Risk Prioritization for a Subset of Domestic Substances List Chemicals Using the RAIDAR Model

Report to Environment Canada

CEMC Report No. 200703

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FINAL REPORT

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1. Introduction

There are approximately 23,000 chemicals on Canada's Domestic Substances List (DSL). In September 2006 the Ministries of Health and the Environment completed the persistence, bioaccumulation and toxicity (PBT) categorization of the DSL as legislated by the Canadian Environmental Protection Act, 1999 (CEPA 1999) [1]. The categorization is a prioritization process and involves the systematic identification of substances on the DSL that should be subject to screening assessments [2]. A large number of substances are subject to further evaluation based on the outcome of the categorization [3]. The screening assessments of substances meeting the categorization criteria are to be undertaken in a timely fashion according to priorities. In order to efficiently accomplish this task, Environment Canada needs to appropriately prioritize the substances for risk assessment based on available information.

The Risk Assessment IDentification And Ranking (RAIDAR) model is a peer-reviewed method developed to assess chemicals for risk at a screening level by estimating the environmental fate, transport, bioaccumulation and exposure to ecological receptors [4]. Selecting a consistent toxicological endpoint C_E and a unit emission rate E_U, the most sensitive risk endpoint is identified and a critical emission rate E_C is then "back-calculated" as a result of that endpoint being reached. E_C can then be compared with the estimated actual emission rate E_A to provide a RAIDAR Risk Assessment Factor (RAF), i.e., RAF = E_A / E_C. The model can be applied to a large number of chemicals in an efficient manner using available physical-chemical property, environmental half-life and toxicity information. The essential role of the model is to synthesize information within a consistent mass balance framework to yield an overall estimate of E_C with respect to the defined endpoint. Thus, substances identified as having the greatest potential concern may be prioritized for more comprehensive assessment. The model output can also be used to indicate substances that are unlikely to be of concern owing to low quantities released to the environment.

This report documents an overview of the RAIDAR model, including recent revisions, and the application of RAIDAR to selected chemicals from the DSL. Environment Canada provided a list of 2,074 DSL chemicals including discrete organics, organometallics, organic-metal salts, inorganics, Unknown or Variable composition, Complex reaction products, or Biological materials (UVCBs), and polymers. Physical chemical property information required by RAIDAR is provided by Environment Canada for 1,387 substances (there are no physical chemical property data available for the remaining 687 substances).

Appendix 1 of this report provides guidance for the types of substances that can be modelled using RAIDAR and the required input data. The model is best suited for discrete organic chemicals that have reliable solubility properties in air, water and organic matter. For example, RAIDAR is not applicable for totally involatile chemicals. Currently, RAIDAR is also not applicable for organometallics, organic-metal salts, inorganics, most UVCBs and polymers.

Appendix 2 of this report provides an overview for the assessment of required input data for reliability. The model results are, of course, only as reliable as the input data, most of which are estimated from quantitative structure-activity relationships (QSARs). The quality assessment methods are applied to the chemicals selected for RAIDAR modelling in this report.

Appendix 3 of this report includes two sections related to the implications of changing the regional scale of the RAIDAR evaluative environment. The first is a largely theoretical analysis and discussion and the second is an illustrative example using a selected DSL chemical.

Appendix 4 is an Excel spreadsheet and provides a summary of selected input data and summary RAIDAR output results. Based on a review of the chemical classes and the input data provided, 1,105 substances are modelled in the evaluative RAIDAR environment. RAIDAR output results include RAFs, E_C, Risk Identification Bins (RIBs), and the most sensitive ecological receptor. Relative risk rankings, i.e., RAF rankings, are based on preliminary DSL quantity information provided by Environment Canada as a surrogate for E_A. The summary model results are provided from 10 different RAIDAR simulations. Five different simulations for fate and transport are calculated, i.e., four mode of entry (MOE) Level III scenarios, and Level II. For each of these five calculations there are two different approaches for addressing the uncertainty of chemical biotransformation in food webs. The first approach assumes no metabolic biotransformation and the second includes estimated rates of metabolic biotransformation in fish, birds and mammals.

The output summary data are discussed in the report. Recommendations are also made for improvements to the required input data and to the model in order that RAIDAR may provide more accurate simulations of fate, exposure and effects, for the prioritization of potential chemical risks to the environment.

2. Overview of the RAIDAR Model

2.1 Chemical concentration and fugacity

RAIDAR is based on the fugacity concept, a brief introduction to which follows.

Chemical concentrations C (mol/m^3) are expressed as the product Zf where f (Pa) is the fugacity and Z ($mol/m^3\cdot Pa$) is the fugacity capacity. The fugacity capacity of a phase depends on the chemical and the nature and temperature of the medium or compartment. Z values quantify the ability of a phase to retain a chemical. The fugacity can be regarded as a partial pressure or the "escaping tendency" of a particular chemical in a particular phase. Chemical uptake and loss processes are defined by a D value (mol/Pa·h), which is essentially a contaminant transport or transformation rate parameter. The rate of chemical transport or flux N (mol/h) is the product Df. It follows that larger D values refer to faster contaminant transport processes. These D values are analogous to rate constants. Full details of the fugacity concept are explained elsewhere [5].

Table 1 provides definitions and calculations for Z values. The model includes the evaluation of hydrophobic chemicals as well as more water-soluble chemicals and ionizing compounds and a three compartment partitioning model is included for biota. In addition to the lipid and water fractions, non-lipid organic matter (NLOM), such as proteins in animals [6, 7] and carbohydrates and cellulose in plants [8], also play a role in partitioning. Thus, the total storage capacity, i.e., Z, for plants and animals in the model is a reflection of the relative contributions of each component as:

$$Z_B = \nu_L Z_L + \nu_{NLOM} Z_{NLOM} + \nu_W Z_W \quad (1)$$

where $Z_{B,}$ $Z_{L,}$ $Z_{NLOM,}$ Z_W are the fugacity capacities of the biota, lipid, NLOM and water, respectively and $\nu_{L,}$ $\nu_{NLOM,}$ ν_W are the volume fractions of the component parts. For foliage and root vegetation Z_{NLOM} is replaced by Z_{NLOC} representing non-lipid organic carbon.

Table 1. Summary of Z values (mol/m^3·Pa) and relevant parameters in the model.

Media	**Z value**	**Parameters and Units**
Air	$Z_A = 1/RT$	R = Ideal Gas Law constant (8.314 Pa·m^3/mol·K) T = temperature (298.15 K)
Aerosol	$Z_Q = Z_A \cdot 0.1 \cdot K_{OA} + Z_A \cdot 0.4 / K_{AW}$	K_{AW} = air-water partition coefficient (dimensionless) = H / RT H = Henry's Law constant (Pa·m^3/mol) K_{OA} = octanol-air partition coefficient (dimensionless) = K_{OW} / K_{AW} K_{OW} = octanol-water partition coefficient (dimensionless) 0.1 = proportionality constant for aerosol organic matter 0.4 = proportionality constant for aerosol aqueous matter
Water	$Z_W = 1/H$ or C^S/P^S	C^S = aqueous solubility (mol/m^3) P^S = vapour pressure (Pa)
Solids	$Z_S = (Z_W \cdot 0.35 \cdot K_{OW} \cdot \nu_{OC} \cdot \rho_S)/\rho_W$	ν_{OC} = volume fraction of organic carbon ρ_S = density of solid (2400 kg/m^3) ρ_W = density of water (1000 kg/m^3)
Lipid	$Z_L = (Z_W \cdot K_{OW} \cdot \rho_W)/\rho_L$	ρ_L = density of lipid (900 kg/m^3)
Nonlipid organic matter	$Z_{NLOM} = 0.035 \cdot Z_W \cdot K_{OW}$	0.035 = proportionality constant for nonlipid organic matter
Nonlipid organic carbon	$Z_{NLOC} = 0.35 \cdot Z_W \cdot K_{OW}$	0.35 = proportionality constant for nonlipid organic carbon
Biota or Diet	Z_B or $Z_D = Z_L \nu_L + Z_{NLOM} \nu_{NLOM} + Z_W \nu_W$	ν_L, ν_{NLOM}, ν_W = volume fraction of lipid, nonlipid organic matter, and water respectively

2.2 Evaluative environment

Figure 1 provides a conceptual overview of the RAIDAR evaluative environment not including humans. The standard area of the regional model is 10^5 km^2. Table 2 lists the "abiotic" and "biotic" components. The model combines fate and transport calculations ("abiotic" processes) followed by food web bioaccumulation calculations ("biotic" processes) and effects concentrations. A description of these models and how they are parameterized follows.

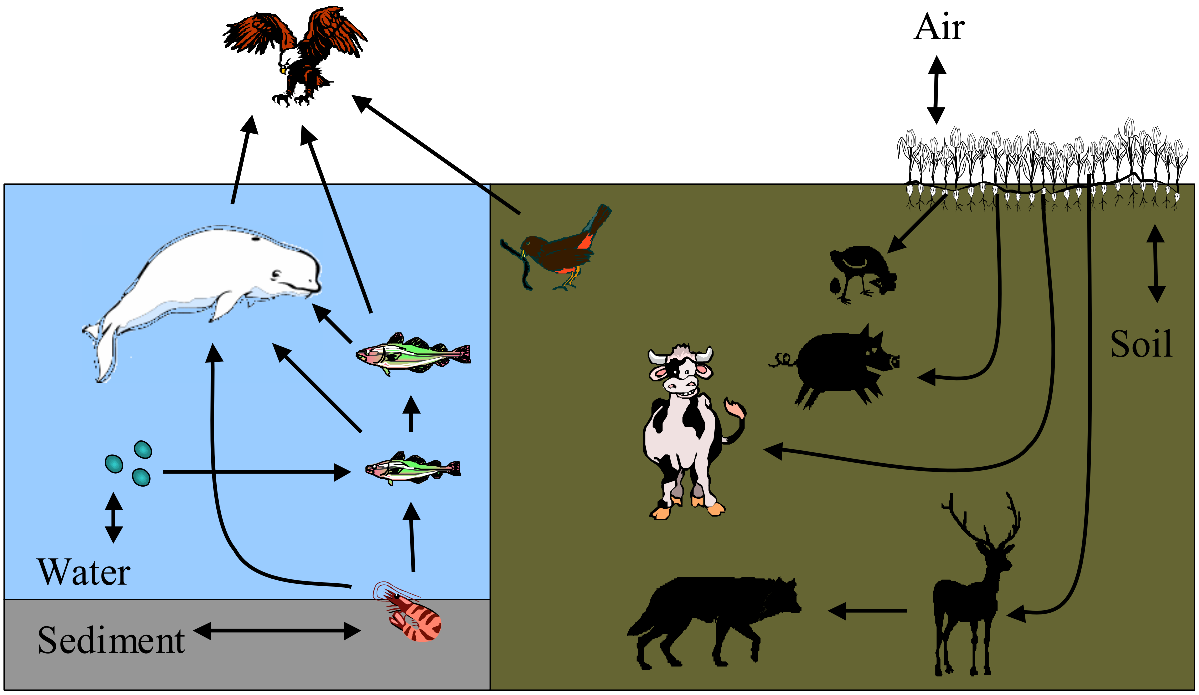

Figure 1. Conceptual overview of RAIDAR (from [4]) modified to not include humans.

Table 2. Abiotic and representative biotic media included in the RAIDAR environment.

“Abiotic” Media	**Vegetation**
Air - bulk	Foliage vegetation (e.g., fruit, grass, nuts)
Water - bulk	Root vegetation (e.g., vegetables, roots)
Soil - bulk	
Sediment - bulk	**Terrestrial Organisms**
	Terrestrial invertebrate (e.g., worm)
Aquatic Organisms	Terrestrial herbivore (e.g., deer)
Plankton (various)	Terrestrial carnivore (e.g., wolf)
Benthic invertebrate (e.g., bivalve)	Avian omnivore – small (e.g., robin)
‘Pelagic-benthic’ fish (e.g., smelt)	Avian omnivore – scavenger (e.g., eagle)
‘Piscivorous’ fish (e.g., salmonid)	Agricultural – swine (e.g., pork)
Aquatic mammal (e.g., beluga whale)	Agricultural – cattle (e.g., beef, dairy)
	Agricultural – poultry (e.g., broiler, hen)

2.3 Fate and transport model

Table 3 summarizes key parameters of the abiotic compartments. Fate and transport of chemical in the abiotic environment are determined by either steady-state Level II or Level III fugacity calculations described in detail elsewhere [5, 9] except as described below. These calculations in “abiotic” media yield an estimated distribution of chemical in air, water, soil and sediment including masses, concentrations and fugacities. These media are essentially parameterized using the well-established EQuilibrium Criterion (EQC) model [9] that also addresses an area of 10^5 km^2 and includes typical compartment properties, residence times and transport parameters. RAIDAR includes chemical degradation at rates defined by the input half-lives in each bulk compartment. Thus, chemical is removed from the environment by degradation and advection processes.

Table 3. RAIDAR abiotic compartments and compositions.

Media	Area, m^2	Depth, m	Volume Fraction	Volume, m^3	Density, kg/m^3
Air (Bulk)	10^{11}	1000		10^{14}	1.19
Air phase			1	10^{14}	1.19
Aerosol phase			2×10^{-11}	2000	2400
Water (Bulk)	10^{10}	20		2×10^{11}	1000
Water phase			1	2×10^{11}	1000
Suspended particle phase			5×10^{-6}	10^{6}	1500
Biota phase			10^{-6}	2×10^{5}	1000
Soil (Bulk)	9×10^{10}	0.2		1.8×10^{10}	1500
Air phase			0.2	3.6×10^{9}	1.19
Water phase			0.3	5.4×10^{9}	1000
Solid phase			0.5	9×10^{9}	2400
Sediment (Bulk)	10^{10}	0.05		5×10^{8}	1280
Water phase			0.8	4×10^{8}	1000
Solid phase			0.2	1×10^{8}	2400

There are some differences in RAIDAR from Level III calculations found in the EQC model as summarized here but given in greater detail elsewhere by Arnot et al. [4]. Notably the process D-value for rain dissolution (D_{Rain}) is calculated based on the relationship between the dimensionless air-water partition coefficient (K_{AW}) and the scavenging efficiency of rain (S_{Rain}) as:

$$D_{Rain} = A \times MTC_{Rain} \times Z_W \quad \text{for } K_{AW} \geq 1 / S_{Rain} \tag{2}$$

$$D_{Rain} = A \times MTC_{Rain} \times S_{Rain} \times Z_A \quad \text{for } K_{AW} < 1/S_{Rain} \tag{3}$$

Where A is the surface area of either water or soil and MTC_{Rain} is the mass transfer coefficient for rain. The Level III model version 2.80 uses equation 2 for all chemicals. Equation 3 limits removal by rain dissolution by setting a maximum value for low K_{AW} chemicals.

Partitioning to aerosols in RAIDAR is derived from a review of aerosol-air partitioning data and models [10] as

$$K_{QA} = 0.1 \times K_{OA} + 0.4 / K_{AW} \tag{4}$$

where $K_{QA,}$ K_{OA} and K_{AW} are the aerosol-air, octanol-air and air-water partition coefficients, respectively. Based on this review, it is estimated that particles are comprised of about 20% organic matter and/or organic carbon. Octanol is used as a surrogate for the organic phase of the particle and it is assumed that the "octanol equivalence" of the organic phase is approximately 0.5, i.e., 10% of the particle is analogous to octanol. There are advantages of using an octanol-air partitioning model as a predictor for aerosol partitioning; however, there is uncertainty as to the extent octanol adequately represents the polar and non-polar classes or organic matter on aerosols [10]. The remaining 80% of the particle is assumed to be equal parts aqueous and inorganic mineral phases, i.e., 40% each. K_{AW} characterizes partitioning from the gas phase to the aqueous phase of the particle. The partitioning model does not account for any partitioning that may occur to non-organic and non-aqueous phases of an aerosol particle, i.e., mineral material, as there are no data available to support the inclusion of this phase in the overall aerosol-air partitioning process.

The advective flow residence time for water in the evaluative EQC environment is increased from 10^4 to 10^5 hours as the residence time for water in the standard EQC environment was originally intended to reflect the rapid flushing form a large volume of water as occurs in the Great Lakes Basin of North America. The revised longer residence time, and thus slower water flow rate, is regarded as more generally applicable.

In the revised version of RAIDAR, Level II bulk air, water, soil and sediment compartments are now identical to the Level III bulk compartments.

2.4 Food web bioaccumulation model

Table 4 summarizes key parameters for the food web compartments. Representative food webs are included to assess chemical exposure routes to receptors in the environment. The food web models take the output from the fate and transport calculations and estimate concentrations and fugacities in some 20 biotic groups including plankton, vegetation, domestic animals, fish and wildlife. This requires data on the nature and quantity of diets, and respiration and growth rates. Essentially, each organism absorbs the chemical by respiring air or water and consuming water and other organisms that may be animal or vegetable in nature. The concentration in each organism is generally calculated using these rates, absorption efficiencies, and the concentration in the respective media. The steady-state concentration in the organism is calculated from an input-output mass balance. The result is an estimate of fugacities and concentrations in the biota.

