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GUIDANCE DOCUMENT ON THE USE OF MULTIMEDIA MODELS FOR ESTIMATING OVERALL ENVIRONMENTAL PERSISTANCE AND LONG-RANGE TRANSPORT

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CHAPTER 1. INTRODUCTION

1. This Guidance Document is addressed to those who are involved in risk assessment and management of chemicals called POPs (persistent organic pollutants) or PBTs (persistent and bio-accumulating toxics). It is about using multimedia models, i.e. generic evaluative models that can calculate overall environmental persistence (P_{ov}) and potential for long-range transport (LTRP) covering multiple compartments such as air, water, sediment and soil: what models you can use to identify and characterize POPs/PBTs, what data to use, and how to use model calculations.

2. POPs and PBTs attract worldwide attention. The UNEP (United Nations Environment Programme) Stockholm Convention on POPs is a prominent example. The Convention includes a procedure for identifying new POPs to be put under the global control. One of the criteria for persistence and long-range transport (LRT) is "scientific evidence" such as model calculations. Multimedia models have been identified, both in scientific and policy communities, as a prominent tool for providing such evidence.

3. P_{ov} and LRTP are relevant to the screening and assessment of chemicals because they indicate whether a chemical has a potential for leading to an exposure burden that will continue into the future time or be displaced to remote regions (Scheringer 2002). A displacement of exposure often implies that benefits and burdens of using a chemical are not distributed equitably between users of the chemical and other parties. This information may have implications for environmental justice. In this context, it is important to understand that toxicity indicators do not provide information on where and when a toxic effect may occur. Indicators addressing the lifetime and mobility of a chemical are required in addition to indicators of toxic effects and bioaccumulation.

4. P_{ov} and LRTP are not intrinsic properties of chemical pollutants, but instead derive from both chemical properties and environmental conditions. They cannot accurately be estimated based on measured environmental concentrations alone even if concentration data are ubiquitous and accurate, which is currently not the case. The required emissions and concentration data are not available and are unlikely to be available in the foreseeable future. In addition, it is desirable to estimate P_{ov} and LRTP characteristics for chemicals that have not yet been introduced into the environment. As a result, P_{ov} and LRTP cannot be measured directly and must be derived from models.

5. Thus, the objective of the document is to provide guidance on how multimedia models can be used in the assessment of POPs/PBTs. It is intended that this guidance be applicable to not only the Stockholm Convention but also other global, regional or national programmes for assessment and management of these substances.

6. The document has been developed as a follow-up activity to the OECD Workshop on the Use of Multimedia Models for the Estimation of Environmental Persistence and Long-Range Transport in the Context of POPs/PBTs Assessment, which was held in Ottawa in October-November 2001 (OECD 2002). The Workshop agreed on the following overall recommendations:

   1. OECD should review the current approaches used for assessment of persistence and long-range transport potential, and identify opportunities for more harmonised approaches. In order to

explore the utility of overall persistence, further work should be carried out to evaluate the uncertainty in the value of overall persistence as a function of the design and parameters of multimedia models.

2. OECD should undertake activities to develop a tiered process for ranking or classification of substances.

3. OECD should, in co-operation with UNEP, develop guidance for users on model applicability and fitness for purposes including information on accuracy, data availability and model adaptations.

4. Intergovernmental organisations, national governments and industry should undertake inter-comparison of multimedia models, as well as comparison to monitoring data, to understand the model uncertainty, identify key needs for refinement, and add consistency across the various levels of complexity of models.

5. A core set of multimedia models should be available and accessible at no cost to the public.

6. The models and the assessment processes should be totally transparent so that all parties can fully appreciate the mechanisms of the decision-making process.

7. The document, as developed by an Expert Group nominated from the OECD member countries and other organizations (member list in Annex 1), directly responds to the third recommendation, and covers the issues raised in the first and second points. Regarding the fourth point, an intercomparison of generic models is being undertaken within the Expert Group. Another intercomparison activity addressing more sophisticated models with geographic resolution is done under the European Monitoring and Evaluation Programme for the UNECE Convention on Long-Range Transboundary Air Pollution.

8. Chapter 2 outlines the regulatory context that has made this Guidance Document necessary. It is demonstrated that although model-based P_{ov} and LTRP are not currently used in regulatory assessments, one can find great opportunities for their future use. This chapter in itself is a concise summary of the persistence and LRT criteria used in international and national programmes.

9. Chapter 3 is an overview of currently available and emerging tools and models. These models are placed in the spectrum of complexity, and the difference in model designs, environmental processes, data needs, and model outputs is discussed. Input data needed to run these models, depending on the characteristics of the substances being modelled, are described with examples of approaches for estimating the data. More specific guidance on data sources is provided in Annex 5.

10. Chapter 4 explains how the estimates of P_{ov} and LRTP can be calculated using multimedia models. Different approaches for calculating P_{ov} and LRTP are described. The sources of difference or uncertainty in model calculation are examined. A “benchmarking” approach to overcome the model dependence is proposed. Several limitations arising from common assumptions in multimedia models are highlighted and discussed.

11. Chapter 5 addresses how these estimates can be used in regulatory and non-regulatory settings, describing tiered approaches for classifying, ranking or assessing substances for P_{ov} and LRTP. It includes examples where multimedia models are used in chemical assessment/management activities, and concludes with guidance on the choice of models and use of model calculations. Conclusions at the end of this chapter regarding the tiered approach, choice of models, and use of relative approach convey the key messages of this Guidance Document.

CHAPTER 2. PREVENTING PBT/POPS POLLUTION THROUGH REGULATORY AND NON-REGULATORY MEANS

2.1 Who are the Users?

12. Potential users of multimedia models for assessing overall persistence (P_{ov}) and long-range transport potential (LRTP) are many and diverse. Given that the objective is reducing/eliminating/preventing use of persistent, bio-accumulating and toxic (PBT) substances and persistent organic pollutants (POPs), the Stockholm Convention on POPs may come to mind first. However, regional organizations, national governments, and other sectors of society, e.g. industry, environmental and public interest groups (NGOs) and academia, are all potential users of the models and this guidance.

13. Several governments, as well as regional economic integration organizations, have established programs for identifying and assessing substances with PBT/POP properties. Similarly, regional and global regimes and organizations have adopted criteria or guidelines for identifying, assessing and managing such substances. The more prominent of these are described briefly in this chapter.

14. National governments have a particularly critical role to play because they engage in a variety of activities designed to improve our ability to protect the environment, as well as change both corporate and personal behavior in pursuit of that objective. The more familiar regulatory ("command and control") methods are still useful and necessary, but voluntary activities are increasingly important. Tools at government's disposal include, for example:

- Regulatory activities ("command and control" methods)

--Reduce or eliminate emissions
--Limit or prohibit uses
--Prevent introduction of substances with unacceptable risk into commerce
--Place suspect substances on public list
--Gather data to support actions

- Non-regulatory activities (pollution prevention)

--Identify safer substitutes and processes
--Promote voluntary use changes, especially for substances with dispersive uses
--Influence personal behavior

15. In addition to understanding that the scope of potential interest in P_{ov} and measures of LRTP is broad, it is important to remember that multimedia models can make useful contributions in other ways. For example, multimedia models for long-range transport and overall persistence can also play a role in the risk assessment of new and existing substances. They can be used during exposure assessment to identify the spatial extent of exposure (i.e. does the substance reside locally or is it transported to remote regions),

environmental partitioning (helpful for identifying media of concern), and residence time in the environment (for determining the potential for acute vs. chronic effects). Multimedia models are useful regardless of whether the activity is regulatory or non-regulatory, or who takes the lead.

2.2 Uses of Multimedia Models

16. Models and their outputs are used for various purposes, e.g. assessing and managing pesticides and industrial chemicals. Governments may use models in programs for screening and assessing new and existing chemicals to identify potential PBTs. In such programs, models may be used as a first step to sort potential candidates for further assessment. A little-publicized feature of the Stockholm Convention on POPs is that nations that have regulatory and assessment schemes for new pesticides or new industrial chemicals and are Parties to the Convention have an obligation to take control measures with new pesticides or industrial chemicals that fulfill the Convention criteria. Similarly, governments that have schemes for assessing existing pesticides or industrial chemicals are obliged to take into consideration the Convention criteria when assessing the substances.

17. Multimedia models can be used for “benchmarking” known pollutants (e.g. DDT, polychlorinated biphenyls, Dioxins and Furans), PBT/POP candidates and new chemicals. Benchmarking is a relative approach for ranking chemicals by comparing model estimates for LRTP and P_{ov} to a suite of chemicals with known LRTP/P_{ov} values. PBT/POP candidates can be ranked in terms of high, medium or low concern for LRTP or P_{ov}. Such approaches have been proposed by Scheringer (1997), Matthies et al (1999) and Beyer et al. (2000). This concept is discussed more fully in Chapter 5 as a way to guide a user to select the appropriate model for his/her purpose and as an approach for using model estimates in regulatory and non-regulatory assessments.

18. Benchmarking may also be the right way (indeed the only reasonable way) to use model-based estimates of P_{ov} and LRTP in the pollution prevention context. This idea has already been implemented in the “PBT Profiler” (http://www.pbtprofiler.net/), an internet-based pollution prevention tool designed to provide screening-level estimates of PBT potential for organic substances.

19. Multimedia models may also be of value in identifying data gaps and pointing to areas where data should be developed (e.g., specific physical-chemical properties, half-lives, partition coefficients), and for forensic as well as liability and compensation purposes. An example of the latter that seems likely to appear in the international arena in the not-too-distant future is the use of LRTP to show that pollution may have originated from a certain distant source (i.e., back tracking to the source). This is an area in which geo-referenced models such as those used to support United Nations Economic Commission for Europe (UNECE) activities may be especially important.

20. Multimedia models also play a role within the chemical industry. They can be used to screen products for PBT properties at an early stage of product development to identify properties of chemical constituents that would cause a concern from an environmental or human health standpoint. Here again pollution prevention considerations are important, and screening tools that give estimates of P_{ov} and LRTP may be an integral part of the review. Whenever they are used for quantitative or semi-quantitative purposes great caution should be exercised and data gathered to confirm or reject model predictions.

21. In some legislatures persistence and/or bioaccumulation *per se* is used as a criterion for taking action on chemicals, while others rely on the risk paradigm and perform fully-fledged risk assessments before taking action. The precautionary approach, which permeates the Stockholm Convention on POPs, shows up also in the assessment of candidate POPs. For example, the POPs review committee must consider processing (i.e. is obliged not to summarily dismiss) substances even when a full data set is not available;

and the Conference of the Parties must decide in a precautionary manner whether to list chemicals under the Convention.

2.3 Global and regional conventions and agreements

2.3.1. Stockholm Convention on POPs

22. The UNEP Governing Council in May 1995 (UNEP, 1995) agreed on an international action plan to protect human health and the environment by the reduction or elimination of POPs. The May 1995 decision targeted a short-list of twelve POPs: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and toxaphene. In 1997 the UNEP Governing Council decided (UNEP, 1997) to establish a negotiating committee to develop a global instrument to address POPs and to initiate a number of immediate actions pertaining to exchanging information, identifying alternatives to POPs, identifying sources and managing and disposing of certain POPs containing materials and wastes. The main outcome of those negotiations was the Stockholm Convention on POPs, which was adopted by 127 countries in Stockholm in May 2001 (UNEP, 2001).

23. The Convention is the first global, legally binding instrument of its kind with scientifically based criteria for potential POPs and a process that ultimately may lead to elimination of a POP substance globally. The criteria for persistence in Annex D of the convention are expressed as single-media criteria as follows:

(i) Evidence that the half-life of the chemical in water is greater than two months, or that its half-life in soil is greater than six months, or that its half-life in sediment is greater than six months; or

(ii) Evidence that the chemical is otherwise sufficiently persistent to justify its consideration within the scope of the Convention.

24. The criteria for LRTP are not expressed as numerical values. The potential for LRT should be assessed from:

- Measured levels in locations distant from the source;
- Monitoring data indicating LRTP has occurred; or
- Fate properties and/or model results demonstrating the potential for LRTP/half-life in air greater than two days.

25. The implications for signatories to the Convention, in their review of new and existing substances at the national level, were mentioned above. Candidate substances to be considered under the Convention are initially screened against the criteria and further assessed based on additional information. Surrogate information may also be submitted for persistence and bioaccumulation, e.g. monitoring data indicating that the bioaccumulation potential is sufficient to warrant consideration of the substance. Point (ii) above ("Evidence that the chemical…within the scope of the Convention") and item 3 under LRTP ("Fate properties and/or model results….") are avenues by which multimedia models in general, and model-derived measures of P_{ov} and LRTP in particular, can be incorporated into the process.

2.3.2. UNECE Long-Range Transboundary Air Pollution (LRTAP) POPs Protocol

26. Under the LRTAP POPs Protocol of the UNECE, selection of new POP substances is to be achieved following the amendment procedure set out in the Protocol and its accompanying Executive Body Decision 1998/2 (UNECE, 1998).

27. Any Party wishing to propose a new substance must provide a risk profile demonstrating the substance's characteristics in relation to given indicative numerical values ("criteria" in other protocols). These characteristics include potential for long-range atmospheric transport; toxicity; persistence, and bioaccumulation. For persistence the single-medium values specified in the Stockholm Convention on POPs are used. Similar to the Stockholm Convention, for each of the above, a surrogate is permitted. For example, as an alternative to the numerical values it might be sufficient to provide "evidence that the substance is otherwise sufficiently persistent to be of concern within the scope of the Protocol". The proposal should contain a summary report that includes information on socioeconomic factors and on e.g., production/uses/emissions; measured environmental levels in areas distant from sources; abiotic and biotic degradation processes and rates; degradation products; and bioavailability.

28. The Executive Body will review the proposal to evaluate inter alia: a) monitoring or equivalent scientific information suggesting long-range transboundary atmospheric transport; and b) whether sufficient information exists to suggest that the substance is likely to have significant adverse human health and/or environmental effects as a result of its long-range transboundary atmospheric transport.

29. Because the LRTAP POPs Protocol explicitly allows surrogate information, the opportunity exists for information from multimedia models, and specifically measures of P_{ov} and LRTP derived from them, to be included. Such information might be incorporated most productively if it were developed in a phased or tiered fashion (i.e. consistent with the recommendations of this guidance document), in parallel with rather than replacing the existing assessment architecture. Here as with the other global and regional conventions, models offer the promise of integrating information in a way that deepens understanding.

2.3.3. OSPAR Convention

30. The Oslo-Paris (OSPAR) Convention for the protection of the marine environment of the North-East Atlantic adopted a "Strategy with regard to Hazardous Substances" at Sintra, in 1998 which aims at the cessation of discharges, emissions and losses of hazardous substances by 2020 in order to achieve 'close to zero'[1] concentrations in the marine environment (OSPAR Commission 1998). Under the OSPAR Convention, a dynamic selection and prioritization scheme for substances that may pose a risk to the marine environment (called DYNAMEC) has been developed (OSPAR Commission 2002). The scheme emphasizes substances with PBT properties and has several steps:

Step 1: Selection of candidates for priority setting.

Step 2: Elaboration of a priority list based on an exposure assessment by using data from monitoring and effects assessment, and scoring by applying a modified EURAM (European Union Risk Ranking Method) procedure.

Step 3: Elaboration of a priority list based on predicted exposure data modeled from production volume, use pattern, distribution within the environmental compartments, persistence, and effects; and scoring, again by applying the modified EURAM procedure.

Step 4: Consolidation/validation of the higher-ranking substances through a comparison of the monitoring- and modeling-based lists, using expert judgment together with additional information. The COMMPS method - Combined Monitoring-based and Modelling-based Priority Setting developed for the EU Water Framework Directive– is employed here.

Step 5: Further detailed consideration, using expert judgment, of the substances ranking the highest in the risk-ranking exercise (step 4), establishing finally a priority list.

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[1] 'close to zero' for synthetic substances and 'close to natural background concentrations' for naturally-occurring substances.

31. Measured concentrations are used as input for the monitoring-based ranking. For the modelling-based ranking the scale of the model is at the European level, which corresponds to the "continental scale" defined in the EU-Technical Guidance Document (European Commission 2003a). Emissions are estimated from production volume, main use category and fractions of release (e.g. closed system, wide dispersive use), while distribution is evaluated by applying the Mackay Level 1 model. Degradation is assessed by taking into account the results of biodegradability testing e.g. ready biodegradability and inherent biodegradability. The EURAM aquatic exposure score may then be calculated.

32. To date, only those initially selected substances for which information on production and use and/or monitoring data were available (203 out of 400) could be ranked. Clearly, the OSPAR activities might gain additional insight from consideration of P_{ov} and LRTP derived from multimedia modeling. Moreover, the assessment and ranking procedures offer several points at which new information could be incorporated.

2.3.4. North American Regional Action Plans (NARAPs)

33. Within the North American Commission for Environmental Co-operation (NACEC) Sound Management of Chemicals (SMOC) initiative, substances with PBT properties are a priority. A three-stage process has been devised for the nomination, evaluation and selection of substances for preparation of NARAPs. (NACEC 2002)

34. Substances are nominated in stage 1 and this can be done by any of the Parties (USA; Mexico; Canada). The nominating Party must provide information in a complete and concise "Nomination Dossier" with key references, following an agreed format.

35. Stage II consists of two phases, namely screening and detailed evaluation. Information gathering is the focus of the screening step, and four basic information requirements must be met before a detailed assessment can be initiated. The four elements are (i) valid monitoring or predicted data pertaining to emissions, effluents or levels in environmental media or biota confirming that the substance may enter, is entering or has entered the North American ecosystem as a result of human activity; (ii) a comprehensive, scientifically sound risk assessment document that characterizes risks to the environment or human health and has national or international acceptance; (iii) adequate measured or predicted data relating to the persistence, bioavailability and bioaccumulation of the substance; and (iv) adequate indirect evidence of the potential for transboundary environmental transport such as persistence in biota/media and volatility, or the availability of direct monitoring evidence of transboundary environmental transport.

36. The stage II detailed evaluation develops the rationale for supporting the selection of a substance as a candidate for regional action. The rationale focuses on the nature and extent or the degree of the problem posed by the nominated substances, and on confirming that there is value added by addressing the substance on a regional basis. As an example, this evaluation must consider the degree to which human health or environmental benefits in North America can be demonstrated as a result of *collective* action. A substance that emerges as a candidate for regional action would then, at the discretion of the Working Group, become the subject of a Draft Decision Document.

37. The NACEC-SMOC process for developing NARAPs allows predictive data. Thus, multimedia model results including P_{ov} and measures of LRTP, though not specifically mentioned, could become part of information dossiers at both the nomination and screening stages. Models would seem especially useful for buttressing arguments that center on concern for transboundary atmospheric transport.

2.3.5. The EU Water Framework Directive (2000/60/EC)

38. The objective of the EU Water Framework Directive (WFD) is the protection of inland surface waters, transitional waters, coastal waters and groundwater, and distinguishes between 'hazardous substances[2]', 'priority substances'[3] and amongst those 'priority hazardous substances'[4]. The directive sets out two different levels for emission controls of substances, depending on whether these substances are grouped among the priority substances or the priority hazardous substances. According to articles 16(1) and 16(6), the measures for priority substances shall be aimed at the progressive reduction of discharges, emissions and losses of the substances concerned. The Commission shall submit proposals for emission controls and environmental quality standards within 2 years of the inclusion on the substance on the list of priority substances.

39. The measures for priority hazardous substances shall be aimed at the cessation or phasing out of discharges, emissions and losses of the substances concerned. The Commission shall submit an appropriate timetable for the implementation of these measures that shall not exceed 20 years.

40. The provisions under the WFD require that the priority substances are selected on the basis of a comprehensive or targeted or, if not available in time, a simplified risk assessment. For the development of the first priority list a procedure named COMMPS (Combined Monitoring-based and Modelling-based priority setting) was developed. COMMPS is to a certain extent comparable to the OSPAR DYNAMEC mechanism but it puts more emphasis on available monitoring data as a prerequisite for substance selection. Furthermore, the number of substances from which the selection was made was very small (less than 300). Currently, the European Commission has adopted a proposal for the list of priority substances and amended its proposal to include priority hazardous substances (European Commission 2001). Priority hazardous substances have been identified taking into account the procedures developed under OSPAR, UNECE and, as far as possible, relevant Community legislation. While many of the substances identified can be characterised as PBT compounds, no specific PBT cut-off criteria have been developed so far. For the revision of the list of priority substances in 2004, it is intended to identify "priority hazardous substances" on the basis of PBT criteria agreed in the European Community.

2.4 Regional and national requirements in new chemicals notification requirements

41. Several nations have implemented or are about to implement new chemical notification requirements that specifically highlight industrial chemicals with PBT properties. In no case do P_{ov} and LRTP currently play any explicit role.

42. The assessment of persistence and bioaccumulation properties for new substances notified in Canada relies on the criteria listed in the *Persistence and Bioaccumulation Regulations* (Canada Gazette 2000). The inherent toxicity (iT) of a new substance is determined and used in the risk assessment. Currently, Environment Canada is examining policy to address new substances that are PBiT, separately from conclusions of the risk assessment. New substances that are assessed as P and B and found "suspected of being CEPA-toxic", that is, found to be of risk to the environment, are subject to the virtual elimination policy described under the *Toxic Substances Management Policy* (TSMP) (Government of Canada 1995).

