (HAPs). The 188 federally listed HAPs present a 30-fold increase in the number of HAPs that must be tracked as compared to the Criteria Air Pollutants (CAPs). Few additional resources are available for HAP inventories, so air agencies need to focus on the HAPs that contribute significant risk. Typically, modeling is necessary to understand which HAPs present the greatest health risks, and accurate modeling is depends on a high quality inventory. To resolve this conundrum, the Maine Department of Environmental Protection (MEDEP) has successfully used a Toxicity-Weighting tool to focus inventory resources towards those HAPs that are likely to be of greatest concern.

The risk posed by a HAP depends upon exposure concentration (the amount of HAP in the air that is breathed), the amount breathed, and the toxicity of the HAP. Toxicity Factors for HAPs are based on the toxicity of each HAP and constants that help determine HAP intake. HAP emissions are a significant factor in determining exposure concentration. Therefore, the toxicity-factor is multiplied by HAP emissions, to derive a relative ranking of HAPs. Emission personnel can then focus QA reviews on those HAPs that have a high-toxicity ranking, and those HAPs whose relative rankings would change significantly when emissions change. Thus, a high quality inventory is available for fate and transport modeling, which ultimately calculates actual risk. Toxicity-factors for HAPs are available on EPA and MEDEP websites.

## **INTRODUCTION: WHY TOXICITY-WEIGHT A HAP INVENTORY?**

Sound air regulation depends on high quality emission inventories, modeling, and ambient air monitoring. Historically, emission inventories have focused on the Criteria Air Pollutants (CAPs). However, as air programs attain milestones in the 1990 Amendments to the Clean Air Act, policy managers are seeking more information on Hazardous Air Pollutant (HAP) emissions. Specifically, the control of HAP emissions under the section 112 “MACT” program is transitioning from implementation of the technology based standards to reviewing the residual risk posed by major facilities that have implemented MACT controls. Likewise, EPA’s area source program is evaluating the risk posed by HAPs from small sources in order to develop appropriate regulations that will reduce the greatest risk for the least cost.

The increased need for high quality HAP data presents challenges for emission inventory programs. Collecting, reviewing and reporting emissions of the six (6) CAPs entails a significant

allotment of resources by federal, state and local air agencies. Increasing inventories by 188 HAPs, or potentially thousands of other Air Toxics (ATs), is a daunting prospect.

Historically, HAP emission inventories have been incomplete and inaccurate. Modeling (based on emissions inventories) to Ambient Air Monitoring results for both the 1999 and 2002 National Air Toxics Assessments (1999 NATA, 2002 NATA) found that the modeling underestimated ambient concentrations.<sup>1,2</sup> A detailed assessment of the HAP inventory in the state of Maine by Maine's Air Toxics Advisory Committee (ATAC), found significant errors in the 1999 National Emissions Inventory (1999 NEI) and the Toxics Release Inventory (TRI) for Maine. Many of these errors resulted in an underestimation of risk for important source sectors.<sup>3</sup> For many missing HAPs, there were no readily available emission factors published by either EPA or trade organizations, suggesting that the underestimation may be national in scope.

In summary, improved HAP emissions inventories are needed despite the workload increase entailed by expanding the number of pollutants 30 fold, and limited or no additional inventory resources for air agencies. The Maine Department of Environmental Protection (MEDEP) developed a "toxicity-weighting" tool that has proven useful for its recent HAP inventory improvement program. This tool has helped MEDEP focus Quality Assurance (QA) reviews on those HAPs that are most likely to increase risk to public health. The toxicity-weighting approach is simple to use, and provides a real time estimation of relative risk, facilitating inventory corrections before undertaking expensive and time-consuming modeling. This results in a resource savings and increased accuracy of the final risk estimates. However, while useful for determining relative risk vis-à-vis other HAPs, toxicity-weighting does not, without modeling, indicate which HAPs pose an unacceptable risk, and it does not predict the location of unacceptable risks. Modeling in conjunction with ambient monitoring is necessary to determine actual exposure concentrations, and thus risk to public health.

## UNDERLYING RISK ASSESSMENT THEORY

The underlying theory for the toxicity-weighting tool is that the risk posed by a given HAP depends upon two main factors: the amount of a HAP that is breathed by an individual (known as "intake"), and the toxicity of the HAP. This relationship is shown in Equation 1.