Table 4. RAIDAR biotic compartments, compositions and key bioaccumulation parameters. The five rates are calculated using equations and parameters in Tables 5 and 6.

Media	Mass, kg	Lipid mass fraction	Water mass fraction	Q, max BMF	Respiration rate, m^3/h	Drinking rate, m^3/h	Feeding rate, m^3/h	Growth rate, m^3/h	Urination rate, m^3/h
Plankton	NA	0.01	0.79	NA	NA	NA	NA	NA	NA
Benthic invertebrate	NA	0.05	0.75	NA	NA	NA	NA	NA	NA
Pelagic-benthic fish	0.1	0.05	0.75	4	8.7E-04	NA	2.1E-07	2.1E-09	NA
Piscivorous fish	2.2	0.15	0.65	8	6.5E-03	NA	3.0E-06	3.0E-08	NA
Aquatic mammal	1000	0.35	0.45	120	8.6E+00	8.4E-04	3.4E-03	3.4E-05	8.4E-04
Foliage vegetation	NA	0.01	0.79	NA	NA	NA	NA	NA	NA
Root vegetation	NA	0.01	0.89	NA	NA	NA	NA	NA	NA
Terrestrial invertebrate	NA	0.02	0.78	NA	NA	NA	NA	NA	NA
Terrestrial herbivore	120	0.1	0.7	4	1.6E+00	3.1E-04	7.6E-04	7.6E-06	3.1E-04
Terrestrial carnivore	80	0.2	0.6	120	1.1E+00	2.2E-04	4.2E-04	4.2E-06	2.2E-04
Avian omnivore - small	0.25	0.05	0.75	10	1.4E-02	9.5E-07	3.0E-06	3.0E-08	9.5E-07
Avian scavenger	4.5	0.1	0.7	60	1.3E-01	7.2E-06	2.6E-05	2.6E-07	7.2E-06
Pork	100	0.2	0.6	6	1.4E+00	2.6E-04	9.9E-04	9.9E-06	2.6E-04
Beef cows	800	0.2	0.6	6	7.2E+00	1.7E-03	4.7E-03	4.7E-05	1.7E-03
Dairy cows	600	0.2	0.6	6	5.7E+00	1.3E-03	4.6E-03	4.5E-05	1.3E-03
Dairy milk	NA	0.04	0.86	NA	NA	NA	NA	NA	NA
Bulk dairy	NA	0.08	0.72	NA	NA	NA	NA	NA	NA
Poultry (broilers)	3	0.1	0.7	6	5.8E-02	5.4E-06	2.9E-05	1.4E-06	5.4E-06
Poultry (hens)	2	0.1	0.7	6	4.3E-02	4.1E-06	2.1E-05	2.1E-07	4.1E-06
Eggs	NA	0.1	0.7	NA	NA	NA	NA	NA	NA

Figure 2 illustrates a conceptual model for major routes of uptake and elimination in representative aquatic and terrestrial organisms. Assuming steady-state conditions, a general mass balance expression written in terms of the flux of chemical into and out of an organism is:

$$\underbrace{D_V f_V + D_D f_D + D_W f_W}_{\text{uptake}} = \underbrace{f_B (D_V + D_E + D_G + D_M + D_U + D_R + D_L)}_{\text{elimination}} \tag{5}$$

where D_V, D_D, D_W, D_E, D_G, D_M, D_U, D_R, D_L represent respiration or ventilation, i.e., uptake from and loss to air or water, uptake from ingestion of food, uptake from ingestion of water, egestion in feces, pseudo-elimination by "growth dilution", loss from metabolism of parent compound, urinary excretion, reproduction losses and lactation D values (where applicable), respectively. f_V is the fugacity in respired air or water, f_D is the fugacity in the diet, f_W is the fugacity in drinking water and f_B is the fugacity in the organism. Fish ventilate water while all other organisms respire air. Dermal uptake and elimination rates are not considered in the model because they are generally slow compared to other rates. Water ingestion and urinary excretion for fish are currently assumed insignificant compared to chemical uptake and elimination at the gill and thus are not included in calculating bioaccumulation in fish.

The rate of fecal egestion can be estimated as:

$$D_E f_B = D_D f_D / Q \tag{6}$$

where Q is the species-specific theoretical maximum biomagnification factor representing biota-feces partitioning. The value varies between species because it is dependent on specific factors related to the digestion process as a result of dietary preferences, the digestibility of the diet and the physiology of the organism. Essentially, Q is a product of a reduction in the volume of diet as it passes through the gastrointestinal tract and an elevation of the biota-to-gut partition coefficient above the biota-to-diet partition coefficient [11]. Q is lower in herbivorous organisms than carnivorous organisms. The algorithms for each bioaccumulation D value are included in Table 5.

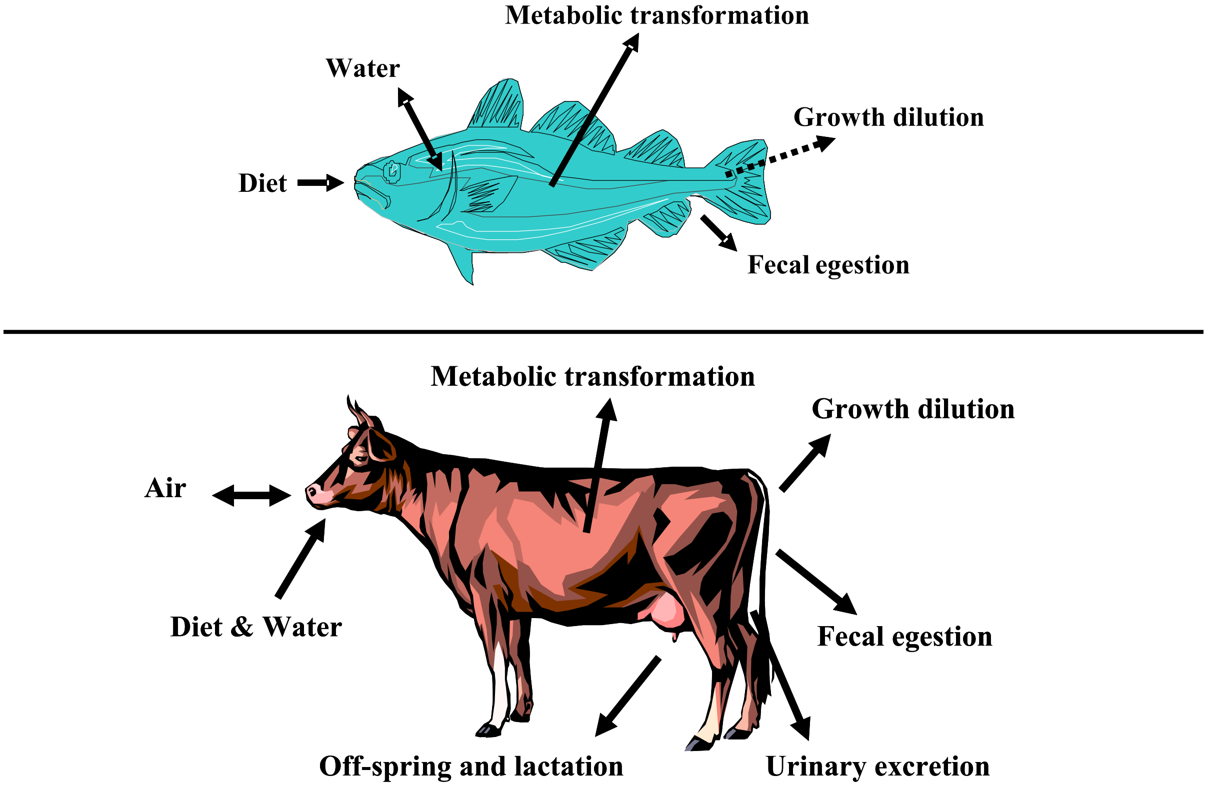

Figure 2. Conceptual overview for major routes of chemical uptake and elimination included in the general bioaccumulation model.

Table 6 provides a summary of the allometric relationships used to describe the specific rates of air inhalation G_V, feeding G_D and water intake G_W for all avian and mammalian species [12] and for feeding G_D and water ventilation G_V for fish [6]. For the allometric feeding rates, a wet weight:dry weight conversion ratio (R_{WD}) of 4:1 is assumed for omnivores and carnivores and a value of 5:1 is assumed for organisms that are primarily herbivorous, i.e., livestock. Some of the coefficients in the allometric feeding rate equations have been revised in the current RAIDAR model. The feeding rate estimates are derived from estimates of metabolic energy requirements and dietary energy contents [12-19]. The wet weight:dry weight conversions are not required for fish as the feeding rate is derived for dietary wet weight. The majority of the allometric relationships describe rate processes as L or kg per day and are converted to m^3/h for the model.

The whole body density of all organisms is assumed to be 1000 kg/m^3. E_V, the environmental medium chemical transfer efficiency, for mammals and birds is assumed to be 1, whereas for fish it is described in Table 5 [20].

The efficiency of chemical uptake from the diet E_D is observed to be greatest in mammals and birds while efficiency is less in fish [6, 11, 21-23]. E_D is a function of the hydrophobicity of the chemical and is observed to decrease for chemicals with log K_{OW} of approximately 6 to 7 and greater in fish and slightly higher in other species. For fish this equation is:

$$E_D = (2.0 + 5 \times 10^{-8} K_{OW})^{-1} \tag{7}$$

and for avian species and mammals:

$$E_D = (1.05 + 10^{-9} K_{OW})^{-1} \tag{8}$$

Table 5. Summary of generic bioaccumulation model D value equations, definitions and units. D values have units of mol/Pa h, efficiencies, E_i, are unitless ratios, rates, G_i, have units of m^3/h.

Equation	Parameter definition
$D_V = E_V G_V Z_W$	D_V – net chemical transport via environmental medium, i.e., air by respiration or water by ventilation
	E_V – environmental medium exchange chemical transfer efficiency
	for fish $E_V = 0.01 + (1/ (1.85 + 155 / K_{OW}))$, for all other organisms, $E_V = 1$
	G_V – gross flow rate for exchange with the environment, i.e., allometric relationships, see Table 6
$D_D = E_D G_D Z_D$	D_D – net chemical transport via diet
	E_D – dietary chemical transfer efficiency, see equations 7 and 8
	G_D – food ingestion rate
	Z_D – weighted sum of Z values of all dietary items
$D_W = E_W G_W Z_W$	D_W – net chemical transport via water ingestion
	E_W – chemical transfer efficiency via water ingestion = 1
	G_W – gross volumetric flow rate for drinking water
$D_E = D_D / Q$	D_E – net chemical transport via fecal egestion
	Q – species-specific theoretical maximum biomagnification factor
$D_G = G_G Z_B$	D_G – growth dilution
	G_G – growth rate
$D_M = V_B Z_B k_M$	D_M – metabolic transformation
	V_B – volume of biota, m^3
	k_M – metabolic transformation rate constant, h^{-1}
$D_U = E_U G_U Z_W$	D_U – chemical transport via urinary excretion
	E_U – chemical transfer efficiency via urinary excretion = 1
	G_U – urinary excretion rate

Equation	**Parameter definition**
$D_R = E_R G_R Z_R$	D_R – chemical transport via reproductive (off-spring) losses
	E_R – chemical transfer efficiency via reproductive losses = 1
	G_R – reproductive loss rate
	Z_R – reproductive Z value
$D_L = E_L G_L Z_M$	D_L – chemical transport via lactation losses
	E_L – chemical transfer efficiency via lactation losses = 1
	G_L – lactation loss rate
	Z_M – lactation Z value

Table 6. Equations and parameters describing respiration (i.e., air or water), food ingestion and water intake (i.e., drinking) rates for fish [6], avian and mammalian [12, 13] species in the model. Rates, G_i, have units of m^3/h, activity factors, AF_i, are unitless. M_B is the ratio of the mass (wet weight, kg) of the organism to that of a 1 kg organism.

Respiration rate (m^3/h) = $G_V = a \cdot M_B{}^{b} \cdot c \;/\; (24\ h/d)$

Organism class	a, m^3/d	b, unitless	c, unitless	Details of c
Fish	*0.98*	*0.65*	$1/(DO)$	DO, dissolved oxygen concentration, mg $O_2/L = (-0.24 \cdot T + 14.04) \cdot OS$ T = mean water temperature = 10 °C OS = oxygen saturation = 0.9 (unitless)
Avian	*0.40*	*0.77*	AF_A	AF_A, avian activity factor = 1.5
Mammals	*0.55*	*0.80*	AF_M	AF_M, mammalian activity factor = 1.5

Food ingestion rate (m^3- wet volume/h), $G_D = a \cdot M_B{}^{b} \cdot c \;/\; (24000\ kg\text{–}dry\ weight.h/m^3.d)$

Organism class	a, kg/d	b, unitless	c, unitless	Details of c
Fish	*0.02*	*0.85*	$e^{0.06T}$	T = mean water temperature = 10°C
Avian – omnivores	*0.05*	*0.75*	R_{WD}	R_{WD}, wet / dry ratio = 4 wet / dry
Mammals – herbivore	*0.1*	*0.75*	R_{WD}	R_{WD}, wet / dry ratio = 5 wet / dry
Mammals – carnivore	*0.07*	*0.82*	R_{WD}	R_{WD}, wet / dry ratio = 4 wet / dry
Mammals – aquatic	*0.07*	*0.82*	R_{WD}	R_{WD}, wet / dry ratio = 4 wet / dry
Swine	*0.15*	*0.75*	R_{WD}	R_{WD}, wet / dry ratio = 5 wet / dry
Beef cow	*0.15*	*0.75*	R_{WD}	R_{WD}, wet / dry ratio = 5 wet / dry
Dairy cow	*0.18*	*0.75*	R_{WD}	R_{WD}, wet / dry ratio = 5 wet / dry
Poultry – broiler	*0.06*	*0.75*	R_{WD}	R_{WD}, wet / dry ratio = 5 wet / dry
Poultry – hen	*0.06*	*0.75*	R_{WD}	R_{WD}, wet / dry ratio = 5 wet / dry

Water intake rate (m^3/h), $G_W = a \cdot M_B{}^{b} \cdot c\ /\ (24000\ L.h/m^3.d)$

Organism class		a, L/d	b, unitless	c, unitless
Avian		*0.06*	*0.7*	*1*
Mammals	terrestrial	*0.1*	*0.9*	*1*
	aquatic	*0.04*		

Table 4 illustrates respiration, feeding, drinking, growth and urination rates derived from the equations described in Tables 5 and 6. These rates are generally comparable with reported empirical food web studies and evaluated models for persistent organic pollutants (POPs) [6, 11, 21, 22, 24]. The theoretical maximum biomagnification factors, lipid contents, wet weights and feeding preferences were based on these empirical and evaluated studies. It is assumed that 1% of an organism's diet is converted to new body mass as a 'growth rate' to calculate growth dilution in Equation 5. An exception is for "broiler" chickens when this value is 5%. For all organisms that drink water, the urinary excretion rate was assumed to be equal to the water intake rate. It was assumed that protein and carbohydrate (i.e., ν_{NLOM}) contribute approximately 20% to most biota, except for root vegetation and dairy milk when this value is assumed to be 10%.

Feeding preferences are presented in Table 7. The diet preferences have been slightly modified from RAIDAR v1.0. The proximate compositions are derived from various sources [14-18]. An allowance for inadvertent uptake of soil with food is included for herbivorous animals and is estimated to be about 1%.

Table 7. Feeding preferences in the representative RAIDAR food webs.

Consumer Consumed	'Pelagic-benthic' fish	'Piscivorous' fish	Aquatic mammal	Terrestrial herbivore	Terrestrial carnivore	Avian - small	Avian - scavenger	Poultry	Pork	Cattle
Foliage vegetation				0.9		0.4		0.95	0.8	0.85
Root vegetation				0.09		0.04		0.05	0.19	0.14
Plankton	0.5									
Benthic invertebrate	0.5		0.3							
'Pelagic-benthic' fish		1	0.4				0.4			
'Piscivorous' fish			0.3				0.15			
Aquatic mammal							0.02			
Soil				0.01		0.01			0.01	0.01
Terrestrial invertebrate						0.55	0.20			
Terrestrial herbivore					1		0.18			
Avian – small							0.05			

Female organisms are known to lower their chemical body burdens of persistent hydrophobic chemicals through reproductive and lactation mechanisms. Thus, to allow for conservative screening level estimates of bioaccumulation, RAIDAR v1.0 was parameterized for "adult male" organisms such that reproductive and lactation losses were not included. The current version of the model addresses reproductive and lactation losses in the general agricultural food web destined for human consumption. These changes are not generally relevant for environmental risk assessment prioritization.

The “single” representative cow in RAIDAR v1.0 has been replaced by a distinct beef cow to estimate chemical concentrations in beef products and by a female cow to estimate chemical concentrations in dairy products. The beef cattle do not include losses for lactation and reproduction whereas the dairy cows do include these mechanisms. Dairy cows are assumed to give birth to one 80 kg calf per year that has one-half the lipid content of the mother, i.e., G_R = 9.1E-06 m^3/h. The representative dairy cow produces 5,900 L of milk per year, i.e., G_L = 6.7E-04 m^3/h. The milk is assumed to consist of 4% lipid, 10% nonlipid organic matter (carbohydrates and protein) and 86% water. “Bulk dairy” is a weighted average of dairy products derived from cow’s milk and is assumed to be 8% lipid, 20% nonlipid organic matter and 72% water.