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[2] PBT substances and other substances giving rise to an equivalent level of concern

[3] Substances identified through comprehensive, targeted or 'simplified' risk assessment. The simplified risk assessment includes a hazard assessment focussing on the aquatic toxicity and the human toxicity via aquatic exposure routes and evidence of widespread environmental exposure.

[4] According to article 16(3), priority hazardous substances are identified by the Commission by taking into account *'the selection of substances of concern undertaken in the relevant Community legislation regarding hazardous substances or relevant international agreements'.*

P_{ov} or LRTP are not routinely part of the assessment of new substances in Canada. However, the intention is to consider these properties more formally in the assessment process once the OECD project for establishing the benchmark procedures (See Sections 4.2.4 and 5.3.1.2) has been completed. The use of multimedia models is not an entirely new concept as the level III model is used for partitioning and establishing a "realistic presence" of a substance in the environmental compartments.

43. In the United States the New Chemicals Program established a PBT category in 1999, with the following definition: PBT chemical substances possess characteristics of persistence (P) in the environment, accumulation in biological organisms (B), and toxicity (T) that make them priority pollutants and potential risks to humans and ecosystems. The PBT category statement describes the boundary conditions, such as fish bioconcentration/bioaccumulation factors and environmental persistence criteria, that determine inclusion in (or exclusion from) the category, and also lists standard hazard and fate tests useful for addressing P, B, and T concerns for new chemicals that fit the category description. Two levels of concern are described, with separate P, B and T criteria for substances with moderate and high PBT concern. The category statement also suggests that multimedia models may be used to integrate estimated emissions to different environmental media. As in Canada P_{ov} and LRTP are not routinely parts of the assessment of new substances. However, the US EPA is likely to consider these properties more formally in the assessment process once the OECD project for establishing the benchmark procedures (See Sections 4.2.4 and 5.3.1.2) has been completed.

44. OECD conducted a survey on approaches in the assessment of new chemicals in different countries, in preparation for an OECD Workshop on new chemicals notification and assessment in 2002. This survey showed that, as in the US, Austria had recently developed criteria for PBT substances that reflected levels of concern. There, new chemicals with PBT properties may be judged persistent and bioaccumulating or very Persistent and very Bioaccumulating (vPvB). As in Canada and the US the P and vP criteria are half-lives in the various environmental compartments. In some other nations, notably Japan and the United Kingdom, there was not formal recognition of PBT substances as a category; nevertheless new chemical notification dossiers were reviewed for the core PBT characteristics of persistence, bioaccumulation and toxicity.

45. The European Commission (2003b) has recently published a proposal for legislation concerning the Registration, Evaluation Authorisation of Chemicals (REACH). Under this proposal, authorization for the use of PBT and vPvB substances and accelerated restriction of their use will be introduced. Proposed criteria for the identification of PBT and vPvB substances are in the same as those in the revised EU Technical Guidance Documents for assessing risks of new and existing chemicals and biocides (European Commission 2003a), reproduced in Section 2.5. This certainly seems like a good opportunity to implement recommendations of this OECD guidance document. Until new legislation is in place, an interim PBT strategy has been agreed within EU member states. This interim strategy has identified PBT criteria; and focuses on the further identification of PBTs and vPvBs among both new and existing substances; and evaluation of an accelerated risk management process.

2.5 Regional and national programs for existing industrial chemicals

46. In the European Union the revised Technical Guidance Document (TGD) on risk assessment of new and existing chemicals and biocides includes PBT and vPvB criteria for the marine risk assessment of existing chemicals (Table 1). The revised TGD also addresses how the P assignment is made for different types of persistence data, including data from Quantitative Structure/Activity Relationships (QSARs)(Table 2). The P criteria are medium-specific degradation half-lives.

Table 1.1. Criteria for identification of PBT and vPvB substances (EU)

Criterion	**PBT-criteria**	**vPvB-criteria**
P	Half-life > 60 d in marine water or > 40 d in freshwater[1)] or half-life > 180 d in marine sediment or > 120 d in freshwater sediment[1)]	Half-life > 60 d in marine- or freshwater or >180 d in marine or freshwater sediment
B	BCF > 2000	BCF > 5000
T	Chronic NOEC < 0.01 mg/l or CMR (having carcinogenicity, mutagenicity or reprotion toxicity) or endocrine disrupting effects	Not applicable

[1)] For the marine environment, risk assessment half-life data for freshwater and freshwater sediment can be overruled by data obtained under marine conditions.

Table 1.2. Overview of P-assignment for different types of biodegradation data (EU)

Type of data	**Criterion**	**Definitive assignment**	**Screening assignment**[1)]
DT50 marine water	> 60 d	vP	-
DT50 freshwater[2)]	> 40 d	P [3)]	-
	> 60 d	vP	-
DT50 marine sediment	> 180 d	vP	-
DT50 freshwater sediment	> 120 d	P [3)]	-
	> 180 d	vP	-
Readily biodegradable [4)]	Yes	Not P	-
	No	-	P or vP
Inherently degradable	Yes	Not P [5)]	-
	No	-	P or vP
QSAR	Thresholds defined for different models.	-	P or vP

1) These screening methods give an "open-ended" categorization of the substance as either being potentially P or vP, which cannot be related to a half-life for biodegradation.
2) Data for estuaries should also be considered in this category.
3) Half-life data in freshwater and freshwater sediment can be overruled by data obtained under marine conditions.
4) Regardless of whether the 10-d window criterion is fulfilled.
5) This only applies to cases where the specific criteria as mentioned in section 4.4.3.3. are fulfilled.

47. In the U.K. the criteria used by the Environment Agency in screening chemicals of concern are described in a document entitled "Managing Chemicals for a Better Environment" (UK Environment Agency 2002), while in the Netherlands criteria for classifying chemicals into categories of concern are described in the Progress Report "Implementation Strategy on Management of Substances", (VROM 2001). The criteria use inherent and ready biodegradability data in combination with BCF, Kow, and ecotoxicity data.

48. The US has established a “PBT Strategy” as a means of coordinating pollution prevention efforts related to existing chemical substances that are priority PBTs. The intended scope is broad but current focus is on “level I” substances listed in the US/Canada Binational Toxics Strategy, which are similar to those included in the Stockholm Convention, and on development of National Action Plans for these substances. Among the Strategy’s explicitly stated principles are that it should address PBT issues in a multimedia fashion; coordinate with and build upon international efforts; and emphasize use of innovative technologies.

49. PBT properties of existing chemicals are also the focus of EPA's Waste Minimization National Plan (WMNP); and special reporting requirements for selected substances on the US pollutant release and transfer registry (PRTR), better known as the Toxics Release Inventory (TRI). By law substances are listed on the TRI based solely on toxicity. However, EPA may highlight other concerns, and does so in this case merely by describing specific substances as PBTs as well as by using lower reporting thresholds, which generate more reporting. Neither of these activities formally incorporates P_{ov} or LRTP, but the TRI rule on PBTs specifically includes level III multimedia modeling as means to achieving a multimedia perspective.

50. In Canada, criteria for persistence, bioaccumulation and inherently toxic (PBiT) are being used by Environment Canada to categorize approximately 23 000 substances listed on the Domestic Substances List (DSL) within a 7-year time frame that commenced on September 14, 1999. *Environment Canada's Guidance for Categorizing Organic Substances on the Domestic Substances List* outlines the process Environment Canada is using to categorize substances listed on the DSL for persistence, bioaccumulation and inherent toxicity to non-human organisms. Those substances found to be persistent or bioaccumulating and inherently toxic will proceed to the second phase, a screening level risk assessment. The definition of "inherently" toxic to non-human organisms is still under consideration by Environment Canada. Categorization and screening are intended for "grandfathered" substances only — substances notified in Canada between 1984 and 1986.

51. Criteria for persistence and bioaccumulation are set out in the Regulations for Persistence and Bioaccumulation (Table 3, Canada Gazette 2000). These criteria were developed from the *Toxic Substances Management Policy* (TSMP) (Government of Canada 1995). The TSMP provides a common science-based management framework for toxic substances in all federal programs and initiatives.

Table 1.3: Criteria for Persistence and Bioaccumulation (Canada)

Persistence [1]		Bioaccumulation
Medium	Half-life	BAF ≥ 5000
Air	≥2 days [2]	Or
Water	≥6 months	BCF ≥ 5000
Sediment	≥1 year	Or
Soil	≥6 months	Log K_{ow} ≥ 5

1) A substance is considered persistent when the criterion is met in any one medium.

2) A substance may be considered as persistent in air if it is shown to be subject to atmospheric transport to remote regions such as the Arctic.

52. The TSMP has two key objectives. The first is the virtual elimination of substances that are persistent, bioaccumulating and found to be "CEPA-toxic" (CEPA-toxic is generally determined using risk assessment) as opposed to "inherently toxic". These substances are called Track 1 Substances. The second objective is life cycle management of other toxic substances to prevent or minimize their release into the environment. These substances are called Track 2 Substances.

2.6 Regional and national regulations on pesticides

53. The OECD recently conducted a survey on data requirements and risk assessment approaches for persistent, bioaccumulating and toxic pesticides (OECD 2002b). The report includes basic information on assessment methods and criteria for defining PBT properties of pesticides. This section summarizes some of its findings.

54. In many countries there are no formal regulatory definitions, but in others, e.g. Australia, Canada and Hungary, half-lives of 6 months in soil and natural waters are commonly accepted environmental persistence criteria for pesticides, as they are for other organic compounds. The 6 months criterion is

common to many global, regional and national assessment protocols for PBTs, especially for the soil compartment (e.g., Stockholm Convention on POPs and Canadian Persistence and Bioaccumulation Regulations). Still others do not specify criteria but give general definitions, for example in terms of residual effects in succeeding crops and soil as a result of use, or the length of time the pesticide can exist in the environment before being destroyed (i.e., transformed) by natural processes.

55. The European Union has established criteria for making decisions on pesticide active ingredients, available in Annex VI of the European Directive 91/414. According to the "Uniform Principles", persistent active substances are those, which exceed the limits defined in chapter 2.5 of the document ("Impact on Environment"). The persistence criteria given are expressed in terms of degradation time (DT) to reach a specified extent of destruction, namely DT90 in the field >1 year in soil and DT50 field >3 months in soil. Some other European countries (e.g. Norway) also apply the EU criteria.

56. In the Czech Republic, the EU persistence criteria for soil are used but only applied if the active ingredient or its metabolites, degradation or reaction products have significant toxicological, ecotoxicological or ecological effects. Although not all respondents in the OECD survey mentioned this "significance criterion", it is probably of broad importance because it seems doubtful that any national authority would ignore toxic impact. For laboratory studies, a pesticide active is considered persistent if non-extractable residues are >70% of the applied quantity of active ingredient after 100 days, and mineralization is <5 %.

57. None of the national authorities that responded in the OECD survey indicated any formal use or recognition of P_{ov} and LRTP derived from multimedia models. One country did note that overall environmental persistence should be "in focus" and that the only true loss mechanism should be degradation - as opposed to persistence in a specific medium in which loss to other media influences how long the substance remains in the medium. This is sound advice but in most cases discussed above, the compartmental persistence criteria either specify degradative losses only (e.g. in the EU "Uniform Principles" just mentioned), or this is implied (e.g. LRTAP POPs). In some cases the judgment of persistence is effects–based (e.g. where persistence is defined as residual toxic effects from a previous application) and here is the possibility that reliance on single-medium P criteria may be shortsighted, especially from the geographic perspective. At the least, national pesticide authorities should consider taking steps to incorporate LRTP into assessments.

2.7 Industry Approaches to PBT Assessment

58. In February 1996, the Chemical Manufacturers Association (CMA) released a guidance document for CMA member companies. The guidance includes information on a process for characterizing and managing both human health and environmental risks linked with chemical manufacturing, by-products and waste materials, which contain PBTs. A screening level evaluation is part of the risk characterization, including numerical values for persistence ($t_{1/2}$ in water = 6 months; $t_{1/2}$ in soil = 1 year) and bioaccumulation (BAF/BCF >5000) but not for toxicity. Toxicity is determined using professional judgement. The criteria were based on available values from other jurisdictions and on available scientific data for substances considered to be PBTs. The process also takes into consideration a substance's potential for long-range transport subsequent to its identification as a PBT.

59. The International Council of Chemical Associations (ICCA) members have committed to sound chemical management and to the reduction of human and environmental risks associated with POPs. The use of most substances identified as POPs have been discontinued or extremely limited by chemical companies within the countries represented by the ICCA. A fundamental conclusion of the ICCA was that the nature of POPs requires that each type of criterion (persistence, bioaccumulation, long-range transport

and reasons for concern with respect to toxicity) be satisfied. Regarding the chosen criteria for POPs the ICCA notes that:

- The criteria for half-life in water should be > 6 (not 2) months, but it should be recognized that this applies to removal of the substance from the environment not merely from the aqueous compartment.

- The criterion for log K_{ow} should be > 5 (not 4) for consistency with the agreed BCF/BAF criterion (which should take precedence),

- With regard to long-range transport, transport without exposure equates to zero risk - therefore the term potential exposure should be retained. Simple advective transport models and the air half-life criterion only consider the potential for a substance to undergo long-range transport. When used as a stand-alone criterion, atmospheric half-life can not identify the potential for a substance transported to remote regions to partition out of the atmosphere and deposit in the biosphere. Substances with a half-life > 2 days that do not partition out of the atmosphere may be transported long distances but will remain in the air and not deposit. If there is no deposition, then there is no potential for exposure to organisms, including humans living in these remote regions.

60. ECETOC have been considering the persistence of chemicals in the environment and have produced a detailed review document (ECETOC, 2003). This document reviews the current approaches for defining, determining or inferring and interpreting the persistence of a substance in the environment. The report identifies factors affecting the persistence of chemicals in the environment and discuss extrapolation from laboratory data to the environment. It also considers ways to improve existing biodegradability tests and reviews abiotic degradation processes.

61. The value of modelling as a tool for targeting degradation testing in relevant environmental compartments is also considered in detail: The report reviews multimedia modelling approaches for the estimation of overall persistence in the environment and concludes that single unit world models with four compartments are the most appropriate tools for evaluating persistence and that more complex models should be reserved for higher tier assessments. If “mode of entry” data are available then level III models are preferred since they allow for the limiting effects of inter-media transport.

62. The ECETOC study proposes a strategy for determining the persistence of a chemical from degradation measurements. The approach is a test and model based strategy, employing a two-stage process (screening and confirmatory) to characterise chemical persistence. This strategy maximises the use of existing degradation data, from standard or non-standard tests, and provides a framework in which data from new test methods can be used in a pragmatic manner to determine overall persistence. Four classes of persistence are proposed ranging from “persistent in the environment” to “easily degradable”. The screening stage aims to identify chemicals that are readily degraded, then for the more persistent substances, a confirmatory stage is applied using multimedia models to help target further testing requirements and to assess the overall persistence of a chemical (a detailed description of the proposed classification is given in ECETOC (2003)).

63. The ECETOC report also considers areas where further work is needed, particularly on the applicability to a wider range of chemicals, improving the knowledge of atmospheric deposition rates, partitioning and degradation in vegetation, OH-radical degradation pathways associated with aerosols and particles and methodologies for incorporating uncertainties in input variables.

CHAPTER 3. MODELS AND INPUT REQUIREMENTS

3.0 Introduction

64. The purpose of this chapter is to introduce the types of multimedia transport and transformation models that are currently available to estimate P_{ov} and LRTP. Because P_{ov} and LRTP are joint properties of chemical pollutants, their emission patterns, and the characteristics of the environment, they cannot be assessed directly from information about the chemical only, or from emissions data. In this chapter, models to determine P_{ov} and LRTP are introduced, before explaining in the next chapter how they are used to calculate these properties. This chapter first considers the models that are available, the data needed for these models and their availability, and concludes with a discussion of how the models differ in spatial/temporal detail and in treating various transport/transformation processes. Most of the models presented in this section are not complex simulation models that might be used for making detailed predictions of concentration, but relatively simple screening models. That is, models that are specifically designed to rank chemicals with regard to P_{ov} and LRTP.

3.1 Accuracy and Uncertainty of Models

3.1.1. What is a model?

65. A model is an artificial reproduction of a system one wishes to study. The behaviour of the model -its "response"- can be observed when various actions, constraints and inputs are imposed on it. Basically, the reason for using a model is that its response is easier to obtain and study than the response of the actual system. Here the system is the global environment, in which a chemical will be distributed and degraded. The model is of course aiming at giving a "faithful" or "reliable" picture of this actual chemical-environment system. What concepts are behind these adjectives?

66. Key concepts for describing models – accuracy, precision, sensitivity and reliability – are defined in Annex 2.

3.1.2. Should we use complex models?

67. Gaining accuracy or reliability (reducing uncertainty) is of course the aim of most model developers. To a certain extent, accuracy generally increases together with the complexity of the model: The more complex the model is, the more elementary mechanisms and the more detailed data/parameters are included – and, consequently, the more detailed output one gets. Section 3.2 will describe two ways of increasing the model complexity.

68. However, a basic principle is that one cannot continuously gain accuracy by increasing the complexity of the models. Beyond a certain level, the amount of data required increases the overall uncertainty of the inputs and therefore the uncertainty of the model. Unless time and resource of the modeller are infinite, a compromise in terms of complexity is necessary to reach an optimum level of uncertainty. For example, it is suggested that there is an optimum spatial resolution for a multimedia model (Wania, 1999). In

environmental sciences, it is difficult to know where this optimum lies and its position will depend on the question to be answered.

3.2 Available Models

69. The nature of environmental processes that transport and remove persistent chemicals requires an approach that describes interactions between the seemingly distinct components of the environmental system. One must treat the atmosphere, hydrosphere, lithosphere and biosphere as an integrated system, not as isolated components. This is referred to as the multimedia approach to describing contaminant fate and transport, as compared to the single-medium paradigm where efforts concentrate on individual media.

3.2.1. Increasing complexity by model structure (level I to level IV)

70. Multimedia fate models synthesize information about partitioning, reaction, and intermedia-transport properties of a chemical in a representative or generic environment. The environment is treated as a set of compartments that are homogeneous subsystems exchanging gas, water, solids, and chemical contaminants with other adjacent compartments. Efforts to develop regional/global contaminant models based on mass balance equations emerged in the late 1970s with the publications of the first edition of Chemodynamics (Thibodeaux, 1979), the environmental segment model (Klöpffer, 1978; Frische et al.,1984) and the seminal papers by Mackay (1979) and Mackay and Paterson (1981, 1982) describing the application of fugacity principles[5] to environmental problems. By the late 1980's multimedia modelling had become more established and was the subject of several reviews, international workshops and studies (Cohen, 1986; PUC, 1986; Allen, 1989; NAS, 1994; Cowan et al., 1995). More recently the issues of persistent pollutants, life-cycle impact assessment, and regional air pollution have motivated further development and application of multimedia modelling. Reported levels of persistent semi-volatile organic compounds and mercury species in vegetation and soil at multiple global sites, in particular in remote areas such the Arctic and Antarctic, have increased interest in more accurate characterizations of chemical transport over regional and global scales.

71. Multimedia models of varying structural complexity can be assembled. Four levels of complexity suggested by Mackay (2001) are summarized in Table 3.1. As one progresses from Level I to Level IV calculations, the fidelity of the calculation to the actual chemical-environment system increases at the cost of additional requirements for input data describing both the environment and the chemical.

Level I Models: Closed System at Equilibrium

72. At the lowest level of complexity, a closed system at equilibrium is modelled. At this level, the concentration of chemicals in multiple media is described by applying a simple mass balance with equilibrium partitioning to a fixed number of moles of chemical in a closed environmental system consisting of a finite number of compartments. The results of the Level I calculation provide insights into the influence of chemical properties on environmental partitioning and a rapid assessment of the environmental media into which the chemical is likely to partition. Because they do not describe several operative processes, Level I models are not directly applicable to calculating P_{ov} and LRTP.

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[5] Fugacity is a criterion of equilibrium and is essentially partial pressure (measured in Pa) and is assumed to be proportional to concentration. Details of the fugacity formalism are described by Mackay (2001). The advantage of fugacity is that for a compartment such as a lake containing water, suspended solids and biota at equilibrium, a single fugacity applies thus a single mass balance equation is written.

Level II Models: Open System at Equilibrium

73. At Level II sources are balanced with removal by chemical transformation and advection at the system boundaries, but the assumption of equilibrium partitioning among compartments is retained. In Level II models, sources are introduced as continuous inputs to the model system, but it is not possible to distinguish releases to different compartments at Level II. Chemical transformations may occur as a result of biotic or abiotic processes that include biotransformation, photolytic decomposition, hydrolytic transformation, and oxidation/reduction. The rate of transformation of contaminants in the environment ultimately determines their potential for persistence. The Level II assumption of equilibrium makes assessment of displacement at compartment boundaries within the environmental system unnecessary. Physical displacement occurs by advection and diffusion. Advective removal refers to chemical displaced by entrainment in a moving medium such as in a moving air mass or a flowing river. The original Level II model assumes steady-state but can be extended to a dynamic transient “Level II dyn” model, which considers explicitly the time course of masses in all environmental media (Trapp and Matthies, 1997). Level II models are the simplest models capable of calculating P_{ov} and LRTP.

