INTERMEDIA TRANSFER FACTORS FOR MODELING THE ENVIROMENTAL IMPACT OF AIR POLLUTION FROM INDUSTRIAL SOURCES

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ABSTRACT

Toxic contaminants emitted to the atmosphere may be transformed and/or transported to other enviromental media such as water, soil, and biota. Many models have been developed to assess the impact of these emissions on human health and ecosystems. These models require input of chemical-specific parameters called intermedia transfer factors (ITFs). This study focuses on assessing the accuracy of ITFs used in modeling the enviromental impact of benzene, 2,3,7,8-TCDD and hexavalent chromium because these chemicals pose significant health risks and are widely emitted from various industrial processes. Many of the IFTs cited in the literature were estimated rather than measured which highlights the need for employing the most accurate estimation techniques available. This study can be used to refine the health risk assessment approach for identifying major enviromental hazards caused by industrial emissions and thus elucidating effective control strategies.

INTRODUCTION

Industrial sources emit a variety of toxic air pollutants which may be transformed and/or transported to other environmental media such as water and soil, and can be accumulated in plants and animals and subsequently impact human health and ecosystems. Because of the potential adverse health effects resulting from human exposure to toxic air pollutants via different exposure pathways, intermedia and trans-boundary migration of pollutants are of international concern and have resulted in more stringent regulation of industrial emissions in developed

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countries. In the U.S., these regulations are based on either the use of best available control technology or the health risk assessment (HRA) process. The HRA process is a useful tool for setting health-based emission standards. With this approach, the most hazardous industrial facilities can be identified and prioritized such that scarce resources for pollution control can be allocated in the most cost-effective manner. This approach has been widely used by U.S. regulatory agencies throughout the 1980's and could be adapted to meet the needs of other industrialized countries.

The HRA process typically incorporates the following elements[1]:

1. Hazard Identification

2. Dose/Response Assessment

3. Exposure Assessment

4. Risk Characterization

The purpose of this study was to refine the multipathway exposure assessment component of the human HRA process by developing an information base on the abiotic and biotic transfer of selected toxic air pollutants between environmental compartments. The study tasks were to: (1) critically review the environmental literature to determine the intermedia transfer factors relevant to the study chemicals; (2) evaluate measured and estimated values; and (3) recommend estimation techniques appropriate to the study chemicals for use in the absence of measured values. The study chemicals for which evaluations have been completed are:

- Benzene

- 2,3,7,8-Tetrachloro-dibenzo-p-dioxin [2,3,7,8-TCDD]

- Hexavalent Chromium [Cr(VI)]

Evaluations are in progress for four additional chemicals, benzo(a)pyrene, methylene chloride, formaldehyde, and mercury.

BACKGROUND

Determination of toxic air contaminant concentrations in different environmental media can be obtained by either pollutant transport modeling or by field measurements. Because of its lower cost and faster time frame compared to field measurements, modeling is often a more attractive approach and many intermedia transport models have been developed to assess the impact of pollutant emissions on human health and ecosystems. These models require input of chemical-specific parameters called intermedia transfer factors.

Despite the appeal of the multipathway exposure analysis and the HRA process, there remains, a great deal of uncertainty in the process, mainly due to deficiencies in our understanding of various intermedia transfer processes[2] and the lack of data in many areas. Major sources of uncertainty in exposure assessment include:

1. Extrapolation of toxicity data in animals to humans;

2. Air dispersion modeling;

3. Estimation of emissions; and

4. Analysis of multimedia exposure.

The uncertainty associated with estimating risk from multimedia exposure to toxic chemicals can be reduced by identifying the input parameters most critical to multimedia analysis and summarizing the most accurate measured values and estimation techniques.

This study focuses on assessing the accuracy of intermedia transfer factors used in modeling of the environmental impact of benzene, 2,3,7,8-TCDD and Cr(VI). These chemicals pose significant health risks because they are known or suspected human carcinogens and are widely emitted from industrial sources. In particular, benzene is used in high volumes by a variety of industries and dioxin and hexavalent chromium are ubiquitous by-products of combustion processes. In addition, these chemicals represent major classes of environmental chemicals. Benzene represents volatile organic chemicals that present significant hazards mainly by inhalation, 2,3,7,8-TCDD represents semi-volatile lipophilic compounds that can bioaccumulate through the food chain posing a hazard from ingestion, and Cr(VI) represents inorganic compounds that exist in the particulate phase that also presents an inhalation hazard. The results of this study should improve the accuracy of multipathway exposure assessment which is important for identifying major environmental hazards caused by industrial emissions and thus elucidating effective control strategies.