The “single” representative poultry organism has been replaced by a “broiler” chicken to estimate chemical concentrations in poultry products and by an “egg-laying hen” to estimate chemical concentrations in eggs. The representative hen is assumed to lay 270 eggs per year, with each egg having a mean mass of 57 grams, i.e., G_R = 1.8E-06 m^3/h. The egg is assumed to have a composition equivalent to that of the hen and the egg and hen are assumed to be equilibrium, i.e., equal f and Z values.

Equation 5 is used to assess bioaccumulation in a range of species with a few exceptions. In screening level models it is often convenient to assume that phases in close contact with one another achieve the same fugacity. When intermedia exchange is fast relative to other loss mechanisms, i.e., growth and degradation, equi-fugacity or bioconcentration occurs. This simplifying assumption avoids the need to calculate rates of intermedia transport or degradation. The fugacities calculated for plankton, benthic invertebrates and terrestrial invertebrates are assumed to be a result of thermodynamic equilibrium with the media in which they reside. Specifically, plankton is at equilibrium with the water, benthic invertebrates are at equilibrium with the sediment and terrestrial invertebrates are at equilibrium with the soil. In some cases this assumption can introduce considerable error, i.e., when growth or degradation rates become greater than intermedia exchange rates. It was previously assumed in RAIDAR v1.0 that foliage and root vegetation were at equi-fugacity with their associated abiotic media [4]; however, most of the edible components of vegetation that are consumed by animals are subject to short growing periods, e.g., 30 - 90 days. Comparatively rapid growth rates and reduced chemical uptake rates through membranes and cell walls, i.e., increased resistances for more hydrophobic chemicals, result in fugacities generally being lower in the plant than the media in which it resides. Thus the revised treatments of foliage and root vegetation to account for competing kinetic rates of uptake and elimination are described.

Chemical concentration in foliage vegetation from air is observed to undergo three key phases [25]. The first is explained by equilibrium partitioning between the plant and the gas phase of air and occurs over a log K_{OA} range from about 3 to 8. Chemical uptake kinetics are reduced in comparison to growth rates for chemicals over a log K_{OA} range from about 8 to 11. Particle deposition from the air to plant surfaces is believed to contribute to chemical concentrations in or on plants for chemicals with log K_{OA} values greater than about 11. The original equation for foliage fugacity in RAIDAR v1.0 has been revised to

$$f_{FV} = f_{BA} \times Z_{BA} / Z_{GA} \times 1/(1 + (K_{OA}/10^{8.5})) \tag{9}$$

where f_{FV} and f_{BA} are respectively, the fugacities in foliage vegetation and bulk air, and Z_{BA} and Z_{GA} are the fugacity capacities for bulk air and the gas phase of air, respectively. A second revision to the estimation of foliage fugacities and concentrations is included in the calculation of the Z value for foliage as

$$Z_{FV} = 0.79 \times Z_W + 0.01 \times Z_L + 0.2 \times Z_{NLOC} \tag{10}$$

This assumes that there is a reduction in foliage concentration as a result of competing uptake and loss rates and that there is a contribution of particle bound deposition and absorption into foliage for high K_{OA} chemicals. This revision provides a better first approximation to the model described by McLachlan 1999 [25] than the previous formulation and is in good agreement with measured data for various foliage plant species [26].

Uptake of chemical by roots from soil is mainly by transpiration of soil pore water into the xylem. The chemical may however be retarded by sorption to the outer layers of the root surface and by depletion of chemical from the pore water in immediate contact with the root. Biotransformation is also possible. Whereas for air-foliage transport K_{OA} is used, K_{OW} is more appropriate for characterizing soil-root transport. Although data are sparse, it is generally accepted that low K_{OW} substances migrate fairly rapidly into roots and may achieve a root fugacity comparable to that of the soil. For very hydrophobic substances there may be insufficient time for equilibration due to the inefficiency of transport of these sparingly soluble substances in water. Growth is also relatively fast. A simple and robust expression that addresses these kinetic issues has been devised as:

$$f_{RV} = f_{BS} \times 1/(1 + (K_{OW}/10^6)) \qquad (11)$$

where f_{RV} and f_{BS} are the fugacities in root vegetation and bulk soil, respectively. A second revision to the estimation of root fugacities and concentrations is included in the calculation of the Z value for root vegetation as

$$Z_{FV} = 0.89 \times Z_W + 0.01 \times Z_L + 0.1 \times Z_{NLOC} \qquad (12)$$

2.5 Model assumptions

Environmental partitioning is modelled using the partition coefficients between air and water, octanol and water and octanol and air by assuming a relationship between organic matter-water and octanol-water partitioning. There is no partitioning to mineral matter. All reactions are treated as first order using the defined half-lives and assuming all chemical in the compartment is available for reaction, i.e., $t_{1/2}=\ln(2)/k$. Rates of transport between compartments are estimated using typical environmental transport parameters such as precipitation rates and mass transfer coefficients. The substance enters the environment only by emission at the specified rate. It leaves the environment by degradation to other species at rates characterized by the half-lives, by advective losses, i.e., by flows of air and water leaving the environment, and by burial in sediments. Only the parent compound is evaluated. Transformed chemical products possess different physical-chemical properties, half-lives and toxicities. Degradation products can be modelled if they are treated separately as a "novel" chemical.

Bioaccumulation is treated by assuming that lipids and octanol are equivalent in solvent properties. For each organism, typical rates of feeding (including dietary preferences), respiration, egestion and growth are assumed and assimilation efficiencies are estimated. A conservative assumption is that no metabolic conversion of chemical occurs in the organisms. If inclusion of metabolic conversion is desired, half-life values for biotransformation are required.

A temperature of 25^{o}C is assumed to apply to both the input data and the evaluative environment. A temperature of 10^{o}C is assumed to estimate allometric relationships for feeding, growth and ventilation for fish in the evaluative environment.

A correction for ionization is not currently included in the model for substances that can dissociate in water for fate and bioaccumulation calculations. Human pharmaceutical uptake studies suggest that ionized species are absorbed to within approximately 3 to 10% of the efficiency of the neutral species [27]. Thus for dietary exposure, model errors for estimating the chemical absorption efficiency for ionizing chemicals in the gastrointestinal tract in the food web calculations are assumed to be minimal. The Henderson-Hasselbalch equation is not valid for estimating the reduced bioavailability of ionizing chemicals to aquatic organisms via the gills as chemical uptake of ionized chemicals is greater than would be estimated using this correction (e.g., [28, 29]). The assumption of "ignoring" potential ionization is believed to provide a conservative method for the uncertainty that this parameter has on model results. Work is ongoing to develop more realistic and robust expressions for partitioning and transport of ionizing chemicals and RAIDAR will be refined as the science progresses.

3. Model Application to DSL Chemicals

3.1 Chemical classes

RAIDAR is currently developed to model discrete organic chemicals that have reliable solubility properties in air, water and organic matter. Currently, RAIDAR is not applicable for organometallics, organic-metal salts, inorganics, most UVCBs and polymers. Appendix 1 of this report provides guidance for the types of substances that can be modelled using RAIDAR and the required input data. Environment Canada has provided physical chemical property information from the DSL database for 1,387 substances. RAIDAR is generally applicable to 1,105 of these substances. Specifically, the model is used for 868 discrete organics, 183 UVCB-organics, and 54 UVCB-biologicals. Discrete organic structures and corresponding property data are provided as surrogates for these 237 UVCB substances.

There are 7 UVCB-biological substances that were not modelled. There are property data for the surrogates chemicals selected to represent the UVCB, but they contain metal components. There are an additional 275 substances with property data available that were not modelled (153 organic-metal salts, 72 organometallics, 29 UVCB-organic-metal salts, and 21 UVCB-organometallics). There are 687 chemicals that do not have any property data and are not suitable for the RAIDAR model (240 inorganics, 2 organometallics, 310 polymers, 18 UVCB-biologicals, 79 UVCB-inorganics, 19 UVCB-organics, 5 UVCB-organic-metal salts, 6 UVCB-organometallics, and 8 UVCB-polymers). We are not aware of any existing screening level mass balance model that can address these substances. They may require individual professional judgment.

3.2 Model input parameters

3.2.1 Physical-chemical properties

RAIDAR requires the following physical-chemical property data: molar mass, MW, aqueous solubility, S, vapour pressure, P, the octanol-water partition coefficient, K_{OW}, and the acid dissociation constant, pKa. As in the EQC model, to ensure internally consistent partitioning behaviour in the model, the octanol-air partition coefficient, K_{OA}, is calculated from the octanol-water partition coefficient and the unitless air-water partition coefficient, K_{AW}, as $K_{OA} = K_{OW} / K_{AW}$, where K_{AW} is P / SRT. Measured physical-chemical property data obtained at 20-25^{o}C are preferable to estimated values but measured values are not available for all of the chemicals. There are measured S, P, and K_{OW} values for 229, 276 and 251 chemicals, respectively. Where measured data were not available, estimates of physical-chemical properties were obtained from EPISUITE [30] as provided by Environment Canada.

The collected physical-chemical property data for the 1,105 chemicals were selected according to the methods described in Appendix 2 and summarized in Appendix 4. Briefly, based on a review of measured data for chemicals in the Syracuse Research Corporation PHYSPROP database and Environment Canada's DSL database, minimum and maximum experimental values (MinEV and MaxEV) were used as cut-off criteria for "extreme" model predictions of physical-chemical properties. The minimum and maximum "cut-off values" for physical-chemical properties were used to replace "extreme" model predictions as input for RAIDAR calculations. These data were flagged, as documented in Appendix 4, because these values are highly uncertain and may require further scrutiny by Environment Canada.

Measurements and estimations of physical-chemical properties provided by Environment Canada and used in this report are for the "salt" forms of certain chemicals. Thus "salt" structures were used as inputs for the EPIWIN models to be consistent with the approach used in the categorization.

3.2.2 Primary transformation half-lives

RAIDAR requires degradation half-life data for bulk air, water, soil and sediment compartments and biotransformation in food webs. Estimates of aerobic aqueous phase biodegradation half-lives were obtained by calibrating BIOWIN model outputs from EPISUITE [30] based on a method previously described in a report to Environment Canada [31]. Briefly, this involves training the numeric outputs from the BIOWIN models to half-lives measured in aerobic environmental compartments. From the 6 half-lives estimated for each chemical, "outliers" were removed upon inspection of the calibrated results. If there is general agreement among the models, i.e., no "outliers" coefficient of variation (CV) is approximately 80% or less, then the average and standard deviation of the calibrated values were calculated. When the CV was greater than 80%, typically one or two of the model estimates were quite different than the rest. These estimates were generally considered as "outliers" and removed and the average and standard deviation were calculated from the remaining model estimates. This generally resulted in the removal of a "high" and "low" value.

Hydrolysis half-lives are applicable for approximately 1% of the chemicals in this study. Hydrolysis half-life estimates were reciprocally combined with the biodegradation half-lives to obtain an overall aqueous aerobic half-life. Aqueous aerobic biodegradation half-lives were extrapolated to bulk soil and bulk sediment compartments using 1:1.5 and 1:6.5 ratios, respectively. There were no considerations for reduction reactions that may occur under anaerobic conditions in the sediment, e.g., nitro group reductions, as these data are not available.

Half-lives in air were estimated for ozone and hydrolysis reactions using AOPWIN of the EPISUITE model [30] provided by Environment Canada. Chemical half-lives in air were estimated by reciprocally combining the AOPWIN hydroxyl radical and ozone half-lives. Air phase ozone reactions are expected for approximately 17% of the chemicals in this study.

The model allows for the input of metabolic biotransformation half-lives for chemicals. There are few data available for the metabolic biotransformation rates for most chemicals. At present there are no established methods or models available to estimate rates of metabolic transformation in biota, although this is an active area of research. In the absence of chemical specific biotransformation information, it is often assumed that there is no metabolic conversion in the food web for hazard and screening level risk assessment. While this is considered to be a conservative approach it can result in the overestimation of exposures to middle and upper trophic level organisms for hydrophobic chemicals that are subject to metabolic conversion in the food web in the RAIDAR model. This results in overestimation of RAFs and priority guidance for these chemicals. To address this we provide simulations with and without estimates of metabolic biotransformation.

Metabolic biotransformation rate constants, i.e., k_M, in all organisms including plants, invertebrates, fish, avian and mammalian species, were assumed by default to be negligible in one series of RAIDAR simulations. This corresponds to a large "fictitious" biotransformation half-life, i.e., 1000 d.

In a second series of simulations, metabolic biotransformation half-life estimates were included for fish, birds and mammals. The general method used to estimate and predict metabolic biotransformation rates in fish is described in greater detail in two previous reports to Environment Canada [32, 33]. Briefly, a large database of metabolic biotransformation half-lives in fish was developed from bioconcentration data using a kinetic model. The metabolic biotransformation rates in the database span about six orders of magnitude, i.e., ~0.0001/d to ~100/d. These data were used to calibrate BIOWIN models to provide chemical specific structure based estimates for metabolic biotransformation in fish. Because of the general lack of data currently available for this parameter and natural variability in the environment an effort was made to make the estimates from BIOWIN "conservative". Lower and upper bound rates in fish were selected as 0.0005/d and 5.0/d, respectively, i.e., four orders of magnitude. Half-life estimates for birds and mammals were obtained assuming the metabolic biotransformation rates in these species are five times faster than in fish (e.g., [34]). A key assumption in these methods is that there are some similarities in the biotransformation potential for many chemicals in various species. This is considered to be a screening level "first step" to obtain reasonable values for this parameter. The selected half-life values for the 1,105 chemicals are summarized in Appendix 4.

As with physical-chemical property data, measurements and estimations of half-lives are for the "salt" form of the molecules. Thus "salts" were used as SMILES inputs for the EPIWIN models to be consistent with the approach used in the categorization.

3.2.3 Effect endpoint

For prioritization ranking with RAIDAR it is necessary to select a common toxicological endpoint for all chemicals to ensure consistent evaluations. There are many toxicological endpoints of relevance for ecological risk assessment; however, there are few measured or modelled data available. Measured and modelled values are generally available for acute lethality, i.e., LC_{50} values in fish. Acute lethality values for the 1,105 chemicals in this report are derived using the toxic ratio approach.

The majority of commercial chemicals are acutely lethal by a narcotic mechanism of toxic action, i.e., "non-specific" (e.g., [35]). This mechanism of toxicity is believed to be consistent for polar and nonpolar narcotic chemicals throughout the biosphere at a critical body residue (CBR_N) of approximately 2 – 8 mmol/kg-wet weight, i.e., central value of 5 (e.g., [36, 37]). Chemicals that have a more specific, i.e., potent, mechanism of toxic action will exert a lethal effect at lower critical body residues, i.e., CBR_S. A toxic ratio (TR) of 10 or greater has been suggested to categorize chemicals that are more acutely potent than narcotics [35, 38] as

$$TR = CBR_N / CBR_X = 5 \text{ mmol/kg} / (BCF \times LC_{50}) \qquad (13)$$

where CBR_X is the critical body residue estimated for all of the chemicals. The BCF is the bioconcentration factor (L/kg-wet weight) and LC_{50} is the iT pivotal value (mmol/L) for the chemical as determined by Environment Canada. Thus, a chemical with a TR greater than 10, i.e., $CBR_X \leq 0.5$ mmol/kg, is considered a toxicant that exerts a specific mode of toxic action and the chemical specific value is used, i.e., $CBR_S = BCF \times LC_{50}$. Chemicals classified as narcotics, i.e., $CBR_X > 0.5$ mmol/kg, are considered to exert a narcotic mechanism and assigned a value 5 mmol/kg. As with all of the input parameters required by the model there are uncertainties as to the precise values for CBR, BCF and iT. Confidence limits for toxicity values of narcotic chemicals span approximately 1 – 2 orders of magnitude and specific mechanisms of action are generally more uncertain, i.e., 2 – 3 orders of magnitude (e.g., [36-38]).

There are 9 measured iT values for algal species and 155 measured iT values from aquatic invertebrates and fish. Algae may be subject to different mechanisms of action, e.g., inhibition of photosynthesis, and these CBRs were treated separately and were applied to algae and vegetation only. The BCFs for the 9 algae data were calculated as

$$BCF_A = K_{OW} \times 0.017 + 0.983 \tag{14}$$

where 0.017 is the lipid-equivalent content of algae and 0.983 is assumed as the remaining, predominantly aqueous, fraction of the organism. The BCFs for the invertebrate and fish data BCF_H were calculated using equation 14 but assuming a lipid-equivalent fraction of 0.05 and an aqueous fraction of 0.95. There were no iT data for 39 chemicals so these were assumed to be narcotics, i.e., a CBR of 5 mmol/kg.

The toxicity (iT) data provided by Environment Canada and used in RAIDAR are for the “no salt” chemical structure. Many of the toxicity models require the “no salt” form as SMILES input. This is consistent with the approach used in the categorization for iT estimates.