**Equation 1:** Generalized Risk Assessment Calculation.

$$\text{Risk} = \text{Intake} * \text{Toxicity}$$

The amount of HAP that a person intakes depends on several factors: the concentration of HAP in the air, how much air a person breathes in a day (which varies with age), and how much time the person spends in the polluted air. The toxicity of a compound depends on the toxic potential (known as "dose – response") of the chemical, and the body weight of the individual breathing the air (which also varies with age). The toxicity of a given HAP is determined by reviewing the effects of accidental or industrial exposure to humans and animal studies. Risk assessors review this data and estimate a "safe" or "reference" exposure for humans. Many of the factors that determine intake and toxicity are relatively constant, and risk assessors have developed default factors for them. By combining the default factors, EPA has simplified inhalation risk calculations so that they are based on two variables: the exposure concentration and toxic potential of the contaminant, as shown in Equation 2.<sup>4</sup>

**Equation 2:** Simplified Risk Calculations for Hazardous Air Pollutants.

$$\begin{aligned} \text{Cancer Risk: } \text{ILCR} &= \text{EC} * \text{IUR} \\ \text{Noncancer Risk: } \text{HQ} &= \frac{\text{EC}}{\text{RfC}} \end{aligned}$$

- Where:
- ILCR- Incremental Lifetime Cancer Risk, or the increased probability (upperbound) of contracting cancer over a lifetime due to exposure to the HAP (unitless). Generally, ILCR less than 1 e-6 (or “1 in a million”) are considered insignificant, while ILCR greater than 1e-4 (or “100 in a million”) are considered significant.
  - HQ- Hazard Quotient, or the potential noncancer hazard posed by a HAP (unitless). A HQ less than one (1) indicates that an adverse non-cancer effect is not likely to occur, while a HQ above 1 means that an adverse health effect is likely to occur after long-term exposure.
  - IUR- Inhalation Unit Risk, or the upper bound estimate of the probability of tumor formation per unit concentration of chemical, expressed in risk per microgram of HAP in a cubic meter of air (ug/m<sup>3</sup>).
  - RfC- Reference Concentration, or exposure level that is not likely to cause deleterious and non-reversible (noncancer) health effects during a chronic exposure period, expressed in mg-HAP/m<sup>3</sup>-air (mg/m<sup>3</sup>)
  - EC Exposure Concentration of HAP in the air that is breathed (ug/m<sup>3</sup>) as determined by modeling emissions (e.g. ASPEN), or from ambient air monitoring.

As seen in Equation 2, risk assessors usually calculate the risk posed by a HAP separately for carcinogens and non-carcinogens. Some compounds, such as benzene and nickel, can cause both a cancer and non-cancer health effect. The IURs and RfCs take into account several default exposure assumptions along with the HAP’s toxicity. EPA’s Office of Air Quality and Planning Standards lists recommended chronic toxicity values for each of the HAPs IURs and RfCs, which is available on its website at: <http://www.epa.gov/ttn/atw/toxsource/summary.html>.

The other important factor in determining a HAP’s impact on human health is the exposure concentration, or concentration of the HAP in the ambient air that a person breathes. Exposure concentration is determined by the amount of HAP that is released, transformation of HAPs as they move downwind, travel time to the exposure point, how long the HAP remains at the exposure point (duration), and how often the HAP moves to the exposure point (frequency). The fate and transport of HAPs is highly complex and variable, and is dependent on the amount and type of chemicals in the air, weather, and terrain.

Models are often used to estimate exposure concentrations. An important input into the model is HAP emissions. Since the influences of weather and terrain cannot be easily simplified, the toxicity-weighting tool was not able to account for these factors. Instead, the toxicity-weighting tool substitutes emission concentration for exposure concentration, since emission concentration is an important component of exposure concentration.

## WEIGHTING EMISSIONS BASED ON TOXICITY

The basis for the toxicity-weighting tool is that the mass of emissions and a HAP's toxicity are two significant factors in determining a HAP's potential impact on public health. Therefore, in the toxicity-weighted emissions approach, the mass of the HAP release (in tons per year) is multiplied times a toxicity factor (unitless) using the formula in Equation 3.