METHODOLOGY

The method of approach for this study consisted of several phases in which key parameters for intermedia transfer analysis were selected, published values for these parameters were collected and critically evaluated, and estimation techniques were evaluated for those parameters for which measured values could not be found in the literature. Intermedia transfer factors that were reviewed for this study are the chemical-specific physicochemical and biochemical properties of the study chemicals which included solubility, vapor pressure, Henry's Law constant, octanol/water and organic carbon/soil partition coefficients, bioconcentration factors, diffusion and mass transfer coefficients, and reaction half-lives in environmental media. Values found in the literature for each of those parameters were critically evaluated according to the following hierarchy:

1. <u>Measured</u> values with <u>known</u> uncertainty (High Reliability)

2. <u>Estimated</u> values with <u>known</u> uncertainty or <u>measured</u> values with <u>unknown</u> uncertainty (Medium Reliability)

3. <u>Estimated</u> values with <u>unknown</u> uncertainty (Low Reliability)

In addition to chemical-specific paramters, non-chemical-specific parameters, such as properties of soil and sediment, depth of water body, and meteorological parameters are also needed as model input parameters. Model-specific assumptions regarding these non-chemical-specific parameters should also be considered when applying multimedia models.

RESULTS

Table 1 presents the multimedia input parameters evaluated in this study along with the degree of reliability (i.e., high, medium, or low) associated with the numerical values reported in the literature for each study chemical. It can be seen from the Table 1 that values for physicochemical parameters appear to be of greatest reliability and values for intermedia transport parameters of lowest reliability. The table also shows that the only multimedia transfer parameters, for air to terrestrial exchange, that apply to Cr(VI) are redox reactions and wet and dry deposition. This indicates that multimedia transfer of inorganic Cr(VI) compounds differs significantly from organic compounds such as benzene and 2,3,7,8-TCDD.

For brevity, the actual values for all parameters were not presented but can be found in reports specific to each study chemical[3,4,5]. The following subsections introduce the concepts of partition coefficients, intermedia transfer parameters and degradation processes. A detailed discussion of these concepts and their influence on transport and degradation processes is provided in respective reports previously mentioned.

Partition Coefficients

The net transport of chemicals from one environmental compartment to another is limited by equilibrium constraints and quantified by partition coefficients. The partition coefficient, H_{ij}, is generally defined as

$$H_{ij} = C_i/C_j \qquad \text{(Eq. 1)}$$

where C_i is the equilibrium concentration in compartment i and C_j is the equilibrium concentration in compartment j.

Intermedia Transport Parameters

Intermedia transport processes occur by either convective transport in a given medium (not addressed in this study) or by interfacial transport from one environmental compartment to another. Interfacial mass transfer coefficients are required to predict the flux of pollutants across the various interfaces and thus its accumulation in the environmental medium of interest. The intermedia transfer parameters considered in this study were diffusion coefficients in air and water, intermedia mass transfer coefficients and deposition flux.

Diffusion Coefficients in Air and Water. Molecular diffusion is the net transport of a molecule within a single phase (e.g. liquid or gas) that results from intermolecular collisions. The diffusive flux due to concentration gradients is defined by Fick's Law:

$$J_A = - D_{AB}\, dC_A / dx \qquad \text{(Eq. 2)}$$

in which J_A is the diffusion flux for compound A (e.g., mg/m^2s), dC_A/dx is the concentration gradient along the x direction and D_{AB} is the diffusion coefficient of A in medium B (e.g., units of cm^2/s).