3.2.4 Emission rates and mode of entry

A unit emission rate of 1 kg/h (8.76×10^{-3} kilotonnes/year) was selected for all model simulations. Level II fate calculations do not require mode of entry information. Level III simulations require mode of entry information. Thus, four different Level III simulations were conducted including emissions strictly to either air, water or soil and a fourth scenario in which 1/3 of the unit emissions are equal to air, water and soil.

Estimates of actual emission rates to calculate the RAFs and RIBs were derived from the reported DSL quantity ranges, i.e., low, medium and high. The three quantity ranges are assumed to be 3.16×10^{-4}, 3.16×10^{-2} and 3.16 kilotonnes/year. There are 4 chemicals that have no reported quantities. The medium range was assumed for these chemicals.

4. Results and Discussion

4.1 RAIDAR data input review

Required RAIDAR model inputs for this report are first briefly reviewed. A thorough review of Environment Canada's DSL database is beyond the scope of this project. The objective is to provide a cursory review of the "reasonableness" of the input data for chemicals that are to be modelled in RAIDAR. In this section a rationale for replacing "extreme" model estimates for physical-chemical property inputs with "cut-off" values and flagging these data are discussed. These data are flagged, as documented in Appendix 4, because these values are highly uncertain and may require further scrutiny by Environment Canada. More details are provided in Appendix 2.

For the DSL categorization, Environment Canada assumed that organic chemicals released to the environment that can form "salts" exist in their "salt form" and based on these distinct properties behave in the environment as the "salt". Many of the toxicity models used to estimate iT values require structural information, i.e., SMILES, in the "acid" form, i.e., "no salt". To maintain consistency with the categorization it was decided that the same SMILES, physical-chemical property, EPISUITE and iT data be used in this project, i.e., "salt" data, for all inputs except for iT measurements and estimates.

4.1.1 Flagging data input

The majority of EPISUITE model estimations employ a "group contribution" method in which fragments of the molecule are used to estimate the whole. It has been noted in a previous report to Environment Canada that the propensity for model errors may increase for larger molecules, i.e., MW > 600 g/mol [31]. Thus, chemicals with a molecular mass greater than 600 have been flagged in the review of selected input data in Appendix 4. "Extreme" physical-chemical properties identified according to the methods described in Appendix 2 were replaced with reasonable "cut-off" values and the data inputs flagged as documented in Appendix 4. Briefly, 52 aqueous solubility values were below the low criterion and were replaced with a value of 10^{-5} mg/L. Two solubility values were above the criterion and were replaced with a value of 10^{6}

mg/L. 372 vapour pressure values were very low or negligible, i.e., 0, and these were replaced with a value of 10^{-9} Pa. Eight vapour pressure values were considered to be high and were substituted with a value of 10^6 Pa. Seven K_{OW} values were less than 10^{-4} and were replaced with this value and 38 K_{OW} values exceeded 10^9 and were replaced with this upper value. Figure 3 illustrates the "chemical-space" occupied by the 1,105 chemicals including the replaced values.

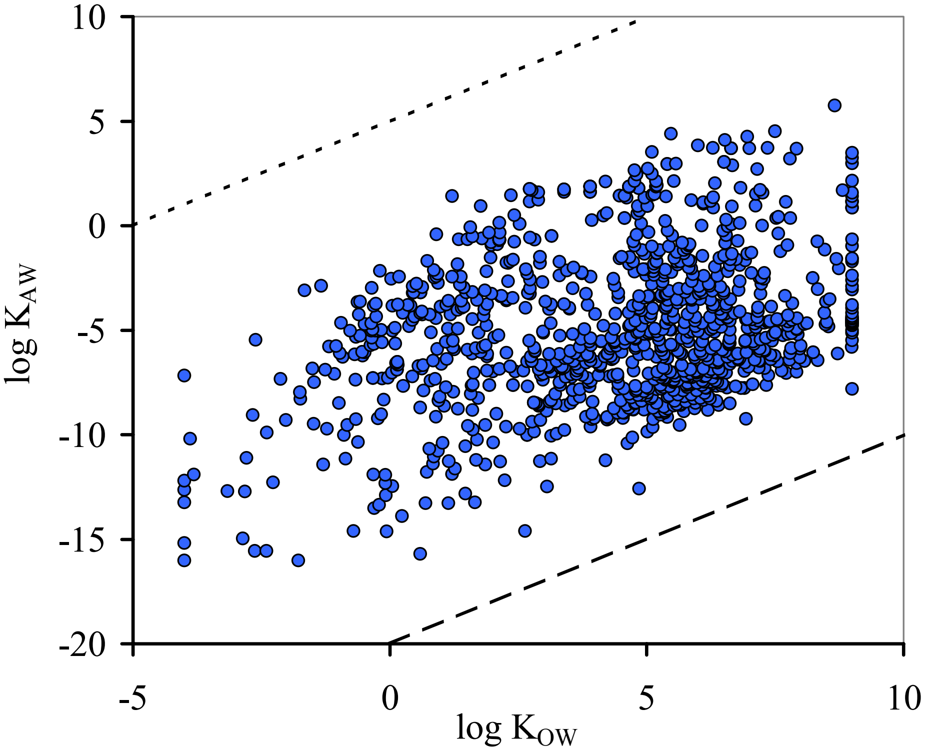

Figure 3. The "chemical space" occupied by the 1,105 chemicals modelled in RAIDAR

There is also uncertainty associated with the estimation of physical-chemical properties for certain chemical classes, i.e., highly fluorinated and organo-silicone chemicals. The "training sets" used in most QSAR models do not contain enough information for these chemicals to give reliable predictions. These chemicals have been identified and flagged in the data input summary sheet and results should be interpreted with these considerations.

Highly reactive chemicals with very short half-lives may not be modelled accurately in the RAIDAR environment. Three chemicals with aqueous, i.e., hydrolysis reaction, half-lives of less than 2 days in water have been flagged. 392 chemicals modelled also have very short half-lives in air, i.e., less than or equal to 0.1 days. These chemicals have been flagged.

It is noteworthy that the RAIDAR environment is an area of 10^5 km^2 and it assumes that the chemical is well mixed throughout this region. In practise, if there is a point source of a very reactive chemical it is likely that only the area in the immediate vicinity of the point source will have significant quantities of chemical. Smaller scale models are more appropriate. For example, air dispersion or river "die-away" models may be preferable. The extent to which the RAIDAR model can be scaled down in area but still yield realistic results is included in Appendix 3.

Chemicals with estimated dimensionless air-water partition coefficients, i.e., K_{AW}, greater than 5 have been flagged. Chemicals that are likely subject to some degree of ionization in the environment have also been flagged in the summary input spreadsheet (Appendix 4).

A review of the iT values indicate that approximately 48% of the iT values selected by Environment Canada for the chemicals modelled in this report are above the reported aqueous solubilities reported in the database. About 31% of the iT values are more than an order of magnitude greater than the reported aqueous solubilities. While the uncertainty in the water solubility data cannot be ignored, this cursory review suggests that there is uncertainty as to the validity of these estimates for these substances. Thus, these chemicals have been flagged.

4.1.2 The "salt" assumption

Solubility is the amount of a solute that will dissolve in a specific solvent under given conditions. The solubility of one substance (usually a solute) dissolving in another (solvent) is generally determined by the intermolecular forces between the solvent and solute, temperature, the entropy of solvation, and the presence and amount of other substances. Perrin et al [39] and

Lee et al [40] suggest a decrease of only 0.11 unit in the pKa for organic acids and bases with a change in ionic strength (μ) from 0 to 0.1. Ionic strength for aqueous phases in the environment typically range from 0.001 – 0.14. Therefore, overall effects from pH and pKa changes due to ionic strength upon speciation are likely to be minimal. This suggests that "salt" forms of DSL chemicals are more likely to behave as either the ionized or the neutral species depending on the pH and the pKa of the chemical. A few examples are provided to illustrate the impacts of the "salt" assumption on modelling results.

Physical chemical property comparisons are provided for the DSL chemicals modelled in this report including a comparison of "salt" and "no salt" formulations. Figure 4 illustrates regressions of water solubility and hydrophobicity from measured and modelled "salt" (4a) and "no salt" (4b) formulations. The regression is notably stronger for the "no salt" form. The "salt" regression also highlights a large number of outliers (within circle) that are in poor agreement. There should be a consistent inverse relationship between water solubility and hydrophobicity. Furthermore, certain chemicals (within circle) treated as "salts" that have apparent "low water solubility", but not proportional "high hydrophobicity", may actually have bioaccumulative properties. These discrepancies are also important for fate and persistence modelling. Figure 5 illustrates a regression of vapour pressures for "salts" and "no salts". The inclusion of a "salt" in the formulation results in large changes in the prediction of the chemicals vapour pressure in comparison to the regression of "regular" chemicals. For example, the vapour pressure may change by approximately 10 orders of magnitude or more.

More specific examples of the differences in the assumption are described below.

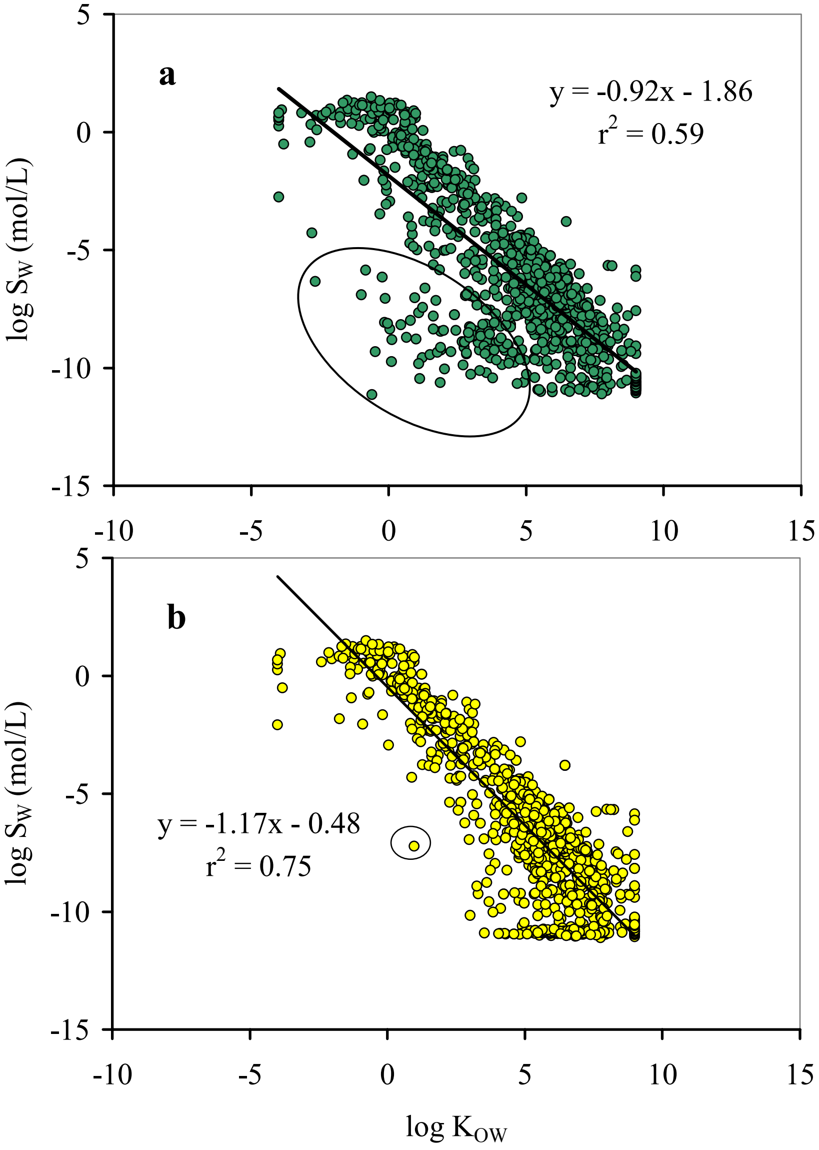

Figure 4. A comparison of aqueous solubility and hydrophobicity for (a) "salt" and (b) "no salt" formulations

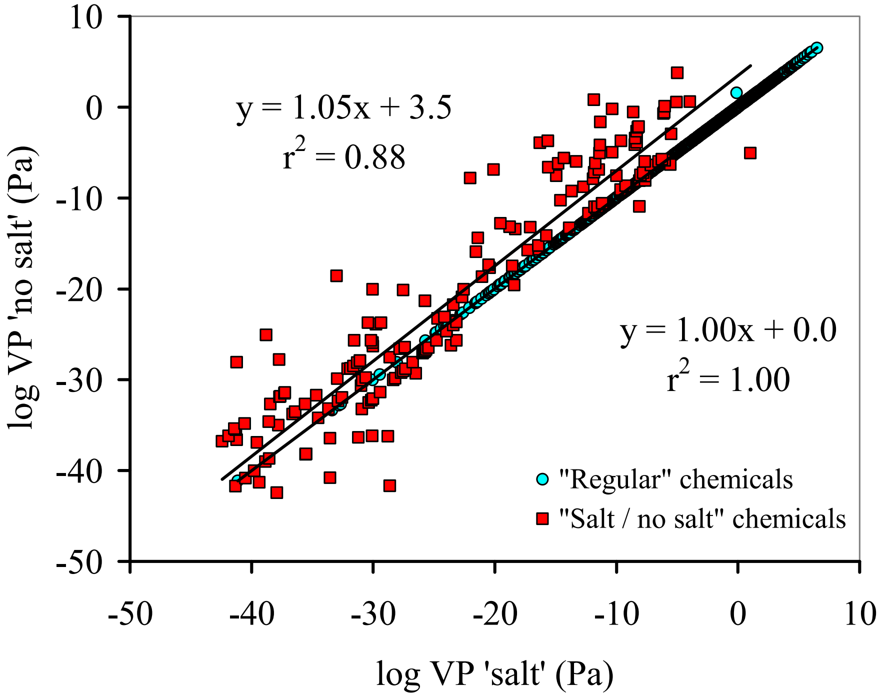

Figure 5. A comparison of measured and modelled vapour pressures for "regular" chemicals and "salt / no salt" chemicals.

A high molar mass "naphthalenesulfonic acid substance" (CAS# 72869-93-3) is treated as a "salt" for the estimation of physical-chemical properties. This results in an estimated water solubility of 15.42 mg/L and a log Kow of –8.62. The neutral form of the acid, "no salt", results in an estimated water solubility of 2 x 10^{-9} mg/L and a log Kow of 6.35. A high molar mass "erythromycin substance" (CAS# 643-22-1) is treated as a "salt" for the estimation of physical-chemical properties in the database. This results in an estimated water solubility of 2 x 10^{-7} mg/L and a log Kow of 7.15. The neutral form of the acid results in an estimated water solubility of 36.58 mg/L and a log Kow of 0.89.

A more detailed example of the differences in chemical form assumptions is discussed for formic acid. Formic acid, sodium salt (CAS # 141-53-7) has an EPIWIN estimated half-life in air of 499.5 days, i.e., no hydroxyl radical and ozone reaction. The neutral form of the molecule has an EPIWIN estimated half-life in air of 20.6 days based on reactions with the hydroxyl radical. The salt has a half-life in water approximately two times greater than the neutral form. The water solubilities are within an order of magnitude of each other (4.3×10^5 and 1.0×10^6 mg/L, respectively) and the K_{OW} of the salt is approximately 3.5 orders of magnitude lower than the neutral form of the acid, i.e., log values of -4.0 and -0.54. The salt form has an estimated vapour pressure of 1.0×10^{-5} Pa and the neutral form has a value of 5.7×10^3 Pa. The resulting air-water partition coefficient for the salt form is approximately eight orders of magnitude less than the neutral form of the acid. RAIDAR Risk Identification Bins (RIBs) are A for Level III emissions to air and equal emissions to air, water and soil for formic acid (salt). In fact, it is the highest ranking chemical under these scenarios. Formic acid, drops from RIB “A” to “E” when the neutral form (“no salt”) of the chemical is used in the model.

Clearly the fate of this chemical is dictated by the assumption of its physical-chemical properties in the environment. The impacts of which will influence the ranking of chemicals by RAIDAR and may influence decisions made by Environment Canada from other programs including the categorization.

We recommend that Environment Canada adopt a consistent approach for selecting physical-chemical properties for substances that may ionize, i.e., “salt/no salt”, as described above. There can also be ambiguity about the use of pKa, the acid dissociation constant, to describe the dissociation of bases. It would be helpful if the assumptions used were documented and examples given of the implications.

4.2 Summary model results

Based on a review of the chemical classes and the input data provided, 1,105 substances are modelled in the evaluative RAIDAR environment. Appendix 4 provides a summary of selected input data and summary RAIDAR output results. The summary model output results are provided from 10 different RAIDAR simulations. This includes Level II calculations (no specific MOE required) and Level III fate calculations (four different MOE scenarios). For each fate calculation, two scenarios are assumed for estimating bioaccumulation in food webs, i.e., (i) no metabolic biotransformation, and (ii) estimates of metabolic biotransformation in fish, birds and mammals. RAIDAR output results include RAFs, E_C, Risk Identification Bins (RIBs), and the most sensitive ecological receptor. Relative risk rankings, i.e., RAF rankings, are also provided for each simulation based on preliminary DSL quantity information provided by Environment Canada as a surrogate for E_A.