**Equation 3:** Conversion of Mass Emissions to Toxicity-Weighted Emission.

$$TWE_{HAP} = W_{HAP} * TF_{HAP}$$

Where:  $TWE_{HAP}$  Toxicity-Weighted Emissions of a given HAP, in Toxicity-Weighted Tons per Year (TW-TPY)  
 $W_{HAP}$  Weight of the given HAP that is emitted to the air in a year, in tons of HAP per year (TPY)  
 $TF_{HAP}$  Toxicity Factor for the given HAP (unitless)

The toxicity-factors for HAPs vary by ten (10) orders of magnitude, so they will have a significant impact on the relative ranking of HAPs. For example, as demonstrated in Table 1, despite relatively low emissions of chromium and naphthalene in Maine, the toxicity of these compounds gives it a relatively high potential for creating an adverse risk when compared to styrene and glycol ethers. Focusing quality assurance efforts on only emission masses (TPY) may mean that significant “risk-driving” HAPs, in this case naphthalene and chromium, would not receive the scrutiny that they merit. Further, significant resources may be expended on verifying high mass emissions, in this case glycol ethers and styrene, which have a much lower potential for public health impacts. By toxicity-weighting the preliminary results of an emission inventory, MEDEP has been able to focus its limited QA resources towards those areas that are most likely, after modeling, to demonstrate a public impact.

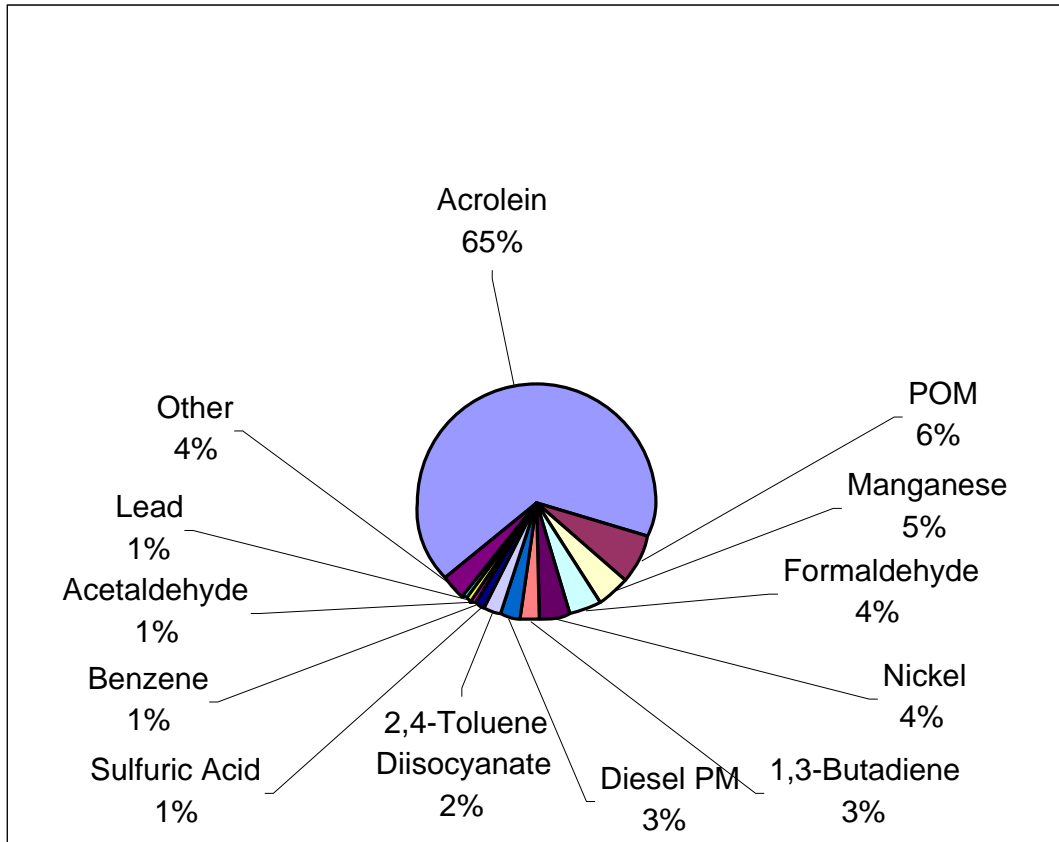
**Table 1:** Comparison of Mass Emissions and Toxicity-Weighted Emissions – 2005 Maine Point Emissions from the Manufacturing Sector for select Hazardous Air Pollutants.