Table 1 - Summary of Selected Multimedia Transfer Parameters

INTERMEDIA TRANSFER PARAMETER	RELIABILITY OF PARAMETER VALUE		
Physicochemical Parameters	Benzene	2,3,7,8-TCDD	Cr(VI)
Water Solubility	High	High	(a)
Vapor Pressure	High	High	(a)
Molar Volume	High	NA	(a)
Density	NA	High	(a)
Melting Point	NA	High	(a)
Boiling Point	High	NA	(a)
Molecular Weight	High	High	(a)
Heat of Vaporization	NA	Medium	(a)
Partition Coefficients			
Henry's Law Constant	High	Low	(a,b)
Octanol-Water Partition Coefficient	High	High	(a,b)
Soil/Water-Organic Carbon Partition Coefficient	Medium	Medium	(a,b)
Bioconcentration Factors	Medium	Medium	(a,b)
Bioaccumulation Factors	Low	Low	(a,b)
Gas/Particle Partitioning	NA	Low	(a,b)
Intermedia Transport Parameters			
Diffusion Coefficients in Air/Water	Medium	Med/Med	(a,b)
Intermedia Mass Transfer Coefficients	Low	Low	(a,b)
Dry Deposition Velocity	Low	Low	Low
Washout (Scavenging) Ratio	NA	Low	Low
Biotransfer Factors	Low	Low	(a,b)
Degradation Rates and Half-lives			
Photooxidation in Air	High	Low	(a,b)
Photolysis in Air/Water	NA	Low/Low	(a,b)
Biodegradation in Water/Soil	Med/Med	Med/Med	(a,b)
Redox Reaction Rates	NA	NA	Medium

NA - Parameter not considered significant for multimedia modeling of study chemical annotated.
High - Indicates measured value with known uncertainty.
Medium - Indicates estimated value with known uncertainty or measured value with unknown uncertainty.
Low - indicates estimated value with unknown uncertainty.
[a]Values are species dependent since Cr(VI) only exists in combination with other elements.
[b]The fate and transport of Cr(VI) is dominated by redox reactions and deposition.

Intermedia Mass Transfer Coefficients. The traditional approach to calculating the flux of a compound between air and water phases is to use the two film theory in which it is assumed that the concentrations immediately on either side of the interface are in equilibrium as can be expressed by a Henry's law constant. The flux, N, in a steady-state process can be expresses as:

$$N = K_G\,(C_g - HC_l) = K_L\,(C_l - C_g/H) \qquad \text{(Eq. 3)}$$

where K_G and K_L are the overall mass transfer coefficients (cm/s) for the gas and liquid phase, respectively, H is unitless Henry's law constant, and C_g and C_l are concentrations in gas and liquid phase, respectively. The overall mass transfer coefficients for the gas and liquid phase can be defined as:

$$1/K_G = k_g + H/k_l \qquad \text{(Eq. 4)}$$

$$1/K_L = 1/k_l + 1/Hk_g \qquad \text{(Eq. 5)}$$

where k_g is a gas-phase exchange coefficient (cm/s), H is the unitless Henry's law constant, and k_l is a liquid-phase exchange coefficient.

Atmospheric Deposition. The total deposition flux from the atmosphere to the terrestrial surface is attributable to dry and wet deposition (scavenging) processes. It is important to distinguish between deposition of a chemical in vapor and particle-bound phases since different transfer mechanisms are involved. The dry deposition flux of a pollutant, (N_A), can be expressed by

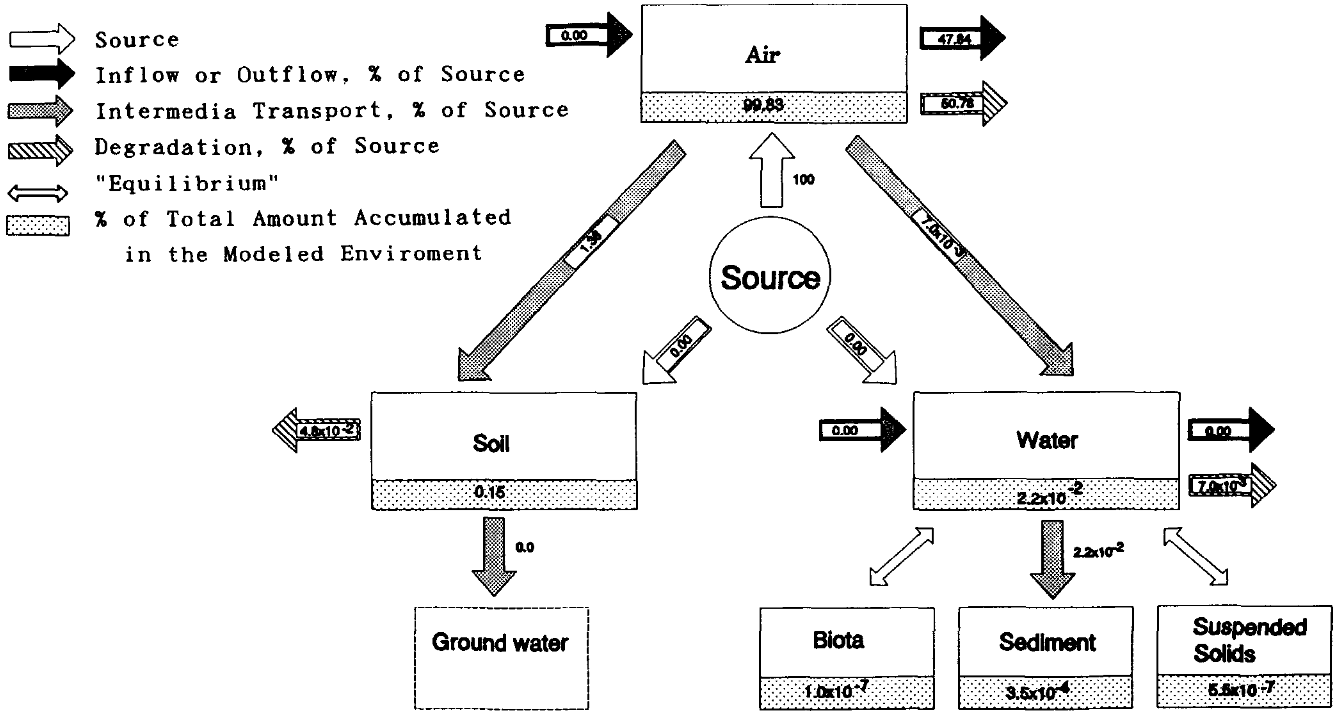
$$N_A = V_d\,C_a \qquad \text{(Eq. 6)}$$