Level III Models: Open System at Steady State and Non-equlibrium

74. A Level III multimedia model includes the rates of inter-media transport between environmental compartments. The mass balance condition is applied to each environmental compartment. This requires quantification of diffusion and advection rates at the compartment boundaries. Although there is no requirement for equilibrium partitioning between adjacent compartments, it is still assumed that chemicals achieve equilibrium partitioning among the available phases within a compartment. Level III models are useful for assessing how a chemical’s mode of entry (ie, whether it is released to air, water or soil) affects P_{ov} and LRTP.

Level IV Models: Dynamic Open System

75. A Level IV model removes the assumption of steady-state conditions. Removal rates and rates of inter-media transport between environmental compartments are used to define a time-dependent description of mass distribution. The rate of chemical input to each compartment can be continuous or time-varying. This makes assessment of transient effects possible, such as seasonal variations in emissions and/or climate and soil conditions.

Table 3.1. Summary of different levels of complexity used to describe multimedia contaminant fate.

Type of compartment calculations	Key assumptions	Information garnered
Level I	• Equilibrium partitioning • Steady state • Closed system	• General partitioning tendencies for persistent chemicals
Level II	• Equilibrium partitioning • Steady state (Could be extended to dynamic) • Open system	• Estimate of overall persistence • Important compartments for removal processes • Relative importance of advection and degradation as removal pathways
Level III	• Non-equilibrium • Steady state • Open system	• Influence of mode of emission on fate and transport

		• Refined assessment of overall persistence and loss pathways
Level IV	• Non-equilibrium • Dynamic • Open system	• Influence of mode of emission on P_{ov} and LRTP • Time course of response of contaminant inventory by compartment to any time-varying conditions

3.2.2. Increasing complexity by a more detailed description of the environment

76. Many so-called generic multimedia fate models are based on environmental parameters that are not representative of any specific geographical area. These generic models are used as a "laboratory" for evaluating the likely behaviour of pollutants and how this relates to basic chemical properties. The focus is on the comparative assessment of chemicals and interpreting how partitioning properties and degradability determine transport and fate processes.

77. In order to increase the fidelity to actual environmental and geographical conditions, multimedia models can be modified in different ways:

- Region-specific multimedia mass balance models have the same framework as generic models but include geographical databases representing a specific political or ecological region.

- Region-specific multimedia models might also include compartments in addition to air, water and soil. Examples are sediments, vegetation and ground water. Multiple soil layers or soil regions, multiple surface water regions and/or layers, and multiple air layers may also be included. Adding more compartments requires additional information to construct the appropriate partition and mass-transfer coefficients.

- Multi-zone models include more spatial resolution by linking several region-specific mass-balance models and have been applied on local, continental and global scales.

- Detailed dynamic models rely on highly resolved, geography referenced data and usually subdivide environmental compartments further in multiple layers

3.2.2.1. Generic Models

78. The term "generic multimedia models" refers to models that define environmental properties and chemical interactions within an environment using default values. The use of default values allows these models to have a wide range of applications without being specific to any particular scenario or geographic location. By adopting those standard conditions, these models allow the focusing of attention on the influence of chemical properties on P_{ov} and LRTP rather than on the influence of a specific environment.

79. "Generic" multimedia models of contaminant fate have been adapted to conduct rapid screening-level assessments of large numbers of chemicals for P_{ov} and LRTP. Webster et al. (1998) describe a generic Level III fugacity model for comparing chemicals in terms of persistence in the entire environment, rather than half-lives in individual media. Bennett et al. (1999) and Pennington (2001a) proposed and applied similar models to calculate multimedia persistence. Generic multimedia models have been adapted for assessing long-range transport potential, for example, by Scheringer (1996) who introduced spatial range as a measure of LRTP, by Bennett et al. (1998) who introduced the concept of "characteristic travel

distance" for multimedia chemicals with further refinements by Beyer et al. (2000) and Beyer and Matthies (2002).

3.2.2.2. Region-Specific Multimedia Fate Models

80. Region-specific multimedia mass balance models have the same framework as generic models but include geographical databases representing a specific political or ecological region. An advantage of region-specific models over generic or evaluative models is that results can be directly compared with reported concentrations of contaminants in a specific area. Examples of regional-scale mass-balance models are ChemCAN, CalTOX, ELPOS and the earlier versions of SimpleBOX.

81. In Europe, the Netherlands National Institute for Public Health and the Environment (RIVM) developed SimpleBOX, a contaminant fate model based on concentrations and first-order rate constants consistent with fugacity concepts (van de Meent, 1992; Brandes et al., 1996). The SimpleBOX model was incorporated into the EUSES framework and became a regional fate model for the European Union. Although the early versions of SimpleBOX represented Europe as a single zone, later versions contained embedded zones—country, continental, and global—and thus can be considered more as a multi-zone model than a one-zone region-specific model.

82. The German Umweltbundesamt extended the regional multimedia distribution model of EUSES to ELPOS (Beyer and Matthies, 2002), which allows the calculation of P_{ov} and LRTP for emission into air or water by using the same model structure, parameters and substance properties. A set of 105 organic compounds including current-use pesticides, POPs and industrial chemicals were evaluated.

83. The California Environmental Protection Agency developed CalTOX (McKone, 1993) for assessing emissions to air, water and soil. The current version of CalTOX includes a geographical database for several specific regions of California, ten ecoregions of the United States and political regions representing forty-eight of its states.

84. At a smaller scale (national to continental), ChemCAN is a generic Level III fugacity model with the addition of a database of environmental parameters for 24 ecological regions of Canada (Mackay et al. 1996). ChemCAN has been evaluated for a limited number of contaminants in the southern Ontario, Canada region (MacLeod et al., 1999) and has also been applied in Japan (Kawamoto et al, 2001).

3.2.2.3. Multi-zone multimedia models

85. Based on the above mentioned generic and regional multimedia models a set of zonal/multi-region models have been developed over the last few years. They consist of a series of regional models that are interconnected by means of advective fluxes in air and water. They can be used to generate more region-specific estimates of LRTP and P_{ov}. Some of these models are reviewed below. It is known that other models exist in geographic regions not described below (e.g. East Asia).

86. A simple version of such a zonal model was developed by Scheringer (1996), who connected a series of generic boxes to form a 1-dimensional band around the globe. Later multi-region models consist of a series of regional models that have zonally distinct environmental conditions (e.g., BETR, GloboPop, CliMoChem). Their objective is to be more realistic by being more detailed, more accurate and less "generic". This principle may be used either at a global scale or at a more local scale.

87. Wania and Mackay (1995) introduced a multimedia global distribution model (GloboPop) with nine connected climate zones. The model has been applied to describe the global fate and transport of the pesticide hexachlorocyclohexane (Wania and Mackay, 1999) with a focus on transport and deposition to the Arctic. Scheringer et al. (2000) developed a similar multimedia model of global contaminant fate to

evaluate how the temperature-driven cold condensation and global fractionation influence the LRTP of persistent organic pollutants (the CliMoChem model).

88. MacLeod et al. (2001) have developed a fugacity-based segmented multi-zone model for North America. This model, referred to as BETR, is built on a framework that links contaminant fate models of individual regions, and is generally applicable to large, spatially heterogeneous areas. The North American environment is modelled as 24 ecological regions, and within each region contaminant fate is described using a 7 compartment multimedia fugacity model. Prevedouros et al (2003) have developed a European version of the BETR model referred to as EVN-BETR, which divides Europe into 54 regions each made up of seven compartments.

89. An emerging area of research is the adaptation of general circulation models that describe geophysical transport of the atmosphere and oceans on a global scale to track persistent chemical contaminants (e.g., EMEP, Hysplit-4, MPI-MCTM). The fate and transport of the contaminants are modelled in relation to geo-referenced entities (land, sea, soil, and vegetation) and the behaviour of the contaminant depends on time, location and mode of entry into the environment. These models put a special emphasis on the atmospheric fate of the substance by including meteorological data at various locations and altitudes (e.g., wind speed, temperature, precipitation rate). The output will be spatially detailed concentrations in environmental compartments over time as well as distribution trends over several years. Also, indicators for persistence and long-range transport potential of substances can be derived from the results of such models (Lammel et al., 2001).

90. It is worth pointing out that these complex dispersion models may be seen as level IV multimedia models with a large number of boxes. All models are based on the principle of conservation of mass, and they often contain similar expressions for some mechanisms (e.g. gas/particle partitioning, atmospheric deposition, degradation). Therefore the various models of increasing complexity might be used complementarily (Wania, 1999).

3.2.3. Selecting the Appropriate Model

91. Multimedia contaminant fate and exposure models can be useful to decision makers because they provide an appropriate quantitative framework to evaluate our understanding of the complex interactions between chemicals and the environment. The greatest challenge for multimedia models is to provide useful information without creating overwhelming demands for input data and producing outputs that cannot be evaluated. It is an important task for multimedia modellers to avoid making a model that has more detail than can be accommodated by existing theory and data while also including sufficient fidelity to the real system to make reliable classifications about the environmental fate and transport characteristics of environmental chemicals.

92. Figure 3-1 summarizes the choices available to modellers and policy makers in making estimates of P_{ov} and LRTP. The Figure shows that the continuum of multimedia models available for estimating P_{ov} and LRTP ranges from very simple (on the left) to complex (on the right) with the extra information needed at each stage shown.

93. Guidance on how to select the appropriate model and a more thorough discussion of how model complexity relates to data needs is given in Chapter 5.

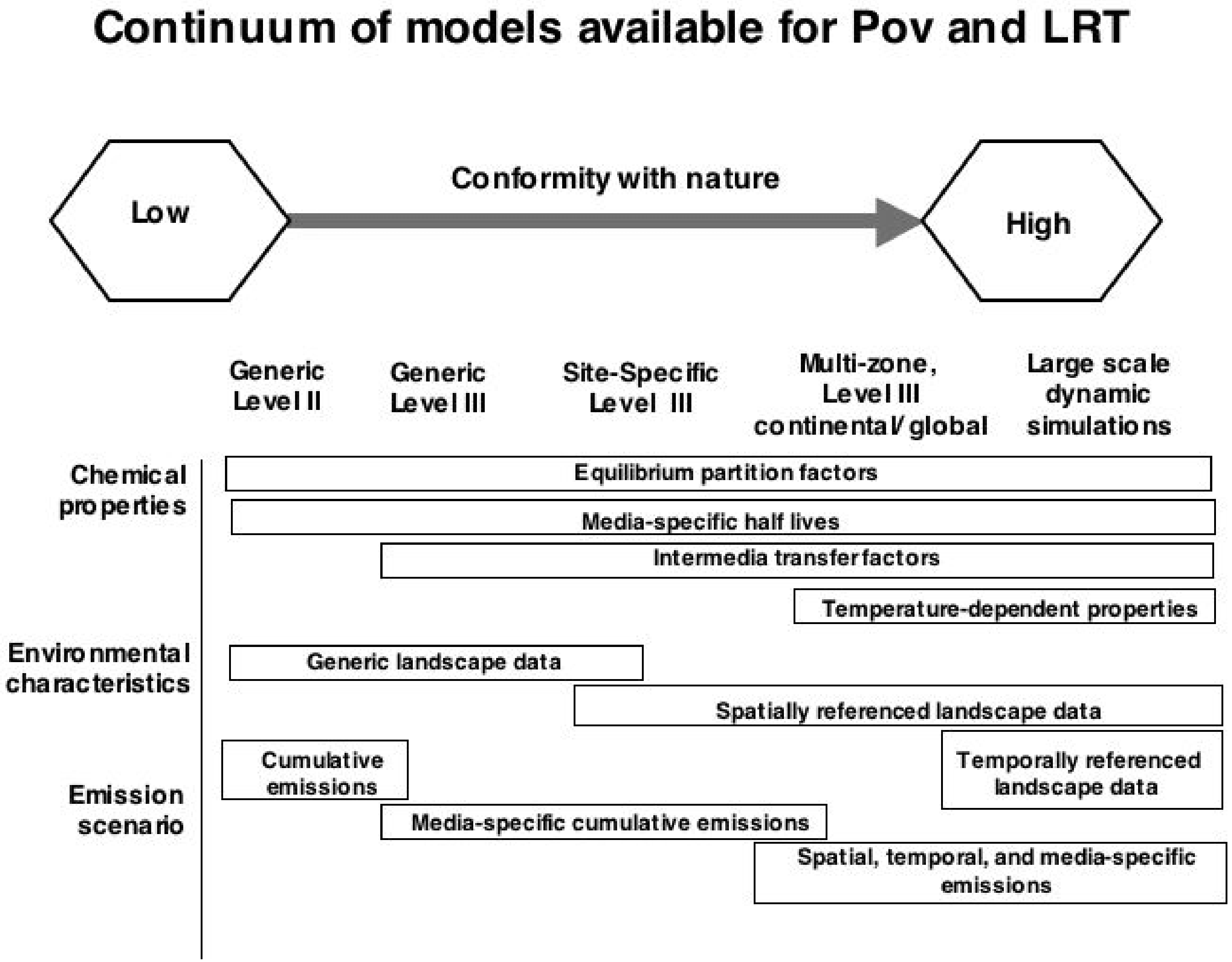

Figure 3-1. An illustration of the continuum of multimedia fate models available for estimating P_{ov} and LRTP.

3.3 Differences Among Models

94. Although the general construction of many multimedia models is based on the same concept, namely the set-up of mass-balance equations for a set of interconnected boxes, there are some "degrees of freedom" where the modeller can define certain features of a model. Therefore, there are important differences between certain models, which should be kept in mind when different results from different models have to be explained. This section provides an overview of the processes by which the models may differ.

3.3.1. Differences in overall model design

95. Models often differ with respect to the model geometry and the types and numbers of compartments included. Important aspects are: the land-to-water ratio, the height of the air compartment, depth of water and soil compartments and the inclusion of compartments such as freshwater sediment or vegetation. The land-to-water ratio determines the dominant properties of the surface media (absorptive capacity, degradation capacity) and the volumes of the compartments determine the relative weight of the compartment-specific loss processes. Accordingly, these factors often account for important differences in model results. In addition, different model purposes require different model designs. For example, models designed for evaluating routes for human exposure such as via food ingestion typically include a more detailed description of compartments such as vegetation that are important to the uptake of a chemical. On the other hand, generic and evaluative models focusing on the overall budget of a chemical in a certain region might include only the "main" compartments of the region while more specific compartments and exposure routes are neglected.

96. Another important feature of a model is whether it assumes steady-state or dynamic conditions (i.e. is it a level III or a level IV model?). Many models are applied at level III and provide a steady-state solution. However, for different chemicals the time-to-steady-state can be significantly different and especially for long-lived chemicals, the steady-state might never be achieved in reality. Therefore, dynamic and steady-state solutions of the same model and for the same chemical can yield very different pictures.

3.3.1.1. Advective and Dispersive Transport

97. Long-range transport can be described by advective or dispersive transport. Advective transport represents a constant mass flux of a "carrier" such as air or water that transports the chemical at a typical wind speed or water current velocity. Dispersive transport is the result of many advective movements of different velocity and orientation. In the long term, it may lead to a homogeneous distribution of a chemical in a given area. Some model approaches consider transport in air and water simultaneously (e.g. Hertwich and McKone 2001; Scheringer et al., 2001) but most calculate separate travel distances for air and water, e.g. ELPOS (Beyer and Matthies, 2002). Stroebe et al. (2003) systematically compare models with single-media transport and models with coupled transport in air and water. In addition, a transport model can be open, i.e. assuming linear transport over any distance, or closed, i.e. circular or spherical with an upper bound for the transport distance. While closed models have an upper bound for possible LRTP values, there is no upper limit for LRTP values calculated in an open model.

98. Only processes leading to an actual loss of the chemical from the environment are included into the calculation of P_{ov}. This obviously applies to all degradation processes. Since advective outflows in air and water as well as inter-compartmental distribution processes only lead to a translocation of chemicals, they are not considered as loss processes. Therefore closed models should be used for the calculation of P_{ov}. Exceptions to this rule are processes that describe the loss of chemicals to the deep sea, through burial into a permanent sediment layer, transfer to the stratosphere, or irreversible transport into the subsurface

environment. In models including these processes they may also be treated as permanent loss processes, in addition to the degradation processes.

3.3.1.2. Equilibrium compartments

99. Some subcompartments are modelled as being at equilibrium with the surrounding compartment, for example particulate matter in water and in air (however, the way in which the particle-associated fractions are calculated might differ between models, see below). With regard to the sediment compartment, some models assume equilibrium between the water column and the sediment, while others treat the sediment as a separate compartment. Additional exchange processes with the water column are particle-associated processes such as resuspension and sedimentation.

3.3.1.3. Temperature-dependence of processes

100. Some models include the possibility to account for the temperature dependence (*T*-dependence) of the degradation rate constants and partition coefficients of the chemicals. While in some cases the user is prompted to enter substance-specific activation energies for the *T*-dependence of the degradation rate constants and, similarly, energies of phase transitions for the *T*-dependence of the partition coefficients, other models assume standard values for these energies. A typical standard value for the activation energy is 20 kJ/mol. For the octanol-water partition coefficient the *T*-dependence is usually assumed to be negligible. This is considered a reasonable assumption because for most chemicals only exchange processes with the gaseous phase show a strong *T*-dependence (due to the strong *T*-dependence of the vapour pressure of chemicals).

3.3.1.4. Formation of transformation products and multispecies cycling

101. Most models do not explicitly account for the formation of persistent transformation products or multiple chemical species (such as ions). Thus, in most cases it is assumed that the disappearance of the parent compound is equivalent to a complete loss of the chemical from the model system. For well characterized chemicals such as DDT that degrade into closely related daughter products this may be addressed by modelling the group of chemicals as a single species (i.e., as “ΣDDT”), assuming a single set of average physico-chemical properties for the mixture. Methods of accounting for the formation of other chemical species and their subsequent fate and behaviour in the environment have been suggested (*e.g.* by Fenner *et al.* 2000 and Cahill *et al.* 2003), but are so far restricted to application to a few case studies due to a lack of information about transformation products formed and their substance-specific properties.

3.3.2. Specific Transport and Transformation Processes

102. All multimedia models address transport and transformation processes with a combination of distribution and degradation models. Among the distribution processes that are addressed in models are atmospheric deposition to soil and water, as well as substance transfer from water to air, soil to air and soil to water. Annex 3 provides a detailed list of the single transport processes considered and discusses how their description can differ between models.

103. Regarding transformation, multimedia models typically make use of one first-order degradation rate constant for the inventory of chemical in each environmental compartment, representing the sum of all degradation processes. It is thus the task of the user to evaluate what processes are influential in each compartment and to add up the corresponding degradation rate constants to obtain one overall degradation rate constant for each compartment. Additionally, the user needs to be aware of the common practice to approximate second-order degradation processes, which are a reasonably correct description for most environmental degradation processes, with pseudo first-order degradation processes.

3.4 Data RequiremeNts and Availability

104. The multimedia transport and transformation models use three sets of input data:

- one describing the properties of the chemicals;
- one describing properties of the environment or landscape receiving the contaminants; and
- one on emissions patterns and mode of entry.

105. The objectives of this section are to identify the data needs, availability, sources and quality indicators of these data for screening models for P_{ov} and LRTP.

3.4.1. Distribution between environmental phases

106. To describe the environmental fate of a chemical, multimedia fate models require quantitative expressions of equilibrium distribution between the various environmental phases. They require expressions for the following phase pairs at least:

- Air-Water
- Air-Atmospheric particulates (aerosols)
- Air-Soil
- Water-Solids (suspended solids, sediments and soil).

107. Over the last decade, several multimedia models have evolve to also require expressions for further compartments and their partition coefficients, for example:

- Air-Vegetation
- Air-Snow.

3.4.1.1. Non-Polar, Non-Ionizing Organic Substances

108. All generic multimedia models for P_{ov} and LRTP assessment rely to some extent on empirical relationships to describe environmental phase partitioning. They are thus strictly only applicable to chemicals for which these empirical relationships hold, i.e. relatively non-polar, non-ionizing chemicals. To make them applicable to other classes of substance, other means to derive partition coefficients between environmental media are needed. For non-polar, non-ionizing organic substances a number of assumptions have been found to be reasonable.

