
Development and Application of Models of Chemical Fate in Canada

Modelling Guidance Document

Report to Environment Canada

CEMN Report No. 200501

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CANADA

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Contribution Agreement 2004-2005

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EXECUTIVE SUMMARY

This document is intended to assist the novice model-user in understanding when, why, and how to use models of chemical fate in the environment.

The complementary nature of monitoring and modelling are described and the role of each is outlined. A key contribution of models is their ability to bring together knowledge about chemical properties, environmental properties, and processes. This facilitates understanding and can highlight knowledge gaps.

Models can be used to establish the entire mass balance of a substance as it is transported, transformed, and bioaccumulated in the environment. They thus enable estimations to be made of certain processes such as volatilization that can not be measure directly. Models can be used to estimate concentrations and fluxes as well as likely time trends in concentrations as a result of changes in emission rates or environmental conditions.

The regulatory background to model use in Environment Canada is described with a brief account of similar approaches in other jurisdictions.

A basic description is provided of principles underlying the use of model, including processes treated, the fugacity concept, the benefits of applying models with increasing degrees or levels of complexity and the contributions of steady-state and dynamic models.

A six-stage process for general evaluations of chemicals is suggested and a number of more specific evaluations are described.

These topics result in a process for using models to establish a general understanding of the behaviour of a chemical in the environment. The emphasis is on organic rather than inorganic chemicals.

The models developed by and available from Canadian Environmental Modelling Network are described and detail is given on model selection and applications. No attempt is made to describe models available from other organisations. The developers of these other models should be consulted directly for information on the nature and applicability of their models.

A number of aspects relating to the interpretation of model results are described including uncertainty, variability, sensitivity, validation, temperature effects, and steady-state and dynamic treatments.

Frequently asked questions are listed with answers and a full list of references is provided.

In total, this document is designed to provide the user, who is not necessarily experienced in model use, with guidance on the use of models for evaluation purposes.

1 INTRODUCTION

1.1 Background

This report is prepared as a part of the Contribution Agreement Development and Application of Models of Chemical Fate in Canada”. It provides guidance on the use of the models in general and it specifically describes the models developed and distributed by members of the Canadian Environmental Modelling Network (CEMN).

1.2 Objectives

The objectives of this report are

- To give an overview of the science of fugacity-based models
- To present a process for understanding the behaviour of a chemical in the environment
- To provide familiarity with CEMN models
- To give guidance on the use of CEMN models especially for the novice user

1.3 Outline

A brief outline of the regulatory background in Canada and around the world is provided.

This report provides basic instructions on the use and interpretation of the environmental fate models produced by the members of the Canadian Environmental Modelling Network.

The role of models in understanding chemical fate in the environment is described including a discussion of the complementary nature of modelling and monitoring.

The fugacity concept is explained and the mathematics of Level I, II, III and IV fugacity models is outlined.

The six-stage process to understand chemical behaviour is described.

A listing of some of the models available from the CEMN is given with details on selected models.

Guidance is given on selecting a model, identifying input data sources, evaluating input data quality, and understanding model outcomes.

2 THE CANADIAN REGULATORY BACKGROUND

2.1 CEPA: The Canadian Environmental Protection Act

The *Canadian Environmental Protection Act, 1999* (CEPA, 1999) is a statute that addresses the responsibility of the Canadian Government to identify potential adverse effects on human health and the environment from chemicals and other substances. CEPA, 1999 provides the federal government with the authority to determine whether chemicals and other substances are “toxic” or capable of becoming toxic in the context of the statute. The Act also provides for a comprehensive “cradle-to-grave” management approach for chemicals and other substances.

2.1.1 Definition of substance

The Canadian Environmental Protection Act, 1999, requires the Ministers of the Environment and of Health to evaluate substances as defined in the Act and is considered key to the protection of the environment. CEPA, 1999 defines substances very broadly and under CEPA as:

“any distinguishable kind of organic or inorganic matter, whether animate or inanimate, and includes

- (a) any matter that is capable of being dispersed in the environment or of being transformed in the environment into matter that is capable of being so dispersed or that is capable of causing such transformations in the environment,
- (b) any element or free radical,
- (c) any combination of elements of a particular molecular identity that occurs in nature or as a result of a chemical reaction, and
- (d) complex combinations of different molecules that originate in nature or are the result of chemical reactions but that could not practicably be formed by simply combining individual constituents,”

and, except for the purposes of sections 66 (the Domestic Substances List), 80 to 89 (New Substances) and 104 to 115 (animate products of biotechnology), includes

- “(e) any mixture that is a combination of substances and does not itself produce a substance that is different from the substances that were combined,
- (f) any manufactured item that is formed into a specific physical shape or design during manufacture and has, for its final use, a function or functions dependent in whole or in part on its shape or design, and

(g) any animate matter that is, or any complex mixtures of different molecules that are, contained in effluents, emissions or wastes that result from any work, undertaking or activity.”

2.1.2 Definition of CEPA toxic

CEPA 1999 requires the Minister of the Environment and the Minister of Health to assess substances in order to determine whether the substance is toxic or capable of becoming toxic. Under the Act (Section 64), a substance is “toxic” if it is entering or may enter the environment in a quantity or concentration or under conditions that:

- (a) have or may have an immediate or long-term harmful effect on the environment or its biological diversity;
- (b) constitute or may constitute a danger to the environment on which life depends; or
- (c) constitute or may constitute a danger in Canada to human life or health.

Substances are assessed by the Ministers of Environment and Health, through the Existing and New Substances Programs jointly administered by Environment Canada and Health Canada.

2.1.3 Legislation for ecological risk assessment of existing substances

Substances assessed under the Existing Substances Program are broadly defined and primarily includes, but is not restricted to those substances found on Canada's original Domestic Substances List (DSL). The original DSL is defined under section 66 and specifies “all substances that the Minister is satisfied were, between January 1, 1984 and December 31, 1986,

- (a) manufactured in or imported into Canada by any person in a quantity of not less than 100 kg in any one calendar year; or
- (b) in Canadian commerce or used for commercial manufacturing purposes in Canada.”

Substances on the original DSL may be given priority for risk assessment through the DSL Categorization Program (ESB 2003). As mandated under Section 73 (a) and (b) of CEPA, 1999, substances on the DSL are categorized as to whether they present to individuals the greatest potential for exposure; or meet the persistence or bioaccumulation criteria, as satisfying the regulations (Canada Gazette, 2000) and are also inherently toxic. Those substances which meet the above criteria will undergo a screening assessment under CEPA, Section 74.

Although the categorization of the substances on the DSL provides a major mechanism to identify substances of potential concern for the environment or human health and subsequent assessment, other substances may be identified for assessment through other mechanisms. Six other mechanisms for substance identification are available and include those found through industry submitted data

(including CEPA, S.70); provincial or international decisions (CEPA, S. 75); public nominations; hazardous classes of substances identified through new substances notifications; emerging science and monitoring; and international assessment or data collection. The Minister is also responsible for compiling a Priority Substances List (PSL) which the Minister considers a priority for risk assessment (CEPA S. 76(1)). Some substances may be exempt from assessment if the substance has already been adequately assessed under another Act of Parliament.

For each substance identified through the mechanisms above, the environmental risk assessment approach will generally follow closely with that described in this document, although some deviations from the approach may occur depending on the purpose and type of assessment and/or the type of substance being assessed. There are also general scientific reviews or investigations (CEPA, Section 68) or support to Ministers and Governor in Council (S. 90), or other scientific reviews for which the Existing Substances Program is responsible.

2.1.4 Legislation for ecological risk assessment of new substances

The New Substances Program is responsible for assessing substances that are defined, by exclusion, through the original DSL (Section 66). Substances that are “new” to Canadian commerce fall under the purview of Parts 5 and 6 of the CEPA, 1999. New substances that are chemicals, polymers and inanimate products of biotechnology are covered in Part 5 of the CEPA, 1999, whereas Part 6 of the CEPA, 1999 deals with new substances that are animate products of biotechnology. This document does not describe the approach for assessing the risk from products of biotechnology.

In CEPA 1999 the approach to the control of new substances is both proactive and preventative, employing a pre-import or pre-manufacture notification and assessment process. When this process identifies a new substance that may pose a risk to health or the environment, the Act empowers Environment Canada to intervene prior to or during the earliest stages of its introduction to Canada. This ability to act early makes the new substances program a unique and essential component of the federal management of toxic substances.

The assessment process begins when Environment Canada receives a New Substances Notification prepared by the company or individual that proposes to import or manufacture a new substance or use it for a Significant New Activity (SNAc). New Substances Notifications must contain all required administrative and technical data and must be provided to Environment Canada by a prescribed date before manufacture or import (Government of Canada, 1994). Notification information is jointly assessed by the Departments of Environment and Health to determine whether there is a potential for adverse effects of the substance on the environment and human health. This assessment, which is considered a risk assessment, must be completed within a specified time, and will reach a conclusion as to whether or not the substance is “toxic” under CEPA. A substance may be notified several times under the New Substances Program depending on the volume of substance manufactured or imported into Canada.

A substance assessed under the New Substances Program may receive several levels of assessment depending on the volume of the substance manufactured or imported into Canada, and whether the

substance is on the non-Domestic Substances List (NDSL). Substances notified at higher volumes (e.g., >5,000 kg/y) contain more information in the notification package and typically require a more detailed assessment, while substances notified at lower volumes (e.g., <5,000 kg/y) often undergo only a preliminary assessment.

The final levels of assessment must meet the higher information requirements of the schedules found in the New Substances Notification Regulation (NSNR) (Government of Canada, 1994). Risk assessment conclusions of lower scheduled assessments may be different than those of the higher Schedules. This document describes the considerations and approaches used to prepare the environmental portion of the risk assessments.

The requirements for notification and assessment in CEPA 1999 do not apply if the new substance is manufactured or imported for a use that is regulated under another Act of Parliament that requires notice and assessment (e.g., Pest Control Products Act). The Governor in Council is responsible for determining that another Act meets these requirements and for placing it on Schedule 2 of CEPA 1999.

Figure 1 provides a schematic representation of how risk assessments for existing and new substances relate to the mandate of substance assessment under CEPA.

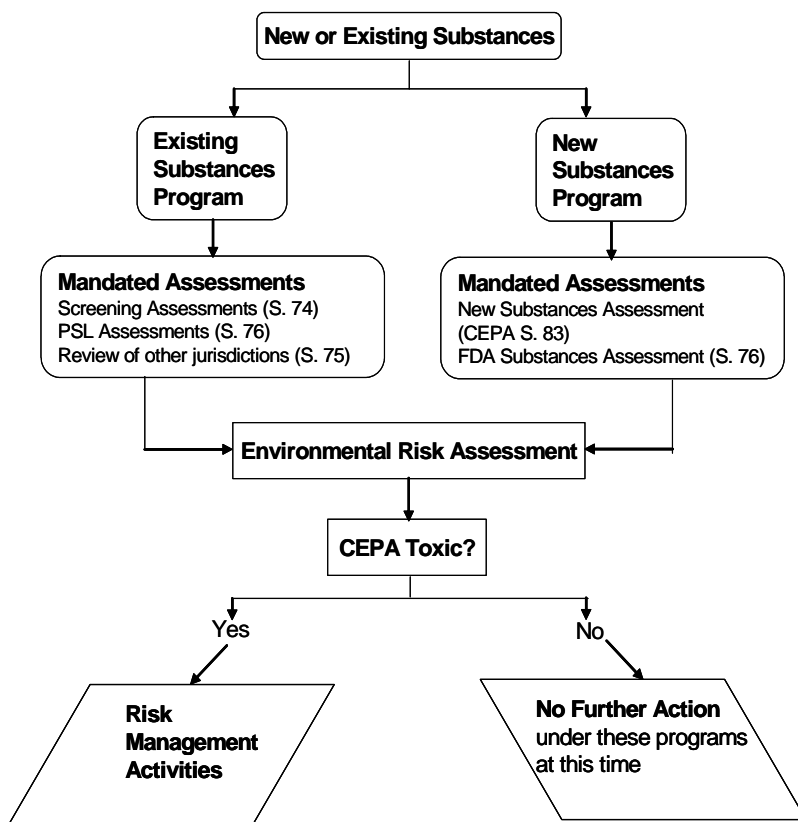


Figure 1: Environmental Risk Assessments (ERA) under CEPA

As the New Substances Notification Regulations are designed for commercial chemicals, a new set of regulations appropriate for the *Food and Drugs Act* products are being developed through the Environmental Assessment Unit (EAU) and the Office of Regulatory and International Affairs, Health Products and Food Branch.

2.2 The Precautionary Principle

Canada has a long-standing history of implementing the precautionary approach in science-based programs related to health and safety, environmental protection, and natural resources conservation. With the increasing emphasis on the adoption of this approach in decision-making, the federal government has been working to develop a set of guiding principles to support consistent, credible, and predictable policy and regulatory decision-making across government when applying the precautionary principle.

During the preparation of an environmental risk assessment, every effort will be made to incorporate the precautionary principle to ensure that decisions are made with a precautionary perspective. The Canadian Environmental Protection Act (CEPA), 1999, specifically addresses the importance of applying the precautionary principle in relation to the assessment and management of substances. In the preamble to the Act and in the introduction under Administrative Duties of the Government of Canada it states that “where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation”. In addition, part V of CEPA, 1999, Section 76.1, which deals specifically with conducting and interpreting the results of a screening or PSL risk assessment, or the evaluation of a decision from another jurisdiction, prescribes the application of the precautionary principle through the statement that “Ministers shall apply a weight of evidence approach and the precautionary principle when preparing and interpreting the results of assessments”.