in which C_a is the mass of the pollutant in the particle phase per unit volume of air, and V_d is the overall chemical deposition velocity which can vary with speed, temperature, humidity, and surface characteristics. The efficiency of scavenging is largely a function of the raindrop size, the aqeous solubility of the chemical in the vapor phase, and the particle size distribution of particle-bound chemicals.

Degradation processes

Reaction rates for individual abiotic and biotic degradation processes can be used to estimate overall environmental degradation half-lives. Degradation rates are determined for an individual chemical or biochemical transformation process within specific media. Environmental degradation reactions are often expressed as the first or "pseudo-first" order reaction rates. Since degradation processes involve chemical changes as opposed to intermedia transport processes which involve the flux of the unchanged chemical through the environment, degradation half-lives for soil, water, and air do not account for intermedia transport of a chemical and are, therefore, not necessarily representative of a chemical's actual persistence within a particular environmental medium[6].

The parameters discussed above are essential for predicting the distribution of chemicals in the environment. As an example, the annual average distribution of benzene in the greater Los Angeles area was estimated using the Spatial Multimedia Compartmental Model developed by Cohen et al.[7]. The results are depicted in Figure 1. The accumulation of benzene in the various



Total Amount Accumulated in the Modeled Enviroment = 66866 kg

Total Source = 585 kg/hour

Figure 1. Multimedia Fluxes and Partitioning of Benzene in Los Angeles

environmental compartments are indicated as a percentage of the total amount present in the atmosphere. Also, the rates of degradation and intermedia transfer rates among the compartments are indicated as the percentage of the estimated emission rate of benzene. As expected, benzene, which is a volatile chemical, resides mostly in the atmosphere (99.8%) with the remainder distributed to the other compartments.

CONCLUSIONS AND RECOMMENDATIONS

Table 2 presents the key findings and conclusions for the study chemicals. The fact that many of the intermedia transfer factors cited in the literature were estimated rather than measured, highlights the need for additional research in this area, and for employing the most accurate estimation techniques available. The use of critically evaluated intermedia transfer factors developed from this study will improve the accuracy of the exposure assessment component of the health risk assessment by incorporating the best available information. The findings of this study may influence the preparation and evaluation of health risks assessments required by various U.S. environmental regulations at the federal, state, and local level.

The HRA approach could be used throughout Eastern Europe to identify and prioritize the industrial facilities that present the greatest risks to public health and are thus in the greatest need of appropriate control technologies. For example, Prague, the capital of the Czech Republic, could benefit from the HRA approach because high population densities are located near potential sources of air toxics[8] (e.g., utilities, cement foundries, steel smelters, aircraft manufacturers, and waste incinerators). The first step towards accomplishing this objective would be to identify the target toxic air pollutants of interest. The U.S. 1990 Clean Air Act Amendments[9] lists 189 such compounds and could provide initial guidance in this area. The next step would be to inventory emission sources and rank sources according to the amounts and toxicity of target compounds emitted. Industrial facilities above some threshold ranking would then perform an HRA using the multimedia exposure principles highlighted in this study, as well as those presented in other guidance documents[1]. Finally, risk managers can use the results of the HRA to target emission controls to an acceptable level of risk (e.g., 10^{-6}, 10^{-5}, or 10^{-4} excess cancers per million people exposed).