109. Sorption to solids in air, water, soil, and sediments is dominated by partitioning or absorption into the organic fractions of these solids. The respective partition coefficients from water and air into this organic fraction can be estimated through simple one-parameter linear free energy relationships (LFERs) of the type:

$$\log K_{\mathrm{Aerosol/Air}} = a \cdot \log P_L + b \qquad \text{(Eq. 3.1)}$$

$$\log K_{\mathrm{Organic\ matter/X}} = a \cdot \log K_{\mathrm{Octanol/X}} + b \qquad \text{(Eq. 3.2)}$$

where K represents a partition co-efficient, P_L is liquid vapour pressure, X is either water or air, and a and b are empirical regression parameters. Examples of such relationships commonly used in multimedia fate models are those for air-aerosol by Junge (1977), Pankow (1987, 1994), Bidleman (1988) and Finizio et al. (1997), water-organic solids in soils and sediments by Seth et al. (1999) and Karickhoff (1979, 1981), air-soil by Hippelein and McLachlan (1998, 2000) and air-vegetation by Tolls and McLachlan (1994) and Kömp and McLachlan (1997). For a review see Boethling and Mackay (2000). The empirical parameters a and b for a particular organic phase are relatively invariant for non-polar organic chemicals.

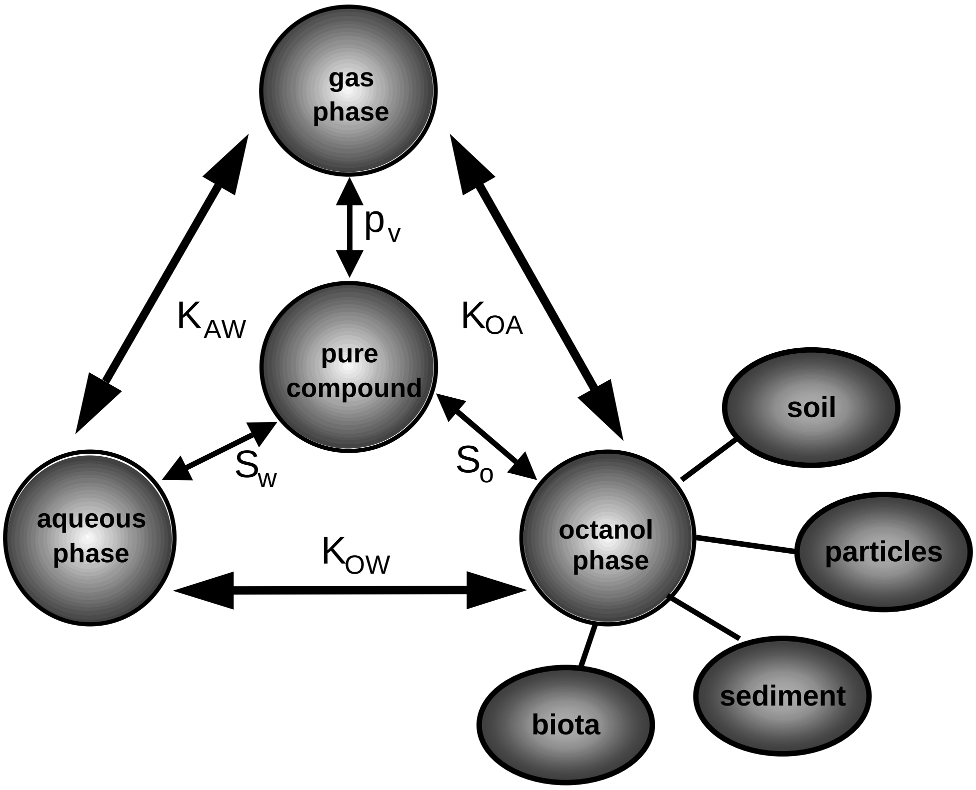

Fig. 3-2 Phase distribution equilibria involving pure phase partition coefficients with importance for describing environmental phase partitioning (K_{AW} air/water partition coefficient, K_{OW} octanol/water partition coefficient, K_{OA} octanol/air partition coefficient. The solid phase is used for soil, sediment, particles and biota).

This implies that these models require a non-polar organic chemical's pure phase partition coefficients K_{AW}, K_{OW}, and K_{OA} to quantify its environmental phase distribution. These three partition coefficients, as well as those partition coefficients involving the pure substance phase (vapour pressure, solubility in water and solubility in octanol) are interrelated as shown in Figure 3-2 (Wania, 2001). They can thus be estimated from each other. This implies that the minimum data requirement for describing phase partitioning of non-polar organic substances is:

- Any two of the three partition coefficients K_{AW}, K_{OW}, and K_{OA}. The third can be estimated from the other two or:
- Any three of the six properties listed in the above figure as long as they do not form a triangle. (For example, if vapour pressure, water solubility and log K_{OW} are known, the remaining partition coefficients can be deduced from these. However, if only vapour pressure, water solubility and log K_{AW} are known, partitioning into organic solids cannot be established).

Ideally, measured information on more than the minimum number of partitioning coefficients should be used when selecting the appropriate model input parameters. This can lead to the problem that the system is over-determined, i.e. various reported properties are not consistent with each other. Beyer et al. (2002) recently suggested the use of algorithms that adjust reported partitioning data in such a way as to assure internal consistency while minimizing the deviation from the original data. These algorithms allow the incorporation of information on the relative certainty associated with the original property data.

Advantages of the LFER approach are:

- experimentally determined data of these properties are often available,
- established internationally accepted technical guidelines exist for the experimental determination of K_{OW}, P_L, and S_W (saturation solubility in water), and
- numerous established quantitative structure property relationships (QSPRs) exist that allow the estimation of K_{OW}, P_L, S_W from molecular structure.

110. It should be cautioned that the experimental methods have limits. Specifically, it is difficult to reliably determine very low vapour pressures ($<10^{-5}$ Pa), very low water solubilities, very high log K_{OW} (>6) and log K_{OA} (>12) values. However, it may not be necessary to determine such extreme values, because:

1. the model result may be insensitive to the actual value of a partition coefficient, as long as it lies beyond a certain threshold. For example, a chemical with log $K_{OA} > 12$ is always particle sorbed in the atmosphere and it may be of little significance to know whether the actual value is 13 or 15.
2. other property values of the same compound are less extreme and can more easily be established. For example, whereas the P_L and S_W of a chemical with very low volatility and water solubility may be difficult to establish experimentally, its K_{AW} may fall in an intermediate range and thus is more easily measured. Note, however, that there are no “established, internationally accepted technical guidelines” for measuring K_{AW}.

3.4.1.2. Polar, Non-Ionizing Organic Substances

111. The approach outlined above for the non-polar substances may also be applicable to polar substances. However, the empirical data that were used to derive existing LFERs usually were restricted to fairly non-polar substances. For example, the LFERs used to describe the phase distribution between air and the organic fraction of aerosol are based on empirical measurements involving almost exclusively PAHs, PCBs, and PCDD/Fs. It is likely that the regression parameters a and b would be different for more polar substances. (In fact, even the regression parameters for air-aerosol partitioning have been found to differ slightly between the PAHs and the chlorinated aromatic compounds.) So far, not enough empirical phase distribution data for polar substances exist that would allow the reliable estimation of their phase distribution from P_L, K_{OW} and K_{OA}.

3.4.1.3. Ionizing Compounds

112. Compounds that ionize in the aqueous phase can be treated as non-electrolytes by multiplying the partition coefficients K_{AW} and K_{OW} for the neutral species by the fraction that is undissociated, which in turn can be calculated from the dissociation constant of the compound pK_A and the pH of ambient water. This assumes that the dissociated form does not volatilise and does not sorb to solids. This model neglects,

however, that the dissociated form might associate with the non-organic part of soil materials such as minerals.

3.4.1.4. Other Compound Classes

113. For many other compound classes, such as metals, surface active substances, extremely water insoluble or involatile substances, polymers, or biological macromolecules the environmental phase distribution can not be estimated using the octanol-based approach outlined for non-ionizing chemicals. For example, their sorption to solids is not necessarily dominated by simple phase partitioning into the organic fraction, but other mechanisms, such as specific surface sorption may become important. It may still be possible to describe them with the help of multimedia models, if the relevant environmental phase distributions can be quantified directly or if different estimation methods exist that allow the estimation of these phase distributions.

114. However, it should be noted that multimedia models are meant to describe the environmental fate of chemicals that distribute notably into more than one environmental phase. For chemicals that occur predominantly in one phase, multimedia models may not be an appropriate tool and the attempt to use them may be misguided. For example, there is not much point in estimating a characteristic atmospheric travel distance for a polymer or a biological macromolecule.

3.4.1.5. Temperature dependence of partition coefficients

115. Most partition coefficients are measured at standard temperature and pressure, but some coefficients, especially those involving partitioning to the gas phase, vary significantly with temperature (Schwarzenbach *et al.* 2003). Some of the multimedia models are set up to adjust partition coefficients when the temperature of the multimedia model application differs significantly from the temperature at which the coefficient has been measured. The user should be aware whether or not such temperature adjustments are employed and whether he has to supply appropriate enthalpies of phase transition or whether standard values are used.

3.4.2. Environmental Degradation

116. Reactivity information (*i.e.* degradation rates) for the various environmental compartments is required to run models. The reaction rates in the various media can either be measured or estimated. Experimentally obtained rate data are preferred over estimated data. The user should be aware that accurate degradation rates are only needed for those compartments in which a significant part of the total chemical mass in the system resides. Because the question of how much of a chemical can be found in which environmental compartment strongly depends on the partitioning properties of the chemical, one way to estimate the presence of a chemical in the different compartments is based on its partition coefficients (see Figure 3-3 below taken from Gouin *et al.* 2000). It has been suggested that for compartments with less than 5% of the chemical mass present, as estimated from partitioning coefficients, a rough estimate of the degradation rate is sufficient (Woodfine *et al.* 2001).

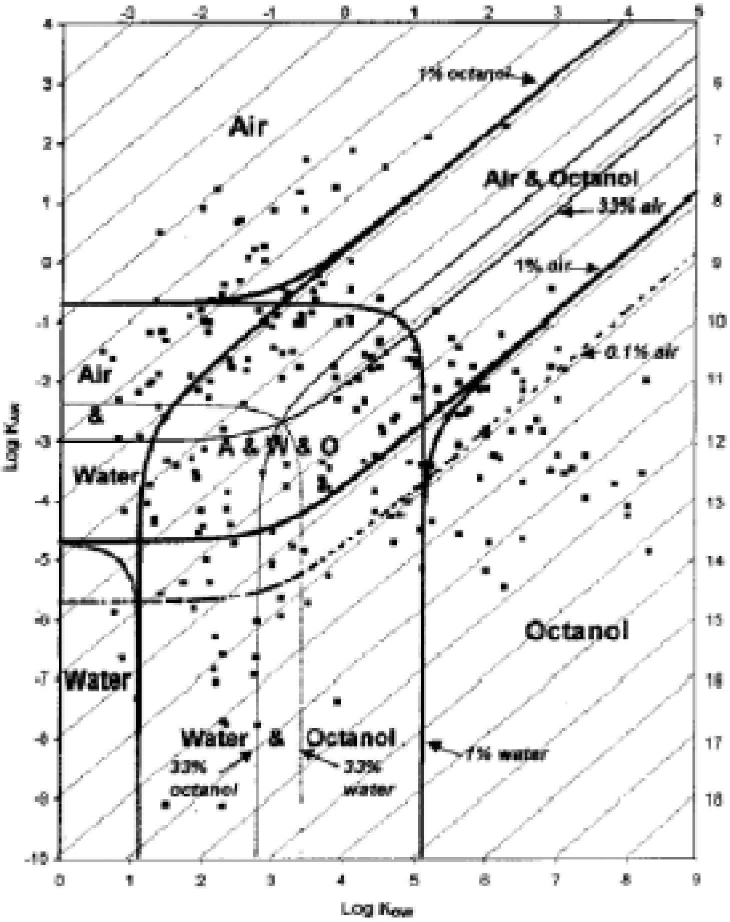

Figure 3-3. Plot of K_{AW} versus K_{OW} showing the distribution of 233 chemicals and lines of fractional distribution among air, water and octanol. This figure is taken from Gouin et al. (2000).

117. Modellers should work to make degradation data as relevant as possible to the natural environment. However, for the majority of chemicals, these types of data are unlikely to be available. For some compartments such as soil and water, results from other test systems such as ready biodegradability tests might be available and could be used as surrogate data to provide estimates of half-lives for modelling. In the absence of any measured data, relevant QSAR estimates can be used as model input. However, use of estimated data will increase the uncertainty of the results. References to guidance documents for data generation, generation of surrogate data, and QSAR estimation sources for parameters described below are given in Annex 4. Half-lives and pseudo-first order rate constants can be interconverted by the relationship $k = \ln 2/t_{1/2}$.

Degradation vs. dissipation When using measured half-lives, users must take care to differentiate between degradation and dissipation half-lives. Only the former are appropriate as inputs into multimedia models, while the latter also includes loss processes other than degradation such as adsorption and transfer to other compartments.

Temperature dependence Degradation processes are temperature dependent, however, most laboratory tests are conducted at standard temperature (20 or 25 °C). Thus it may be necessary to extrapolate rate constants for higher-tier models to other than the measured temperatures using the Arrhenius equation. For screening level multimedia models standard temperature is assumed.

3.4.2.1. Degradation in Air

118. In the atmosphere, photooxidation by reaction with hydroxyl radicals will generally be more important than direct photolysis because most substances do not have absorbance in the relevant wavelength region for direct photolysis. Ozone and nitrate radicals react photochemically, but these reaction rates are usually much smaller than those with hydroxyl radicals. However, these other processes can be dominant for some classes of chemicals and under certain conditions. Experimental values exist for about 600 organic substances measured in the gas phase (see for example the literature review of Klöpffer and Daniel 1991). To estimate missing data, it is common to calculate these rate constants with the software programme AOPWIN (Atmospheric Oxidation Program, Meylan and Howard, 1999).

119. Many organic chemicals have low vapour pressures ($<10^{-3}$ Pa) so that they sorb to aerosols in the atmosphere to a considerable degree. For such semi-volatile chemicals, the OH rate constant is difficult to measure and only a few experimental data exist so far. To represent the reactivity of such semi-volatile chemicals with OH radicals, the conservative assumption is that the adsorbed fraction is not subject to OH-radical degradation. Research is needed either to confirm or disprove this assumption. The gas-phase fraction subject to degradation is calculated by the Junge (1977) equation or more recently by the approach of Finizio et al. (1997) and Harner and Bidleman (1998) using K_{AO}-based models.

3.4.2.2. Degradation in Water

120. The degradation pathways in water include hydrolysis, direct and indirect photolysis and biodegradation. The overall degradation rate constant is calculated as the sum of these three rate constants. But users should note that measurements of one process may also implicitly include the contribution of other processes.

121. Biodegradation is the dominant degradation process in water for most nonpolar organics, but hydrolysis and photolysis can be dominant for some classes of reactive organic chemicals. An internationally accepted standard test for measuring biodegradation rate constants in water is only available for seawater (OECD Test Guidelines 306). Tests for hydrolysis are usually conducted in sterilized water in darkness at different pH levels. From such measurement series rate constants for reaction with H_2O, OH^- and H_3O^+ are determined. The rate of hydrolysis always increases with temperature. Direct photolysis can occur in water, but only plays a role for substances that absorb light at wavelengths greater than 290 nm because of the overlap with the spectrum of sunlight. The photolysis degradation rate depends upon the light absorption properties of the compound and upon the light intensity of the respective geographical region and the season (OECD 1997, 2000). The photolysis degradation rate in natural waters can be estimated using the model ABIWAS 2.0, which is based on a model developed by Frank and Klöpffer (1989).

122. Multimedia models require half-lives. The OECD biodegradability tests provide qualitative results. For those cases where the only biodegradability information available stems from ready biodegradability tests, e.g. conducted according to OECD guidelines, the EU countries and the US EPA provide guidelines on how to translate these qualitative results into half-lives for different compartments. Table 3-2 shows the standard definitions for deriving half-lives in water from the result of ready biodegradability tests used by the EU, and Table 3-3 lists corresponding rules used by the US EPA for programs such as the high production volume chemicals (HPVC) program (US EPA-OPPT, 2003).

Table. 3-2 First order rate constants and half-lives for biodegradation in surface water estimated based on results of screening tests on biodegradability according to European Comission (2003).

Study result	**Rate constant ($kbio_{water}$) [d^{-1}]**	**Water Half-life [d]**
Ready biodegradable	0.047	15
Ready, but failing the 10-d window	0.014	50
Inherent biodegradable	0.0047	150
Not biodegradable	0 ($6.93 \cdot 10^{-7}$ EUSES-default)	To be determined (~ 1000000 EUSES-default)

Table. 3-3 First order rate constants and half-lives for biodegradation in surface water estimated based on results of ready and inherent biodegradability test results according to US EPA-OPPT (2003).

READY TEST RESULT (% biodegradation)	**Inherent test result**	**Rate constant ($kbio_{water}$) [d^{-1}]**	**Water half-life [d]**
pass test		0.1400	5
fail test, but ≥40%		0.0690	10
fail test, ≥20%, but <40%	≥70%	0.0230	30
	≥20%, but <70%	0.0069	100
fail test, <20%	<20%	0.0000	10,000 or other appropriate default for no biodegradation

QSAR models can also be used to estimate the biodegradation potential of a substance. However, available models (e.g., BIOWIN, CATABOL, TOPKAT) do not estimate the half-lives of queried substances. An extrapolation from model output to half-lives is required. Currently, the only approach available to do this was developed by the Syracuse Research Corporation (SRC, 2003) for use in the PBT-Profiler program and is based on BIOWIN's Ultimate Survey Model (USM). According to this method, half-lives in days are assigned to BIOWIN USM "word" output as follows:

"hours" = 0.17
"hours to days" = 1.25
"days" = 2.33
"days to weeks" = 8.67
"weeks" = 15
"weeks to months" = 37.5
"months" = 60
"recalcitrant" = 180

3.4.2.3. Degradation in Soil

123. Degradation possibilities in soil consist of hydrolysis in interstitial water, photodegradation in the soil top-layer, and biodegradation. The overall degradation rate constant is calculated as the sum of these three rate constants—hydrolysis, photodegradation and biodegradation. Biodegradation is the dominant process in soil for most nonpolar organics, but hydrolysis and photolysis can be dominant for some classes of organic chemicals. There are test methods available to determine biodegradability in soil (OECD guidelines 307). However, data on soil biodegradation do not exist for many organic chemicals other than pesticides. Degradation varies considerably as a function of soil type, hydrological status, temperature and geographic location. Where no soil data are available, results from biodegradability tests in water may be used to estimate half-lives in soil. In the EU, a scheme to predict half-lives for (bulk) soil from standardized biodegradability tests in water that includes variation with solids/water partitioning has been developed (European Commission 2003a) and is summarized in Table 3-4. When extrapolating half-lives from the results of ready and inherent biodegradation tests, the USEPA has proposed the same multiplier value for soil as for water (i.e., 1) for the HPVC program. In the PBT profiler program, however, the US EPA applies a fixed ratio of 1:2 for estimating the half-life in soil from that in water according to the output from the BIOWIN USM. The 1:2 ratio reflects a more recent analysis of available data and the 1:1 ratio in HPVC program needs to be updated.

Table. 3.4 Half-lives for biodegradation in surface soil in days estimated based on results of screening tests on biodegradability and based on water-solid partition coefficient Kp_{soil} according to European Commission (2003a).

Kp_{soil} [$L \cdot kg^{-1}$]	Soil half-lives [d]		
	Study results		
	Readily biodegradable	Readily biodegradable, failing 10-d window	Inherently biodegradable
≤ 100	30	90	300
>100, ≤ 1000	300	900	3000
>1000, ≤ 10000	3000	9000	30000

There are tests available to determine photodegradation rates on soil. It might also be possible to estimate these values. As with photolysis in water, direct photolysis only plays a role for substances that absorb light at wavelengths greater than 290 nm, because of the overlap with spectrum of sunlight.

3.4.2.4. Degradation in Sediment

124. Data on biodegradation in sediments do not exist for many chemicals and therefore the half-life for the model must be estimated. In the current EU approach, the half-life in sediment is estimated to be 10 times that in soil. When extrapolating half-lives from the results of ready and inherent biodegradation tests, the USEPA has proposed that a multiplier of four be applied to the water half-life for the HPVC program. In the PBT profiler program, the US EPA applies a fixed ratio of 1:9 for estimating the half-life in anaerobic sediment from that in water as generated by the BIOWIN USM. The 1:9 ratio reflects a more recent analysis of available data and the 1:4 ratio in HPVC programs needs to be updated.

3.4.2.5. Degradation in Vegetation

125. Some researchers have determined that vegetation is an important factor affecting the atmospheric transport and persistence of organic pollutants, see for example Wania and McLachlan (2001). Foliage can effectively filter organic substances from the atmospheric gas phase and subsequent litter fall transports pollutants to the soil. Two processes related to vegetation can reduce atmospheric transport of volatile and semi volatile substances:

1. Partitioning from the gas phase to leaves and subsequent litter fall (scavenging) and

2. Enhanced degradation in and on plants/leaves.

126. Several researchers have assumed that metabolism in plant tissue is less relevant to non-ionic, airborne substances. Photodegradation of substances sorbed on foliage may be more important for some lipophilic compounds (Bennett et al, 1998). Half-lives or degradation rates are available for only a very small number of substances and plant species. If the vegetation partitioning and degradation are considered an important pathway for semi-volatile organic substances, then research is needed to provide more insight in these processes and to produce degradation rate constants.