Historically, and as described in this document, the application of the precautionary principle is and will continue to be an integral part of the environmental risk assessment process. The application of the precautionary approaches in the environmental assessment is made through conservative assumptions or quantitative adjustments for uncertainty regarding adverse fate or toxic effects to the environment or to adjust for the unknown or inaccurate exposure scenarios. As a practical example, in the effects assessment stages, a precautionary approach may manifest itself through the selection of the lowest, most protective quantitative measurement or estimate from the available data, or through the application of conservative “assessment” factors which will lower the effect concentration even more to account for data limitations. For the development of the exposure scenarios, precautionary assumptions are often applied through the assumption of large or maximum use or release volumes and or, through the development of potential use or release scenarios.

2.3 Framework for the Environmental Risk Assessment (ERA) of Substances Under CEPA

The environmental risk assessment of substances occurs through three main phases. The first phase called pre-screening and prioritization provides a means for triaging substances so that they may be prioritized for further assessment. The second phase, called the assessment phase, involves

characterizing the environmental exposure of a substance and the potential effects of a substance to non-human biota. The final phase is the risk characterization phase and it involves determining the risk potential of a substance according to a weight of evidence for exposure and effects. Throughout the Environmental Risk Assessment (ERA) process, data are collected to support the assessment as needed. Most data are collected during the pre-screening and prioritization phase and the assessment phase. Dialogue with interested parties (e.g., regulatory managers, industry, and public) is also conducted throughout the ERA as needed and may result in the re-iteration of an ERA as a result of new ideas or data. Figure 2 provides an overview of the process for conducting the ERA of substances.

2.3.1 Pre-screening and prioritization phase

The pre-screening and prioritization phase provides an initial first impression of the potential concern a new or existing substance may pose to the environment. The intent of this stage is to provide a rapid initial evaluation of a substance based on specific properties of the substance (e.g., persistence, bioaccumulation and toxicity) as well as information on the use, import/manufacture volume, how the substance may enter the environment and the multi-media fate of the compound. The results of pre-screening and prioritization can also be used to help set out a plan for the ERA of a substance.

The level of detail of pre-screening and prioritization may vary between substances depending on programs needs and the level of information available for a substance. For example, the pre-screening of new substances is largely based on examination of a chemical's structure, key chemical properties, import/manufacture volume and intended use. This information is combined to give an overall qualitative assessment of the priority of the new substance. For existing substances, a scoring procedure involving several parameters may be used to provide a sequential method of determining the priority of a substance for assessment. Regardless of the level of detail of the pre-screening and prioritization a dialogue among risk assessors and managers is undertaken to ensure that there is consensus on which substances are a priority.

2.3.2 Environmental fate phase

Once a substance is released to the environment from an anthropogenic activity, it becomes important to understand where a substance will reside in the environment, how much of it will reside there and for how long. Along with knowledge of how a substance enters the environment (i.e., mode-of-entry), how much and how often, understanding the environmental fate allows an assessor to understand which environmental compartments are expected to contain the substance and consequently which organisms may be exposed. Key physical-chemical properties of a substance can be used to help determine environment fate (e.g., organic carbon partitioning coefficient, Henry's Law Constant, bioconcentration factor, degradation half-lives). These properties can be entered into a multimedia model to provide a better understanding of the partitioning behaviour of a substance within and between environmental compartments and the overall residence time in a compartment.

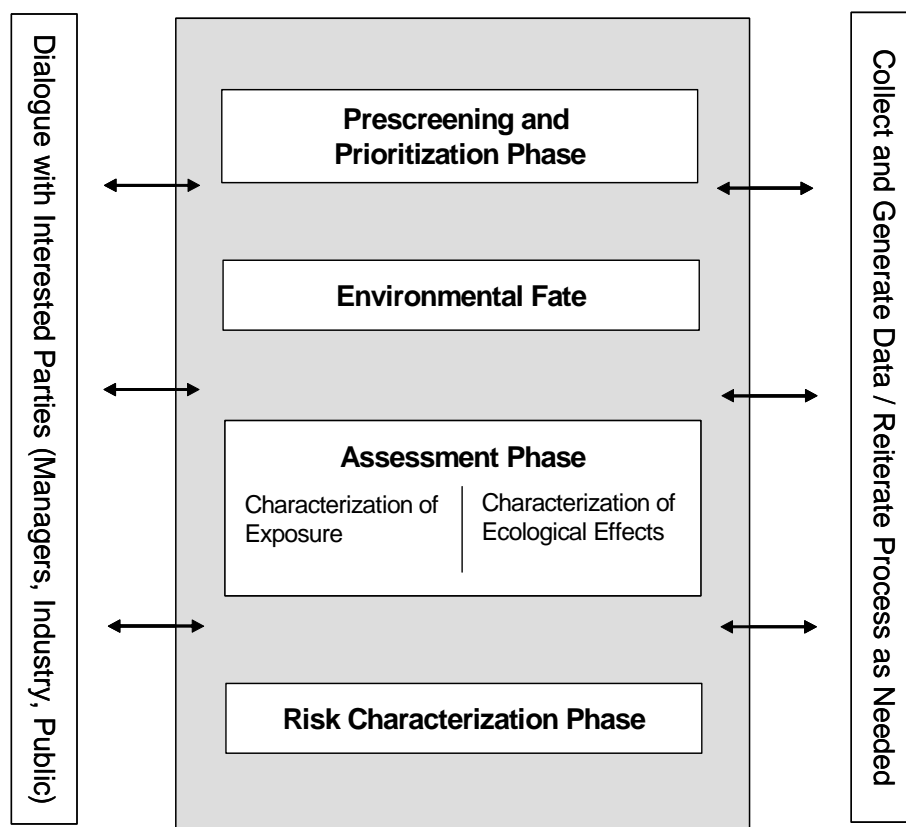


Figure 2: Framework for Conducting the Environmental Risk Assessment (ERA) of New and Existing Substances

2.3.3 Assessment phase

The assessment phase consists of two main parts characterization of exposure and characterization of ecological effects.

Exposure assessment characterizes the potential contact or co-occurrence of stressors (in this case chemicals) with receptors (non-human target biota). Travis et al. (1983, cited in Barnhouse et al. 1986) defines exposure assessment for toxic chemicals as the “determination of the toxic materials in space and time at the interface with target populations”. This is a very broad definition, but is nevertheless important because it implies that the goal of exposure assessment is the determination of a chemical concentration(s) in the environment that is considered toxic or presents a risk to non-human biota. Extrapolating from this definition, it can also be held that regardless of how inherently toxic a chemical can be, without organism exposure, there is no risk. Generally, estimates of exposure are conservative and are based on reasonable worst-case scenarios that err on the side

of caution. The principles of pollution prevention under CEPA are implemented in the exposure assessment by examining all reasonably anticipated future uses and related exposures.

Effects assessment characterizes the type and magnitude of ecological effects resulting from environmental exposure to a chemical or a combination of chemicals. Often, in risk assessments, the most sensitive receptor is used as the baseline from which to determine potential hazards to more than one species. Often the type and magnitude of ecological effects is determined based on measurement endpoints (e.g., median lethal concentration, median effects concentration for reproduction). These endpoints correlate to the protection goals for the assessment (referred to as assessment endpoints) and are used to evaluate potential threats to populations of species in the environment. Ultimately, the effects assessment aims to derive the concentration of a substance in the environment at which no effects are observable in target biota.

During the assessment phase, experimental and predicted data are collected or generated using QSARs or environmental models. A re-iteration of the exposure or effects assessment may be undertaken if there is sufficient concern for the substance or new data have been supplied or collected. As with the pre-screening and prioritization phase, dialogue with interested parties (e.g., other assessors, managers, industry) is also performed to ensure that the characterization of exposure and ecological effects is based on the best available information.

2.3.4 Risk characterization

The risk characterization phase brings together the information from the exposure assessment and effects assessment with the aim of concluding whether a substance poses a risk to non-human biota. The potential risk of a substance can be estimated using simple approaches such as the quotient method or can be based on several lines of evidence (e.g., PBT properties of a substance) for both biotic and abiotic endpoints.

The risk characterization phase also includes a qualitative assessment of the potential risk a substance poses to the environment and will reach a conclusion on the toxicity of a substance as defined under CEPA.

The risk characterization phase also points out where data gaps and uncertainties exist in the assessment and how these factors impact the quality of the assessment. A re-iteration of the assessment may be undertaken

2.4 The Need for a Multimedia Approach to Environmental Fate in ERA

In recent years, the characterization of uncertainty in ecological risk assessment has received much attention and has become increasingly important regardless of the level of assessment performed. Tools for characterizing uncertainty range from relatively simple qualitative approaches to complex probabilistic designs. The ecological risk assessment of new substances in Canada uses a screening level approach. Characterization of uncertainty at the screening level becomes very important because typically fewer data are available and used to estimate risk.

In 1998 and 1999 the New Substances Division of Environment Canada undertook two studies to examine qualitatively the uncertainties associated with the exposure assessment of new substances in Canada (BEC 1999a; BEC 1999b). In the first study, a characterization of the data gaps and short comings of the aquatic driven exposure assessment process was conducted. Specifically, a characterization of the uncertainties associated with: (1) the estimation of release concentration, (2) fate and distribution, and (3) release, fate and distribution in non aquatic media was described. One of the key recommendations from the first study was that a multi media approach to conducting the exposure assessment of new substances in Canada was needed in order to address releases to media other than the water column. Although water column release and exposure form the basis for determining the predicted environmental concentration of a new substance, releases to other media do occur and are appropriate (e.g., accumulation in soils) but are not routinely considered. In the second study, a strategy for dealing with the key data gaps and short comings that contribute to exposure uncertainty was detailed. In this study a preliminary approach to conducting the multi media exposure assessment (MMEA) of new substances was outlined.

The New and Existing Substances Branches of Environment Canada have acted on the MMEA recommendation and strategy, which ultimately, led to the development of guidance for MMEA of substances under CEPA (BEC 2001). Since 2001 many new multimedia tools and approaches have been developed. In particular, as the Existing Substances Program embarks on the risk assessment of substances categorized as persistent or bioaccumulative and inherently toxic, Environment Canada recognized the need for up to date and detailed guidance on multimedia models and their use in risk assessment. The result is this guidance document which is intended to be a evolving piece of work that will be updated periodically as new techniques and understanding develop in the unit world.

2.5 Practices in Other Jurisdictions

Practices in the US are generally similar to those in Canada in a scientific sense but the legislative framework, the Toxic Substances Control Act, is different. Reference should be made to the USEPA, Office of Prevention, Pesticides and Toxic Substances for guidance on current practices.

Chemical assessment in Europe is conducted by the European Chemicals Bureau (ECB) located in Ispra, Italy. This organization collects information on chemicals used in Europe and prepares priority lists. Priority substances are then allocated for assessment to specific member nations of the European Union. Assessment reports are published and make recommendations on whether or not some regulatory activity is deemed desirable. In recent years emphasis has been on “high production volume” chemicals. It is suggested that the reader consult the ECB website (<http://ecb.jrc.it>) for details of the assessment process (EUSES), priority lists, and technical guidance documents. The assessment relies on the “SimpleBox” model developed by RIVM in the Netherlands.

Other national and international agencies also conduct assessments and provide guidance on model use, notably Japan, the OECD, and UNEP.

3 MODELS AS A CONTRIBUTION TO UNDERSTANDING ENVIRONMENTAL FATE

3.1 What models can do for you

When seeking to understand the behaviour of chemicals in the environment, there is a consensus that it is no longer satisfactory to begin production and discharge before having some degree of assurance of the absence of risk. This has been learned from the tragedies of the past as highlighted so elegantly by Rachel Carson (1962) in her book “Silent Spring”. Models provide a fast and inexpensive mechanism for bringing together the best of current science on chemical fate processes in the environment, with chemical properties data collected in the laboratory setting or from QSARs.

This should not be seen as excluding monitoring of in-use chemicals. For in-use and historic-use chemicals, monitoring and modelling should play complementary roles. In the modelling context, monitoring is critical for the continuing evaluation and improvement of the science on which the models are based. Monitoring, in turn, benefits from the insights provided by modelling. Monitoring programs contribute to the scientific understanding of environmental processes; better models are developed; all with the ultimate benefit of improved chemical management.

As focus shifts from those substances already identified as problematic to a more preventive and protective role, the weaknesses of existing science in explaining chemical behaviour become evident. For example, the models which have long been used for such substances as PCBs may not adequately describe fluorinated substances.

Historically, monitoring and modelling have primarily been conducted for the more populated regions of North America and Europe. As global concern shifts from the immediate surroundings of these affluent regions to the third world as a potential source and the polar regions as potential destinations for contaminants, new environmental processes become important. The effects of temperature, snow fall, and ice cover require improved representation within the models. Monitoring and laboratory studies are required to facilitate the quantification of cold climate processes.

There are two fundamentally different types of models used in understanding chemical fate. The first are statistical, knowledge-based models or correlations such as those contained in the EPIWIN suite where similarities in properties imply similarities in behaviour. The second are mechanistic, process-based models. Nearly all of the models developed by the CEMN are process-based models of chemical fate.

Process-based models are a convenient way of bringing together the existing science in a simple format to calculate expected chemical behaviour. Models need to be continually tested for validity and challenged by monitoring programs and updated as the science existing at the time of model development is shown to be inadequate for emerging chemicals or emerging concerns.

The models of the CEMN are founded upon the fundamental law that mass is neither created nor destroyed, and therefore, these models are known as “mass balance models”.

A mass balance environmental model can:

- i) reveal likely relative concentrations, i.e., it is useful for monitoring purposes by indicating likely relative concentrations between media such as air, water, and fish.
- ii) show the relative importance of loss processes, i.e., the process rates that we need to know most accurately
- iii) link loadings to concentrations, i.e., identify key sources and ultimately their effects
- iv) enable time responses to be estimated, i.e., how long recovery will take
- v) generally demonstrate an adequate scientific knowledge of the system

Models are often not necessary when the sources, fate and effect are obvious, but they become more valuable as situations become more complex, subtle, and with multiple sources. The user can also play “sensitivity games” to determine what is most important and what is less important.

Models of the type described in this report can be used for the following general purposes.

