

Appendix E Determination of Chemicals for Multipathway Analysis

E.1 Introduction

The AB-2588 program assesses the risk from airborne chemicals that are often emitted by facilities at high temperature and pressure in the presence of particulate matter. Some of these chemicals will be emitted and remain in vapor form. The inhalation cancer risk and noncancer hazard from such volatile chemicals are likely to be much greater than the risk from other possible exposure pathways. Other chemicals, such as semi-volatile organic or metal toxicants, can either be emitted as particles, form particles after emission from the facility, or adhere to existing particles. Some chemicals will partition between the vapor and particulate phases. Some chemicals such as PAHs have been found to have a portion of the particle associated mass in reversible equilibrium with the vapor phase and a portion irreversibly bound (Eiceman and Vandiver, 1983). Chemicals in the particulate phase can be removed from the atmosphere by settling, which can be enhanced by coalescence into larger particles with greater mass.

There are a number of exposure pathways by which humans may be exposed to airborne chemicals in addition to inhalation. Particulate associated chemicals can be deposited directly onto soil, onto the leaves of crops, or onto surface waters. Crops may also be contaminated by root uptake of chemicals. Livestock such as chickens, pigs and cows may be contaminated by inhalation of such chemicals or by consumption of contaminated feed, pasture, or surface waters. Humans may be exposed to these chemicals through inhalation, consumption of crops, soil, surface waters, meat, eggs and dairy products. Infants may be exposed through consumption of human breast milk.

E.2 Criteria for Selection of Chemicals for Multipathway Analysis

Chemicals listed in Appendix A, "Substances for Which Emissions Must be Quantified" that have been previously reported to be emitted by facilities in California under the Air Toxics "Hot Spots" Act were considered as candidates for multipathway analysis. From the chemicals meeting this criteria, chemicals which had been considered in the past to be multipathway chemicals or were thought to be likely candidates were selected for further analysis. We evaluated the extent to which chemicals might be particle bound. Two models were used to determine the fraction of airborne chemical that is in the particle phase, the Junge-Pankow adsorption model and the Koa absorption model.

E.2.1 The Junge-Pankow Adsorption Model as a Means of Determining Gas-Particle Partitioning

Junge (1977) developed a theoretical model for the partitioning of the exchangeable fraction of an airborne chemical between the vapor and particulate phases in the ambient air.

$$\theta = \frac{bS^{(p)}}{P_L^{s_L} + bS^{(p)}} \quad (\text{Eq. E-1})$$

Where:

θ = fraction of the total mass of chemical on the particle phase
(unitless)

b = a constant (mm Hg cm³/cm²)

$S^{(p)}$ = total surface area of particle per unit volume of air (cm²/cm³)

$P_L^{s_L}$ = saturation pressure of the liquid chemical at ambient
temperature (mm Hg)

Junge (1977) did not distinguish between solid and liquid phase vapor pressures. Pankow (1987) recognized the importance of using the liquid phase vapor pressure. When the chemical of interest is a solid at the temperature of interest, the subcooled liquid vapor pressure must be used. The subcooled liquid vapor pressure is an extrapolation of the saturated liquid vapor pressure below the melting point where the compound actually exists as solid (Boethling and McKay, 2000). The subcooled liquid vapor pressure can be estimated using the following equation:

$$P_L^{s_L}/P_s^{s_s} = \exp[\Delta S_f (T_m - T)/RT] \quad (\text{Eq. E-2})$$

Where:

$P_L^{s_L}$ = sub cooled liquid vapor pressure of the liquid chemical at
ambient temperature (Pascal).

$P_s^{s_s}$ = saturated vapor of the solid at room temperature

ΔS_f = entropy of fusion (J/mol K)

T_m = melting point temperature (K)

T = ambient temperature (K)

R = gas constant (8.3143 joules/K mole)

Values for ΔS_f may be obtained in the literature. In cases where a literature value is not available a default value of 56.45 has been suggested by Boethling and McKay (2000).

The percentage of the total mass of chemical (vapor plus particulate fraction) is determined by multiplying θ times 100. The percentage of the total mass of

chemical that is in particulate phase is determined in part by the concentration of particles in the air. For our purposes, we used an average concentration of particles in urban air determined by Whitby (1978). The concentration of particles was $1.04 \times 10^{-4} \mu\text{g}/\text{cm}^3$. The surface area per μg of particle was assumed to be $0.05 \text{ cm}^2/\mu\text{g}$. Thus the $S^{(p)}$ is calculated to be $5.2 \times 10^{-6} \text{ cm}^2/\text{cm}^3$. The value of b used is the default value of $0.1292 \text{ mm Hg cm}^3/\text{cm}^2$ recommended by Pankow (1987).