3.4.3. Environmental Characteristics

127. The types of data needed for environmental characteristics include meteorological data such as average annual wind speed, deposition velocities, air temperature, and depth of the mixing layer; hydrological data, such as annual rainfall, runoff, soil infiltration, ground-water recharge, surface water depth, sediment loads; and soil properties, such as bulk density, porosity, water content, erosion rates, and root zone depth. Generic models for estimating P_{ov} and LRTP generally supply default values for these environmental characteristics. Section 4.2 of this report considers how variation in environmental characteristics impacts model results.

3.4.4. Emission Scenarios

128. The emissions scenarios indicate the fraction of a chemical that is released to air, water and soil. Knowledge of the mode of entry is required in Level III and Level IV models to estimate overall environmental persistence. There are a number of ways to obtain mode of entry.

129. Conditions for estimating releases to different compartments are described in Emission Scenario Documents (ESDs). OECD is working on developing ESDs responding to various categories of industry or use of chemicals. There are also national and regional ESDs, most notably those included in the EU Technical Guidance Document (European Commission 2003a). For a first rough estimate for the mode of entry, emission tables (so called A-tables) are also available in the EU Technical Guidance Document.

130. Information on how a chemical is used may also be employed to estimate the relative importance of its releases to air, water and land. In some cases it may also be possible to estimate the mode of entry for a chemical based on information for an analogue chemical that has similar physical/chemical properties and uses.

131. Pollutant Release and Transfer Register (PRTR) inventories provide probably the most extensive release and transfer data for chemicals emitted to air, water and land. From those data one can calculate the mass fraction of a chemical's release to air, water and soil and therefore its mode of entry. Many OECD countries that have or are developing PRTR programmes collect release and transfer data for a large number of chemicals for the following types of releases: air stack and fugitive releases, direct surface water releases and indirect surface water releases through waste water treatment systems, storm water releases,

disposal to land by underground injection, farm treatment, surface impoundments, landfills, and accidental releases. Parties to the UNECE LRTAP Convention are to provide annual inventories. In addition some countries estimate releases from traffic and other sources.

132. Sometimes, medium-specific measurements of releases may be available. For example, in the United States the US EPA Air Program collects monitoring data for certain chemicals.

133. It is important to consider the whole life cycle of the substance, as significant emissions may occur at different stages of the life cycle and these emissions may be to different media. The release fractions used should relate to total emissions. The different sources of information listed below may only relate to certain stages. Data sources relating to mode of entry include:

- OECD Emission Scenario Documents (http://www.oecd.org/ehs)
- Individual Country Emission Scenario Documents (overview in OECD Use and Release Database, http://webdomino1.oecd.org/ehs/urchem.nsf)
- OECD Compendium of PRTR Release Estimation Techniques (http://www.oecd.org/ehs)
- Individual Country PRTR Guidance Documents on Estimating Releases
- Individual Country Media Specific Programmes.
- Preliminary review of emission data sources for release estimation and development of emission scenario documents (CEFIC LRI, 2001)

3.4.5. Data Availability and Quality

3.4.5.1. Availability

134. Reactivity and environmental partitioning data can be obtained from a variety of sources as discussed earlier. In many countries regulations on pesticides and new industrial chemicals require industry to provide most of the key data as set out in the Annex 4 to run generic multimedia models. However, the situation is different for the bulk of existing industrial chemicals for which experimental data need to be searched out in the scientific literature, in handbooks, company catalogues, material safety data sheets, and databanks. More data are becoming available through the Internet . Selected data sources are listed in Annex 5.

3.4.5.2. Quality criteria and uncertainty

135. Once a set of possible input data for a given substance has been collected, it must then be reviewed for reliability. If both experimental and estimated data are available, it is generally recommended that the experimental data be preferred over the estimated values. Second, it should be checked whether internationally accepted test methods had been used in acquiring that data. A number of other factors should also be considered when assessing the reliability of the data including (for a detailed listing of quality criteria see Kollig (1988)):

- Replication and reproducibility
- Consistency between independent results

- Consistency with those of structurally similar substances or homologues
- For environmental partition coefficients, whether the values fall within the acceptable range of the test method
- For reactivity data, if the results are based on laboratory measured values, how they are extrapolated to represent environmental half-lives.

136. The resulting data collections will still exhibit considerable variance. In general, the variance for substance-specific partition coefficients will be found to be lower than the variance in degradation rates. This is due to the fact that degradation rates are subject to both measurement uncertainty and environmental variability. When deriving average values of collected data for entering as model input parameters, averages should be calculated as geometric means instead of arithmetic means, in particular for degradation rates.

137. Regarding the quality of QSAR methods to estimate missing substance-specific input data, in some methods, such as the EPISuite (Meylan and Howard, 1999), information is supplied about the scope and quality of the training and the validation set but for many QSAR methods this information is not provided. When the reliability of the predictions is described, it is usually expressed as standard deviations indicating the logarithmic deviation of the measured values from those predicted. However, these standard deviations give no indication about the ability of the method to predict values for substance classes other than those used to develop and test the correlation. To obtain QSAR predictions that are as reliable as possible, users must make sure that the structure of the compound in question is well covered within the training set of the QSAR and that the training set contains data that have been verified.

138. To summarize, it is recommended that model users employ the following data hierarchy scheme when choosing input data for multimedia models:

1. Experimental data derived using an acceptable test protocol (e.g., OECD test guidelines), if a guideline exists for the endpoint in question[6].
2. Measured data derived from other "acceptable" methods
3. Close structural analogue[7]
4. Reliable QSAR prediction
5. Default value/expert judgment.

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[6] For example, for biodegradation, for a long time there have been only ready biodegradation tests available, which, as indicated above, do not provide the needed half-lives. This has now changed with the finalization of some guidelines for determining biodegradation rates (e.g. OECD 306-308). However, because these tests are quite expensive, the data situation is not expected to considerably improve over the next few years.

[7] A close analogue should preferably contain most, if not all, of the same structural features as the queried substance. Structural differences that occur should be minimal, and the structures should preferably differ only by a "least affecting fragment". This means that the difference of the effect on (or contribution to) the physical-chemical property between the differing fragments should not be large.

CHAPTER 4. CALCULATING OVERALL PERSISTENCE IN THE ENVIRONMENT AND LONG-RANGE TRANSPORT POTENTIAL WITH MULTIMEDIA MODELS

4.1 Role of multimedia models in calculating P_{ov} and LRTP

139. Operational definitions of overall persistence in the environment (P_{ov}) and "long-range transport potential" (*LRTP*) have been proposed by a group of experts (Klecka *et al.* , 2000), following a SETAC Pellston Conference in Fairmont Hot Springs, Canada. These definitions make use of the multimedia fate modeling principles described in the previous chapter.

4.1.1. Persistence

140. The Fairmont group offered two definitions for persistence (Van de Meent *et al.* , 2000):

- *Overall residence time at steady state*. The calculated overall residence time (P_{ov}) of a substance in a multimedia environment is taken as a measure of persistence:
$$P_{ov} = \tau_{overall} = \frac{\Sigma M_i}{\Sigma(M_i \cdot k_i)} = \frac{1}{\Sigma(\varphi_i \cdot k_i)} = \frac{1}{\ln 2 \cdot \Sigma(\varphi_i / t_{½ i})}$$
where M_i is the mass inventory, φ_i the mass fraction, k_i the first-order transformation rate constant, and $t_{½,i}$ the half life of the substance in medium i. Defined this way, P_{ov} is the mass-distribution weighted average environmental residence in time units. As for most substances transformation rates follow the order: air >> water > sediment/soil, persistence is greatest for substances that predominantly reside in sediment and soil, which is the case for many of the classical hydrophobic POPs. Given the single-media transformation rates, inter-media distribution is the key to overall persistence in the environment. In principle, the mass distributions can be obtained from field measurements. However, practical solutions use multimedia modelling, as described in the previous chapter. Any multimedia fate model capable of doing steady-state (level II or III) calculations can be used for this purpose.

- *Clearance time*. The period (time units) needed for a specified reduction (50%, 95%) of the mass of substance in the environment upon cessation of emissions was proposed as measure of persistence. Calculation of clearance time requires models with transient (Level II dyn or level IV) modelling capabilities. Probably because of this greater computational requirement, this definition of persistence has not been used widely.

4.1.2. Transport potential

141. Three possible definitions are proposed by the Fairmont group for the long-range transport potential:

- *Eulerian approach*. The most refined option proposed involves the use of spatially resolved mass balance modeling. As a result of simultaneous advection, dispersion and degradation, continuous emission from a point or area results in a steady spatial distribution. The spatial range (length units) in which 95% of the substance resides is used as a measure of *LRTP*. Although the Fairmont group specifically referred to Scheringer's 1-dimensional circulinear modeling approach (Scheringer 1996), in which this spatial range is expressed as a dimensionless fraction of the Earth's circumference, any spatially resolved multimedia model can be used to apply the Eulerian approach to *LRTP*-assessment. Two metrics that are calculated with the Eulerian approach, too, are the Arctic Contamination Potential (Wania 2003) and the Great Lakes Transport Efficiency defined by MacLeod et al. (2002a). These metrics focus on the fraction of the chemical emitted that is deposited to the surface media in a target region (the Arctic or the Great Lakes Basin).

- *Mixed-compartment approach*. A less computationally demanding option is to use the same multimedia models that are used for calculating P_{ov}. In this option *LRTP* is calculated as the spatial scale (length units) of a region out of which 50% of the substance is transported to the rest of the world by advection with air and/or water. At steady state, the emission mass flow of a substance into an open regional system is balanced by the sum of degradation mass flows within the system and advective transport mass flows (with air and water) out of the system. The ratio of transport and degradation mass flows is characteristic of the transport potential. The spatial scale for which transport precisely matches degradation is called the characteristic scale. For some chemicals partitioning into the less mobile media (water, sediment, soil) is so rapid and extensive that transport out of the system may not reach 50% at any scale. This is particularly so in case chemicals are emitted to soil. Therefore, Hertwich (1999) and Van de Meent *et al.* (2000) proposed to directly take the transport-degradation ratio for a reference spatial scale as a measure of *LRTP*. In this alternate definition, *LRTP* is dimensionless. Other variations on this theme are the mobility index by Van de Meent *et al.* (1993, 1994), the Arctic Accumulation Potential by Wania (2003) and efficiency of transport into the Great Lakes as used by MacLeod *et al.* (2002a). This type of *LRTP*-measure can be taken from the output of any standard level III multimedia model.

- *Lagrangian characteristic travel distance approach*. As a third option, the Fairmont group proposed the characteristic travel distance. This is the distance that a substance can travel in air or water before the mass emitted is reduced (by transformation or inter-media transport) to 37% (1/*e*) of the original mass (Bennett et al, 1998, Beyer et al., 2000, Beyer and Matthies, 2002)). Like the characteristic scale, characteristic travel distance is expressed in units of length. It has been shown that the concepts of characteristic travel distance and characteristic scale are equivalent. In case of advection in one compartment only, the distance that a parcel of air or water has travelled when the amount of chemical that it contains is reduced to 1/e of the original mass, is equal to the spatial scale for which transport and degradation exactly balance (Van de Meent et al, 2000). The characteristic travel distance in air or water is related to P_{ov} at steady-state (Beyer et al. 2000). A similar concept was used as "atmospheric half length" by Van Pul *et al.* (1998). Calculation of characteristic travel distance is optionally offered as an output of some models (*e.g.* ELPOS, Bennett's model; REFS). In these models, characteristic travel distance is calculated using the same process descriptions as used in standard multimedia models.

4.2 Influence of substance properties, modeling assumptions and emission scenarios on P_{ov} and LRTP

142. It follows from the above operational definitions that, P_{ov} and LRTP depend on the substances properties (as desired), but also on the model used and the emission scenario applied.

4.2.1. Substance properties

143. As described in the previous section, P_{ov} is a function of the degradation rate constants and the intermedia partition coefficients. The same is true for LRTP, because in order to be transported, a chemical needs to be (i) sufficiently long-lived (persistent), and (ii) present to a considerable extent in a mobile medium (air, water). Therefore, P_{ov} and LRTP are well-behaved (although not necessarily simple) functions of the single-media half-lives and intermedia partition coefficients.

4.2.2. Modeling assumptions

144. There is an obvious direct relationship between inter-media mass distribution and the compartment volumes. These volumes (air mixing height, relative surface areas, compartment depths) are set as part of the model definition, and differ between the multimedia models. In addition to these quantitative differences in model parameterizations, there are structural differences between the models: they differ in the way spatial differences are described - in addition to the unit-world model introduced by Mackay (TaPl3), regional model (ELPOS), nested models (EUSES/SimpleBox), and spatially resolved models (Globo-POP, CliMoChem, BETR, IMPACT 2000, Lammel's model, Hemispheric MSC-E model; REFS) are being used. Also, differences in time-averaging of environmental variables (diurnal, seasonal variabilities) can affect P_{ov} ranking (Lammel, 2004).

145. Models also differ in the way inter-media transport processes are modelled (*e.g.*, some models consider vegetation, others do not). These differences in assumptions and choices, which underlie the models, result in different P_{ov} and LRTP values being calculated for the same substances.

146. Specific examples of such differences in modelling assumptions are listed below:

Particle-bound fraction in air

147. Different algorithms are in use for estimating the fractions of substance in gaseous and aerosol-associated form in the atmosphere, leading to differences in degradation- and deposition rates. The two approaches, based on either liquid vapour pressure or K_{OA}, have been evaluated as to be equivalent (Xiao and Wania, 2003).

Partitioning to sediment and soil

148. Different empirical relationships between K_{OW} and K_{SW} may lead to significant differences in inter-media partitioning.

Mixing depths/heights

149. Different mixing heights and depths are chosen in different models. Some models (CalTOX, ELPOS, SimpleBox) offer chemical-specific penetration depths for this purpose. This may significantly influence the effect that exchange processes have on concentrations in the compartments.

Vegetation

150. Some models have a vegetation compartment, while others don't. Also, vegetation is modelled differently in different models (the ELPOS model offers optional consideration of vegetation). It should be noted that for some substances, this may lead to very different P_{ov} and/or LRTP (Scheringer and McKone, 2003; Wegmann et al, 2004).

Continuous or intermittent rainfall

151. Most multimedia models assume a continuous light rainfall. Hertwich (1999) showed that, for less volatile chemicals (air-water partition coefficient K_{AW} below 10^{-4}), the mass fractions contained in the different compartments of a model can be highly different depending on whether there is rain washout or not. The air compartment is affected most significantly by this effect. Hertwich calculated the exact amount of a chemical that is contained in the air (or any other compartment) if rain is intermittently "switched on and off" in a model, i.e. representing more realistic rain conditions. This amount is obtained as the average over time of the concentration as a function of time. To calculate this exact time averaged-amount, a dynamic (level IV) model is required. It is possible, however, to approximate the exact value by the average of the amounts that are contained in the air with rain on and with rain off. This means that the result of the dynamic calculation can be estimated from the steady-state results from the two model versions with rain on and off.

152. Depending on the relationship between the degradation rate constant in air, the rain washout rate, and the degradation rate constants in water and soil, the fraction of the chemical in air can be higher or lower in the model with intermittent rain than in the model with continuous rain.

153. The main implication of these results is that significantly different fractions in air can be obtained for chemicals with K_{AW} below 10^{-4} if a steady-state model with continuous rain or the combination of two models with rain on/off (intermittent rain) is used. Because the fraction in air also occurs in the expressions for the overall persistence, the characteristic travel distance, and the spatial range (Beyer *et al*. 2000, Bennett *et al.* 2001), the rain assumption also affects the results for these quantities.

4.2.3. Emission scenario

154. P_{ov} and LRTP generally depend on the environmental compartment to which the chemical is released, since this influences the intermedia mass distribution at steady state. However, most chemicals have multiple and variable uses. Reasonable options for P_{ov} and LRTP assessment of substances are

i) Estimation of a realistic emission scenario if reliable information is available, e.g. from emission scenario documents,

ii) Calculation of P_{ov} and LRTP for an "intermediate" scenario in which the chemical is emitted in equal amounts to all relevant compartment, or

iii) Calculation of three scenarios with separate emissions to air, soil and water in order to cover the three most extreme values possible.

155. The latter option would lead to assessments of the kind "if emitted to air, P_{ov} would be equal to the P_{ov} of substance X when emitted to air, or to the P_{ov} of substance Y when emitted to soil".

4.2.4 Addressing the model dependence by systematic model comparison

156. The effect of model assumptions and emission scenarios on calculated P_{ov} and LRTP has been addressed by Wania and Mackay (2000). Wania and Dugani (2003) compared four multimedia models with respect to the LRTP results obtained for suites of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs). It appeared that different models/model geometries produced different absolute values for P_{ov} and LRTP, but that relative rankings of substances were affected to a much lesser extent.

157. On the basis of these findings, a scientific workshop was recently held under the auspices of the OECD Expert Group on Multimedia Models to develop methods for producing model-independent P_{ov} and LRTP values. The Workshop recognized that in all models, P_{ov} and LRTP are rather complex functions of the physical-chemical substance properties. These functions are different from one model to another,

although similar. Differences in model outputs for the same substance vary, depending both on models that are compared, and the physical-chemical properties of the substance. There is no simple formula or procedure for transforming model-specific outputs into universal, model-independent outputs. As a solution, the Workshop examined a model comparison procedure, in which P_{ov} and LRTP values were calculated for 3175 hypothetical substances that represent the entire universe of chemicals, and ranking them for these values. Calculation was done on several different models, and it appeared that different models ranked the hypothetical substances at satisfactorily similar positions on the P_{ov} and LRTP scales, reflecting their true (model-independent) positions in the chemical universe. Significant differences in the rankings from different models can be explained by different model assumptions. This approach can be used for assessing P_{ov} and LRTP of real chemicals (See Section 5.3.1.2). The report of the Workshop and its follow-up activities will be published by OECD (http://www.oecd.org/env/riskassessment).

4.3 Sensitivity and uncertainty

4.3.1. Sensitivity

158. Sensitivity, uncertainty and other related concepts are defined in Annex 2. Systematic sensitivity analysis yields insight into the most influential parameters, by changing each of the input parameters in a systematic way (e.g. changing one parameter by ±1%, ±3%, ±6%, ±10%, then changing another parameter by ±1%, ±3%, ±6%, ±10%, etc): these parameters should be known with highest precision (Morgan and Henrion, 1990). It is widely recognized that parameter sensitivities in multimedia models can be very different for different substances and different scenarios (i.e. emission pattern, temperature, correlation models used etc.).

159. A good overview on the sensitivity of P_{ov} and LRTP calculations with multimedia models can be found in Beyer and Matthies (2002). They calculate sensitivities of P_{ov} and LRTP for several chemicals with ELPOS, considering substances with a wide range of physical-chemical properties. They assume that all emissions are into the air compartment and investigate the local sensitivity for a 10% change in the input parameters. They identify a set of environmental and chemical parameters that are often “on top of the sensitivity list”. The list is given in Table 4.1.

Table 4.1: Substance properties that typically have great influence on P_{ov} and LRTP, assuming 100% emission into air.

	P_{ov}	LRTP
Substance parameters	Degradation rate in air Degradation rate in soil Vapor pressure Kow	Degradation rate in air Vapor pressure Water solubility
Environmental Parameters	Height of air compartment Rain rate Density of soil solids Mass transfer coefficient soil-air	Wind speed Height of air compartment Rain rate “Aerosol parameters”

160. As a rule, sensitivities of P_{ov} depend strongly on the mass distribution, i.e. on the partitioning behavior of the substance and on the emission pattern. To decide which are the most influential substance properties and environmental parameters, it is thus most informative to first roughly investigate the mass distribution (see Webster *et al* (1998), for simple rules of thumb). However, the height of the air compartment is nearly always an important influencing factor, as are the degradation rates in all compartments. For emission into air the degradation rate in air often shows the strongest influence. If other emission patterns are assumed, degradation rates and other parameters describing the respective emission compartments become more sensitive.

161. Because LRTP is mainly determined by processes in the air compartment, sensitivities for LRTP tend to be similar for most substances. On the substance parameter side, it is often degradation rate in air and the vapour pressure that determine LRTP. Exceptions are the very hydrophilic substances, where the rain rate becomes important, and strongly ad- or absorbing substances, where particle-related processes, i.e. "aerosol parameters", become important. The most influential environmental parameters are wind speed and the height of the air compartment.

4.3.2. Uncertainty

162. Uncertainty in calculated model output originates from different sources, e.g. uncertainty or -variability in input parameter values. Small uncertainties in sensitive model parameters may contribute greatly to the overall uncertainty in model output, whereas great uncertainties in insensitive parameters may not have dramatic effects. Systematic uncertainty analysis yields the contributions of individual parameters to the overall output uncertainty.