Table 8 summarizes the RIB distributions for all simulations assuming no metabolic biotransformation in the food webs. Table 9 summarizes the RIB distributions for all simulations including estimates of metabolic biotransformation in the food webs. The RAFs span from approximately 12 to over 16 orders of magnitude depending on the scenario.

Table 8. A summary of Risk Identification Bin (RIB) counts from 5 different RAIDAR simulations assuming no metabolic biotransformation in the food webs.

	Model Scenario				
	LII	LIII AWS	LIII A	LIII W	LIII S
RIB	Count	Count	Count	Count	Count
A	0	1	3	0	1
B	3	33	14	29	3
C	49	157	57	171	38
D	194	351	203	413	126
E	522	424	449	326	376
F	210	113	265	118	488
G	127	26	114	48	73

RIB = A: RAF $\geq 10^2$; B: $10^0 \leq$ RAF $< 10^2$; C: $10^{-2} \leq$ RAF $< 10^0$; D: $10^{-4} \leq$ RAF $< 10^{-2}$; E: $10^{-6} \leq$ RAF $< 10^{-4}$; F: $10^{-8} \leq$ RAF $< 10^{-6}$; G: RAF $< 10^{-8}$

Table 9. A summary of Risk Identification Bin (RIB) counts from 5 different RAIDAR simulations including estimates of metabolic biotransformation in the food webs.

	Model Scenario				
	LII	LIII AWS	LIII A	LIII W	LIII S
RIB	Count	Count	Count	Count	Count
A	0	0	1	0	0
B	1	6	10	2	2
C	15	62	19	64	17
D	79	193	82	197	81
E	251	365	256	457	313
F	450	439	456	308	457
G	309	40	281	77	235

RIB = A: RAF $\geq 10^2$; B: $10^0 \leq$ RAF $< 10^2$; C: $10^{-2} \leq$ RAF $< 10^0$; D: $10^{-4} \leq$ RAF $< 10^{-2}$; E: $10^{-6} \leq$ RAF $< 10^{-4}$; F: $10^{-8} \leq$ RAF $< 10^{-6}$; G: RAF $< 10^{-8}$

Most of the chemicals modelled in this report fall in the lower priority bins. The data summarized in Table 8 indicate that on average, assuming no metabolic biotransformation in the food webs, approximately 60% of the 1,105 chemicals modelled in this report have RAFs $< 10^{-4}$ and approximately 10% of the chemicals have RAFs $\geq 10^{-2}$. Table 9 indicates that when estimates of metabolic biotransformation are included in the food webs, more than 80% of the 1,105 chemicals modelled in this report have RAFs $< 10^{-4}$ and less than approximately 5% of the chemicals have RAFs $\geq 10^{-2}$.

Figure 6 illustrates that there can be some bias introduced to the risk prioritization by assuming no metabolic biotransformation, i.e., RAFs show a slight increase with increasing hydrophobicity. The merit of including the estimates of metabolic biotransformation in the prioritization is that there is no apparent bias in RAFs as a function of hydrophobicity. The metabolic biotransformation estimation method is intended to provide reasonable, yet conservative, estimates of rates; however, the method is preliminary.

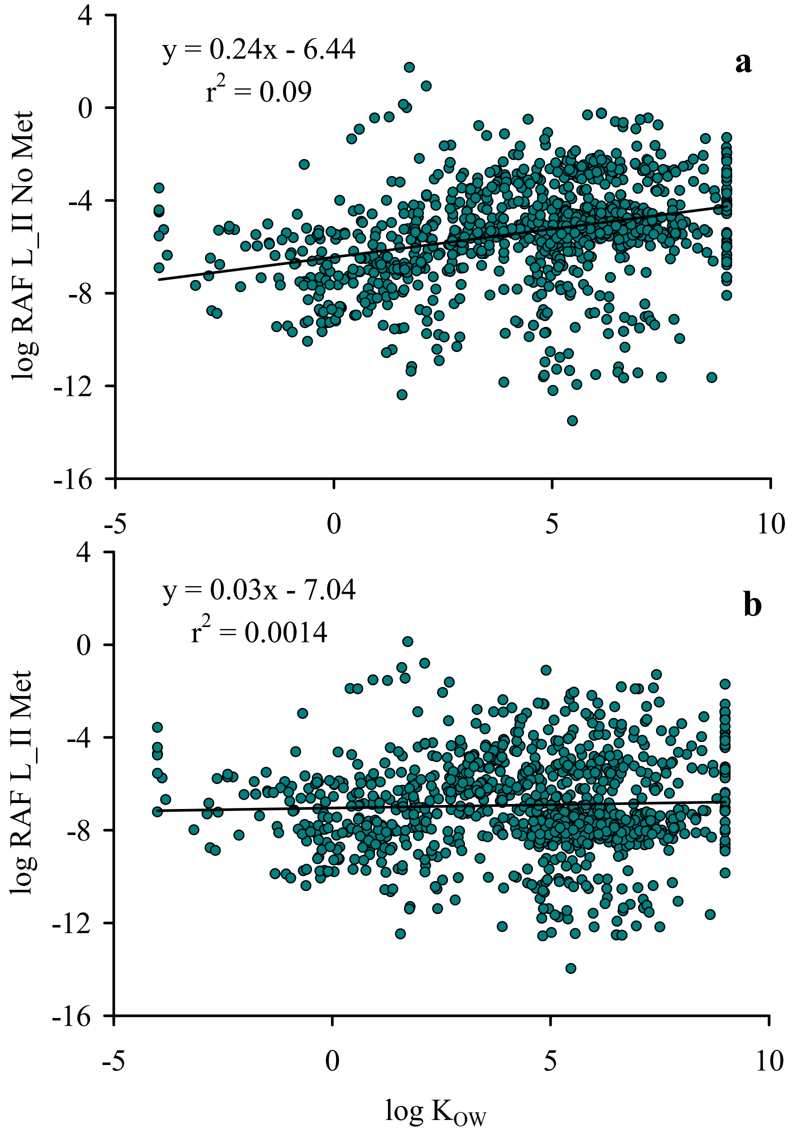

Figure 6. A comparison of model bias as a function of hydrophobicity (a) assuming no metabolic biotransformation, and (b) including estimates of metabolic biotransformation.

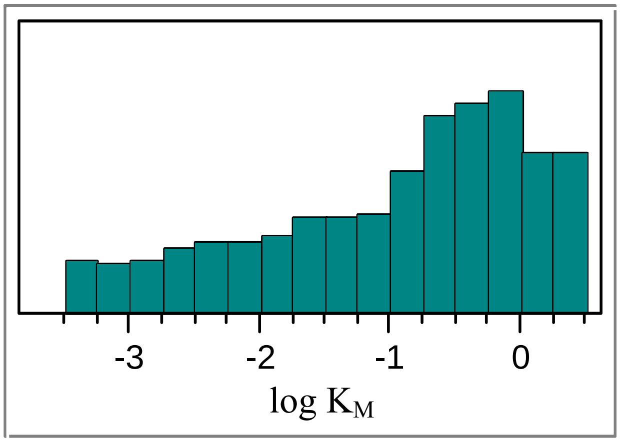

Figure 7. The distribution of estimated metabolic biotransformation rates (k_M) in fishes for the 1,105 chemicals.

The apparent metabolic biotransformation rates appear reasonable based on preliminary testing and visual inspection of structures and rates in our *in vivo* database. The same issues regarding errors for very large chemicals in EPIWIN predictions will be translated to these estimates as well. The errors for the larger molecules are conservative, i.e., low k_M values. Figure 7 illustrates the frequency distribution of the metabolic biotransformation rates estimated in fish for the 1,105 chemicals modelled in this report.

4.3 Guidance on non-RAIDAR model chemicals

Please see Appendix 1.

4.4 Adjusting regional area

Please see Appendix 3.

5. Summary and Recommendations

A total of 1,105 chemicals provided by Environment Canada are readily modelled by RAIDAR. Certain physical-chemical properties and iT values are flagged for further inspection by Environment Canada. This report documents a screening review of the required input data for the modelled chemicals; a thorough review is beyond the scope of this project.

It is recommended that a more comprehensive review of physical-chemical property and toxicity values in the Environment Canada DSL database be conducted. The discrepancy between the current approach for iT estimates ("no salt") in comparison to other estimates, i.e., physical-chemical properties and half-lives ("salt"), is raised. Key assumptions may influence decision making on prioritizing chemicals for comprehensive risk assessments. It is highlighted that key assumptions regarding the form of certain substances in the environment, i.e., "salt" or "no salt", can have significant effects on all model predictions. We recommend that the validity of the "salt form" assumption be further reviewed as this will have implications for RAIDAR results as well as other risk prioritization programs at Environment Canada and Health Canada.

The results obtained from the RAIDAR model, and indeed any mass balance model, are dependent on reliable inputs. Despite the described uncertainties in current DSL data and extrapolations, the results of this report suggest that large-scale applications of RAIDAR can provide guidance for priority setting. Specifically, RAIDAR RAFs for the 1,105 chemicals studied span 12-16 orders of magnitude. Where applicable, chemicals may be re-ranked with Environment Canada's database of "actual emission rates" using the critical emission rate information provided.

The model is intended to prioritize chemicals for risk assessment; however, it is also identifies key areas of uncertainty and data gaps, e.g., physical-chemical properties and half-lives. RAIDAR brings together key elements of a risk assessment at a screening level and can quantify many uncertainties as well as risk. For chemicals that are being considered for further evaluation, RAIDAR can help prioritize information gathering where it is most needed in an efficient manner. Uncertainty and sensitivity analyses with RAIDAR can be used to prioritize data needs for risk assessment programs. RAIDAR can also provide guidance for monitoring programs.

Unfortunately, for chemicals that cannot currently be modelled by RAIDAR there is little practical guidance that can be given as to priority setting based on the scope of this project and the data available.

Research is ongoing to prioritize the assumptions of the RAIDAR model to identify which are the most important, i.e., the treatment of ionizing chemicals and further evaluating biotransformation rate estimation methods. This is intended to focus further research efforts to reduce uncertainty in risk assessment modelling.

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7. Appendix 1: Input Data for the RAIDAR Model

7.1 Introduction

The RAIDAR model is envisaged as being used by a variety of individuals from different organizations and with different skills. It is thus important that those using the model do so properly and with an appreciation of its strengths, limitations and assumptions. The candidate substances range considerably in properties and in the quantity and quality of available substance-specific data. It is thus necessary that the user be fully informed about the data required for the class of substance being addressed, the assumptions being made and the modelling approach being taken.

In this Appendix an attempt is made to categorize the diverse chemicals on the Domestic Substances List (DSL) and suggest the appropriate input data.

7.2 Chemical categories and data requirements

Table A1.1 lists 14 categories of substances that are encountered in the DSL. For modelling purposes they are grouped into four classes. The four model classes (I - IV) are based on the modelling approach that will be adopted for that type of compound and the nature of the information that is likely to be available. This selection directs the model to accept and process the data correctly.

For class I, data are required for partitioning to all media. For class II, no data are required for air because the substance is involatile. For class III and class IV, the model either can not be run because no significant partitioning occurs or “custom” evaluation is required and direct use of RAIDAR is unlikely to be successful.

Table A1.1. Chemical categorization groups, examples of specific chemical substances and model classes.

Chemical Categorization Groups		Examples	Model Class
1	Reactives	Chlorine, acetic anhydride	IV
2	Conventional organics	Cyclohexanol	I
3	Dissociating organic acids	Carboxylic and phenolic acids	I
4	Dissociating organic bases	Amines	I
5	Gases	Methane	I
6	Involatile organics	Azo dyes, surfactants	II
7	Insoluble organics	Waxes, silicones	III
8	Elements	Copper	IV
9	Inorganic ionizing chemicals, cation of concern	Chromium chloride	IV
10	Inorganic ionizing substances, anion of concern	Sodium cyanide or benzoate	IV
11	Organo-metallic substances	Methyl mercury	IV
12	Geochemically stable substances	Manganese or silicon oxides	IV
13	UVCBs	Turpentine oil, distillates	IV
14	Polymers	Polyvinyl acetate	IV

- UVCBs - Unknown or Variable Composition, Complex Reaction Products, or Biological Materials

Group 1: Reactive Substances

Properties of this group

The substance has a short reaction half-life, i.e., zero to 10 hours. As a result, the "parent" substance has insufficient time to partition between media or be transported any significant distance in the environment. Impacts will be entirely local. Multimedia evaluative models such as RAIDAR are not applicable. Examples of substances in this group are various peroxides which react rapidly, gases such as chlorine and ozone, and acid anhydrides which react or degrade rapidly with water. The "daughter" product(s) may, however, be of concern, but they must be evaluated separately using substance-specific properties. The "daughter" will, of course, have quite different properties from the "parent" and can only be evaluated using property data specific to the "daughter".

Model application and data requirements

No modelling is possible, thus they are assigned to class IV.

Group 2: Conventional Organic Substances

Properties of this group

Included in this group are hydrocarbons, alcohols, ketones and other substances containing, for example, halogen substituents which have measurable vapour pressures, boiling and melting points, solubilities in water (which can be very low), and octanol-water partition coefficients (K_{OW}). They have a known, unique molecular structure and a unique set of physical chemical properties that can be measured or estimated. They usually contain the elements carbon, hydrogen, oxygen, the halogens, nitrogen, sulfur and phosphorus. They do not have dissociating acidic or basic groups such as carboxylic acids or amines. These substances are addressed in Groups 3 and 4. No pKa value(s) are thus applicable. The substance is a liquid or solid at normal environmental temperatures such as 25^{o}C, i.e., the boiling point exceeds 25^{o}C. If the substance has a boiling point lower than 25^{o}C it is classified as a gas (Group 5). If it has no vapour pressure it should be treated as Group 6. If it has no reported solubility in water (as often applies to substances of very high molecular weight) it should be treated as Group 7.

Model application and data requirements

For modelling purposes the substance falls into class I. The following properties are required at the evaluation temperature of 25°C:

Substance name or identifier,

Molar mass (g/mol),

Solubility in water (mg/L) and vapour pressure (Pa), (or dimensionless air-water partition coefficient, $K_{AW,}$ calculated from these two properties or from the Henry=s Law Constant, H ($Pa.m^3/mol$)),

Log octanol-water partition coefficient, log K_{OW},

Degradation half-lives in air, water, soil and sediment (hours),

Metabolic biotransformation half-lives in fish, avian species and mammals (hours), if available.

The octanol-air partition coefficient is calculated as K_{OW}/K_{AW}.

Group 3: Dissociating Organic Acids

Properties of this group

Substances in this category usually contain one or more phenolic, carboxylic or sulfonic acid groups. Examples are phenols and aliphatic acids. The neutral form of the molecule can be designated R-H where R is an organic molecule comprising carbon, oxygen, hydrogen and possibly sulfur, nitrogen and phosphorus. When dissolved in water, the molecule may ionize to form hydrogen ion H^+ and an anion R^-:

$$R\text{-}H \leftrightarrow R^- + H^+$$

The molecule may have several hydrogens that can dissociate.

To estimate the behavior of this type of substance it is essential to have available, in addition to the conventional partition coefficients, an estimate of the dissociation constant, generally designated as pKa. Typical values for chlorinated phenols range from 4 to 8. It is the relative magnitudes of pKa and pH, the environmental acidity, which determine the extent of dissociation.

As a result of this tendency to dissociate the substance may exist in its non-ionic (NI) protonated or neutral form and its ionic (I) de-protonated or charged anionic form. These forms have different properties, for example the neutral form may evaporate from water, but the ionic form does not evaporate. It is thus essential to calculate the fractions in each form. This is done using the Henderson Hasselbalch equation that gives the I/NI ratio in water as:

$$I/NI = 10^{(pH - pKa)}$$

The pH is assumed to be 7.0 in the environment and pKa is the logarithmic dissociation constant. Note that if the substance has several pKa values, the one corresponding to the primary or first dissociation process should be used. This has the lowest value of pKa. For example, if values of 5, 8 and 11 are given, it is best to use 5 and ignore the others, at least for the present screening purposes.

The model calculates the I/NI ratio in the water phase for the specified pKa by assuming a pH of 7.0. Further, it will be assumed that the ionic form does not evaporate from water, sorb to organic matter, or bioaccumulate into lipids. This ratio is assumed to apply in all water phases in the environment.

There can be ambiguity about the values of the solubility in water and K_{OW}. If experimental data are used, the pH should also have been specified to clarify if the properties are those of the non-ionized or non-ionized plus ionized forms. If the latter applies, the solubility and K_{OW} of the non-ionized form should be calculated and these values entered as input. The model will then "correct" for ionization. If the data are from an estimation method, the values generated will correspond to the molecular structure provided to the method. For example, a SMILES notation should refer to the non-ionized form, not the ionized form. These data can be input directly. The model will assume that the estimated data apply to the non-ionized form and it will "correct" for ionization.

Model application and data requirements

For modelling purposes this substance falls into Class I, and specifically as an organic acid substance that may ionize. The model estimates the distribution of this substance in four compartments, air, fresh water, soil, and sediment using a steady-state approach as described earlier for Group 2 substances. The data required by the model are those listed earlier and the dissociation constant, pKa, at the evaluation temperature of 25^oC.

