Appendix E

Determination of Chemicals for Multipathway Analysis

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. The settling of smaller particles 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. 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” which 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 chose chemicals on the basis of whether they might be particle bound.

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.

$$\theta = \frac{bS^{(p)}}{P^s_L + bS^{(p)}}$$

Where:

θ = fraction of the total mass of chemical on the particle phase (unitless)
b = a constant (mm Hg cm^3/cm^2)
$S^{(p)}$ = total surface area of particle per unit volume of air (cm^2/cm^3)
P^s_L = saturation pressure of the liquid chemical at ambient temperature (mm Hg)

Junge (1977) did not distinquish 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:

$$P^s_L/P^s_s = \exp[\Delta S_f (T_m-T)/RT]/RT$$

Where:

P^s_L = sub cooled liquid vapor pressure of the liquid chemical at ambient temperature (Pascal).
P^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 fractions) 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 1.04×10^{-4} $\mu g/cm^3$. The surface area per μg of particle was assumed to be 0.05 $cm^2/\mu g$. Thus the $S^{(p)}$ is calculated to be 5.2×10^{-6} cm^2/cm^3. The value of b used is the default value of 0.1292 mm Hg cm^3/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 the best available to develop criteria 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). OEHHA has decided that chemicals with less than 0.5% of the total mass in the particle-associated fraction will not be considered for multipathway analysis. 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. 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 (with the exception of elemental mercury).

These metals include lead, mercury compounds, selenium, manganese, zinc, lead, 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 some cases the saturated vapor pressure at a temperature at or near ambient temperature (25°C) the air/particle coefficient could not be calculated. For PAHs it appears that naphthalene (2 fused rings) did not have a significant percentage of the total mass in the particle phase. However, anthracene (3 fused rings) did have a significant fraction of total mass (1.57 %) in the particulate fraction. We therefore concluded that for the PAHs we would include all compounds (including those for which we did not locate vapor pressures) with three or more fused rings for multipathway analysis.

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 (q)	% Particulate (of total mass)
4,4'methylene dianiline	1.0	197	1	NA	NA
o-cresol	0.28*	38.2,	2	$2.44X10^{-6}$	2.44×10^{-4}
m-cresol	0.39**	25	2	$1.71x10^{-6}$	$1.71x10^{-4}$
p-cresol	0.37**	25	2	$1.81x10^{-6}$	$1.81x10^{-4}$
Cellosolve	5.63***	25	3	$1.19x10^{-7}$	$1.19x10^{-5}$
Cellosolve acetate	2.12***	25	3	$3.17x10^{-7}$	3.19E-05
Mercury	$1.20x10^{-3}$***	25	4	$5.6x10^{-4}$	0.056
Hexachlorocyclohexanes (Lindane)	$1.18 x10^{-4}$**	20	5	$5.66x10^{-3}$	0.57
Phthalates					
Diethylhexylphthalate	$1.97 X10^{-7}$***	25	3	$7.73x10^{-1}$	77.3
Chlorobenzenes					
Chlorobenzene	12.2***	25	6	$5.53x10^{-8}$	$5.53x 10^{-06}$
p-Dichlorobenzene	0.65***	25	6	$1.03x10^{-6}$	$9.93x10^{-05}$
m-Dichlorobenzene	2.30***	25	6	$1.03x10^{-6}$	$1.03x10^{-4}$
o-Dichlorobenzene	0.39***	25	6	$1.71x10^{-6}$	$1.71x10^{-4}$
1,2,3-Trichlorobenzene	0.39*	40	6	$1.71x10^{-6}$	$1.71x10^{-4}$
1,2,4-Trichlorobenzene	0.45*	38	6	$1.48x10^{-6}$	$1.48 x10^{-6}$
1,2,3,4-Tetrachlorobenzene	$6.58 x 10^{-2}$*		6	$1.02x10^{-5}$	$1.02x10^{-3}$
1,2,3,5-Tetrachlorobenzene	0.14*		6	$4.82x10^{-6}$	$4.82x10^{-4}$
Pentachlorobenzene	$6.67 x 10^{-3}$*	25	6	$1.01x10^{-4}$	$1.01x10^{-2}$
Hexachlorobenzene	$2.96 x 10^{-4}$*	25	6	$2.96x10^{-4}$	$2.96x10^{-2}$