- i) to maximize our understanding of a monitored system.
- ii) to obtain the best possible understanding of the likely behaviour of a substance not yet being monitored or not yet in production.
- iii) to enhance a monitoring program by providing guidance on the likely behaviour of the substance of interest.
- iv) to evaluate the results of a monitoring program and test for any systematic error in the chemical analysis, e.g., mis-reported units.

3.2 Environmental processes and pathways

There are three environmental processes or pathways to be considered in a mass balance model; transformation or degradation processes, advection processes that move the chemical out of the modelled system, and exchange processes between environmental media or compartments.

3.2.1 Transformation

A substance can be effectively removed from consideration by being transformed through a chemical reaction. This is often described as degradation and first-order reaction kinetics are assumed in analogy with radioactive decay. These reactions include photolysis, oxidation, hydrolysis, and biodegradation.

Cautionary note:

Our focus here is on the degradation of the original or “parent” chemical. The “daughter” product of any degradation reaction may or may not be more persistent, bioaccumulative, or toxic than the parent substance and thus may merit further investigation.

3.2.2 Advection

Advection processes such as wind transport and river currents can effectively remove a substance from the modelled system by transporting it to a different location.

Cautionary note:

The substance may be more or less of a problem in the new location and thus may merit further investigation.

3.2.3 Intermedia exchange

Exchange between environmental media can occur by a multitude of processes including diffusion, rain dissolution, wet and dry aerosol deposition, runoff, and sedimentation and resuspension. Depending on the specific model other processes may be included. The importance of each process is highly dependent upon the chemical being investigated.

3.3 Fugacity concept

3.3.1 Origins, meaning, and usefulness

Fugacity was introduced by G.N. Lewis in 1901 as a criterion of equilibrium. It is similar to chemical potential, but unlike chemical potential, it is proportional to concentration.

Fugacity, which means escaping or fleeing tendency, has units of pressure and can be viewed as the partial pressure which a chemical exerts as it attempts to escape from one phase and migrate to another. In many respects, fugacity plays the same role as temperature in describing the heat equilibrium status of phases and in revealing the direction of heat transfer.

The application of the fugacity concept to environmental models is fully described in the text by Mackay (2001).

When equilibrium is achieved a chemical reaches a common fugacity in all phases. For example, when the fugacity of benzene in water is equal to its fugacity in air, we may conclude that equilibrium exists. However, these common fugacities will correspond to quite different concentrations. If the fugacity in water exceeds that in the air, benzene will evaporate until a new equilibrium is established.

The use of fugacity instead of concentration thus immediately reveals the equilibrium status of a chemical between phases and the likely direction of diffusive transfer. Further, the magnitude of the fugacity difference controls the rate of transfer, by for example evaporation.

The relationship between fugacity (f , Pa) and concentration (C , mol/m³) is given mathematically in equation (1)

$$C = Zf \quad (1)$$

where Z is a “fugacity capacity” or Z value with units of mol/m³·Pa.

When performing fugacity calculations, the SI units of mol/m³ are used for all concentrations. It is therefore necessary to convert from mg/L for concentrations in water, or mg/kg or µg/g for concentrations in solid phases. A knowledge of the density (kg/m³) of the solid phases is required.

3.3.2 Defining Z values

A Z value expresses the capacity of a phase, or environmental medium, for a given chemical. Z values are large when the chemical is readily soluble in a phase, i.e., the phase can absorb a large quantity of the chemical. A low Z value indicates that the phase can accept only a small quantity of chemical, i.e., the chemical is “less-soluble” in the phase.

To establish Z values for each chemical in each phase, the process usually starts in the air phase. In the air, the Ideal Gas Law is applied.

$$PV = nRT \quad (2)$$

where P is pressure, or fugacity in our case, V is the volume of the air, n is the number of moles of the chemical, R is the gas constant (8.314 Pa·m³/mol·K), and T is absolute temperature (K). Since $C = n / V$, and $C = Zf$ equation 2 can be re-written in fugacity terms as

$$Z_A = 1/RT = C_A / f_A \quad (3)$$

the subscript A referring to the air phase. Z_A is thus about 0.0004 mol/m³·Pa for all chemicals in air.

A partition coefficient is the ratio of the concentrations in two environmental media at equilibrium, thus it is the ratio of the Z values of the two media. For example, the air-water partition coefficient, K_{AW} , is

$$\begin{aligned} K_{AW} &= C_A / C_W \\ &= Z_A f_A / Z_W f_W \end{aligned} \quad (4)$$

and since K_{AW} is measured when f_A equals f_W , i.e., at equilibrium,

$$K_{AW} = Z_A / Z_W \quad (5)$$

In general,

$$K_{ij} = Z_i / Z_j \quad (6)$$

Using the partition coefficients and previously calculated Z values, it is thus possible to calculate Z values for the chemical in other media such as soil, fish, and sediment if dimensionless partition coefficients are known.

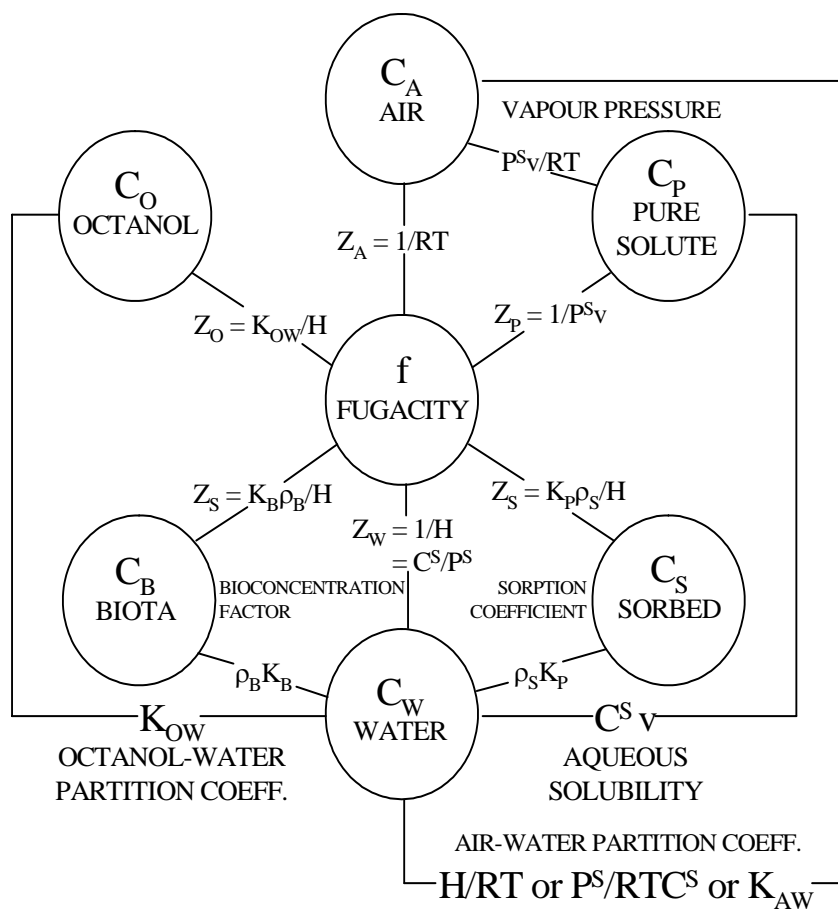
Cautionary Note:

Care must be taken to ensure that the partition coefficients are dimensionless because many are reported in dimensional units such as L/kg, i.e., a ratio of a solid phase concentration (mg/kg) to a liquid phase concentration (mg/L). The preferred units of both concentrations when calculating partition coefficients are mol/m³ or g/m³. This ensures that the partition coefficient is dimensionless.

A very convenient and important description of chemical hydrophobicity or lipophilicity is K_{OW} , the octanol-water partition coefficient, which is the ratio of Z in octanol to Z in water. Octanol is commonly used as a surrogate for lipids and organic matter in the environment. Hydrophobic chemicals such as DDT or PCBs have K_{OW} values of about a million implying that Z_O is about a million times Z_W , i.e., the water phase has a very limited capacity for the chemical. The chemical is thus “water hating” or hydrophobic. K_{OW} is used in correlations to describe partitioning from water into lipids of fish and other organisms and into natural organic carbon such as humic material. It is also used to correlate toxicity data for a variety of chemicals.

Correlations have been developed for several partition coefficients for organic chemicals as a function of chemical properties such as solubility in water, K_{OW} and vapour pressure. These can be exploited to give “recipes” for Z values. Caution must be exercised when using these correlations for chemicals of unusual properties such as ionizing acids or bases, detergents, dyes and polymers. Figure 3 is a summary of expressions which can be used to estimate Z values, detailed justification being given in Mackay (2001). Notable is the use of K_{OW} to estimate K_{OC} the organic carbon partition coefficient which is the key to the estimation of soil-water and sediment-water partition coefficients for many compounds.

Pure solutes are rarely present in the environment except as a result of chemical spills. The Z value for a pure solute is thus of more academic than practical interest. The fugacity of a pure solute is its vapour pressure, P^S (Pa). The concentration (mol/m³) is the reciprocal of the molar volume, v (m³/mol). It follows that Z is $1/(P^S v)$.



Definition of Fugacity Capacities

Compartment	Definition of Z, mol/m ³ Pa	
Air	$1/RT$	$R = 8.314 \text{ Pa m}^3 / \text{mol K}$ $T = \text{temperature, K}$
Water	$1/H$ or C^S/P^S	$H = \text{Henry's law constant, Pa m}^3 / \text{mol}$ $C^S = \text{aqueous solubility, mol/m}^3$ $P^S = \text{vapour pressure, Pa}$
Solid Sorbent (e.g. soil, sediment, particles)	$K_p \rho_s / H$	$K_p = \text{solid-water partition coefficient, L/kg}$ $\rho_s = \text{density of solid, kg/L}$
Biota	$K_B \rho_B / H$	$K_B = \text{biota-water partition coefficient, L/kg}$ or $\text{bioconcentration factor (BCF), L/kg}$ $\rho_B = \text{density of biota, kg/L}$ (often assumed to be 1.0 kg/L)
Pure Solute	$1 / P^S v$	$v = \text{solute molar volume, m}^3/\text{mol}$

Figure 3: Relationships between Z values and partition coefficients and summary of Z value definitions.

3.4 An exploration of Levels

It is useful to explore the behaviour of a chemical in the environment through a series of models of increasing complexity. The simpler models are easiest to understand and have fewest data requirements. As the complexity of the models increase, they become more challenging to understand and the data requirements increase. When more input data must be estimated, the reliability of the model output may become compromised. By stepping through a series of models of increasing complexity, understanding of the chemical's behaviour can be maximized while the likelihood of gross mis-representation is minimized.

Here the assumptions for the four levels of complexity are described. These calculations are embodied in a set of model software, each named for the level it contains, and in other software for specific purposes. The software is described later.

3.4.1 Level I: simple equilibrium partitioning calculations

It is simplest to begin by assuming a closed environment with a constant amount of chemical present at equilibrium between the environmental media. This "pop can" environment has no mechanisms for chemical to be added or removed. There are no degradation or advection processes. There is no active transport between environmental media; to return to the heat capacity analogy used previously, the can has been on the shelf for long enough to have reached a constant temperature. In fugacity terms, this assumption of equilibrium means that a single fugacity exists in the environment, i.e., in a four-compartment environment where A is air, W is water, E is soil or "earth", and S is sediment,

$$f_A = f_W = f_E = f_S = f \quad (7)$$

A Level I model combines chemical partitioning (measured or estimated) data to give the Z values in each medium in the environment and, more importantly, the chemical's partitioning tendency. The inter-media surface areas are not needed because equilibrium is assumed between well-mixed volumes of media.

The partitioning behaviour of a chemical can be most readily depicted and understood with a chemical space diagram such as that shown later in Figure 4.

Some algebra

M is total moles of chemical in the environment, V_i is volume, and C_i is concentration for compartment i and all summations are over all i.

$$M = \sum V_i C_i = \sum V_i Z_i f_i \quad (8)$$

and since all f_i are equal and can be designated f by equation (7)

$$M = f \sum V_i Z_i \quad (9)$$

or

$$f = M / \sum V_i Z_i \quad (10)$$

This is a Level I calculation.

The calculation sequence is

- given the partition coefficients of a chemical, Z values can be determined
- given compartment volumes, $Z_i V_i$ can be determined
- given an amount of chemical present, f can be determined from equation (10), and
- from f, all concentrations, $C_i = Z_i f$ and all amounts $m_i = C_i / V_i$ can be determined.

As a final check, the sum of all m_i must equal the total amount of chemical present.

A simple worked example for DDT in a water body such as a lake is given in Appendix D.

3.4.2 Level II: equilibrium partitioning with loss processes

The modelled complexity of the environment at equilibrium can be increased by including the loss processes of advection and degradation. Advection includes mechanical removal processes such as achieved by air and water currents and is characterized by a flow rate, G (m³/h). Degrading reactions can include both chemical reactions and biologically-mediated degradation, and are characterized by a half-life, τ (h) or rate constant, k (1/h) = $\ln(2) / \tau$. A set of transport or transformation values known as fugacity rate constants or D values (mol / Pa h) are calculated as $D = G Z$ or $D = k V Z$ where V (m³) is the volume of the medium. Since the equilibrium assumption is maintained in Level II calculations, there is no dependence on the medium to which the chemical is emitted; and total emission into the environment is sufficient to describe chemical entry to this system. Again, the inter-media surface areas are not needed as equilibrium is assumed between well-mixed volumes of media.

Some algebra

E is emission rate in mol/h

$$E = \sum D_i f_i \quad (11)$$

and by equation (7) and re-arranging equation (11)

$$f = E / \sum D_i \quad (12)$$

This is a Level II calculation.

The calculation sequence is

- use the Z values from Level I
- given compartment volumes, rate constants, and flow rates, all D_i values can be determined
 - for advection processes, A: $D_{iA} = G_i Z_i$

- for reaction processes, R: $D_{iR} = k_i V_i Z_i$
 - given an emission rate, f can be determined from equation (12), and
 - from f , all concentrations, $C_i = Z_i f$ and all rates $D_i f$ can be determined.
- As a final check, the sum of all loss rates $D_i f$ must equal the emission rate.