Group 4: Dissociating Organic Bases

Properties of this group

Included in this group are amines which associate with a hydrogen ion to form an ionic species such as a quaternary amine ion. The parent compound can be designated RNH_2 and it reacts as follows:

$$RNH_2 + H^+ \leftrightarrow RNH_3^+$$

To estimate the behavior of this type of substance it is essential to have available, in addition to the conventional partition coefficients, an estimate of the dissociation constant, generally designated as pKa. It is the relative magnitudes of pKa and pH, the environmental acidity, which determine the extent of dissociation.

Model application and data requirements

The substance is treated, for modelling purposes as being in Class I, and specifically as an organic base that may ionize. The model estimates the distribution of this substance in four compartments, air, fresh water, soil, and sediment using a steady-state approach as described earlier for Group 2 and 3 substances. The data required by the model are those listed earlier and the dissociation constant, pKa, at the evaluation temperature of 25^oC.

Group 5: Gases

Properties of this group

These substances have boiling points below the evaluation temperature of 25^oC. Included are inorganic gases such as nitrogen and sulfur oxides, hydrocarbons with four or less carbons, freons and halogen gases. If the gas reacts rapidly with water it should be treated in Group 1 (reactive substances). Substances in this group are likely to partition primarily into the atmosphere and they tend to evaporate rapidly from soils and water.

Model application and data requirements

This substance is treated, for modelling purposes as being in Class I. Data required by the model at the evaluation temperature of 25°C are as listed earlier for Group 2 substances. Two properties are of particular importance and the corresponding data must be carefully selected. Vapour pressure P (Pa) and solubility in water S (mg/L) are used to estimate the air-water partition coefficient K_{AW}. Alternatively, K_{AW} may be entered directly thus avoiding the need for individual P and S data. A problem can arise because S may be measured at atmospheric pressure thus P is 101,325 Pa, or it may be measured at a higher vapour pressure such as 200,000 Pa. It is essential to know which solubility applies. The other data required are molar mass, octanol-water partition coefficient and compartment transformation half-lives.

Group 6: Involatile Organic Substances

Properties of this group

This group includes involatile substances such as surfactants and dyes. The substances may have a negligible vapour pressure and thus no air-water partition coefficient. The dyes are designed to react with, sorb to, or dissolve in, materials such as fabrics, papers and plastics. In many cases they are sparingly soluble in water and solubility may not be available. The octanol-water partition coefficient may also be in doubt. Those of high molar mass may have a low and possibly unknown vapour pressure. They may also dissociate in water, i.e., they have reported pKa values.

If reliable data are available for both solubility and vapour pressure they should be treated as Class I substances and assigned to Group 2. If the chemicals have solubility data but no vapour pressure they can be treated as Class II and should be assigned as Group 6. If they have vapour pressures but no solubility they should be treated as Class III and assigned to Group 7. If neither are available they should be considered as Class IV and assigned to Group 12.

Model application and data requirements

For modelling purposes these substances fall into class II. The following properties are required at the evaluation temperature of 25°C:

Substance name or identifier,
Molar mass,
Log octanol-water partition coefficient, log K_{OW},
The air-water partition coefficient is assumed to be negligible, i.e., 10^{-11},
An octanol-air partition coefficient will be calculated and will be very large, i.e., 10^{11},
Degradation half-lives in water, soil and sediment (hours),
Metabolic biotransformation half-lives in fish, avian species and mammals (hours), if available.

Group 7: Insoluble Organic Substances

Properties of this group

Many of these substances are of petroleum origin or they are natural oils from vegetable or animal sources. Included are silicones, waxes, greases and solid oils which liquefy above 25°C. They may comprise several individual chemical substances, often in variable quantities. Some may also be classified as UVCBs. They have boiling points or vapour pressures thus they do partition into air, but they have negligible solubility in water, thus no partition coefficients with respect to water can be defined. Because of the low concentrations in water existing bioaccumulation equations do not apply.

Model application and data requirements

These chemicals are Class III and classified as “model-difficult”. A custom evaluation is required and it is not recommended that RAIDAR be used for assessments.

Group 8: Elements

Most of the elements of atomic number less than 18 (argon) are reactive and form either gases or other substances when in contact with water. Most of the other elements are metals or metalloids. They may be essentially inert unless converted to an ionic form.

Model application and data requirements

Because of the unique properties of these elements, and because some are highly toxic, a custom evaluation is required and it is not recommended that modelling be attempted. They are thus assigned to class IV.

Group 9: Inorganic ionizing substances, cation of concern

Properties of this group

Included in this group are inorganic substances that have measurable solubilities in water and thus form concentrations of metal ions in solution. The primary concern is for the environmental fate of these ions. Examples are soluble Cu, Pb, Zn, Ni and Co ions or compounds. Ammonium salts are best treated as Class 10 in which allowance is made for chemical conversion of the ion.

Model application and data requirements

Because of the unique nature of these substances RAIDAR is not recommended for use. The reason for this is that ion partitioning is influenced by pH, oxidation status, the nature and concentration of organic matter which may be in dissolved, colloidal or particulate form, competition from other metals (notably Ca and Mg) and the presence of mineral oxides and sulfides. The simplifications and generalizations that apply to organic substances do not apply. They are thus assigned to class IV.

Group 10: Inorganic ionizing substances, anion of concern

Properties of this group

Included in this group are inorganic substances that have measurable solubilities in water and thus can establish concentrations of anions in solution. Examples are cyanide and benzoate ions. It is these anions that are of concern.

Model application and data requirements

These substances are not recommended for RAIDAR modelling since they require “custom” evaluation. They are thus assigned to class IV.

Group 11: Organo-metallic substances

Properties of this group

Included in this group are substances in which a metal moiety is covalently bound to an organic moiety. These chemicals do not ionize, but they may be subject to chemical conversion to other species including metal ions. Examples are certain iron, tin and cobalt organo-metallic and organo-mercury compounds.

Model application and data requirements

The behaviour of organo-metallic compounds is sufficiently complex and the species are of such toxicity that separate evaluation is required and it is recommended that RAIDAR not be used. They are thus assigned to class IV.

Group 12: Geochemically stable substances that are involatile and sparingly soluble in water

Properties of this group

Included in this group are mineral oxides, sulfides, silicates, carbonates and other geochemically stable substances, insoluble dyes and pigments. Examples are silicon dioxide (sand), aluminum silicates such as clays, carbonates and sulfates such as lime and gypsum. They are usually crystalline and display negligible solubilities in water. They are also involatile. As a result they remain in the same chemical form during environmental exposure although strong acid or alkaline conditions or heat may result in chemical changes. They have no tendency to partition into other media. If ingested, they are probably egested without any significant assimilation.

Model application and data requirements

Little information can be gained by modelling their fate thus they are assigned to Class IV and no modelling is undertaken.

Group 13: UVCBs (Unknown or Variable Composition, Complex Reaction Products and Biological Materials)

Properties of this group and assessment strategies

Included in this group are various petroleum distillates and natural oils and waxes. The assessment depends on knowledge of the chemical composition and on the available property data. Biologicals should not be modelled. The following strategy is suggested.

1. The UVCB can be treated as a single substance with defined properties. This substance may be an ingredient of the mixture or it may be a specific substance with similar properties, or it may be fictitious but has appropriate estimated properties. If the required property data are available the UVCB is treated as a single Class I substance and assigned to Group 2.

2. The UVCB can be treated as a mixture of defined proportions of two or more substances of defined identity and properties (e.g., x% and y% but care must be taken to establish if the percentage is on a mass, volume or molar basis). An evaluation is done for each of the substances in turn and the final concentrations are weighted according to the fractions present in the original UVCB. This final weighting must be done "by hand" by the user. In the interests of simplicity, the number of substances should be minimized. Several of Group 2 evaluations are thus required.

3. A "worst case" substance is selected, probably on the basis of its toxicity. The entire mixture is treated as consisting of that substance. In the event that the substance is say 10% of the total, then the concentrations can be adjusted by this percentage. The substance is then evaluated as Group 2.

4. If the above options are not applicable the UVCB is assigned to Class IV and no modelling is possible.

Group 14: Polymers

Properties of this group and assessment strategies

Included in this group are high molar mass weight polymers such as polyvinyl chloride (PVC), polyethylene and methylmethacrylate. Many of these are stable and essentially involatile and insoluble in water, thus they do not experience partitioning or appreciable degradation. There may be concern about residual monomer or plasticizing or other agents but these should be treated as the specific chemical substance, generally as group 2. Some have polar groups resulting in appreciable solubility in water. Others may be present in emulsion form. Because of their unique properties modelling is not recommended.

Summary of Required Input Data

Class I "Conventional organic substances and includes organics, dissociating organic acids and bases, gases, organic oils and some organic dyes"

Molar mass, solubility in water, vapour pressure (or K_{AW}), K_{OW}, half-lives in environmental and biological compartments, and pKa if applicable.

Class II "Non volatile organic substances"

Molar mass, partition coefficients between water and soil, sediment, water particulates and biotic phases. Half lives in water, soil and sediment and biota.

Class III "Non soluble but possibly volatile organic substances"

The model is not recommended for use.

Class IV "Pigments, minerals, inorganic ionizing chemicals, organo-metallics, etc"

The model is not recommended for use.

8. Appendix 2: Input Data Reliability

8.1 Introduction

In this appendix guidance is provided on data reliability, especially with a view to identifying values that are outside the typical range of values, i.e., they are “extreme”. Most of the DSL data have necessarily been obtained from existing Environmental Substances Databases or from estimation or quantitative structure-activity relationship (QSAR) methods, especially using the EPA sponsored EPI Suite programs from the Syracuse Research Corporation (SRC). Although numerous QSARs have been published in the literature, they are often specific to classes of compounds, thus their applicability to substances outside the training set is uncertain. The EPI Suite programs are thus very valuable sources of data on a wide variety of compounds. The prediction methods are based mostly on group or bond contribution schemes based on linear free energy assumptions in which the molecule is broken down into a number of “building blocks” and each “block” is assigned a property. These are added in quantities dependent on the number of “blocks” present in quantities dictated by the input information which may be a SMILES entry to characterize molecular structure. In some cases adjustments are made to characterize features such as the proximity of functional groups. Often, empirical data are provided which are, by definition, more accurate if done properly. It is generally accepted that empirical data should be used in preference to predicted data.

8.2 Limiting and extreme values of data

When scrutinizing the input data it is desirable as a first step to identify for each property a Minimum Credible Value (MinCV) as a value below which any estimated values should be regarded as highly suspect. The actual value may truly lie below the MinCV, but its magnitude is highly uncertain. A Maximum Credible Value (MaxCV) can also be identified. More thorough scrutiny could involve comparison of two or more properties that lie between these limits. For example, a low solubility generally results in a high K_{OW}, thus a high solubility and a high K_{OW} may be inconsistent. A value of 10^{-9} Pa is regarded as a minimum *experimental* value (MinEV) of a measured vapour pressure and reflects a figure below which very few experimental data have been reported, although some values below this have probably been measured accurately in a research setting. A value of 10^{-10} Pa is regarded as a minimum *credible* value (MinCV) and reflects the figure below which, it is believed, no accurate data have been reported. Values below this may be real, but they are highly suspect since they are beyond present experimental or predictive limits.

A procedure that is being increasingly implemented in environmental fate models is to provide the user with a warning if the suggested value lies between the MinEV and the MinCV, but it will accept the value. For values below the MinCV a warning is also issued and the user is presented with two options. Either the MinCV is substituted for the suggested value or the user is required to substitute another value, which may be the originally suggested value. When the program is run in batch mode the MinCV should, we suggest, be automatically substituted and the output flagged that this has been done. For any value below the MinEV the output is also flagged. The aim is to impart credibility to the program by forcing it to acknowledge that in the range of extreme values there may be a calculation that is subject to considerable error. This facility does not presently exist within the RAIDAR model and for this project extreme estimated physical-chemical values have been replaced with minimum and maximum values.

These limiting values must be selected using professional judgment. Values are suggested here for discussion purposes but scrutiny by others is desirable. Consideration should be given to the policy implications of this approach since it raises issues about the credibility of the assessment. For example, if a value below the MinCV is obtained from an estimation method or suggested by industry, is the assessor justified in using it or substituting another value? Are the suggested MinEV and MinCV reasonable reflections of the state of the science?

Class I Substances

We address and make suggestions about seven properties namely, (1) vapour pressure, (2) solubility in water, (3), air-water partition coefficient, (4) octanol-water partition coefficient, (5) dissociation constant, pKa, (6) molecular weight, (7) degradation half-lives.

(1) Vapour pressure data

Vapour pressure, preferably expressed in Pa, is essentially the solubility of the substance in air or in a gas phase. It can be regarded as indicative of the concentration in the gas phase in equilibrium with the pure solid or liquid substance. Vapour pressures are meaningful for substances that have critical temperatures above environmental temperatures. As a result, substances such as methane do not possess a vapour pressure at 25°C since liquid and gaseous methane can not co-exist at 25°C. Other volatile substances such as propane can exist as liquids at 25°C but since their boiling point is lower than 25°C, the liquid can only exist at higher than atmospheric pressures. A vapour pressure can be measured at 25°C but it will exceed atmospheric pressure of approximately 10^5 Pa. For solid substances the vapour pressure reported may be of the solid or in some cases of the hypothetical sub-cooled liquid. The user should be clear about the state of the chemical in such situations since errors can result from mis-interpretation of data.

Vapour pressure is primarily used in models to calculate the air-water partition coefficient, K_{AW}, also using the solubility in water. For gases, the solubility in water depends on the pressure of the gas (Henry's Law), thus to calculate K_{AW} requires assurance that the vapour pressure and solubility refer to the same temperature and pressure. Often vapour pressure is estimated using a chromatographic retention time method that actually measures an air-substrate partition coefficient. This can be correlated against vapour pressure using reference substances of known vapour pressure. These estimated vapour pressures are of the liquid state chemical, even when the substance is solid. It is erroneous to calculate K_{AW} from a ratio of a liquid vapour pressure to a solid solubility. In some cases the solubility of gases is measured and reported at atmospheric pressure. The data must be scrutinized to assure that the data are consistent in this regard. One approach is to enter K_{AW} or a Henry's Law Constant directly. Fortunately, there are few gases on the DSL list thus it is not an onerous task to check each one for consistency. Any DSL vapour pressure exceeding a MaxCV of 10^5 Pa should be carefully assessed.

The experimental determination of low vapour pressures is very demanding because concentrations in the gas phase are very low. Rarely are pressures lower than 10^{-9} Pa actually measured, although data from higher temperatures (at which pressures are higher) can be extrapolated down to lower temperatures and GC retention time methods can be used. A pressure of 10^{-9} Pa corresponds to about 10^{-13} g/L or less than 1 pg/L. These substances are sparingly volatile, their concentrations in air are very difficult to measure and when present in the vapour phase they are mainly associated with aerosol particles. Examples are benzo(a)pyrene and DDT. Pigments and dyes are particularly problematic in this regard because there is little or no incentive to measure their vapour pressure, few data are available and estimation methods are suspect.

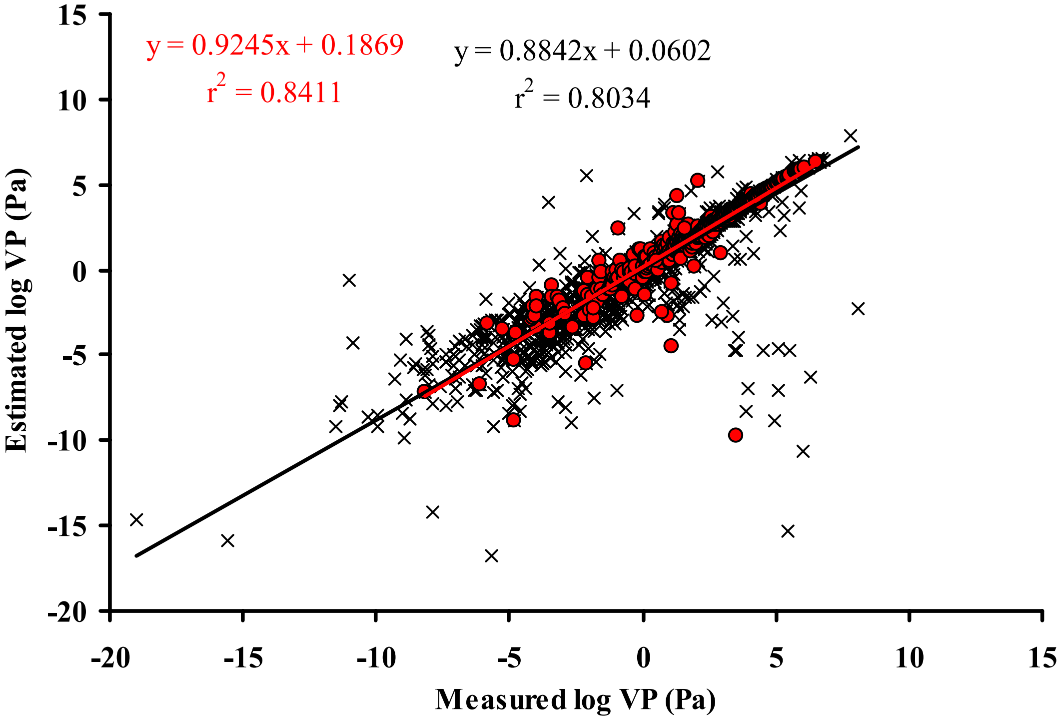

Figure A2.1. A comparison of estimated and measured vapour pressure values for organic chemicals in the DSL (red circle) and SRC (black cross) databases (see Table A2.1).