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

Chemical	Vapor Pressure (mm Hg)	Temp. (°C)	Ref. (Vapor Press.)	Air/Particle Partition Coefficient (q)	% Particulate (of total mass)
PAHs					
Benzo{a}Pyrene	9.23×10^{-8}*	25	7	8.79×10^{-1}	87.9
Benzo[a]anthracene	4.07×10^{-6}*	25	7	1.42×10^{-1}	14.2
Benzo[b]fluoranthene	1.59×10^{-07}	25	7	8.09×10^{-1}	80.9
Benzo[k]fluoranthene	3.7×10^{-8}*	25	7	9.48×10^{-1}	94.8
Dibenz[a,h]anthracene	6.07×10^{-11}**	25	7	1.00×10^{0}	100
Indeno[1,2,3-cd]pyrene	1.19×10^{-9}**	25	8	9.98×10^{-1}	99.8
Naphthalene	0.31*	25	7	2.14×10^{-6}	2.14×10^{-4}
Acenaphthene	3.02×10^{-03}*	25	7	2.23×10^{-5}	2.23×10^{-3}
Acenaphthylene	6.67×10^{-03}	25	7	1.00×10^{-4}	0.01
Anthracene	4.2×10^{-06}*	25	7	1.57×10^{-2}	1.57
Chrysene	8.81×10^{-8}**	25	7	8.84×10^{-1}	88.4
Chlorophenols					
Pentachlorophenol	1.73×10^{-3}*	25	2	3.88×10^{-4}	3.88×10^{-2}
2,4,6-Trichlorophenol	2.8×10^{-02}*	25	2	2.34×10^{-5}	2.34×10^{-3}
2,4,5-Trichlorophenol	4.59×10^{-02}*	25	2	1.46×10^{-5}	1.46×10^{-3}
Nitrosoamines					
N-Nitrosodiethylamine	8.60×10^{-1}***	20	1	7.81×10^{-7}	7.81×10^{-5}
N-Nitrosodimethylamine	8.1***	20	2	8.29×10^{-8}	8.29×10^{-6}
N-Nitrosodiphenylamine	4.12×10^{2}**	25	2	1.63×10^{-9}	1.63×10^{-7}
N-Nitrosodi-n-butylamine	3.00×10^{-2}***	20	9	2.24×10^{-5}	2.24×10^{-3}
N-Nitrosodi-n-propylamine	4.15×10^{-1}***	20	2	1.62×10^{-6}	1.62×10^{-4}
N-Nintrosopyrrolidine	7.20×10^{-02}***	20	9	9.2×10^{-6}	9.2×10^{-4}