A simple worked example of DDT in a water body is given in Appendix E.

3.4.3 Level III: steady-state with multimedia transport

By removing the equilibrium assumption, the model complexity and data demands are again increased. The steady-state assumption, i.e., the absence of change over time, is retained. Without the equilibrium assumption the chemical's fugacities in each medium generally differ and, it is now necessary to describe active transport processes between environmental media. These can include processes such as diffusion, volatilization, deposition, resuspension, and runoff and require a variety of input data depending on the details of the environment modelled. For example, media volumes are no longer sufficient. The inter-media surface areas are needed to calculate many of these transfer process rates. In general, $D = A U Z$ where U is the transport velocity for the process in units of m/h and A is the area of the exchange surface in m^2 . Medium-specific emission rates, E_i , are now required because the results are strongly dependent on the receiving medium or media, i.e., the "mode-of-entry". This more complicated calculation will yield the same results as a Level II calculation if the chemical is rapidly transported between media such that all media have the same fugacity - the key assumption of Level II.

Some algebra

E_i are the emissions into each medium i , $D_{i,j}$ are the fugacity rate constants for chemical transfer from medium i to medium j . Since chemical mass is conserved, the amount entering each medium must equal the amount removed by either transport into another medium or by one of the loss processes of advection and degradation.

$$\text{Entering} = \text{Advection} + \text{Degraded} + \text{Transferred} \quad (13)$$

Losses in medium i are given by

$$D_{iT} = D_{iA} + D_{iR} + \sum D_{i,j} \quad (14)$$

$$E_i + \sum D_{j,i} f_j = f_i D_{iT} \quad (15)$$

Note that $\sum D_{j,i} f_j$ is the sum of the rate of input from other compartments j to compartment i . Re-arranging equation (15) gives

$$f_i = (E_i + \sum D_{j,i} f_j) / D_{iT} \quad (16)$$

We thus obtain for n media, n equations with n unknown fugacities and we can solve them for all fugacities, from which concentrations, amounts and rates are calculated.

Note that we can have as many boxes as we like - the limitation is our ability to estimate D values, not computing power.

This is a Level III calculation.

The calculation sequence is

- obtain the Z values from Level I, and D_{iA} and D_{iR} from Level II
- given the necessary transfer process information, calculate all D_{ij}
- given all emissions, E_i , the set of mass balance equations (16) will yield the set of fugacities, and
- from all f_i , all concentrations, $C_i = Z_i f_i$ and the total removal rate from the environment $\Sigma(D_{iA} f_i + D_{iR} f_i)$ can be determined.

As a final check, the total removal rate must equal the sum of the emission rates, ΣE_i and each compartment should also display a mass balance with inputs equalling outputs.

A simple worked example for DDT in a water body is given in Appendix F.

3.4.4 Level VI: dynamic

This next level of complexity, Level IV, includes change over time, i.e., it does not assume steady-state. Here a single emission such as a spill may be followed through time, or the effect of emission reductions examined in detail. Sufficient input data is often difficult to obtain and erroneous estimates can lead to false conclusions. Thus, it is important to follow a progression of increasing model complexity and data demands to anticipate the likely dynamic behaviour prior to performing such calculations.

Some algebra and some calculus

For a time-varying emission to medium i, $E_i(t)$, mass balance dictates that all chemical entering medium i must be accounted for through transport into another medium or by one of the loss processes of advection and degradation **or** must become a part of the inventory of chemical in medium i. Thus the amount of chemical in medium i at time t is given by

$$m_i(t) = m_i(t-1) + \Delta t \, dm_i/dt \quad (17)$$

$$dm_i/dt = d(f_i V_i Z_i)/dt = \text{rate of chemical entering} - \text{rate of chemical leaving} \quad (18)$$

or assuming volumes and Z values are constant

$$V_i Z_i \, df_i/dt = E_i(t) + \Sigma D_{j,i}(t) f_j(t) - f_i(t) D_{iT}(t) \quad (19)$$

In equation (19) the left-hand side is the inventory change and the terms on the right-hand side are direct emission to the compartment, transport to the compartment, and losses from the compartment.

D_{IT} is the total of all loss D values by reaction, advection, and intermedia transport. A dynamic calculation for constant emissions, if continued for a long enough period, will achieve the steady-state condition and results will be equivalent to those from the Level III calculation.

There are thus n simultaneous linear differential equations. They can be solved analytically but it is often easier to solve them by numerical integration. The result is the time-course of concentrations in each medium.

3.4.5 Summary of Levels

Table 1: Summary of Levels of complexity in multimedia models

Level	Assumptions
I	Closed system Defined chemical amount Equilibrium between media ==> one fugacity
II	Single chemical emission rate Reaction and advective loss processes Equilibrium between media ==> one fugacity
III	Chemical emission rates and mode-of-entry Reaction and advective loss processes Non-equilibrium between media ==> different fugacities Steady-state system, i.e., unchanging with time
VI	Dynamic system, i.e., changing with time

3.5 A Six-Stage Process to Understanding Chemical Fate

In 1996, Mackay et al (1996a) outlined a 5-stage process to understand the behaviour of a substance in the environment. The five stages are: (1) chemical classification, (2) acquisition of discharge data, (3) evaluative assessment of chemical fate, (4) regional or far-field evaluation, and (5) local or near-field evaluation. A sixth stage was suggested by MacLeod and Mackay (1999) in which an exposure evaluation would be conducted.

Recently, in recognition of the challenges of obtaining the emission data for stage 2, it has been suggested that target emissions can be calculated from critical concentrations to evaluate risk. A more detailed discussion of this risk evaluation is given later.

This process generates an increasing understanding of the chemical of interest. Often sufficient information will be generated early in the process and the final stages will be unnecessary, or allow simplifying assumptions to be made without loss of accuracy. For example, when gathering the data for stage 1, it may become evident that the substance is not multimedia in nature but partitions

exclusively to only one or two environmental media. In such a case, the degradation half-lives in the media to which it does not partition may be assumed to be infinite (i.e., the rate is zero) and do not need to be measured or estimated.

This gradual increase in data requirements and complexity facilitates the mental assimilation of the information generated. By plotting the partitioning properties of a substance much may be learned. By calculating the substance's fate in an evaluative environment, key processes can be identified.

It is argued by some that all the information may be generated by using a single, complex and realistic model. This assumes that all of the required input data are available. It assumes that all the process information encoded in the model is correct and applicable. It assumes that the greatest realism is always required and that the results will always be interpretable.

It is well-established that as models increase in realism and complexity, the data demands increase; data demands that are often impossible to satisfy except through estimation methods. As more input data are estimated, the reliability of the results becomes compromised. Also, as the complexity of the model increases, the results become more challenging to interpret and thus more prone to mis-interpretation.

For these reasons, we recommend that simpler models be applied first and the complex models only used when necessary.

Occam's razor or the Principle of Parsimony

Essentia non sunt multiplicanda praeter necessitatem

"What can be done with fewer (assumptions) is done in vain with more"

3.5.1 Stage 1: Chemical classification and physical data collection

Partitioning

For convenience in modelling, three chemical types have been defined (Mackay et al, 1996a). this allows these chemicals to be treated by multimedia models such as those developed by the CEMN. The defining characteristics and some examples are given in Table 2. Table 3 gives the typical property data required for a chemical of each defined type. Data sources and estimation methods are suggested later in this section.

Table 2: Chemical types are based on partitioning behaviour.

Type	Partitions into	Z	Equilibrium criterion	Examples
1	all media	non-zero in all media	fugacity	most organic chemicals (e.g., chlorobenzenes, PCBs) including ionizing chemicals
2	not air	\approx or = 0 in air	aquivalence	cations, anions, involatile organic chemicals, and surfactants
3	not water	\approx or = 0 in water	fugacity	very hydrophobic compounds (eg., long-chain hydrocarbons, silicones)
4	not air and not water	\approx or = 0 in air and water	none	polymers
5				speciating chemicals (e.g., mercury)

Type 4 substances tend to remain in their original state as a solid in the environment thus modelling of the type described in this document does not serve a useful purpose. It should be noted that polymers may contain unreacted monomer and other additives such as plasticisers that are of possible concern. These substances may degrade to form other chemicals that can have adverse effects.

Type 5 substances display complex environmental fate and require case-specific evaluation.

Table 3: Typical physical chemical property data required for each chemical type

Type	Data required
1	molar mass, data collection temperature, solubility in water, vapour pressure, and octanol-water partition coefficient (K_{OW}) and possibly pK_a
2	partition coefficients from solids or organic carbon to water
3	partition coefficients from solids or a pure phase to air

Aquivalence

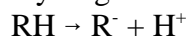
The Z values for Type 2 chemicals are calculated using the equivalence approach (Mackay 2001). Since the vapour pressure and the air-water partition coefficient may be zero, Z for water becomes infinite if calculated as for Type 1. Therefore, calculation starts by defining Z for water as 1.0. All other Z values are deduced from the Z value for water and the partition coefficient of the phase with respect to water.

Ionizing Chemicals

Organic acids and bases such as phenols, carboxylic acids, and amines, may dissociate or ionize in the environment. As a result of this tendency to dissociate an acidic substance may exist in its non-ionic protonated or neutral form and its ionic de-protonated, or charged, form. Bases behave similarly but the protonated form is charged. 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.

The simple, first order approach of Shiu et al (1994) and Mackay et al (2000) to quantifying these fractions is briefly described below.

The neutral form of an acid molecule can be designated RH 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^-



The molecule may have several hydrogens that can dissociate. No correction is made for the effect of cations other than H^+ . It is assumed that dissociation takes place only in aqueous solution, not in air, organic carbon, octanol or lipid phases. Some ions and ion pairs are known to exist in the latter two phases, but there are insufficient data to suggest a general procedure for estimating quantities.

The dissociation constant is defined as follows.

$$K_a = [R^-] [H^+] / [RH] \quad (20)$$

so

$$pK_a = \log ([R^-] [H^+] / [RH]) \quad (21)$$

Typical values of pKa for chlorinated phenols range from 4 to 8. It is the relative magnitudes of pKa and pH, the environmental acidity, that determine the extent of dissociation.

Rearranging equation (20) gives

$$\begin{aligned} \log ([R^-] / [RH]) &= \log I = -\log [H^+] + \log K_a \quad (22) \\ &= pH - pK_a \end{aligned}$$

where I is the ratio of the ionized to non-ionized concentrations, pH is $-\log [H^+]$ and pKa is $-\log K_a$. Note that base 10 logarithms are used. This leads to the Henderson Hasselbalch equation

$$I = 10^{(pH - pK_a)} \quad (23)$$

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, use 5 and ignore the others, at least for screening purposes.

Assuming a pH of 7.0 and 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.

As a result of ionization, 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-ionised or non-ionised plus ionised forms. If the latter applies, the solubility and K_{OW} of the non-ionised form can be calculated. 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 used in QSARs will normally refer to the non-ionised form, not the ionised form

Models treating ionizing chemicals normally require the solubility of neutral species either from an estimation method or measured.

For the general case of a pKa measured at an acidity of pH_d , where the subscript d represents the data pH, the ionic to non-ionic ratio at of pH_d is

$$I_d = 10^{(pH_d - pKa)} \quad (24)$$

thus the non-ionic fraction is

$$x_{N_d} = 1 / (1 + I_d) \quad (25)$$

and the ionic fraction is

$$x_{I_d} = I_d / (1 + I_d) \quad (26)$$

The Z_{T_d} for both species in water at the pH of the data collection is $1/H_d$, therefore the Z for the ionic fraction is

$$Z_{I_d} = x_{I_d} \times Z_{T_d} \quad (27)$$

Similarly the Z for the non-ionic fraction is

$$Z_{N_d} = x_{N_d} \times Z_{T_d} \quad (28)$$

But, the Z for the non-ionic fraction is unaffected by the pH of the water and therefore, at the pH of the environment (e) is given by

$$Z_{N_e} = Z_{N_d} = x_{N_d} \times Z_{T_d} \quad (29)$$

The Z for the ionic fraction, at the pH of the environment, is given by

$$Z_{I_e} = I_e Z_{N_e} \quad (30)$$

And finally, the Z for both species together, at the pH of the environment, is

$$Z_{T_e} = Z_{N_e} + Z_{I_e} \quad (31)$$

To calculate the D values for the loss and transfer processes care must be taken to use the Z value relating to the species participating in the process.

The same arguments apply to bases. Rather than use the constant K_b it is usual to express it also as K_a , noting that $pK_a + pK_b = 14$.

Note that in the Handbook by Mackay et al (2000) the aqueous solubilities selected are primarily those of the non-ionic form.

Degradation

Chemical transformation, or degradation, can be considered to be the decomposition of the substance of interest into water, carbon dioxide, and inorganic compounds, however, only primary degradation, i.e., the degradation causing a change in the identity of the substance, is considered here. The daughter compounds are normally considered separately from the parent compound as they have a completely different set of properties, including a different toxicity, and thus a different priority.

Degradation is normally characterized as a first-order reaction and quantified by a reaction rate constant, k_i (1/h), or a half-life, τ_i (h) = $\ln(2)/k_i$ in each environmental medium, i. Degradation occurs by processes such as photolysis, hydrolysis, oxidation and biodegradation. The rates of these processes are strongly dependent upon environmental conditions such as temperature, solar insolation, and the nature and activity of the microbial community. Thus degradation data are characterized by a high inherent variability. For a more detailed discussion of natural variation in degradation half-lives consult Boethling and Mackay (2000) or Webster et al (1998). Various researchers have sought to acknowledge this variability by defining degradation classes and including a range of values in each class. For example, Syracuse Research Corporation (SRC), uses an semi-quantitative scheme based on designations of hours (4.1 h) , hours to days (30 h), days (56 h), days to weeks (208 h), weeks (360 h), weeks to months (900 h), months (1440 h), and “recalcitrant” (3600 h) (ref). Another is the lognormal classification scheme of Mackay et al (2000) and Webster et al (2003) as shown in Table 4.