163. The results of an uncertainty analysis depend on the types of distribution functions chosen to represent the variance in the input parameters and on the assumed spread of these distribution functions (Lessmann, 2003). Three studies have explicitly focused on quantifying the uncertainty of P_{ov} and LRTP (Bennett *et al.*, 2001; Beyer and Matthies, 2002; Fenner *et al.*, 2003). In these studies 30 to 70 compounds with diverse partitioning behaviour have been investigated. All three studies used Monte Carlo simulations to deduce so-called 80% or 90% confidence intervals. An x% confidence interval indicates that x percent of possible results will lie within the given interval when all model parameters are varied to the extent that they are uncertain. Model users who wish to estimate the uncertainty of their results can use Table 4.2, in which typical uncertainty intervals for P_{ov} and LRTP, calculated with three different models, are given[8].

Table 4.2: Confidence factors for P_{ov} and LRTP, as obtained from uncertainty analysis for up to 70 compounds with diverse partitioning behavior.

	P_{ov} Confidence factor	***LRTP*** Confidence factor
Bennett *et al.* 2001, advective model	---	10-40
Bennett *et al.* 2001, diffusive model	---	2-5
Beyer and Matthies, 2002	3-30	4-50
Fenner *et al.* 2003	10-20	2-4

164. Confidence factors typically cover one to two orders of magnitude for both P_{ov} and LRTP. As an exception, the confidence factors for LRTP obtained with the diffusive model in Bennett *et al.* (2001) and the model used in Fenner *et al.* (2003) are smaller, *i.e.* less than one order of magnitude. In both cases, the uncertainty analysis was conducted with the ChemRange model (Scheringer *et al.* 2002) that has an upper limit for LRTP that corresponds to 95% of the circumference of the earth. In contrast, the advective models used in Bennett *et al.* (2001) and Beyer and Matthies (2002) assume no upper limit for LRTP.

165. These confidence ranges are large, relative to inter-substance differences, which complicates ranking of substances in terms of their absolute P_{ov} and LRTP values.

166. Beyer and Matthies (2002) and Fenner *et al.* (2003) studied how much each input parameter in a model contributes to the overall uncertainty. Knowing this helps in identifying those parameters that should be known best in order to achieve accurate modeling results.

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[8] People wanting to perform a simple uncertainty analysis of their own modeling results should be aware that, besides the rather complex Monte Carlo simulations, easier to use analytical approximation methods are available for uncertainty analysis (e.g. MacLeod et al. 2002b).

167. For emission to air, Beyer and Matthies (2002) found that similar input parameters as identified in the sensitivity analysis also show the highest contributions to overall uncertainty. These are: degradation in air, vapour pressure and water solubility on the substance parameter side, and height of the air compartment, wind speed and rain rate on the environmental parameter side. Additionally, for substances with high affinity for the organic phase (*i.e.* logKow>3), the half-life in soil is also important to P_{ov}.

168. As in the sensitivity analysis, the question of which parameters contribute most to the overall uncertainty depends strongly on substance properties and emission patterns. Therefore, Fenner *et al.* (2003) have studied substance-to-substance differences in sensitivity and uncertainty. For this purpose they grouped chemicals into groups with similar partitioning properties, in analogy to Gouin et al. (2000) (see Figure 3.3), and then evaluated those input parameters contributing most to overall uncertainty for each group separately. The results are collected in Table 4.3 and should be useful to the user as a compendium to identify the most influential input parameters for the chemical investigated.

Example: What are the most influential input parameters for the calculation of P_{ov} for a chemical with K_{OW}=3.5 and K_{AW}=-4?

1. Go to Figure 3.3 and find out that the chemical belongs to the air-octanol-water partitioning group

2. Go to Table 4.3 and find out that for this group the degradation rates in soil and air and the mass transfer coefficient between soil and air are the most influential parameters.

3. Carefully check your degradation data in soil and air and try to determine them as reliably as possible because the outcome of your model will greatly depend on these values.

169. Some general rules for LRTP can be deduced from Table 4.3. For most groups, the processes in air dominate (*i.e.* degradation rate in air on the substance parameter side, and OH radical concentration in air, eddy diffusion coefficient in air and mass transfer coefficients for diffusive exchange to air on the environmental parameter side). Exceptions are substances with a strong affinity for the organic phase, for which aerosol deposition and deep-sea particle deposition become influential for *LRTP*, and very hydrophilic substances, which are washed out from the atmosphere by rain.

170. Table 4.4. can be regarded as summary of Table 4.3. It indicates how much the three groups of input parameters, namely partition coefficients, degradation rates and landscape parameters contribute to the overall uncertainty. It shows that most of the output uncertainty stems from uncertainty in the degradation rates (61-97% for P_{ov}, 27-84% for *LRTP*, see Table 4.4). Thus, if precise results are needed, gathering in-depth knowledge on degradation rates would be most effective.

Table 4.3: In this table parameters that contribute more than 4% to the overall uncertainty of P_{ov} or LRTP are listed. They are identified separately for six groups of substances with different partitioning behavior between the phases air, water and octanol (used as proxy for the soil compartment) [9] ***(e.g. a chemical belonging to the air-octanol group is a chemical that partitions mainly to the atmosphere and into the soil compartment). These results are strictly speaking only applicable if emission into soil is assumed.***

P_{ov}						
	Air	*Air-Water*	*Air-Octanol*	*Octanol*	*Octanol-Water*	*Air-Octanol-Water*
Most influential substance parameters	Degradation rate in air Degradation rate in soil	Degradation rate in water Degradation rate in air Degradation rate in soil	Degradation rate in soil	Degradation rate in soil	Degradation rate in soil Degradation rate in water	Degradation rate in soil Degradation rate in air
Most influential environmental parameters	OH· concen-tration in air OC content in soil Mass transfer coefficient soil-air	Mass transfer coefficient soil-air				Mass transfer coefficient soil-air

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[9] Substances partitioning largely to water were omitted from this list since results for this type of substance were felt to be possibly in error as a result of the modeling assumption of continuous rain (see also section 4.2.2).

LRTP

	Air	*Air-Water*	*Air-Octanol*	*Octanol*	*Octanol-Water*	*Air-Octanol- Water*
Most influential substance parameters	Degradation rate in air Degradation rate in water Kaw	Degradation rate in air	Degradation rate in air Degradation rate in water Kaw Kow	Degradation rate in air Degradation rate in water Kaw Kow	Degradation rate in air Degradation rate in water Kaw Kow	Degradation rate in air Degradation rate in water
Most influential environmental parameters	OH· concen-tration in air Eddy diffusion coefficient in air Mass transfer coefficient water-air	OH· concen-tration in air Eddy diffusion coefficient in air Mass transfer coefficient water-air	OH· concen-tration in air Eddy diffusion coefficient in air Mass transfer coefficient water-air Mass transfer coefficient soil-air	OH· concen-tration in air Eddy diffusion coefficient in air Rain rate “Aerosol parameters” “Deep sea deposition parameters”	OH· concen-tration in air Eddy diffusion coefficient in air Rain rate “Aerosol parameters”	OH· con-centration in air Eddy diffusion coefficient in air Mass transfer coefficient soil-air

***Table 4.4:* In this table it is indicated which type of parameter contributes most to the overall uncertainty of P_{ov} or LRTP. The percentages of contribution are identified separately for six groups of substances with different partitioning behavior between the phases air, water and octanol (used as proxy for the soil compartment)[10] (e.g. a chemical belonging to the air-octanol group is a chemical that partitions mainly to the atmosphere and into the soil compartment). These results are strictly speaking only applicable if emission into soil is assumed.**

P_{ov}

	Air	*Air-Water*	*Air-Octanol*	*Octanol*	*Octanol-Water*	*Air-Octanol-Water*
Contribution of degradation rates	61%	85%	97%	97%	96%	88%
Contribution of partition coefficients	5%	2%	0%	0%	1%	2%
Contribution of environmental parameters	34%	13%	3%	3%	3%	10%

LRTP

	Air	*Air-Water*	*Air-Octanol*	*Octanol*	*Octanol-Water*	*Air-Octanol- Water*
Contribution of degradation rates	84%	80%	78%	55%	27%	84%
Contribution of partition coefficients	1%	0%	3%	5%	18%	1%
Contribution of environmental parameters	15%	20%	19%	40%	55%	15%

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[10] Substances partitioning largely to water were omitted from this list since results for this type of substance were felt to be possibly in error as a result of the modeling assumption of continuous rain (see also section 4.2.2).

4.4 Limitations

171. The limitations for use of current multimedia fate models for calculating P_{ov} and *LRTP* can be made transparent by discussing the basic assumptions made in these models.

Well-mixed compartments

172. The most fundamental assumption of this type of model is that relatively large, internally well-mixed compartments are used to represent the environmental media. This implies that the spatial and also the "functional" resolution of the models is relatively low ("functional resolution" refers to the number and types of processes covered by a model). In other words, the models represent an average situation but do (in most cases) not reflect a certain region at a certain time. This kind of simplification is helpful because the complexity of environmental systems is very high and a detailed representation of this complexity leads to models that are complex as well and, therefore, difficult and time-consuming to set up and use. Moreover, spatially and temporally resolved emissions, which are needed at the same level of complexity with distribution (Berding et al, 2000), are unavailable for almost all chemicals.

173. On the other hand, the simplified approach of box models implies that the models cannot be used to predict pollutant concentrations with high spatial and temporal resolution, *i.e.* for specific locations and points in time. However, with some qualifications, the model results can be applied to reality: (i) If information on the release pattern of a chemical is available, "realistic" release terms can be used in the model and the concentrations obtained reflect – with the limitation that only averages over relatively large regions and long times can be obtained – the actual concentration of a chemical in the different media considered (the model results might thus coincide with a chemical's concentration at a single location at a specific time, but the modeller can never know when and if they do). (ii) Even if a model is used with idealized release scenarios such as a single point source, it should provide some general trends of the pollutant behaviour that might in a similar way be found in reality. It has to be kept in mind, however, that this "evaluative" use of a multimedia model does not even aim to predict actual concentrations but is intended to provide an understanding of the environmental processes and their interplay and of how the chemical properties determine the model outcome.

Number and type of chemical species covered

174. The next two assumptions concern the way in which the mass-balance equations for the different boxes of a multimedia model are set up. Most models are built upon a set of mass-balance equations only for a single chemical species circulating between the different compartments of a model. The parameters occurring in these mass-balance equations are derived from environmental parameters such as particle deposition rate constants and a set of substance-specific parameters that are very similar for most models, namely partition coefficients and first-order degradation rate constants. This set-up is appropriate for a single, non-polar organic chemical because the environmental behaviour of such a chemical can indeed be described by partition coefficients and degradation rate constants.

175. At this point, the following limitations become obvious: Most models cannot be applied to chemicals that form different chemical species such as transformation products of the parent compound, the anions of acidic compounds, or different forms of metal complexes. To describe such systems of chemicals, the mass-balance equations of a multimedia model need to be extended so that the formation of other species than the parent compound is accounted for. There are a few examples of such models (Fenner *et al.* 2000, Cahill *et al.* 2003).

Substance properties used to determine parameters of mass-balance equations

176. Another aspect is the question of whether the environmental behaviour of a chemical can be adequately described in terms of partition coefficients and first-order degradation rate constants. For metals, too, mass-balance equations for environmental compartments can be set up but it might be necessary to determine the parameters of these equations in terms of other substance properties than Henry's law constant, octanol-water partition coefficient, and rate constants for chemical and biological degradation. Therefore, models requiring these types of substance properties cannot easily be applied to metals (in addition to the fact that most metals form different chemicals species in the environment).

Steady state

177. A fourth assumption that is important for many models, but not as fundamental as the first three assumptions, is the assumption of the system being at steady state. In principle, the set of mass-balance equations of a multimedia model can be solved dynamically, *i.e.* for the concentrations of the chemical(s) as functions of time, or under the assumption of steady-state. The steady-state solution refers to a state that is achieved only after a "sufficiently" long time (for example, the time to reach at least 95% of the steady-state concentrations in all compartmetns can be calculated). On the one hand, the steady-state solution is easier to obtain than the full concentration functions. On the other hand, the time to steady state might be long or even very long for chemicals with slow processes such as a low degradation rate constant in soil or variable release/emission patterns. In such cases, the steady state might never be achieved in reality or even as an evaluative sketch of a chemical's environmental fate it might be misleading. The steady state assumes that all compartments are completely "filled" with the chemical so that outflow balances inflow. For "slow" compartments such as soil, this state might be reached only after several decades. This means that for chemicals with slow processes, a dynamic calculation should be performed in addition to the steady-state solution.

CHAPTER 5. APPLICATION OF MULTIMEDIA MODELS IN CHEMICAL ASSESSMENT

5.0 Introduction

178. Chapter 2 presents regulatory and non-regulatory uses of multimedia models for estimating LRTP and P_{ov}. Chapter 3 describes the mechanics of multimedia models and Chapter 4 discusses the interpretation of their outputs. This chapter explains how the results from models may be applied in regulatory and non-regulatory settings in order to assess chemicals. This chapter discusses how users might select a model according to their needs - e.g. confidence level required - but also their constraints - e.g. data available.

179. Section 5.1 explains in what context multimedia models are applied and how they can complement more simple approaches such as the use of single media half-lives. Section 5.2 illustrates the available continuum of models of increasing complexity (as a complement to Chapter 3) and also shows how reliability, confidence level, data needs and range of applicability are likely to vary with model complexity. Section 5.3 focuses on the ways of using LRTP and P_{ov} as the main outputs of these models, but it will be shown in 5.3.3 that other model outputs may also be used for supporting an evaluation process. Practical examples of the application of multimedia model will be given in Section 5.4. Section 5.5 summarises this chapter.

5.1 Why use a multimedia model?

5.1.1. The main uses of multimedia models: screening and assessment

180. As discussed in Chapter 2, multimedia models (and other fate models for single media) may be used by both regulatory and non-regulatory users. The non-regulatory users can be academics, non-government organisations or the chemical industry. The two major types of use of multimedia models results are:

1. when a substance is under development by the chemical industry and

2. when substances are being assessed as new or existing substances (including pesticides) by regulators at the national, regional or global level.[11]

181. Based on their predictive capability, the aim of multimedia models is to help their users in determining the overall hazard or risk a substance poses to the environment or to humans. Consequently, it is very important to select an appropriate multimedia model to use in chemical assessment and to determine how the results from the models can be applied.

182. Two kinds of evaluation may be addressed:

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[11] The consequences may be limitations in production amount, prohibiting a specific production process, restrictions in uses, etc.- see examples in 5.4.

1. (1) Chemical screening: The objective is to identify substances of concern among a large set of substances. Chemical screening can also refer to broader approaches that result in the same goal, e.g. ranking the chemicals comparatively to each other or establishing priority classes. This process is generally based on the specific properties of the substances (e.g. half-lives). It may solely rely on estimated data or may involve a combination of measured and estimated data.

2. (2) Risk assessment: This consists of characterising the risk that a substance poses to human and non-human organisms by considering its inherent toxicity and the potential for exposure. For each compartment of the environment, the calculation of a predicted concentration, or exposure value, is compared to an effect concentration. Here the predictive capability of some models is required.

The present chapter will focus on these two purposes.

5.1.2. Why simple approaches may not be sufficient

183. The half-life of a chemical in a given compartment of the environment can be used as an indicator for persistence. Moreover, under certain assumptions its half-life in air can be used as a surrogate for LRTP. These single-media half-lives can be compared to numerical regulatory criteria. In the framework of the Stockholm Convention on POPs and the POPs Protocol under the LRTAP Convention (Long-Range Transboundary Air Pollution), thresholds are given for single-media half-lives, namely:

- Persistence is indicated by a half-life in soil > 6 months or a half-life in water > 2 months.

- LRTP is indicated by a half-life in air > 2 days (see also Tables 1-3, Chapter 2).

184. This is the simplest approach and is common among global, regional and national POP/PBT initiatives. It is used in many regulatory agencies because such data are available for many chemicals and can be produced through standardised methods.

However, this simple approach may not be sufficient for several reasons, among them:

(1) Partitioning properties are not taken into account. For example, assessment based on half-life in a medium to which the substance is unlikely to partition may lead to over-protection in terms of persistence. P_{ov} is a better indicator of persistence in the environment as a whole

(2) Mode of entry is not taken into account. For example, the persistence of a substance with a long half-life in soil compared to its half-life in water will be greater if it is discharged directly to soil, than if the initial emission is to water. Effect of medium to which emissions occur may not be explicitly considered when using single-medium half-lives; whereas, use of a level III multimedia model mandates that it be addressed.

(3) Half-life in air is only one parameter that affects long-range transport. Multimedia models are the most appropriate way to assess LRTP because they consider important variables in addition to air half-life.

(4) Half-life data are often unavailable. Use of surrogate data and additional efforts to obtain half-life data will benefit from multimedia models in the sense that, by indicating potential environmental fate these models can focus attention media half-lives that are greatest value in obtaining P_{ov}.

5.1.3. Can monitoring fill the gap?

185. Monitoring is another potential source of support for regulation. In the Conventions cited above, measurements in remote regions provide a type of information that may be used as evidence of LRTP. In addition, results from monitoring in a given compartment of the environment or in a given living species may bring evidence for a substance being "of concern" – either at a local of a global level.

186. However, in order to yield meaningful data, such studies involve the large financial costs of samplings and analyses, and the cost of lost opportunity due to the long time required to complete the sampling and analysis. Moreover, it is unrealistic to assume that monitoring studies can adequately cover the large number of chemicals and geographic areas needed to identify chemicals of concern and assess the hazard and risk posed by these chemicals. Multimedia models are a more efficient way for doing this. They are also helpful in designing monitoring studies for chemicals that are predicted to pose a risk.

5.2 Selecting a model

5.2.1. Complexity of available models

187. The evaluation of a substance –mainly its fate in the environment– can be performed using a range of modelling approaches, from simple to more complex. The simplest approach, described in 5.1.2, refers to estimating LRTP using estimated or measured atmospheric half-life and persistence using single media half-lives. Beyond this, a wide spectrum of multimedia models of increasing complexity is available. In Chapter 3 the basics of these models were presented in a detailed manner, and their increasing complexity was explained, both in terms of model structure (from level II to level IV) and in terms of description of the environment (generic models, region specific models or multi-zone models, spatially detailed dynamic models).

188. Clearly, the most basic models provide several advantages, in that they are simple, quick to use, do not require much modelling expertise and are not resource or data intensive. Yet, if the available data and the user's expertise are sufficient, the evaluation can be carried out with a more complex tool, with a higher spatial and temporal resolution, which will potentially be more accurate or more informative. Hence the outputs of different models are likely to be complementary. A user may select a model from the spectrum at any point and does not have to begin with a simple model and progress to a more complex model.

189. Table 5.1 gives an overview and a possible classification of some of these models through increasing levels of complexity.

Table 5.1: Summary of Model Complexity, Associated Requirements and Outputs

Level of Model Complexity	**Example of Model**	**Data Requirements and Sources**	**Type of Model Output**	**Example of Application**
Simplest—non model-based approach	Single medium half-life	Estimated* or measured half-life in specific media	Medium-specific half-lives	Compare half-lives to regulatory criteria (e.g., half-life in air >2 days = potential for LRT) for such activities as the screening of large inventories of chemicals for PBT/POP properties
Simple	Generic multi-media models (e.g., TaPL3, ELPOS,	Estimated* or measured physical-chemical	CTD, spatial range, Various values of LRTP P_{ov},	CTD or spatial range used to identify substances with high LRTP in PBT/POP programs or screening level risk

	Chemrange, Simplebox, EQC)	properties, half-lives and partition coefficients	media partitioning information	assessment of new and existing substances; P_{ov} used with media partitioning information to identify relevant exposure media and exposure duration
Intermediate complexity	Multimedia models with regional or zonal distinctions (e.g., EVN-BETR, CliMoChem, GloboPoP)	Estimated* or measured physical-chemical properties, half-lives and partition coefficients; environmental properties for zones	Various values of LRTP; P_{ov}; media partitioning information for specific zones; chemical loading in different climatic zones ; some models provide global distributions based on assumed emission patterns	Screening-level risk assessment and more detailed risk assessment for regional areas and emission patterns ; Global distributions may be applied on a larger scale
More Complex	Spatially explicit dynamic models (e.g., EMEP, G-CIEMS, POPCYCLING-Baltic)	Measured physical-chemical properties, half-lives and partition coefficients; GIS-referenced data	Concentrations of chemicals across locations according to time trends	Detailed risk assessment for specific locations or regions and emission patterns

* The term “estimated” refers to model input data derived using QSARs, extrapolation procedures (e.g., media specific half-lives extrapolated from ready biodegradation test or biodegradation QSAR results) or through the use of a closest analogue approach.

Abbreviations : CTD= characteristic travel distance ; PBT = persistent, bioaccumulative and toxic ; POP = persistent organic pollutant ; LRTP= long-range transport potential ; P_{ov} = overall persistence (derived from a multimedia model by definition).

5.2.2. Factors to consider when selecting a model

5.2.2.1. Reliability and confidence

190. In judging the acceptability of any model for a specific chemical and release scenario, it is important to address the interaction among precision, accuracy, and confidence. Reliability includes precision and accuracy and is a measure of model performance. These concepts of are defined in Annex 2. But it is noted here that a there is not necessarily a one-to-one relationship among precision, accuracy, and confidence. For example making a model trivially simple can maximize its precision but not its accuracy. A complex model can be more accurate and instil confidence, but if there is no reliable data available to match its input needs, it will be neither precise or reliable. The choice of models is not only driven by their reliability, but will be based on the user’s confidence in the model. “Confidence” is more subjective than "reliability" and depends not only on the model but also on the way it is used.