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

Chemical	Vapor Pressure (mm Hg)	Temp. (°C)	Ref. (Vapor Press.)	Air/Particle Partition Coefficient (q)	% Particulate (of total mass)
PCBs					
Aroclor 1016	$1.50x10^{-3}$*	25	6	$4.48x10^{-4}$	$4.48x10^{-2}$
Aroclor 1221	$1.50x10^{-2}$*	25	6	$4.48x10^{-5}$	$4.48x10^{-03}$
Aroclor 1232	$4.05x10^{-03}$***	25	6	$1.66x10^{-4}$	0.17
Aroclor 1242	$4.13x10^{-04}$***	25	6	$1.63x10^{-4}$	0.16
Aroclor 1248	$3.33x10^{-04}$***	25	6	$1.66x10^{-3}$	0.17
Aroclor 1254	$7.73x10^{-05}$***	25	6	$8.62x10^{-3}$	0.86
Aroclor 1260	$4.40x10^{-06}$***	25	6	$1.32\ x10^{-1}$	13.2
Dioxins and Furans					
2,3,7,8 Tetrachlorodibenzo-p-dioxin	$4.5x10^{-7}$*	20	7	$5.97x10^{-1}$	59.7
2,3,7,8 Tetrachlorodibenzofuran	$9.21x10^{-7}$*	25	7	$9.97x10^{-1}$	99.7
1,2,3,4,7 Pentachlorodibenzodioxin	$5.9x10^{-7}$**	25	7	$5.42x10^{-1}$	54.2
2,3,4,7,8 Pentachlorodibenzofuran	$1.63x10^{-7}$*	25	7	$4.22x10^{-1}$	42.2
1,2,3,4,7,8 Hexachlorodibenzo-p-dioxin	$5.89x10^{-9}$*	25	7	$9.17x10^{-1}$	91.7
1,2,3,4,7,8 Hexachlorodibenzofuran	$6.07x10^{-8}$*	25	7	$9.89x10^{-1}$	98.9
1,2,3,4,6,7,8 Heptachlorodibenzo-p-dioxin	$7.68x10^{-9}$*	25	7	$9.76x10^{-1}$	97.6
1,2,3,4,6,7,8 Heptachlorodibenzofuran	$1.68x10^{-8}$*	25	7	$9.76x10^{-1}$	97.6
1,2,3,4,7,8,9 Heptachlorodibenzofuran	$9.79x10^{-9}$*	25	7	$9.87x10^{-1}$	98.7
1,2,3,4,5,6,7,8 Octachlorodibenzofuran	$1.95x10^{-9}$*	25	7	$9.97x10^{-1}$	99.7
1,2,3,4,5,6,7,8 Octachlorodibenzo-p-dioxin	$2.08x10^{-9}$*	25	7	$9.97x10^{-1}$	99.7

*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)

1. IARC (1986) Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. World Health Organization, International Agency for Research on Cancer: Geneva. 1972 - present. (multivolume work) 39:348. (as cited by the Intermedia Transport Predictor software developed for the California Air Resources Board by Yorem Cohen, Arthur Winer and Robert Van de Water, UCLA.)
2. Donald Mckay, Wan-Ying Shiu and Kuo-Ching Ma Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Volume IV Oxygen, Nitrogen, and Sulfur Containing Compounds. CRC Lewis: Boca Raton, 1992.
3. McKone TE, Daniels JI, Chiao FF, Hsieh DPH (1993) Intermedia Transfer Factors for Fifteen Toxic Pollutants Released in Air Basins in California. California Air Resources Board, Report No. UCRL-CR-115620. (as cited by the Intermedia Transport Predictor software developed for the California Air Resources Board by Yorem Cohen, Arthur Winer and Robert Van de Water, UCLA.)
4. Cohen, Y., Winer A.M., Creelman, L., Stein, E., Kwan, A., Chu, J., Development of Intermedia Transfer Factors for Toxic Air Pollutants, California Air Resources Board Contract No. A032-170, vol I-VII, 1994.
5. Toxicological Profile for Hexachlorocylcohexanes. US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR): Atlanta, GA. (as cited by the Intermedia Transport Predictor software developed for the California Air Resources Board by Yorem Cohen, Arthur Winer and Robert Van de Water, UCLA.)
6. Donald Mckay, Wan-Ying Shiu and Kuo-Ching Ma Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Monoaromatic Hydrocarbons, Chlorobenzenes and PCBs Vol. 1. Lewis Publishers: Chelsea, MI., 1992
7. Donald Mckay, Wan-Ying Shiu and Kuo-Ching Ma Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins and Dibenzofurans, Vol. 3. Lewis Publishers: Chelsea, MI.,1992
8. Montgomery JH, Welkom LM (1990) Groundwater Chemicals Desk Reference. Lewis Publishers: Chelsea, MI. (as cited by the Intermedia Transport Predictor software developed for the California Air Resources Board by Yorem Cohen, Arthur Winer and Robert Van de Water, UCLA.)
9. Klein RG (1982) Toxicol. 23:135-48. (as cited by the Hazardous Substances Data Bank, National Library of Medicine, October, 1996)

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-nitrosdimethylamine, 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 dianiline [1]
creosotes
diethylhexylphthalate
hexachlorocyclohexanes
PAHs (including but not limited to the following:)[2]

- anthracene
- benzo[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
- indo[1,2,3-cd]pyrene

[If mixtures are not reported as specific PAHs, then they should be treated as benzo(a)pyrene]

The following PAHs were excluded for multipathway analysis based on physico-chemical properties:

- naphthalene
- acenaphthene
- acenaphthylene

PCBs [3]

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

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

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

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

beryllium and compounds
cadmium and compounds
chromium VI and compounds
inorganic arsenic and compounds
lead and compounds
nickel and compounds
mercury and compounds[5]

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[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] From OEHHA analysis (Table E1), it is clear that PAHs with three rings or greater should be included in multipathway analysis. OEHHA therefore has included some compounds on this list for which air/particle coefficients were not calculated in Table E1.