HAP	TF	TPY	TW-TPY
Sulfuric Acid	72	9,007	648,512
Glycol Ethers	3.6	83	298
Styrene	0.072	67	5
Acrolein	3600	61	218,357
Naphthalene	6400	17	106,747
Chromium & Compounds	86000	1	99,556

The toxicity-weighted inventory also allows for easy comparison across various HAPs or emission sectors. By allowing an “apples-to-apples” comparison between numerous HAPs with varying toxicities, vast amounts of data can be summarized into a few charts and graphs. This approach was used by MEDEP to enable a diverse stakeholder group to reach agreement on the

nature of air toxic risks in Maine, and the next steps necessary to resolve air toxic issues. Two examples of charts summarizing Maine’s HAP inventory are shown in Figure 1 and Figure 2.

**Figure 1:** Maine preliminary 2005 toxicity-weighted emission inventory by pollutant.

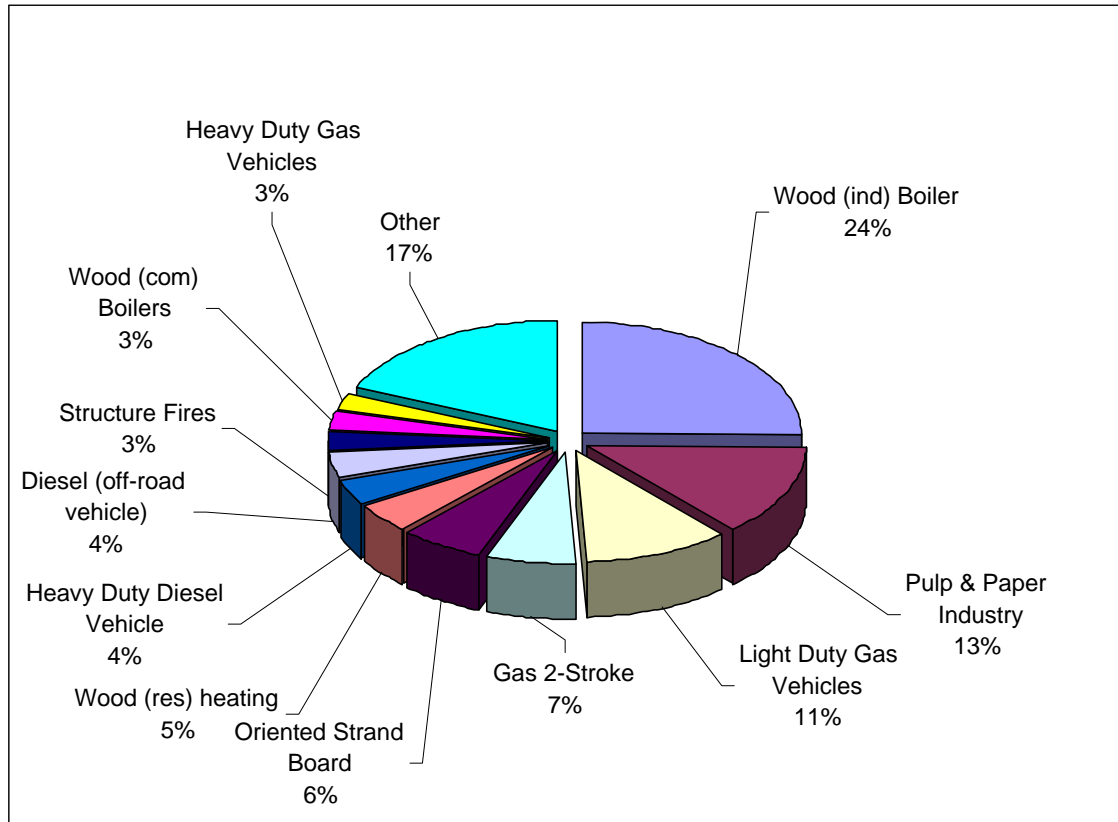


### Derivation of Toxicity-Factors

#### Risk Screening Environmental Indicators Model

In 2003, the Maine DEP established a stakeholder group, the Air Toxics Advisory Committee (ATAC), to review available information on air toxics in Maine and assess potential risk to the public. The ATAC determined that the best approach to assessing potential risk from HAPs was to first toxicity-weight the states emissions inventory. For a toxicity factor, a Public Health Subcommittee selected the toxicity-factors used in EPA’s Risk-Screening Environmental Indicators (RSEI) model. The Public Health Subcommittee selected the RSEI toxicity-factors because EPA frequently updates the factors based on the latest toxicity information, they were available for most of the air toxics contained in the state’s HAP inventory, and they provide a method of evaluating carcinogens and non-carcinogens at the same time. EPA developed the RSEI model to assess the risk of releases reported in the Toxics Release Inventory (TRI). To derive the toxicity-factors for the RSEI model, EPA assessed a hierarchy of toxicity information, and derived a common risk weighting scale.