It should be noted that the particle bound associated fraction of some semi-volatile organic toxicants has been found to consist of a non-exchangeable fraction and a fraction which equilibrates with the vapor phase (Bidleman and Foreman, 1987). The equation of Junge (1977) only addresses the exchangeable fraction. This means that the actual fraction of the total mass that is particle bound material may be somewhat higher than the theoretical model which Junge (1977) proposed. The partitioning of semi-volatile organic toxicants between the vapor phase and particles has been experimentally investigated by Bidleman et al. (1986) and Bidleman and Foreman (1987). High volume sampling has been done in several cities in which the particulate and vapor fractions have been collected on filters and adsorbents. This work has supported the validity of the theoretical model of Junge (1977).

The Junge (1977) and Pankow (1987) model appears to be a reasonable model to determine which chemicals emitted by facilities in the AB-2588 program should undergo multipathway analysis. The liquid or subcooled liquid vapor pressure at ambient temperatures determines the fraction of chemical that will be particle associated. The vapor pressure is available for most of the chemicals for which the determination needs to be made.

It should be noted that the Junge (1977) model was designed to look at the partitioning of chemicals between the particle and vapor phases under equilibrium conditions in the atmosphere. The initial conditions under which particle formation may occur as chemicals are emitted into the atmosphere may be different from the conditions assumed by Junge (1977). The chemicals of concern in the AB-2588 program may be emitted at high temperatures and pressures in the presence of a high concentration of particulate matter. Such conditions may favor partitioning of mass toward the particulate fraction. It is also possible that such conditions might favor the formation of a greater fraction of non-exchangeable particle associated chemical which is not taken into account in the Junge (1977) equation. The rapid cooling from high temperature to ambient temperature may also influence the percent of total mass which is particle bound in ways that are not accounted for in the simple equilibrium model of Junge (1977).

E.2.2 The Octanol-Water Partition Coefficient as a Means of Determining Gas-Particle Partitioning

In the past 15 years, there have been advances in the understanding of the partitioning of semi-volatile organic compounds between the gas phase and the organic condensed phase on airborne particles, using the octanol-water partition coefficient as a predictor of gas particle partitioning in the environment. Because the equation for estimating partitioning involves the octanol/air partition coefficient (K_{OA}), this model is referred to as the K_{OA} absorption model, while the Junge-Pankow is known as an adsorption model. Several studies have described the octanol/air partition coefficients for chlorobenzenes, PCBs, DDT, PAHs and polychlorinated naphthalenes (PCNs) (Harner and MacKay, 1995; Komp and McLachlan, 1997; Harner and Bidleman, 1998).

K_{OA} is defined as $K_{OA} = C_o/C_A$, where C_o (mol/L) is the concentration of the compound in 1-octanol and C_A (mol/L) is the gaseous concentration at equilibrium. For the calculation, K_{OA} can be derived as $K_{OA} = K_{OW}/K_{AW} = K_{OW}RT/H$, where K_{OW} is the octanol/water partition coefficient, K_{AW} is the air/water partition coefficient, H is the Henry's Law constant (J/mol), R is the ideal gas constant (J/mol/K), and T is the absolute temperature (degrees K) (Komp and McLachlan, 1997).

The particle/gas partition coefficient (K_P) is defined as $K_P = C_p/C_g$, where C_p is the concentration on particles (ng/ μ g of particles), and C_g is the gas-phase concentration (ng/m³ of air) (Harner and Bidleman, 1998). The relation between K_P and K_{OA} is defined as:

$$\log K_P = \log K_{OA} + \log f_{om} - 11.91 \quad (\text{Eq. E-3})$$

where, f_{om} = organic matter fraction of the particles.

The fraction (ϕ) of compound in the particle phase is

$$\phi = K_P (\text{TSP}) / [1 + K_P (\text{TSP})] \quad (\text{Eq. E-4})$$

where, TSP = total suspended particle concentration.

Using $f_{om} = 20\%$ (Harner and Bidleman, 1998) and the afore-mentioned average concentration of particles in urban air determined by Whitby (1978), TSP = $1.04 \times 10^{-4} \mu\text{g}/\text{cm}^3 = 104 \mu\text{g}/\text{m}^3$, we obtained the percentage of compound on particles ($\phi \times 100$) for selected chemicals through the K_{OA} absorption model, presented as the last column in Table E.1 below. For many chemicals, the values compare well with those obtained with the Junge-Pankow adsorption model.