Figure A2.1 compares estimated vapour pressures with corresponding measured values from DSL and SRC databases. There are very few measured values below 10^{-9} Pa. In some cases there is a very large discrepancy between estimation methods and empirical data.

Table A2.1 lists further summary statistics and selected minimum and maximum values used in this report. In summary, data below a MinEV of 10^{-9} Pa should be carefully scrutinized and data below a MinCV of 10^{-10} Pa should be viewed with extreme caution. The implications of using extreme values and substituted limiting values should be understood, preferably by undertaking a specific sensitivity analysis.

Table A2.1. Statistical summary of vapour pressure measurements and estimates from the DSL and SRC databases and selected values (n - number of measured observations in databases for selected temperature ranges).

Vapour pressure, P (Pa)	DSL database	SRC database
n	439	1839
Experimental temperature range	18-32°C	15-32°C
Measured minimum value	6.67E-09	1.07E-19
Measured maximum value	3.27E+06	1.29E+08
Estimated minimum value[a]	1.99E-10	1.80E-17
Estimated maximum value[a]	3.44E+05	7.08E+07
Minimum estimated value for all DSL chemicals	1.87E-43	N/A
Maximum estimated value for all DSL chemicals	7.08E+07	N/A
Selected minimum value for RAIDAR model	1.00E-09	N/A
Selected maximum value for RAIDAR model	1.00E+05	N/A

[a] corresponding to the measured values

(2) Solubility in water

As with vapour pressure, problems arise with both the high and low values. Substances such as ethanol are totally miscible with water thus no solubility can be measured, or is meaningful. In such situations the DSL data show values of 10^6 mg/L which is simply the density of water. From a physical-chemical perspective the key quantity is the infinite dilution activity coefficient of the substance in water. This can be measured, usually from the Henry's Law Constant. Assuming a value of 10^6 mg/L can be misleading but when this value is used in models it probably leads to the correct conclusion regarding fate.

Many organics are sparingly soluble in water, experimental values extending down to about 10^{-4} mg/L or 10^{-4} g/m^3. It is very difficult to measure these values because even a minute quantity of colloidal or pure phase material in the water phase can confound the determination. Extreme care is required to eliminate such problems. These substances also tend to associate with vessel surfaces and the air-water interface causing experimental problems. Pigments and dyes are problematic because, by their very nature, they are sparingly soluble in water.

Figure A2.2 compares estimated aqueous solubility values with corresponding measured values from DSL and SRC databases. The plot illustrates that few measured solubilities lie below 10^{-5} mg/L or g/m^3. The lower limit for reliable measurement and prediction is about 10^{-5} mg/L thus any lower values should be treated as suspect.

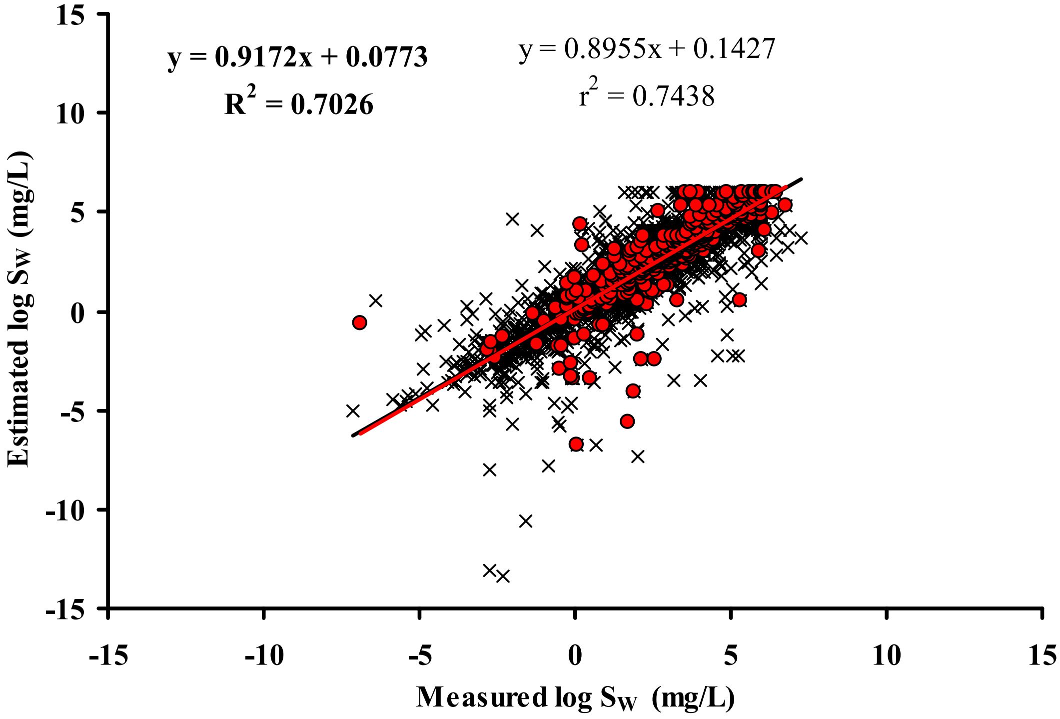

Figure A2.2. A comparison of estimated and measured aqueous solubility values for organic chemicals in the DSL (red circle) and SRC (black cross) databases (see Table A2.2).

Table A2.2 lists further summary statistics and selected minimum and maximum values used in the report. We suggest a MinEV of 10^{-5} mg/L and a MinCV of 10^{-6} mg/L. Model results obtained above the MaxCV of 10^{6} mg/L value should be flagged and if a more accurate assessment is justified an empirical value of K_{AW} should be sought. In summary, any solubilities above 10^{5} mg/L or below 10^{-5} mg/L should be carefully scrutinized.

Solubility is used in conjunction with vapour pressure to estimate the air-water partition coefficient, K_{AW}, thus it is preferable to input this value directly. Thus if both quantities are suspect, their ratio is doubly suspect. It may be desirable to consider limits on K_{AW} calculated from low values of vapour pressure and solubility.

Table A2.2. Statistical summary of aqueous solubility measurements and estimates from the DSL and SRC databases and selected values (n - number of measured observations in databases for selected temperature ranges).

Aqueous solubility, S (mg/L)	DSL database	SRC database
n	380	2444
Experimental temperature range	15-30°C	15-30°C
Measured minimum value	1.35E-07	7.40E-08
Measured maximum value	6.14E+06	1.82E+07
Estimated minimum value[a]	1.61E-07	4.27E-14
Estimated maximum value[a]	1.00E+06	1.00E+06
Minimum estimated value for all DSL chemicals	0	N/A
Maximum estimated value for all DSL chemicals	1.00E+06	N/A
Selected minimum value for RAIDAR model	1.00E-05	N/A
Selected maximum value for RAIDAR model	1.00E+06	N/A

[a] corresponding to the measured values

(3) Octanol-water partition coefficient

Again, problems arise with high and low values. It is very difficult to measure log K_{OW} values above 7 and few reliable data extend beyond 8. Predicted values above 9 should be regarded as suspect. The experimental problem is avoidance of the formation of micelles in the water phase which may contain some octanol and associated dissolved chemical. Indeed octanol is to some extent a surface active substance. There is some debate as to whether log K_{OW} values in the range of 11 to 12 and above are even possible because molecules which are so hydrophobic may not be very soluble in octanol or in lipid phases. This debate is somewhat academic because there are doubts about the extent to which octanol can be used to indicate partitioning into lipids and organic matter for such substances, this being the primary incentive for using K_{OW}.

This issue is important because K_{OW} is used to estimate bioaccumulation in plants and animals, thus using an erroneously high value may overestimate exposure via dietary sources. This is offset to some extent by expressions in models that reduce assimilative efficiencies for high K_{OW} range and by the onset of reduced bioavailability.

It is possible to have very low K_{OW} values, less than 1.0, thus log K_{OW} can be negative. For example, lysine (CAS 56-87-1) has a log K_{OW} of -3.05 and a glycine salt (CAS 64-02-8) has a predicted value of -13.17. The implication is that these substances prefer to dissolve in water, rather than octanol. Models will thus predict little or no sorption to soils, sediments or biota which may be correct, but the absolute values of sorption should be regarded as suspect. It seems likely that these substances will partition into the aqueous phases associated with these sorbents, for example into the aqueous blood phase of animals or transpiration streams of plants.

Figure A2.3 compares estimated octanol-water partition coefficients with corresponding measured values from DSL and SRC databases. There are very few measured values below 10^{-4} and very few measure values above 10^{9}, thus these values seem reasonable as the MinEV and MaxEV, respectively. It is suggested that a MinCV be 10^{-5} and a MaxCV be 10^{10}.

Table A2.3 lists further summary statistics and selected minimum, i.e., 10^{-4}, and maximum, i.e., 10^{9}, K_{OW} values used in the report. Values below and above this range should be flagged and carefully scrutinized.

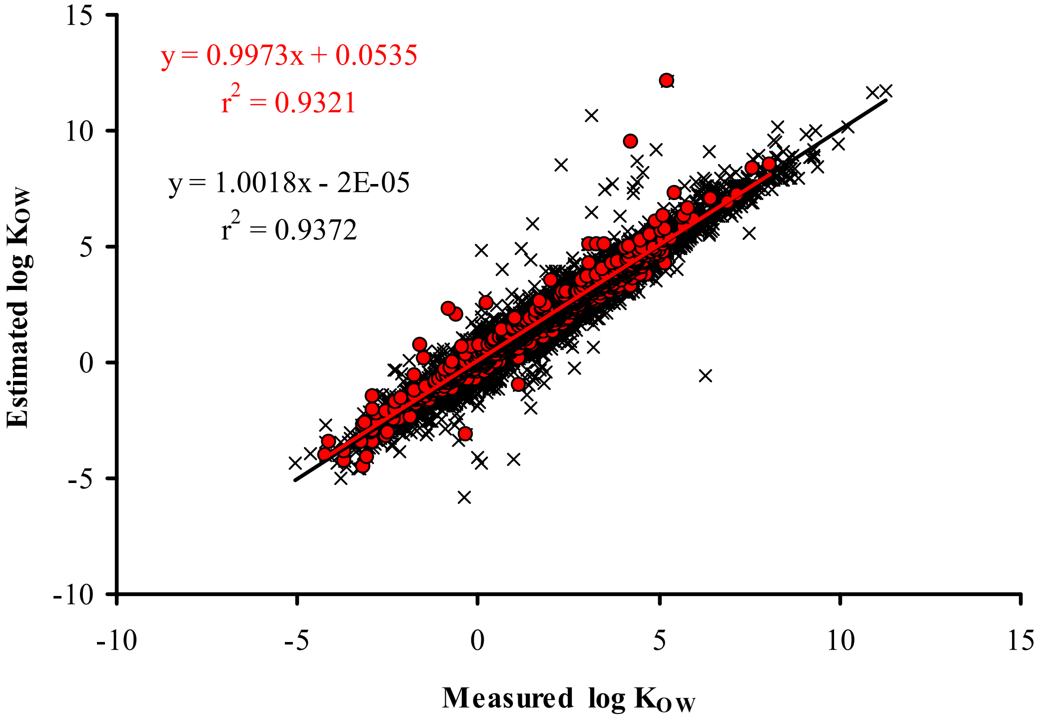

Figure A2.3. A comparison of estimated and measured logarithmic octanol-water partition coefficient, log K_{OW}, for organic chemicals in the DSL (red circle) and SRC (black cross) databases (see Table A2.3).

Table A2.3. Statistical summary of octanol-water partition coefficient, K_{OW}, measurements and estimates from the DSL and SRC databases and selected values (n - number of measured observations in databases for selected temperature ranges).

Log K_{OW} (unitless)	DSL database	SRC database
n	888	11135
Experimental temperature range	15-30°C	15-30°C
Measured minimum value	-4.2	-5.8
Measured maximum value	8.06	11.29
Estimated minimum value[a]	-4.49	-5.8
Estimated maximum value[a]	12.11	12.11
Minimum estimated value for all DSL chemicals	-22.46	N/A
Maximum estimated value for all DSL chemicals	48.68	N/A
Selected minimum value for RAIDAR model	-4.0	N/A
Selected maximum value for RAIDAR model	9.0	N/A

[a] corresponding to the measured values

(4) Air-Water partition coefficient

In some cases the dimensionless air-water partition coefficient, K_{AW}, or the Henry's Law Constant, H, is used directly. K_{AW} is H/RT where R is the gas constant and T is the absolute temperature. Most organics have K_{AW} values below 1, and only very volatile but sparingly soluble substances, such as freons, have higher values. Oxygen has a K_{AW} of approximately 30 and is an extreme case. There are estimation methods for K_{AW} but there are few estimations for DSL chemicals, i.e., about only 200 of the 11,000 organics. It is suggested that a MaxEV of 5 be adopted with a MaxCV of 50. No minimum values are suggested.

(5) Dissociation constant pKa

This value can be calculated quite accurately for many organic molecules including acids and bases, the latter usually being reported as pKa rather than pKb since (pKa + pKb) is 14. The ratio of ionic (I) to non-ionic (NI) species is calculated using the Henderson-Hasselbalch equation, namely:

$$\log(I/NI) = pH - pKa$$

where pH is that of the solution. When pH equals pKa the ratio is 1.0. Relatively low values of pKa, say 4, imply extensive ionization at environmental pH values of 6 to 7.

Some compounds have multiple pKa values derived from several functional groups or several extents of dissociation but the lowest value generally dominates and it is common to ignore the higher values, except when high accuracy is justified.

The difficulty is not the physical chemistry but rather using the "I/NI" ratio correctly in the model. The usual assumption for organics is that only the non-ionic (neutral) form participates in sorption to organic media such as lipids and humic materials. This is known to be erroneous because the ions do partition but a generally applicable predictive approach for sorption of ionic species is not available. It is certain that the ionic form will interact with other ionic moieties in mineral and organic phases but quantifying these processes is problematic. As a result predictions of partitioning from the aqueous phase should be viewed with caution, especially if the I/NI ratio exceeds 10.

(6) Molecular weight (or more correctly, molar mass)

This property should have an unequivocal value, but in some cases there is a question about the identity of the substance. For example, on the DSL CD-ROM "methane, sodium salt" (CAS 124-41-4) is attributed a molar mass of 32.4 which is the molar mass of methanol. Formic acid, calcium salt is assigned a value of 46.3, the value for formic acid. It appears that in such cases the contribution of the metal has been ignored. For UVCBs this quantity is particularly problematic since the substance is usually a mixture of variable composition. In some cases the mixture is identified as being of two dissimilar substances such as a metal salt and an organic mixture. There seems to be little alternative to a check of these data by a competent and skeptical chemist.

(7) Half-lives

Half-lives for transformation reactions in air are generally calculated from QSARs describing the rates of reaction with hydroxyl radicals, ozone and oxides of nitrogen. Because of the extensive empirical database these values are regarded as quite accurate. It should be noted that use of a half-life assumes first-order behaviour but these reactions are generally second order with an assumed constant concentration of the oxidizing agent. The problem is that the concentration of the oxidizing agent that can be diurnally and seasonably variable. The inputs selected for this report assume a 12 hour sunlight period.

Much longer half-lives exist in water, soils and sediments. This issue is not as important as it may appear because these persistent substances are often removed from the regional environment by advection rather than reaction, except from soils and sediments. It is common practice to estimate a biodegradation half-life in water then apply a ratio to that in soil and sediment. For example, the US EPA recently revised its practice of using a water:soil:sediment ratio of 1:1:4 to a ratio of 1:2:9. This should be viewed as a convenient, approximate expedient to be used in the absence of actual empirical data. Ratios of 1:1.5:6.5 were selected for these simulations. When there is reaction by other mechanisms such as hydrolysis these rate data should also be included as was done in this study.

Any half-life less than 0.1 to 0.2 days (2.4 to 4.8 hours) indicates a very reactive substance which will not survive long enough to migrate widely throughout the environment. It can best be classified as “reactive” and there is little justification for modelling. It may, however, be desirable to model the degradation product. For example, phosphate esters are assigned half-lives in air of about 0.1 days thus presumably the ester linkage is rapidly severed releasing the organic moiety which will likely survive for a longer period of time.

At this time we are unable to suggest limiting values, but this should be addressed.

8.3 Summary and recommendations

Given the necessity of assessing a large number of substances and the paucity of empirical data on their partitioning and reactivity properties, it is necessary to use estimation methods. These methods are generally based on a “training set” of well-studied substances, but they are necessarily being applied to substances with structures and properties outside the range of the “training set”. There is thus a significant potential for error when estimating properties. This can translate into error in fate and exposure estimation and in prioritization.

A *minimal response* is simply to flag any predicted extreme properties as being outside the range of accepted values. The assessment results obtained using such data should be flagged as possibly erroneous and a cautionary note can be added to the assessment.