**Figure 2:** Maine preliminary 2005 toxicity-weighted emission inventory by source.



However, the ATAC noted that the factors used to derive the common weighting scale “maintain the equivalency between cancer and noncancer scores that was established in the Hazard Ranking System (HRS) scoring methodology used in EPA’s Superfund program”<sup>5</sup> Therefore, the factors are based on a Hazard Quotient (HQ) of 1 and an Incremental Lifetime Cancer Risk (ILCR) to  $2.5 \times 10^{-4}$ , as shown in Equation 4.

**Equation 4: RSEI Toxicity Factors**

$$\text{Cancer Risk: } TF_{\text{carc}} = \frac{ILCR}{IUR} = \frac{2.5e-4}{IUR}$$

$$\text{Noncancer Risk: } TF_{\text{noncarc}} = HQ * RfC = 1 * RfC = RfC$$

$$\text{RSEI Toxicity Factor: } TF_{\text{RSEI}} = \text{The Greater of } TF_{\text{carc}} \text{ or } TF_{\text{noncarc}}$$

Where:	$TF_{\text{carc}}$	RSEI toxicity Factor based on carcinogenic properties of a given HAP
	$TF_{\text{noncarc}}$	RSEI toxicity Factor based on noncarcinogenic properties of a given HAP
	$TF_{\text{RSEI}}$	RSEI toxicity Factor based on both carcinogenic and non-carcinogenic properties of a given HAP
	ILCR	Incremental Lifetime Cancer Risk, or the increased probability (upperbound) of contracting cancer over a lifetime due to exposure to the HAP (unitless)
	HQ	Hazard Quotient, or the potential noncancer hazard posed by a HAP (unitless).
	IUR	Inhalation Unit Risk, or the upper bound estimate of the probability of tumor formation per unit concentration of chemical, expressed in risk per microgram of HAP in a cubic meter of air ( $\text{ug}/\text{m}^3$ ).
	RfC	Reference Concentration, or exposure level that is not likely to cause deleterious and non-reversible (noncancer) health effects during a chronic exposure period, expressed in $\text{mg-HAP}/\text{m}^3\text{-air}$ ( $\text{mg}/\text{m}^3$ )
	EC	Exposure Concentration of HAP in the air that is breathed ( $\text{ug}/\text{m}^3$ ) as determined by modeling emissions or from ambient air monitoring

### Updating Select RSEI Toxicity Factors

When the Maine Air Toxics Initiative (MATI) began, the latest available RSEI factors had not been updated in two years. Maine Center for Disease Control (MECDC) reviewed the underlying data the RSEI toxicity-factors for some 70 HAPs. These were the HAPs of greatest concern in the mid 1980's, for which the MECDC had established interim ambient air guidelines.<sup>6</sup> In cases where updated toxicological information was available, MEDEP updated the RSEI toxicity factor. The updated Toxicity Factors are available on the MATI website at: <http://www.maine.gov/dep/air/toxics/mati-archive.htm>.

### Chromium Toxicity Factor

It is important to note that Chromium is generally found in the environment as trivalent chromium (Chromium III or Cr III) or hexavalent chromium (chromium VI or Cr VI), as determined by its valence state. Chromium III is much less toxic and more prevalent than chromium VI. The major target organ for both forms of chromium is the respiratory tract. The body converts some chromium (VI) to chromium (III).<sup>7</sup> The Toxicity Factor in RSEI for Chromium is specific to either Chromium III or Chromium VI. Since these factors vary by an order of magnitude, to accurately weight an inventory, the total chromium must be speciated into chromium (VI) and chromium (III).