A number of studies have been published which evaluated gas-particle partitioning in the urban environment under equilibrium conditions where there were existing particles from a variety of sources (e.g. diesel exhaust, road dust). Existing particles are thought to have a lipid bilayer into which gaseous chemicals can equilibrate. There is some question whether chemicals emitted

from a stack would have time to interact with existing urban particles before reaching nearby receptors. Also, in some cases particulate matter in the air around facilities may not be present in very high concentrations.

E.3 Fraction in particle phase to be considered for multipathway analysis

OEHHA has decided that if either the Koa model or the Junge-Pankow model shows a chemical as $\geq 0.5\%$ particle-bound, we will consider it for multipathway assessment. The 0.5% is a relatively small percentage of the total mass. This percentage was chosen in part to compensate for the uncertainties involved in extrapolation of the Junge (1977) model to the conditions under which particles may be formed in the stacks of facilities. Thus chemicals with vapor pressures greater than 1.34×10^{-4} mm Hg at 25° C will not be considered for multipathway analysis. An exception to this rule is the inclusion of hexachlorobenzene (HCB) for multipathway analysis, even though its calculated percentage of total mass in the particulate phase is expected to be below 0.5%. The criteria for including HCB are discussed in Section E.3 below. It should be noted that the chemicals for which noninhalation pathway risks are a significant fraction of the total risk are metals, PAH's, PCB's, polychlorinated dibenzo-p-dioxins and furans. These chemicals have much higher percentages of total mass in the particulate fraction than 0.5%.

There are some toxic compounds without measurable vapor pressure at 25° C such as the metals and their compounds. These metals include lead, mercury compounds, nickel, selenium, fluoride, beryllium, arsenic, chromium VI and cadmium. These toxicants are included on the list of chemicals for multipathway analysis.

In Table E.1 we have calculated the air/particle partition coefficients of the compounds emitted by facilities for which it appeared possible that a significant fraction of the total mass could be in the particulate fraction. In cases where the saturated vapor pressure at a temperature at or near ambient temperature (25° C) is not available; the air/particle coefficient can be calculated using modern tools such as USEPA's SPARC.

For PAHs, consideration for multipathway analysis is largely confined to PAHs with 4 or more fused rings because a significant fraction of their total mass is in the particle phase. Naphthalene contains 2 fused rings and is included in the Hot Spots program as a carcinogen. However, it does not have a significant percentage of its total mass in the particle phase, so is not considered for multipathway analysis. The PAHs with 3 fused rings (e.g., phenanthrene, fluorine, acenaphthene) are also predominantly found in gaseous form and the data are currently too limited or inadequate to list any of them as carcinogens. Laboratory studies of sludge-amended soils containing PAHs have also shown significant loss through volatilization only for PAHs with less than 4 fused rings (Wild and Jones, 1993). Thus, speciated analysis for PAHs that include only the compounds with 4 or more fused rings can be used for multipathway assessment.

Table E1 Calculation of Air/Particle Coefficients and Percent of Particle Associated Total Mass for Selected Chemicals.