In such flagged cases, and assuming that an evaluation is required, two general approaches can be adopted. First, the raw data can be adopted and used in the assessment, the risk of error accepted and the results flagged appropriately. Second, the extreme data point can be adjusted by hand to the boundary of the extreme region to render it in a region in which the model is known to give realistic results. Again the result should be flagged. This second option has the advantage that it will be clear that the results are being influenced by this intervention and are thus somewhat artificial, but it can be asserted that the fate and exposure assessment probably leads to the correct general conclusion regarding the sources and order of magnitude of the exposures.

Both approaches justify, if not require, that the model be tested with data lying in the extreme region to establish that it is robust and does not give unreasonable results.

9. Appendix 3: Implications of Changes in Scale of the RAIDAR Model

9.1 Introduction

In this appendix the issue of how the RAIDAR model can be used to describe the fate of chemicals at a variety of scales, i.e., areas differing from the "standard" value of 10^5 km^2, especially as the area is reduced in an attempt to simulate smaller regions experiencing more intense chemical use or release. The appendix has two parts. In the first part the theory of how changes in scale are expected to affect the model results is discussed. In the second part the RAIDAR model is applied at various scales to a selected chemical and the results are discussed.

9.2. Theoretical analysis

The "standard" RAIDAR model simulates the fate of chemicals in an area of 10^5 km^2. This area contains water bodies of area 10^4 km^2 or 10% of the total area. The height of the atmospheric compartment is 10^3 m and the water depth is 20 m. The advective flows of air and water into and out of the region are defined using residence times of 100 h for air and 10^5 h for water.

The volume of air is thus 10^5 km^3 or 10^{14} m^3 and the volume of water is thus 200 km^3 or 200 x 10^9 m^3. The flow rates are these volumes divided by the corresponding residence times, namely

Air	10^3 km^3/h or 10^{12} m^3/h
Water	0.002 km^3/h or 2 x 10^6 m^3/h

This flow rate of air corresponds to a velocity of air through the "side" of the atmosphere which has an area of about 300 km by 1 km or 300 km^2 (the square root of 10^5 km^2 is approximately 300 km). The air velocity is thus 10^3 km^3/h divided by 300 km^2 or approximately 3 km/h which is a low but reasonable wind speed. Alternatively this velocity can be calculated as the ratio of the width of the environment (300 km) to the residence time of the air (100 h).

Regarding water flow, for comparison the St. Lawrence River flow is approximately 8000 m^3/s or 2.88 x 10^7 m^3/h, which is about an order of magnitude larger than the value used in RAIDAR. We believe using this value would distort the results by implying excessive dilution of the water resulting from high advective flow. The default RAIDAR rainfall of 0.876 m/year over the area of 10^{11} m^2, results in a precipitation flux of approximately 10^{11} m^3/year or 10^7 m^3/h which is a factor of 5 greater than the water flow rate. The lower flow rate was selected to introduce a degree of conservativeness in the model and is, we believe, appropriate for evaluative purposes.

During the development of the original EQC and RAIDAR model various areas, depths, volumes and residence times were considered and the values ultimately selected are viewed as being conservative and thus appropriate for priority setting and preliminary evaluation purposes.

If the user elects to reduce the area of the environment, say by a factor of 10 to 10^4 km^2 and retains the same emission rate, height, depth and residence times then the flow rates of air and water will be reduced by a factor of 10. This will cause rates of advective loss to be reduced and the masses, concentrations and exposures of chemical in the environment will increase. The magnitude of this increase will likely be less than a factor of 10 because rates of degrading reactions will increase as a result of the increase in chemical inventory. Essentially, the chemical is constrained to smaller area and will increase in concentration.

If the user compensates for the slower advection rates by also reducing the residence times by a factor of 10 this will retain similar advective flows and chemical quantities will not increase as much, but the increase will depend on the relative rates of advection compared to internal losses by reaction and intermedia transfer. It is noteworthy that reducing both the area and residence time by a factor of 10 implies that the flow velocity of air will increase by a factor of approximately 3 because the "side of the square" changes to 100 km (instead of approximately 300 km) and the transit time will be 10 h (instead of 100 h), thus the velocity increases to 10 km/h (instead of 3 km/h). This can be demonstrated mathematically using the simple mass balance in Figure A3.1, which applies to air. A similar argument can be applied to the water balance.

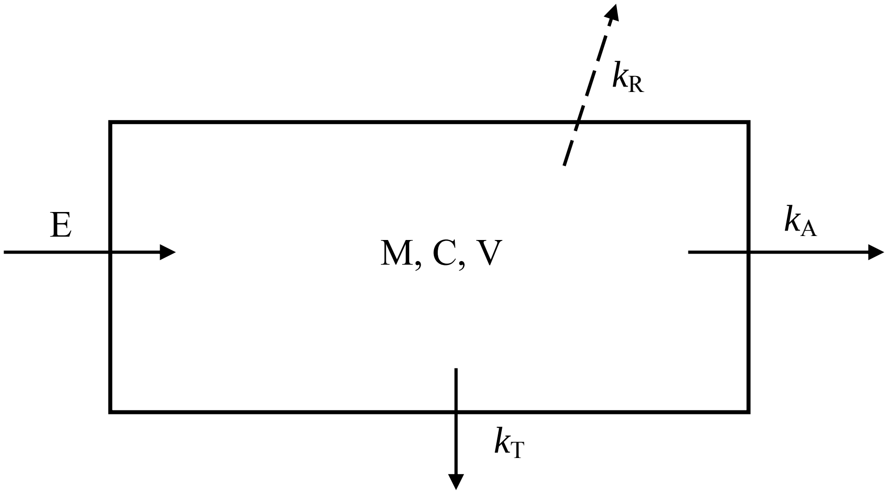

Figure A3.1. An illustration of the steady state mass balance for chemical input and output in a defined multimedia compartment, e.g., air.

A steady-state mass balance gives

$E = M(k_A + k_R + k_T)$

where E is the emission rate, M is the mass in the air, C is the concentration in air, V is the air volume and M = CV. The rate constants are k_A for advection which equals $1/\tau$ where τ is the residence time, k_R is for reaction and k_T is for irreversible transfer to other media. The reaction rate constant is independent of the size of the environment and the flow rate. The transfer rate constant k_T can be shown to be U/h where U is a transfer velocity (m/h) and h is the height or depth of the compartment. It is affected only if the atmospheric height or water depth is changed.

Applying these equations to two conditions subscripted s for the standard conditions and i for the new conditions it can be shown that

$C_i/C_s = (E_i/E_s)(V_s/V_i)(k_R + k_T + 1/\tau_s)/(k_R + k_T + 1/\tau_i)$

If we introduce factors F for the change from s to i of F_A for area with equal height, i.e., (V_i/V_s) and F_T for advection residence time, i.e., (τ_i/τ_s) and F_E for E_i/E_s and we designate $(k_R + k_T)$ as K

$C_i/C_s = (F_E/F_A)(1 + K\tau_s)/(1/F_T + K\tau_s)$.

In the earlier examples F_A and F_T were 0.1 corresponding to a factor of 10 decrease in both area and residence times. This equation has the following properties. If F_E is 1.0 (equal emissions) and K is small compared to τ_s (most loss is by advection) then if C_i/C_s is approximately F_T/F_A and C will be unchanged if these factors are equal. The change in area is compensated for by the change in residence time. If F_E is 1.0 and K is large compared to τ_s (most loss is internal), usually because of fast reaction, then C_i/C_s is $1/F_A$ and an increase in area causes a proportional decrease in C. The amount of chemical in the environment is unchanged but the concentration falls because of greater dilution in a larger volume.

For intermediate situations the concentration changes but not proportionally to F_T or inversely proportionally to F_A. As the environment becomes larger this increase produces a less than proportional decrease in C. For the case of most interest in which the size of the environment decreases (say by a factor of 10) and both F_A and F_T are less than 1, i.e., both are 0.1, than C will increase. For example if $K\tau_s$ is 1.0, i.e., rates of internal and advective losses are equal, than a factor of 0.1 change in F_A and F_T will cause C to increase by a factor of 10 x 2/11 or 1.8. Internal loss processes become less important and advection becomes more controlling. Specifically, whereas in the standard case advection and internal losses were equal, advection now accounts for 91% of the losses and internal processes account for 9%. This undoubtedly reduces the ability of the RAIDAR model to discriminate between chemicals because all chemicals are subject to advective losses, regardless of chemical properties.

The model can however be used to estimate concentrations in regions differing in size from the standard environment. This requires careful selection of residence times. The obvious and simple strategy is to increase or decrease both area and residence time by the same factor, but with an awareness that advection will become more important.

9.3 Limits to area reduction

As the area becomes very small the assumption of the 10^3 m atmospheric height becomes unrealistic. Reducing the atmospheric height to 100 m has the effect of causing more chemical to transfer to soil, vegetation and water. Ultimately as the area is reduced in size to 10 km across or less a conventional plume dispersion calculation becomes more appropriate as detailed in the text by Turner[1].

A plot of the Pasquill-Gifford vertical dispersion parameter against downwind distance (e.g. Fig. 2.4 of Turner) shows that for stability classes B and C, the height of 10^3 m is reached at a downwind distance of about 10 km. At shorter distances the chemical plume is not capable of mixing to the entire atmospheric height. At 1 km the plume may reach only 100 m. In our judgment, the following recommendations can be made regarding scales.

Standard scale of 300 km	10^3 m applies and simulation is satisfactory
Reduced scale of 100 km	10^3 m applies and simulation is satisfactory
Reduced scale of 30 km	10^3 m applies and simulation marginally satisfactory
Reduced scale of 10 km	10^3 m applies and simulation becomes suspect: a plume dispersion calculation should also be done
Reduced scale of 3 km	10^3 m simulation is unsatisfactory and a plume dispersion calculation is required

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[1] Turner D.B. (1994) Workbook of atmospheric dispersion estimates: an introduction to dispersion modeling. Second edition. Lewis publishers, CRC Press, Inc., Boca Raton, FL.

9.3.1 Illustrative example

We apply the RAIDAR model to a typical chemical (toluene) to illustrate the effect of reduction in area of the evaluative environment. The area of water is assumed to be a constant proportion of the total area, i.e., 10^{-1}, and a constant unit emission rate to air of 1 kg/h is used. Table A3.1 summarizes the selected physical-chemical properties and environmental half-lives of toluene used for this example.

Table A3.1. Summary of physical-chemical property and half-life data for toluene.

Parameter	Value	Units
Molar mass	92.14	g/mol
Vapor pressure	3785	Pa
Aqueous solubility	573	g/m^3
log K_{OW}	2.73	unitless
Half-life in air	2.04	d
Half-life in water	14	d
Half-life in soil	28	d
Half-life in sediment	84	d

In the standard RAIDAR environment of 10^5 km^2 the rate constants, d^{-1}, are

Reaction	$k_R = 0.24$
Advection	$k_A = 0.34$
Transfer	$k_T = 0.001$

Table A3.2 summarizes rate constants, mass, concentration, and percent losses in the air compartment of the RAIDAR environment as a function of reducing the evaluative area and by reducing the advective residence times in proportion to the area decrease, i.e., factor of 10. The rate constant for advection increases proportionally to the reduction in total evaluative area, whereas the rate constants for reaction and internal transfer are unchanged. As the area is reduced the loss by advection becomes greater, the mass in air is reduced and the concentration in air is increased but these changes are disproportionate to the increase in the advection rate. Loss from reaction becomes less by approximately the order at which the decrease in mass occurs until loss by advection dominates, i.e., area of 10^2 km^2. Loss from the internal transfer is insignificant for this chemical.

In these simulations for each 10-fold decrease in regional area, the flow velocities for air and water increase by a factor of about 3. The air flow velocity increases as the area is reduced because the transit time falls by a factor of 10 for each change in area but the transit distance falls only by a factor of $10^{1/2}$. As a result, a decrease by a factor of 100 in area causes an increase by a factor of 10 in air flow velocity. Reducing the area below 10^4 km^2 results in a severe loss in the ability of the model to discriminate between chemicals of different reactivity.

Further simulations were conducted in which the flow velocities remain consistent, i.e., wind speed of 3 km/h for all scenarios, by reducing the advective residence times by a factor of about 3 for each 10-fold reduction in area as

$$\tau_i = \tau_s/[(V_s/V_i)^{1/2}]$$

This is the same as reducing the advective residence times in proportion to the length of the side of the environment, i.e., square root of the area. Table A3.3 summarizes rate constants, mass, concentration, and percent losses in the air compartment of the RAIDAR environment as a function of reducing the evaluative area using this approach. Now the advection rate constant increases by a factor of about 3 rather than 10 for each 10-fold reduction in area. The rate constants for reaction and irreversible transfer remain the same as in the previous example. The mass of chemical in air decreases by a factor of about 2 when the evaluative area is reduced from 10^5 to 10^4 and then decreases by a factor of about 3 as advection in air dominates the total loss from the evaluative regions. The percent loss by reaction is initially about the same as the decrease in mass. The reduction in mass of chemical in air is initially affected directly by the degree to which chemical is lost by reaction until total loss is dominated by advection. This is viewed as a more realistic approach since it avoids excessive advective losses. As a result a reduction in area to about 10^3 km^2 appears feasible.

9.4 Summary

The effect of reducing the area of the RAIDAR environment has been investigated both theoretically and by actual operation of the model. If the area is reduced, the best strategy is to reduce the air and water residence times as well but not in proportion. A realistic reduction in these residence times is in proportion to the square root of the area, i.e., proportional to the side of the environment. This effectively retains constant air and water velocities.

Table A3.2. Summary of changes in rate constants, mass, concentration and percent losses for the air compartment as a result of reducing the RAIDAR evaluative environment "regional" area. The reaction rate constant is held constant. The advection residence time τ_A is reduced in proportion to the area causing k_A to increase since $k_A = 24/\tau_A$. The emission rate is constant at 1 kg/h into air. Reducing the area causes a decrease in mass but an increase in concentration. Advection becomes more important as the area is reduced.

Area km^2	Side km	τ_A h^{-1}	k_A d^{-1}	k_R d^{-1}	k_T d^{-1}	Mass kg	Concentration g/m^3	Loss by advection %	Loss by reaction %	Loss by transfer %
10^5	316	100	0.24	0.34	0.001	41.4	4.1×10^{-10}	41	59	0
10^4	100	10	2.4	0.34	0.001	8.76	8.8×10^{-10}	88	12	0
10^3	31.6	1	24	0.34	0.001	0.1	9.9×10^{-10}	99	1	0
10^2	10	0.1	240	0.34	0.001	0.01	1.0×10^{-9}	100	0	0
10^1	3.16	0.01	2400	0.34	0.001	0.01	1.0×10^{-9}	100	0	0

Table A3.3. Summary of changes in rate constants, mass, concentration and percent losses for the air compartment as a result of reducing the RAIDAR evaluative environment "regional" area and maintaining consistent flow velocities for air and water. In all cases the air flow velocity is 3.16 km/h. The advection rate constant increases as the area decreases but not proportionally.

Area	Side	τ_A	k_A	k_R	k_T	Mass	Concentration	Loss by advection	Loss by reaction	Loss by transfer
km^2	km	h^{-1}	d^{-1}	d^{-1}	d^{-1}	kg	g/m^3	%	%	%
10^5	316	100	0.24	0.34	0.001	41.4	4.1×10^{-10}	41	59	0
10^4	100	31.6	0.76	0.34	0.001	21.8	2.2×10^{-9}	69	31	0
10^3	31.6	10	2.4	0.34	0.001	8.8	8.8×10^{-9}	88	12	0
10^2	10	3.16	7.6	0.34	0.001	3.0	3.0×10^{-8}	96	4	0
10^1	3.16	1	24	0.34	0.001	1.0	9.9×10^{-8}	99	1	0

10. Appendix 4: Summary Input and Output_RAIDAR.xls

Summary required input data and RAIDAR output data are provided in a separate spreadsheet.

For the 1,105 chemicals that could be modelled, the selected input data are summarized in the worksheet "Selected P_C property_comments". This includes the chemical names, CAS#, SMILES notations ("salt form"), physical chemical properties, half-lives, critical body residues (CBR), and estimated actual emission rates E_A, i.e., "DSL Quantity", used to calculate RAIDAR Risk Assessment Factors (RAFs). Input values that were flagged, and occasional comments, as discussed in the report, are also included.

Summary RAIDAR output data for simulations assuming negligible metabolic biotransformation rates in fish, birds and mammals are included in the worksheet "Output_no met". Summary RAIDAR output data for simulations including estimates for metabolic biotransformation rates in fish, birds and mammals are included in the worksheet "Output_met". These sheets include the chemical names, CAS#, SMILES notations ("salt form"), estimated actual emission rates E_A, i.e., "DSL Quantity", used to calculate RAIDAR Risk Assessment Factors (RAFs). For each simulation, i.e., 10 scenarios, and for each modelled chemical the critical emission rate E_C, RAF, Risk Identification Bin (RIB), and the most sensitive ecological receptor (endpoint) are provided. For each scenario the chemicals are ranked from 1 to 1,105.

The list of chemicals provided by Environment Canada that could not be modelled by RAIDAR at this time are in the worksheet "Not modelled".