Table 4: Lognormal degradation classification scheme.

Class	Mean half-life (hours)	Range (hours)
1	5	<10
2	17 (~ 1 day)	10 - 30
3	55 (~ 2 days)	30 - 100
4	170 (~ 1 week)	100 - 300
5	550 (~ 3 weeks)	300 - 1000
6	1700 (~ 2 months)	1000 - 3000
7	5500 (~ 8 months)	3000 - 10000
8	17000 (~ 2 years)	10000 - 30000
9	55000 (~ 6 years)	30000 - 100000
10	(> 11 years)	> 100000

Cautionary note:

The absence of degradation gives an infinite half-life. In practical terms, this can be represented by the very large half-life value of 10^{11} hours which translates to a negligible reaction rate. A half-life of zero, by contrast, indicates an infinitely fast reaction process. Most CEMN models prohibit the unrealistic entry of a zero half-life.

Data sources and estimation methods

For chemicals that have been studied, there are some excellent compilations of data such as Mackay et al (2000), Verschuere (2001), and the Handbook of Environmental Fate and Exposure Data for Organics by Howard (1989, 1990, 1991, 1993, and 1997).

In the absence of data, estimation methods must be used to determine chemical partitioning properties. These methods should be used with caution and with a knowledge of the limitations of the method. A very brief overview is provided here. For more information, the reader is referred to Boethling and Mackay (2000), and Mackay (2001). Some estimation methods are included in the EPI Suite software (available from http://www.syrres.com/esc/est_soft.htm or <http://www.epa.gov/oppt/exposure/docs/episuitedl.htm>).

Henry's Law Constant, H ($\text{Pa m}^3/\text{mol}$)

The air-water partition coefficient, K_{AW} , is H / RT where R is the gas constant, 8.314 Pa/m^3 , T is temperature (K), and H can be estimated from the vapour pressure, P (Pa), and the water solubility, S (mol/m^3), (Mackay 2001). Note that both P and S must be of the same state, i.e., solid (S) or liquid

(L). That is, $H = P_L / S_L$ or $H = P_S / S_S$. For substances with a melting point greater than 25 °C, i.e., solids at room temperature, a fugacity ratio, F, can be defined from the melting point, MP, and the temperature at which P_S was measured (normally about 25 °C).

$$F = e^{(6.79 \times (1-MP/T))} \quad (32)$$

The sub-cooled liquid vapour pressure, P_{SL} is then P_S / F and $H = P_{SL} / S_L$

Organic Carbon Partition Coefficient, K_{OC} (L/kg)

The organic carbon - water partition coefficient, K_{OC} (L/kg), can be estimated from either K_{OW} , or the water solubility, S.

Table 5: K_{OC} estimation methods

Estimation	Source
K_{OC} (L/kg) = 0.41(kg/L) K_{OW}	Mackay 2001
K_{OC} (L/kg) = 0.35(kg/L) K_{OW}	Seth et al 1999
equations of the form $\log K_{OC} = a \log K_{OW} + b$ with various values of a and b	Boethling and Mackay 2000 p153 Table 8.1
equations of the form $\log K_{OC} = a \log S + b$ with various values of a and b	Boethling and Mackay 2000 p154 Table 8.2

Soil and Sediment - Water Partition Coefficients

The partitioning between the solid fraction of soil or sediment, and water, can be obtained as a measured equilibrium partition coefficient, K_p (L/kg) = C_s (mg/kg) / C_w (mg/L). Using the density of the solids, a dimensionless partition coefficient can be determined. For example, for soil,

$$K_{Soil\ Solids, Water} = K_p \text{ (L/kg)} \rho_{Soil\ Solids} \text{ (kg/m}^3\text{)} / (1000 \text{ L/m}^3\text{)} \quad (33)$$

where $\rho_{Soil\ Solids}$ is the density of soil solids and 1000 L/m³ is a volumetric conversion.

It is also possible to estimate K_p from K_{OC} as

$$K_p \text{ (L/kg)} = y K_{OC} \text{ (L/kg)} \quad (34)$$

where y is the mass fraction of organic carbon present in the soil solids (i.e., dry soil) (Boethling and Mackay 2000; Mackay 2001). There are four assumptions that must apply to use this estimation method, otherwise K_d should not be estimated using this equation.

- 1 - sorption is exclusively to the organic component of the soil (or sediment)
- 2 - all soil (or sediment) organic carbon has the same sorption capacity per unit mass
- 3 - equilibrium is observed in the sorption-desorption process
- 4 - desorption isotherms are identical.

Aerosol - Air Partition Coefficient

Aerosol - air partitioning is not normally measured for evaluation purposes. It can be measured in the environment by measuring concentrations in air before and after filtration. It is variously estimated as shown in Table 6.

Table 6: K_{OA} estimation methods

Estimation	Source
$K_{QA} = 6 \times 10^6 / P_L$	Mackay 2001
$K_p (m^3/\mu g) / K_{OA} = B$ where B is $b \times 10^{-12}$ thus $K_{QA} = K_{OA} \times \rho_Q (kg/m^3) \times b \times 10^{-3} (m^3/kg)$ b is approximately 1.5 for most persistent organics	Finizio et al 1997
$\log K_p = (a * \log K_{OA}) + b$ or $K_{QA} = K_{OA}^a \times \rho_Q (kg/m^3) \times 10^{(b+9)} (m^3/kg)$ a is approximately 0.55 and b is -8.23 for most persistent organics	Finizio et al 1997
$\log K_p (m^3/\mu g) = \log K_{OA} - 12.61$ or $K_{QA} = K_{OA} \times \rho_Q (kg/m^3) \times 10^{-3.61} (m^3/kg)$	Bidleman and Harner, 2000

Due to the small volume of aerosols present, the amount of chemical sorbed is small. For substances with a high K_{OA} , the concentration may be high and scavenging may be an important transport vector for removal of the substance from the air. For low K_{OA} substances, partitioning to aerosols is relatively unimportant. When K_{OA} is very large, i.e., 10^{10} and above, most chemical in the atmosphere is likely to be sorbed to aerosols. Benzo[a]pyrene is an example.

Biota - Air and Biota - Water Partition Coefficients

Partitioning between the abiotic and biotic media in the environment is not normally measured. Partitioning between biota (B) and the air or water is usually estimated assuming partitioning to only the lipid fraction. If this assumption is not true, some other estimation method should be used. For aquatic biota such as fish, if a lipid fraction of 0.05 is assumed, then the partitioning coefficient, $K_{BW} = 0.05 K_{OW}$. Similarly for vegetation, if the leaves are assumed to have a lipid fraction of 0.01, the leaf-air partition coefficient, $K_{BA} = 0.01 K_{OA}$. For roots, a root-water partition coefficient may be estimated in the same way.

Degradation

As for chemical partitioning properties, there is a variety of data sources including those listed above. Specific to degradation data is the Handbook of Environmental Degradation Rates (Howard, 1991). Estimation methods have also been developed. A review of existing methods and suggestions for their application are given in a companion document to this report (Arnot et al, 2005). Some estimation methods are included in the EPI Suite software (<http://www.epa.gov/opptintr/exposure/docs/episuite.htm>).

Toxicity

It is important to identify the potential for concern regarding the toxicity of the substance. If a substance is unlikely to have toxic effects at the expected concentrations, it may not warrant further investigation. A substance with a higher probability of toxic effects should be investigated first, and more fully.

To a first approximation there are three methods of expressing toxicity.

First is to define a concentration external to the organism that will cause a specified effect such as lethality or failure to reproduce. The aquatic LC50 and the occupational Threshold Limit Value (TLV) in air, **applicable to occupational exposure**, are examples.

Second is a dose, often expressed in mg/kg body weight per day, which causes an effect. This is widely used in human toxicology. The dose may be the product of a concentration in food and the quantity of food consumed per day.

Third is the delivered dose or the internal concentration or quantity or critical body residue of chemical causing the effect. For example, a chemical that exerts toxicity by narcotic or baseline toxicity does so at a concentration in the body of 1 to 5 mmol/kg body weight. The concentration may also be in a specific tissue within the organism. Generally, chemicals which have similar modes of toxic action have similar internal concentrations at the same effect level. Obviously the calculation of this concentration requires a bioaccumulation or even a pharmacokinetic model.

The issue evaluating toxicity is beyond the scope of this Guidance but it is useful for the modeller to know how the results are to be used in the evaluation of toxic effects. Many believe that the future of environmental toxicology lies in calculating the third metric of toxicity, namely the critical body residue required to cause the specified mode of toxic action. The mode of action can, in principle, be predicted from molecular structure.

3.5.1 Stage 2: Acquisition of discharge data

This is typically a very challenging task. For many substances of concern, discharges are dispersed and highly population and culturally dependent. The components of automobile exhaust are typical of this group of substances. At the other extreme are substances discharged at point-sources, often industrial in nature. Where such discharge data exist they may be incomplete or suited only local-scale evaluations.

3.5.2 Stage 3: Evaluative assessment of chemical fate

Armed with the data collected in stages 1 and 2 of this 6-stage process, modelling is now both possible and useful. An examination of the behaviour of the substance in a generic or “evaluative” environment increases our understanding without requiring regional properties and in a way that can be compared across regulatory jurisdictions. This can be preformed with a models such as the 3-part set Level I, Level II, Level III or the EQC model that combines the calculations of the other three but with less flexibility for the user. (See Section 4.3.1 to 4.3.4 for details on these models.) For an evaluative assessment a unit amount or rate of emission can be used as absolute concentrations are not the focus of this stage of the six-stage process.

The area for an evaluative assessment should be large enough that wind dispersion does not dominate the distribution of concentrations to the exclusion of all other information. In the EQC model an area of 10^{11} m² or 10^5 km². This is about the size of southern Ontario or twice the size of Nova Scotia. This is large enough to show chemical exchange behaviour in the environment. If as area on the order of a few kilometres square is used, local sources and wind patterns will dominate and a dispersion model should be used. One can consider two extremes of scale, for very small areas losses are entirely dominated by advection but for the entire globe degradation losses dominate. Degradation and advection losses become equal when the reaction half-life is similar to the advection residence time. The smaller value dominates since it reflects a faster process.

In the Level I calculations, the partitioning properties of a chemical are used to show the environmental media in which it will tend to be present. The term “realistic presence” has been used to designate an amount of at least 5% in an environmental medium (Webster et al 2004a; Woodfine and Mackay 2001; Environment Canada 2003). A multimedia chemical is realistically present in more than one environmental medium. For single-medium chemicals, i.e., chemicals with a realistic presence in only one medium, multimedia models are neither needed nor useful. The fate of a single-medium chemical is limited to processes occurring solely in that medium (advection and degradation). Multimedia models should only be used if the chemical is realistically present in at least two environmental media.

The “realistic presence” concept has been suggested as a rational method of avoiding demands for data which prove to be of little or no value. If a chemical is present only to the extent of say 2% in a medium it is unlikely that the overall fate of the chemical, especially its persistence, will be affected by rates of degradation in that medium. It can thus be argued that no degradation rate data are needed and a zero degradation rate (infinite half-life) can be assumed. The 5% cut-off has been established by experience but is somewhat arbitrary. (Woodfine and Mackay 2001, Webster et al 2004a).

In the Level II calculations, the partitioning and degradation properties of a chemical are combined to give a first estimate of the relative importance of each removal process, and the longevity or persistence (P) and long-range transport potential (LRT) of the chemical. While current Level II models do not explicitly calculate LRT it can be calculated manually as the product of an assumed wind speed (km/h), the overall residence time of the chemical (h), and the ratio of the amount in air

to the total amount in the system. The values of P and LRT should be considered in the context of the values for ranking against other chemicals. The absolute value P and LRT calculated by these models are not meaningful.

For multimedia chemicals that are not realistically present in at least two media as identified in the Level I calculations, the same simplifying assumptions regarding the degradation data requirements for Level II calculations may be made. For example, if a chemical does not partition appreciably into air, the degradation half-life in air can be assumed to be infinite, i.e., assume no degradation of the chemical in a medium in which it is not present. This assumption represents a reduction in the data requirements while having a minimal impact on the model results (Woodfine and Mackay 2001, Webster et al 2004a, Environment Canada 2003).

In a Level III calculation, the partitioning and degradation properties of the chemical are combined with intermedia transport process information. In the absence of the equilibrium assumption, the relative emission rates to each environmental medium becomes essential information because the results are often strongly dependent on the mode-of-entry. It is common practice among researchers, when these relative emission rates are not known, to perform a separate Level III calculation for a unit emission into each potential receiving medium and focus on the worst-case scenario. Thus if there are three potential receiving media, the calculations are performed three times, once for each medium as receiving a unit emission. The results of the three scenarios are compared and the assessor can then focus on the worst-case, e.g., the unit emission to air. Identifying the worst-case scenario will require a knowledge of the target organism and exposure routes. Of course, if emission mode-of-entry data are available they should be used.

From the Level III model and using the evaluative environment the relative importance of each transport and removal process can be ascertained for the chemical and emission scenario under investigation. The importance of each process is chemical and emission scenario dependent and can not be determined in a general way. Consider for example, a chemical with a high K_{OA} emitted to air. This chemical will sorb strongly to aerosols and wet and dry aerosol deposition will be important. Rain rate will be important as it affects the rain scavenging of this aerosol-associated chemical. The dissolved fraction of the rain deposited fraction of chemical will be relatively less important and depends on the K_{AW} of the chemical.

Level III calculations also provide values for P and LRT. When the relative emission rates to each environmental medium are known, this represents an improvement on the estimate provided by the Level II calculations. It is not yet clear that there is any benefit from these estimates of P and LRT where the relative emission rates are not known, at least with some degree of confidence. The value of LRT is, again, not meaningful in an absolute sense but should be compared to the values for other chemicals to provide a ranking. The value of P, while meaningful, may also usefully be compared between chemicals.