[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. We are currently investigating the possibility of identifying the particulate phase PCBs based on the degree of chlorination.

[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.

[5] Elemental mercury is treated as a multipathway chemical despite the fact the vapor pressure indicates it would not be a multipathway chemical because atmospheric transformations may take place which would decrease the vapor pressure to the point where deposition onto particles may occur.

Table E3 Specific Pathways to be Analyzed for Multipathway Chemicals

Chemical	Soil Ingest.	Dermal	Meat, Milk & Egg Ingest	Fish Ingest	Expos Veg. Ingest.	Leafy Veg. Ingest.	Prot. Veg Ingest.	Root Veg. Ingest.	Water Ingest	Breast Milk Ingest.
4,4'-methylene dianiline	X	X		X	X	X			X	
Creosotes	X	X		X	X	X			X	
Diethylhexylphthalate	X	X		X	X	X			X	
Hexachlorocyclohexanes	X	X		X	X	X			X	
PAHs	X	X	X	X	X	X			X	
PCBs	X	X	X	X	X	X			X	X
Cadmium & compounds	X	X	X	X	X	X	X	X	X	
Chromium VI & compounds	X	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	
Lead & compounds	X	X	X	X	X	X	X	X	X	
Mercury & compounds	X	X	X	X	X	X	X	X	X	
Nickel	X	X	X		X	X	X	X	X	
Dioxins & furans	X	X	X	X	X	X			X	X

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.3 Breast Milk Pathway

An algorithm has been developed for quantifying exposure to semivolatile organic chemicals in breast milk as explained in Chapter 5. The breast milk pathway is assessed for the first one year of life, which is a much shorter exposure duration than other pathways. A contaminant must be present in breast milk in relatively high concentrations for the breast milk pathway dose to be a large fraction of the dose from other pathways.

A key determinant of the concentration in breast milk is the $t_{1/2}$ of the chemical in the mother's body. Chemicals with a short maternal $t_{1/2}$ are unlikely to reach a high enough concentration to deliver a high enough dose in breast milk to be a very large fraction of the dose delivered by other pathways such as inhalation. There are a number of factors that will determine maternal $t_{1/2}$. Lipophilic, poorly metabolized, non-volatile chemicals such as dioxin will tend to have long maternal half lives. Such chemicals tend to be sequestered in body fat, very slowly eliminated by metabolism and cannot be eliminated through the lung.

The risk from metals from the breast milk pathway is not currently considered in the "Hot Spots" program because an algorithm for determining concentration in breast milk is not currently available. It is likely that each metal would need to be separately addressed. OEHHA is currently considering approaches to this problem.

OEHHA proposes that organic chemicals be considered for inclusion in the breast milk pathway only if they are lipophilic enough to be reasonably described by a default partition coefficient into body fat of 0.9. The $t_{1/2}$ of chemicals in the mother's body appears to largely determine the ratio of the dose of chemical delivered via the breast milk pathway to the dose delivered by the inhalation route. If the breast milk pathway delivers a dose which is likely to be less than 1% of the inhalation dose then the chemical will be excluded from consideration. The equations for determining the average daily dose delivered by the breast milk pathway and the equation for determining the breast milk contaminant concentration can be arranged to determine the $t_{1/2}$ of the chemical which would give an average daily breast milk dose (mg/kg/day) which is 1 percent or greater of the total average daily dose (mg/kg/day) which would be delivered to a 70 kg person. For the sake of simplicity, we considered the dose to be that which would be delivered by the inhalation route only with an air concentration of 1 $\mu g/m^3$.