### Derivation of Missing RSEI Risk Factors

When a RSEI toxicity factor was not available for a given compound, the MEDEP consulted with MECDC and derived a toxicity factor in one of two ways. If sufficient toxicity information was available on the compound in EPA's Integrated Risk Information System (IRIS), then ATAC derived a toxicity factor using the same protocols that were used to derive the RSEI toxicity factor. These protocols are described in the "User's Manual for RSEI Version 2.1".<sup>5</sup> If insufficient information existed, a factor was derived using the hierarchy that was developed by the MECDC in April of 2004 for establishing the Maine Ambient Air Guidelines. This Hierarchy is, from highest to lowest preference, toxicity data from:

- UR and RfCs from EPA's Integrated Risk Information System (IRIS),
- UR and Reference Exposure Levels (RELs) from the California's Office of Health Hazard Assessment (CA-OHHA),
- chronic Maximum Recommended Levels (MRLs) from the Agency for Toxic Substances and Disease Registry (ATSDR),
- Threshold Limit Values (TLVs) from the American Conference of Industrial Hygienists (ACGIH), adjusted for exposure to the general population, and
- As a last resort, toxicity data for oral exposure from the above sources.<sup>8</sup>

#### Selecting a Toxicity Factor for Polycyclic Organic Matter (POM)

The ATAC's Public Health Subcommittee also established a toxicity factor for Polycyclic Organic Matter (POM), also known as Polycyclic Aromatic Hydrocarbons (PAHs). The Subcommittee evaluated available POM emissions and toxicological data to derive a toxicity factor of 6400 (unitless).<sup>9</sup> The POM toxicity factor is based on the World Health Organization's unit risk of 90 per mg/m<sup>3</sup> for benzo(a)pyrene, which was used 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 combustion sources. Additional support for the factor came from a California EPA finding that children had greater exposures and toxicological susceptibility to POM.<sup>10</sup>

#### Selecting a Toxicity Factor for Diesel Particulate Matter (DPM)

Additionally, the Public Health Subcommittee developed a toxicity factor for diesel particulate matter (DPM), based on toxicological data. The subcommittee developed a range of toxicity weights from 360 to 2100. The lower toxicity weight (360) is based on noncancer effects, which were derived from a EPA Reference Concentration for chronic exposure to DPM. The higher toxicity weight (2100) is based on cancer effects and is derived from an Inhalation Unit Risk for DPM developed by California's Environmental Protection Agency (CA-EPA).<sup>11</sup>

#### **Conversion of Toxicity Factors to Relevant Risks for Maine**

One issue that arose through the MATI process was that the RSEI factors weigh non-carcinogens more heavily than carcinogens than the MEDEP generally does when making risk based decisions. Rather than the cancer and non-cancer risks used in the federal superfund program, Maine DEP generally establishes acceptable risk for air toxics at a HQ of 1 or an ILCR of 10<sup>-5</sup>. These endpoints are the basis for the Maine Ambient Air Guidelines, which are established by the Maine CDC.<sup>8</sup> Recently, Maine DEP in consultation with ME CDC adjusted the toxicity-factors used in the Maine Air Toxics Initiative to be consistent with these guidelines. The adjustments were made according to the formulas in Equation 5.



**Equation 5:** Derivation of Maine Specific Toxicity Factors.

$$\frac{HQ_{MAAG}}{HQ_{RSEI}} = \frac{ILCR_{MAAG}}{ILCR_{RSEI}} \rightarrow HQ_{MAAG} = HQ_{RSEI} * \frac{ILCR_{MAAG}}{ILCR_{RSEI}}$$

$$HQ_{MAAG} = HQ_{RSEI} * \frac{1e-5}{2.5e-4} = \frac{HQ_{RSEI}}{25}$$

MATI Toxicity Factor:  $TF_{MATI} = \text{The Greater of } TF_{carc} \text{ or } TF_{noncarc}$

Where: $HQ_{MAAG}$	Hazard Quotient used to establish the Maine Ambient Air Guidelines = 1
$HQ_{RSEI}$	Hazard Quotient used to establish the toxicity-factors in EPA's Risk Screening Environmental Indicators Model = 1
$ILCR_{MAAG}$	Incremental Lifetime Cancer Risk, used to establish the Maine Ambient Air Guidelines = 10 in a million, or $10^{-5}$ .
$ILCR_{RSEI}$	Incremental Lifetime Cancer Risk, used to establish the toxicity-factors in EPA's Risk Screening Environmental Indicators Model = 250 in a million or $2.5e-4$ .
$TF_{carc}$	Toxicity Factor based on carcinogenic properties of a given HAP
$TF_{noncarc}$	Toxicity Factor based on noncarcinogenic properties of a given HAP
$TF_{MATI}$	Maine Air Toxic Initiative revised Toxicity Factor based on both carcinogenic and non-carcinogenic properties of a given HAP