Finally, Level III calculations using an evaluative environment can be compared to monitored concentration data. This must be done with some care and acknowledging the inherent error that will be caused by the properties of the evaluative environment not matching those of the region where

the data were collected. There are some advantages to this pseudo-regional modelling. First, monitoring data from a variety of regions can be combined. For example, much of the northern US, southern Canada, and western Europe all have somewhat similar environments. Thus when monitoring data are sparse, data from all of these regions can be combined and the model results compared to the range of monitored values. It is of particular interest to compare the relative concentrations, that is, if the monitored concentration in the soil samples is ten times that of the water samples, is this seen in the model results? This type of comparison may point to selective sampling where only locations of high concentration need be monitored.

3.5.3 Stage 4: Regional or far-field evaluation

Regional or far-field evaluations with region-specific environmental properties provide the first set of concentrations for direct comparison to monitoring data collected in a specified area such as Southern Ontario, or Northern BC.

The ChemCAN model was developed for this purpose and contains a database of properties for 24 regions of Canada. For consistency and comparison the database also contains the standard EQC environment.

As for an evaluative assessment, a region should be defined as an area large enough that wind dispersion does not dominate to the exclusion of all other information. Local hot spots are not treated. It is important when defining a region for this stage in the process to specify an area large enough that advective flow-through will not dominate the chemical removal processes such that all intermedia and degradation effects are obscured. In ChemCAN the Canadian regions range in size from 2176000 km² for the Arctic and North Nunavut region to 80190 km² for the B. C. - South Pacific Maritime region. This is large enough to show chemical exchange behaviour in the environment. If an area on the order of a few kilometres square is used, local sources and wind patterns will dominate and a dispersion model should be used. A region should not be defined with an area of less than about 100 km by 100 km, or 10000 km².

Using too large an area will also lead to erroneous results as the assumption of a single well-mixed air compartment will be violated. As a general rule, the area should not be greater than about 1000 km by 1000 km or 1000000 km². Larger areas should be sub-divided and each section considered separately with wind and river currents acting as transport mechanisms between the sections.

Cautionary Note:

Defining an area less than 10000 km² or greater than 1000000 km² in a regional model may not give meaningful results.

A regional model calculates the average conditions over the region since each environmental medium is treated as a single, well-mixed box and thus has only one concentration for the whole region. These models are not suited to treating point-source releases. Dispersed contaminant sources such as vehicle emissions, releases from consumer products, and historic discharges of persistent contaminants may be understood using a regional-scale model.

Cautionary Note:

Regional models are not suited to treating point-source emissions (e.g. an industrial stack) unless there are numerous point sources (e.g. household chimneys). The model may not give meaningful results.

For a regional model, the relative emission rates to each environmental medium are not sufficient. The absolute discharge rates to each should be known. If these rates are unknown or uncertain but good monitoring data are available, a unit emission with the correct relative emission rates may be used. By scaling the results to obtain the concentration in the best characterized environmental medium the estimated emissions may be compared with reported emissions.

Cautionary Note:

Sampling programs, especially for environmental media such as soil or sediment give only the conditions found locally and are often located in areas suspected of being contaminated and thus may reflect a higher than average concentration of contaminant.

Global modelling is a further extension of the far-field model and is discussed later.

3.5.4 Stage 5: Local or near-field evaluation

Local or near-field models are useful for focussing attention on areas known to have higher than average concentrations of the chemical of interest, or the immediate effect of a local point-source such as a production plant. Local scale models typically treat areas of less than a few kilometres square. Examples of such near-field models are atmospheric dispersion models, water quality models for rivers and lakes, soil fate models (as routinely used in pesticide registration and regulation), and groundwater models.

Cautionary Note:

Defining an area greater than 1000 km² or less than 30 km² in a local-scale model may not give meaningful results.

Local-scale abiotic evaluation

Included in this category of model are the lake model QWASI, and the agricultural field model BASL4 (described in a companion report, Hughes et al 2005). Dispersion models may also be local-scale models, however, these are single medium models and therefore are the domain of other researchers outside the CEMN.

Local-scale biotic evaluation

Included in this category of models are various types of mathematical relationships used to quantify chemical transfer from the abiotic environment into biota such as plants and animals. Several types of bioaccumulation models are described including empirical models, mechanistic models, physiologically-based pharmacokinetic models (PBPK) and food web bioaccumulation models. Empirical models are typically derived by fitting a mathematical relationship to empirical data. For example, quantitative structure-activity relationships (QSAR) provide estimates based on the physical chemical property of the chemical (e.g., K_{ow}). Mechanistic bioaccumulation models include equations that quantify the mass balance of chemical uptake and elimination in a single organism. These models generally consider an organism as either a single compartment (i.e., whole body) or two compartments (i.e., body and gastrointestinal tract). Bioaccumulation models have been developed and parameterized for a number of species including zooplankton, invertebrates, marine mammals, terrestrial mammals, amphibians and birds as well as various plant species ranging from algae to agricultural crops and forests. PBPK models are further developed mechanistic models that include multiple compartments within an organism (e.g., brain, liver, kidney, muscle etc). Thus PBPK models can provide estimates of chemical concentrations in specific tissues as distinct from a whole body concentration. They require significantly more organism-specific information (e.g., tissue perfusion and blood flow rates) than the less detailed bioaccumulation models. For many chemicals and organisms equilibrium within the organism occurs quickly and techniques such as lipid normalization can provide tissue based estimates in the absence of data required for PBPK models. Food web bioaccumulation models consist of a collection of single organism bioaccumulation models that are interconnected by feeding relationships reflecting those observed in the natural environment.

Cautionary Note:

Most bioaccumulation models have been developed for poorly metabolized non-ionic organic chemicals. For chemicals that are metabolized, reliable estimates of the metabolic transformation rate are required. There is greater uncertainty in model predictions for ionizing chemicals. Metals should be modelled using appropriate metal bioaccumulation models. These require metal-specific parameters.

Stage 6: Risk evaluation

A full treatment of risk evaluation is beyond the scope here but it generally involves comparison of a calculated or measured concentration with a concentration known to cause an adverse effect. The ratio of these concentrations is often referred to as a risk quotient or a PEC/PNEC (predicted effect concentration/predicted no-effect concentration) ratio. This quotient or ratio should be as small as possible.

3.6 Other models addressing specific issues

3.6.1 Global modelling

In some circumstances, a model calculation of a chemical's fate on a global scale may be required. This is generally only of interest for substances of high environmental persistence and mobility. One of the advantages of a global modelling approach is that no spatial boundary conditions need to be specified (e.g. there is no need to specify possibly highly uncertain concentrations in media advected into the model region). For virtually all chemicals the global environment can be considered a closed system. Also, as there is only one global environment, model users can typically rely on a default environmental scenario. However, when simulating the real fate of a chemical on a global scale, global emission information is required, which is often difficult to obtain. A variety of global modelling approaches for persistent organic chemicals have been presented (Scheringer and Wania, 2003).

3.6.2 Groundwater

New substances that are water soluble, have low sorptive capacity and are released directly to soil at depth from a use activity such as oil and gas exploration, may come into contact with groundwater and be transported to surface water bodies via groundwater recharge. This is not expected to be a common occurrence for new substances in Canada since relatively few new substances fit the above description. However, a simplified groundwater transport model that assumes a homogeneous soil and other default transport parameters (e.g., hydraulic conductivity) can be used to model a generic situation in which a water soluble compound is released directly to soil in the vicinity of a surface water body (e.g., wetland). This model should be viewed as a first cut and may require more site specific information on soil and groundwater conditions, if available.

In 1996, the Canadian Council of Ministers of the Environment's (CCME's) Subcommittee on Environmental Quality Guidelines for Contaminated Sites developed a generic groundwater transport model to estimate the potential for soil contaminants to impact surface water bodies via groundwater recharge (Appendix C and D, CCME 1996). The model is worked backwards so that a new substance risk assessor can input the Critical Toxicity Value or CTV (formerly called the Concentration of Concern) and back calculate the concentration in groundwater that would cause an exceedence of the CTV in a surface water body recharged by the groundwater.

$$Y = DF \times CTV(K_d + \theta_m)$$

where,

Y = critical soil concentration (mg/kg)

DF = dilution factor (default = 50)

CTV = critical threshold value (mg/L)

K_d = soil-water partition coefficient

θ_m = soil moisture content (default = 41%
from Level III model)

The general equation of the model is given below.

The model is presented in detail in Appendix G and requires information on the physical-chemical properties of the new substance, particularly the K_d . The risk assessor should check to determine if application of the groundwater model is appropriate. Site-specific circumstances may dictate that a groundwater transport pathway is not of concern at a particular site. For instance, it should be known if there is a surface water body within a relatively short distance of where the new substance is released to the sub-soil compartment.

In the ChemCAN model (version 6.00) an estimate is made of groundwater concentration as follows. The soil pore water concentration is calculated, then it is assumed to be reduced in the aquifer by a factor $(1 + K_{ow}/500)$. For example, if K_{ow} is 500 then the estimated groundwater concentration is half the pore water concentration. This should be regarded as only an approximate screening level calculation to obtain an order of magnitude value for the level of contamination of groundwater.

3.6.3 Global warming potential

In Canada's National Action Program on Climate Change, Canadian Federal, Provincial, and Territorial Governments identified climate change as a major sustainable development issue. Canada was one of over 180 countries to sign the Framework Convention on Climate Change at the United Nations Conference on Environment and Development in Rio de Janeiro in June 1992. Canada ratified the Convention on March 21, 1994 and is working on its current commitment to stabilize greenhouse gas emissions at 1990 levels by the year 2000.

Global warming potential (GWP) is the ratio of the warming caused by a substance to the warming caused by a similar mass of carbon dioxide over a period of time. While any time period can be selected, the 100 year GWPs recommended by the IPCC and employed by the United States for policy making and reporting purposes were used in this report (IPCC 1996). The GWP of CO₂ is defined to be 1.0. CFC-12 has a GWP of 8,500, while CFC-11 has a GWP of 5,000. Various HCFCs

and HFCs have GWPs ranging from 93 to 12,100. Water, a substitute in numerous end-uses, has a GWP of 0. A table of GWPs estimated for various greenhouse gases can be found at:

[http://yosemite.epa.gov/OAR/globalwarming.nsf/UniqueKeyLookup/LHOD5MJTD8/\\$File/2003-final-inventory_annex_s.pdf](http://yosemite.epa.gov/OAR/globalwarming.nsf/UniqueKeyLookup/LHOD5MJTD8/$File/2003-final-inventory_annex_s.pdf)

More detailed information on the estimation of GWP using simple climate models is described by the Intergovernmental Panel on Climate Change (IPCC) in a series of technical papers on climate change (IPCC 1997).

Typically, the GWP of a new substance will be provided by the Notifier (when appropriate) based on 20, 100 and 500 year estimates. The atmospheric lifetime of the substance should also be provided based on model calculations. Many GWP estimates for new substances will be provided for HFCs, HFEs, HCFCs, and PFCs. These estimates can be used to evaluate the potential for global warming based on the intended use and release of the substance. The substance may regulatory control solely based on its GWP.

3.6.4 Ozone depletion potential

In 1987 Canada and other countries signed the Montreal Protocol on Substances that Deplete the Ozone Layer. The Protocol in essence, describes the phase out of CFC and other ozone depleting substances by countries that ratified the protocol. The ozone depletion potential (ODP) is the ratio of the impact on ozone of a substance compared to the impact of a similar mass of CFC-11. Thus, the ODP of CFC-11 is defined to be 1.0. Other CFCs and HCFCs have ODPs that range from 0.01 to 1.0. The halons have ODPs ranging up to 10. Carbon tetrachloride has an ODP of 1.2, and methyl chloroform's ODP is 0.11. HFCs have zero ODP because they do not contain chlorine.

The ODP potential of a substance suspected of having ODP (e.g., contains chlorine, bromine and no hydrogen) should be specified by the Notifier or if not, should be obtained from the Notifier. However, because of the phase out of ozone depleting substances under the Montreal Protocol, chemical companies in Canada are seeking replacements to ODP substances. As a result, it is not likely that many new CFC-type substances will be notified in Canada. Rather, replacements such as HFCs, HFEs, HCFCs will be more common. These substances have low ODP but high GWP.

More information on the estimation of ODP can be found in the Scientific Assessment of Ozone Depletion by the World Meteorological Organization (WMO) (WMO 1998).

3.6.5 Chemical Space Diagrams

When assessing chemical behaviour it is often useful to identify the chemical's location on a chemical space diagram (Gouin et al., 2000; Meyer et al., 2005). Two such diagrams are in current use. First is a plot of $\log K_{AW}$ vs $\log K_{OW}$ as shown in Figure 4a. If the partition coefficients are internally consistent (Cole and Mackay, 2000; Beyer et al., 2002), i.e. if the effect of the mutual solubility of water and octanol on the chemical's solvation in water and octanol is neglected, then the diagonals shown in Figure 4a correspond to lines of constant K_{OA} or K_{OW} / K_{AW} . Second is a plot of $\log K_{AW}$ vs $\log K_{OA}$ as shown in Figure 4b. The diagonals correspond to lines of constant K_{OW} .