191. Concerning mechanistic models, in principle the less uncertainty a model brings the higher the confidence should be. However, models with a low accuracy might still be used with high confidence if accuracy is limited by available data and the goal of the user is consistency more than fidelity. For example, when carrying out a risk assessment, it is quite common to run a simple model with conservative options, by maximising some parameters, in order to be sure -or confident enough- that the output is greater than reality (e.g. for the exposure). The result is certainly inaccurate, but the confidence level of the user is high because he is confident of avoiding "false negatives". Besides, in the case of a chemical

screening with a simple multimedia model the absolute values (concentrations in the environment) need not be proved accurate (or conservative) to be useful, since the objective is to compare substances.

5.2.2.2. Data needs, resource intensity and range of applicability

192. Theoretically, a user should consider the degree of model complexity required to answer his questions in combination with the accuracy of the results he needs and the level of confidence he wishes (these factors are presented in Figure 5.1). However, it is likely that the level of model complexity selected by a user will mostly depend on data requirements, compared to the amount of data available and on the accuracy of these data.

193. Simple models require fewer data and are less resource intensive but can be less accurate than more sophisticated models. The selection of a more complex model generally aims at increasing the overall confidence of predictions as well as the accuracy of results (e.g. concentrations in more sub-compartments; results with higher spatial or temporal resolution). But this greater confidence is not guaranteed unless the model has been correctly validated (or evaluated against measured data) and the accuracy of input data is sufficient. Generally, increasing the complexity of the model will increase the data needs as follows :

- More data on the environment itself which is described with more accuracy (in a more detailed way).

- Improved data on the substance itself, which means more accurate data on its physical-chemical properties.

- More quantitative data related to the release of the substance, e.g. tonnage, mode of entry.

- More field data in order to validate the model results. The more complex a model is, the more data the developer of the model needs in order to calibrate and to validate it. However, a user is generally not obliged to go into such considerations, if his confidence level in the model is sufficient.

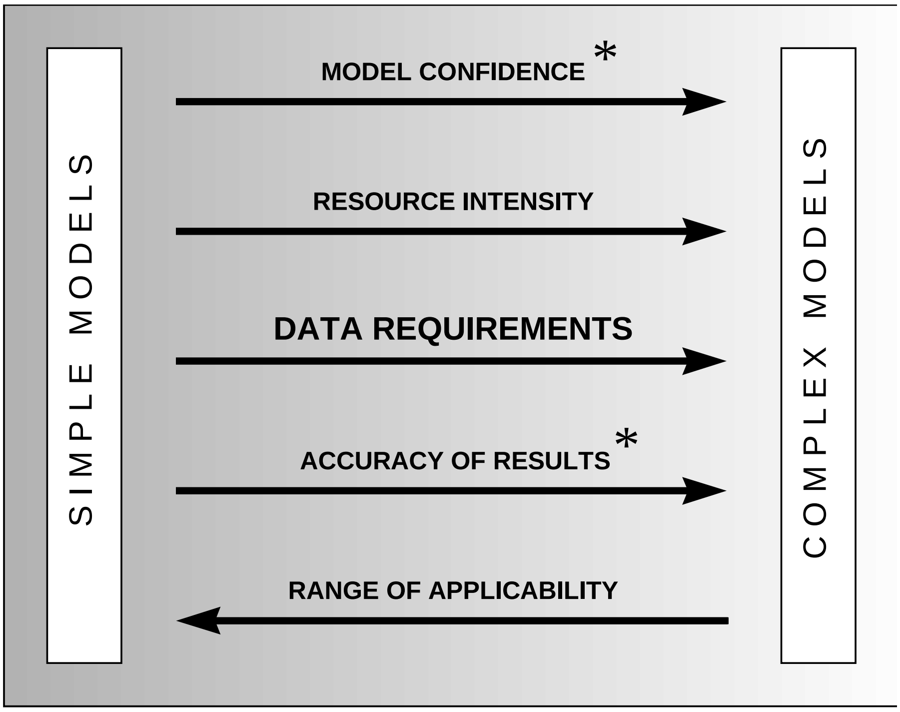
194. For many chemicals, especially new ones, too few data will be available to run the more complex models. Accordingly, a simple model requiring few data inputs is typically used. For example, with a level I or level II model, the mode of entry is not necessary since it will have no influence on the distribution between the compartments. Besides, a generic Level II model will typically, but not always, rely on estimated values from QSARs or extrapolation approaches to generate the needed partition coefficients and degradation data.

195. With more complex models these data are more and more replaced by data measured in the laboratory. To run the models the data measured in the laboratory are then supposed to be representative of environmental conditions. For example the results of the laboratory test on ready biodegradability are transferred to the biodegradation of the substances in the compartments water, soil and sediment. As highlighted in Chapter 3 this is of course afflicted with large uncertainties, because of the artificiality of ready biodegradability tests, mineral nutrient test media, test substance as sole carbon source, temperature dependence, etc.

196. At a detailed level of risk assessment, spatially explicit multimedia models may be employed to better understand the fate of a chemical over time and within specific regions according to known emission patterns. Generally, the major weakness of these most complex models is their data needs: firstly the amount of monitoring data that are needed by the model developers for their validation, and secondly, for any user, the amount of accurate input data that are needed for running them.

197. Of course the time and money needed for a study increases with the number of data to be gathered. The level of expertise needed for running a more complex model and for managing more data are also higher. As a result, complex models have a more limited range of applicability across users than more simple generic models. Figure 5.1 represents a graphical interpretation of this idea.

Figure 5.1 : Spectrum of Model Complexity and Associated Factors



(*) *As described in the text, the increase in accuracy and in model confidence exists only up to an "optimum" level of complexity*

198. It should always be decided for each individual case whether a higher level of complexity in the model will provide a valuable increase of scientific knowledge, with enough confidence, as compared to the effort needed. The refinement of the evaluation can take place at a higher level through an improvement of the data set. A "purposeful improvement" of the data set means that only data that are important for the refinement should be generated (Pennington, 2001b). This can be achieved for example by using the results of a simple model (e.g. distribution between the compartments) before refining the data required for running a more complex model: see Section 5.3.3 for more details.

199. As shown in section 4.2.3, there is also an interaction between the choice of the emission scenario and the use of the models. For example, a modeller who is interested in being as close as possible to reality has to use a realistic emission scenario for the three compartments air, soil and water, based on reliable information. This is especially true if he uses a region-specific model. Alternatively, other users may perform simpler calculations with only one default scenario (e.g assuming 100% emission into air because air is a mobile compartment and this is likely to lead to the greatest LRTP - conservative estimation) or with three scenarios with separate emissions to air, soil and water in order to cover the most extreme values possible for P_{ov} and LRTP. In this case a generic model is appropriate.

5.3 Using the model outputs in chemical assessment

5.3.1. Absolute and relative approaches

5.3.1.1. Absolute approach

200. There are two approaches to using estimates of LRTP and P_{ov}. The first approach, often referred to as the absolute approach (OECD 2002a), determines if a substance passes or fails by comparing the model results for the substance to thresholds, which have to be chosen *ex-ante* by the competent authority. Those substances that pass the criteria are not considered further or may receive a low priority for further assessment. Those substances that fail the criteria may be given a high priority for further investigation or in some cases may require immediate action. For example, in the case of the authorisation of a new substance, reducing the production amount may be sufficient to reach a level "of no concern".

201. In risk assessment where the calculation of a predicted concentration is compared to an effect concentration, the absolute approach is the only possibility. However, the absolute approach can also be used in chemical screening.

202. The choice of the thresholds has to be conservative, in order to avoid evaluating a substance “of concern” as that "of no concern". The lower the level of complexity, the less accurate the representation of reality is, and the more conservative the criteria should be. In principle this should produce few or no false negatives (i.e. will be conservative), but potentially a high number of false positives (Pennington 2001b). It should be underlined that so far P_{ov} has not been used in absolute approaches for regulatory purposes, owing to the lack of multimedia criteria for persistence.

5.3.1.2. Relative approach (benchmarking approaches)

203. The current limitation of the former procedure is that the absolute approach necessitates the establishment of absolute criteria for P_{ov} and LRTP. Contrary to criteria in terms of single-media half-lives, this is problematic because it has been proven that different models, even if similar in complexity, are likely to give different absolute values as outputs for the same chemical (Wania and Mackay, 2000).

204. Hence a second approach, which is referred to as the relative approach, has been proposed for chemical screening (OECD 2002a). In this approach, a suite of chemical benchmarks is first defined, each of them being well known in terms of risk assessment: P_{ov} and LRTP estimates are then carried out for these benchmarks. Secondly, the chemical of concern is ranked or classified relative to this suite of chemical benchmarks using the same model. This procedure enables assessment of the substance, by considering its ranking in terms of P_{ov} or LRTP among the well-known benchmark chemicals. The relative approach can be likened to the process of establishing calibration standards in the laboratory. Examples of chemical ranking and classification approach are described by Matthies et al (1999), Beyer et al. (2000) and Bennett et al. (2001). Relative approach may also be applicable when the desired outcome is the screening of a large set of existing chemicals, to establish priority classes of substances for further assessment or action.

205. As explained in Section 4.4, project is on-going, in conjunction with the OECD Multimedia Modelling Expert Group, to establish a more precise benchmarking procedure for producing model-independent P_{ov} and LRTP in order to evaluate substances. The study concludes that a range of different models ranked 3175 hypothetical substances in satisfactorily similar positions. The Expert Group proposes to use this ranking as a way to position the P_{ov} and LRTP calculated for a specific substance against values calculated for this set of benchmark substances. This amounts to calibrating P_{ov} and LRTP scales using the set of hypothetical substances. Further guidance for this procedure will be included in the report of the

Workshop and the follow-up activities (to be made available from http://www.oecd.org/env/riskassessment).

5.3.2. Tiered use of models

206. As explained earlier, models are to be selected from a wide range of complexity. It is advisable to use multimedia models in a tiered approach due to resource and data limitation, especially in the context of a regulatory assessment, which may result in a decision for the substance of interest. This approach refers to a stepwise procedure during the evaluation of a problem, each tier or level representing a stage of complexity. The higher the tier, the more complex the model used. Hence, this approach necessitates:

1. The selection of several models from the spectrum of complexity;

2. The choice of decision rules, in order to go from one tier "up" to the next one. At each stage, or tier, the outputs of the model are used to determine if a chemical “passes” or “fails” given criteria.

207. The whole procedure can be seen as an iterative process. This principle is illustrated in Figure 5.2. A reasonable number of tiers in an assessment could be 3 or 4. At any Tier N, a model of appropriate complexity is used to calculate P_{ov} and LRTP. These values are compared with defined thresholds and/or benchmarks. If it is shown that the chemical is of no concern, the assessment stops there. If not, the assessment proceeds to the next tier N+1, with higher level of complexity and accuracy. Particular attention is needed for defining the final tier, because a regulatory decision is to be made if the substance still proves to be of concern after an evaluation at this final level.

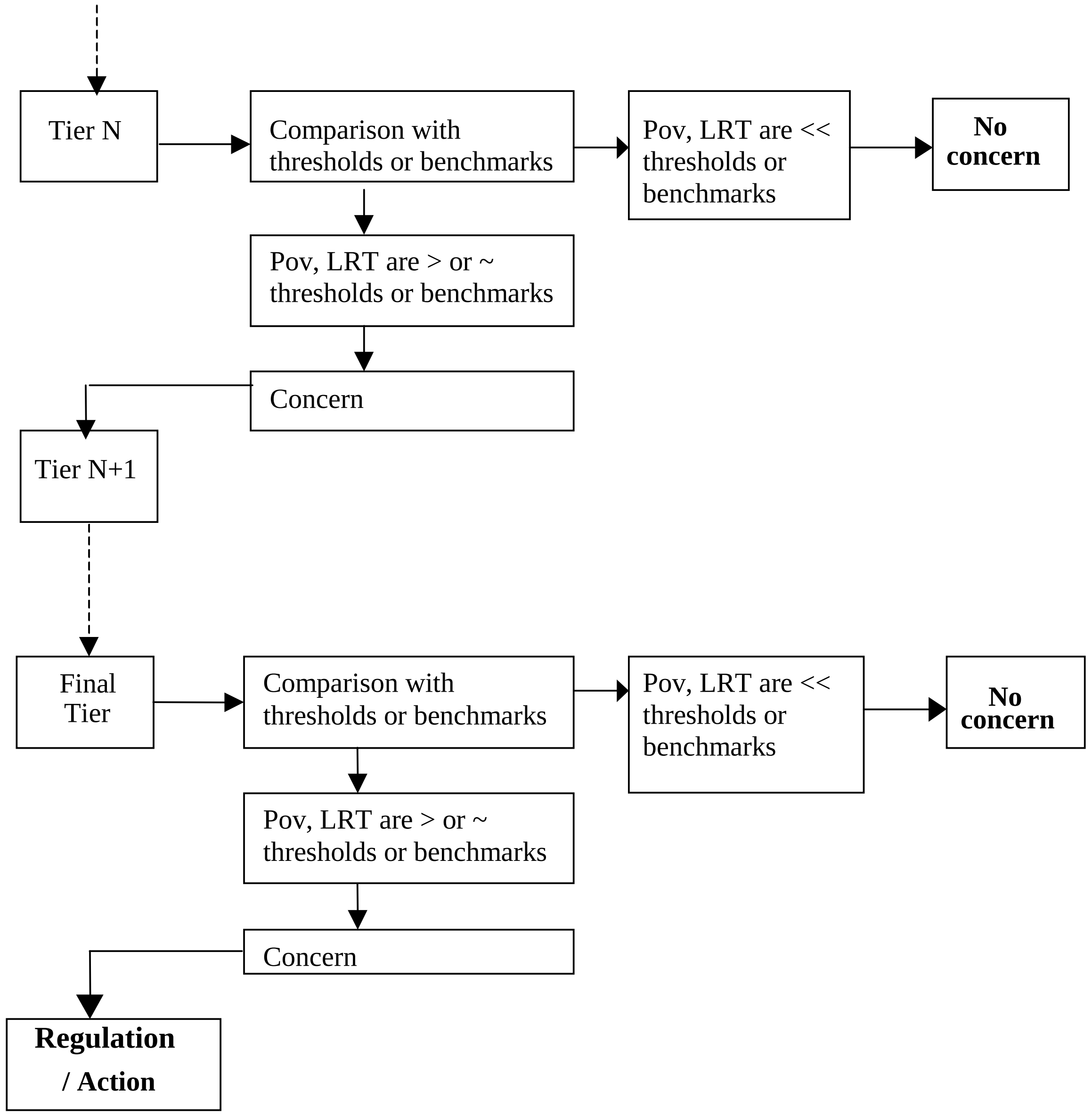
208. Generally, an evaluation will begin with the lowest stage, especially for new substances, since the available data are limited. However, if enough reliable data are available, the evaluation can begin at a higher level of complexity. At the lower stages data gaps can be identified, and these (if any) should be addressed as part of the refinement of the evaluation at higher levels.

209. An exact separation between the individual tiers is not always rigorously possible for all substances, due to different data availability, and case by case study is generally needed. For example, in the case of a new chemical a modeller may be unable to complete the next "tier" properly, if he does not have the refined data necessary – he may then introduce a kind of intermediate level instead by running the more complex model with conservative assumptions.

210. It should be noted that Figure 5.2 describes only the general principle of a tiered approach. Design of tiers and selection of models should be done according to the needs of the assessors, taking into account the characteristics of different levels of models described in Chapter 3 and Section 5.2. This document does not aim at *a priori* guidance on specific tiers or models.

Figure 5.2 - Illustration of the principles of the tiered approach

In bold characters : ways out of the process



5.3.3. Using other outputs than P_{ov} and LRTP

211. The key outputs of multimedia models are LRTP and P_{ov}. In order to complete the understanding of the behaviour of chemicals in the environment we can also use some other outputs of the models.

212. A good example is the distribution of a substance among the different compartments, expressed in percentages. A generic multimedia model can be used to identify those media that are expected to contain the major amount of a substance according to the partitioning results generated by the model. This helps determine which media will be of concern in the exposure assessment, e.g. in order to focus on organisms that inhabit these media. This output can be useful to guide future sampling and monitoring programs.

213. Such results can also orient an ongoing risk assessment study. Single media half-lives can be said to be more relevant for those media in which the substance will be present in a significant amount. If, for example, a substance has only a very small tendency for distribution into soil, then the measurement of the degradation in soil is not very important. In such a case the use of a QSAR is sufficient, even if using a more complex model. This is a practical example for a "purposeful improvement" of the data set mentioned in 5.2.2.

214. Other multimedia estimates can be important in the exposure assessment of a new substance. For instance, the definition of “long-range transport” may not be as important as determining where a substance is largely deposited during transport. This can help define the geographical scale of the risk assessment and help delineate potential hotspots. Estimates of LRTP can also be combined with the octanol-air partition coefficient (K_{OA}) or the octanol-water partition coefficient (K_{OW}) to determine if a new substance is likely to be detected in the terrestrial or aquatic food chains of sensitive species. This will establish the need for generating more information on effects or detailed site-specific exposure.

215. The exposure concentrations derived from multimedia models may be useful in themselves. These estimated concentrations may be accurate only to an order of magnitude or less, but even then they may be useful in a screening level assessment to determine if there is a large margin of safety, or which chemicals need to be prioritised for more detailed assessment.

216. Outputs from detailed and complex models have not been used directly for supporting a regulatory process at a national or global level. However, they are used in order to support more local actions and policies (e.g. North-American Great Lakes, Baltic sea) or to help in refining the evaluation of the previous stages and answer questions like: Are there some specific regions of concern? Are there some peaks of concentration in summer or in winter? etc.

5.4 Examples of the Application of P_{ov} and LRTP in Pollution Prevention

217. To illustrate the potential applications of P_{ov} and LRTP in the world of pollution prevention, examples have been selected that span the range of non-regulatory and regulatory uses identified in Chapter 2. These are presented below.

5.4.1. Non-Regulatory Users

218. Non-regulatory users of multimedia models include the chemical industry (including industry-sponsored organisations such as CEFIC and ECETOC), the public, non-governmental organizations and academia. In terms of pollution prevention, the chemical industry stands to benefit the most from use of models for LRTP and P_{ov}. The chemical industry is aware that “environmentally friendly” chemical substitutes and processes will be more acceptable to their customers, the general public, NGOs and

regulators (e.g., green chemistry). A chemical substitute must however be an economically viable alternative to existing products in a company's inventory.

219. When a new substance is under development by a chemical company, many of the physical-chemical properties, degradation and partitioning data may not have been derived, but it may still be desirable to understand the environmental fate of the substance before further development proceeds. The substance under development may be screened using simple models or generic multimedia models relying on QSAR predictions to fill data inputs. The use of results from multimedia modelling that relies solely on QSAR estimates as model input obviously creates a level of uncertainty that is difficult to quantify (i.e. estimates from estimates). However, the absolute accuracy of results may not be the point of the exercise; rather the results can be viewed as a basic screening of the environmental fate and behaviour of the substance prior to proceeding in earnest with commercial development [12]. The same can be said for regulatory applications of multimedia models using QSAR predictions as model input.

220. Consequently, in the absence of regulatory demands, multimedia models and other screening tools can promote voluntary changes in the chemical industry and serve to increase post-development product stewardship. This is the impetus behind the PBT Profiler in the US. The PBT Profiler was developed as a voluntary screening tool to identify pollution prevention (P2 Assessment Framework) opportunities for chemicals without experimental data. Primarily it is used by the chemical industry (although anyone can use it to screen a substance) during product pre-development stages to help identify chemicals that may potentially persist, bioaccumulate and be toxic to aquatic life (i.e. are PBT candidates). The Profiler uses a level-III multimedia model to decide which is the "predominant" environmental medium for a given substance and the substance is assigned high, medium or low (H/M/L) for persistence based on whether the substance is predicted to exceed set persistence criteria for that medium. P_{ov} is calculated and displayed but not used to determine H/M/L. Tools like the Profiler could easily take the next step by telling the user how the given substance compares to familiar substances, i.e. substances with data, and whose behaviour is in general known (benchmark approach). The same applies to LRTP, which the Profiler presently does not calculate.

221. Similarly the ECETOC proposed strategy for assessing the persistence of chemicals in the environment includes the use of multimedia models for assessing overall persistence and for targeting the need for further testing (ECETOC 2003); but the strategy presently does not address P_{ov} and LRTP.

5.4.2. Regulatory Users

222. Regulatory users include users complying with global and regional conventions and agreements (e.g. Stockholm Convention, NARAPs) and national governments responsible for the management of both new and existing industrial chemicals and pesticides. As mentioned previously, the application of multimedia models for LRTP and P_{ov} can be useful to regulators for both hazard-based chemical screening activities and risk assessment.