Chemical	Vapor Pressure (mm Hg)	Temp. (°C)	Ref. (Vapor Press.)	Air/Particle Partition Coefficient (θ)	% Particle Phase	
					Junge-Pankow model	K _{OA} model
4,4-Methylene dianiline	1.0	197	1	NA	NA	31.5
o-Cresol	0.28*	38.2,	2	2.44x10 ⁻⁶	2.44x10 ⁻⁴	4.65x10 ⁻³
m-Cresol	0.39**	25	2	1.71x10 ⁻⁶	1.71x10 ⁻⁴	6.64x10 ⁻³
p-Cresol	0.37**	25	2	1.81x10 ⁻⁶	1.81x10 ⁻⁴	5.45x10 ⁻³
Cellosolve	5.63***	25	3	1.19x10 ⁻⁷	1.19x10 ⁻⁵	6.38x10 ⁻⁵
Cellosolve acetate	2.12***	25	3	3.17x10 ⁻⁷	3.19x10 ⁻⁵	3.40x10 ⁻⁵
Mercury (elemental)	1.20x10 ^{-3***}	25	4	5.6x10 ⁻⁴	0.056	NA****
Hexachlorocyclohexanes (Lindane)	1.18x10 ^{-4**}	20	5	5.66x10 ⁻³	0.57	6.39x10 ⁻²
Phthalates						
Diethylhexylphthalate	1.97x10 ^{-7***}	25	3	7.73x10 ⁻¹	77.3	98.9
Chlorobenzenes						
Chlorobenzene	12.2***	25	6	5.53x10 ⁻⁸	5.53x10 ⁻⁶	1.09x10 ⁻⁵
p-Dichlorobenzene	0.65***	25	6	1.03x10 ⁻⁶	9.93x10 ⁻⁵	9.96x10 ⁻⁵
m-Dichlorobenzene	2.30***	25	6	1.03x10 ⁻⁶	1.03x10 ⁻⁴	4.24x10 ⁻⁵
o-Dichlorobenzene	0.39***	25	6	1.71x10 ⁻⁶	1.71x10 ⁻⁴	6.53x10 ⁻⁵
1,2,3-Trichlorobenzene	0.39*	40	6	1.71x10 ⁻⁶	1.71x10 ⁻⁴	3.30x10 ⁻⁴
1,2,4-Trichlorobenzene	0.45*	38	6	1.48x10 ⁻⁶	1.48x10 ⁻⁶	2.88x10 ⁻⁴
1,2,3,4-Tetrachlorobenzene	6.58x10 ^{-2*}		6	1.02x10 ⁻⁵	1.02x10 ⁻³	1.39x10 ⁻³
1,2,3,5-Tetrachlorobenzene	0.14*		6	4.82x10 ⁻⁶	4.82x10 ⁻⁴	3.41x 0 ⁻⁴
Pentachlorobenzene	6.67x10 ^{-3*}	25	6	1.01x10 ⁻⁴	1.01x10 ⁻²	7.36x10 ⁻³
Hexachlorobenzene	2.96x10 ^{-4*}	25	6	2.96x10 ⁻⁴	2.96x10 ⁻²	1.53x10 ⁻²

Table E1 Calculation of Air/Particle Coefficients and Percent of Particle Associated Total Mass for Selected Chemicals.

Chemical	Vapor Pressure (mm Hg)	Temp. (°C)	Ref. (Vapor Press.)	Air/Particle Partition Coefficient (θ)	% Particle Phase	
					Junge-Pankow model	K _{OA} model
PAHs						
Naphthalene (2 fused rings)	0.31*	25	7	2.14x10 ⁻⁶	2.14x10 ⁻⁴	3.46x10 ⁻⁴
Acenaphthene (3 fused rings)	3.02x10 ⁻³ *	25	7	2.23x10 ⁻⁵	2.23x10 ⁻³	4.34x10 ⁻³
Acenaphthylene (3 fused rings)	6.67x10 ⁻³	25	7	1.00x10 ⁻⁴	0.01	7.55x10 ⁻³
Anthracene (3 fused rings)	4.2x10 ⁻⁶ *	25	7	1.57x10 ⁻²	1.57	6.78x10 ⁻²
Benzo[a]anthracene (4 fused rings)	4.07x10 ⁻⁶ *	25	7	1.42x10 ⁻¹	14.2	8.15
Chrysene (4 fused rings)	8.81x10 ⁻⁸ **	25	7	8.84x10 ⁻¹	88.4	4.82x10 ⁻⁵
Benzo[a]pyrene (5 fused rings)	9.23x10 ⁻⁸	25	7	8.79x10 ⁻¹	87.9	60.2
Benzo[b]fluoranthene (5 fused rings)	1.59x10 ⁻⁷	25	7	8.09x10 ⁻¹	80.9	NA****
Benzo[k]fluoranthene (5 fused rings)	3.7x10 ⁻⁸ *	25	7	9.48x10 ⁻¹	94.8	79.9
Dibenz[a,h]-anthracene (5 fused rings)	6.07x10 ⁻¹¹ **	25	7	1.00x10 ⁰	100	NA****
Indeno[1,2,3cd]-pyrene (6 fused rings)	1.19 x10 ⁻⁹ **	25	8	9.98x10 ⁻¹	99.8	NA****
Chlorophenols						
Pentachlorophenol	1.73x10 ⁻³ *	25	2	3.88x10 ⁻⁴	3.88x10 ⁻²	76.9
2,4,6-Trichlorophenol	2.8x10 ⁻⁰² *	25	2	2.34x10 ⁻⁵	2.34x10 ⁻³	NA****
2,4,5-Trichlorophenol	4.59x10 ⁻⁰² *	25	2	1.46x10 ⁻⁵	1.46x10 ⁻³	NA****
Nitrosoamines						
N-Nitrosodiethylamine	8.60x10 ⁻¹ ***	20	1	7.81x10 ⁻⁷	7.81x10 ⁻⁵	2.67x10 ⁻⁵
N-Nitroso-dimethylamine	8.1***	20	2	8.29x10 ⁻⁸	8.29x10 ⁻⁶	NA****
N-Nitroso-diphenylamine	4.12x10 ² **	25	2	1.63x10 ⁻⁹	1.63 x10 ⁻⁷	NA****
N-Nitrosodi-n-butylamine	3.0x10 ⁻² ***	20	9	2.24x10 ⁻⁵	2.24x10 ⁻³	NA****
N-Nitrosodi-n-propylamine	4.15x10 ⁻¹ ***	20	2	1.62x10 ⁻⁶	1.62x10 ⁻⁴	2.75x10 ⁻⁴
N-Nitrosopyrrolidine	7.2x10 ⁻⁰² ***	20	9	9.2x10 ⁻⁶	9.2x10 ⁻⁴	NA****