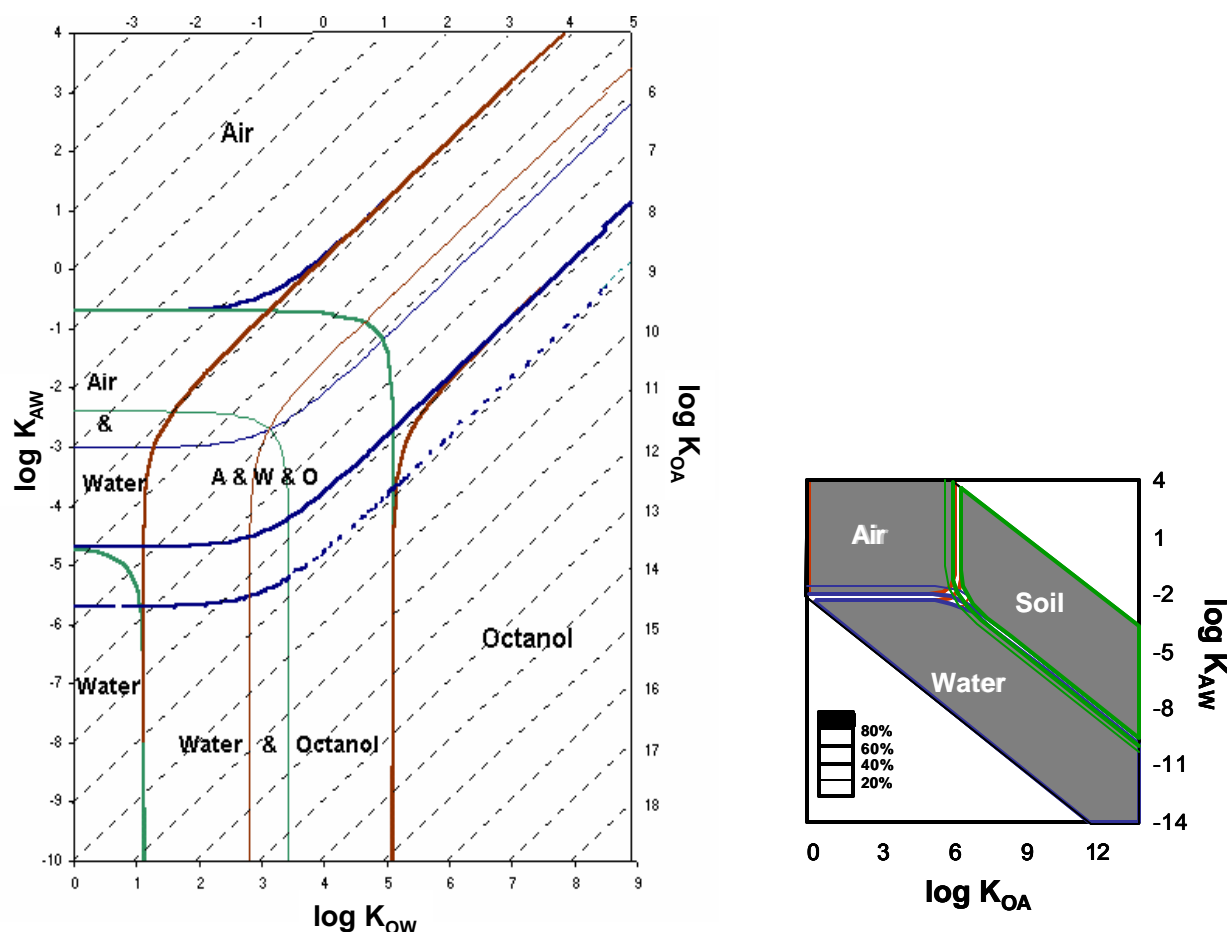


Figure 4: Chemical space diagrams (a) is the $\log K_{AW}$ vs $\log K_{OW}$ plot; (b) is the $\log K_{AW}$ vs $\log K_{OA}$ plot

By placing the chemical on such a plot it becomes apparent which environmental compartment, or compartments if the chemical partitions equally between two or more compartments, will likely be important in assessing the chemical fate of the substance. In this method an equilibrium steady-state mass balance model (Level I) is used to identify into which environmental compartment a substance

will most likely partition. A useful simplification is to view the environment (for partitioning purposes) as volumes of air, water, and octanol. The octanol represents organic matter in soil and sediment. The environment is divided into compartments of air, water and octanol, where the octanol compartment represents the organic carbon content associated with surface media, commonly represented by the soil and sediment compartments. For example the partitioning between water and organic carbon, K_{OC} , can be estimated as $0.35 \times K_{OW}$ (Seth et al., 1999).

Knowing the volume ratios of each environmental compartment, as well as the partition coefficients, K_{AW} and K_{OW} , it is possible to determine the mass fraction, F , of a chemical in each medium by

$$F_i = (V_i K_{iW} / (K_{WW} V_W + K_{AW} V_A + K_{OW} V_O))$$

where the subscript i is air, water or octanol, K_{WW} is 1.0 and V is the volume. The volume ratios for air:water:octanol used by Gouin et al. (2000), and adopted here, are respectively 650 000:1300:1. This method is useful for identifying where a substance will partition, which is useful for identifying the environmental half-lives that are most likely influencing the overall persistence of the substance, as described by performing a Level II calculation. For instance, if a substance is found to have a mass fraction in a particular compartment that is greater than 99%, then it is likely that the half-lives for the other environmental compartments will have a negligible influence on the overall persistence, overall, and can therefore be ignored.

It is important to note that the mass fraction of a substance for a particular environmental medium, as determined using the equation shown above, will be strongly influenced by the volume fractions used. Thus, the partitioning behaviour of a substance will largely depend on the environment into which it is emitted, and may vary from region to region. Also notable, is the temperature dependence of the partition coefficients, K_{AW} , K_{OW} and K_{OA} . Typically, the position of a chemical substance in the chemical space will shift to the lower right in Figure 4a in response to decreasing temperatures (Beyer et al., 2003).

As an illustration of the use of these diagrams we describe below their use in calculating the Arctic Contamination Potential.

The Globo-POP model (which is described in detail later) has been used in the context of predicting which chemicals have the potential to reach and accumulate in the Arctic environment. An indicator, termed Arctic Contamination Potential (ACP) was defined as the ratio of a chemical present in Arctic surface media relative to the total globally emitted (eACP) or accumulated (mACP) amount of a chemical (Wania, 2003, 2004). The eACP can be interpreted as indicator of LRT, which is independent of the emission amount and which can be compared directly with simpler LRT indicators such as the characteristic travel distance or the spatial range. The mACP on the other hand is indicating what fraction of the total global inventory is present in Arctic latitudes. Even for completely persistent substances eACP and mACP are not necessarily the same, because loss processes other than degradation may result in the total globally accumulated amount being smaller than the total globally emitted amount. This applies in particular to substances that sorb to suspended solids, which can be transferred to the deep sea or buried fresh water sediments (Wania, 2004).

The numerical value of the ACP quotients is dependent on the time and location of chemical release into the global environment. For comparative and predictive investigations it is therefore useful to use a standardized emission scenario. This generic emission scenario assumes that the zonal distribution of emissions mirrors the latitudinal distribution of the human population (Wania, 2003). It further assumes continuous steady emissions over a one (ACP1) or ten (ACP10) year time period. The eACP10 is most suitable for comparing chemicals in terms of their LRT behaviour, and is the form of the ACP that was used in intercomparison studies with other LRT assessment models (Fenner et al., 2005). Among the current LRT assessment methods, the ACP/Globo-POP approach is unique in taking into account the spatial and temporal variability of temperature on the globe. This has an impact both on chemical persistence (because of the zonal dependence of degradation rates) and gas phase-condensed phase distribution, which in turn affects air-surface exchange and thus transport and accumulation. Consequently, model intercomparison studies (e.g. Fenner et al., 2005) reveal that assessment results for both P and LRT potential by Globo-POP can deviate quite substantially from those of simpler assessment techniques. The Globo-POP approach also considers transport in both atmosphere and ocean, and can deal with different modes of emission. However, it is limited in terms of the partitioning properties of the substances that can be evaluated. Specifically, very volatile ($\log K_{OA} < 3$) and very water soluble substances ($\log K_{AW} < -5$) lead to model instability and can therefore not be simulated.

One approach to find the substances with highest potential for accumulation in remote cold regions seeks to identify the hypothetical combination of chemical distribution and degradation properties which lead to maximum ACP values. If one first neglect the influence of degradation properties, it is possible to first focus on the distribution characteristics. As in Globo-POP these are expressed in terms of K_{OA} , K_{AW} and K_{OW} , ACP results for perfectly persistent chemicals can be displayed in two dimension partitioning maps (Figure 5, Wania, 2003) as introduced earlier in this document.

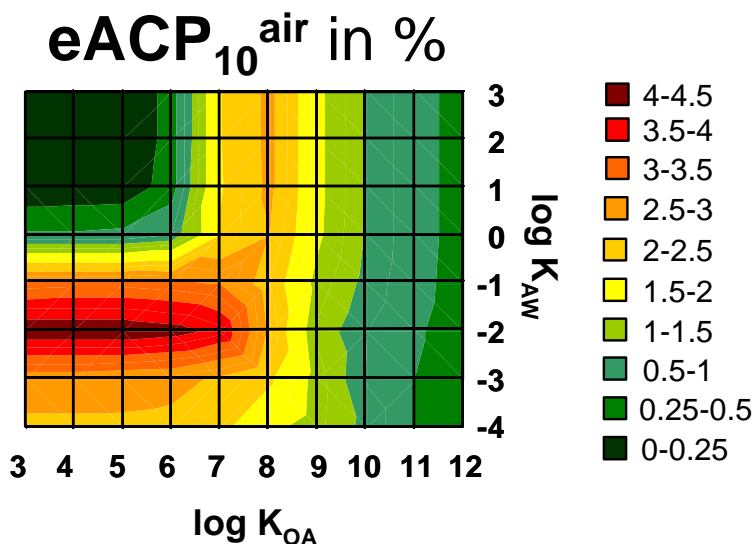


Figure 5: Arctic Contamination Potential

The ACP of a perfectly persistent organic chemical tends to be higher for two combinations of partitioning properties: relatively volatile ($\log K_{OA} < 9$) and water soluble ($4 > \log K_{AW} > -0.5$) substances and substances which are semi-volatile ($6.5 < \log K_{OA} < 10$) and relatively hydrophobic ($\log K_{AW} > -3$). Very volatile chemicals with $\log K_{OA} < 6.5$ and $\log K_{AW} > -0.5$ remain in the atmosphere even under Arctic temperature conditions, whereas very involatile chemical with a $\log K_{OA} > 10$ are efficiently and irreversibly deposited with atmospheric particles before reaching the Arctic (Wania, 2003).

As a result, the ACP can be rapidly estimated for any persistent chemical from its location on the chemical space diagram. It is believed that such diagrams can be used in other contexts in which partitioning properties are important.

4 CEMN MODELS

4.1 Model Development Process and Implementations

Model development is an ongoing and iterative process. Laboratory and field measurements lead to an understanding of processes of chemical transfer and transformation. The mental model resulting from this understanding is captured as a set of equations for the processes that are generally considered to be important. The physical representation of a mental model may take any one of a variety of forms, most often spreadsheets are used by the researchers as they develop their understanding of the processes individually and in context. The ease with which equations and parameters may be modified in a spreadsheet make it a very useful tool for model implementation during the development stages. Once the set of equations is established, “software” can be developed. Software is distinguished by its independent nature; it is complete in itself and does not require external software (such as Excel®) to operate. Good software development ensures model stability, the complete repeatability of results regardless of the user, and is contained in a functional framework. Ideally, the visual appearance of the model should coincide with the user’s mental model of the system being represented. While some CEMN models are in spreadsheet form, many are software.

4.2 Models Available

In this section, the currently available CEMN models are listed, and details given on selected models. The reader should consult the CEMN member websites (listed in Section 6) for updates. CEMN models are available only from the developers.

Table 7: List of available models

CEMC Models Currently Available (http://www.trentu.ca/cemc)				
	Version	Released	Model Format	Key Information; To answer questions of the type -
AirWater	2.00	2004	W	air-water exchange characteristics of a chemical based on its physical chemical properties and total air and water concentrations
	1	1991	B	
ChemCAN	6.00	2003	W	region-specific multimedia fate; database of Canadian regions; user may add new regions Q: Are the documented emissions sufficient to account for the measured concentrations of current chemical "B"?
ChemSCORER	1	2002	E	a rapid assessment of environmental hazard and ranks the chemical for P, B, T, and LRT against a set of reference chemicals

Format Codes: W = Windows software; E = Excel® spreadsheet; B = DOS BASIC

CEMC Models Currently Available (<http://www.trentu.ca/cemc>) - continued

	Version	Released	Model Format	Key Information; To answer questions of the type -
EQC	2.02	2003	W	evaluative multimedia fate; combines LI, LII and LIII calculations; facilitates a progressive understanding of a chemical's fate in a standard environment Q: In general terms, how will the (new) chemical "A" behave in the environment?
Fish	2	2004	W	single organism model treats the steady-state uptake and release of an organic chemical by a fish
	1	1991	B	
Foodweb	1	1991	B	contaminant flux through an aquatic foodweb
Generic	1	1991	B	early version of EQC
Level I	3.00	2004	W	multimedia partitioning
Level II	2.17	1999	W	multimedia partitioning and fate, assuming equilibrium
Level III	2.70	2004	W	multimedia partitioning and fate, assuming steady-state
Level I, II, III	1	1991	B	earlier version of the above set of software
QWASI	2.80	2002	W	Focus on aquatic environment (lake); aquatic fate, assuming single well-mixed waterbody and steady-state
	1	1991	B	Q: What is the concentration of chemical "C" in Dexe Lake?
RateCon	1	1991	B	designed to predict the fate and recovery times of contaminants in the Great Lakes; similar to QWASI but not using the fugacity concept
Sediment	2	2004	W	calculates the water-sediment exchange characteristics of a chemical based on its physical chemical properties and total water and sediment concentrations
Soil	2	2004	W	very simple assessment of the relative potential for degrading reaction, evaporation, and leaching of a pesticide applied to a surface soil
	1	1991	B	
STP	2.1	2004	W	engineered system sewage treatment plant
	1	1991	B	Q: What are the key removal processes for chemical "D" in a defined STP?
TaPL3	3.00	2003	W	Transport and persistence estimations P and LRT in multimedia environment, assuming steady-state Q: How do the persistence and LRT of the chemicals in this set compare?