FUTURE RESEARCH NEEDS

To improve the accuracy of the exposure assessment component of the HRA process, additional research is warranted in the following areas:

- More measured values of known accuracy are needed for intermedia transfer parameters.
- Improved estimation techniques are needed for predicitng bioconcentration factors, intermedia transfer parameters, and degradation processes in the absence of measured values.
- The sensitivity of multimedia pathway exposure models to various intermedia transfer factors should be established.
- The particle size distribution and chemical mass distribution for major emission sources of the study chemicals should be determined.

TABLE 2 - KEY FINDINGS AND CONCLUSIONS FOR STUDY CHEMICALS[a]

MAJOR FINDINGS	BENZENE	2,3,7,8-TCDD	Cr(VI)
Physicochemical Parameters			
The most important physicochemical parameters are molecular weight, vapor pressure, and solubility because they can be used to predict other parameters such as Henry's law constant, octanol-water partition coefficient, organic carbon partition coefficient, bioconcentration factors, etc., in the absence of measured values.	X	X	X
Partition Coefficients			
When correlations derived from regression analysis, it is important to verify that the value of the input parameter is within the range of applicability of the correlation.	X	X	
Air-to-leaf uptake may be a significant exposure pathway for vegetation ingestion.	X		
The current uses of bioconcentration factors generally assume that measured chromium is present as *Cr(VI), although the trivalent form* would be favored in biota.			X
Note inconsistency in terminology between bioconcentration and bioaccumulation.	X	X	X
There is a lack of experimental data on accumulation *in vegetation due to wet deposition.*		X	
Intermedia Transfer Parameters			
Intermedia transfer factors for specific chemicals are often applicable to homologous compounds.	X	X	
The *concept of biotransfer factors* should be revisited since they are based implicitly on the assumption of steady state conditions.	X	X	
The transport of benzene is dominated by gaseous and dissolved aqueous phase process.	X		
There is a lack of experimental data on diffusion coefficients, mass transfer coefficients, dry and wet deposition velocities, and biotransfer factors.	X	X	
Resuspension of particle-bound chemicals, which may be a significant exposure pathway, is currently not considered in most exposure models.		X	X
The distribution of chemical between gas and particle-bound phases and the mass *distribution* of a chemical as a function of particle size is critical in determining the relative importance of various transport mechanisms.		X	

TABLE 2 - KEY FINDINGS AND CONCLUSIONS FOR STUDY CHEMICALS[a]

MAJOR FINDINGS	BENZENE	2,3,7,8-TCDD	Cr(VI)
There is a lack of data on chemical mass distribution in particles and particle size distribution from major emission sources.		X	X
Dry and wet deposition are important processes for the removal from the atmosphere.		X	X
Erosion and aquatic transport of sediments appear to be dominant transport mechanisms for sorbed chemicals in aquatic systems.		X	
Degradation Processes			
Specific loss mechanisms (transport or degradation) for different environmental media were often not clearly identified and distinguished for the overall half-life values reported in the literature.	X	X	
The major degradation process for benzene is in the atmosphere by reaction with the OH radical.	X		
Degradation process depends on so many different factors that it may be inappropriate to attempt to characterize the degradation half-life by a single number.	X	X	
Photochemical degradation and OH radical attack are important processes for removal from the atmosphere.		X	
There was a lack of experimental data on atmospheric degradation and photolysis in water.		X	
The likely transformation of Cr(VI) to Cr(III) by redox reactions is an important degradation pathway.			X
Biodegradation is the most significant loss mechanism in soil and aquatic systems.	X		
Exposure Assessment			
Bioavailability of air toxics from various matrices should be considered with regard to its strong dependence on solubility and vapor pressure.	X	X	X
Human exposure to Cr(VI) by ingestion of animals (including fish) is unlikely due to reduction of Cr(VI) within animals.			X
Where exposure to Cr(VI) is considered critical to the outcome of a risk assessment, measurements of redox potential of impacted may be advisable			X

[a] X - Indicates that the key finding applies to the study chemical annotated.

- Complete the evaluation of parameters for all 189 compounds defined as air toxics listed in the Clean Air Act.

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