Table E1 Calculation of Air/Particle Coefficients and Percent of Particle Associated Total Mass for Selected Chemicals.

Chemical	Vapor Pressure (mm Hg)	Temp. (°C)	Ref. (Vapor Press.)	Air/Particle Partition Coefficient (θ)	% Particle Phase	
					Junge-Pankow model	K _{OA} model
PCBs						
Aroclor 1016	1.50x10 ^{-3*}	25	6	4.48x10 ⁻⁴	4.48x10 ⁻²	1.63x10 ⁻³
Aroclor 1221	1.50x10 ^{-2*}	25	6	4.48x10 ⁻⁵	4.48x10 ⁻³	6.53x10 ⁻⁴
Aroclor 1232	4.05x10 ^{-3***}	25	6	1.66x10 ⁻⁴	0.17	2.84x10 ⁻³
Aroclor 1242	4.13x10 ^{-4***}	25	6	1.63x10 ⁻⁴	0.16	1.13x10 ⁻²
Aroclor 1248	3.33x10 ^{-4***}	25	6	1.66x10 ⁻³	0.17	5.17x10 ⁻²
Aroclor 1254	7.73x10 ^{-5***}	25	6	8.62x10 ⁻³	0.86	0.142
Aroclor 1260	4.40x10 ^{-6***}	25	6	1.32x10 ⁻¹	13.2	1.23
Dioxins and Furans						
2,3,7,8 Tetrachloro-dibenzo-p-dioxin	4.5x10 ^{-7*}	20	7	5.97x10 ⁻¹	59.7	10.7
2,3,7,8 Tetrachloro-dibenzofuran	9.21x10 ^{-7*}	25	7	9.97x10 ⁻¹	99.7	5.18
1,2,3,4,7 Pentachloro-dibenzodioxin	5.9x10 ^{-7**}	25	7	5.42x10 ⁻¹	54.2	85.7
2,3,4,7,8 Pentachloro-dibenzofuran	1.63x10 ^{-7*}	25	7	4.22x10 ⁻¹	42.2	28.4
1,2,3,4,7,8 Hexachlorodibenzo-p-dioxin	5.89x10 ^{-9*}	25	7	9.17x10 ⁻¹	91.7	78.7
1,2,3,4,7,8 Hexachloro-dibenzofuran	6.07x10 ^{-8*}	25	7	9.89x10 ⁻¹	98.9	30.4
1,2,3,4,6,7,8 Heptachlorodibenzo-p-dioxin	7.68x10 ^{-9*}	25	7	9.76x10 ⁻¹	97.6	83.3
1,2,3,4,6,7,8 Heptachloro-dibenzofuran	1.68x10 ^{-8*}	25	7	9.76x10 ⁻¹	97.6	52.8
1,2,3,4,7,8,9 Heptachloro-dibenzofuran	9.79x10 ^{-9*}	25	7	9.87x10 ⁻¹	98.7	NA****
1,2,3,4,5,6,7,8 Octachloro-dibenzofuran	1.95x10 ^{-9*}	25	7	9.97x10 ⁻¹	99.7	97.1

Table E1 Calculation of Air/Particle Coefficients and Percent of Particle Associated Total Mass for Selected Chemicals.