Format Codes: W = Windows software; E = Excel® spreadsheet; B = DOS BASIC

CEMC Models Currently Available (<http://www.trentu.ca/cemc>) - continued

	Version	Released	Model Format	Key Information; To answer questions of the type -
PBPK	1	2003	E	Physiologically-Based Pharmacokinetic model, describes disposition of contaminants within the human body
Multi-species	1	2003	E	fate of a chemical with up to 3 other chemical species (reversible or irreversible conversion)
High resolution Multi-species	4.1	2003	E	multi-species chemical, more highly resolved and segmented environment

Format Codes: W = Windows software; E = Excel® spreadsheet; B = DOS BASIC

Wania Models Currently Available (<http://www.utsc.utoronto.ca/~wania>)

All are Windows software in format.

	Version	Released	Key Information
LSER-Level III	1	2003	calculates Z-values using linear solvation energy relationships (LSERs) rather than partitioning properties such as water solubility, vapour pressure, K_{ow}
Cozmo-POP	1	2000	dynamic multimedia fate and transport model describes the long-term fate of POPs in a coastal environment or the drainage basin of a large lake
Cozmo-POP 2	2	2005	increased and flexible spatial resolution of the aquatic environment and the improved description of the sediments and the processes associated with sediments
Globo-POP	1	1995	glo

ERTG Models Currently Available (<http://www.rem.sfu.ca/toxicology/>)

All are Excel® spreadsheet format.

	Version	Released	Key Information
BAF-AqWeb-Site	1	1993	site-specific aquatic food web bioaccumulation
BAF-AqWeb-Site	2	2004	site-specific aquatic food web bioaccumulation
BAF-AqWeb-QSAR	1	2003	generic aquatic food web bioaccumulation

Cautionary Note:

The entries in the chemical databases included with most software models listed here can be modified therefore it is the responsibility of the user to ensure that the values are correct by consulting a reference such as that of Mackay et al. (2000).

4.2.1 Choosing a model

When choosing the model for a particular task the parameters of the task, the expectations, and the acceptability of assumptions must be considered.

For general assessments not specific to a particular location, models such as EQC are helpful for gaining a general impression of the likely behaviour of a substance. These models are most useful for chemicals that are multimedia in nature, i.e., realistically present in all environmental media.

In chemical assessments, for single-medium substances, i.e., substances with a realistic presence in only one environmental medium, a model with a detailed description of processes in that medium should be used to understand the likely behaviour of the substance. For example, a very volatile substance with a low K_{OA} and a high K_{AW} is likely to be present only in air. For such a substance a dispersion model will provide an estimate of concentrations in the air at various distances from the source. For such a substance, a multimedia model such as EQC which gives an average concentration in air over a large area, would require more input information without providing the spatial detail available from the dispersion model.

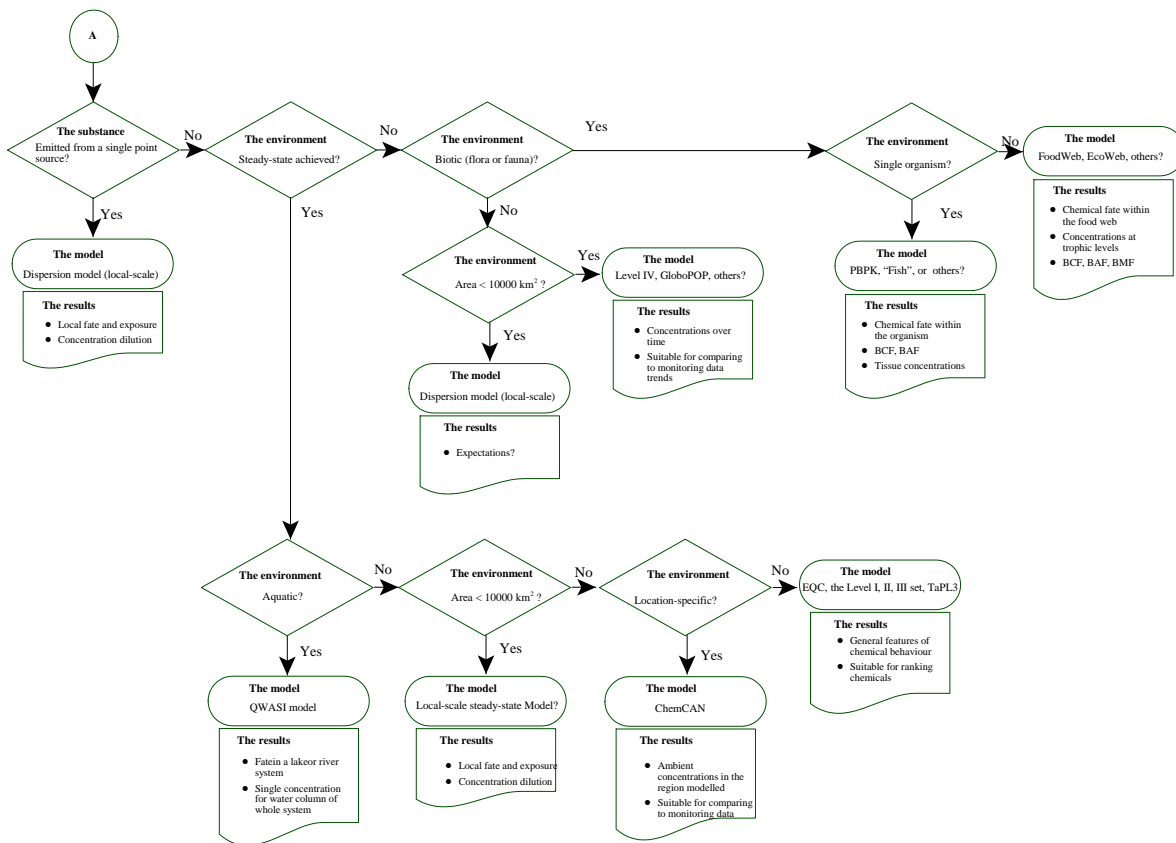
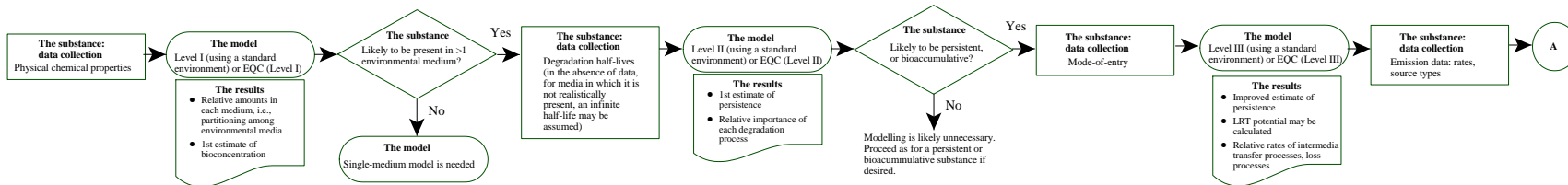
For a discharge to a river or lake, a water quality model such as QWASI gives an estimate of average concentrations in the water and sediment. Again, this is more useful in this case than a model such as EQC. If the substance being discharged is very volatile, QWASI gives an estimate of volatilization but assumes a fixed (user-specified) concentration in the air. To better determine the concentration in the air, a model which calculates this value must be used.

Some guidance is provided with each model as to the original intended uses of the model. Using a model for a purpose other than that for which it was designed may cause it to give mis-leading results and should be avoided. A careful examination of the equations in a model can assist in determining the appropriateness of a model for a purpose.

Some models such as Level III, EQC, TaPL3, and ChemCAN contain many of the same equations; they all contain Level III calculations. The differences are the result of a progressive increase in our understanding of environmental processes, the intended uses of the model, and the needs of the project(s) underway during the development of the model. The Level III model is a general implementation of the Level III calculations and can be made to mimic many of the results from the other three. However, it is easier to use ChemCAN, for example, when modelling chemical fate in Southern Quebec.

Figure 6 illustrates a suggested modelling process and decision tree that the user may find helpful.

Modelling Process and Decision Tree



4.3 Details on Selected CEMN Models

4.3.1 Level I Model (Version 3.00)

Model Overview

A Level I simulation is of the equilibrium distribution of a fixed quantity of conserved (ie. non-reacting) chemical, in a closed environment at equilibrium, with no degrading reactions, no advective processes, and no intermedia transport processes (e.g. no wet deposition, or sedimentation). The medium receiving the emission is unimportant because the chemical is assumed to become instantaneously distributed to an equilibrium condition.

Physical-chemical properties are used to quantify a chemical's behaviour in an evaluative environment. Three types of chemicals are treated in this model: chemicals that partition into all media (Type 1- excluding ionizing chemicals), involatile chemicals (Type 2), and chemicals with zero, or near-zero, solubility (Type 3). Details on chemical Types are given in Section 3.5.1.

Level I assumes a simple, evaluative, closed environment with user-defined volumes and densities for the following seven homogeneous environmental media (or compartments): air, water, soil, sediment, suspended particles, fish and aerosols.

If one of the environmental media, soil for example, is removed by reducing its volume to zero, then the chemical will partition among the remaining media. That is, the amount of chemical, expressed as a percentage of the total dose, will increase in each of air, water, sediment, suspended particles, fish and aerosols. The total amount of chemical remains the same. A feature of the model is that even with a zero volume of a medium, soil in this example, a concentration is still calculated for the zero volume medium. This is the concentration the medium would have if it were present. This is possible since equilibrium is assumed and thus the fugacity of the medium is known and the concentration is the product of the fugacity, f , and the fugacity capacity, Z , of the medium which is independent of the presence of the medium.

The required model input data and a list of results are given in Table 8.

A complete description of the Level I calculations is given in the textbook on fugacity models by Mackay (2001).

Intended Uses

This model is useful for establishing the general features of a new or existing chemical's behaviour. A Level I calculation gives the general impression of the likely media into which a chemical will tend to partition and an indication of relative concentrations in each medium and between sub-compartments in each medium. For example, a Level I calculation can be used to investigate the phase distribution of organic chemicals in the atmosphere at equilibrium, that is the relative distribution between gas phase, atmospheric particles, and water droplets. The results can again be displayed in partitioning space maps as discussed in Section 3.5.1 Similarly, Level I calculations can be used to investigate the equilibrium phase distribution within a soil (i.e. between the soil organic

matter, and pore air and pore water). The results of changes in chemical and environmental properties may be explored. This model is not suited to local-scale assessments such as the area around a stack.

Table 8: Level I input data and results

Chemical Properties:
<p>chemical name, molar mass, data temperature</p> <p>Type 1 chemicals (excluding ionizing substances)</p> <p>water solubility, vapour pressure, log K_{ow}, melting point</p> <p>Type 2 and 3 chemicals</p> <p>partition coefficients</p>
Environmental Properties:
<p>volumes and densities for all seven media</p> <p>organic carbon content for soil, sediment, and suspended particles</p> <p>fish lipid content</p>
Emissions:
<p>chemical amount</p>
Model Output:
<p>partition coefficients</p> <p>Z values</p> <p>fugacity of the system</p> <p>relative concentrations and amounts for each compartment</p> <p>a summary diagram</p>

Cautionary Note:

The concentrations and amounts reported by the Level I model are proportional to the arbitrary quantity of chemical introduced into the system. Therefore, the absolute values should not be used but rather the values relative to each other and the total amount, specifically, the amount as a % of the total quantity of chemical.

4.3.2 Level II Model (Version 2.17)

Model Overview

A Level II simulation describes a situation in which a chemical is continuously discharged at a constant rate and achieves a steady-state and equilibrium condition at which the input and output rates are equal. Degrading reactions and advective processes are the loss or output processes treated. Intermedia transport processes (eg. no wet deposition, or sedimentation) are not quantified. The medium receiving the emission is unimportant because the chemical is assumed to become instantaneously distributed to an equilibrium condition.

Physical-chemical properties are used to quantify a chemical's behaviour in an evaluative environment. Three types of chemicals are treated in this model: chemicals that partition into all media (Type 1- excluding ionizing chemicals), involatile chemicals (Type 2), and chemicals with zero, or near-zero, solubility (Type 3). Level II assumes a simple, evaluative environment with user-defined volumes and densities for the following homogeneous environmental media (or compartments): air, water, soil, sediment, suspended particles, fish and aerosols. "Fish" is a generic aquatic biotic organism.

Three residence times are calculated, an overall value, T_O , and individual residence time attributable to reaction only, T_R , and advection only, T_A . Note that $1/T_O$ equals the sum of $1/T_R$ and $1/T_A$. The relative contribution of advection and reaction to the total removal of chemical depends strongly on the size of the system as noted in Section 3.5.2. However, consideration of advection and reaction rates allows for the calculation of chemical persistence. It provides a first estimate of overall environmental persistence, which is a critical property of the chemical. It also shows which loss processes are likely to be most important. A fast reaction or short half-life may not be significant if relatively little of the chemical is subject to this reaction by virtue of its partitioning. The potential for the chemical to be subject to long-range atmospheric transport is also indicated by the magnitude of the air advection loss. While this version of the Level II model does not explicitly calculate LRT it can be calculated manually as the product of an assumed wind speed (km/h), the overall residence time of the chemical (h), and the ratio of the amount in air to the total amount in the system as was done for the collaboration with Fenner et al (2005) . The global chemical persistence is best indicated by the reaction residence time, whereas the local persistence is indicated by the overall residence time.

Note that in this version, reaction half-lives are requested for all seven media. In previous versions reactions in only four media were treated. In the absence of data, the half-lives for suspended particles and fish can be assumed to be equal to that of the water, and that of aerosols can be assumed to be equal to that of air.

The advective residence time selected for air applies to aerosols and the residence time for water applies to suspended sediment and fish. The advective residence time of aerosols, suspended particles and fish cannot be specified independently of the air and water residence times. These residence times are the time that the air, for example, spends in the modelled system. It is related to the prevailing wind direction and the distance across the region in that direction. Since only the