$$Emi = \frac{1\ \mu g/m^3 * 20\ m^3 * 0.001}{70\ kg}$$

$$Cm = \frac{DoseIm * 25{,}500*(ABW)}{DermE * F * Yr}$$

$$Cm = 1.53 \text{ X } 10^{-3} \text{ (mg/kg milk)}$$

$$t_{1/2} = \frac{f_2 * 0.693 * Cm}{Emi * f_1 * f_3}$$

$$t_{1/2} = 32.1 \text{ days}$$

Where: Emi = average daily maternal intake of contaminant from all routes
70 = default value for maternal weight
20 m^3 = default maternal breathing rate
0.001 = conversion factor μg to mg

Cm = Concentration of contaminant in mother's milk (mg/kg milk)
DoseIm = Average daily dose through ingestion of mother's milk (3.08×10^{-4} mg/kg*day)
25,550 = lifetime, 70 years (days)
ABW = average infant body weight (6.5 kg)
DermE = daily breast milk ingestion rate (0.9 kg/day)
F = frequency of exposure (365 days)
Yr = breast feeding period (1 year)
$t_{1/2}$ = half life of contaminant in the mother (days)
f_2 = fraction of the mother's weight that is fat (0.33)
f_1 = fraction of contaminant that partitions to mother's milk (0.9)
f_3 = fraction of fat of mother's milk (0.04)

This calculation reveals that with the current model organic chemicals with a $t_{1/2}$ less than 32 days will have average daily dose from the breast milk pathway less than 1% of the average daily dose from all other routes of exposure. Table E4 has the list of chemicals that should be considered in the breast milk pathway according to this criteria. $T_{1/2}$ values are not available for all chemicals. Professional judgment was used to exclude some chemicals not likely to have a $t_{1/2}$ of 32 days or greater.

PAHs were previously considered in the breast milk pathway (CAPCOA, 1993). PAHs represent a class of compounds for which information on the body $t_{1/2}$ does not appear to be available for humans. OEHHA has found some literature on benzo[a]pyrene and 3-methylcholanthrene Benzo[a]pyrene is lipophillic but extensive metabolism and excretion take place in rats (Hecht et al. 1979). Approximately 75% of an orally administered dose was excreted in 48 hours. In the same study 8.6 μg benzo[a] pyrene consumed by humans was not detected as the parent compound in the feces. This may indicate that the benzo[a]pyrene was metabolized and therefore not detected. The benzo[a]pyrene orally administered to the human volunteers was not radiolabelled. In guinea pigs about one third of an intravenously administered dose was excreted within 4 hours (Bowes and Renwick, 1986). The transfer of an orally administered dose of 3-methylcholanthrene and benzo[a]pyrene to breast milk in rats was 0.19% in rats (West and Horton, 1976). In rabbits 0.0003% of an oral dose of benzo[a]pyrene and 3-methylcholanthrene was transferred to breast milk (Clive and Horton, 1976). In the same study in sheep 0.01% of an oral dose of benzo[a]pyrene and 3-methylcholanthrene transferred was transferred to breast milk. These studies indicate that the breast milk pathway in humans is likely to contribute a small fraction of the total dose received from all pathways for a 9, 30 or 70 exposure to airborne benzo[a]pyrene. OEHHA is recommending that PAHs not be evaluated by the breast milk pathway.

Table E-4 Chemicals for Which The Breast Milk Pathway Should be Considered

Chemical	Human Body $T_{1/2}$ (Days)	Reference
Dioxins and furans	2,117	1
PCBs	1,460	2

1. Poiger, H and Schlatter, C. Pharmacokinetics of 2,3,7,8-TCCD in man. Chemosphere 15: 1489-94, 1986.

2. Davies, D. and Mes. J. Comparison of the residue levels of some organochlorine compounds in breast milk of the general and indigenous Canadian population. Bull. Environ. Conta. Toxicol. 39: 743-749, 1987.

E.4 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. Chemicals with 0.5% of the total mass or more in the particulate fraction at 25° C are considered by OEHHA to be multipathway chemicals. This corresponds to toxicants with a vapor pressure of 1.34×10^{-6} mm Hg. 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.

E.5 References

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