Chemical	Vapor Pressure (mm Hg)	Temp. (°C)	Ref. (Vapor Press.)	Air/Particle Partition Coefficient (θ)	% Particle Phase	
					Junge-Pankow model	K _{OA} model
1,2,3,4,5,6,7,8 Octachlorodibenzo-p-dioxin	2.08x10 ^{-9*}	25	7	9.97x10 ⁻¹	99.7	93.6

- | | | |
|-------------------------|-------------------------|---------------------------------|
| 1. IARC, 1986; | 5. ATSDR, 2005; | 8. Montgomery and Welkom, 1990; |
| 2. McKay et al. 1992a; | 6. McKay et al., 1992b; | 9. Klein, 1982 |
| 3. McKone et al., 1993; | 7. McKay et al., 1992c; | |
| 4. Cohen et al., 1994; | | |

*Indicates subcooled liquid vapor pressure

**Indicates subcooled liquid vapor pressure estimated according to Boethling and McKay, 2000, page 238.

***Indicates Psat liquid (substance is a liquid at 25 °C)

****Not available because Kow and/or Henry's Law constant not found

For the nitrosamines, we were not able to locate saturated vapor pressures for N-nitrosomethylethylamine, N-nitrosomorpholine, and N-nitrosopiperidine. We were able to find saturated vapor pressures for N-nitrosodiethylamine, N-nitrosodimethylamine, N-nitrosodiphenylamine, N-nitrosodi-n-butylamine, N-nitrosodi-n-propylamine and N-nitrosopyrrolidine. None of these compounds had particle associated percentages above 0.5%. N-nitrosopyrrolidine was structurally similar to N-nitrosomorpholine and N-nitrosopiperidine. N-nitrosopyrrolidine has a particle associated percentage of 9.2×10^{-4} . This is well below the 0.5% that we selected as our cutoff. We therefore felt that N-nitrosomorpholine and N-nitrosopiperidine were unlikely to have a particle bound percentage above 0.5% and thus we excluded these compounds from multipathway consideration. N-nitrosomethylethylamine did not appear likely to have a particle bound percentage above N-nitrosodiethylamine, N-nitrosodimethylamine or N-nitrosodi-n-butylamine. All of these nitrosamines are well below the 0.5% cutoff.

Table E2. Chemicals for Which Multipathway Risks Need to be assessed.

4,4'-methylene dianiline¹

creosotes

diethylhexylphthalate

hexachlorobenzene

hexachlorocyclohexanes

pentachlorophenol

PAHs (including but not limited to the following):²

benz[a]anthracene

benzo[b]fluoranthene

benzo[j]fluoranthene

benzo[k]fluoranthene

benzo[a]pyrene

dibenz[a,h]acridine

dibenz[a,j]acridine

7H-dibenzo[c,g]carbazole

7,12-dimethylbenz[a]anthracene

3-methylcholanthrene

5-methylchrysene

dibenz[a,h]anthracene

dibenzo[a,e]pyrene

dibenzo[a,h]pyrene

dibenzo[a,i]pyrene

dibenzo[a,l]pyrene

chrysene

indeno[1,2,3-cd]pyrene

PCBs³

Polychlorinated dibenzo-p-dioxins {PCDDs} (including but not limited to the following, but excluding dioxins with less than four chlorines):⁴

2,3,7,8 tetrachlorodibenzo-p-dioxin

1,2,3,7,8 pentachloro-p-dioxin

1,2,3,4,7,8 hexachlorodibenzo-p-dioxin

1,2,3,6,7,8 hexachlorodibenzo-p-dioxin

1,2,3,7,8,9 hexachlorodibenzo-p-dioxin

1,2,3,4,6,7,8 heptachlorodibenzo-p-dioxin

1,2,3,4,5,6,7,8 Octachlorodibenzo-p-dioxin

Table E2. Chemicals for Which Multipathway Risks Need to be Assessed (Cont.).

Polychlorinated dibenzofurans {PCDFs} (including but not limited to the following, but excluding dibenzofurans with less than four chlorines:)⁴

- 2,3,7,8 tetrachlorodibenzofuran
- 1,2,3,7,8 pentachlorodibenzofuran
- 2,3,4,7,8 pentachlorodibenzofuran
- 1,2,3,4,7,8 hexachlorodibenzofuran
- 1,2,3,6,7,8 hexachlorodibenzofuran
- 1,2,3,7,8,9 hexachlorodibenzofuran
- 2,3,4,6,7,8 hexachlorodibenzofuran
- 1,2,3,4,6,7,8 heptachlorodibenzofuran
- 1,2,3,4,7,8,9 heptachlorodibenzofuran
- 1,2,3,4,5,6,7,8 Octachlorodibenzofuran

Metals, semi-metals and inorganic compounds

- arsenic and arsenic compounds
- beryllium and beryllium compounds
- cadmium and cadmium compounds
- soluble compounds of chromium VI
- fluoride and soluble fluoride compounds
- lead and inorganic lead compounds
- inorganic mercury compounds
- nickel and nickel compounds
- selenium and selenium compounds

¹ The saturated vapor pressure at 25°C or close to 25°C is not available to our knowledge. The other evidence available, a melting point of 91.5°C and a boiling point of 398-399 °C (Merck, 1989) indicate that it is very likely that a very significant fraction of the chemical emitted into the air would be in the particulate phase. In addition the vapor pressure at 197 °C is only 1 mm (IARC, 1986).