The most recent toxicity-factors are available on the Maine Air Toxics Initiative Website at: <http://www.maine.gov/dep/air/toxics/mati-docs.htm>

**RECOMMENDED STEPS TO IMPROVE TOXICITY FACTORS**

While developing the toxicity-weighting tool, the MEDEP noted several additional factors that are not taken into account by the toxicity-weighting factors. Adjustments to account for persistence and bioaccumulation should be developed.

**Persistence**

There is great variation in the speed with which compounds will degrade once emitted into the biosphere. Some will last a matter of minutes, and others will remain for several decades. Those compounds that do not readily degrade will remain in the biosphere such that emissions from each inventory year become additive. The toxicity-weighted emissions discussed in this paper do not take this persistence into account.

The ATAC explored simplistic factors, such as an Air Toxic's half-life in air, to account for persistence. However, many chemical properties and weather conditions affect a chemical's residence time in the atmosphere. Furthermore, other compounds, particularly metals, may not remain in the atmosphere, but will remain in terrestrial or aquatic ecosystems once deposited. A sophisticated modeling of all of these factors was beyond the scope of the MATI project, and a simplified protocol was not readily available to quantify persistence. Therefore, the ATAC had to account for persistence in a qualitative manner. Manganese, Lead, Cadmium, Chromium,

Arsenic, Cyanide & Compounds, other metals, Chloroform, Carbon Tetrachloride, Ethylene Dichloride and Ethylene Dibromide are examples of persistent HAPs.

### **bioaccumulation**

In a process known as “bioconcentration” or “bioaccumulation”, over time some chemicals will increase in body tissue concentration after being ingested, inhaled, or absorbed. Bioconcentration occurs whenever an animal’s tissue absorption level of a chemical exceeds the rate of metabolism (breakdown) and excretion of that chemical. Thus, over time, an animal may have a greater concentration of the contaminant in its tissue than the surrounding contaminated environment. Further, predators are exposed to greater tissue concentrations as they moving up the food chain. Dioxin, and methyl- mercury are two compounds that are know to be highly bioaccumulative. Often these compounds will concentrate in the fatty tissue of an animal.

Bioconcentration is an important property of some HAPs that was not quantified in the Toxicity-Weighting approach taken by ATAC, nor was this factor included in the 1996 or 1999 NATA Risk Assessments. The ATAC explored simplistic approaches, such as applying bioconcentration factors for media such as water and sediment, but found that these factors were not relevant or appropriate. A more sophisticated modeling of all of the factors that influence bioaccumulation was beyond the scope of the MATI project, so the ATAC conducted a qualitatively assessment. However, State agencies and EPA should explore the possibility of developing Toxicity Factors that take bioaccumulation into account.

### **CONCLUSIONS**

The Maine DEP has found the toxicity-weighting tool to be a simple and easy way to prioritize data for quality assurance reviews and refinement, both saving resources and providing an inventory that will more accurately predict risks to public health when modeled. EPA and other state, local and tribal air agencies should consider using toxicity-factors as a QA tool for HAP inventories.

While developing this tool, the MEDEP notes several additional factors that are not taken into account by the toxicity-weighting factors. EPA along with state, local and tribal air agencies should explore the possibility of improving toxicity-factors to take into account persistence and bioaccumulation.

### **ACKNOWLEDGEMENTS**

The Maine DEP thanks Maine CDC for its technical support in the MATI process, the development of Ambient Air Guidelines, and development of toxicity-factors. MEDEP also thanks EPA for financial and technical assistance with the Maine Air Toxics Initiative, and for providing the basic risk assessment and inventory tools that are necessary to undertake this work. We also thank the ATAC members for their valuable insight into inventory improvements in general, and the toxicity-weighting process specifically.

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**KEY WORDS**

Air Modeling

Air Toxics

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HAP

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Maine Air Toxics Initiative

Quality Assurance

Toxicity Factors

Toxicity Weighting