5.4.2.1. Global and Regional Levels

223. At the global level, the Stockholm Convention, the UNECE LRTAP and OSPAR Convention, outlined in Chapter 2, provide opportunities for the incorporation of P_{ov} and LRTP derived using a multimedia model. The three mandates mention the principles of "long-range transport" potential and "persistence". The criteria concerning exposure are complemented with information concerning effects

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[12] It is noted that knowledge of QSAR reliability and "appropriateness" for the chemical being modeled (i.e., is the substance modeled well by the QSAR or is it difficult to model ?) will improve the quality of the input data as QSAR predictions will be closer to "true" values.

(hazard), such as results of tests in (eco)toxicology, bio-concentration factors BCF and/or K_{OW} (as a surrogate for the estimation of bioaccumulation). Currently, these Conventions use single-media half-lives as measures of persistence or long-range transport but they do not exclude the use of modelling results or “surrogate” information to provide evidence for these properties.

224. In the UNECE LRTAP Protocol for instance, it will be possible to use P_{ov} generated using a generic multimedia model, in addition to single-media persistence values, in order to provide a weight of evidence when nominating a new POP candidate. The partitioning information from the model would also provide useful information for the risk profile that is required for a POP candidate. When determining the LRTP of a POP candidate, a generic or zonally distinct multimedia model (e.g. Chemrange, GloboPop) could be used to generate LRTP estimates that could be applied with half-life estimates in air to create a weight of evidence for LRTP. Information from such a model would also increase the understanding of the fate of a POP candidate from sources to areas of deposition. Results from models may also be used to direct monitoring activities under the global conventions or possibly to “backtrack” to sources of emission.

225. In the framework of European Union regulation, in the case of new substances the exposure-relevant basic data set must be supplied by industry (e.g. vapor pressure, water solubility, the octanol-water partition coefficient). The advantage is that these data are generated by standardized test guidelines and are therefore valid. Then a screening risk assessment of the substance is led by an expert –who reports to all member states– by comparing predicted exposure values (PEC : Predicted Environment Concentrations) with ecotoxicological values (PNEC : Predicted No Effect Concentrations) in each compartment. If this assessment shows a reason for concern (i.e. PEC/PNEC equal to 1 or greater than 1), a refinement of the risk assessment is needed. This refinement consists of using the same model but refining the input data, e.g. by providing more specific effect data, more accurate data on the releases, etc. In case the maximum feasible refinement still raises a concern, then the notification of the substance may be refused, but in most cases a discussion will begin with the industry in order to reduce the releases of the substance: limitations in the production amount, prohibiting a specific production process, restrictions in uses, etc. The case of an immediate refusal of the notification is rare, given that the studies were led previously by the industry. The process of refinement of the evaluation is different from the concept of "tiered approach" since (i) the same model is used and (ii) case by case study is the rule, no "level" is formalized.

226. This risk assessment will consider the whole life cycle of the chemical, and will be driven according to the EU Technical Guidance Document. The assessment is carried out with a model (EUSES) which includes a level III model (SimpleBox). Hence, although not included in the regulation, P_{ov} and LRTP could easily be calculated: this was done with the development of the model ELPOS (Beyer and Matthies, 2002). In contrast, up to now the evaluation of persistence of new and existing chemicals is being carried out using the single media half lives whereas the evaluation of LRTP is not considered. For existing chemicals there are often many data available, but their reliability is often questionable. Sometimes, there are also monitoring data available in order to validate the model estimates, and the regulator can impose specific monitoring programmes. For pesticides the situation is similar to new substances, but additionally, various measured field data have to be supplied by industry (e.g. K_{OC}, Soil half-life).

5.4.2.2. National level

1. At a national level, Canada, for example, could use generic models for LRTP in PBT screening to “categorize” the 23,000 existing substances on the Domestic Substance List (DSL) for persistence, because Canada includes LRTP as an indicator of persistence in air (see Table 3, Chapter 2). However, P_{ov} cannot currently be used as a tool for categorizing the substances on the DSL because Canada has chosen to use single media half-lives to determine persistence in air, water, sediment and soil.

2. P_{ov} is likely to be beneficial in the risk assessment of new and existing substances. This allows environmental evaluators to employ a generic multimedia model for P_{ov} and LRTP (e.g. EQC Level III, TaPL3, Chemrange). For example, new substance notifications received in Canada contain a substantial amount of physical-chemical information and fate data and the mode of entry is typically known. Because the risk assessment of a new substance in Canada must assess the persistence of the compound under review, estimates of P_{ov} can be used as a more environmentally relevant measure of persistence (i.e., since it considers partitioning, advection and reaction). However, to use P_{ov} in this manner, chemical benchmarks will be needed. P_{ov} must be related to known persistent or non-persistent chemicals so that some “real world” context can be given to the estimate of P_{ov} within the risk assessment. This should become feasible in the near future, since it is the objective of the ongoing Expert Group activity on benchmarking to provide this information. P_{ov} can also be combined with other degradation estimates (e.g., from BIOWIN) to provide a weight of evidence for determining environmental persistence.

3. Realistic presence has been defined by Woodfine and Mackay (2001) for use in determining the partitioning and persistence of organic substances on Canada’s Domestic Substances List. The authors suggested that if less than 5% of a substance is found to partition to a medium, the medium specific half-life criterion for categorizing a substance for persistence need not be considered due to lack of presence in that medium. Although the utility of the exact figure of 5% still has to be confirmed, the interesting idea is to help to save time and money when refining an evaluation by setting priorities in the data requirements.

5.5 Conclusion

227. Concerning the gradation in model complexity and its proper use:

- Multimedia models are among the most appropriate tools for chemical screening as well as risk evaluation and some of their major outputs –P_{ov} and LRTP– are useful indicators. For interpretation purposes, other outputs of the models are also helpful, e.g the distribution between the different compartments enables to identify the media in which the chemical is present in a significant amount. Outputs from detailed, complex models can refine the evaluation or backup local actions.

- A wide spectrum of multimedia models of increasing complexity is available. Simple "generic" models and spatially detailed models are complementary and they currently have similar representations of individual processes.

- From this spectrum a few classes of models of similar complexity can be presented. In the context of a regulatory assessment, the general principle of a "tiered approach" can be defined as a stepwise procedure during the evaluation of a problem, each level (or "tier") representing a stage of complexity. The higher the tier, the more complex the model used.

- Concerning accuracy and level of confidence:

- The accuracy of a model represents its capacity to give a result that tends to centre on the true answer (even if it is not precise). Increasing model complexity generally aims at increasing the accuracy of the results, but also leads to a need for a greater amount of more accurate input data, as well as a higher level of user expertise. The choice of a model should always be driven by the objective of the user as well as his constraints in terms of data and resource availability.

- One cannot always gain accuracy by complicating a model, but unless there is adequate and reliable data for this more complex model both the precision of and confidence in the model will diminish. When data is limited, one can resort to, a conservative approach that does not necessarily need high accuracy.

- It should be always decided for each individual case whether a higher level of complexity in the model (e.g. the next higher tier in case of a tiered approach) will provide a valuable increase of scientific knowledge, and with enough confidence, as compared to the effort needed.

- Concerning absolute and relative approaches :

- Due to the difficulty of establishing absolute criteria for P_{ov} and LRTP, use of benchmark substances is strongly encouraged Evidence for the inclusion of a new POP or PBT candidate based on its relative ranking to a known substances would improve the likelihood of the model results being understood and accepted by decision makers. This is to be confirmed by the final report from the Bilthoven Workshop in June 2003.

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ANNEX 2: DEFINITION OF KEY TERMS

The **accuracy** of a model can be defined as follow : The closer the response of the model is to the response of the actual system, the more accurate the model is. In principle, the accuracy of a model can be determined by measuring the gap between these two answers. The specific problem concerning environmental sciences, however, is that one cannot measure reality, because it is too complex and too unstable (or time-dependent). Hence it is difficult to prove the accuracy of an environmental model.

The **precision** of a model is a different concept, rather related to the reproducibility of its response, when running the model several times with slightly changing inputs. In principle, a model can be very precise even if not accurate.

The **uncertainty** of a model addresses both concepts of accuracy and precision. It includes the uncertainty of the input data as well as the sources of uncertainty which are inherent to the model structure: e.g. the elementary processes which are not taken into account, the simplification of processes through mathematical equations, the limitation in spatial or temporal definition, etc.

The **uncertainty of the input data** is due to both the **errors** in measurements and the impossibility to account for the **environmental variability** with time and space in the real system.

The **sensitivity** of a model refers to the extent to which model output is affected by changing the value of an input parameter.

Directly related to the concept of precision, the **sensitivity analysis** of a model consists in studying the evolution of its response after changing each input parameter in a standardised way (e.g. from –10% to +10%). Hence the sensitivity of the various parameters can be compared (see examples in Chapter 4). In principle, this can be done independently from the actual ranges of variation of the parameters in the real world, contrary to an uncertainty analysis: An **uncertainty analysis** of a model consists in studying the evolution of its response after changing each input parameter according to its realistic variation (variability) in the actual system.

The **reliability** of a model may be defined as the opposite to its overall uncertainty. Hence it is the result of an objective analysis of the model.

The **confidence** in the model refers to a judgement by the users of the model – either personal or consensual – on how much they can rely on the model output for certain purposes. The concept of confidence can be illustrated by a Wilhelm Tell metaphor. Before shooting, Wilhelm Tell should have been confident in his own skills at archery. Evidence of his reliability and accuracy would be demonstrated after his shot (and repeated successful shots).

Concerning models in general, the management of confidence is more natural with a statistical model, because it will never give an answer without the related **confidence interval**, e.g.: "the answer of the model is 25, with 90% confidence level that the answer in the real world would be between 22 and 30".

ANNEX 3: DISCUSSION OF INDIVIDUAL TRANSPORT AND TRANSFORMATION PROCESSES

Degradation processes

Most models prompt the users to enter one first-order degradation rate constant for the chemical in each environmental compartment, representing the sum of all degradation processes. It is thus the task of the user to evaluate what processes are influential in each compartment and to add up the corresponding degradation rate constants to obtain one overall degradation rate constant for each compartment. Additionally, the user needs to be aware of the common practice of approximating second-order degradation processes, which are a reasonably correct description for most environmental degradation processes, with pseudo first-order degradation processes. This simplification is reasonable for processes such as hydrolysis or photooxidation when contaminant concentrations are low. In the case of biodegradation, however, the use of pseudo first-order rate constants conceals the large variance in the biomass factor, i.e. to what extent a viable microbial community is available that is able to degrade the chemical in question.

The degradation rate constants in each environmental compartment are usually weighted with the fraction of the substance that is available for a specific degradation pathway. For example, it is assumed that in the air compartment only that part of the substance that is not associated with aerosol particles is subject to photooxidation. In a similar way, models differ sometimes with respect to the treatment of the degradation processes in the soil. While some attribute an overall degradation rate constant, mostly deduced from an estimate of biodegradability of the substance that applies to the entire substance mass in soil, others apply the degradation processes such as hydrolysis or biodegradation to the fraction in pore water only. To correctly use the models in this respect, one would need to know whether the degradation rate constants have been measured or estimated for bulk soil or the pore water fraction only. In most cases, however, that information is not available.

Distribution processes

Among the distribution processes that are addressed in models are atmospheric deposition to soil and water, transfer from soil to air and water, transfer from water to air and exchange processes between water and sediment.

- *Atmospheric deposition* to soil and water includes the following processes:

- Wash out
- Wet deposition
- Dry deposition

In the atmosphere, the particle-bound fraction of a chemical is subject to both dry and wet deposition. Dry deposition is governed by turbulent diffusion. The gaseous fraction is subject to equilibration with tropospheric water and subsequent washout by precipitation. Also, the gaseous fraction is subject to the diffusive exchange with the soil and water compartments according to the partition coefficients between soil and air, and soil and water (i.e. the Henry's law constant), respectively. The following differences in the description of these processes can be encountered among different models:

- The particle-associated fraction is modeled according to the Finizio K_{OA} model (representing absorption) or according to the Junge model (representing adsorption).
- There is continuous (most models) or periodic rainfall (Hertwich, 1999)

- The two-resistance model used to address diffusive phase exchange is based either on substance-specific or generic mass transfer coefficients (MTC)
- In some models, sorbed phase transport in the soil is included (McLachlan et al. 2002), which increases the rate of the air-soil exchange and leads to higher deposition mass fluxes.

- *Water to air transfer*

always includes diffusion according to the two-resistance model (substance-specific or generic MTC) and, in some models, also spray drift from the oceans.

- *Transfer from soil to Air*

- Volatilization from pores filled with water and pores filled with air
- Volatilization from the soil sorbed phase

The distribution from soil to air always includes diffusion according to the two-film resistance model (substance-specific or generic MTC). In some models (McLachlan et al. 2002) bioturbation by earthworms and other soil organisms is included as an additional process within the soil matrix that enhances the air-soil exchange.

- *Transfer from soil to water*

- Leaching of the dissolved fraction
- Runoff of the particle-bound fraction

Most models include leaching of the dissolved and runoff of the particle-bound fraction with rainwater. Some scale the leaching and runoff rate with the amount of rainfall, others use constant rates. Models also differ with respect to whether they multiply the rates by the respective dissolved and solid-bound fractions or whether they apply the rate to the bulk mass in soil.

- *Transfer from water to soil*

- Infiltration of irrigation water

Some models such as ChemCan and CalTOX allow surface water transport from suface and/or ground water to soil to account for irrigation (or flooding). In CalTOX this pathway is only included in the assessment of transfers to vegetation for human dose calculations, but this pathway is not included in the mass-balance model.

- *Tansfer from water to sediment*

- Particle settling
- Diffusion

Apart from differing values for the settling constant, most models seem to use a version of the surface-mixed sediment layer model to model these processes (Schwarzenbach et al. 1993). As mentioned in the general comments, in some models the sediment is not an independent compartment itself but is assumed to be at equilibrium with the water compartment.

- *Transfer from sediment to water*

- Resuspension
- Diffusion

Apart from differing values for the resuspension constant, most models seem to use a version of the surface-mixed sediment layer model to model these processes (Schwarzenbach et al. 1993). As mentioned in the general comments, in some models the sediment is not an independent compartment itself but is assumed to be at equilibrium with the water compartment.

ANNEX 4: KEY DATA SET TO RUN A GENERIC MODEL

Substance Identity

Common name
CAS Number
Molecular weight
SMILES Code

Substance Data

Property	Dimension	OECD Test Guideline	Example QSAR Method/Model
Properties of pure substance			
Melting point	C	OECD 102	MPBPVP (SRC[13])
Vapour pressure	Pa	OECD 104 (Draft update 2003)	MPBPVP (SRC)
Water solubility	mg/L	OECD 105	WSKOWWIN (SRC)
Dissociation constant, pKa	---	OECD 112	Pkalc (PALLAS[14] ?); pKa (ACD[15])
Partition coefficient			
Octanol/water partition coefficient	---	OECD 107 OECD 117 OECD 122 (Draft 2000)	KOWWIN (SRC); CLOGP[16]; PROLOGD (kow for dissociable substances-PALLAS); ProLogP - (PALLAS); logKow - (OASIS FORECAST[17]); logKow (ACD)
Optional partition coefficient			

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[13] Syracuse Research Corporation

[14] Compudrug Chemistry Limited.

[15] Advanced Chemistry Development Limited

[16] BioByte Corporation

[17] Mekenyan et al. Lab of Mathematical Chemistry, Bourgas, Bulgaria

Property	**Dimension**	**OECD Test Guideline**	**Example QSAR Method/Model**
Air/water partition coefficient	---	Mackay et al. 2000	HENRYWIN (SRC)
Air/octanol partition coefficient	---	Harner and Bidleman (1998); Harner and Mackay (1995)	
Adsorption coefficient	L/kg	OECD 106 OECD 121	KOCWIN (SRC); KOC (ACD)
Degradation rate constant			
Photooxidation	Rate constant ($d^{-1)}$	OECD Draft (2000)	AOPWIN (SRC)
Water Direct photolysis	Rate constant (d^{-1})	OECD Draft (2000)	ABIWAS 2.0[18]
Water Hydrolysis	Rate constant (d^{-1})	OECD 111	HYDROWIN (SRC)
Water Biodegradation	Rate constant (d^{-1})	OECD 301 (ready) OECD 302 (inherent)	BIOWIN (SRC) OASIS CATABOL[19] TOPKAT[20]
Aerobic Mineralisation in Surface Water		OECD 309	
Soil Biodegradation	Rate constant (d^{-1})	OECD 304A OECD 307	---
Photodegadation on soil	Rate constant (d^{-1})	US EPA No 835.2410 OECD Draft Test Guideline (2002)	
Sediment	Rate constant (d^{-1})	OECD 308	---
Vegetation foliar dissipation	Rate constant (d^{-1})	US EPA No. 875.2100	
Mode of entry			
Mode of entry	Percent emission into air, water, soil	---	---

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[18] Frank, Klöpffer: 1989

[19] Mekenyan et al. Lab of Mathematical Chemistry, Bourgas, Bulgaria

[20] Oxford Molecular Group

ANNEX 5: SELECTED DATA SOURCES

Handbooks

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Company Catalogs

Aldrich company
Merck company
Fluka Chemie AG, Buchs/Switzerland
Etc.

Material Safety Data Sheets

Website of University of Vermont, http://siri.uvm.edu/msds
Sicherheitsdatenblätter: http://www.verwaltung.uni-mainz.de/dua/eusdb.html
International Chemical Safety Card (ICSC):
http://www.ilo.org/public/english/protection/safework/cis/products/icsc

Databases Available by Subscription

IUCLID - International Uniform Chemical Information Database, European Chemicals Bureau, Ispra/Italy

AQUASOL, Arizona Database of Aqueous Solubility
http://www.pharmacy.arizona.edu/outreach/aquasol/index.html

Design Institute for Physical Property Data (DIPPR) Database
http://www.cas.org/ONLINE/DBSS/dipprss.html

MedChem Database (CLOGP Database)
http://www.daylight.com

Databases with Free Web Access

ARS Pesticide Properties Database (PPD)
http://wizard.arsusda.gov/acsl/ppdb.html

Oregon State University Extension Pesticide Properties Database
http://ace.orst.edu/info/nptn/ppdmove.htm

Physical Properties Database (PHYSPROP)
http://esc.syrres.com/interkow/physdemo.htm

NIST Chemistry WebBook
http://webbook.nist.gov/chemistry

Alternative Solvents Database
http://solvdb.ncms.org

Environmental Fate Databases (EFDB) (this database comprises the ones below)
  CHEMFATE, Syracuse Research Corporation
  http://www.syrres.com

  DATALOG, Syracuse Research Corporation
  http://www.syrres.com

  BIOGEG
  Syracuse Research Corporation: http://www.syrres.com

  BIOLOG
  Syracuse Research Corporation: http://www.syrres.com

Environmental Chemicals Data and Information Network Databank (ECDIN)
http://ecdin.etomep.net (link not working)
National Pesticide Telecommunications Network (NPTN)
http://ace.orst.edu/info/nptn

Chemfinder.com
http://www.chemfinder.com ; http://chemfinder.cambridgesoft.com

Interactive Learning Paradigms (ILPI) MSDS Website
http://www.ilpi.com/msds

GINC = Global International Network on Chemicals
http://www.nihs.go.jp/GINC/index.html

Hazardous Substances Databank
http://www.toxnet.nlm.nih.gov Adelaide University Library:

Library University of Adelaide/Australia
http://library.adelaide.edu.au/guide/sci/Chemistry/env.html

UNEP Chemicals: International Register of Potentionally Toxic Chemicals (IRPTC), Geneva:
http://www.chem.unep.ch/irptc : Inventory of Information Sources, Internet Guide.

COMMPS Databank (EU): Combined Monitoring-based and Modelling-based Priority Setting.
http://www.umweltbundesamt.de/wasser/themen/stoffhaushalt/wrrl.htm, and
http://www.iuct.fhg.de/commps/commps_2.zip (=ACCESS 97 databank)

OECD EXICHEM Databank
http://www.olis.oecd.org/exichem.nsf

OECD HPV Database
http://cs3-hq.oecd.org/scripts/hpv/

National Institute of Technology and Evaluation, Japan: Chemical Management Center:
http://www.safe.nite.go.jp (English site under construction).

Chemical Inspection and Testing (CITI) Japan
Biodegradation and Bioaccumulation Data of Existing Chemicals
Biodegradability and Estimates
http://www.cerij.or.jp

AIST databases, including Computed Property Data Base for Molecules
http://www.aist.go.jp/RIODB/riohomee.html

IPCS INCHEM
WHO International Programme on Chemical Safety (IPCS): ILO, WHO, UNEP
http://www.inchem.org

QSAR Handbooks and Articles

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North American Commission for Environmental Cooperation,
http://www.cec.org/programs_projects/pollutants_health/smoc

OECD Test Guidelines, http://www.oecd.org/env/testguidelines

OSPAR Convention, http://www.ospar.org

Stockholm Convention on Persistent Organic Pollutants; www.pops.int

UNECE Convention on Long-range Transboundary Air Pollution, http://www.unece.org/env/lrtap/

UNEP Chemicals POPs page, http://www.chem.unep.ch/pops/