² PAHs with three or more fused rings (Table E2) are to be assessed for multipathway analysis. If PAH mixtures are reported instead of speciated PAHs, then the cancer potency of the entire mixture should be treated the same as benzo(a)pyrene.

³ PCBs is inclusive of all Aroclor mixtures. The information in Table E1 indicates that some of the Aroclor mixtures do not have significant air/particle coefficients. However, it is difficult to determine vapor pressures on mixtures of compounds. OEHHA therefore is proposing to include all of the Aroclors in the list of chemicals for multipathway analysis. The percentage of some individual PCBs in the particulate phase has been measured in air samples (Horstmann and McLachlan, 1998). The particulate phase of tetrachlorinated PCBs (PCB 152) can be expected to be around 1.4%, and increasing to 11.3% for the heptachlorinated PCBs (PCB 180)

⁴ From OEHHA analysis (Table E1), it is clear that all polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans should be included in the multipathway analysis.

Table E3 Specific Pathways to be Analyzed for Multipathway Chemicals

Chemical	Soil Ingestion.	Dermal	Meat, Milk & Egg Ingest	Fish Ingestion	Exposed Veg. Ingest.	Leafy Veg. Ingest.	Protected. Veg. Ingest.	Root Veg. Ingest.	Water Ingest	Breast Milk Ingestion.
4,4'-methylene dianiline	X	X			X	X			X	
Creosotes	X	X	X	X	X	X			X	
Diethylhexylphthalate	X	X	X	X	X	X			X	
Hexachlorocyclohexanes	X	X	X	X	X	X			X	
Hexachlorobenzene	X	X	X	X	X	X			X	
PAHs	X	X	X	X	X	X			X	X
PCBs	X	X	X	X	X	X			X	X
Pentachlorophenol ^a										
Dioxins & furans	X	X	X	X	X	X			X	X
Inorganic arsenic & cmpds	X	X	X	X	X	X	X	X	X	
Beryllium & compounds	X	X	X	X	X	X	X	X	X	
Cadmium & compounds	X	X	X	X	X	X	X	X	X	
Chromium VI & cmpds	X	X	X ^b	X	X	X	X	X	X	
Lead & compounds	X	X	X	X	X	X	X	X	X	X
Inorganic mercury cmpds	X	X	X	X	X	X	X	X	X	
Nickel & compounds	X	X	X	X	X	X	X	X	X	
Fluoride & compounds	X	X	X		X	X	X	X	X	
Selenium and cmpds	X	X	X	X	X	X	X	X	X	

^a To be assessed by pathway

^b Cow's milk only. No multipathway analysis for meat and egg ingestion

OEHHA is recommending that all of the chemicals chosen for multipathway analysis be included in the soil ingestion and dermal pathways. The soil t1/2 values needed to determine concentration in the soil are found in Appendix G. The variates need for the dermal pathway are found in Chapter 6 and Appendix F.

The meat (beef, chicken, pork), cow's milk and egg pathways are listed in one column because the lipid solubility and half-life in the body are common factors which determine if these compounds will be present in these three pathways in appreciable concentrations in the fat of meat, milk and eggs.

E.4 Evidence for Inclusion of Hexachlorobenzene for Multipathway Assessment

In the previous Hot Spots Guidance document, semi-volatile substances with less than 0.5% of their total mass in the particle-associated fraction was not considered for multipathway analysis. Although this is a reasonable cut-off for semi-volatile substances predominantly in the gas phase, an exception is made for hexachlorobenzene (HCB). From Table E1, the Junge model shows HCB with a particle/gas ratio of only 0.0296% at 25 °C. Normally, this would exclude HCB from multipathway analysis. However, actual field measurements of the air/particle partitioning of HCB in Table E.4 shows that the compound is often found in particle form above 0.5%.

The greater than expected particle fraction for HCB is a likely result of environmental conditions at the locations assessed for HCB. The adsorption of HCB on aerosols and subsequent deposition depends on the vapor pressure, the amount and surface area of aerosol particles, and the relevant environmental temperature (Ballschmiter and Wittlinger, 1991). Colder temperatures and greater airborne particulate levels would increase the particle/gas ratio of HCB. In fact, Ballschmiter and Wittlinger (1991) suggested that the particle fraction found at -8 °C (3.5%) in a rural region will be similar to the particle fraction in urban areas with higher particulate levels and an air temperature of 15 °C.

Table E.4. Field study vapor/particle distributions of HCB

Study	Particle fraction Concentration (% particle)	Gas phase Concentration (% gas)
Popp et al., 2000 ^a Leipzig area Roitzsch area Greppin area	0.8 pg/Nm ³ (0.9%) 0.5 pg/Nm ³ (0.3%) 2.6 pg/Nm ³ (0.9%)	83.1 pg/Nm ³ (99.1%) 145.6 pg/Nm ³ (99.7%) 280.6 pg/Nm ³ (99.1%)
Horstmann and McLachlan, (1998) ^b	0.43 pg/m ³ (0.2%)	210 pg/m ³ (99.8%)
Lane et al., 1992 ^c Turkey lake Pt. Petre	3 pg/m ³ (4.1%) 2 pg/m ³ (2.8%)	71 pg/m ³ (95.9%) 69 pg/m ³ (97.2%)
Ballschmiter and Wittlinger, 1991 ^d	4 pg/m ³ (3.5%)	110 pg/m ³ (96.5%)
Bidleman et al., 1987 ^e 20 °C 0 °C	(nd) ^f (0.1%) (nd) (0.7%)	(nd) (99.9%) (nd) (99.3%)

^a Air samples collected near chlorobenzene-contaminated sites of Bitterfeld region in Germany over a two-week period during the summer of 1998.

^b Air samples collected over one year in a forest clearing in Germany from May 1995 to April 1996.

^c Air samples collected during spring, summer, and fall of 1987 in rural regions of Ontario, Canada.

^d Air sample taken at a mean ambient temperature of -8 °C outside a small village near a major road in Germany

^e Data collected from Stockholm, Denver and Columbia. Vapor phase component possibly overestimated due to volatilization (blowoff) from the particle phase in the sampler.

^f No concentration data was provided.

In addition, Foreman and Bidleman (1987) have suggested that field measurements of HCB particle fractions may be greater than in laboratory settings because sources in the environment includes combustion-derived HCB particle incorporation. Similar to dioxins, combustion of organic material that includes chlorinated substances has been suggested as a primary source of HCB.

Nevertheless, the minor particle fraction of the HCB results in Table E.4 may still not be sufficient to support a multipathway analysis. However, when the extreme environmental persistence of this compound relative to other predominantly gaseous semi-volatile substances (i.e., nitrosamines and chlorophenols) is taken into account, it appears that even a fraction of the compound depositing in the particle bound phase could result in measurable levels in sediment and soil with possible accumulation over time. Field studies at Lake Superior, a relatively pristine water body in which organics deposit primarily from atmospheric sources, have found that HCB accumulated in water, sediment and fish tissue samples (Eisenreich et al., 1981). In particular, the strong retention of HCB to sediment

particulates in the water allowed much of the historical burden to become immobilized in bottom sediments, with a concomitant reduction in the levels of HCB found in the surface waters.

More evidence for HCB's persistence in soil was observed in a laboratory study. Aerial application of HCB in a greenhouse with simulated pasture conditions showed that HCB volatilized fairly rapidly from plant and soil surfaces (Beall, 1976). Only 3.4% of HCB remained in the top 2 cm of soil 19 months after spraying. Residues on the grass grown in the soil volatilized considerably faster, with only 1.5% remaining on the plants after two weeks, and <0.01% at 19 months. However, no significant reduction in HCB was found in the deeper 2-4 cm layer of soil after 19 months, showing HCB to be persistent within the soil, including a resistance to microbial degradation and leaching. The immobilization of HCB within the soil is due to its high K_{ow} , leading to strong adsorption to the soil organic fraction.

E.5 Summary

The theoretical model of Junge (1977) uses the liquid or subcooled liquid vapor pressure to determine the percentage of the total airborne mass of chemical that is particulate. The Koa model uses the octanol-water coefficient as a predictor of gas particle partitioning in the environment. Chemicals with 0.5% of the total mass or more in the particulate fraction at 25°C by either model are considered for multipathway analysis by OEHHA. A list of multipathway chemicals for the AB-2588 program is provided in Table E2. The percentage of the total mass in the particulate phase and the air/particle partition coefficients for these chemicals and a few other selected chemicals are presented in Table E1.

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